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Assessment of soil phosphorus status and management of phosphatic fertilisers to optimise crop production

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ASSESSMENT OF SOIL PHOSPHORUS STATUS AND MANAGEMENT OF PHOSPHATIC FERTILISERS TO OPTIMISE CROP PRODUCTION

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FOREWORD

Phosphorus (P) is an essential plant nutrient, and its deficiency in soils severely restricts crop yields. Tropical and subtropical soils are predominantly acidic and often extremely deficient in phosphorus. Moreover most of these soils possess a high phosphate sorption capacity. Strongly sorbed or fixed phosphate is unavailable for plant uptake. Therefore, substantial P inputs are required for optimum plant growth and adequate food and fiber production.

Manufactured water-soluble P fertilizers, like superphosphates, are the commonest P inputs. However, in most developing countries these P fertilizers are not produced locally but are imported, and their supplies to resource-poor farmers in rural areas are limited. Many phosphate-bearing mineral deposits exist worldwide. Several developing countries with P-deficient tropical acid soils have important phosphate rock deposits, that is the raw material for the production of P fertilizers. Thus, under certain soil and climatic conditions, direct application of phosphate rocks (PRs) is an agronomically and economically sound alternative to the use of expensive superphosphates.

In spite of extensive research on the application of PR to acid soils in temperate regions, there is scant information on the potential of local PR sources in tropical and subtropical regions. Phosphate rocks vary widely in their mineralogical, chemical and physical properties and consequently in their reactivity and agronomic potential. It is, therefore, necessary to assess the relative agronomic effectiveness of the indigenous and imported PRs using the commercially available superphosphate as a reference. Also, changes in the soil available P when amended with PR products and water-soluble P fertilizers need to be properly monitored with suitable soil P testing methods for the provision of adequate P fertilizer recommendations.

During the 1980's, some local PR sources were evaluated in the FAO Fertilizer Programme. The idea of a project on PR evaluation was first conceived in 1991 and prompted by developments in promising technologies to enhance the agronomic effectiveness of PRs, which needed to be properly evaluated and tested in a research network. The Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture convened a Consultants meeting in May 1993 in Vienna to review recent advances on this topic and to define the objectives for a Co-ordinated Research Project (CRP) entitled The Use of Nuclear and Related Techniques for Evaluating the Agronomic Effectiveness of P Fertilizers, in Particular Rock Phosphates, which was implemented from 1993 through 1998. Research focused on technologies to enhance the agronomic effectiveness of natural and modified PR products applied to crops grown in acid soils. ^{32}P isotopic techniques were utilized to gather quantitative and precise information on phosphate behavior in the soil-plant system, and the efficacy of PR management practices. In this context, the technical support provided by the FAO/IAEA Agriculture and Biotechnology Laboratory, Seibersdorf, Austria and the Centre d'Etudes Nucleaires, Cadarache, France, was crucial for the implemention of these activities.

The IAEA thanks the French Government for its generous financial support to initiate the project, and to later expand the network to include participants from eastern European countries. The project also received financial support from the Institut Mondiale du Phosphate (IMPHOS) to carry out standard characterization of the soils and PRs utilized in the project and to field test PRs of known reactivity.

F. Sikora edited the TECDOC for publication. The IAEA officer responsible for this publication was F. Zapata of the Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture.

EDITORIAL NOTE

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SUMMARY

Most acid soils of the tropics and subtropics show a widespread phosphorus (P) deficiency and high P sorption capacity, and therefore require substantial P inputs for optimum plant growth and production of food and fiber. Manufactured water-soluble P fertilizers such as superphosphates are commonly recommended to correct P deficiency, but most developing countries import these fertilizers, which are often in limited supply for resource-poor farmers. In addition, sustainable intensification of agricultural production in these regions necessitates the addition of P inputs not only to increase crop production but also to improve soil P status to avoid further soil degradation. Therefore, it is imperative to explore alternative P inputs. In this context, the use of phosphate rocks is particularly attractive under some conditions to develop an effective and economic phosphate management program.

Geological deposits of phosphate-bearing minerals are distributed worldwide. Phosphate rock (PR) deposits have been found in many developing countries of Asia, Africa and Latin America. However, few large deposits are commercially mined for use as raw materials for manufacturing P fertilizers. The use of locally available resources is an important factor in the development of a sustainable agriculture. Their use for direct application as a finely-ground product, though recommended, is not practiced in these regions due to the lack of adequate information on the reactivity of the PRs (potential for direct application) as well as their agronomic effectiveness (P supply to soils and crops). It is well known that the PRs show different reactivity as a result of their extremely variable chemical and mineralogical composition. In addition to P, they also contain a wide range of chemical elements, some of which are beneficial (nutrient supply), while others have long term harmful effects.

The agronomic effectiveness (capacity of P supply to crops) of PRs depends not only on inherent factors, but also on the soil conditions and plants/crop genotypes utilized. In terms of improving the soil P status, they have both immediate and residual effects, which can be better measured in a crop rotation or within a cropping systems context. To optimize their utilization as alternative P sources, it is necessary to develop and utilize new technologies to enhance the agronomic effectiveness of less reactive PRs. In some cases, this is done through chemical processing such as partial acidulation and the preparation of compacted granulated formulations of mixtures of PR and superphosphate. There is also the potential to utilize biological approaches such as selected plant genotypes, which possess better natural or improved mechanisms in the rhizosphere for P acquisition from PRs; incorporation of organic residues and agro-wastes together with PRs; inoculation with improved micro-organisms, etc.

In addition to conventional techniques, the radioisotope ^{32}P was employed as a tracer in several studies at different stages of the project to obtain quantitative and precise information on the dynamics of P in the soil when amended with PRs and water-soluble P fertilizers (^{32}P isotopic exchange kinetics) and the value of management practices employed to enhance the agronomic effectiveness of PRs in greenhouse and field studies (^{32}P isotope dilution techniques such as L and A values). The utilization of these techniques required trained technical staff with skills and expertise and laboratory facilities for handling and measuring the radioisotope. The required support in terms of research, training and analytical services was provided by the FAO/IAEA Agriculture and Biotechnology Laboratory, Seibersdorf, Austria, and the “Centre d’Etudes Nucleaires”, Cadarache, France.

Within the above context, a Co-ordinated Research Project on “The Use of Nuclear and Related Techniques for Evaluating the Agronomic Effectiveness of Phosphatic Fertilizers, in Particular Rock Phosphates” was implemented during the period 1993-1998. The main objectives of this project were:

(a) To assess the initial available soil P status and fertilizer-induced changes when amended with PR products and water-soluble P fertilizers in a variety of agro-ecosystems using conventional (chemical) and isotopic techniques.
(b) To quantitatively evaluate the uptake and utilization of P fertilizers, in particular PR-based products by crops grown under a variety of soil and climatic conditions. Thus, the project aimed to evaluate the agronomic effectiveness of natural PR deposits and where necessary, finding ways/means of enhancing their effectiveness.
(c) To obtain agronomic and economic recommendations on the use of P fertilizers, in particular PR-based products in acid soils.

The work plan of the project was implemented in a logical sequence in three phases. Few of the research projects included all three phases. However, depending on the availability of resources and staffing, each project had aspects of P research tailored to local needs and conditions. In its initial phase the project activities focused on the first objective to evaluate the performance of routine chemical methods for assessing available P in soils amended with PR products and water-soluble P fertilizers. The participants to characterize soil P dynamics parameters using the ^{32}P isotope exchange technique collected more than 100 soil samples. Available soil P was determined by the routine chemical (extraction) method utilized in each country. Other methods such as resin and iron strips were also tested. The core activities of the project were implemented during the second phase. Most participants carried out preliminary experiments in the greenhouse to evaluate the agronomic potential of local and imported PR sources using the ^{32}P isotope dilution and conventional techniques. Technological and biological approaches to enhance the agronomic effectiveness of PRs were also investigated. During the final phase, some participants conducted field experiments to gather information on the agronomic effectiveness of PRs under a variety of soil and climatic conditions. PRs of known reactivity were provided by IMPHOS. A minimum data set was collected for validating the P submodel of the DSSAT family of crop models.

The research network comprised 12 contract holders from Brazil, Chile, China, Cuba, Ghana, Indonesia, Kenya, Malaysia, Romania, Thailand, Venezuela and Vietnam; and 6 agreement holders from USA (IFDC and University of Kentucky), France (CIRAD and CEN, Cadarache), Australia (CSIRO) and Spain (CSIC, Granada). During the final phase of the project, five contractors from Belarus, Hungary, Lithuania, Poland and Russian Federation were incorporated.

The results obtained in the project provided new information on the chemistry of soil P, tests for available soil P, phosphate nutrition of crops, agronomic effectiveness of PRs and P fertilizer recommendations with particular emphasis on the utilization of PR sources. Due consideration was also given to environmental issues. The research results are summarized according to the objectives of the Project with an additional Section for the eastern European studies.

Soil P availability studies, including environmental issues related to PR application

The performance of several chemical extraction methods for determining available soil P was studied using the ^{32}P isotopic exchange kinetics method as the reference. The majority of soils in the study were Ultisols, Inceptisols and Oxisols. With regard to the chemical extractants, it was found that in most cases Bray 1, Bray 2, Oniani, Mehlich I, Mehlich III over-estimated available P in PR-amended soils compared with water-soluble P fertilized soils while E_1 (isotopic), resin, Olsen, Pi strip, 0.5N NaOH, NH_4^+ hepta-Molybdate, and Colwell provided good estimates of P availability in PR-amended soils compared with water-soluble P fertilized soils. In the high P-fixing Oxisols in Brazil, Bray 1 and Mehlich III performed well in PR-amended soils. In near neutral Alfisols of Cuba, Bray 1 underestimated P availability in PR-amended soils compared with water-soluble P fertilized soils.

It was concluded that there is no single soil P test that can be universally used to estimate available P in soils amended with PR and water-soluble P fertilizers. The Pi test works well in determining available soil P in soils amended with either PR or water-soluble P fertilizer, as evidenced by laboratory and greenhouse studies at IFDC and comparisons with E_1 (Malaysia). A modification of the method was made using 0.02 M KCl instead of 0.01 M $CaCl_2.2H_2 0$ for use in soils treated with PR and superphosphate. Precautions need to be taken to avoid background P concentrations in the reagents utilized and to completely remove any soil particle from the strips.

The ^{32}P isotopic exchange kinetic method was very valuable to assess P dynamics in soil with or without the addition of P fertilizer. It provides a good description of soil P status, i.e. intensity $(C_{p)}$, quantity (E_1) and capacity (Q) factors. The soil P fixation capacity can also be also determined from these measurements. The evaluation made after about one month of incubation of soil and P fertilizer can be used to predict the agronomic effectiveness of P fertilizers. Furthermore, the method can be used to identify various kinetic pools of soil P and their changes with time. This isotopic method was applied to almost all soils used in the network. The technique needs to be properly adjusted according to the soil type. The quantity parameter E_1 was used as a reference value for comparisons in P availability studies. Errors were found to be significant in determining E_1 values due to very low C_p values that can occur in low available P or high P-fixing soils (Australia, Chile, China, Venezuela).

It was concluded that the criteria for a “good” chemical extractant method for available soil P are: rapid, reproducible, sensitive to changes in Quantity and Intensity, and extract a similar proportion of bioavailable P (Q/I) across a range of crops, soils and management practices. Further P availability studies with tropical acid soils need to be done and several recommendations were also made to perform these.

The plant-availability and soil loading effects of fluorine, Cd and other heavy metals in soils amended with PRs and water-soluble P fertilizers need to be addressed in long term field studies. In the short term, Cd availability to plants grown on soils amended with PR is lower than in soils amended with fertilizer products formed from PR acidulation. A continual application of reactive PRs to pastures in Australia resulted in fluoride accumulation in the top-layer of the soil, although the herbage F concentrations were not affected by fertilizer type or soil/site factors. Further studies are needed to follow the potential of F toxicity to animals. The plant concentrations of the radionuclides ^{90}Sr and ^{137}Cs was reduced in Chernobyl contaminated soils amended with PRs. Further research is needed to study the specific mechanisms for this effect. Reactive PR-amended soils showed decreased soil acidity and increased exchangeable Ca, thus showing some remediating effect on low buffer capacity, highly weathered, acidic soils.

Evaluation of the relative agronomic effectiveness of PR products

Greenhouse and field evaluation studies were carried out using conventional and ^{32}P isotope dilution methods. The relative agronomic effectiveness (RAE) was measured in terms of response (dry matter, total P uptake or P derived from the fertilizer) with a standard fertilizer for comparison, usually triple superphosphate. Also the AE was evaluated through the use of substitution ratios, i.e. the number of kg P as PR, which are equivalent to 1 kg P as superphosphate. Initial work evaluated the AE of natural PRs, in particular those locally available and follow-up investigations studied several processes to enhance their AE. The results were analyzed in relation to the main factors affecting the AE of the PRs for direct application as follows:

- Inherent characteristics of the PR: Most PRs used in the network were of sedimentary origin. The most important characteristic for determining the PR reactivity was the P solubility of the PR, which depends on the degree of the carbonate isomorphic substitution for phosphate in the apatite structure. This information can be obtained from the mineralogical analysis and total chemical composition or the solubility indices, as measured by 2% citric acid or 2% formic acid.
- Soil characteristics: The main soil groups included in the evaluation tests were in order of importance: Ultisols, Inceptisols, and Oxisols and to a lesser extent Alfisols, Mollisols, and Spodosols. It was found that the utilization of PR is most effective in soils of low pH (less than 5.0), low available soil P, high CEC, and low exchangeable Ca and high organic matter content. These soil characteristics greatly affect the dissolution of PRs and consequently their effectiveness.
- Plant factors: The RAE of natural PR and modified PR products depends on the rate of P applied and crop species. Phosphate rocks were found to be more effective with crops having a long growth cycle, or subsequent crops of a rotation, nitrogen fixing crops, and crops with root systems that can release/exudate organic acids such as canola, lupin, etc. The strategy recommended was to identify species/crop cultivars/lines that can efficiently use the P from PRs and include them in the crop rotation for improving the P status of the overall soil/plant system.

Low to medium reactive PRs are not suitable for direct application to crops but their AE can be greatly enhanced by preparing modified products through partial acidulation (PAPR), granulating PR and superphosphates or preparing mixtures of PR with a water-soluble P source or organic materials, as shown by work carried out in Venezuela (Ultisol and Oxisol), China (Ultisol), Cuba (Alfisol), Brazil (Ultisol and Oxisol), and Thailand (Ultisol). The enhancement effect of a water-soluble P fertilizer on the P uptake from a medium reactive PR by maize and cowpea was also demonstrated by means of ^{32}P isotopic techniques in the USA (Ultisol).

The AE of PR can be also enhanced through biological approaches such as: (i) the identi-fication of suitable plant genotypes with efficient P acquisition and their inclusion in crop rotations, as done in China and Chile; (ii) the inoculation of trees with mycorrhizal fungi and P solubilizing bacteria, as shown by the work done in Spain (shrubs) and Kenya (small N-fixing trees); (iii) the use of mixtures of PRs with composting/fermentation products of agrowastes; and (iv) the AE of PRs can be further increased by mycorrhizal fungi inoculation, as shown by work done in Spain. Here again several areas of further research were identified and recommended.

Field evaluation of PR products

The final evaluation of the PR products was made in a network of field experiments in selected locations (benchmark soils) to study the interactive effects of soil, climate, and crop management factors on the AE of the PRs. These experiments, although laborious and time-consuming, should be established in farmers' fields (on-farm trials) or in fields close to farmers' conditions. They should be done at the cropping system level to gather information on the immediate and residual effect of PRs on the actual yield response and to evaluate the economic benefits. Field experiments were also carried out to validate the P submodel for integrating basic PR, soil, plant and climatic factors and for extrapolating the results to other agro-ecological conditions. A set of data from these experiments was collected and a database was created to validate the P submodel.

Field experiments were carried out under rain-fed conditions on a wide variety of soil types, the majority being acid soils (pH less than 5.5) with low available P, and also under diverse climatic conditions ranging from tropical to temperate. The evaluation of PRs was made utilizing specific plant/crop species, for instance maize (Venezuela, Hungary), sorghum (Venezuela), sugar cane (Cuba), lowland rice (Indonesia), upland rice (Brazil), soybean (Brazil), common bean (Cuba), cowpea (Brazil), winter wheat (Hungary), pastures (Australia), buckwheat (China), barley (Russian Federation, Lithuania, Hungary), peas (Hungary), beet (Lithuania), Eucalyptus (Brazil), pine (USA), fast-growing trees (Kenya) or crop rotations/cropping systems such as soybean-maize rotation (Thailand), wheat-maize-soybean rotation (Romania), alfalfa/corn intercrop (Spain), rice-soybean-mungbean rotation (Indonesia). The application of PR and water-soluble P fertilizers gave a good yield response. Evaluation criteria other than dry matter, grain yield, and P uptake were also estimated in some studies such as the ability of PR to reclaim disturbed, acidic land and the uptake of Cd, F, and radionuclides such as ^{137}Cs and ^{90}Sr in Chernobyl-contaminated areas. The field experiments confirmed the efficacy of the ^{32}P isotopic techniques in providing precise and quantitative information on P uptake by plant from various PR sources and for assessing differences between the experimental treatments. Recommendations for the continuation of ongoing experiments and further field studies were made. Some of these will be undertaken in the follow-up co-ordinated research project on tropical acid soils.

Phosphate studies in eastern Europe

Five contractors from this subregion joined the project in 1996. Incubation studies were conducted with soil samples amended with soluble P fertilizers and PR, and the fate and behavior of the applied P was followed with the routine soil P testing (chemical) methods. In one study (Poland), a comparative assessment of the routine method was made utilizing the ^{32}P isotope exchange kinetics technique as a reference.

In most countries, greenhouse experiments were carried out with different soils, crops and P fertilizer treatments to evaluate the efficiency of locally available P fertilizer sources. No significant differences in the efficiency of superphosphate and reactive, finely-ground PR sources were found in acid soils, mostly Spodosols. In some countries, field experiments were either established or continued (long term trials) to compare different sources of P. Results similar to the greenhouse experiments were found. Greenhouse and field experiments were carried out in Byelorussia and Russia to investigate the effect of P fertilizers as a counter-measure on plant uptake of the radionuclides ^{90}Sr and ^{137}Cs from Chernobyl- contaminated soils. The application of P fertilizers including PR sources reduced by 1.2 fold the ^{137}Cs concentration and up to 2 times the ^{90}Sr concentration in barley plants. Further studies are needed to confirm this finding and investigate the mechanism involved.

The participation of these contractors in the CRP contributed substantially to enhance their knowledge and expertise on P fertilization and updating of methods for soil P testing through exchange of information and collaborative links with well-established laboratories in phosphate research.

Concluding remarks

The study of the dynamics of soil P, in particular the “plant-available P” over time is an essential pre-requisite for providing adequate P fertilizer recommendations and to evaluate the benefits derived from the applied P fertilizer. Several routine soil P tests and ^{32}P exchange kinetic methods were utilized to assess the bioavailable P in soils amended with PR and water-soluble fertilizers. No single chemical extraction method was found suitable for all soils and fertilizers. The Pi strip method showed promising results but more work is needed with tropical acid soils. The ^{32}P exchange kinetics method allowed a complete characterization of the P dynamics in the soil and provided basic information for modeling the dynamics of soil P. This technique has been further refined for use in tropical acid soils.

The agronomic effectiveness of PR was mainly dependent on solubility (reactivity), which is related to the degree of carbonate substitution for phosphate in the apatite structure. Rock phosphates with low reactivity are unsuitable for direct application to annual crops. Research carried out in Venezuela, China, Cuba, Brazil, and Thailand demonstrated that AE could be increased by partial acidulation or by mixing with organic materials or a water-soluble source. AE can be also enhanced through biological approaches involving inoculation with mycorrhizal fungi and rhizobacteria. The AE of PR was also dependent on crop species, being particularly effective on crops such as canola and lupin, which exude organic acids from their roots. The AE of PR is higher on soils with low pH, low available P, low exchangeable Ca, high cation exchange capacity and high organic matter content. The ^{32}P isotopic techniques were a powerful tool to determine these main factors affecting the AE of PRs.

From the data obtained from field experiments and the standard characterization of PRs and soils used in the network, a database was created. The tested P submodel was found to be unsuitable for the experimental work of the project. It is therefore, necessary to develop a simple model for a decision support system for direct application of PRs. In this context, due consideration should be given to socio-economic criteria for adoption of the recommended PR technologies. Further field studies on P cycling and budgets/balances in cropping systems are needed to validate the new model. Also, the proper characterization of soils and PR materials is required to have a clear understanding of the factors influencing the AE of PR products and to provide adequate recommendations for their direct application.

Investigations carried out in this Project have demonstrated the potential for using PR sources as alternative P inputs. ^{32}P isotope techniques are invaluable tools not only to provide unique information on the soil P dynamics but also to develop novel technologies to enhance the agronomic effectiveness of natural and modified PR materials. Thus, ^{32}P isotope techniques were utilized to get a better understanding of the behavior of P in the soil-plant system and as a reference for conventional techniques.

Particularly noteworthy was the success in identifying technologies for enhancing the AE of less reactive PR sources. Several chemical and biological approaches were tested and found to be effective in enhancing the AE of PRs in acid soils, but work remains to investigate other approaches or combinations at the cropping system level. The findings of this project are relevant to the follow-on CRP on Tropical Acid Soils, which will continue this research but in a broader context with focus on the savannas of Africa and Latin America. The employment of PRs combined with suitable acid-tolerant and P-efficient plant genotypes would be a key component for improving the soil fertility status and developing sustainable agricultural production systems in the sub-humid and humid tropics.

Part I

STANDARD CHARACTERIZATION STUDIES

STANDARD CHARACTERIZATION OF PHOSPHATE ROCK SAMPLES FROM THE FAO/IAEA PHOSPHATE PROJECT

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Abstract. Phosphate rocks (PR) are phosphate-bearing minerals that vary widely in their inherent characteristics and consequently their agronomic potential. In the framework of a FAO/IAEA networked research project, the evaluation of the agronomic effectiveness of natural and modified PR products under a variety of soil climate and crop management conditions was carried out. The characterization of phosphate rocks is the first and essential step in evaluating their suitability for direct application. If several PR sources are utilized, standardized methods should be used for comparison purposes to determine their agronomic potential. This paper describes the standard characterization of phosphate rock products utilized in the project, in particular the mineralogical and crystallographic analyses, physical analyses, chemical composition and solubility in conventional reagents. A total of 28 phosphate rock samples from 15 countries were collected and analyzed in specialized laboratories. The data on mineralogy, chemical composition and solubility in conventional reagents are closely interrelated. An arbitrary classification of the reactivity of the PR samples was made based on the solubility indices in conventional reagents. On another hand, the results of the crystallographic parameters, calculated indices of absolute solubility, specific surface and porosity reflect the variability of the physical state and the sample pre-conditioning treatment of the analyzed products. A proper characterization of phosphate rock samples should provide the maximum of basic information that can be obtained in a cost-effective manner in normal chemical laboratories. Based on the results of this characterization, the following determinations are recommended: a description of the sample, major elemental (total P, Ca, Mg) composition, solubility in conventional reagents (neutral ammonium citrate, citric and formic acid) and particle size analysis. The classification of PR samples for direct application as fertilizers requires the definition of standards. It should be noted that the European standards are very strict with regard to solubility and particle size. The studies carried out under this project are part of the efforts to provide some guidelines for the provision of such standards in other environmental conditions, in particular tropical acid soils. Follow-up studies are required to evaluate the agronomic effectiveness of the PR, i.e. actual performance of the PR under study as affected by a specific set of soil, crop, climate and management conditions. In a final phase, it would be required to relate the results agronomic potential from the study with those of actual agronomic effectiveness and several other socioeconomic criteria for developing adequate Decision Support Systems for PR application.

1. INTRODUCTION

In many acidic soils in developing countries, P deficiency is the main limiting factor for crop production and, therefore, requires the application of P fertilizers for optimum plant growth and production of food and fibre. However, in most developing countries superphosphates, which are the commercially available phosphatic fertilizers, are not produced locally and their supplies to resource-poor farmers is rather limited [1]. On the other hand, many developing countries possess deposits of phosphate rock (PR) minerals [2]. Many years of research have shown that PR can be used for direct application in agriculture and it is most effective when used in acid P-deficient soils. [3]. As this is commonly the case in most tropical soils, direct application of PR is considered an agronomic and economically attractive alternative to the use of more expensive water-soluble P fertilizers such as superphosphates [1, 4].

Considering the direct application of PR products, several factors affect their agronomic effectiveness or their capability to supply phosphorus to crops. These have been extensively described in several reviews for temperate [3] and tropical agriculture [1]. The various factors may be grouped into three main categories, i) inherent PR factors, ii) soil factors and iii) plant factors. The PR products or materials differ widely in their geological origin, mineralogical, chemical and physical properties and consequently in their effectiveness [1, 5, 6]. It is, therefore, essential to identify and select PR products of good quality and suitable for direct application, in particular to tropical acid soils [7].

In the frame of the FAO/IAEA networked research project on "The use of nuclear and related techniques for evaluating the agronomic effectiveness of P fertilizers, in particular rock phosphates" the agronomic effectiveness of natural and modified PR products was evaluated under different soil, climate and crop conditions [8]. In addition to the individual characterization studies performed by the participating investigators, a standard characterization of the soils and PRs employed in the project was carried out with financial support of the World Phosphate Institute. The standard characterization was conducted to obtain direct and comparable information on the suitability of PRs for direct application and to better interpret the results from the agronomic evaluation, including the creation of a database for using a phosphate model.

This paper describes the standard characterization of phosphate rock products utilized in the project, in particular the mineralogical and crystallographic analyses, the chemical composition and solubility in conventional reagents, and the physical analyses. The results are synthesized and additional correlation studies are presented. Also, guidelines for their characterization are given.

2. MATERIALS AND METHODS

A total of 28 phosphate rock samples from 15 countries were collected for mineralogical as well as chemical and physical analyses (Table I). From these, two were granulated, 11 ungrounded and 15 ground samples. The exact origin of the products, and the treatments performed, if any, were not specified. Eight extra samples (2 PRs from Venezuela and 6 imported PRs from Malaysia) were received only for mineralogical characterization.

The majority of samples were reported to be phosphate rocks of commercial grade, after washing or beneficiation. Some have been directly obtained from the mine deposits, others have undergone some manufacturing process such as partially acidulation (Venezuela) or fusion (Brazil).

The chemical analyses, including solubility in conventional reagents and the physical analyses (particle size, specific area and porous volume) were performed at the "Centre d'Etudes et de Recherches des Phosphates Minéraux", CERPHOS, Casablanca, Morocco [9]. The specific methods used are indicated in Table II. The mineralogical and crystallographic determinations were made at the "Centre de Recherches Pétrographiques et Géochimiques" of the "Centre National de Recherches Scientifiques" (CNRS), Nancy, France, by X-ray diffraction on compacted, non-oriented powder preparations. A total of 32 samples were analysed for mineralogical content.

3. RESULTS AND DISCUSSION

The results from the analyses performed on the PR samples have been grouped according to the type of analyses.

First of all, it should be noted that the available general information on the phosphate rock samples is very poor and incomplete. In many countries phosphate rocks are not available on a commercial scale. A description of the phosphate rock should include the origin of the rock sample (country and location of the deposit), type of deposit (geological formation), and pre-treatment/conditioning of the sample, if any, i.e. washing, grinding, beneficiation, heating, degree and kind of acidulation, granulation, etc. Most of this information can be obtained from the supplier.

The full set of analytical data for the mineralogical and crystallographic determinations, chemical and solubility in conventional reagents and textural analysis is not given in this paper. Rather, the summary tables from these results are presented and discussed.

3.1. Mineralogy

The main mineral content of the PR samples is shown in Table III. Apatite is the predominant mineral averaging 75%, ranging from 46–56% (China-Jingxiang, Russia, Brazil-Patos) to 90-95% (Togo 1, Morocco 2, Tunisia 2). These values are roughly equivalent to the percentage P_2O_5 content (Table VII).

Two other minerals of interest to agriculture are calcite and dolomite as sources of Ca and Mg. A relatively high content of calcite is observed for Morocco 3, Jordan 1, and Jordan 3 (14%) and Venezuela-Monte Fresco (28%). Dolomite content is high in Thailand-Racha Buri (34%), Morocco 1 (22%), and China-Jingxiang (21%), resulting also in high contents of CaO and MgO (Table VI). It is expected that these phosphates when applied in acidic soils would produce an important liming effect due to its Ca and Mg supply [10, 11].

Conversely, useless silica (quartz) contents are high in Russia PR (40%), Venezuela-Navay (35%), Brazil-Patos (30%) and China-Jinning (27%), Venezuela-Riecito (24%) and China-Jinxiang (23%). This mineral constitutes generally an exogangue, and needs to be removed in order to increase the P_2O_5 content of the final product and to decrease transportation and grinding costs [12, 3].

TABLE I. LIST OF PHOSPHATE ROCK (PR) SAMPLES UTILIZED IN THE PROJECT

PR Denominations	Country/Origin	Source	Analysis
ALGERIA	Algeria	IMPHOS	MINER/CHEM/PHY
MOROCCO 1	Morocco	IMPHOS	MINER/CHEM/PHY
MOROCCO 2	Morocco	IMPHOS	MINER/CHEM/PHY
MOROCCO 3	Morocco	IMPHOS	MINER/CHEM/PHY
TUNISIA 1	Tunisia	IMPHOS	MINER/CHEM/PHY
TUNISIA 2	Tunisia	IMPHOS	MINER/CHEM/PHY
TUNISIA 3	Tunisia	IMPHOS	MINER/CHEM/PHY
JORDAN 1	Jordan	IMPHOS	MINER/CHEM/PHY
JORDAN 2	Jordan	IMPHOS	MINER/CHEM/PHY
JORDAN 3	Jordan	IMPHOS	MINER/CHEM/PHY
SENEGAL	Senegal	IMPHOS	MINER/CHEM/PHY
MINJINGU	Tanzania	IMPHOS	MINER/CHEM/PHY
TOGO 1-COMMERCIAL	Togo	IMPHOS	MINER/CHEM/PHY
TOGO 2-HIBOGAN	Togo	IMPHOS	MINER/CHEM/PHY
PATOS	Brazil	Participant CRP	MINER/CHEM/PHY
YOORIN	Brazil	Participant CRP	CHEM
BAHIA INGLESA	Chile	Participant CRP	MINER/CHEM/PHY
TRINIDAD DE GUEDES	Cuba	Participant CRP	MINER/CHEM/PHY
NAVAY	Venezuela	Participant CRP	MINER
RIECITO	Venezuela	Participant CRP	MINER/CHEM/PHY
RIECITO PAPR	Venezuela	Participant CRP	CHEM
MONTE FRESCO	Venezuela	Participant CRP	MINER
MAARDU	Estonia/Lithuania	Participant CRP	MINER/CHEM/PHY
POLPINO	Russia	Participant CRP	MINER/CHEM/PHY
JINGXIANG	China	Participant CRP	MINER/CHEM/PHY
JINNING	China	Participant CRP	MINER/CHEM/PHY
RACHA BURI	Thailand	Participant CRP	MINER/CHEM/PHY
PETCHA BURI	Thailand	Participant CRP	MINER/CHEM/PHY

TABLE II. LIST OF STANDARDS METHODS FOR PR SAMPLES OF DIRECT APPLICATION

Chemical Element	Method
P_20_5 TOTAL ISO 6598	Dissolution of the sample using hydrochloric-nitric acid digestion. After dissolution, precipitation of the orthophosphate ions as quinoleine phospho-molibdate, the acid solution is passed at about 75°C through a filter, washed, dried with acetone. The obtained precipitate is weighed.
CaO	Dissolution of the sample using perchloric acid. The calcium is chelated in alcaline medium using excesss amounts of EDTA. This excess is titrated with a calcium solution of known concentration in the presence of magnesium to make the change more visible.
MgO	Dissolution of the sample using perchloric acid digestion. Measurement of the magnesium content, by Atomic Absorption Spectrometry (AAS) with an air/acetylene flame , in presence of lanthanum nitrate as matrix modifier and at a wave length of 285.2 nm, or alternatively by Inductively Coupled Plasma-Emission Spectrometry (ICP-ES).
K_2O	Dissolution of the sample using perchloric acid digestion. Measurement of the potassium content by AAS with an air/acetylene flame at a wavelength of 766.5 nm, or alternatively by ICP-ES.
Na_2O	Dissolution of the sample using perchloric acid digestion. Measurement of the sodium content by AAS with an air/acetylene flame at a wavelength of 766.5 nm, or alternatively by ICP-ES.
Fe_2O_3	Dissolution of the sample using perchloric acid digestion. Measurement of the iron content by AAS with an air/acetylene flame at a wavelength of 372 nm, or alternatively by ICP-ES.
Al_2O_3	Dissolution of the sample using perchloric acid digestion. Measurement of the aluminium content by AAS with an air/acetylene flame at about a wavelength of 309.3 nm, or alternatively by ICP-ES.
SiO_2	Dissolution of the sample using hydrofluoric acid digestion. Measurement of the silica content by AAS with a nitrous oxide/acetylene flame at a wavelength of 251 nm.
SO_3	Dissolution of the sample using perchloric acid digestion. The concentration of sulphates is determined either by turbidity (precipitation of $BaSO_4$ by the reaction of sulphate ions present in the solution and a calibrated $BaCl_2$) or by ICP-ES.
Cu	Dissolution of the sample using perchloric acid digestion Measurement of the copper content by AAS in an air/acetylene flame at a wave length of 324.8 nm or alternatively by ICP-ES.
Mn	Dissolution of the sample using perchloric acid digestion. Measurement of the manganese content by AAS in an air/acetylene flame at a wave length of 279.5 nm or alternatively by ICP-ES.

TABLE II (CONTINUED)
LIST OF STANDARDS METHODS FOR PR SAMPLES OF DIRECT APPLICATION

Chemical Element	Method
Zn	Dissolution of the sample using perchloric acid digestion Measurement of the zinc content by AAS in an air/acetylene flame at a wave length of 213.9 nm, or alternatively by ICP-ES.
Cd	Dissolution of the sample using perchloric acid digestion Measurement of the cadmium content by AAS in an air/acetylene flame at a wavelength of 228.8 nm, or alternatively by ICP-ES.
Cr	Dissolution of the sample using perchloric acid digestion Determination of the chromium content by ICP-ES or alternatively by colorimetry (in acid medium the bichromate ions $Cr_2\ O_7$ produce in reaction with diphenylcarbazide a violet color that is measured by Spectrophotometry at a wavelength of 540 nm).
Ni	Dissolution of the sample using perchloric acid digestion Measurement of the nickel content by AAS in an air/acetylene flame at a wave length of 232 nm, or alternatively by ICP-ES.
F	Dissolution of the sample by nitric acid. Determination of the fluorine concentration with an ionometer using a fluoride specific electrode.
Solubility test citric acid/ formic acid (EEC Method)	Extraction of phosphorus from ground and sieved (to 63 microns) phosphate samples using citric acid or formic acid solution while shaking at a temperature of about 20°C.
Solubility test citric acid (New Zealand Meth.)	Extraction of phosphorus from ungrounded phosphate samples with a solution of citric acid while shaking at a temperature of about 20°C.

3.2. Crystallography

The results of *a* and *c* axes of the hexagonal crystal of the apatite contained in the PR samples are presented in Table IV. The unit cell *a* dimension is indicative of the degree of carbonate substitution for phosphate, decreasing as the mole ratio of CO_3/PO_4 increases. Thus, the axis is a key factor determining the chemical reactivity of the PR containing carbonate apatite [13, 6].

The composition of carbonate-apatites can be expressed by the following general formula [14, 5]:

$Ca_{10-i-j}\ Na_i\ Mg_j\ (PO_4)_{6-x}\ (CO_3)_x\ F_{2+0.4x}$
where, Ca can be substituted by Na and Mg,
and PO_4 can be substituted by CO_3 and F.

These isomorphic substitutions modify the crystallographic parameters. A particular feature is the F content. The PR with a high degree of isomorphic substitution of carbonate for phosphate has a F content near or higher than that of theoretical fluor-apatite to charge balance the replacement of carbonate for phosphate [15].

TABLE III. MINERALOGICAL COMPOSITION OF PHOSPHATE ORES (IN %)

Phosphates	Apatite	Calcite	Dolomite	Quartz	Feldspar	Kaolinite	Mica
Algeria	84		10	2.5			
Morocco 1	65		22	12			
Morocco 2	93		1.5	2.5			
Morocco 3	82	14					
Tunisia 1	85	2	3	3			
Tunisia 2	90	4	1.5	1.5			
Tunisia 3	85	6	1	6			
Jordan 1	70	14		12			
Jordan 2	80	4		11			
Jordan 3	73	14		11			
Senegal	83	3		11			
Minjingu	80	3					
Togo 1, Commercial	95			3			
Togo 2, Hibogan	80			13		1.5	
Brazil 1, Patos	55			30	2	2.5	5
Bahia Inglesa	62			18	13		1.5
Trinidad de Guedes	85	2.5		7			
Riecito	70	1		24	5		
Monte Fresco	65	28		7			1
Navay	60			35	2.5	1.5	
Maardu	70	3.5	5.5	17	1		
Polpino	56			40			2
Jingxiang	46	8	21	23	1		
Jinning	58		11	27			3
Malaysia - Jordan	85	7		7			
Malaysia - China	80		4.5	13			2
Malaysia - Tunisia	82	4	4.5	2.5			
Malaysia - N. Carolina	90			6.5			
Malaysia - Christmas Island	88		2				
Malaysia - Morocco	85	8	1.5	1.5			1.5
Thailand - Racha Buri	50	3	34	6		2	
Thailand - Petcha Buri	85	8					1.5

From the value of the *a* axis it is possible to calculate the coefficients of the general formula, using the following empirical relations:

$$a = 9.374 - 0.204\ [x/(6-x)]$$

$$CO_3/PO_4 = [x/(6-x)]$$

$$i = 1.327\ [x/(6-x)]$$

$$j = 0.515\ [x/(6-x)]$$

Table V shows the calculated empirical formulae of the different apatites under study. All but three PR samples (Morocco 3, Jordan 1 and Russia) show different degrees of isomorphic substitution in their structure confirming their carbonate apatite nature. It may be also noted that the ratio CO_3/PO_4 increases in the PRs with high CO_3 isomorphic substitution as well as the F content. Almost all, except those mentioned above, can be considered as “excess fluorine” PRs because they contain fluorine in excess of the two moles per formula weight [15]. However, they do not exceed three that may cause injury to grazing stock through fluorosis.

TABLE IV. CRYSTALLOGRAPHIC PARAMETERS OF APATITES (UNIT CELL DIMENSION IN ANGSTROMS, Å)

Phosphates	a axis	c axis
Algeria	9.339	6.904
Morocco 1	9.360	6.904
Morocco 2	9.339	6.896
Morocco 3	9.366	6.904
Tunisia 1	9.346	6.904
Tunisia 2	9.353	6.904
Tunisia 3	9.339	6.900
Jordan 1	9.366	6.904
Jordan 2	9.353	6.900
Jordan 3	9.353	6.900
Senegal	9.391	6.904
Minjingu	9.339	6.888
Togo 1, Commercial	9.384	6.896
Togo 2, Hibogan	9.377	6.904
Patos	9.394	6.888
Bahia Inglesa	9.339	6.892
Trinidad de Guedes	9.318	6.884
Riecito	9.415	6.904
Monte Fresco	9.394	6.908
Navay	9.380	6.900
Maardu	9.394	6.900
Polpino	9.366	6.912
Jingxiang	9.377	6.888
Jinning	9.349	6.884
Malaysia - Jordan	9.366	6.904
Malaysia - China	9.387	6.896
Malaysia - Tunisia	9.339	6.900
Malaysia – N. Carolina	9.339	6.892
Malaysia - Christmas Island	9.394	6.896
Malaysia - Morocco	9.360	6.904
Thailand - Racha Buri	9.391	6.890
Thailand - Petcha Buri	9.429	6.896

Several authors have attempted to relate chemical reactivity of sedimentary apatites to their mineralogical characteristics. Thus, indices of absolute solubility, which are defined as the ratio between the percentages of soluble P in a given reagent (neutral ammonium citrate, citric acid, formic acid) to the total P content of the apatite, can be calculated. By this way, the variations in the apatite content of the ores, and the P content in the apatite can be eliminated. Based on a study with 50 phosphate rocks, using the same *a* axis the following relations have been proposed to estimate indices of absolute solubility [14]:

Neutral ammonium citrate = $421\ (9.369 - a)$
Citric acid = $611\ (9.378 - a)$
Formic acid = $1.091\ (9.376 - a)$

TABLE V. EMPIRICAL FORMULAE OF APATITES

Phosphates	Ca	Na	Mg	PO_4	CO_3	F	CO_3/PO_4
Algeria	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Morocco 1	9.875	0.090	0.035	5.614	0.385	2.154	0.069
Morocco 2	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Morocco 3	9.929	0.051	0.020	5.773	0.226	2.090	0.039
Tunisia 1	9.749	0.181	0.070	5.275	0.724	2.289	0.137
Tunisia 2	9.813	0.135	0.052	5.439	0.560	2.224	0.103
Tunisia 3	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Jordan 1	9.929	0.051	0.020	5.773	0.226	2.090	0.039
Jordan 2	9.813	0.135	0.052	5.439	0.560	2.224	0.103
Jordan 3	9.813	9.135	0.052	5.439	0.560	2.224	0.103
Minjingu	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Bahia Inglesa	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Trinidad de Guedes	9.496	0.363	0.141	4.707	1.292	2.516	0.274
Polpino	9.929	0.051	0.020	5.773	0.226	2.090	0.039
Jingxiang	9.778	0.161	0.062	5.344	0.655	2.262	0.123
Malaysia - Jordan	9.929	0.051	0.020	5.773	0.226	2.090	0.039
Malaysia - Tunisia	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Malaysia - N. Carolina	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Malaysia - Morocco	9.875	0.090	0.035	5.614	0.385	2.154	0.069

The data on calculated indices of absolute solubility using the "*a* axis" of PR are presented in Table VI. Based on these criteria, the most reactive PR products were Trinidad de Guedes from Cuba, followed by Algeria, Morocco 2, Tunisia 3, Tanzania, and Chile. It should be also noted that there were some limitations to these calculations. From a total of 33 determinations of the *"a* axis", only 19 could be used. The other values were higher than 9.374 Å and, thus would produce negative values. Among the 19 useful values, seven were identical, thus the technique was not sensitive enough to discriminate among PR sources. For this reason, it was not possible to draw clear conclusions with regard to their chemical reactivity from the crystallographic analysis.

Thus, the crystallographic analysis provides valuable information for determining the reactivity of phosphate rocks. Indeed, the dimensions of the unit-cells *a* and *c* of the apatite are indicators of the size of the crystals and their degree of substitution. The reactivity and chemical solubility would increase with the carbonate substitution for phosphate [13, 6, 1].

These results provide a good theoretical basis for the grouping of PR samples. However, it should be noted that sedimentary phosphate rocks are complex mineral mixtures and even PRs from the same deposit may contain apatite with widely differing properties. The carbonate-fluorapatites are metastable and can be modified under the combined effects of weathering, metamorphism and time [15].

On another hand, these determinations are expensive and require specialized laboratories and skilled staff, therefore, they should be reserved only for basic studies to characterize main phosphate deposits.

3.3. Chemical analysis

The data from the elemental quantitative analysis provide a complete picture of the chemical composition in terms of major elements (P, Ca, Mg), intermediate (Si, F, Fe, etc.) and microelements, (Zn, Cu, Ni, Mn). The full data are not shown.

TABLE VI. INDICES OF ABSOLUTE SOLUBILITY OF PHOSPHATE ROCKS CALCULATED FROM *a* AXES (IN % OF THEORETICAL P_2O_5 CONTENT)

Phosphates	Neutral Ammonium Citrate	Citric Acid	Formic Acid
Algeria	12.63	23.82	46.91
Morocco 1	3.79	10.99	17.45
Morocco 2	12.63	23.82	46.91
Morocco 3	1.26	7.33	10.91
Tunisia 1	9.69	19.55	32.73
Tunisia 2	6.74	15.27	25.09
Tunisia 3	12.63	23.82	46.91
Jordan 1	1.26	7.33	10.91
Jordan 2	6.74	15.27	25.09
Jordan 3	6.74	15.27	25.09
Minjingu	12.63	23.82	46.91
Bahia Inglesa	12.63	23.82	46.91
Trinidad de Guedes	21.49	36.66	63.27
Polpino	1.26	7.33	10.91
Jinning	8.42	17.71	29.45
Malaysia - Jordan	1.26	7.33	10.91
Malaysia - Tunisia	12.63	23.82	46.91
Malaysia – N. Carolina	12.63	23.82	46.91
Malaysia - Morocco	3.79	10.99	17.45

A summary of the main elemental composition of the studied PR samples is given in Table VII. The total P_2O_5 contents are very variable, ranging from 15–17% (Russia, Chile) to 35–36% (Senegal, Togo), with an average of 27%. Phosphate rocks containing less than 20% P_2O_5 need to be beneficiated, in order to bear the transportation costs. According to European regulations, a minimum of 25% P_2O_5 is required [16].

The CaO contents varied from 24% (Russia) to 52% (Morocco 3), with an average of 41%. Most PR contains values above average. Phosphate rocks suitable for direct application supply more calcium than phosphorus to the soil, thus having some amendment effect [17].

The MgO contents (3–4% in Thailand Racha Buri and China Jingxiang) are not negligible and probably come from dolomite. Brazil 2 Yoorin, with 12% MgO, corresponds to a manufactured product, i.e., fused phosphate.

The CO_2 contents, with an average of 4%, may be originated from two sources, i.e., free carbonates and isomorphic substitution in the apatite. In the case of China JX (12%) and Thailand RB (11%), it probably comes from carbonates (dolomite).

The SiO_2 contents confirm the significant presence of quartz minerals in PR. Russia, China JN, and Brazil 1, Patos PR had 46%, 36%, and 31% SiO_2, respectively (data not shown).

Concerning microelements content, it is noticeable that Brazil 2, Yoorin ranks first for most of these elements and that both PR samples from Thailand, RB and PB are very rich in Mn and Zn. The Cd content seems not to be a problem, with an average of 17 ppm, and only three PR products have more than 50 ppm (Senegal, Togo, Morocco 2).

Regarding the chemical analyses, the major elements (P, Ca, Mg and CO_2) can be determined routinely in chemical laboratories and the information provided is useful for agricultural purposes [17]. The P_2O_5 is essential for calculating the rates of PR application and the CaO and MgO for estimating the potential amendment effect of the PR. In this study, the average contents of CaO and P_2O_5 in the PR samples were 41% and 27%, respectively.

TABLE VII. CHEMICAL COMPOSITION (IN %)

Phosphates	P_2O_5	CaO	MgO	CO_2
Algeria	28.90	47.95	1.46	7.66
Morocco 1	26.65	44.02	2.24	8.29
Morocco 2	31.84	50.05	0.41	5.35
Morocco 3	32.05	52.01	0.27	6.59
Tunisia 1	29.55	48.23	0.47	6.14
Tunisia 2	30.29	49.63	0.51	5.88
Tunisia 3	28.12	47.39	0.45	6.59
Jordan 1	30.62	47.67	0.25	4.28
Jordan 2	30.64	47.39	0.30	3.74
Jordan 3	30.32	50.47	0.23	6.24
Senegal	35.51	50.05	0.06	1.96
Minjingu	28.73	42.90	1.91	4.37
Togo 1, Commercial	36.09	49.77	0.10	1.78
Togo 2, Hibogan	27.92	38.70	0.29	1.25
Patos	25.45	31.40	0.21	0.45
Yoorin	17.69	27.06	12.70	0.71
Bahia Inglesa	17.22	28.88	0.72	3.92
Trinidad de Guedes	31.09	45.71	0.23	3.21
Riecito	29.45	38.98	0.08	2.23
Riecito PAPR 40%	26.37	30.56	0.13	0.89
Maardu	30.08	44.30	0.83	4.37
Polpino	15.07	24.68	0.32	2.94
Jingxiang	19.24	35.47	3.93	12.30
Jinning	21.39	30.98	0.95	2.67
Racha Buri	23.23	38.27	4.92	11.72
Petcha Buri	34.81	46.27	0.05	4.72

3.4. Solubility in conventional reagents

The results of the solubility tests in neutral ammonium citrate, 2% citric acid and 2% formic acid, are presented in Table VIII (values expressed in % of total P_2O_5). These are the three commonly used extractants for measuring solubility of PR. Comparisons of these solubility tests have been made by some authors [18].

The solubility of PR is measured in conventional reagents such as organic acids, which simulates the extraction power of the root similar to the determination of available soil P. Neutral ammonium citrate is a mild extractant that generally gives a good correlation with P uptake by plants and it is recommended in the USA [19]. On the contrary, relatively strong extractants such as citric (used in Brazil) and formic (used in Europe) acids usually extract more phosphorus because of the higher acidity of these extracts. Of these, the 2% formic acid is much more concentrated than the others because of differences in molecular weight.

TABLE VIII. SOLUBILITY TESTS IN CONVENTIONAL REAGENTS
(% OF TOTAL P_2O_5)

Phosphates	Neutral Ammonium Citrate	Citric Acid	Formic Acid
Algeria	23.0	38.6	71.2
Morocco 1	26.0	38.4	60.4
Morocco 2	20.2	33.1	60.1
Morocco 3	16.7	29.9	56.5
Tunisia 1	27.6	41.7	75.8
Tunisia 2	22.7	41.3	72.5
Tunisia 3	21.3	40.3	73.6
Jordan 1	33.1	26.0	27.4
Jordan 2	24.0	36.2	55.9
Jordan 3	31.1	31.2	52.1
Senegal	12.4	21.5	25.6
Minjingu	28.9	44.9	69.9
Togo 1 Commercial	13.6	20.1	19.8
Togo 2 Hibogan	15.4	24.6	23.8
Patos	6.4	22.0	18.1
Yoorin	80.2	99.2	77.6
Bahia Inglesa	34.3	51.6	60.1
Trinidad de Guedes	23.1	29.3	25.5
Riecito	12.1	32.5	32.8
Riecito PAPR 40%	31.6	58.5	54.3
Maardu	29.1	28.5	32.9
Polpino	31.8	48.2	46.8
Jingxiang	6.6	8.8	11.6
Jinning	16.5	24.2	24.0
Racha Buri	37.0	55.6	64.4
Petcha Buri	25.7	38.9	51.9

A first classification was made based on the combination of these three solubility tests. The PR samples in study were classified into four distinct groups according to their reactivity (Table IX-A).

The European solubility standards for phosphates as fertilizers are very strict. A minimum of 55% solubility in 2% formic acid is required [16]. Table IX-B displays the classification of the PR samples according to their solubility in 2% formic acid. Four categories of long-term reactivity were identified (Table IX-B).

Both classifications provide a similar but not identical grouping of the PR samples in study. The first one, using the solubility data in the three reagents, expresses the average short and long term effects of PR whereas the second, with only formic acid solubility, appears to be more related to the long-term effect of PR.

It should be also pointed out that these classification data based on chemical solubility in conventional reagents are quite different from the classification using the indices of absolute solubility (Table VI).

All these solubility determinations can be made in normal chemical laboratories. At least the solubility in formic acid should be determined because it is stable, reproducible, easy to handle and the results enable to discriminate the chemical reactivity of different phosphates. It is advisable, however, to use more than one solubility test in evaluating the PR chemical reactivity [5, 20].

TABLE IX. CLASSIFICATION OF PR REACTIVITY ACCORDING TO SOLUBILITY INDICES IN CONVENTIONAL CHEMICAL REAGENTS AND SOLUBILITY IN FORMIC ACID

A) CONVENTIONAL CHEMICAL REAGENTS

Group I	Group II	Group III	Group IV
Racha Buri	Jordan 3	Maardu	Jinning
Tunisia 1	Jordan 2	Jordan 1	Senegal
Bahia Inglesa	Petcha Buri	Morocco 3	Togo 2
Minjingu	Morocco 2	Trinidad de Guedes	Togo 1
Tunisia 2		Riecito	Jingxiang
Tunisia 3			
Polpino			
Algeria			
Morocco 1			

B) FORMIC ACID

Group I (> 70%)	Group II (60-70%)	Group III (50-60%)	Goup IV (< 50%)
Tunisia 1	Minjingu	Morocco 3	Polpino
Tunisia 2	Racha Buri	Jordan 2	Maardu
Tunisia 3	Bahia Inglesa	Jordan 3	Riecito
Algeria	Morocco 1	Petcha Buri	Jordan 1
Yoorin	Morocco 2		Senegal
			Trinidad de Guedes
			Jinning
			Togo 2
			Togo 1
			Patos
			Jingxiang

3.5. Particle size distribution

The results of the particle size analysis in % of product passing through 45, 90, 165 and 320 microns sieves are presented in Table X. As the physical state of the initial samples was quite different (ground, ungrounded, granulated), it is not possible to make a direct comparison of the results across samples. For example, Morocco 3, ungrounded, had only 4.5% passing through 45 microns, while Estonia, finely ground, has 100% passing through all sieves. In this case, each phosphate should be examined individually and related to its agronomic effectiveness. From the data of Table X, it may be noted that 14 PR samples (about 60%) have 80% of the product passing through a 165 microns sieve. This determination is important and easy to be made.

In general, several reports indicate that P availability from PR is enhanced with increasing fineness of grinding. However, it is reported that a general cut-off point for most PR appears to be 100-mesh (150 microns) sieve [3]. Thus, there is no need to grind PR more finely than required for 80–90% of the product to pass 100-mesh [1]. According to European standards, PR products to be utilised as fertilizers should be finely ground, i.e. 90% of the product should pass through a 63 microns sieve and 99% of the product should pass through a 125 microns sieve [16].

Data on specific surface and porosity (volume of porous space) of the PR samples are not shown. These values depend on the origin of the PR and, also the degree of fineness.

TABLE X. PARTCIEL SIZE DISTRIBUTION OF PHOSPHATE FRACTIONS UNDER 400 MICRONS (IN % OF PRODUCT PASSING THROUGH)

Phosphates	45 microns	90 microns	165 microns	320 microns
Algeria	10.1	19.8	62.2	91.1
Morocco 1	35.3	47.9	69.1	92.2
Morocco 2	9.3	13.2	42.8	86.5
Morocco 3	4.5	7.3	30.9	80.9
Tunisia 1	69.1	83.8	97.2	100
Tunisia 2	68.8	80.2	90.9	97.9
Tunisia 3	63.8	76.9	91.5	98.6
Jordan 1	14.9	23.5	45.5	83.9
Jordan 2	62.4	87.0	98.3	100
Jordan 3	28.7	40.3	55.5	86.1
Senegal	8.6	31.1	61.5	90.1
Minjingu	55.2	75.6	89.5	97.3
Togo 1 Commercial	9.3	20.3	60.2	92.6
Togo 2 Hibogan	71.1	93.3	100	100
Patos	64.4	88.5	99.4	100
Bahia Inglesa	54.9	82.3	99.0	100
Trinidad de Guedes	13.1	16.2	29.4	77.5
Riecito	65.7	85.2	98.2	100
Maardu	100	100	100	100
Polpino	63.3	72.5	82.3	94.6
Jingxiang	59.5	71.6	83.2	94.9
Jinning	73.8	92.9	100	100
Racha Buri	66.2	84.8	97.7	100
Petcha Buri	45.9	61.5	76.6	93.2

3.6. Correlation studies

Attempts were made to relate some parameters determined in the characterisation, in particular to interpret the solubility data, which are considered indices of PR reactivity.

First, a correlation between the solubility measured in conventional reagents and the calculated indices of absolute solubility was run with the following results:

neutral ammonium citrate	r = 0.15
citric acid	r = 0.07
formic acid	r = 0.14

No relationship between both solubility groups was found. These results are in contrast to previous studies [5, 6]. It is likely that the crystallographic data were not sufficiently sensitive to discriminate between PR sources, thus the calculated indices of absolute solubility are not good indicators of their reactivity.

Secondly, the following correlations between the measured solubility in conventional reagents were made:

formic acid vs. neutral ammonium citrate	r = 0.56
formic acid vs. citric acid	r = 0.72
citric acid vs. neutral ammonium citrate	r = 0.89

The simple linear correlation coefficients show some relationship but they are not very close. This may be explained by the fact that the PR samples belong to contrasting solubility groups, thus each group requiring partial linear regression analysis. It was not possible to separate them further into different groups due to the lack of sufficient information on the PR samples. Other studies indicate that the presence of free carbonates in the PRs interfere with the solubility measurements [18].

Thirdly, correlations were made between the data of solubility in formic acid and other parameters, as follows:

formic acid vs. CO_2 content	$r = 0.26$
formic acid vs. specific surface	$r = 0.31$
formic acid vs. porous volume	$r = -0.05$
specific surface vs. porous volume	$r = 0.24$

In the first correlation, no relationship was found. Here again, the PR samples belong to carbonate-apatites, with different degrees of isomorphic substitution and in some PRs, the CO_2 content represented mainly the free carbonates (Tables V and VII). Regarding the parameters of the physical analysis, specific surface and porous volume, the samples in study had contrasting particle size distribution due to the pre-treatment/conditioning of the samples received from the participants (Table X).

4. CONCLUSIONS

The characterization of phosphate rocks is the first and essential step in evaluating their suitability for direct application. If several PR sources are utilized, standardized methods should be used for comparison purposes to determine their agronomic potential.

The data on mineralogical and chemical composition and solubility in conventional reagents are closely interrelated. An arbitrary classification of the reactivity of the PR samples in four categories was made based on the solubility indices in conventional reagents. On another hand, the results of the crystallographic parameters, calculated indices of absolute solubility, specific surface and porosity reflected the large variability of the physical state resulting from preconditioning treatment of the received samples.

A proper characterization of phosphate rock samples should provide the maximum of basic information that can be obtained in a cost-effective manner by routine analysis in chemical laboratories. The following determinations are recommended: description of the sample, major elemental (total P, Ca, Mg) composition, solubility in conventional reagents (neutral ammonium citrate, citric and formic acid) and particle size analysis.

The classification of PR samples for direct application as fertilizers requires the definition of standards. The European standards were found to be very strict for this purpose. The studies carried out under this project should be considered as attempts to provide some guidelines for the provision of such standards in other conditions, in particular tropical acid soils where the PRs show great agronomic potential.

Follow-up studies are required to evaluate the agronomic effectiveness of the PR, i.e. actual performance of the PR under study as affected by a specific set of soil, crop, climate and management conditions. In a final phase, it would also be important to relate the results of this study with those of the agronomic effectiveness and several other socio-economic criteria for developing adequate PR Decision Support Systems.

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REFERENCES

[1] HAMMOND, L.L., CHIEN, S.H.; MOKWUNYE, A.U., Agronomic value of unacidulated and partially acidulated phosphate rocks indigenous to the tropics. Adv. Agr. **40** (1986) 89-140.

[2] British Sulfur Corporation Limited. 1987. World Survey of Phosphate Deposits. 5th edition, London.

[3] KHASAWNEH, F.E., DOLL, E.C., The use of phosphate rock for direct application to soils. Adv. Agron. **30** (1978) 159-206.

[4] CHIEN, S.H.; FRIESSEN, D.K., Phosphate rock for direct application. In: TVA Workshop on Future Directions for Agricultural Phosphorus Research, 47-52. Bulletin Y-224, Tennessee Valley Authority, Muscle Shoals, Alabama (1972).

[5] LEHR J.R., Mc CLELLAN, G.H., A revised laboratory reactivity scale for evaluating phosphate rocks for direct application. Bull. Y43, Nat. Fert. Develop. Center, TVA, (1972) 36 pp.

[6] TRUONG BINH, et al., Caractérisation et comparaison des phosphates naturels tricalciques d'Afrique de l'Ouest en vue de leur utilisation directe en agriculture. Agron. Trop. XXXIII-2, Avril-Juin (1978), 136-145.

[7] CHIEN, S.H., MENON, R.G., Factors affecting the agronomic effectiveness of phosphate rock for direct application. Fert. Res.**41** (1995) 227-234.

[8] ZAPATA, F., Evaluating the Agronomic Effectiveness of phosphate rock materials through the use of nuclear and related techniques: Main results and experiences from a past FAO/IAEA Co-ordinated Research Project. In: Management and Conservation of Tropical Acid Soils for Sustainable Crop Production. In IAEA TECDOC 1159, Vienna, Austria, (2000) 91-100.

[9] Centre d' Etudes et de Recherches des Phosphates Minéraux (CERPHOS). Principes de méthodes d'analyses chimiques appliquées sur des échantillons de phosphates pour application directe. Casablanca. Maroc (1995).

[10] JADIN, P., TRUONG BINH, Efficacité de deux phosphates naturels tricalciques dans deux sols ferrallitiques acides du Gabon.Café Cacao Thé. **31** (4) (1987) 291-302.

[11] HELLUMS, D.T., CHIEN, S.H., TOUCHTON, J.T. Potential agronomic value of calcium in some rock from South America and West Africa. Soil Sci. Am. J. **53** (1989) 459-462.

[12] BAUDET, G., TRUONG, B., FAYARD, C., SUSTRAC, G., La filière phosphate: du mineral à l'engrais, principaux points de repère. Chron. Rech. Min. **484** (1986) 19-36.

[13] CHIEN, S.H., Thermodynamic considerations on the solubility of phosphate rocks. Soil Sci. **123** (1977) 17-121.

[14] Mc CLELLAN, G.H., LEHR, J.R., 1969. Crystal chemical investigation of natural apatites. Am. Min. **54** (1969) 1374-1391.

[15] McCLELLAN, G.H., Van KAUWENBERG, S.J. Relationship of Mineralogy to sedimentary phosphate rock reactivity. In: Proc. Workshop on Phosphate Sources for Acid Soils in the Humid Tropics of Asia., 6-7 November 1990, Kuala Lumpur, Malaysia, p.1-17. Malaysian Society of Soil Science, KL, Malaysia (1992).

[16] Association Française de Normalisation (AFNOR). Matières fertilisantes et supports de culture. Troisième édition. (1991).

[17] TRUONG, B., CISSE, L., Appréciation de la valeur fertilisante des phosphates de Matam (Senegal). Agro. Trop. **40** (3) (1985) 230-238.

[18] CHIEN, S.H., HAMMOND, L.L., A comparison of laboratory methods for predicting the agronomic potential of phosphate rocks for direct application. Soil Sci. Soc. Am. J. **42** (1978) 935-939.

[19] Association of Official Analytical Chemists (AOAC). Official Methods of Analysis. 12th edition. Washington, DC. (1970).

[20] DIAMOND, R.B., Views on marketing of phosphate rock for direct application. In: Proc. Seminar on Phosphate Rock for direct application, Haifa, Israel, pp.448-463.

STANDARD CHARACTERIZATION OF SOILS EMPLOYED IN THE FAO/IAEA PHOSPHATE PROJECT

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Abstract

In the frame of the FAO/IAEA networked research project, the agronomic effectiveness of natural and modified phosphate rock (PR) products was evaluated using nuclear and related techniques under a variety of soil, climate and management conditions. In addition to the local soil analyses, it was decided to make a standard characterization of the soils employed in the project to gather direct and comparable information on the relevant soil properties affecting the suitability of PRs for direct application and to better interpret the results from the agronomic evaluation, including the creation of a database for phosphate modelling. This paper describes the standard characterization of soils, that was mainly made at CIRAD, Montpellier, France. A total of 51 soil samples were analyzed from15 countries including Belarus (1), Brazil (2), Chile (3), China (20), Cuba (2) Ghana (6), Hungary (2), Indonesia (3), Kenya (1), Malaysia (1), Poland (1), Romania (2), Russia (1), Thailand (3) and Venezuela (3).

Methods of analyses used for the soil characterization included textural class, pH, chemical analysis for total N and P, and exchangeable elements (CEC, saturation). Available P was measured using 4 methods including Olsen, Bray II, Pi paper and Resin. Available P measurements using resin method were made at CENA, Piracicaba, Brazil. The soil P dynamics was described using the ^{32}P isotope exchange kinetic method at CEN Cadarache, France with the same soil samples.

As a result of the worldwide distribution of the soils employed in the project, the results showed a very large diversity in each of the measured soil characteristics. The analysis of the data focused on the most representative tropical acid soils, i.e. Ultisols and Oxisols. Inceptisols have also been included because most of them were acid and located in the tropics and subtropics. Results are synthesized and analyzed with particular emphasis on: i) identification of the most relevant soil characteristics affecting PR dissolution and their agronomic potential in tropical acid soils; and ii) suitability of methods for routine testing of available P in these soils. The study demonstrates that pH and soil P status parameters, in particular P fixation capacity index and P concentration in aqueous extract are the main soil properties affecting PR dissolution in these tropical acid soils. Additional related characteristics are clay content, organic matter content, and % Ca saturation. In the case of high P fixing soils, it would be also useful to have information on total and extractable Fe and Al.

The methods of determination of available P were only relatively compared. In order to compare the P measured by these methods (extracting solutions or isotopic method) and the P actually available to the crop, yield data of field experiments are needed, as well as the response of the crops to the P fertilization. Further studies are needed with PR application to tropical acid soils to: a) establish relationships between crop yields and soil P supply in field experiments, and ii) group soils P supply into categories based on the probability of crop response to P fertilization.

1. INTRODUCTION

Phosphorus (P) deficiency is widespread in acid soils of the tropics and subtropics. Also, most of these soils have a high P sorption capacity. Thus, they require substantial inputs of P fertilizers for adequate crop growth and optimum production of food and fibre. Manufactured P fertilizers like superphosphates are mostly imported and supplies to the resource-poor farmers are limited and expensive. Many phosphate-bearing mineral deposits exist worldwide. Phosphate rocks vary widely in mineralogical, chemical and physical properties, and consequently in their reactivity and agronomic potential. Under certain conditions, direct application of phosphate rocks (PRs) is an agronomic and economically attractive alternative to the use of manufactured phosphatic fertilizers. Upon application of a PR to a soil, both the rate of P dissolution and fate of the released P are affected by the soil properties determining the chemical reactions and the P demand by the growing crops. Among the soil properties, soil pH, exchangeable Ca, P-sorption capacity and organic matter are reported to be the main factors affecting the agronomic potential of PRs [1].

Recognizing the importance of overcoming main constraints to agricultural production in the tropics and subtropics, the Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture established a research network of 21 participating scientists from developing and industrialized countries and implemented a project during 1993-1998 with a main objective to evaluate the agronomic effectiveness of rock phosphates through the use of P-32 and related techniques [2]

Participating scientists represented benchmark sites with regard to the worldwide distribution of chemical infertile acid soils especially in the tropics and subtropics in order to test the agronomic effectiveness of indigenous and imported PRs under a variety of soil and crop conditions. As part of the project, participating countries performed a characterization of the soils and PRs utilized in their research. In addition, a standard characterization of the soils and PRs employed in the project was made with financial support of the World Phosphate Institute (IMPHOS) to gather direct and comparable information on the factors affecting the suitability of PRs for direct application and to better interpret the results from the agronomic evaluation, including the creation of a database for phosphate modelling.

This paper describes the standard characterization of the soils employed in the project. Results are synthesized and analysed with particular emphasis on: i) identification of the most relevant soil characteristics affecting PR dissolution and their agronomic potential in tropical acid soils; and ii) suitability of methods for routine P testing in these soils.

2. MATERIALS AND METHODS

A total of 51 soil samples from 15 countries participating in the FAO/IAEA Co-ordinated Research Project on "The use of nuclear and related techniques for evaluating the agronomic effectiveness of P fertilizers, in particular rock phosphates" were collected for chemical and physical analyses. All samples were surface (topsoil) soil samples used for routine soil P testing. The full list of soil samples grouped according to the geographical region of origin is shown in Table I. Their worldwide distribution was as follows: 27 samples (53%) were from Asia, 10 (20%) from Latin America, 7 (14%) from Africa and 7 (14%) from Europe.

The routine physical and chemical analyses of the soil samples were carried out at the "Unité Sols et Eaux, Centre de Coopération Internationale en Recherche Agronomique pour le Développement" (CIRAD), Montpellier, France. All the analyses were performed on the "fine earth" fraction (samples passed through a 2 mm sieve). The determination of the physical and chemical properties was made following the French standard methods briefly described below [3].

2.1. Particle size distribution

Automatic granulometer GRANULOSTAT: Standard method AFNOR X 31-107. Destruction of the organic matter by wet digestion using hydrogen peroxide (H_2O_2). Soils were dispersed and suspended in sodium hexa-metaphosphate [40 g/l] and anhydrous sodium carbonate Na_2CO_3 [10 g/l]. Clay and silt particles were determined by sedimentation using a Robinson pipette. Sand particles separated from the clay and silt by a sieve and subsequently fractionated by wet sieving (rinsing the sample with water in a nest of sieves). The following particle size fractions were considered:

Clay	< 2 μm
Fine silt (Silt F)	2 μm–20 μm
Coarse silt (Silt C)	20 μm–50 μm
Fine sand (Sand F)	50 μm–200 μm
Coarse sand (Sand C)	200 μm–2000 μm

TABLE I. GEOGRAPHICAL DISTRIBUTION OF SOILS USED FOR FIELD EXPERIMENTS

Geographical Region	Country	Location	Soil Taxonomy	
Africa	Ghana	Abena	Oxisol	Typic Haplorthox
Africa	Ghana	Ankasa	Oxisol	Typic Haplorthox
Africa	Ghana	Ayinase	Oxisol	Typic Haplorthox
Africa	Ghana	Boi	Oxisol	Plinthic Eutrodox
Africa	Ghana	Kwaben	Ultisol	Typic Hapludult
Africa	Ghana	Tikobo	Ultisol	Typic Hapludult
Africa	Kenya	Kakamega	Ultisol	Typic Hapludult
Asia	China	Changxing	Inceptisol	Typic Haplaquept
Asia	China	Gaonan	Aridisol	Typic Calciorthid
Asia	China	Guangzhou	Inceptisol	Typic Haplaquept
Asia	China	Huazhou	Ultisol	Typic Hapludult
Asia	China	Jingde	Ultisol	Typic Hapludult
Asia	China	Jinhua	Ultisol	Typic Hapludult
Asia	China	Jinxian	Inceptisol	Anthraquic Eutrocrept
Asia	China	Kunming (red clay)	Inceptisol	Typic Eutrocrept
Asia	China	Kunming (shale)	Ultisol	Typic Hapludult
Asia	China	Liujiang	Alfisol	Typic Rhodudalf
Asia	China	Taihe	Inceptisol	Anthraquic Eutrocrept
Asia	China	Yangling	Mollisol	Typic Haplustoll
Asia	China	Yingtan	Ultisol	Typic Hapludult
Asia	China	Yiyang	Ultisol	Typic Hapludult
Asia	China	Yongdeng	Mollisol	Typic Calciustoll
Asia	China	Yuzhong	Entisol	Typic Ustipsamment
Asia	China	Zhanjiang	Inceptisol	Typic Eutrocrept
Asia	China	Zunyi 26	Ultisol	Typic Hapludult
Asia	China	Zunyi 27	Entisol	Typic Udorthent
Asia	Indonesia	Batu Marta	Ultisol	Typic Paleudult
Asia	Indonesia	Pasar Jumat	Ultisol	Typic Kandiudult
Asia	Indonesia	Pusaka Negara	Inceptisol	Endoaquept
Asia	Malaysia	Rengam	Ultisol	Typic Paleudult
Asia	Thailand	Kho Hong	Ultisol	Kandiudult
Asia	Thailand	Pak Chong	Ultisol	Oxic Paleustult
Asia	Thailand	Warin	Ultisol	Oxic Paleustult
Europe	Belarus	Minsk	Spodosol	Sod Podzolic
Europe	Hungary	Kompolt	Mollisol	Typic Hapludoll
Europe	Hungary	Szentgyörgyvölgy	Alfisol	Typic Ochraqualf
Europe	Poland	Pulawy	Histosol	Eutric Histosol
Europe	Romania	Albota	Alfisol	Typic Agrudalf
Europe	Romania	Sanandrei	Mollisol	Typic Agrudoll
Europe	Russia	Bryansk	Spodosol	Sod Podzolic
Latin America	Brazil	Piracicaba 1	Oxisol	Hapludox
Latin America	Brazil	Piracicaba 2	Oxisol	Hapludox
Latin America	Chile	Metrenco	Ultisol	Paleo Humult
Latin America	Chile	Pemehue	Inceptisol	Distrandept
Latin America	Chile	Santa Barbara	Andosol	Haploxerand
Latin America	Cuba	Ciego di Avila/Epica	Alfisol	Orthic Paleustalf
Latin America	Cuba	Ciego de Avila/Univ	Alfisol	Orthic Paleustalf
Latin America	Venezuela	El Pao	Ultisol	Typic Paleustult
Latin America	Venezuela	Valle La Pascua	Ultisol	Typic Paleustult
Latin America	Venezuela	Yaracuy	Ultisol	Typic Paleustult

2.2. pH

The pH in H_2O was determined in a suspension of soil and water with a ratio of 1:2.5 (soil:water). The suspension was stirred from time to time and pH measured after 2 hours of equilibration with a potentiometer. The pH in KCl was measured in the same way as the pH in water, except 1 M KCl solution was used instead of H_2O.

2.3. Total carbon

Following standard method NF ISO 10694 of June 1995: "Dosage du carbone organique et du carbone total après combustion sèche (analyse élémentaire)". Dry combustion (950°C with oxygen) of the sample. Resulting CO_2 is analysed using an infrared cell. (*Automatic Analyser LECO CHN 600*).

2.4. Total nitrogen

Oxidation of the sample in an induction oven following standard method NF ISO 13878 of July 1998: "Détermination de la teneur totale en azote par combustion sèche (analyse élémentaire)" and resulting N is analysed using a thermal conductivity cell. (*Analyser LECO PF 428*).

2.5. Total phosphorus

Dissolution of the sample ("Mise en solution totale par attaque acide") was made according to the standard NF X 31-147 of July 1996 and analysis ("Dosage du phosphore") according to the standard NF ISO 11263 of July 1995. Digestion of the sample with HF/HNO_3 was performed in a microwave oven. Phosphorus was analysed using a colorimetric method (Molybdenum blue) with an automatic analyser *Alliance Integral.*

2.6. Cation exchange capacity

The CEC method used hexamine-cobalt trichloride ($Co\ (NH_3)_6\ Cl_3$) [4]. Soil (3.5 g) was shaken in 70 ml of solution of hexamine-cobalt trichloride for 2 hours. The concentration of this solution should be adjusted taking into account the forecasted CEC of the sample between 2 and 5 CEC. The pH is measured on an aliquot of the solution after centrifugation after filtering the remaining suspension. Ca, Mg, K, Na, Al and Mn are analysed in the filtrate using ICP (Inductively Coupled Plasma). The CEC is calculated after titration of the cobalt remaining in the solution.

2.7. Available phosphorus

2.7.1. P Olsen [5] and P Bray II [6]

Bray II and Olsen methods were chosen as reference chemical extraction methods for the project and performed on the soil samples received.

For Olsen P, 5 g of soil are suspended in 100 ml of sodium bicarbonate 0.5M $NaHCO_3$, pH = 8.5 and the suspension shaken for 30 minutes. The P content in the filtrate is analysed using colorimetric method (Molybdenum blue), with an automatic analyser *Alliance Integral.*

For Bray II P, 2 g soil mixed with 14 ml of the P extracting solution consisting of 0.03 mole/L sodium fluoride (NaF) and 0.1 mole/L of HCl and shaken for 40 seconds. After filtration, the P content is analysed using a colorimetric method (Molybdenum blue with boric acid) with an automatic analyser *Alliance Integral*.

2.7.2. P iron strips, Pi [7, 8]

In this method iron hydroxide impregnated paper strips are utilised as sink for phosphate ions in solution. It is a method to testing for available soil phosphorus developed at IFDC. The latest modified version was used for the analyses [8].

2.7.3. P resin [9]

The analyses for available P by the resin method were performed on some samples at the Centre for Nuclear Energy in Agriculture (CENA), Piracicaba, Brazil, thanks to the collaboration of T. Muraoka. Results are given in mg P/dm^3 of soil.

2.7.4. ^{32}P exchange kinetics method [10]

J.C. Fardeau made the analyses by the ^{32}P exchange kinetics method at the "Centre d'études nucléaires" (CEN), Cadarache, France. The E_1 value or quantity factor, i.e. the amount of isotopically exchangeable phosphate within one minute, was utilised as index of available soil P.

3. RESULTS AND DISCUSSION

3.1. Soil characteristics

Table II shows the soils grouped according to the Soil Classification (Soil Taxonomy), their specific field location in the country and degree of weathering. Although almost all main soil orders of the Soil Taxonomy were represented, the predominant ones were Ultisols (39%), Inceptisols (18%), Oxisols (12%) and Alfisols (10%). Since the native soil P status, in particular forms and stability of soil P is determined to a great extent by the degree of weathering, they have been divided into three categories: Highly Weathered (HW), Slightly Weathered (SW) and Little Weathered (LW). The first category comprised Ultisols, Oxisols and Spodosols; the second group Inceptisols, Andosols, Mollisols, and Alfisols whereas the last category included all other soils, like Entisols, Aridisols, and Histosols. It was expected that this grouping would reflect the effect of the pedogenesis on P chemistry and fertility [11].

Table III presents the data of the particle size analysis, textural class and other characteristics such as organic matter (OM), total nitrogen (N) content and C/N ratio. The soils are listed according to increasing sand content.

Table IV contains the data on soil pH (water and KCl), exchangeable cations (bases, Al and H), the sum of exchangeable bases (S), the cation exchange capacity (CEC = T), the base saturation (%BS or S/T) and the Ca saturation (% Ca/T). The soils are listed according to increasing pH values in H_2O.

Table V displays several parameters for assessing the soil P status. In addition to total P, data on available soil phosphorus measured by Olsen, P Bray II, P iron paper and P resin methods are shown. Some parameters, like quantity E_1 and fixation index (r_1/R) obtained with the ^{32}P exchange kinetics method are also indicated.

The analysis of the data focused on the most representative tropical acid soils, i.e. Ultisols and Oxisols. Inceptisols were also included because most of them were acid and located in the tropics and subtropics.

3.2. Soil properties considered suitable for PR dissolution

Plant roots will take up phosphate ions from the soil solution. Phosphate rocks, which are mainly apatite, are recommended for direct application to acid soils but they are water-insoluble P sources. They have first to be dissolved in soils to release phosphate ions. From mass action law controlling the dissolution reaction of phosphate rocks in acid soils, it may be noted that the dissolution depends on the chemical potential in the soil solution of the following components: a) hydroxide ions expressed through pH values, b) calcium ions, and c) phosphate ions [12]. The results obtained from the main soil characteristics influencing these chemical potentials were analysed.

TABLE II. SOIL CLASSIFICATION AND WEATHERING DEGREE

Soil Taxonomy		Country	Location	Weathering degree
Alfisol	Typic Rhodudalf	China	Liujiang	SW
Alfisol	Orthic Paleustalf	Cuba	Ciego de Avila/Epica	SW
Alfisol	Orthic Paleustalf	Cuba	Ciego de Avila/Univ	SW
Alfisol	Typic Ochraqualf	Hungary	Szentgyörgyvölgy	SW
Alfisol	Typic Agrudalf	Romania	Albota	SW
Andosol	Haploxerand	Chile	Santa Barbara	SW
Aridisol	Typic Calciorthid	China	Gaonan	LW
Entisol	Typic Ustipsamment	China	Yuzhong	LW
Entisol	Typic Udorthent	China	Zunyi 27	LW
Histosol	Eutric Histosol	Poland	Pulawy	LW
Inceptisol	Distrandept	Chile	Pemehue	SW
Inceptisol	Anthrogenic Eutrocrept	China	Changsha	SW
Inceptisol	Typic Haplaquept	China	Changxing	SW
Inceptisol	Typic Haplaquept	China	Guangzhou	SW
Inceptisol	Anthraquic Eutrocrept	China	Jinxian	SW
Inceptisol	Typic Eutrocrept	China	Kunming (red clay)	SW
Inceptisol	Anthraquic Eutrocrept	China	Taihe	SW
Inceptisol	Typic Eutrocrept	China	Zhanjiang	SW
Inceptisol	Endoaquept	Indonesia	Pusaka Negara	SW
Mollisol	Typic Haplustoll	China	Yangling	SW
Mollisol	Typic Calciustoll	China	Yongdeng	SW
Mollisol	Typic Haplodoll	Hungary	Kompolt	SW
Mollisol	Typic Agrudoll	Romania	Sanandrei	SW
Oxisol	Hapludox	Brazil	Piracicaba 1	HW
Oxisol	Hapludox	Brazil	Piracicaba 2	HW
Oxisol	Typic Haplorthox	Ghana	Abena	HW
Oxisol	Typic Haplorthox	Ghana	Ankasa	HW
Oxisol	Typic Haplorthox	Ghana	Ayinase	HW
Oxisol	Plinthic Eutrodox	Ghana	Boi	HW
Spodosol	Sod Podzolic	Belarus	Minsk	HW
Spodosol	Sod Podzolic	Russia	Bryansk	HW
Ultisol	Paleo Humult	Chile	Metrenco	HW
Ultisol	Typic Hapludult	China	Huazhou	HW
Ultisol	Typic Hapludult	China	Jingde	HW
Ultisol	Typic Hapludult	China	Jinhua	HW
Ultisol	Typic Hapludult	China	Kunming (shale)	HW
Ultisol	Typic Hapludult	China	Yingtan	HW
Ultisol	Typic Hapludult	China	Yiyang	HW
Ultisol	Typic Hapludult	China	Zunyi 26	HW
Ultisol	Typic Hapludult	Ghana	Kwaben	HW
Ultisol	Typic Hapludult	Ghana	Tikobo	HW
Ultisol	Typic Hapludult	Kenya	Kakamega	HW
Ultisol	Typic Paleudult	Indonesia	Batu Marta	HW
Ultisol	Typic Kandiudult	Indonesia	Pasar Jumat	HW
Ultisol	Typic Paleudult	Malaysia	Rengam	HW
Ultisol	Kandiudult	Thailand	Kho Hong	HW
Ultisol	Oxic Paleustult	Thailand	Pak Chong	HW
Ultisol	Oxic Paleustult	Thailand	Warin	HW
Ultisol	Typic Paleustult	Venezuela	El Pao	HW
Ultisol	Typic Paleustult	Venezuela	Valle La Pascua	HW
Ultisol	Typic Paleustult	Venezuela	Yaracuy	HW

TABLE III. GRANULOMETRY (TEXTURAL CLASSES), ORGANIC MATTER, ORGANIC CARBON, TOTAL N AND C/N RATIO (SOILS LISTED ACCORDING TO INCREASING % SAND CONTENT)

Country	Location	Soil Taxonomy	Clay %	Silt F %	Silt C %	Sand F %	Sand C %	Sand %	Textural Class	O M %	O C %	N %	C/N
China	Yangling	Mollisol	25.2	37.5	32.8	3.5	1.0	4.5	Silty Loam	1.9	1.1	0.10	11.3
Indonesia	Pusaka Negara	Inceptisol	61.0	27.5	6.7	2.9	1.9	4.8	Clay	3.6	2.1	0.18	11.9
Romania	Sanandrei	Mollisol	42.5	22.2	29.0	5.7	0.6	6.3	Silty Clay	2.4	1.4	0.15	9.1
China	Changxing	Inceptisol	32.6	36.2	23.3	6.5	1.4	7.9	Silt Clay Loam	2.2	1.3	0.16	8.3
Indonesia	Pasar Jumat	Ultisol	70.5	14.2	5.3	7.3	2.7	10.0	Clay	3.0	1.7	0.19	9.3
China	Jingde	Ultisol	60.1	17.8	11.7	6.1	4.3	10.4	Clay	2.6	1.5	0.14	10.6
Hungary	Kompolt	Mollisol	38.8	24.5	25.0	9.4	2.5	11.8	Silt Clay Loam	3.7	2.2	0.18	12.4
China	Yuzhong	Entisol	18.3	26.4	41.0	13.3	1.0	14.3	Silty Loam	3.7	2.1	0.24	9.0
Hungary	Szentgyörgyvölgy	Alfisol	19.4	25.5	40.1	9.4	5.6	15.0	Silty Loam	2.4	1.4	0.14	10.3
China	Jinxian	Inceptisol	27.8	39.7	16.2	7.5	8.8	16.3	Silt Clay Loam	3.0	1.8	0.18	9.8
China	Zunyi 27	Entisol	42.4	32.2	9.0	14.2	2.2	16.4	Silty Clay	1.3	0.8	0.08	9.8
China	Gaonan	Aridisol	17.4	32.4	32.8	17.1	0.4	17.5	Silty Loam	1.7	1.0	0.07	13.7
China	Zunyi 26	Ultisol	31.1	27.9	23.1	14.3	3.6	17.9	Silt Clay Loam	2.3	1.4	0.14	9.8
Chile	Pemehue	Inceptisol	34.5	32.7	14.6	11.6	6.6	18.2	Silt Clay Loam	13.4	7.8	0.64	12.2
Belarus	Minsk	Spodosol	13.7	18.7	49.1	16.4	2.2	18.6	Silt Clay Loam	1.4	0.8	0.09	9.2
China	Liujiang	Alfisol	44.2	23.7	10.1	9.4	12.7	22.1	Clay	2.3	1.3	0.14	9.8
Thailand	Pak Chong	Ultisol	32.7	30.8	13.7	13.1	9.7	22.8	Clay Loam	1.5	0.9	0.08	10.6
Chile	Metrenco	Ultisol	47.6	16.0	13.4	13.6	9.4	23.0	Clay	10.1	5.9	0.36	16.2
Cuba	Ciego de Avila/Univ	Alfisol	67.6	5.2	4.0	12.2	11.0	23.2	Clay	3.0	1.7	0.18	9.5
China	Yingtan	Ultisol	45.5	19.6	11.6	17.0	6.3	23.3	Clay	0.6	0.3	0.05	5.9
Cuba	Ciego de Avila/Epica	Alfisol	65.8	6.9	1.7	11.2	14.4	25.6	Clay	2.7	1.6	0.19	8.4
Romania	Albota	Alfisol	26.8	27.4	18.7	15.8	11.4	27.2	Loam	2.1	1.2	0.11	10.8
China	Yongdeng	Mollisol	14.4	24.3	33.3	17.7	10.3	28.0	Silty Loam	3.0	1.7	0.17	10.2
China	Jinhua	Ultisol	39.7	17.7	12.9	9.6	20.1	29.7	Clay Loam	1.3	0.7	0.08	9.3
Indonesia	Batu Marta	Ultisol	27.3	14.7	27.5	26.7	3.8	30.5	Loam	2.8	1.6	0.13	12.3
China	Kunming (red clay)	Inceptisol	51.7	9.9	7.0	21.8	9.6	31.4	Clay	2.5	1.4	0.15	9.9
Chile	Santa Barbara	Andosol	11.7	31.5	25.2	22.6	9.0	31.6	Silty Loam	8.4	4.9	0.37	13.4

Country	Location	Soil Taxonomy	Clay %	Silt F %	Silt C %	Sand F %	Sand C %	Sand %	Textural Class	O M %	O C %	N %	C/N
China	Taihe	Inceptisol	20.7	30.2	13.0	20.2	15.9	36.1	Loam	2.1	1.2	0.14	9.1
China	Yiyang	Ultisol	34.0	17.3	12.2	24.0	12.4	36.4	Clay Loam	3.8	2.2	0.18	11.9
Kenya	Kakamega	Ultisol	42.7	10.2	3.9	10.0	33.2	43.2	Clay	3.1	1.8	0.13	13.9
Malaysia	Rengam	Ultisol	47.2	4.1	3.3	11.1	34.3	45.4	Sandy Clay	2.5	1.5	0.12	12.6
China	Guangzhou	Inceptisol	38.5	6.7	3.1	6.3	45.4	51.7	Sandy Clay	1.6	0.9	0.07	12.6
China	Zhanjiang	Inceptisol	26.4	7.3	9.5	19.9	36.9	56.8	Sandy Clay Loam	1.4	0.8	0.09	9.5
China	Kunming (shale)	Ultisol	19.2	10.1	12.7	54.2	3.9	58.1	Sandy Loam	3.7	2.2	0.13	16.8
Russia	Bryansk	Spodosol	17.8	9.9	12.7	42.8	16.8	59.6	Sandy Loam	2.6	1.5	0.13	11.4
Ghana	Boi	Oxisol	30.0	4.1	4.9	36.7	24.3	61.0	Sandy Loam	4.0	2.3	0.20	11.7
Venezuela	El Pao	Ultisol	17.2	5.9	11.3	46.1	19.5	65.6	Sandy Loam	1.9	1.1	0.10	11.5
Thailand	Kho Hong	Ultisol	11.8	9.4	10.6	51.1	17.1	68.2	Sandy Loam	2.5	1.5	0.12	12.1
China	Huazhou	Ultisol	13.7	5.3	11.4	54.3	15.3	69.6	Sandy Loam	1.0	0.6	0.07	8.5
Ghana	Abena	Oxisol	21.2	4.5	2.8	9.8	61.7	71.5	Sandy Loam	2.6	1.5	0.12	13.1
Poland	Pulawy	Histosol	10.6	12.7	4.3	15.2	57.1	72.3	Sandy Loam	20.4	11.9	0.96	12.4
China	Changsha	Inceptisol	10.0	6.2	10.6	23.3	49.9	73.2	Loamy Sand	4.2	2.4	0.24	10.3
Thailand	Warin	Ultisol	5.9	1.8	12.6	58.7	20.9	79.6	Loamy Sand	0.4	0.2	0.02	13.8
Ghana	Ankasa	Oxisol	15.6	2.8	1.9	12.3	67.4	79.7	Loamy Sand	1.9	1.1	0.10	11.0
Ghana	Ayinase	Oxisol	12.2	4.1	3.2	16.2	64.3	80.5	Loamy Sand	3.0	1.7	0.15	11.6
Brazil	Piracicaba 1	Oxisol	11.1	2.3	4.8	57.5	24.3	81.8	Loamy Sand	1.1	0.6	0.06	10.0
Brazil	Piracicaba 2	Oxisol	11.3	1.9	5.0	60.0	21.8	81.8	Loamy Sand	1.0	0.6	0.05	10.4
Venezuela	Yaracuy	Ultisol	6.7	4.0	7.0	35.0	47.3	82.3	Loamy Sand	0.6	0.3	0.04	7.3
Ghana	Tikobo	Ultisol	10.9	2.1	4.1	31.9	51.0	82.9	Loamy Sand	1.9	1.1	0.10	11.4
Venezuela	Valle La Pascua	Ultisol	6.8	3.4	6.6	39.3	43.9	83.2	Loamy Sand	0.6	0.4	0.04	9.0
Ghana	Kwaben	Ultisol	6.5	2.1	4.1	43.3	44.0	87.3	Sand	3.1	1.8	0.15	12.3

Silt F = fine silt, Silt C = coarse silt, Sand F = fine sand, Sand C = coarse sand, OM = organic matter, OC = organic carbon, N = nitrogen, C/N = carbon/nitrogen ratio.

TABLE IV. SOIL pH, EXCHANGEABLE CATIONS, SUM OF EXCHANGEABLE BASES (S), CEC (T), % BASE SATURATION (S/T), % CALCIUM SATURATION (Ca/T) (SOILS GROUPED ACCORDING TO INCREASING pH_{H2O} VALUES)

Country	Location	Soil Taxonomy	pH H_2O	pH KCl	Ca	Mg	K	Na	Mn	Al	H	S	T	S/T	Ca/T
					-------------------		------cmol(+)/kg		-------------------		-------------------		-------	%	%
Thailand	Kho Hong	Ultisol	4.20	3.45	0.25	0.09	0.06	0.03	0.04	1.25	0.32	0.43	2.16	19.9	12
Venezuela	Yaracuy	Ultisol	4.20	3.70	0.54	0.31	0.05	0.07	0.01	0.18	0.04	0.97	1.22	79.9	44
China	Kunming (red clay)	Inceptisol	4.25	3.90	1.68	0.30	0.05	0.02	0.09	0.72	0.16	2.05	3.70	55.4	45
Poland	Pulawy	Histosol	4.36	3.85	10.01	2.73	1.19	0.22	0.03	0.60	0.22	14.15	12.7		79
Ghana	Boi	Oxisol	4.40	3.60	0.45	0.46	0.09	0.08	0.02	1.03	0.30	1.08	3.02	35.8	15
Ghana	Abena	Oxisol	4.55	3.60	0.33	0.33	0.09	0.08	0.01	1.09	0.24	0.82	2.61	31.6	13
Malaysia	Rengam	Ultisol	4.60	4.00	0.24	0.17	0.14	0.03	0.01	1.24	0.15	0.59	2.10	28.1	11
China	Yiyang	Ultisol	4.65	3.80	1.09	0.42	0.24	0.16	0.19	1.22	0.12	1.91	3.34	57.0	33
China	Yingtan	Ultisol	4.70	3.80	0.49	0.26	0.12	0.05	0.01	6.40	0.19	0.92	10.6	8.7	5
China	Zhanjiang	Inceptisol	4.75	3.90	0.49	0.19	0.04	0.07	0.01	0.80	0.09	0.79	2.61	30.3	19
China	Guangzhou	Inceptisol	4.85	3.95	0.67	0.08	0.22	0.11	0.01	0.62	0.07	1.07	1.81	59.1	37
Venezuela	Valle La Pascua	Ultisol	4.85	3.95	0.24	0.20	0.04	0.01	0.01	0.25	0.09	0.49	0.93	52.6	26
China	Jinhua	Ultisol	4.90	3.80	1.84	0.23	0.08	0.05	0.12	1.48	0.11	2.20	5.46	40.3	34
Ghana	Ankasa	Oxisol	4.95	4.05	0.45	0.30	0.08	0.07	0.01	0.66	0.11	0.90	2.13	42.4	21
Indonesia	Batu Marta	Ultisol	4.95	3.95	1.56	0.74	0.13	0.04	0.02	0.78	0.16	2.46	3.66	67.2	43
China	Kunming (shale)	Ultisol	4.95	3.90	1.32	0.37	0.23	0.04	0.09	0.82	0.09	1.95	2.95	66.4	45
Ghana	Ayinase	Oxisol	5.00	3.75	0.37	0.40	0.08	0.07	0.01	0.92	0.17	0.92	2.56	36.1	14
Kenya	Kakamega	Ultisol	5.00	4.15	1.18	0.31	0.13	0.11	0.16	1.03	0.09	1.74	3.19	54.4	37
China	Changxing	Inceptisol	5.05	4.10	8.05	2.23	0.09	0.18	0.21	0.10	0.06	10.55	12.2	86.3	66
Ghana	Tikobo	Ultisol	5.05	4.15	1.17	0.43	0.07	0.06	0.01	0.13	0.06	1.72	1.85	93.0	63
China	Huazhou	Ultisol	5.25	4.30	0.96	0.23	0.14	0.08	0.02	0.07	0.03	1.41	2.16	65.3	44
Thailand	Warin	Ultisol	5.30	4.00	0.36	0.20	0.04	0.01	0.07	0.11	0.06	0.61	0.72	84.5	50
China	Zunyi 26	Ultisol	5.30	4.35	5.75	1.17	0.43	0.09	0.21	0.08	0.04	7.44	8.98	82.9	64
Romania	Albota	Alfisol	5.40	4.10	8.34	1.40	0.22	0.10	0.18	0.15	0.07	10.06	11.2	89.6	74
Romania	Sanandrei	Mollisol	5.50	4.55	16.19	4.37	0.25	0.07	0.22	0.00	0.01	20.87	22.1	94.5	73

Country	Location	Soil Taxonomy	pH H_2O	pH KCl	Ca	Mg	K	Na	Mn	Al	H	S	T	S/T %	Ca/T %
					-------------------		------cmol(+)/kg		-------------------		-------------------		-------		
Russia	Bryansk	Spodosol	5.55	4.45	4.61	0.99	0.32	0.07	0.17	0.06	0.04	5.99	5.96	100	77
China	Jinxian	Inceptisol	5.55	4.55	3.93	0.66	0.14	0.09	0.07	0.03	0.02	4.83	4.99	96.8	79
Ghana	Kwaben	Ultisol	5.60	4.60	1.77	0.73	0.23	0.06	0.01	0.01	0.03	2.78	2.90	96.1	61
China	Changsha	Inceptisol	5.70	4.70	7.40	0.63	0.12	0.12	0.19	0.06	0.02	8.27	10.7	77.6	69
China	Taihe	Inceptisol	5.75	4.75	2.37	0.74	0.08	0.07	0.02	0.01	0.01	3.26	3.51	92.9	68
Venezuela	El Pao	Ultisol	5.80	4.65	1.12	3.14	0.23	0.07	0.06	0.02	0.05	4.55	5.23	87.1	21
Chile	Pemehue	Inceptisol	5.80	4.70	4.08	0.81	0.34	0.09	0.04	0.03	0.03	5.32	6.07	87.7	67
Hungary	Szentgyörgyvölgy	Alfisol	5.80	4.55	4.57	0.69	0.19	0.03	0.15	0.13	0.01	5.49	5.98	91.9	76
China	Jingde	Ultisol	5.90	4.90	5.65	1.37	0.27	0.04	0.16	0.00	0.01	7.33	9.38	78.1	60
Chile	Metrenco	Ultisol	6.00	4.80	10.65	1.64	0.34	0.08	0.14	0.00	0.02	12.71	14.9	85.4	72
Belarus	Minsk	Spodosol	6.05	5.00	3.68	1.33	0.13	0.01	0.05	0.07	0.01	5.15	5.44	94.6	68
Chile	Santa Barbara	Andosol	6.05	5.15	1.88	0.31	0.11	0.07	0.01	0.00	0.00	2.37	2.66	89.2	71
Hungary	Kompolt	Mollisol	6.15	5.10	24.31	4.34	0.30	0.01	0.09	0.33	0.02	28.95	29.9	96.9	81
Indonesia	Pusaka Negara	Inceptisol	6.15	5.30	20.85	11.50	1.00	0.54	0.70	0.00	0.00	33.89	35.8	94.7	58
Indonesia	Pasar Jumat	Ultisol	6.40	5.20	7.88	2.43	0.36	0.58	0.37	0.00	0.00	11.26	14.5	77.6	54
Brazil	Piracicaba 2	Oxisol	6.40	4.90	1.28	0.32	0.07	0.03	0.02	0.03	0.01	1.70	1.74	97.8	74
Thailand	Pak Chong	Ultisol	6.70	5.70	6.60	0.85	0.22	0.07	0.05	0.01	0.00	7.73	7.82	98.8	84
Cuba	Ciego de Avila/Univ	Alfisol	6.80	5.70	8.83	3.39	0.22	0.13	0.02	0.00	0.00	12.57	13.5	93.0	65
Brazil	Piracicaba 1	Oxisol	6.95	5.10	1.55	0.36	0.12	0.04	0.01	0.01	0.00	2.07	2.06	100	75
Cuba	Ciego de Avila/Epica	Alfisol	7.10	6.10	7.81	2.81	0.59	0.12	0.01	0.00	0.00	11.34	11.8	96.2	66
China	Liujiang	Alfisol	7.30	6.45	22.79	1.72	0.10	0.18	0.01	0.00	0.00	24.79	25.8	96.0	88
China	Zunyi 27	Entisol	7.40	6.75	17.36	0.95	0.16	0.06	0.01	0.00	0.00	18.53	20.2	91.6	86
China	Yuzhong	Entisol	8.20	7.55	10.22	0.94	0.35	0.09	0.01	0.00	0.00	11.60	12.2	94.9	84
China	Gaonan	Aridisol	8.45	7.80	7.62	1.55	0.44	0.41	0.01	0.00	0.00	10.01	9.11	100	84
China	Yangling	Mollisol	8.45	7.45	14.21	2.33	0.34	0.22	0.01	0.00	0.00	17.10	16.3	100	87
China	Yongdeng	Mollisol	8.50	7.75	10.94	1.85	1.45	0.16	0.01	0.00	0.00	14.40	13.8	100	79

TABLE V. SOIL PHOSPHORUS STATUS CHARACTERISTICS: TOTAL P AVAILABLE P ACCORDING TO DIFFERENT METHODS, E_1 AND FIXATION INDEX r_1/R (SOILS LISTED ACCORDING TO INCREASING E_1 VALUES)

Country	Location	Soil Taxonomy	P total	P-Olsen	P-Bray 2	P-Iron	P resin	E_1	r_1/R
			mg P/kg		mg P/kg		mg P/dm^3	mg P/kg	
Venezuela	Yaracuy	Ultisol	85	3.4	5.3			0.29	0.550
Venezuela	El Pao	Ultisol	110	2.3	2.8			0.36	0.160
China	Kunming (shale)	Ultisol	281	5.6	16.5	2.3	5.9	0.49	0.160
Brazil	Piracicaba 1	Oxisol	171	3.6	18.0	1.5	4.3	0.54	0.100
Ghana	Tikobo	Ultisol	138	4.5	12.9	1.0	4.6	0.75	0.370
Ghana	Ankasa	Oxisol	116	4.2	13.4	0.1	5.0	0.81	0.160
Ghana	Abenia	Oxisol	127	3.5	13.1	0.5	6.2	0.92	0.190
China	Yuzhong	Entisol	1200	55.9	149.6	3.7	11.2	1.00	0.130
Thailand	Warin	Ultisol	63	2.0		0.5	2.5	1.10	0.610
Ghana	Ayinasi	Oxisol	118	7.9	19.8	0.9	9.0	1.10	0.340
Ghana	Kwaben	Ultisol	138	14.0	43.4	4.3	12.4	1.30	0.680
Venezuela	Valle La Pascua	Ultisol	83	3.7	4.1			1.40	0.740
China	Huazhou	Ultisol	310	17.9	46.9	4.4	12.7	1.40	0.140
Ghana	Boi	Oxisol	226	3.7	21.2	0.3	4.6	1.50	0.160
Chile	Metrenco	Ultisol	659	4.3	3.3	2.1	12.4	1.50	0.018
China	Yangling	Mollisol	710	8.2	121.1	6.5	10.5	1.50	0.140
Thailand	Pak Chong	Ultisol	252	4.0		4.3	11.2	2.20	0.089
China	Taihe	Inceptisol	431	23.6	118.3	11.6	28.6	2.20	0.300
China	Gaonan	Aridisol	645	13.0	97.7	12.2	25.1	2.20	0.115
Cuba	Ciego de Avila/Epica	Alfisol	392	5.9	9.6	2.0	20.5	2.40	0.045
China	Liujiang	Alfisol	508	5.8	19.5	2.4	19.9	2.50	0.033
China	Jinxian	Inceptisol	318	7.0	24.5	1.9	9.3	2.60	0.017
China	Yiyang	Ultisol	572	17.4	49.2	3.1	19.2	2.60	0.045
Malaysia	Rengam	Ultisol	81	3.5	6.8			3.00	0.190
Kenya	Kakamega	Ultisol	458	4.2	13.4	1.9	7.1	3.75	0.012
Brazil	Piracicaba 2	Oxisol	165	3.2	19.1	0.8	3.7	3.90	0.017
Belarus	Minsk	Spodosol	417	23.1		26.1	36.3	4.40	0.340

Country	Location	Soil Taxonomy	P total	P-Olsen	P-Bray 2	P-Iron	P resin	E_1	r_1/R
			mg P/kg		mg P/kg		mg P/dm^3	mg P/kg	
China	Zhanjiang	Inceptisol	167	3.3	6.1	0.5	2.5	4.50	0.015
Chile	Santa Barbara	Andosol	1730	11.2	2.2	10.8	14.6	4.60	0.011
China	Guangzhou	Inceptisol	133	3.4	12.6	3.1	3.4	5.60	0.011
China	Zunyi 27	Entisol	888	31.0	145.0	13.5	75.5	5.95	0.270
Poland	Pulawy	Histosol	510	97.9		43.2	74.8	6.10	0.680
Hungary	Kompolt	Mollisol	303	17.2		26.3	37.6	6.30	0.180
China	Changxing	Inceptisol	297	9.6	19.5	2.3	10.5	6.70	0.006
China	Zunyi 26	Ultisol	599	26.9	184.6	7.3	33.2	8.30	0.019
Chile	Pemehue	Inceptisol	1893	12.8	4.7	6.9	23.6	8.30	0.015
China	Jingde	Ultisol	1041	20.3	34.6	21.6	81.9	8.70	0.680
China	Changsha	Inceptisol	750	11.1	23.0	15.5	89.4	8.80	0.082
Hungary	Szentgyörgyvölgy	Alfisol	751	39.4		44.4	59.6	9.00	0.370
China	Kunming (red clay)	Inceptisol	904	42.3	111.0	1.4	26.1	9.00	0.008
Romania	Albota	Alfisol	495	15.3	26.6	8.5	25.8	9.75	0.260
China	Yongdeng	Mollisol	1150	58.2	427.7	38.5	111.8	16.40	0.590
China	Jinhua	Ultisol	388	6.3	25.1	1.6	1.8	20.30	0.004
China	Yingtan	Ultisol	235	1.6	2.4	0.0	1.8	22.00	0.002
Thailand	Kho Hong	Ultisol	120	5.8	10.8	2.7	3.4		
Indonesia	Batu Marta	Ultisol	175	3.8	17.2	2.1	6.5		
Cuba	Ciego de Avila/Univ	Alfisol	259	2.1	2.2	0.7	5.3		
Russia	Bryansk	Spodosol	376	30.2		8.4	14.9		
Romania	Sanandrei	Mollisol	485	6.0	11.0	4.0	11.8		
Indonesia	Pusaka Negara	Inceptisol	570	15.2	51.5	4.5	46.6		
Indonesia	Pasar Jumat	Ultisol	640	10.6	6.1	1.6	25.8		

3.2.1. Soil pH

Soil pH is reported as one of the most predictive properties of PR dissolution, in particular when it is combined with determination of Al (pyrophosphate soluble Al) and Fe (oxalate extractable) in the soil [13]. Furthermore, it has been found in Australia that soil acidity titratable to pH 6 is the most highly predictive property of PR dissolution in a wide range of soils. This acidity considers the supply of protons from organic matter and surfaces of soils minerals [14].

The soils in the study were grouped according to their pH values in water and their distribution as shown in Table VI.

The results of Table VI indicate that 86% of the soils in the study had pH<6.0 and thus, a high probability for PR dissolution. The few soils with pH above 6.0 were also acid soils but lime-amended. These values, however, should be critically examined in conjunction with the pH buffering capacity of the soil, which is stronger in heavy textured soils and soils with high organic matter content [13].

TABLE VI. DISTRIBUTION OF SOILS ACCORDING TO SOIL pH (H_2O)

SOIL	PH <5.0	pH 5.0-6.0	PH >6.0	Range
ULTISOLS	10	8	2	4.20 - 6.70
INCEPTISOLS	3	5	1	4.25 - 6.15
OXISOLS	4	0	2	4.40 - 6.95
TOTAL	17 (49%)	13 (37%)	5 (14%)	

3.2.2. Colloidal particles

The content and type of colloidal particles of the soils determine the physico-chemical characteristics of the soils, thus affecting the PR dissolution rates. Properties like water holding capacity, CEC, pH-buffering capacity mentioned above, phosphate sorption (adsorption/desorption) rates and intensity are dependent on the soil colloidal fractions.

Under this heading, an analysis has been made of the content of both mineral and organic colloidal fractions. The distribution of soils according to the mineral colloidal fraction, clay content alone and fine particles (%clay + %fine silt), are given in Table VII.

From Table VII, it may be observed that the majority of Inceptisols have very high clay (>20%) and fine particle contents (>30%). Ultisols showed a balanced distribution with regard to fine particles and clay content while in the Oxisols the contents of clay and fine particles were the lowest.

An analysis of the soils distribution according to the organic matter content is also shown in Table VII. In the highly weathered tropical acid soils, which contain low activity clays (1:1 type) and iron and aluminum oxides, the organic matter plays an important role affecting the P sorption capacities of these soils [15].

Organic P is a significant fraction of total soil P in these soils when uncultivated [11]. However, when these soils are brought under cultivation or fallows are eliminated, there is a widespread and serious depletion of organic matter affecting overall soil fertility.

TABLE VII. DISTRIBUTION OF SOILS ACCORDING TO CLAY CONTENT, FINE PARTICLE (CLAY+FINE SILT) CONTENT, AND ORGANIC MATTER

CLAY CONTENT

SOIL	<20%	20–40%	>40%	Range
ULTISOLS	9	5	6	5.9–70.5
INCEPTISOLS	1	6	2	10.0–61.0
OXISOLS	4	2	-	11.3–30.0
TOTAL	14 (40%)	13 (37%)	8 (23%)	

FINE PARTICLES (CLAY + FINE SILT)

SOIL	<30%	30–60%	>60%	Range
ULTISOLS	9	6	5	7.7–84.7
INCEPTISOLS	1	3	5	16.2–88.5
OXISOLS	5	1	-	13.2–34.1
TOTAL	15 (42%)	10 (29%)	10 (29%)	

ORGANIC MATTER CONTENT

SOIL	<1.5%	1.5–2.5%	>2.5%	Range
ULTISOLS	6	6	8	0.40–10.1
INCEPTISOLS	1	4	4	1.40–13.4
OXISOLS	2	1	3	1.00–4.00
TOTAL	9 (26%)	11 (31%)	15 (43%)	

About half (43%) of the soils in study showed high organic matter content because they were uncultivated or under fallow. As indicated above, this may have implications on soil P testing due to the close association of organic P and soil P fertility status of these soils [11]. On the other hand, these soils may be considered suitable for fertilization with PR because of their greater pH buffering capacity and supply of protons.

3.2.3. Calcium status

Concentration of Ca in soil solution and Ca buffering capacity of the soil can affect PR dissolution. Exchangeable Ca has been utilized as an indicator of the Ca status in soils. This parameter, however, was found to be a minor predictive variable explaining the PR dissolution in soils [16].

In this study, both exchangeable Ca and sum of exchangeable bases were related to the cation exchange capacity of the soils to estimate their respective % Ca saturation and % base saturation. The distribution of the soils according to these parameters is shown in Table VIII.

The distribution patterns for both % Ca saturation and % base saturation are similar, i.e. 66% of the soils have low and medium Ca and base saturation. The low Ca and base saturation in soil provides suitable conditions for PR dissolution. However, some 34% showed abnormally high Ca and base saturation levels, probably due to the application of lime amendments to these tropical acid soils.

3.2.4. Phosphate status

Phosphate factors considered are total P content, concentration of P (phosphate) in the soil solution and P buffering capacity. In this study, the concentration of P in the soil extract (intensity factor C_P) and the instantaneous P adsorption (fixation) parameter, as determined by the ^{32}P exchange kinetics method was utilized as indicators for the last two factors.

TABLE VIII. DISTRIBUTION OF SOILS ACCORDING TO
% CALCIUM SATURATION AND % BASE SATURATION

% CALCIUM SATURATION

SOIL	<45%	45–60%	>60%	Range
ULTISOLS	11	4	5	5–84
INCEPTISOLS	2	2	5	19–69
OXISOLS	4	-	2	15–75
TOTAL	17 (49%)	6 (17%)	12 (34%)	

% BASE SATURATION

SOIL	<60%	60–85%	>85%	Range
ULTISOLS	7	8	5	8.7–98.8
INCEPTISOLS	3	1	5	30.3–96.8
OXISOLS	4	-	2	31.6–100
TOTAL	14 (40%)	9 (26%)	12 (34%)	

The soil distribution according to the total P (mg P kg^{-1} soil) content is shown in Table IX. The ranges for establishing the soil categories were arbitrarily selected considering the levels normally found in highly weathered tropical acid soils. Considering an average content of 1500 mg P kg^{-1} soil total P for a normal soil, the large majority of the soils in this study can be considered to have low inherent P fertility.

For the application of the ^{32}P exchange kinetics method, a soil suspension in water is prepared using a 1:10 soil:water ratio [10]. The phosphate (P) concentration (ppm) in the soil water extract was utilized as an indicator of the P concentration in soil solution. The distribution of the soils according to this parameter is given in Table IX.

Three categories (low, medium and high) were established according to arbitrary critical levels. However, the low (<0.02 ppm P) and the intermediate (0.02–0.2 ppm P) categories can be considered as very low and low respectively. Thus, 91% of the soils had very low and low P concentrations in soil extracts. Only 9% were high, probably due to the residual effect of past P fertilization or bush fallow (i.e. in the Oxisols [11]). All Inceptisols showed poor P concentrations in the soil extracts.

In the ^{32}P exchange kinetics method, the ratio r_1/R is determined, where r_1 is the ^{32}P activity remaining in solution after 1 minute of exchange and R, the ^{32}P activity introduced at time t = 0. This instantaneous adsorption index can be used to estimate the soil phosphate (P) fixing capacity (as the inverse of this ratio or R/r_1) and its determination is recommended in routine analysis of soil P fertility status [17]. Soils were also distributed according to this parameter, as shown in Table IX.

Almost all Inceptisols showed an extremely high P fixation capacity and most Oxisols, intermediate P fixation capacity. Ultisols had P fixation capacities across all categories.

For a wide range of soils with well-crystalized mineral components (clays and oxides) and low amorphous materials, this P fixation capacity index was found closely related to the soil content of clay and dithionate-citrate extractable iron oxides [17]. Particular care must be taken in Oxisols strongly enriched in Fe oxides but containing goethite crystals larger than those normally found for pedogenic Fe oxides [18].

TABLE IX. DISTRIBUTION OF SOILS ACCORDING TO TOTAL P CONTENT, P CONCENTRATION IN SOIL EXTRACTS, AND P FIXATION CAPACITY INDEX

TOTAL P (mg/kg)

SOIL	<500	500–1000	>1000	Range
ULTISOLS	15	4	1	63–1041
INCEPTISOLS	5	3	1	133–1893
OXISOLS	6	-	-	116–226
TOTAL	26 (74%)	7 (20%)	2 (6%)	

P CONCENTRATION IN SOIL WATER EXTRACTS (mg/L)

SOIL	<0.02	0.02–0.2	>0.2	Range
ULTISOLS	11	6	1	0.0027–0.59
INCEPTISOLS	5	2	-	0.004–0.066
OXISOLS	4	-	2	0.0013–0.36
TOTAL	20 (65%)	8 (26%)	3 (9%)	

P FIXATION CAPACITY INDEX (R/r_1)

SOIL	<5	5–10	>10	Range
ULTISOLS	6	4	7	0.018–0.740
INCEPTISOLS	1	-	7	0.008–0.030
OXISOLS	1	4	1	0.017–0.340
TOTAL	8 (26%)	8 (26%)	15 (48%)	

The P buffering or the P adsorption capacity of the soil is considered to play a major role in PR dissolution in soils [19]. Some authors consider it more important than the pH buffering capacity of the soil. Sometimes, when both P and pH buffering capacities are positively correlated it is not possible to ascertain the relative importance of the two properties in promoting PR dissolution [13].

This study demonstrates that pH and soil P status parameters, in particular P fixation capacity index and P concentration in aqueous extract, are the main soil properties affecting PR dissolution in these tropical acid soils. Additional related characteristics are clay content, organic matter content, and % Ca saturation. In the case of high P fixing soils, it would also be useful to have information on total and extractable Fe and Al.

3.3. Suitability of methods for soil P testing

Many factors influence plant growth and its P uptake. Plant roots take up orthophosphate ions from the soil solution. However, mass flow (the absorption of water from soil solution by the plant) can only explain 5–10% of the total P uptake. This means that a large fraction of phosphate ions taken up by the roots is desorbed from the solid phase of the soil during plant growth. Thus, available P can be defined as the phosphate ions that may leave the soil particles and enter into soil solution for uptake by the root hairs. The quantity of available P is therefore, the fraction of total soil P that could be made available for plant uptake and not the actual quantity of P extracted or removed by a crop [20].

Phosphorus fertilizer recommendations are based on the crop yield responses to increasing applications of P fertilizer in defined soils and environments. To calculate the optimum P fertilizer rate to be applied to a crop, it is necessary to estimate the soil available P. There are many routine methods for soil P testing to determine available soil P. Most routine methods are based on the extraction capacity of several chemical compounds simulating the P uptake by roots. A chemical extractant when added to a soil will react with the predominant P forms of that soil; thus when changing either soils or extractants, the P extracted will differ widely. No single chemical method is suitable for all soils. In this study two common extractant methods were utilized which included Olsen and Bray II.

Other methods for soil P testing are based on the exchange reactions of phosphate ions in the soils. One of these utilized in this study measures available P by anion exchange resins. Another exchange method employed for the quantification of available soil P is the ^{32}P exchange kinetics method, based on the Brownian motion principle of phosphate ions in a soil suspension (1:10 soil:water ratio). The soil P status is characterised through the determination of the intensity, quantity and capacity factors. The quantity factor (E_1 value), that is the amount of phosphate ions exchangeable after one minute of exchange is considered the available soil P.

Another method utilises iron oxide-coated filter paper (Pi) strips as sinks or collectors for the P in the soil suspension. From preliminary studies, this Pi method appears attractive for routine P testing in a wide range of soils.

The soils in study were classified into categories of low, medium and high content of available soil P based on arbitrary critical limits. The distribution of the soils is shown for the Olsen, Bray II, Pi, P resin, and ^{32}P exchange kinetics methods in Table X.

Data on amounts of available P obtained by Olsen and Bray II methods are different due to contrasting extracting power of the solutions utilised in these methods. However, the distribution pattern of the soils according to the available amounts is quite similar. The majority (some 60%) of soils have low P availability, whereas soils with medium and high availability are more or less equally represented (20% each). Considering their natural soil P fertility (total P content), it may be inferred that some of them, in particular those with high available P have received P fertilizers in the past.

In general, the results of iron strip P (Pi) showed a similar trend as indicated above for the chemical extraction methods but with a slightly higher number of soils (Ultisol and Inceptisol) on the medium and high availability category.

The distribution of soils according to P availability by the resin was similar to the one described above for the extraction and Pi methods; with about 60% for the low available P category and the rest more or less similarly distributed between medium and high available P categories. However, the distribution within the soil groups was most close between the Pi and P resin methods.

The amounts of available soil P determined by the exchange methods of resin and isotopic exchange kinetic varied widely, as indicated by the range and critical limits. A close examination of the E values revealed that some data, in particular those of the Inceptisols and one Oxisol with very high P fixation capacity were overestimated. The parameters determined by the isotopic method are largely influenced by the P fixing capacity of the soils [21]. Reclassifying these outliers as low available, the distribution of soils was as follows: low (23 or 74%), medium (6 or 19%) and high (2 or 6%). A particular limitation in most tropical acid soils is their very low P concentration in soil solution complicated by their high P fixing capacity and interference of colloidal particles, making it difficult to obtain accurate and reliable data on intensity and quantity factors (JC Fardeau, personal communication). Further studies are needed to improve these determinations such as use of ionic chromatography [22]

In this study, a preliminary evaluation of methods for available P was made but limited to a relative comparison of the laboratory tests. No greenhouse and field data from the agronomic testing were included. The participants of the project have conducted this study as part of their own work. In summary, no conclusion can be made in this study on the suitability of the methods for soil P testing due to the lack of data on the agronomic evaluation. Further investigations on PR application to tropical acid soils, under well-defined management conditions, i.e: cropping system, cultivation, fallow, and P fertilization history, are needed to: a) establish relationships between crop yields and soil P supply in field experiments, and ii) group soil P supply into categories based on the probability of crop response to P fertilization.

TABLE X. DISTRIBUTION OF SOILS ACCORDING TO
OLSEN P, BRAY II P, IRON STRIP P (Pi), RESIN P, AND E_1 VALUES

OLSEN P

	<7	7–14	>14 mg P/kg	Range
ULTISOLS	14	2	4	1.6–26.9
INCEPTISOLS	2	4	3	3.3–42.3
OXISOLS	5	1	-	3.2–7.9
TOTAL	21 (60%)	7 (20%)	7 (20%)	

BRAY II P

	<20	20–40	>40 mg P/kg	Range
ULTISOLS	14	2	4	2.4–184.6
INCEPTISOLS	4	2	3	4.7–118.3
OXISOLS	5	1	-	13.1–21.2
TOTAL	23 (66%)	5 (14%)	7 (20%)	

IRON STRIP P (Pi)

	<2	2–4	>4 mg P/kg	Range
ULTISOLS	10	5	5	0–21.6
INCEPTISOLS	3	2	4	0.5–15.5
OXISOLS	6	-	-	0.1–1.5
TOTAL	19 (54%)	7 (20%)	9 (26%)	

RESIN P

	<10	10–20	>20 mg P/dm^3	Range
ULTISOLS	12	4	4	1.8–81.9
INCEPTISOLS	3	1	5	2.5–89.4
OXISOLS	6	-	-	3.7–9.0
TOTAL	21 (60%)	5 (14%)	9 (26%)	

E_1 VALUES

	<2	2–4	>4 mg P/kg	Range
ULTISOLS	9+2	4	2	0.29–8.70
INCEPTISOLS		2	6	2.0–9.0
OXISOLS	5	1	-	0.81–3.9
TOTAL	16 (52%)	7 (23%)	8 (26%)	

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REFERENCES

[1] KHASAWNEH, F.E., DOLL, E.C., Use of phosphate rock for direct application. Adv. Agron. **30** (1978) 159-206.

[2] ZAPATA, F., Evaluating agronomic effectiveness of phosphate rocks using nuclear and related techniques: Results from an FAO/IAEA Coordinated Research Project. In: IAEA TECDOC 1159, IAEA, Vienna (2000) 91-100.

[3] AFNOR, Recueil de Normes “Qualité des sols”, volume 1 (566 pages) and 2 (408 pages). ISBN 2-12-213141-1, 1999 (http://www.afnor.fr).

[4] ORSINI, L., REMY, J.C., Utilisation du chlorure de cobaltihexamine pour la détermination simultanée de la capacité d’échange et des bases échangeables des sols. Bulletin de l’AFES, Science du Sol (1976) 269-275.

[5] OLSEN, S.R., COLE, C.V., WATANABE, F.S., DEAN, L.A., Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ. 939. US Gov. Print Office, Washington DC. (1954).

[6] BRAY, R.H., KURTZ, L.T., Determination of total, organic, and available forms of phosphorus in soil. Soil Sci. **59** (1945) 39-45.

[7] MENON, R.G., CHIEN, S.H., HAMMNOND, L.L., The Pi soil phosphorus test. A new approach to testing for soil phosphorus. IFDC Ref. Manual R-7 International Fertilizer Development Center, Muscle Shoals, Alabama, USA (1989) 10 p.

[8] HABIB, L., CHIEN, S.H., MENON, R.G., CARMONA, G., Modified Iron Oxide-Impregnated Paper Strip Test for soils treated with Phosphate Fertilizers. Soil Sci Soc Am. J. **62** (1998) 972-976.

[9] RAIJ, B. VAN, QUAGGIO, J.A., Metods de analise de solo para fins de fertilidade. Boletim Tecnico No.81. Instituto Agronomico de Campinas, Brasil (1983) 30 p.

[10] FARDEAU, J.C.; GIRAUD, G., MAROL, C., Bioavailable soil P as a key to sustainable agriculture. Functional model determined by isotopic tracers. In: Proc. Int. Symp. on Nuclear and related techniques in soil-plant studies on sustainable agriculture and environmental protection. IAEA, STI/PUB/947, Vienna (1995) 131-144.

[11] SHARPLEY, A.N., TIESSEN, H., COLE, C.V., Soil phosphorus forms extracted by soil tests as a function of pedogenesis. Soil Sci. Soc. Am. J. **51** (1987) 362-365.

[12] CHIEN, S.H., Reactions of phosphate rocks with acid soils of the Humid Tropics. In: Proc. Workshop “Phosphate sources for Acid Soils in the Humid Tropics”, Kuala Lumpur, November 1990. Malaysian Soc. of Soil Science, Kuala Lumpur (1992) 18-29.

[13] GILKES, R.J., BOLLAND, M.D.A., The Australian Experience with Rock Phosphates: Limitations and Explanations. In: Proc. Workshop “Phosphate sources for Acid Soils in the Humid Tropics”, Kuala Lumpur, November 1990. Malaysian Soc. of Soil Science, Kuala Lumpur (1992) 177-205.

[14] KANABO, I.A.K., GILKES, R.J., The role of soil pH in the dissolution of phosphate rock fertilizers. Fert.Res.**12** (1987) 165-174.

[15] YAMUREMYE, F., DICK, R.P., Organic amendments and phosphorus sorption by soils. Adv. Agron. **56** (1996) 139-185.

[16] HUGHES, J.C., GILKES, R.J., The effect of soil properties and level of fertilizer application on the dissolution of Sechura Rock Phosphate in some soils from Brazil, Colombia, Australia and Nigeria. Aust.J.Soil Res.**24** (1986) 219-227.

[17] FROSSARD, E., FELLER, C., TIESSEN, H., STEWART, J.W.B., FARDEAU, J.C., MOREL, J.L., Can an isotopic method allow for the determination of the phosphate-fixing capacity of soils? Commun. Soil Sci. Plant Anal. **24** (1993) 367-377.

[18] OWUSU BENNOAH, E., SZILAS, C., HANSEN, H.C.B., BORGAARD, O.K., Phosphate sorption in relation to Aluminium and Iron Oxides of Oxisols from Ghana. Commun. Soil Sci. Plant Anal. **28** (1997) 685-697.

[19] BOLLAND, M.D.A., BARROW, N.J., Effect of level of application on the relative effectiveness of rock phosphate. Fert. Res.**15** (1988) 181-192.

[20] FARDEAU, J.C., Dynamics of phosphates in soils. An isotopic outlook. Fert. Res. 45 (1996) 91-100.

[21] XIONG LIMING, FARDEAU, J.C., ZHOU ZHIGAO, Suitability of isotopic kinetic approach to assess phosphorus status and bioavailability of major acidic soils soil in subtropical China. Pedosphere **7** (1997) 11-118.

[22] SINAJ, S., MACHLER, F., FROSSARD, E., FAISSE, C., OBERSON, A., MOREL, C., Interferences of colloidal particles in the determination of orthophosphate concentration in soil water extracts. Commun. Soil Sci. Plant Anal. **29** (1998) 1091-1105.

Part II

STUDIES FROM WESTERN EUROPE AND NORTH AMERICA

THE USE OF ^{32}P DILUTION TECHNIQUES TO EVALUATE THE EFFECT OF MYCORRHIZAL INOCULATION ON PLANT UPTAKE OF P FROM PRODUCTS OF FERMENTATION MIXTURES INCLUDING AGROWASTES, *Aspergillus niger* AND ROCK PHOSPHATE

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Abstract. Some microorganisms, such as filamentous fungi, are capable of solubilizing rock phosphate products, which are a less costly alternative to conventional P fertilizers used so far in agriculture. However, metabolizable C compounds must be supplied to the microbes to solubilize rock phosphate (RP). On another hand, huge quantities of organic materials are produced by cultivated plants every year and their residues became agrowastes, which may often pose significant environmental problems. An atractive approach to solubilize RP would therefore, be the application of microorganisms possessing a high acid-producing activity in fermentation processes based on agrowastes. In this context, *Aspergillus niger* was successfully cultivated on sugar beet (SB) waste material supplemented with 3.0 g/l RP acidifying the medium by releasing citric acid and thus decreasing the pH to 3.0–3.5. At the end of the solid-state fermentation process, the product contained mineralized (69%) organic matter, RP solubilized to 224 µg/ml and fungal mycelium. A series of microcosms greenhouse experiments were then carried out aimed at evaluating the effectiveness of such product, added at a rate of 5% (v/v), to a neutral, calcareous, P-deficient soil. Clover (*Trifolium repens)* inoculated or not with an arbuscular mycorrhizal fungus, was the test plant. It was shown that the product improved plant growth and P acquisition. Mycorrhizal inoculation further enhanced the effectiveness of the fermentation product. The use of the isotopic ^{32}P dilution technique showed a lowering of the specific activity of the treated plants, thus indicating that plants benefited from P solublilized from RP by the microbial treatments applied in this experiment. The reported biotechnological approach offers a potential application for sustainability purposes.

1. INTRODUCTION

In the natural plant environment (the biosphere, including soil) all the biogenic elements are normally present but not in amounts and availability states required for a high and safe production. In addition, it is well known that land degradation, with a concomitant deterioration of soil fertility, exacerbates further the stagnation or decline of agricultural production [1]. This is the situation of the Mediterranean soils where the combined result of the climate characteristics and the anthropogenic environmental effects has led to disruptions of the vegetation cover and soil structure. The main problems of Mediterranean soils are low contents of organic matter and soluble P, and degraded physical-chemical and biological soil properties, such as soil aggregation and microbial functioning [2]. In conventional, high input agriculture, nutrient deficiencies are remediated and controlled by using fertilizers to establish a proper nutrient balance. However, in view of current developments in sustainability, efforts are concentrated on elaboration of agro-techniques that involve a rational exploitation of soil microbial activities, organic matter amendments and the use of less expensive, though less bioavailable, sources of plant nutrients, like rock phosphate (RP) and agrowastes, which may be made available by microbiologically-mediated processes [3, 4].

It is accepted that there is no substitute of RP as a source of P and with the current trend for a reduced use of agrochemicals; a renewed interest on direct application of RP has arisen [4]. However, and particularly for non-acidic soils, a minimum processing is required before application. Even when the soil acidity is below 5.5–6.0 it has been shown that after four years of annual surface application is when RP could be as effective as superphosphate [5]. Therefore, cropping situations should be manipulated in a way that will permit an effective use of RP, particularly in soils with neutral to slightly acid pH values, as the majority of Mediterranean soils.

Based on the extensive literature on RP research, it is postulated that the processing of RP materials can be approached in two main ways. The first one is to search environmentally mild methods of solubilization before RP application to the soil. Here, the biological methods are considered as the most promising, but more studies should be done using inexpensive organic substrates and highly metabolically active microorganisms operating in economically-attractive and technologically-accepted processes. The second line of studies should be oriented towards direct application of RP to the soil together with microorganisms, both organic acid-producers and mycorrhizal fungi, using technologies that may permit their large-scale application with the existing agricultural machinery. Here, the soil management practices should ensure adequate microbial survival and functioning. Therefore, both approaches are based on the use of natural sources of nutrients and energy.

As the plants grow, besides the harvestable products, huge quantities of residues are also produced. Some residues, in fact agrowastes, may often pose a significant environmental problem, but also their lignocellulosic material is a potentially valuable source of energy. Breakdown by acid-producing microorganisms should be the biotechnological answer allowing using this abundant natural and renewable material [6].

During recent years several investigations on microbially mediated RP solubilization were carried out to study the possibility of combining the capability of some fungal microorganisms to grow on agrowastes and to solubilize simultaneously RP by organic acids released during the fermentation process [7-12]. The aim of the work reported here was to assess the effect of applying the resulting fermentation products in a soil-plant system, together with a mycorrhizal inoculum, by using the ^{32}P dilution techniques.

2. MATERIALS AND METHODS

2.1. Fermentation experiment

2.1.1. Microorganism

The strain NB2 of *Aspergillus niger* used throughout this study was selected from 20 acid-producing fungal cultures and shown to produce only citric acid on complex substrates [13].

2.1.2. Treatments, culture media and fermentation conditions

Four treatments were established as follows: [i] sugar beet wastes (SB); [ii] SB with rock phosphate (RP); [iii] SB with *A. niger*; [iv] SB with RP and *A. niger*, all of them mixed with 50 ml Czapek's mineral solution in 250 ml Erlenmeyer flasks. Sugar beet waste material was ground in an electrical grinder, passed through a 1 mm sieve and used at a concentration of 100g/l. Treatments ii and iv were supplemented with RP [finely ground, 100-mesh, fluorapatite from Morocco with 12.8% total P] at a rate of 3.0 g/l. All mixtures were sterilized at 120°C for 30 min. Treatments iii and iv were inoculated with 1.2×10^7 spores of *A. niger*/flask. All treatments [in triplicate] were incubated statically at 30°C for 20 days and further applied in the soil-plant experiment.

2.1.3. Analytical methods

A. niger mycelia growth was determined by weighing the mycelium, which was carefully separated from the culture medium, washed, and dried in an oven at 100°C. Growth rate change during the incubation process was determined dividing the difference between the previous and actual mycelia weight value by the respective time difference [(mycelia growth at day 6th minus mycelia growth at day 3d)/6-3]. Medium pH was measured with a glass electrode and titratable acidity was determined by titrating each sample to pH 7.0 with 0.1M NaOH. The weight loss of lignocellulose during the incubation was calculated on the basis of ash [500°C] content [16] and presented as a percent of mineralization. Lignin, cellulose and hemicellulose contents were measured [17]. Oxidizable carbon was measured by a wet oxidation method [18], total carbon was determined from the ash [18], and total nitrogen was estimated by the Kjeldal method. The citric acid content was determined by a micro colorimetric method [19]. Phosphorus content was determined by the molybdo-vanadate method [20].

2.2. Soil–plant experiment

2.2.1. Experimental design, test soil, plant and microbial inoculation

The treatments used in this experiment were as follows: [i] SB: control; [ii] SB with RP; [iii] SB with *A. niger*; [iv] SB with RP and *A. niger*, all of them inoculated or not with the arbuscular mycorrhizal (AM) fungus *Glomus deserticola* (total Nº of treatments=8). The products from treatments [i-iv] as described in 2.1.2 were mixed with a steam-sterilized soil-sand mixture (1:1, v/v) and left for equilibration for 4 weeks at room temperature. The topsoil (0-20 cm) from a field of the Granada (Spain) province was used. The main characteristics were pH 7.5; 8 μg P/g [Olsen test]; organic carbon 0.46%; total N 0.046% and E.C. 1.89. SB and RP (microbially treated or not) were added to the soil at a rate supplying 5 g SB/100 g soil and 0.15 g RP/100 g soil/sand mixture.

Three seedlings of *Trifolium repens* were transplanted in each pot (d=12.2 cm; 500 g capacity) inoculated or not with the AM fungus *G. deserticola* and all pots received 1 ml (10^8 cells/ml) of *Rhizobium trifoli* suspension. The AM inoculum consisted of 5 g of spores, mycelium and mycorrhizal root fragments and was applied to each one of the corresponding pots in the bottom of a 5-cm-deep planting hole. The plants were grown in a green house under day/night cycle of 16/8 h, 21/15°C, 50% relative humidity. Throughout the experiment, the pots were weighed every day and water loss was replaced by watering on top of the soil.

The ^{32}P isotope dilution technique [14] was utilised for the studies. An aliquot containing 592 kBq ^{32}P pot^{-1} was added to obtain sufficient activity in the plant material. To prepare the ^{32}P-labelled carrier solution the total activity required for the experiments was added as carrier-free ^{32}P to a known volume of carrier solution (KH_2PO_4) with 10 mg P kg^{-1} [15]. Labelling was done by thoroughly mixing the soil with 10 ml pot^{-1} of ^{32}P-labelled carrier solution.

2.2.2. Analytical methods

Plants were harvested after 6 weeks. Shoot dry weight was recorded after drying at 70°C. Shoot P content was determined by a molybdo-vanadate method [20]. The percentage of mycorrhizal infection was estimated by microscopic examination of stained root samples [21, 22]. The ^{32}P activity in the plant material was measured using the Cerenkov effect in a liquid scintillation analyser Packard Tri-Carb 300. Counts were expressed in Bq and corrected for counting efficiency (50%). The specific activity SA of P in the plant material was then calculated by considering the radioactivity per amount of total P content in the plant and expressed in Bq mg P^{-1}. Data were processed by analysis of variance and Duncan's test ($P \leq 0.05$).

3. RESULTS AND DISCUSSION

3.1. Fermentation stage

Aspergillus niger grew well on medium containing SB waste material as a substrate and a rapid mycelial growth was recorded at the beginning of the cultivation period followed by a slow growth phase (Table I). The initial (first 3 days) average growth rate was 0.19 g/flask/day and 0.02 g/flask/day during the second week. It increased again thereafter and the total biomass produced on medium supplemented with RP was 20% higher than that of 1.0 g/flask obtained [7] on the medium without RP. Mycelial growth and titratable acidity production paralleled in the first half of the process resulting in a maximum solubilization (76%) of the rock phosphate. However, after this period the fungus started to produce spores, indicating adverse conditions for acid productivity. This caused a slow decrease in titratable acidity with a corresponding decrease in soluble P production.

Biomass growth on the lignocellulosic substrate tested in this study was higher than that under liquid culture conditions using the same strain of *A. niger* [13]. Other authors applying sugarcane bagasse [23] and vinasse [24] have reported similar results. The most likely explanation is the the presence of

TABLE I. MYCELIAL GROWTH, TITRATABLE ACIDITY AND ROCK PHOSPHATE SOLUBILIZATION BY *Aspergillus niger* CULTIVATED ON SUGAR BEET WASTE

Time (days)	Biomass (g/flask)	Titratable acidity (mmol/l)	Citric acid (% of total acidity)	Phosphate conc. (μg/ml)	Soluble P/ total P (%)
3	0.57±0.12	38.2±1.4	100	47.4±1.6	12
6	0.68±0.08	60.6±0.7	98	172.6±0.8	44
10	0.77±0.05	72.2±0.6	92	292.2±2.3	76
15	0.89±0.05	58.8±1.1	87	276.8±3.1	71
20	1.20±0.10	48.1±0.2	71	224.0±0.9	58

TABLE II. COMPOSITION OF SUGAR BEET WASTE[1] SUSPENSION TREATED WITH *Aspergillus niger* AFTER A 20-DAY CULTIVATION

	Cellulose (%)	Hemicellulose (%)	Lignin (%)	pH	Mineralization (%)
Initial	29.0	23.0	5.0	7.2	-
20 d	17.0	4.2	4.2	3.2	69

[1] Total carbon: 55%; Oxidizable carbon: 16%; Total nitrogen: 1.7%

sufficient amounts of nutrients in the initial period of cultivation and some lignocellulolytic activity (Table II) bearing in mind the ability of *A. niger* to degrade such kind of substrates [23]. The specific conditions provided by the microorganism/air/water interface during this type of cultivation [23], determined a level of acidity, which was sufficient to overcome the neutralizing effect of RP and its solubilization.

It should be noted that the measured phosphate concentration in the solution probably corresponded to the amount that was not consumed by the mycelium. The addition of RP to the cultivation medium affected the behavior of *A. niger,* particularly its growth and citric acid production.

Although a high percentage of mineralization of SB waste was achieved, a careful assessment and further studies should be done in order to find a better compromise between the level of degradation and concentration of soluble phosphate before the resulting system is applied in soils with different characteristics.

3.2. Soil-plant experiment

Dry matter responses and P content of shoots of non-mycorrhizal and mycorrhizal *T. repens* after the addition of microbially-untreated SB with or without RP and previously cultivated SB (with or without RP) by *A. niger* are presented on Fig. 1 and Fig. 2, respectively.

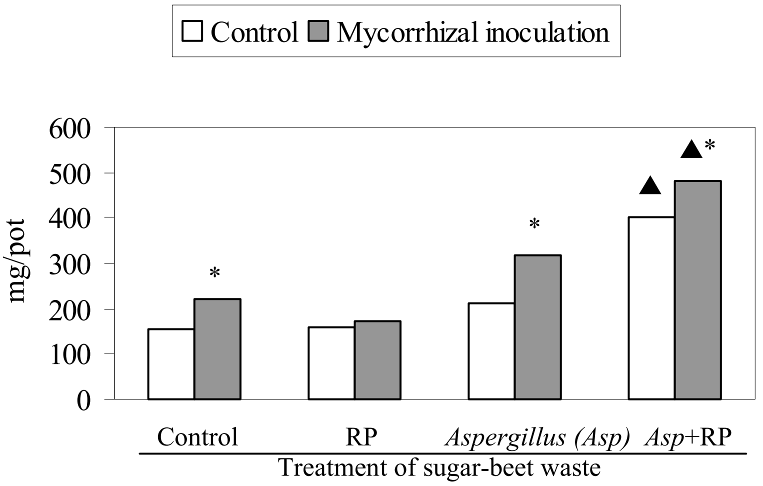

*Fig. 1. Shoot dry weight of Trifolium plants grown for 42 days as affected by fermentation-resulting products and mycorrhizal inoculation. * Denotes significant differences in mycorrhizal response. ▲ Denotes significant differences in RP response.*

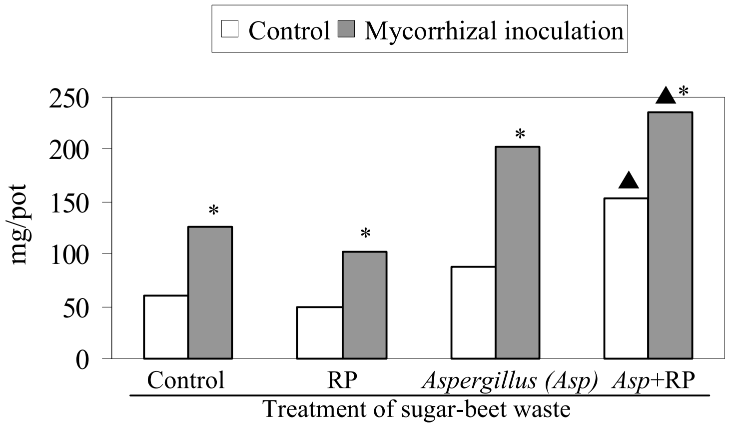

*Fig. 2. Shoot P content of Trifolium plants grown for 42 days as affected by fermentation-resulting products and mycorrhizal inoculation. * Denotes significant differences in mycorrhizal response. ▲ Denotes significant differences in RP response.*

The addition of SB alone or in combination with RP in the absence of *A. níger* did not have a significant effect on plants weight of either, non- and mycorrhizal soil-plant system. However, plant P acquisition was favored by *G. deserticola* in the respective treatments. The addition of microbially precultivated SB without RP increased plant weight of *T. repens* and almost doubled its P content compared with the control and SB with RP treatments. These effects could be related to the low pH of the mixture due to the presence of citric acid. Although the soils in Southern Spain have a high phosphate-fixing capacity, it was reported recently that the addition of citric acid increased phosphate concentrations in solutions of alkaline soils, this effect being detectable even after 140 days [25]. A significantly high growth and P shoot content was found in plants grown in soil amended with the lignocellulosic substrate with RP and *A. niger* mixture. This observation was even more pronounced in plants inoculated with *G. deserticola*. The triple combination between *A. niger, R. trifoli* and *G. deserticola* caused a response in plant growth and P uptake of both non-mycorrhizal and mycorrhizal plants, respectively, but the inclusion of RP in the system enhanced this effect. The assumption that *A. niger* can provide additional nutrient amounts derived from the mycelium cannot explain the lower plant growth and P uptake in the treatment without RP and AM inoculation. This work confirms the important role of mycorrhizal fungi and particularly their synergistic effect in combination with P-solubilizing microorganisms, as reported previously [26].

The effects of certain combinations of treatments produced a lowering in the SA of the clover plants (Fig. 3). This lowering was clearer in AM-inoculated plants, particularly when RP was a component of the fermentation mixture. It could be argued that the treatments having the lower SA values suggest that the plant is using extra ^{31}P released from otherwise unavailable P sources [14]. The phosphate-solubilizing activity of *A. niger*, could in part release P ions from the added RP and the AM external mycelium was transferring to the plant ^{31}P released from RP particles, therefore inducing a lowering in the $^{32}P/^{31}P$ ratio [26, 27]. Therefore, the lowering in the specific activity is indicating solubilization of RP by the microbial activities applied in the reported biotechnological approach.

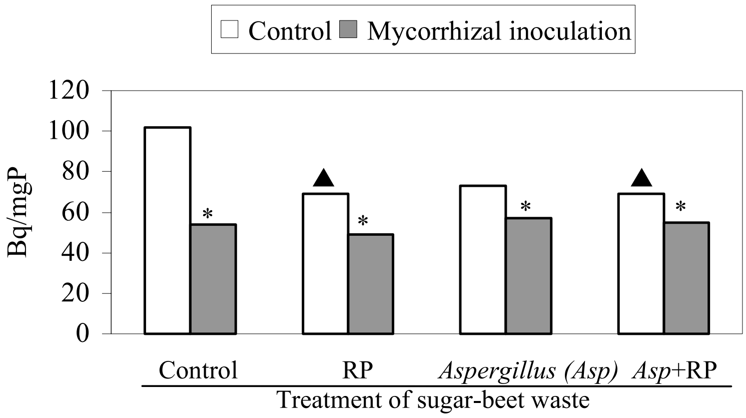

*Fig. 3. Specific activity of Trifolium plants grown for 42 days as affected by fermentation resulting products and mycorrhizal inoculation. * Denotes significant differences in mycorrhizal response.*
▲ Denotes significant differences in RP response.

4. CONCLUSIONS

The biological solubilization of RP using the metabolic, acid-producing activity of the filamentous fungus *A. niger* during its cultivation on sugar beet waste material and further application of the resulting mixture appears to be effective in a neutral, calcareous soil as shown by the isotopic (^{32}P) dilution technique. The interaction between a biotechnological practice (triple inoculation with *R. trifoli, A. niger* and *G. deserticola*) and a low-input technology (RP addition to the system) demonstrates the potential application of such combined approaches in improving sustainable nutrient supply to plants.

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REFERENCES

[1] Current world fertilizer situation and outlook 1996/7-2002/2003. FAO (electronic version) (1998) 1-32.
[2] JEFFRIES, P., BAREA, J.M., Biogeochemical cycling and arbuscular mycorrhizas in the sustainability of plant-soil systems, In S. Gianinazzi, H. Schuepp (eds). Impact of Arbuscular Mycorrhizas on Sustainable Agriculture and Natural Ecosystems, Verlag, Basel, (1994) 101-115.
[3] IYAMURENYE, F., DICK, R.P., Organic amendments and phosphorus sorption by soils, Adv. Agron. **56** (1996) 139-185.
[4] RAJAN, S.S.S., WATKINSON, J.H., SINCLAIR, A.G., Phosphate rocks for direct application to soils, Adv. Agron. **57** (1996) 77-159.
[5] GHANI, A., RAJAN, S.S.S., LEE, A., Enhancement of rock phosphate solubility through biological processes, Soil Biol. Biochem. **26** (1994) 127-136.

[6] VASSILEV, N., BACA, M.T., VASSILEVA, M., Plant lignocelluloses and decomposition by fungi: From Nature to industrial use, Mycol. **8** (1994) 113-115.

[7] VASSILEV, N., BACA, M.T., VASSILEVA, M., FRANCO, I., AZCÓN, R., Rock phosphate solubilization by *Aspergillus niger* grown on sugar beet wastes, Appl. Microbiol. Biotechnol. **44** (1995) 546-549.

[8] VASSILEV, N., FRANCO, I., VASSILEVA, M., AZCÓN, R., Improved plant growth with rock phosphate solubilized by *Aspergillus niger* grown on sugar beet waste, Biores. Technol. **55** (1996) 237-241.

[9] VASSILEV, N., FENICE, M., FEDERICI, F., AZCÓN, R., Olive mill waste water treatment by immobilized cells of *Aspergillus niger* and its enrichment with soluble phosphate, Process Biochem. **32** (1997) 617-620

[10] VASSILEV, N., VASSILEVA, M., AZCÓN, R., FENICE, M., FEDERICI, F., BAREA J.M., Fertilizing effect of microbially treated olive mill wastewater on *Trifolium* plants, Biores. Technol. **66** (1998) 133-137.

[11] VASSILEVA, M., VASSILEV, N., AZCÓN, R., Rock phosphate solubilization by *Aspergillus niger* on olive cake-based medium and its further application in soil-plant system, W.J. Microbiol. Biotechnol. **14** (1998) 281-284.

[12] RODRIGUEZ, R., VASSILEV, N., AZCÓN, R., Increases in growth and nutrient uptake of alfalfa grown in soil amended with microbially-treated sugar beet waste, Appl. Soil Ecol. **330** (1998) 1-7.

[13] VASSILEV, N., VASSILEVA, M., GANCHEV, I., Citric acid production by *Aspergillus niger* on starch hydrolysate media, Acta Microbiol. Bulg. **18** (1986) 62-67.

[14] ZAPATA, F., AXMANN, H., ^{32}P isotopic techniques for evaluating the agronomic effectiveness of rock phosphate materials, Fert. Res. **41** (1995) 189-195.

[15] ZAPATA, F., Isotope techniques in soil fertility and plant nutrition studies, In: G. Hardarson (ed), Use of nuclear techniques in studies of soil-plant relationships, International Atomic Energy Agency, Vienna, Austria.

[16] KUMAR, N., SIGN, K., Chemical and microbiological changes during solid substrate fermentation of wheat straw with *Coprinus fimetatus,* Biol. Wastes **33** (1990) 231-242.

[17] GOERINGH, K., VAN SOEST, P.J., Forage fiber analysis, Agriculture Handbook 379. Agriculture Research Service, USDA, Washington, DC, 1-12.

[18] NELSON, D.W., SOMMERS, L.E., Total carbon, organic carbon, and organic matter. In: A.L. Page, R.H. Miller, D.R. Keeney (eds.), Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties. SSSA, ASA, Madison, Wisconsin, (1982), 539-577.

[19] TAUSSKY, H.H., A micro colorimetric method for the determination of citric acid. J. Biol. Chem. **181** (1949) 195-198.

[20] LACHICA, M., AGUILAR, A, YANEZ, J., Analisis foliar. Metodos analiticos utilizados en la Estación Experimental del Zaidín, An. Edafol. Agrobiol. **32** (1973) 1033-1047.

[21] PHILLIPS, J.M., HAYMAN, D.S., Improved procedure for clearing roots and staining parasitic and vesicular arbuscular mycorrhizal fungi for rapid assessment of infection, Trans. Brit. Mycol. Soc. **55** (1970) 159-161.

[22] GIOVANNETTI, M., MOSSE, B., An evaluation of techniques for measuring vesicular-arbuscular mycorrhizal infection in roots, New Phytol. **84** (1980) 489-500.

[23] ORIOL, E., SCHETTINO, B., VINEGRA-GONZALEZ, G., RAIMBAULT, M., Solid state culture of *Aspergillus niger* on support, J. Ferment. Technol. **66** (1988) 57-62.

[24] NAHAS, E., BANZATTO, D.A., ASSIS, L.C., Fluorapatite solubilization by *Aspergillus niger* in vinasse medium, Soil Biol. Biochem. **22** (1990) 1097-1101.

[25] GERKE, L., Phosphate, aluminum, and iron in the soil solution of three different soils in relation to varying concentrations of citric acid, Z. Pflanzenernahr. Bodenk. **155** (1992) 17-22.

[26] TORO, M., AZCÓN, R., BAREA, J.M., Improvement of arbuscular mycorrhiza development by inoculation of soil with phosphate-solubilizing rhizobacteria to improve rock phosphate bioavailability (^{32}P) and nutrient cycling, Appl. Environ. Microbiol. **63** (1997) 4408-4412.

[27] TORO, M., AZCÓN, R., BAREA, J.M., The use of isotopic dilution techniques to evaluate the interactive effects of *Rhizobium* genotype, mycorrhizal fungi, phosphate-solubizing rhizobacteria and rock phosphate on nitrogen and phosphorus acquisition by *Medicago sativa,* New Phytol. **138** (1998) 265-273.

EVALUATION OF AVAILABLE PHOSPHORUS AND CADMIUM ASSOCIATED WITH PHOSPHATE ROCK FOR DIRECT APPLICATION

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Abstract

Three greenhouse experiments were conducted to evaluate available P and Cd associated with the use of phosphate rock (PR) for direct application. These experiments were: (1) “Estimation of Phosphorus Availability to Maize and Cowpea From Phosphate Rock as Enhanced by Water-Soluble Phosphorus;” (2) “Modified Iron Oxide-Impregnated Paper Strip (Pi) Test for Soils Treated With Phosphate Fertilizers;” and (3) “Effect of Acidulation of High Cadmium Containing Phosphate Rocks on Cadmium Uptake by Upland Rice.”

In the first experiment, a medium-reactive Central Florida phosphate rock (PR) was used. The effectiveness of P sources in terms of increasing dry-matter yield and P uptake followed the order of TSP ≥ (PR + TSP) > PR for maize and TSP = (TSP + PR) > PR for cowpea. P uptake from PR in the presence of TSP was higher than P uptake from PR applied alone. With respect to P uptake from PR applied alone, the corresponding relative increase in P uptake from PR due to TSP influence was 165% for maize and 72% for cowpea. In the second experiment, a highly reactive North Carolina PR was used. Both Bray I and the Pi test (with $CaCl_2$) underestimated available P from PR with respect to TSP. Available P estimated by the Pi test with KCl was more closely related to P uptake with both PR and TSP. More P was extracted from PR by the Pi test with KCl than with $CaCl_2$, whereas no effect was observed for TSP. In the third experiment, a low-reactive Togo PR and a highly reactive North Carolina PR were used. Both PRs were fully acidulated to SSP and Togo PR was also partially acidulated with H_2SO_4 at 50% level to PAPR. Cd uptake by rice grain followed the order of NC-SSP > NC-PR and Togo-SSP > Togo PAPR > Togo PR. The results also showed that most of the Cd uptake was retained in rice root and straw. Total uptake of Cd, Ca, and P by the rice plant was higher from NC-PR than from Togo-PR. Cd concentration in rice grain showed no significant difference between NC-PR and Togo-PR, whereas Cd concentrations in root and straw were higher with NC-PR than that with Togo-PR.

1. INTRODUCTION

In 1993, the Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture launched a 5-year Co-ordinated Research Project (CRP) on “The Use of Nuclear and Related Techniques for Evaluating the Agronomic Effectiveness of Phosphate Fertilizers, in Particular, Rock Phosphate.” IFDC was invited to participate in this CRP as a collaborative institution. During the 5-year period, IFDC conducted three major experiments to contribute to meet part of the objectives of this CRP. These experiments were: (1) “Estimation of Phosphorus Availability to maize and Cowpea From Phosphate Rock as Enhanced by Water-Soluble Phosphorus;” (2) “Modified Iron Oxide-Impregnated Paper Strip (Pi) Test for Soils Treated With Phosphate Fertilizers;” and (3) “Effect of Acidulation of High Cadmium Containing Phosphate Rocks on Cadmium Uptake by Upland Rice.”

The purpose of this paper is to present a summarized report on the three experiments conducted by IFDC. More detailed information can be found in the three papers published in scientific journals [1-3].

2. EXPERIMENT 1: ESTIMATION OF PHOSPHORUS AVAILABILITY TO MAIZE AND COWPEA FROM PHOSPHATE ROCK AS ENHANCED BY WATER-SOLUBLE PHOSPHORUS

2.1. Literature review and objective

Although direct application of phosphate rock (PR) may be a cost-effective means to supply phosphorus (P), PRs with low and medium reactivity often do not perform as well as soluble P fertilizers in terms of yield response of food crops [4-7]. One practice that has been reported to increase the plant's utilization of low- and medium-reactivity PR is to supply the early P requirement of the crop with water-soluble P fertilizer. By doing so, the plant would have better root development and, in turn, would be able to utilize PR more effectively than could a plant treated with PR alone [8]. The additional P can be supplied by compacting water-soluble P fertilizers, such as TSP, with PR or by partially acidulating PR with H_2SO_4 or H_3PO_4 [9-12].

Quantitative estimation of P availability from PR in soil as enhanced by water-soluble P has not been reported. Because of possible interactions (priming effect) among water-soluble P, PR, and soil P, use of radioactive ^{32}P as a tracer is essential to distinguish P availability from soil P, PR, or water-soluble P. The objective of this study was to use ^{32}P as a tracer to estimate quantitatively the enhancement effect of water-soluble P (TSP) on P availability applied from a medium-reactivity PR to maize and cowpea grown on an acid soil.

2.2. Materials and methods

The soil used was a Hartsells silt loam classified as a Typic Hapludult (Table I). The soil was air-dried and screened to less than 2 mm. The PR used was a finely ground (<0.15 mm or 100 mesh) Central Florida PR (CFPR). Its total P and citrate-soluble P were 14.2% and 1.4%, respectively. Radioactive ^{32}P-tagged TSP was prepared by adding ^{32}P-labeled H_2PO_4 to CFPR. After curing, the TSP aggregates were crushed and ground to powder (<0.15 mm), which had a total P content of 18.8%. The specific activity of the ^{32}P-tagged TSP was 43.6 MBq g^{-1} P at the time of planting the crops in the greenhouse.

One mL of ^{32}P solution with radioactivity of 1,850 MBq was diluted to 5 L in a KH_2PO_4 solution containing 20 mg P L^{-1}. The specific activity of the diluted solution was 0.37 MBq ^{32}P mL^{-1}. Four kg of soil was mixed thoroughly with 80 mL of the diluted ^{32}P solution and 720 mL of water. The soil was then equilibrated for 1 week and mixed with CFPR at 0, 12.5, 25, 50, 100, and 200 mg P kg^{-1}. A second set of 4-kg soil samples was mixed separately with CFPR and ^{32}P-tagged TSP at total P rates of 12.5, 25, 50, 100, 200, and 400 mg P kg^{-1}. The P ratio of CFPR:TSP was fixed at 50:50. A third set of soil samples was mixed with ^{32}P-tagged TSP at P rates of 12.5, 25, 50, 100, and 200 mg P kg^{-1}. Phosphorus added at 400 mg P kg^{-1} contained 200 mg P kg^{-1} as CFPR and 200 mg P kg^{-1} as ^{32}P-tagged TSP. This treatment was used to compare with the application of 200 mg P kg^{-1} as CFPR alone or 200 g P kg^{-1} as ^{32}P-tagged TSP alone.

Additional nutrients were added to each pot at constant rates as follows: 200 mg N kg^{-1} as urea for maize (*Zea mays* L.) and 20 mg N kg^{-1} as urea for cowpea (*Vigna unguiculata* L.), 150 mg K kg^{-1} as K_2SO_4. Other nutrients were added at adequate levels. The pots were placed in a randomized block design with three replicates for each treatment.

TABLE I. SELECTED SOIL PROPERTIES OF THE HARTSELLS AND HIWASSEE SOILS

Soil Properties	Hartsells	Hiwassee
pH (1:1 soil/water)	5.0	5.6
Organic Matter (g kg^{-1})	37	19
Clay content (g kg^{-1})	200	340
Extractable P (mg kg^{-1})		
Bray I	2.0	0.9
Pi-test	3.9	2.9
Effective cation exchange Capacity (cmol$_c$ kg^{-1})	4.7	3.9

Six seeds of maize were planted in each pot, and water was added on a daily basis to bring the soil to approximately 80% of field capacity. After germination, the maize plants were thinned to three plants per pot. Six weeks after planting, the aboveground portions of the maize plants were harvested. For cowpea, three seeds inoculated with a commercial inoculant (Nitragin) were planted in each pot and thinned to one plant after germination. The aboveground portions of the cowpea plants were harvested at the flowering stage (approximately 45 days after planting).

The plant materials were ground using a Wiley mill, and samples were digested with a mixture of HNO_3 and $HClO_4$. Phosphorus concentration in the plant digests was determined using the ammonium molybdate-ascorbic acid method. The activity of ^{32}P in the plant digests was measured by a liquid scintillation counter. Radioactivity counts were corrected for background and for decay to the days of planting when the ^{32}P was applied to the soil.

Based on the isotopic dilution method, the amount of P uptake by the plants from soil, CFPR, and ^{32}P-tagged TSP were calculated as described by Chien et al. [1].

Various response functions were used to describe the relationship between crop yield or P uptake and rate of P applied from three different P sources. Because the experimental data of all three P sources could not be fitted with the same response function containing only a one-term coefficient for the independent variable (i.e., rate), the ratio of the two fitted coefficients could not be used to calculate the relative agronomic effectiveness (RAE) as suggested by Chien et al. [3]. Instead, the method of averaging values across all P rates was used.

The index RAE was defined as:

$$RAE(\%) = (Y_1 – Y_0) / (Y_2 – Y_0) \times 100$$

where
Y_1 = Yield or P uptake obtained with CFPR or (CFPR + TSP),
Y_2 = Yield or P uptake obtained with TSP, and
Y_0 = Yield or P uptake obtained with check (no P added).

To compare treatment effects among various P sources, values of LSD were calculated ($P = 0.05$) and used to detect the significant differences in average values of P uptake across all P rates.

2.3. Results and discussions

The average values of dry-matter yield and P uptake across P rates for maize and cowpea are shown in Tables II and III. For maize, the effectiveness of P sources in terms of increasing dry-matter yield and P uptake followed the order of TSP > (CFPR + TSP) > CFPR. The lower effectiveness of CFPR than that of TSP was due to its lower solubility. Chien and Friesen using the same PR reported a similar result [7]. Mixing CFPR and TSP at a P ratio of 50:50, however, significantly increased dry-matter yield and P uptake. The RAE increased from 31% with CFPR to 83% with (CFPR + TSP) in dry-matter yield and from 37% with CFPR to 86% with (CFPR + TSP) in P uptake. For cowpea, the effectiveness of P sources followed the order of TSP = (CFPR + TSP) > CFPR (Tables II and III). The RAE increased from 55% with CFPR to 98% with (CFPR + TSP) for dry-matter yield and from 50% with CFPR to 92% with (CFPR + TSP) for P uptake.

The calculated values of P uptake by maize or cowpea from CFPR applied alone or as (CFPR + TSP) are shown in Figs 1 and 2.

It can be seen that P uptake from CFPR in the presence of TSP was significantly higher than that from CFPR applied alone. In other words, water-soluble P from the applied TSP enhanced P uptake from CFPR when CFPR was mixed with TSP. For example, at 100 mg P kg^{-1} of CFPR applied, P uptake by maize from CFPR applied alone was 2.30 mg P pot^{-1}, whereas the P uptake from CFPR applied in the presence of TSP was 7.49 mg P pot^{-1} (Fig. 1). The same comparison for P uptake by cowpea was 3.04 mg P pot^{-1} with CFPR alone versus 5.06 mg P pot^{-1} with (CFPR + TSP) (Fig. 2).

TABLE II. DRY-MATTER YIELD AND RELATIVE AGRONOMIC EFFECTIVENESS (RAE) OBTAINED WITH VARIOS P SOURCES FOR MAIZE AND COWPEA

P Source	Maize		Cowpea	
	Dry-Matter Yield[2] g pot^{-1}	RAE %	Dry-Matter Yield[2] g pot^{-1}	RAE %
Check	1.07	0	0.60	0
CFPR[1]	4.10	31	3.85	55
CFPR + TSP	9.13	83	6.45	98
TSP	10.78	100	6.55	100
LSD 0.05	1.32	-	1.22	-

[1] CFPR = Central Florida phosphate rock.

[2] Averaged across P rates.

TABLE III. PHOSPHORUS UPTAKE AND RELATIVE AGRONOMIC EFFECTIVENESS (RAE) OBTAINED WITH VARIOUS P SOURCES FOR MAIZE AND COWPEA

P Source	Maize		Cowpea	
	P Uptake[2] mg P pot^{-1}	RAE %	P Uptake[2] mg P pot^{-1}	RAE %
Check	1.15	0	0.79	0
CFPR[1]	9.12	37	8.72	50
CFPR + TSP	19.93	86	15.38	92
TSP	23.00	100	16.70	100
LSD 0.05	3.97	-	3.65	-

[1] CFPR = Central Florida phosphate rock.

[2] Averaged across P rates.

At a given rate of PR applied, the difference between P uptake from PR applied alone and P uptake from PR applied with TSP represents the quantitative estimation of the enhancement effect of water-soluble P (TSP) on the effectiveness of PR. The average increase in P uptake from CFPR due to TSP influence, across all the PR rates applied, was 3.48 mg P pot^{-1} for maize and 1.38 mg P pot^{-1} for cowpea (Table IV). With respect to CFPR applied alone without TSP, the relative increase in P uptake from CFPR due to TSP influence was 165% for maize and 72% for cowpea (Table IV). The result thus shows a significant beneficial effect of adding water-soluble P to increase the effectiveness of PR utilization by crops.

The CFPR and TSP were applied separately to the soil in the present study, because of their physical separation, the chemical interaction between CFPR and TSP as reported by Mokwunye and Chien [14] was probably negligible. Instead, the enhancement effect was most likely due to an increased early plant-root development, as induced by water-soluble P, which enabled the plant to use PR more effectively than could a plant treated with PR alone [8].

TABLE IV. THE AVERAGE INCREASE IN P UPTAKE BY MAIZE AND COWPEA FROM CFPR AS ENHANCED BY TSP

P Source	P Uptake From CFPR	
	Maize	Cowpea
	- - - - - - - - - - - - - mg P pot^{-1}	- - - - - - - - - - - -
CFPR[1] alone (A)	2.11	1.93
CFPR + TSP (B)	5.59	3.31
(B-A)	3.48	1.38
(B-A)/(A), %	165	72

[1] CFPR = Central Florida phosphate rock.

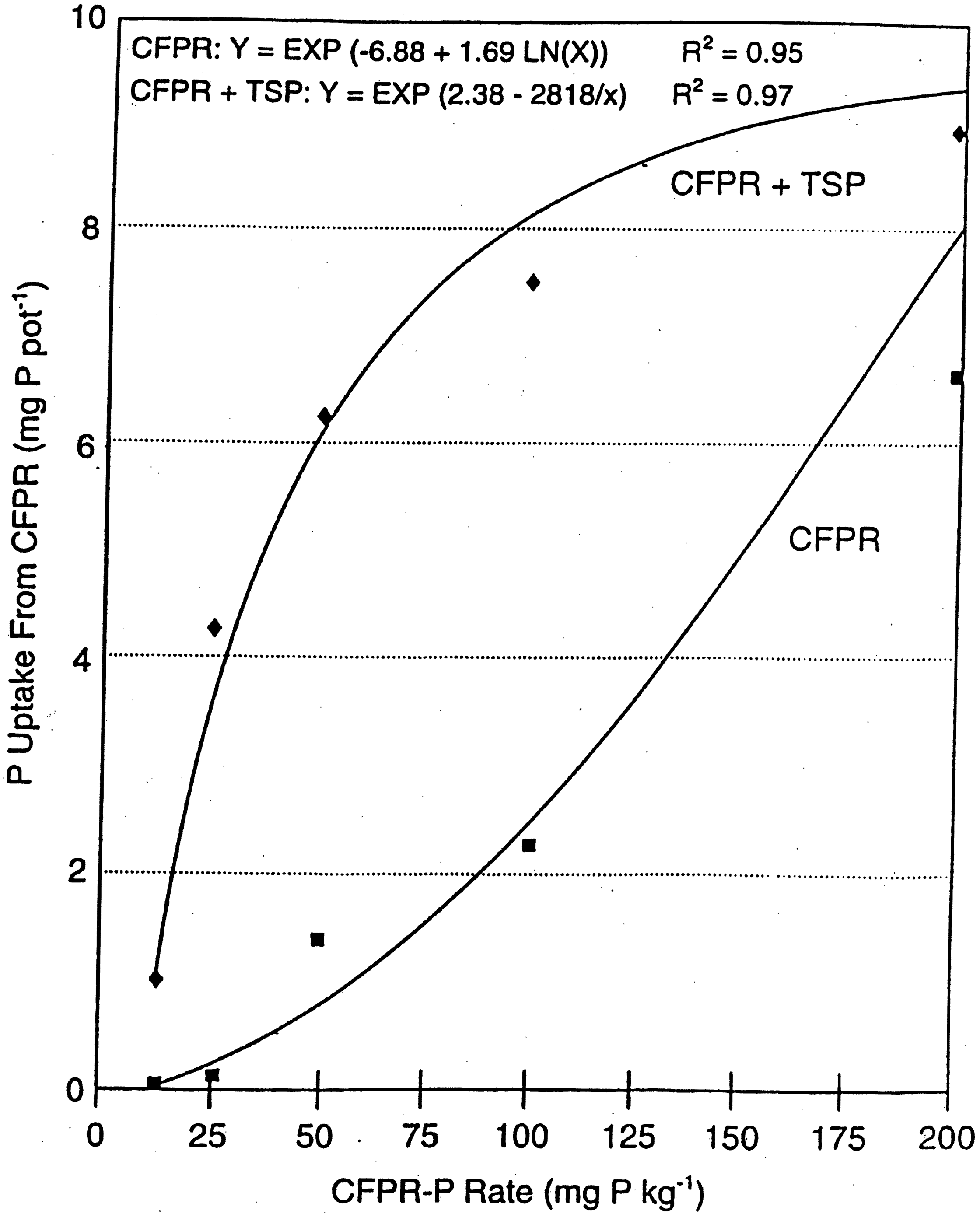


Fig. 1. Phosphorus uptake by maize from Central Florida phosphate rock (CFPR) alone or from CFPR in the mixture of CFPR and TSP (CFPR + TSP).

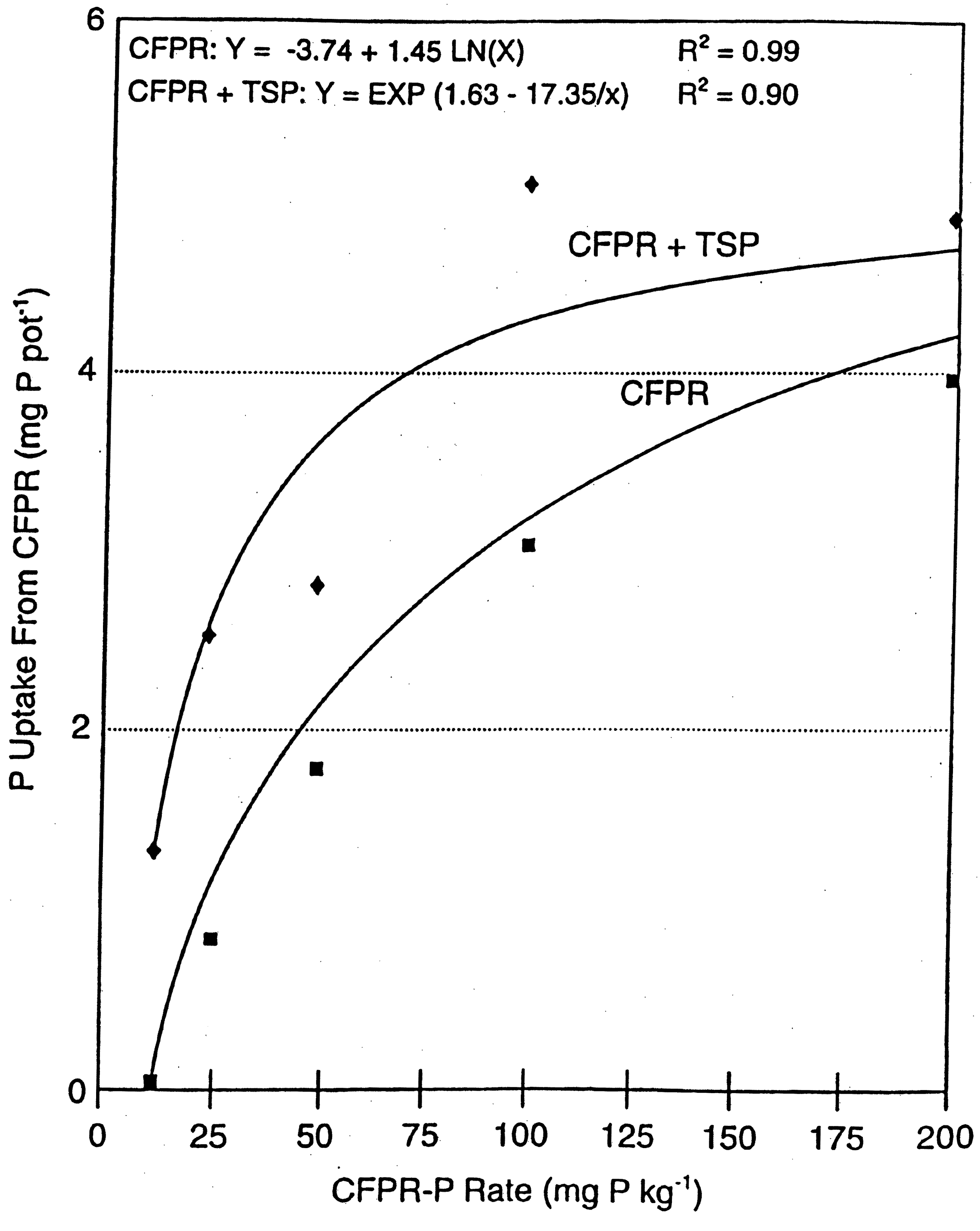


Fig. 2. Phosphorus uptake by cowpea from Central Florida phosphate rock (CFPR) alone or from CFPR in the mixture of CFPR and TSP (CFPR + TSP).

3. EXPERIMENT 2: MODIFIED OXIDE-IMPREGNATED PAPER STRIP TEST FOR SOILS TREATED WITH PHOSPHATE FERTILIZERS

3.1. Literature review and objective

The iron oxide-impregnated paper strip (Pi) test is a relatively new approach to evaluate available phosphorus (P) in soils [15, 16, 17, 18]. The Pi test was first introduced by Menon et al. [19] to measure available P in four soils pre-incubated with phosphate rock (PR) or triple superphosphate (TSP) before cropping with maize. Compared with other conventional soil tests (Bray I, Bray II, Mehlich I, Olsen, and resin), the Pi test had the highest correlation between dry-matter yield or P uptake and soil available P when all the soils P sources, and rates of application were pooled. Thus, the use of the Pi test has been suggested as an alternative to the conventional soil tests to measure available P in soils treated with PR-based fertilizers or TSP [18, 20-22]. In all of the studies, however, the ranges in plant yield or P uptake and Pi-P obtained with TSP were much wider than those obtained with PR. To evaluate critically whether PR and TSP follow the same relationship when crop response is plotted against Pi-P in soil, the ranges in crop response and Pi-P with PR and TSP should be approximately the same.

The objective of this study was to evaluate the use of the Pi test for available P from soils treated with PR and TSP. The emphasis of the study was to investigate whether the same relationship between crop response and Pi-P could apply to both PR and TSP.

3.2. Materials and methods

Two soil samples were collected from the surface (0-20 cm) layer of Hartsells silt loam and Hiwassee clay loam (Table I). Finely ground (-0.15 mm; -100 mesh) North Carolina (NC) PR and a commercial-grade, granular TSP were used. North Carolina PR had 130 g kg^{-1} of total P and 30 g kg^{-1} soluble P in neutral ammonium citrate. The total P of TSP was 201 g kg^{-1} of which 167 g kg^{-1} was water-soluble and 34 g kg^{-1} was citrate soluble.

Amounts of NC-PR and TSP were mixed with 4 kg of soil to give P rates at 0, 25, 50, 75, 100, 125, 150, 200, and 300 mg P kg^{-1}. The soils were then incubated for 2 weeks in the greenhouse with mean temperature approximately at 30°C. Soil moisture was maintained at approximately 80% of field capacity by watering daily.

After incubation, approximately 100 g of soil samples were taken from each pot for P analysis. Urea and KCl were then mixed with the incubated soils at 200 mg N kg^{-1} and 200 mg K kg^{-1}, respectively. Other nutrients were added to all the treatments at adequate levels. The pots were placed in a randomized block design with three replications for each treatment.

Six seeds of maize (variety Funks 4765) were planted per pot, and the plants were thinned to three plants per pot after germination. At 5 weeks after planting, the aboveground parts of the plants were harvested, dried in an oven at 60°C for 10 days, and weighed. The plant materials were ground using a Wiley mill, and the samples were digested with a mixture of H_2SO_4 and H_2O_2.

Phosphorus in the soils was extracted by Bray I and Pi tests. The Pi paper strips were prepared by neutralization of $FeCl_3$ with NH_3 vapor [15]. However, the Pi paper strips were washed with water to remove NH_4Cl before being used, as recommended by Chardon et al. [17]. For the Pi test, a 1.0-g soil sample was shaken with one Pi strip (without using a nylon sheath) in 40 mL of 0.01 M $CaCl_2$ solution for 16 hours. The Pi strip was then taken out and washed free of soil, and the P sorbed by the strip was dissolved in 40 mL of 0.1 M H_2SO_4 [15]. A modified Pi test, in which 0.01 M $CaCl_2$ was placed with 0.02 M KCl was used to study the effect of Ca^{2+} and K^+ ions on PR dissolution during soil extraction. The amounts of P in the plant digest and soil extracts were determined using the ammonium molybdate method with ascorbic acid as the reducing agent.

3.3. Results and discussions

There was no significant difference in dry-matter yield of maize obtained with NC-PR and TSP in Hartsells soil (Fig. 3a). In Hiwassee soil, TSP was more effective than NC-PR in increasing dry-matter yield (Fig. 3b).

There were two distinct lines when P uptake by maize was plotted against Bray I-P extracted from the two soils treated with NC-PR and TSP (Fig. 4). The NC-PR line above the TSP line suggests that the Bray I test underestimates available P from NC-PR with respect to TSP, as first reported by Barnes and Kamprath [23].

Similar to the Bray I test, a plot of P uptake by maize against the Pi test with 0.01 M $CaCl_2$ resulted in two distinct lines for NC-PR and TSP (Fig. 5). The NC-PR line was above the TSP line, suggesting the Pi test with $CaCl_2$ also underestimates available P from NC-PR with respect to TSP to yield the same amount of P uptake. Thus, the conclusion drawn by Menon et al. [19] that the Pi test with $CaCl_2$ measured available P from PR and TSP similarly was incorrect, as evidenced from the present study. The explanation for the underestimation of available P from NC-PR with respect to TSP by the Pi test with $CaCl_2$ is that $CaCl_2$ decreased PR dissolution during the Pi extraction through the Ca common-ion-effect. Since the undissolved PR provided most of the P nutrient to the plant whereas reaction products of TSP in the form of Fe-Al-P provided available P, a decrease in NC-PR dissolution during the Pi extraction with $CaCl_2$ resulted in less available P from NC-PR than that from TSP. During plant growth, however, NC-PR and TSP were equally effective in providing available P to soil solution for plant uptake in Hartsells soil and 91% as effective as TSP in Waverly soil. Therefore, less available P was measured by the Pi test with $CaCl_2$ from NC-PR than from TSP for a given amount of P uptake.

If $CaCl_2$ was responsible for the underestimation of available P from NC-PR with respect to TSP by the Pi test, then the Pi test should be suitable to evaluate available P from NC-PR and TSP if $CaCl_2$ was replaced by KCl, which does not have the common-ion-effect on PR dissolution. This hypothesis was confirmed as a single line was obtained for both NC-PR and TSP when P uptake was plotted against Pi-extractable P with 0.02 M KCl (Fig. 6). Thus, the Pi test with 0.02 M KCl measured the same amount of available P from NC-PR and TSP to yield the same amount of P uptake from NC-PR and TSP.

The above discussions and conclusions on the use of the Pi test were based on P uptake data. Similar patterns were also observed when dry-matter yield data were plotted against available P extracted from NC-PR and TSP by the Pi test with $CaCl_2$ or KCl (data not shown). Therefore, it can be concluded that replacing $CaCl_2$ with KCl in the modified Pi test should be more suitable for evaluating available P from soils treated with PR and TSP. The other effective soil test for PR and TSP is the use of a mixture of cation and anion exchange resin membrane [24]. All other soil tests have been found unsuitable for PR and TSP treated soils [20, 21].

4. EXPERIMENT 3: EFFECT OF ACIDULATION OF HIGH CADMIUM CONTAINING PHOSPHATE ROCKS ON CADMIUM UPTAKE BY UPLAND RICE

4.1. Literature review and objective

Potential cadmium (Cd) uptake by food crops from applied phosphate (P) fertilizers has become an important environmental issue because of the potential health hazards to human life from consuming foods that may contain a significant amount of Cd. Numerous studies have investigated the Cd uptake by crops from P fertilizers [25,26]. In most of the studies, water-soluble P fertilizers such as TSP and DAP were used.

Reactive PR has been shown to be suitable for direct application to acid soils [4, 5, 27]. For those PRs that are not suitable for direct application because of their low reactivity, partial acidulation of PR is a technology that can produce agronomically effective P fertilizers [5, 28, 29]. Little information is available in the literature on Cd uptake by crops from either PR or partially acidulated PR (PAPR).

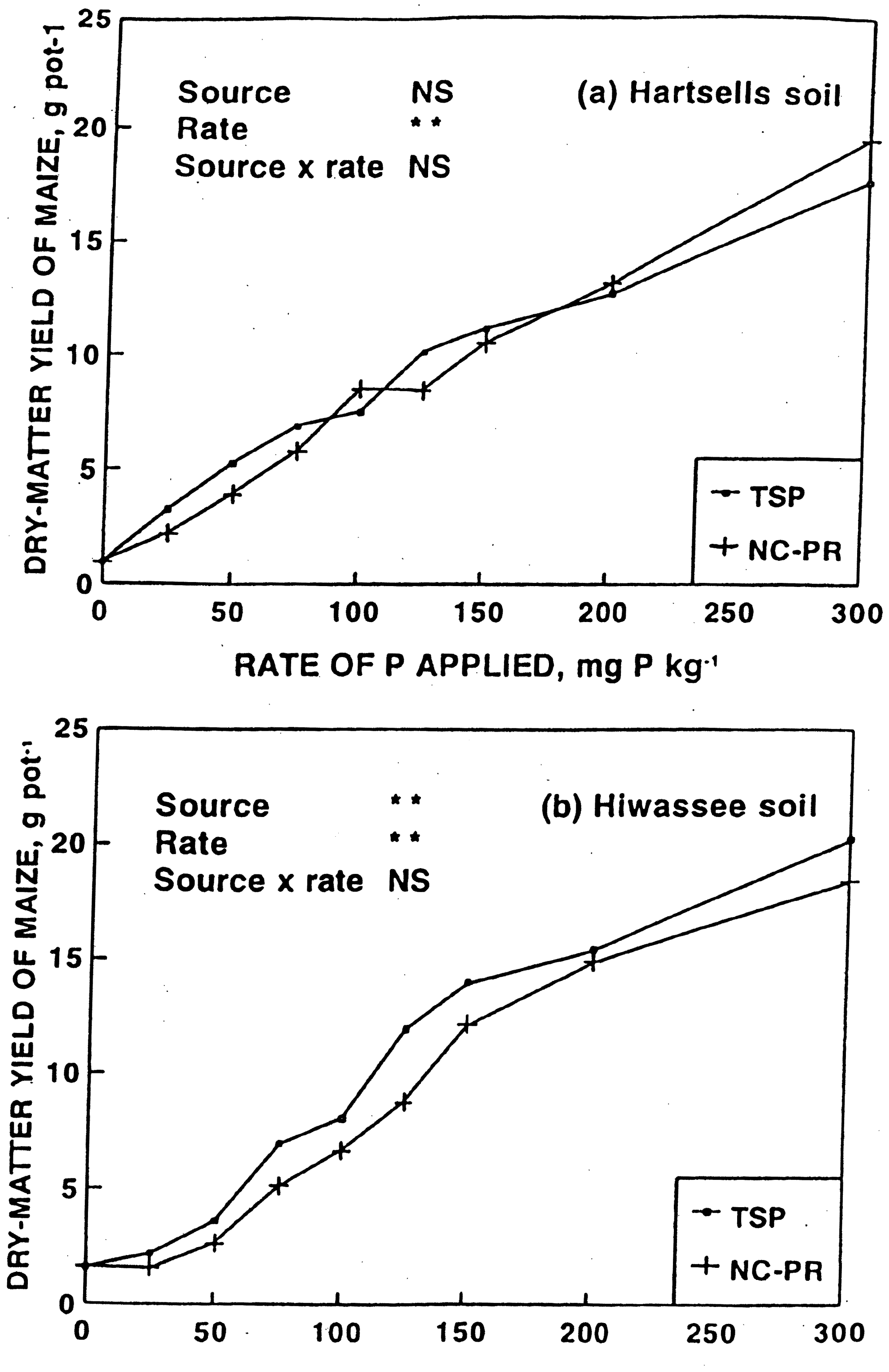


Fig. 3. Dry-matter yield of maize obtained with TSP and NC-PR in Hartsells and Hiwassee soils.

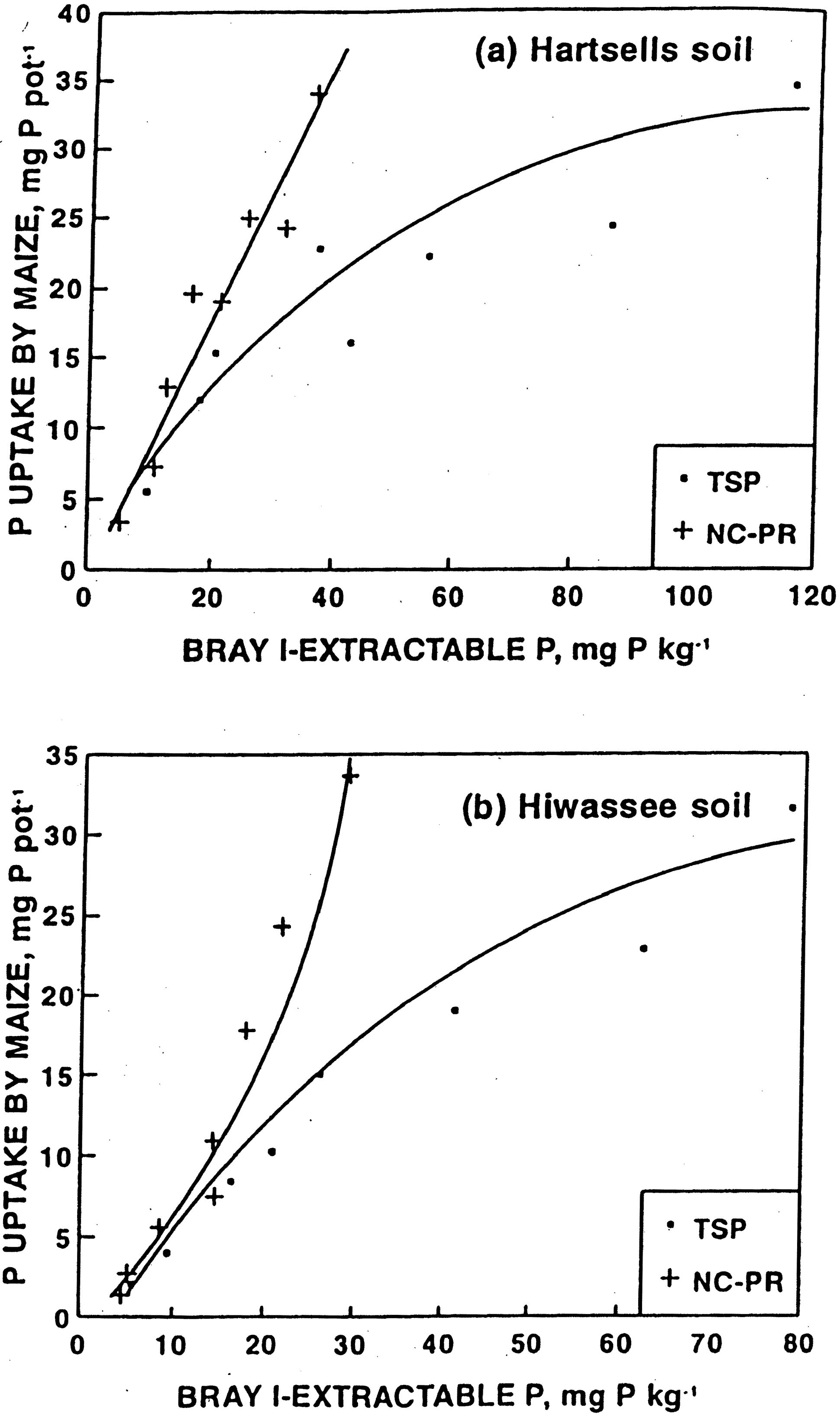


Fig. 4. Relationship between P uptake by maize and Bray I-extractable P in two soils treated with TSP and NC-PR.

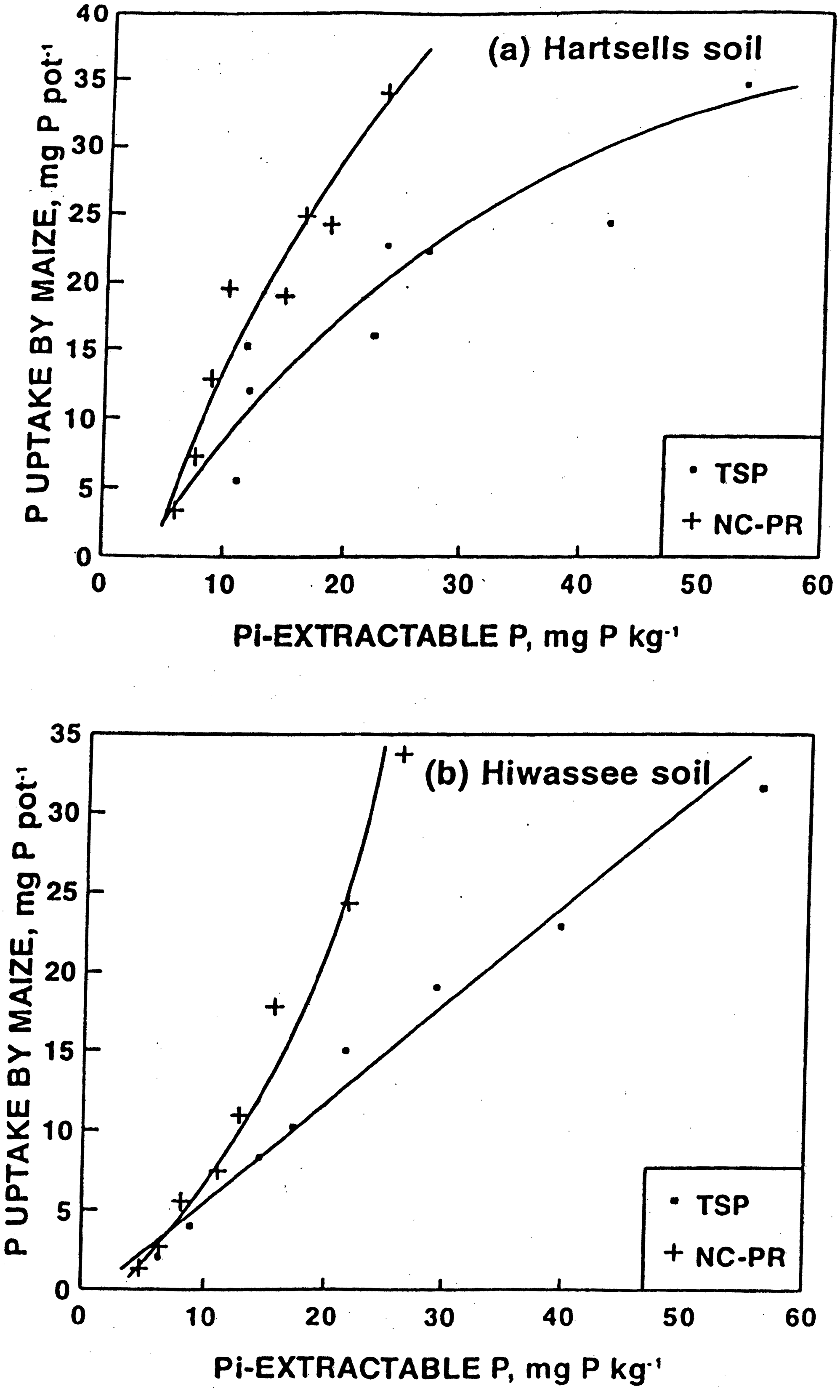
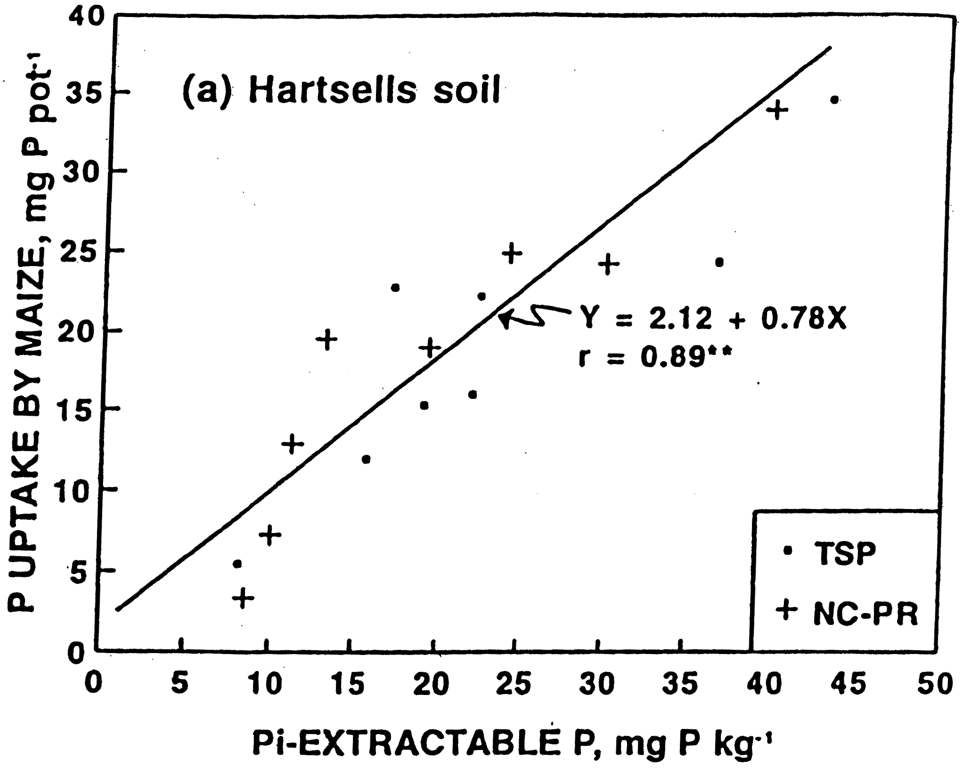


Fig. 5. Relationship between P uptake by maize and Pi-P (0.01 M $CaCl_2$) in two soils treated with TSP and NC-PR.



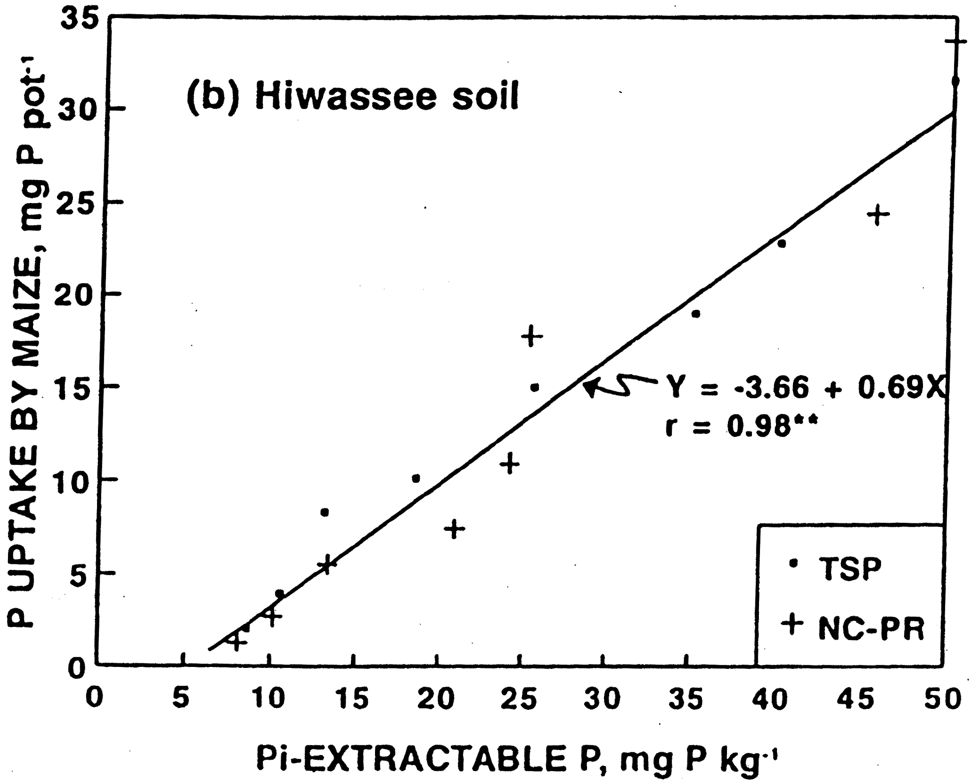


Fig. 6. Relationship between P uptake by maize and Pi-P (0.02 M KCl) in two soils treated with TSP and NC-PR.

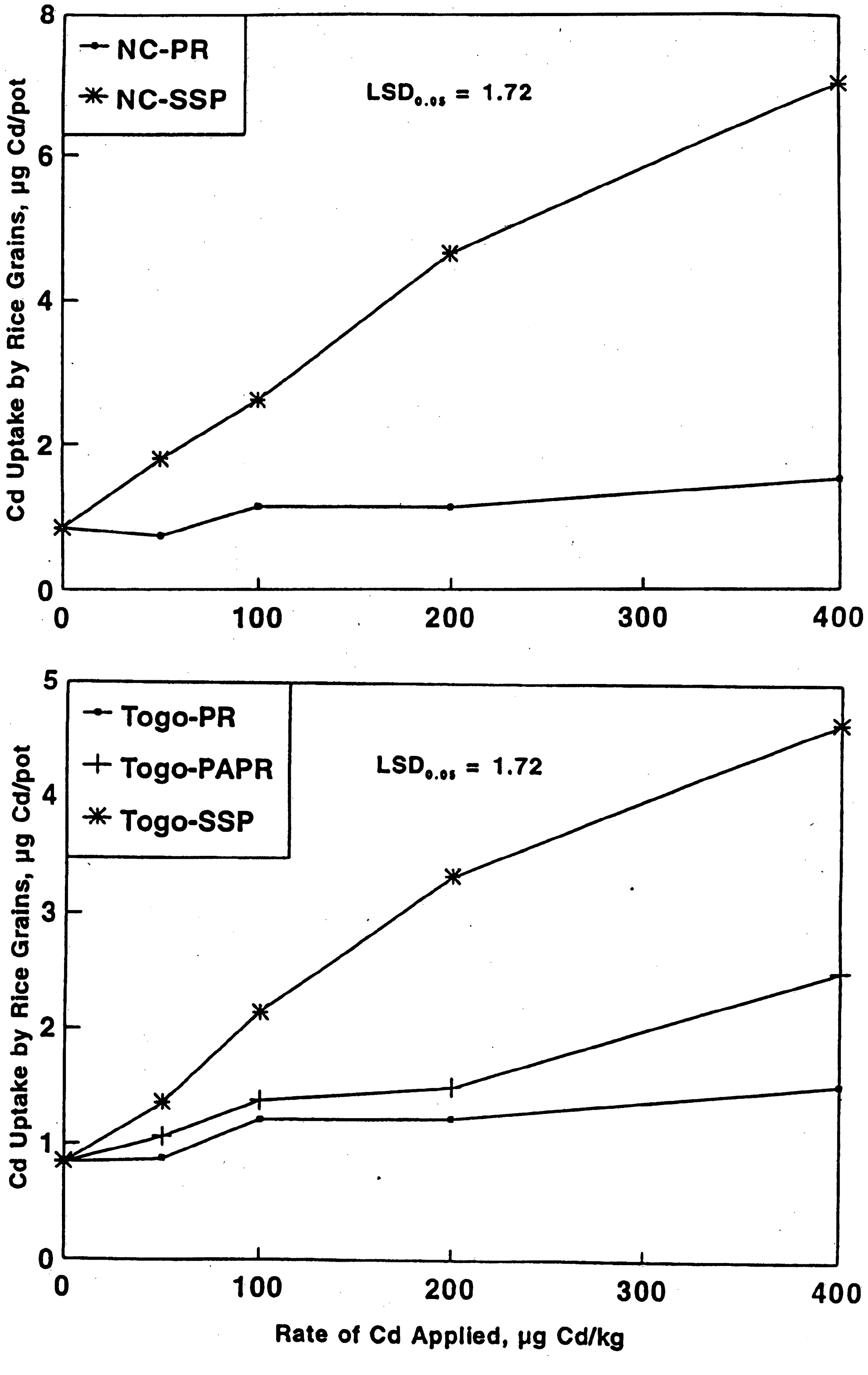


Fig. 7. Cd uptake by rice grains from (a) NC-PR and NC-SSP and (b) Togo-PR, Togo-PAPR, and Togo-SSP in Hartsells soil.

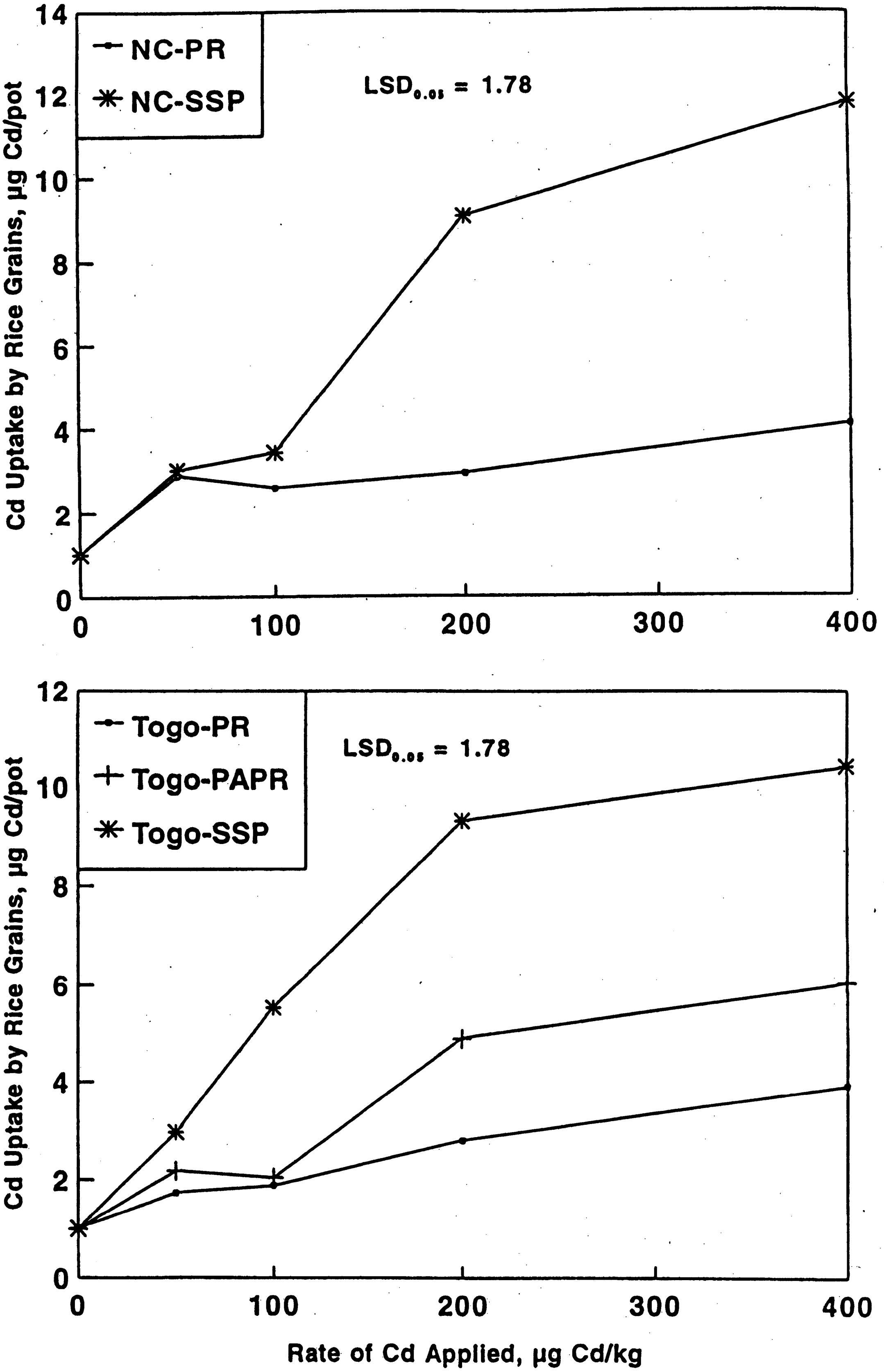


Fig. 8. Cd uptake by rice grains from (a) NC-PR and NC-SSP and (b) Togo-PR, Togo-PAPR, and Togo-SSP in Hiwassee soil.

The objective of this study was to investigate the effect of acidulation of PR on Cd uptake by an upland rice crop. Two PRs having high Cd content were used in this study. In this study, the application of a large amount of water-soluble P as reagent-grade of KH_2PO_4, which does not contain Ca and Cd, and using the P fertilizers containing Cd as sources of Cd under the conditions where P was not a limiting factor on the plant growth, eliminated the confounding effect of P and Cd uptake [30].

4.2. Materials and methods

The NC-PR that was used was unground with a particle size distribution of 85% in the range between 1.18 mm and 150 mm and 15% smaller than 1.18 mm. Togo-PR was finely ground through 1.18 mm. PAPR and SSP were produced by acidulating ground (smaller than 1.18 mm) Togo and NC PRs with H_2SO_4 at 50% (only Togo-PR) and 100% levels in a nongranular run form. The P and Cd contents of P fertilizers are shown in Table V. Two acid soils, Hartsells and Hiwassee (Table I), were used in the greenhouse experiment.

TABLE V. PROPERTIES OF P AND Cd CONTENTS OF P FERTILIZERS USED

P Source	Total P	H_2O-P	Citrate-P	Total Cd	DTPA-Cd
	- - - - - - - - - - - - (%) - - - - - - - - - - - - - -			- - - - - - (mg Cd/kg) - - - - - -	
NC-PR	13.3	0.0	2.8	47.0	0.2
NC-SSP	6.3	5.8	0.5	24.7	18.7
Togo-PR	16.0	0.0	2.0	54.0	1.7
Togo-PAPR	12.3	4.8	1.8	35.7	6.8
Togo-SSP	9.2	8.7	0.5	31.5	19.7

Phosphate fertilizers in amounts required to give total Cd rates of 0, 50, 100, 200, and 400 μg Cd/kg were mixed with 4 kg of soil. All of the treatments also received 200 mg P/kg as KH_2PO_4. Constant rates of other nutrients were added at adequate levels to each pot. The pots were placed in a randomized block with three replications for each treatment. Ten rice seeds were planted and thinned to one seedling per pot. Soil moisture was maintained at 80% of field capacity by watering daily. The rice crop was grown to maturity and harvested.

Rice grain samples were taken from all the treatments whereas rice straw and root and soil samples were taken only from the check (no Cd added) and 400 μg Cd/kg treatments. After harvesting the aboveground plant parts, soil in the pots was carefully washed with water on a screen to obtain soil-free root samples. The plant samples (grain, straw, and root) were dried in a forced-air cabinet at 65^{o}C for 10 days followed by grinding. To determine Cd, Ca, and P uptake by plant, the ground plant samples were ashed in the furnace at 400^{o}C. The ash was then dissolved with 5 N HNO_3 at 50^{o}-60^{o}C. Cadmium in the soil samples was extracted with a DTPA solution, as described by Baker and Amacher [31]. Cadmium and Ca in the ashed plant samples and soil DTPA extracts were determined by using an inductively coupled plasma (ICP) spectrometer. Phosphorus concentration in the ashed plant samples was determined by using the ammonium molydate-ascorbic acid method.

4.3. Results and discussions

Analysis of variance (ANOVA) of rice yield data showed that source and rate of P were statistically nonsignificant (data not shown). Thus, there was no P response as expected since all the treatments including the check received a very high rate of P (200 mg P/kg) as KH_2PO_4. Therefore, it would be expected that there should be no confounding effect of P and Cd uptake by upland rice.

Uptake of Cd by rice grains on Hartsells and Hiwassee soils increased with the rate of Cd applied to the soils. The increase of Cd uptake was most pronounced with NC-SSP and Togo-SSP followed by Togo-PAPR. NC-PR and Togo-PR resulted in the lowest Cd uptake (Figs. 7 and 8). This corresponds with the findings that DTPA-Cd levels in NC-SSP and Togo-SSP were higher than those in NC-PR and Togo-PR (Table V).

Table VI shows Cd uptake by rice roots, straw, and grains from various Cd sources at the 400 µg Cd/kg rate. It can be seen that most of the Cd take-up was retained in rice roots and straw. In Hartsells soil, Cd uptake by rice grains was less than 3% of total Cd uptake by rice. In Hiwassee soil, the value was less than 10%. Data in Table VI indicate that Cd uptake by rice increased as the degree of PR acidulation increased. Acidulation of PR also increased DTPA-extractable Cd in soils, and there was a significant relationship between Cd uptake by rice and soil DTPA-Cd (data not shown).

The results of Cd uptake suggest that if unacidulated PRs (e.g., NC-PR) and partially acidulated PRs (e.g., Togo-PAPR) are as effective as fully acidulated P sources (e.g., SSP) under certain soil and crop conditions [5, 29], these water-insoluble and partially water-insoluble P sources are not only more cost effective, but also they may contribute less Cd uptake by crops than the use of water-soluble P sources. In a previous study, it was observed that rice grain yields obtained with NC-PR, NC-SSP, Togo-PAPR, and Togo-SSP were about the same at a rate of 200 mg P/kg applied to Hiwassee soil (Table VII). Both Cd uptake by rice grains and Cd concentration in grains followed the order of NC-SSP > NC-PR and Togo-SSP > Togo-PAPR (Table VII). The Cd concentration in grains obtained with NC-SSP was approximately twice more than that obtained with NC-PR. Similar results were observed with Togo-SSP and Togo-PAPR.

Table VIII shows total uptake of Cd, Ca, and P by rice plant (root, straw, and grain) from NC-PR and Togo-PR. Similar to Cd uptake, uptake of Ca and P was higher from NC-PR than that from Togo-PR. Because the reactivity of NC-PR is higher than that of Togo-PR (Table V), it suggests that Cd is associated with Ca and P in the same apatite structure, rather than as a discrete Cd mineral (e.g., $CdCO_3$). The presence of Cd in apatite structure is most likely through the isomorphic substitution of Cd^{2+} for Ca^{2+} [32]. Data in Table VIII points out that highly reactive PR (e.g., NC-PR) provides not only more available P but also more available Cd as compared with the low-reactive PR (e.g., Togo-PR). However, there was no significant difference in Cd concentration in grains of upland rice using NC-PR and Togo-PR on both soils, whereas Cd concentrations in roots were higher with NC-PR than those with Togo-PR in both soils (Table IX). Concentration of Cd in rice straw was higher with NC-PR than that with Togo-PR in Hiwassee soil. It should be pointed out that potential Cd toxicity to human health from Cd-contaminated food crops is based on Cd concentration in edible parts of crops rather than on total Cd uptake by crops. Table IX shows that both highly reactive NC-PR and low-reactive Togo-PR resulted in the same quality of rice grains in terms of Cd contamination with respect to human health.

TABLE VI. CADMIUM UPTAKE BY RICE, ROOT, STRAW,
AND GRAIN AND DTPA-EXTRACTABLE Cd IN SOILS AT 400 µg Cd/kg RATE

		Cd Uptake				
Soil	Cd Source	Root	Straw	Grain	Total	Soil DTPA-Cd
		- - - - - - - - - - -- (µg Cd/pot)	- - - - - - - - - - - - -			(µg Cd/g)
Hartsells	Check	21.4	12.0	0.84	34.2	0.023
	NC-PR	51.1	17.6	1.5	70.2	0.055
	NC-SSP	204	195	7.0	406	0.123
	Togo-PR	37.9	16.3	1.5	55.7	0.027
	Togo-PAPR	98.3	54.2	2.5	155	0.088
	Togo-SSP	194	133	4.6	331	0.166
	($LSD_{0.05}$)	(26.9)	(21.1)	(2.2)	(31.0)	(0.010)
Hiwassee	Check	1.2	9.4	1.0	11.6	0.011
	NC-PR	52.5	57.4	4.1	114	0.094
	NC-SSP	12.	181	11.8	313	0.106
	Togo-PR	23.2	31.8	3.9	58.9	0.025
	Togo-PAPR	54.7	95.7	6.0	156	0.067
	Togo-SSP	137	189	9.6	336	0.136
	($LSD_{0.05}$)	(14.9)	(23.9)	(5.6)	(22.5)	(0.015)

TABLE VII. RICE GRAIN YIELD AND Cd UPTAKE
FROM VARIOUS P SOURCES ON HIWASEE SOIL

P Source	P Rate (mg P/kg)	Cd Rate (μg Cd/kg)	Grain Yield[1] (g/pot)	Cd Uptake by Grain[1] (μg Cd/pot)	Cd Concentration in Grain[1] (μg Cd/g)
NC-PR	200	70.5	25.3 A	1.68 B	0.066 B
NC-SSP	200	79.0	24.5 A	3.25 A	0.135 A
Togo-PAPR	200	57.8	27.6 A	1.44 B	0.051 B
Togo-SSP	200	69.3	25.6 A	2.88 A	0.114 A

[1] Values followed by same letter in each column are not significantly different (P = 0.05).

TABLE VIII. TOTAL Cd, Ca AND P UPTAKE BY RICE PLANT (ROOT, STRAW, AND GRAIN)
FROM TWO PRs AT 400 μg Cd/kg RATE

PR Source	Cd Uptake[1]		Ca Uptake[1]		P Uptake[1]	
	Hartsells	Hiwassee	Hartsells	Hiwassee	Hartsells	Hiwassee
NC-PR	70.2 A	114 A	339 A	276 A	166 A	236 A
Togo-PR	55.7 B	58.9 B	265 B	207 B	125 B	170 B

[1] Values followed by same letter in each column are not significantly different (P = 0.05).

TABLE IX. CADMIUM CONCENTRATION IN ROOT, STRAW, AND GRAIN OF RICE PLANT
OBTAINED FROM TWO PRs AT 400 μg Cd/kg RATE

Soil	Cd Source	Cd Concentration[1]		
		Root	Straw	Grain
		- - - - - -- - - - - - -	(mg Cd/kg)	- - - - - - - - - - - - -
Hartsells	NC-PR	1.568 A	0.304 A	0.056 A
	Togo-PR	1.055 B	0.273 A	0.054 A
Hiwassee	NC-PR	2.021 A	0.995 A	0.216 A
	Togo-PR	0.624 B	0.518 B	0.159 A

[1] Values followed by same letter in each column are not significantly different (P = 0.05).

5. CONCLUSIONS

Use of the ^{32}P isotope dilution technique is a powerful tool to study the agronomic efficiency of PR as enhanced by water-soluble P. The modified iron oxide-impregnated paper strip (Pi test) by replacing 0.01 M $CaCl_2$ with 0.02 M KCl is an effective soil P test for both PR and water-soluble P. Acidulation of Cd-containing PR clearly increases Cd uptake by crops. If unacidulated PR or partially acidulated PR are agronomically as effective as fully acidulated PR, these water-insoluble or partially water-soluble P sources may also contribute less to Cd uptake by crops than the use of water-soluble P sources.

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REFERENCES

[1] CHIEN, S.H., MENON, R.G., BILLINGHAM, K.S., Estimation of phosphorus availability from phosphate rock as enhanced by water-soluble phosphorus, Soil Sci. Soc. Amer. J. **60** (1996) 1173-1177.

[2] HABIB, L. CHIEN, S.H., MENON, R.G., CARMONA, G., Modified iron oxide- impregnated paper strip test for soils treated with phosphate fertilizers, Soil Sci. Soc. Amer. J. **62** (1998) 972-976.

[3] IRETSKAYA, S.I., CHIEN, S.H., MENON, R.G., Effect of acidulation of high cadmium containing phosphate rocks on cadmium uptake by upland rice, Plant Soil **201** (1998) 183- 188.

[4] KHASAWNEH, F.E., DOLL, E.C., The use of phosphate rock for direct application to soils, Adv. Agron. **30** (1978) 159-206.

[5] HAMMOND, L.L., CHIEN, S.H., MOKWUNYE, A.U., Agronomic value of unacidulated and partially acidulated phosphate rocks indigenous to the tropics, Adv. Agron. **40** (1986) 89-140.

[6] CHIEN, S.H., SALE, P.W.G., HAMMOND, L.L., "Comparison of effectiveness of various phosphate fertilizer products," *In* Phosphorus Requirements of Sustainable Agriculture in Asia and Oceania, International Rice Research Institute, Los Baños, Philippines, (1990) 143-156.

[7] CHIEN, S.H., FRIESEN, D.K., "Phosphate rock for direct application," *In* Future Directions for Agricultural Phosphorus Research (SIKORA, F.J., ed.), TVA, Muscle Shoals, Alabama, USA, (1990) 47-52.

[8] CHIEN, S.H., HAMMOND, L.L., Agronomic evaluation of partially acidulated phosphate rocks in the tropics: IFDC's experience, Paper Series IFDC-P7, International Fertilizer Development Center (IFDC), Muscle Shoals, Alabama, USA (1988) 10 pp.

[9] CHIEN, S.H., SOMPONGSE, D., HENAO, J., HELLUMS, D.T., Greenhouse evaluation of phosphorus availability from compacted phosphate rocks with urea or with urea and triple superphosphate, Fert. Res. **14** (1987) 245-256.

[10] MENON, R.G., CHIEN, S.H., Phosphorus availability to maize from partially acidulated phosphate rocks and phosphate rocks compacted with triple superphosphate, Plant Soil **127** (1990) 123-128.

[11] MENON, R.G., CHIEN, S.H., GADALLA, A.N., Phosphate rocks compacted with superphosphate versus partially acidulated phosphate rocks as phosphorus sources to beans and rice, Soil Sci. Soc. Am. J., **55** (1991) 1480-1484.

[12] KPOMBLEKOU, K., CHIEN, S.H., HENAO, J., HILL, W.A., Greenhouse evaluation of phosphate fertilizers produced from Togo phosphate rock, Comm. Soil. Sci. Plant Anal. **22** (1991) 63-73.

[13] CHIEN, S.H., SALE, P.W.G., FRIESEN, D.K., A discussion of the methods for comparing the relative effectiveness of phosphate fertilizers varying in solubility, Fert. Res. **24** (1990) 149-157.

[14] MOKWUNYE, A.U., CHIEN, S.H., Reactions of partially acidulated phosphate rock with soils form the tropics, Soil Sci. Soc. Am. J. **44** (1980) 477-482.

[15] MENON, R.G., CHIEN, S.H., HAMMOND, L.L., The Pi soil phosphorus test: A new approach to testing for soil phosphorus, IFDC Reference manual R-7, International Fertilizer Development Center (IFDC), Muscle Shoals, Alabama, USA (1989) 10 pp.

[16] MENON, R.G., CHIEN, S.H., HAMMOND, L.L., Development and evaluation of the Pi soil test for plant-available phosphorus, Comm. Soil Sci. Pl. Anal. **21** (1990) 1131-1150.

[17] CHARDON, W.J., MENON, R.G., CHIEN, S.H., Iron oxide-impregnated filter paper (Pi test): A review of its development and methodological research, Nutr. Cycl. in Agroecosystems **46** (1996) 41-51.

[18] MENON, R.G., CHIEN, S.H., CHARDON, W.J., Iron oxide-impregnated filter paper (Pi test): A review of its application, Nutr. Cycl. in Agroecosystems **47** (1997) 7-18.

[19] MENON, R.G., HAMMOND, L.L., SISSINGH, H.A., Determination of plant available phosphorus by the iron hydroxide-impregnated filter paper (Pi) soil test, Soil Sci. Soc. Am. J. **53** (1989) 110-115.

[20] PERROTT, K.W., SAGGAR, S., MENON, R.G., Evaluation of soil phosphate status where phosphate rock based fertilizers have been used, Fert. Res. **35** (1993) 67-82.

[21] MENON, R.G., CHIEN, S.H., Soil testing for available phosphorus in soils where phosphate rock-based fertilizers are used, Fert. Res. **41** (1995) 179-187.

[22] RAJAN, S.S.S., WATKINSON, J.H., SINCLAIR, A.G., Phosphate rocks for direct application to soils, Adv. Agron. **57** (1996) 77-159.

[23] BARNES, J.S., KAMPRATH, E.L.J., Availability of North Carolina rock phosphate applied to soils, Tech. Bull. No. 229, North Carolina Agric. Exp. Stn., Raleigh, North Carolina (1975) 23 pp.

[24] SAGGAR, S., HEDLEY, M.J., WHITE, R.E., GREGG, P.E.H., PERROTT, K.W., CORNFORTH, S., Development and evaluation of an improved soil test for phosphorus. II. Comparison of the Olsen and mixed cation-anion exchange resin in tests for predicting the yield of ryegrass grown in pots, Fert. Res. **33** (1992) 135-144.

[25] MORTVEDT, J.J., Cadmium level in soils and plants from some long-term soil fertility experiments in the United States of America, J. Environ. Qual. **16** (1987) 137-142.

[26] MORTVEDT, J.J., Heavy metal contaminants in inorganic and organic fertilizers, Fert. Res. **43** (1996) 55-61.

[27] CHIEN, S.H., MENON, R.G., Factors affecting the agronomic effectiveness of phosphate rock for direct application, Fert. Res. **41** (1995) 227-234.

[28] SCHULTZ, J.J., Sulfuric acid-based partially acidulated phosphate rock: Its production, cost, and use, Tech. Bull. IFDC T-31, International Fertilizer Development Center (IFDC), Muscle Shoals, Alabama (1986) 30 pp.

[29] CHIEN, S.H., MENON, R.G., Agronomic evaluation of modified phosphate rock products: IFDC's experience, Fert. Res. **41** (1995) 197-209.

[30] CHIEN, S.H., MENON, R.G., "Dilution effect of plant biomass on plant cadmium concentration as induced by application of phosphate fertilizers," *In* Fertilizer and Environment, VIII International Symposium C.I.E.C., Instituto de Recursos Naturales y Agrobiologia, Salamanca, Spain, (1994) 106 p.

[31] BAKER, D.E., AMACHER, M.C., Nickel, copper, zinc, and cadmium, *In* Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties, (PAGE, A.L., ed.), Amer. Soc. of Agron., Madison, Wisconsin, USA (1982) 323-336.

[32] SERY, A., MANCEAU, A., GREAVES, G.N., Chemical state of Cd in apatite phosphate ores as determined by EXAFS spectroscopy, Am Mineral **81** (1996) 864-873.

EFFECTIVENESS OF NORTH CAROLINA PHOSPHATE ROCK AND FERTILIZER TABLETS IN RECLAIMING DISTURBED LAND IN COPPER BASIN, TENNESSEE, USA

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Abstract. Open smelting of copper ore about 100 years ago resulted in approximately 9,300 ha of disturbed land with severely eroded acidic soils at Copper Basin, Tennessee, USA. A field study was initiated in 1992 to compare revegetation from surface application of North Carolina phosphate rock (PR) and triple superphosphate (TSP) at 20, 59, and 295 kg P ha^{-1}, and determine benefits of fertilizer tablets. Measurements included survival and growth of transplanted pine seedlings, ground cover from an aerially seeded grass/legume mixture, and soil acidity. Tree survival was greater than 87% with no difference among treatments. When fertilizer tablets were not used, tree height and diameter increased with increasing soil P rates with growth maximized at 59 kg P ha^{-1}. After 96 and 240 d, there was no difference between PR and TSP with respect to growth of loblolly pine. After 960 days, PR caused greater tree growth compared to TSP. Weeping love grass provided the most ground cover, and its growth was stimulated with fertilizer tablets and P application. Fescue, lespedeza, and black locust trees responded more to PR than to TSP. Soil pH increased, and 0.01-M $SrCl_2$ extractable Al decreased, with increasing rate of PR. The molar ratios of Ca:Al in 0.01-M $SrCl_2$ soil extracts were also greater with PR compared to TSP. Decreased soil acidity, increased growth of loblolly pines, and increased diversity of ground cover vegetation from PR application makes PR a suitable material for reclaiming extremely acidic soils. Fertilizer tablets had an effect of improving loblolly pine growth when no P was surface applied. However, with surface P application of 59 kg ha^{-1} as PR, fertilizer tablets did not add any additional benefit to loblolly pine growth. Some improvement in tree growth was observed using fertilizer tablets with P applied as TSP at 59 kg ha^{-1}. Fertilizer tablets did greatly improve ground coverage of weeping love grass. Use of fertilizer tablets in reclamation efforts in conjunction with adequate surface P application may benefit growth and ground coverage of weeping love grass but, depending on the P source used, would provide little to no benefit to loblolly pine trees in early stages of growth.

1. INTRODUCTION

Phosphate rock is a good source of P for crops growing in acid soils, in particular for for perennial crops because of its slow dissolution over time. Land in the Copper Basin, Tennessee, USA is disturbed, resulting from past copper mining activities and further degraded, mainly by erosion. The soils are severely eroded and acidic [1]. Revegetation of disturbed lands is currently an area of environmental concern and active research. Phosphate rock is a superior source for supplying P to plants when the P fixing capacity is very high [2], as observed in Copper Basin soil with salt-extractable Al as high as 300 mg/kg. Phosphate rock would appear to be well suited for supplying P to trees and grasses planted in this area during reclamation efforts. In addition to supplying P, the higher Ca to P weight ratio in phosphate rock (approximately 2) compared to water soluble fertilizers (TSP = 0.67) would result in greater Ca addition to soil per unit of P applied. Calcium added to the soil may increase the Ca:Al molar ratio in soil solution, thus contributing to control the effects of Al toxicity on plant growth [3].

Fertilizer tablets have been developed to provide a slow release of nutrients to trees when added to soil when transplanting tree seedlings [4]. Fertilizer tablets and sludge placed in slits in soil close to transplanted tree seedlings were found to greatly improve early growth of sweetgum, sawtooth oak, black locust, black alder, and loblolly pine planted at the Copper Basin when compared to controls without tablets or sludge [5, 6]. Current reclamation practices in the Copper Basin involve the use of fertilizer tablets in addition to aerial application of fertilizers to the soil surface at the time of planting [1]. Although studies by Berry [5, 6] proved the effectiveness of using fertilizer tablets without any surface application of fertilizer, the utility of fertilizer tablets when also broadcasting fertilizer remains in question.

A study was conducted at the Copper Basin to determine the effectiveness of broadcasting North Carolina phosphate rock on the soil surface compared to triple superphosphate (TSP) during revegetation efforts. In addition to comparing P sources, the benefit of applying fertilizer tree tablets was evaluated with concurrent surface application of fertilizer.

2. MATERIALS AND METHODS

The experimental site was in the Copper Basin area in Tennessee behind the Copperhill High School. Baseline soil chemical characteristics were determined in soil collected at 0 to 15 cm depth in each of the experimental plots prior to implementing treatments. Soil pH was determined with 1:1 soil:water paste and a glass electrode. Cation exchange capacity was determined with the pH 7 NH_4OAc extraction methods. Exchangeable Al was determined with 50 ml of 1 N KCl added to 5 g soil, shaken for 30 minutes, filtered through Whatman 42 paper, and analyzed in the filtrate via atomic absorption spectroscopy. The 0 to 15 cm soil depth at the site had a soil pH of 4.5 ± 0.1 s.u. and exchangeable Al content of 191 ± 70 mg/L. The cation exchange capacity and base saturation were 1.7 cmol/kg and 2.4%, respectively.

The study consisted of plots having dimension of 7.3 x 9.1 m^2. The treatments consisted of 4 P application rates of 0, 20, 59, or 295 kg/ha P using North Carolina PR or TSP. In addition to the P source and rate, an additional treatment was including which consisted of using or not using a fertilizer tablet with each tree during transplantation. The experimental design was a randomized complete block with split plots. The split plot treatment was using or not using fertilizer tree tablets. The control treatment with 0 kg/ha P was only used once in each split plot with the application of 20, 59, and 295 kg/ha P with PR or TSP to result in 7 experimental units in each split plot. With two split plot treatments (with or without fertilizer tablet) and 4 replications, the total number of experimental plots was 56.

The experimental plots were prepared and established in March 1992. Before any fertilizer addition or planting, the site was sub soiled with 2-foot rippers on a crawler-type tractor. The TSP and PR treatments were hand applied to each plot. In addition, 112 kg/ha N and 112 kg/ha K were broadcast by hand over each plot as NH_4NO_3 and KCl fertilizer. Loblolly pine seedlings (*Pinus taeda*) were obtained from a local nursery at the 1-0 seedling stage and were not inoculated with mycorrhizal fungi. Twenty tree seedlings were planted 2 m apart from one another in each plot, which resulted in 4 rows along the longer dimension of each plot. The tree seedlings were planted with a hand-held device that created a slit in the soil where the root mass of the seedling was placed. Another slit was created parallel to the previous slit to tampon soil up against the root mass. For the treatments with fertilizer tablets, a 21 g fertilizer tablet was placed in the second slit. The fertilizer tablets had a grade of 20-10-5. Nitrogen consisted of urea formaldehyde. The tablets also contained 2.6, 1, and 0.35% Ca, S, and Fe. The calcium carbonate equivalence of the tablets was 5%. Each plot was planted with 20 pine seedlings spaced 6 feet apart. A commercial seed mixture containing 46% sericea lespedeza (*Lespedeza cuneata*), 16% Kobe lespedeza (*Lespedeza striata*), 27% Kentucky 31 tall fescue (*Festuca arundinacea*), 4% weeping love grass (*Eragrostis curvula*), and 6% tree-black locust (*Robinia pseudoacacia*) was aerially applied at 84 kg/ha.

The experimental site was visited during November or December of 1992, 1993, and 1994, which was 96, 240, and 960 days, respectively, after preparing the site. During each of these visits, measurements were made and samples were collected for laboratory analyses. During each of the visits, tree height and trunk diameters were measured. Tree height was determined with a 1-m rule and trunk diameter was determined 2.5 cm from the soil surface using a digimatic caliper. The predominance of vegetative ground coverage was determined using the line intersect method with a kit developed by the National Resource Conservation Service. The method involves stretching a line on the ground with beads every 18 cm on the line and counting the number of beads intersected by a particular plant species as viewed directly from the top. The number of beads showing an intersection divided by the total number of beads times 100 provides a good approximation on the percent coverage of plant species. Three lines were laid out in each plot exactly in between the four rows of pine trees.

Vegetative intersections with 150 beads were possible in each plot. Loblolly pine survival rates were measured by counting the number of live trees in each plot. The number of black locust trees in each plot was counting during the 1994 visit.

During the visits in 1992 and 1993, soil was collected from 0 to 2.5-cm depths in each plot. Several samples were taken in each plot and composited to obtain a representative sample. The soil was collected in plastic bags and transported to the lab. The soil was air- dried and ground to pass a 2 mm screen. The soil was extracted for Bray P using 2 g soil and 20 ml of Bray solution, shaken for 60 minutes, and filtered through Whatman 42 filter paper. The filtrate was analyzed for P via ascorbic acid colorimetric procedure [7]. Soil pH was determined using 1:1 soil:water paste and a glass electrode. Soil solution Al and Ca was extracted with 0.01 M-$SrCl_2$ where 10 g soil was added to 20 ml of extractant, shaken for 60 minutes, and filtered through Whatman 42 paper. The filtrate was analyzed for Al and Ca via atomic absorption spectroscopy.

During the visit in 1993, loblolly pine needles were collected from the last fully elongated flush in each of the plots. Several samples were collected in each plot to obtain a representative sample. The pine needles were brought back to the lab, dried in paper bags at 60°C, and ground in a Wiley mill to pass a 60-mesh screen. Total nitrogen was determined via Kjehldahl digestion [8] and NH_4^+ analyses via segmented flow colorimetry. For P, K, Al, and Ca analyses, 0.5 g of tissue was dry-ashed at 450°C and dissolved in 6 M HCl. The digestate was analyzed for P using the ascorbic acid colorimetric procedure [7]. The digestate was analyzed for K, Al, and Ca using atomic absorption spectroscopy.

3. RESULTS AND DISCUSSION

3.1. Plant growth

After 96, 240, and 960 days, tree growth responded to increasing levels of P application without application of fertilizer tablets, with maximum growth reached at 59 kg/ha P (Fig. 1).

Phosphate rock and TSP caused similar response in loblolly pine after 96 and 240 days. Phosphorus sources, P rates, and fertilizer tablets had no effect on tree survival. Survival rates were above 87% for all treatments (data not shown). There was little response to PR or TSP with fertilizer tablets. No benefits were observed using both fertilizer tree tablets and surface application of PR at 59 kg/ha P. After 960 days, PR caused greater tree growth than TSP at a P application rate of 59 kg/ha, when fertilizer tree tablets were not used.

The vegetative coverage of the grasses, tall fescue and weeping love grass, decreased with time (Figs. 2 and 3). After 96 days, the highest fescue coverage approached 20% but was reduced to levels below 3% after 960 days. Weeping love grass coverage was much higher at approximately 80% after 96 days and was reduced to 60% in the best growing plots after 960 days. Although fertilizer tablets did not appear to benefit tree growth with surface P application at 59 kg/ha P, there were noticeable effects on ground cover of weeping love grass. The percent ground coverage of weeping lovegrass was greater with fertilizer tablets than without them, indicating the weeping love grass may have utilized nutrients within the fertilizer tablets. The result was puzzling since ground cover was measured in between the tree rows (3' from the sides of each tree row) where the utilization of the nutrients in the fertilizer tablets would appear to be limited. Either weeping lovegrass had an extensive rooting system, or the fertilizer tablets solubilized with rain events and N and K got washed throughout the plot. Greater surface applications of N and K may have minimized the effect of fertilizer tablets on weeping love grass growth. Phosphate rock caused greater fescue coverage compared to TSP at the highest rate of P application. There was no difference between P sources in ground coverage of weeping love grass.

Vegetative ground coverage of the leguminous plants, lespedeza and black locust, are shown in Figs. 4 and 5. Unlike fescue and weeping lovegrass, coverage of the legumes increased with time. No lespedeza was observed at 96 days, but increased to 22% in the best growth plots after 960 days.

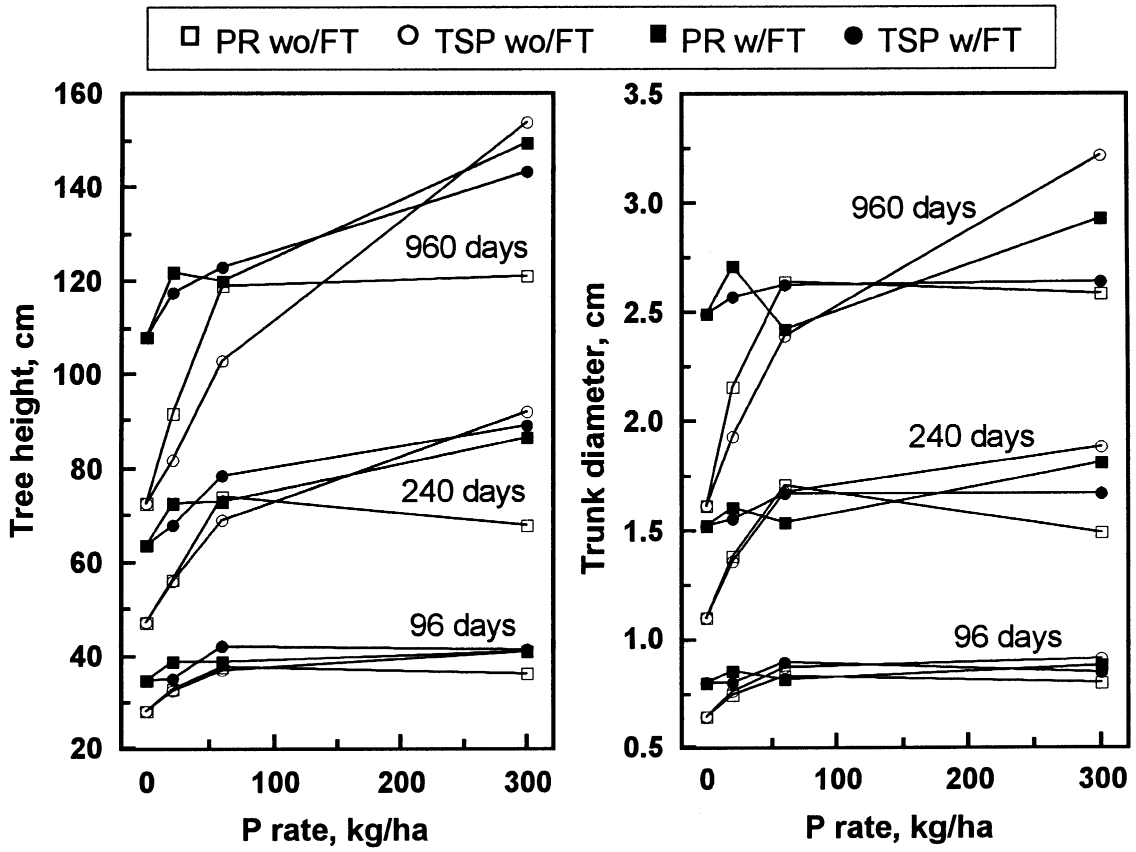

Fig. 1. Loblolly pine height and trunk diameter as affected by various soil application rates of PR and TSP, with or without application of fertilizer tree tablets (FT), at 96, 240, and 960 days after site preparation.

Very few black locust trees were observed after 240 days, but several were observed and counted after 960 days. Phosphate rock was a better P source for growth of lespedeza and black locust. Legumes produce an acidic rhizosphere, which makes them well suited to utilize P in PR [9]. The greater growth of legumes in the PR treatments was probably due to the acidic rhizosphere having a greater ability to solubilize apatite in PR compared to aluminum phosphates formed in soil with application of TSP. Use of PR improved vegetative diversity of ground cover species by increasing legume growth. Since legumes can fix atmospheric nitrogen, the improved legume growth from PR addition has important long-term consequences for the developing ecosystem.

3.2. Soil chemistry

Phosphate rock caused a greater increase in soil pH compared to TSP (Fig. 6). Phosphate rock contains P as PO_4^{3-}. When PR dissolves in soil, PO_4^{3-} can hydrolyze water to form HPO_4^- and $H_2PO_4^-$, which causes an increase in the pH due to release of OH^-:

$$PO_4^{3-} + H_2O \text{ <---> } HPO_4^{2-} + OH^-$$
$$PO_4^{3-} + H_2O \text{ <---> } H_2PO_4^- + 2\ OH^-$$

Although slight, PR had a liming effect due to the above reactions. As phosphorus in TSP is present as $H_2PO_4^-$, TSP dissolution in soil had no effect on soil pH.

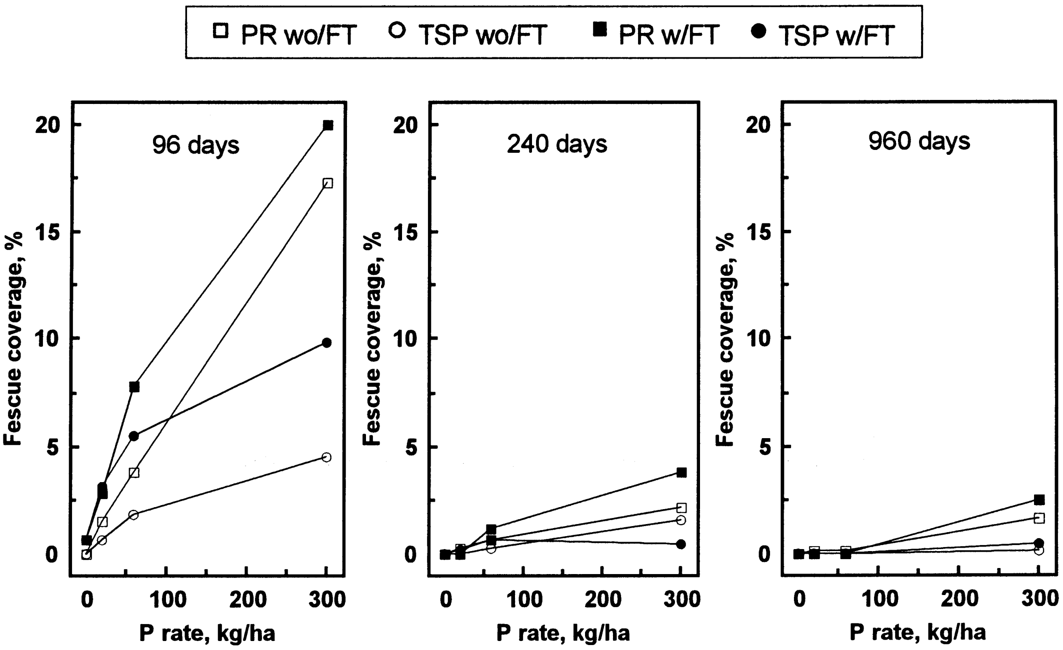

Fig. 2. Fescue coverage in experimental plots as affected by by various soil application rates of PR and TSP, with or without application of fertilizer tree tablets, at 96, 240, and 960 days after site preparation.

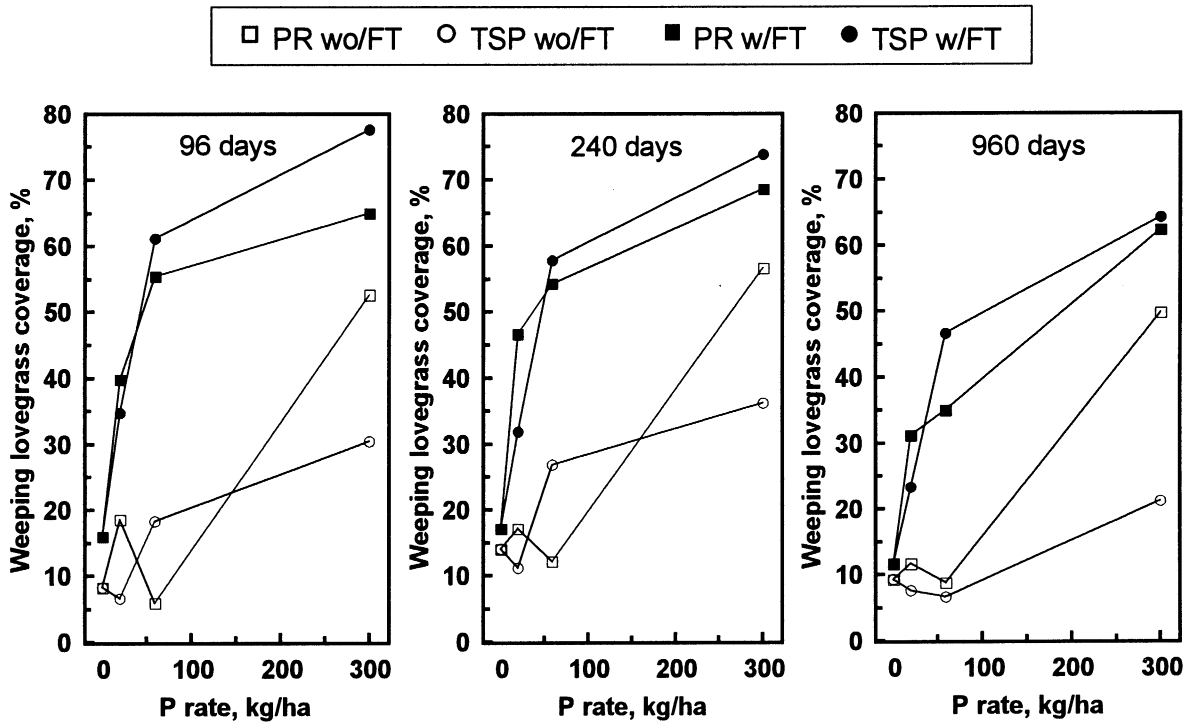

Fig. 3. Weeping lovegrass coverage in experimental plots as affected by various soil application rates of PR and TSP, with or without application of fertilizer tree tablets, at 96, 240, and 960 days after site preparation.

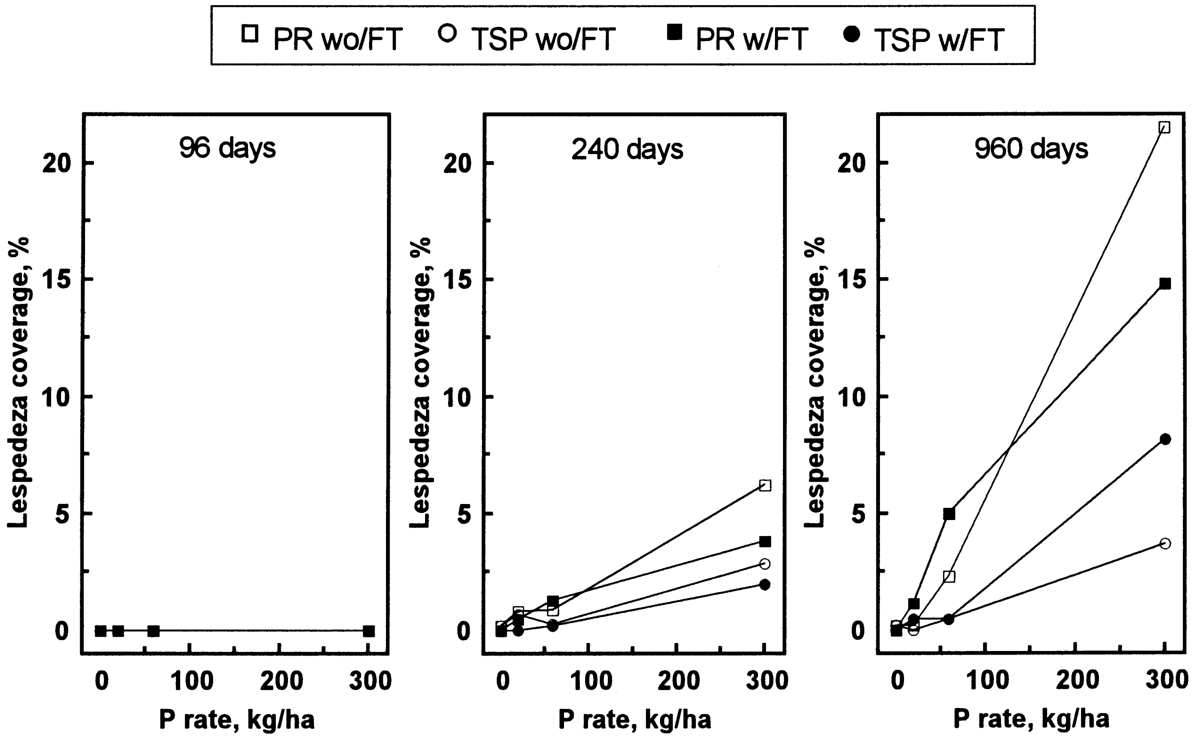

Fig. 4. Lespedeza coverage in experimental plots as affected by various soil application rates of PR and TSP, with or without application of fertilizer tree tablets, at 96, 240, and 960 days after site preparation..

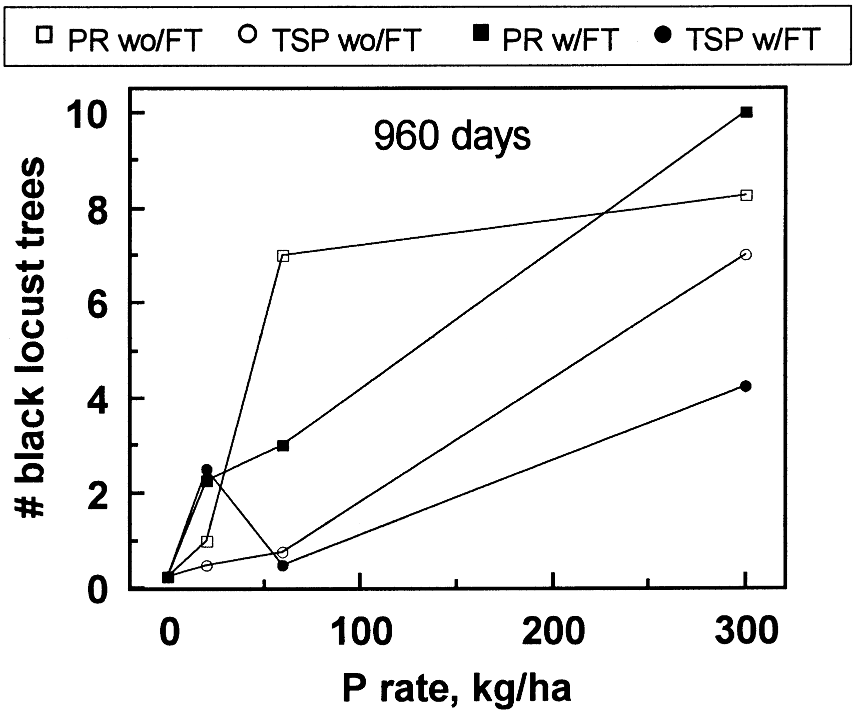

Fig. 5. Number of black locust trees in each experimental plot as affected by various soil application rates of PR and TSP, with or without application of fertilizer tree tablets, at 960 days after site preparation.

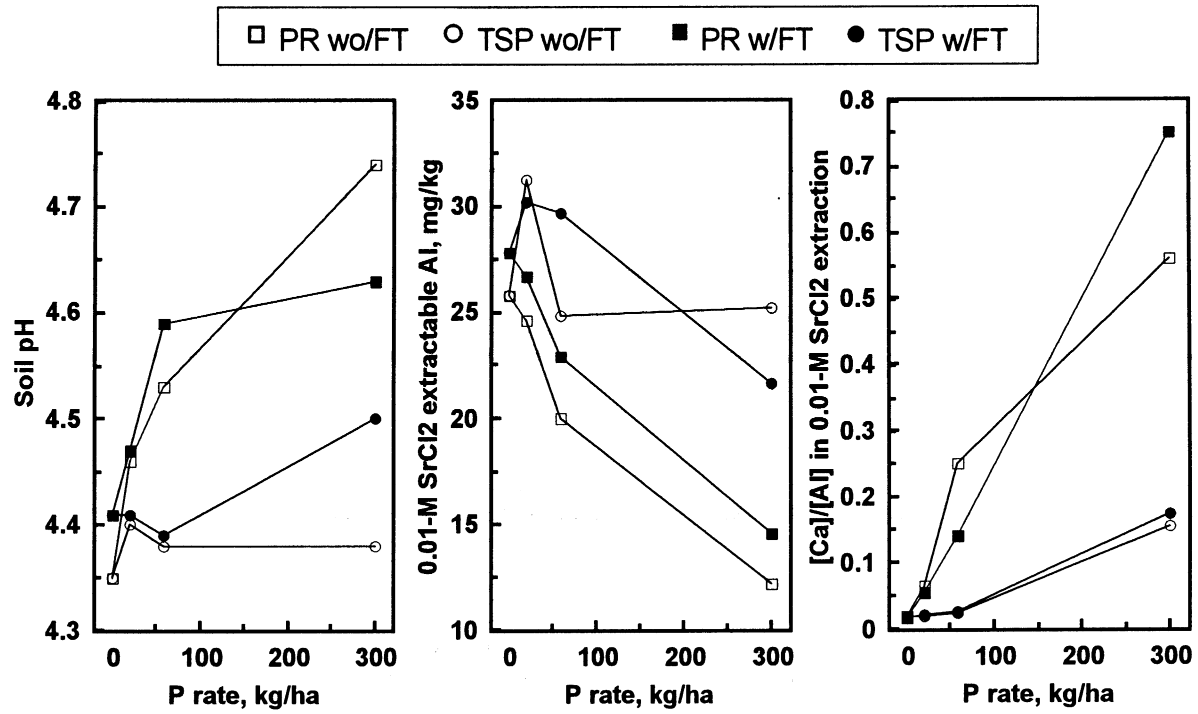

Fig. 6. Soil pH, 0.01-M $SrCl_2$ extractable soil Al, and Ca:Al molar ratios in 0.01-M $SrCl_2$ of surface 2.5 cm soil 240 days after site preparation as affected by various soil application rates of PR and TSP, with or without application of fertilizer tree tablets.

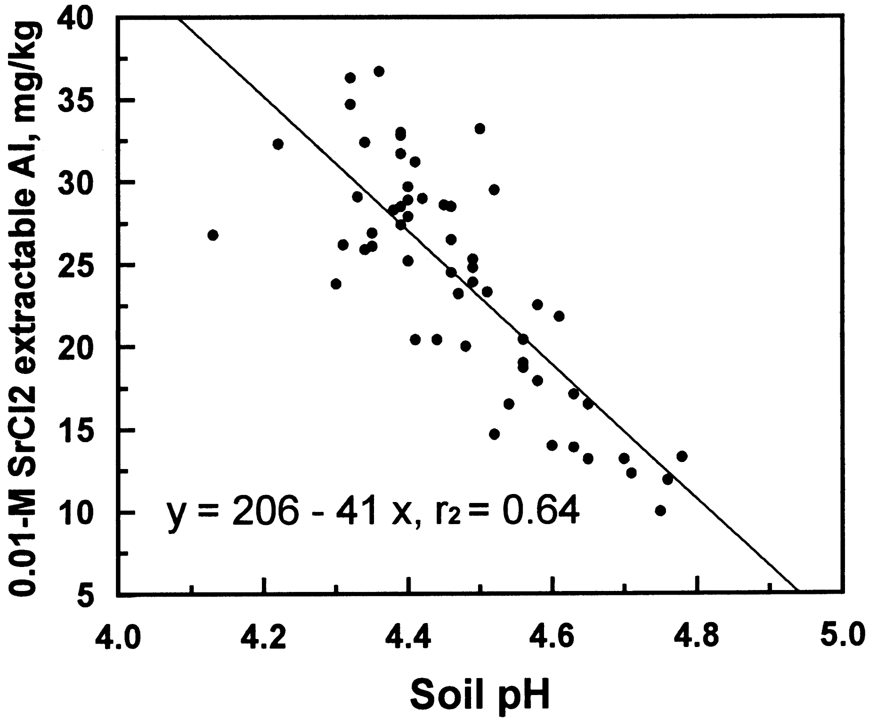

Fig. 7. Correlation between 0.01-M $SrCl_2$ extractable soil Al and soil pH in the surface 2.5 cm soil 240 days after site preparation.

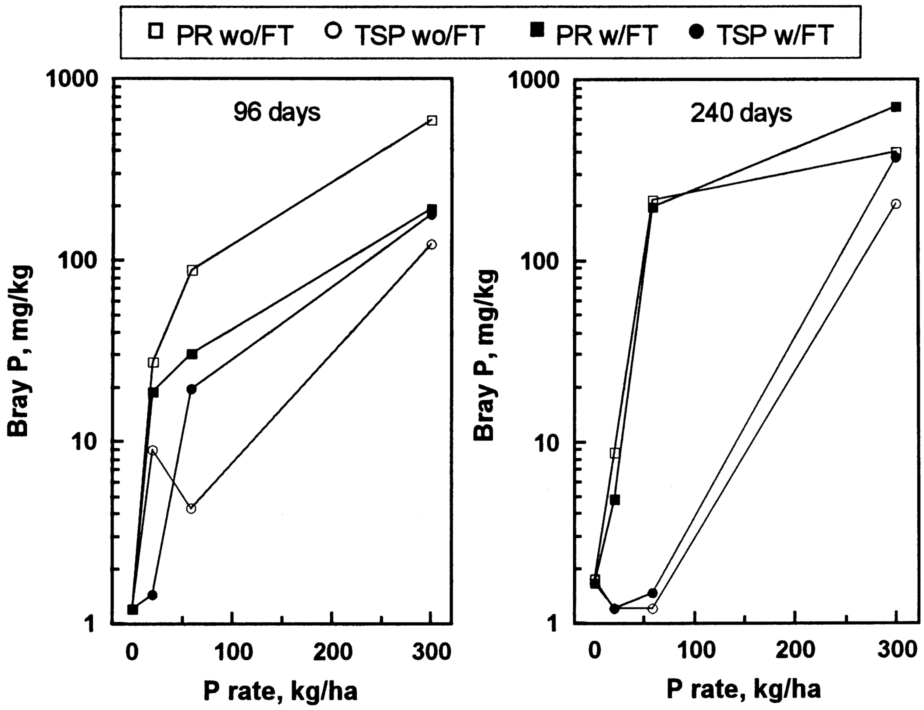

Fig. 8. Soil Bray P in surface 2.5 cm soil 240 days after site preparation as affected by various soil application rates of PR and TSP, with or without application of fertilizer tree tablets.

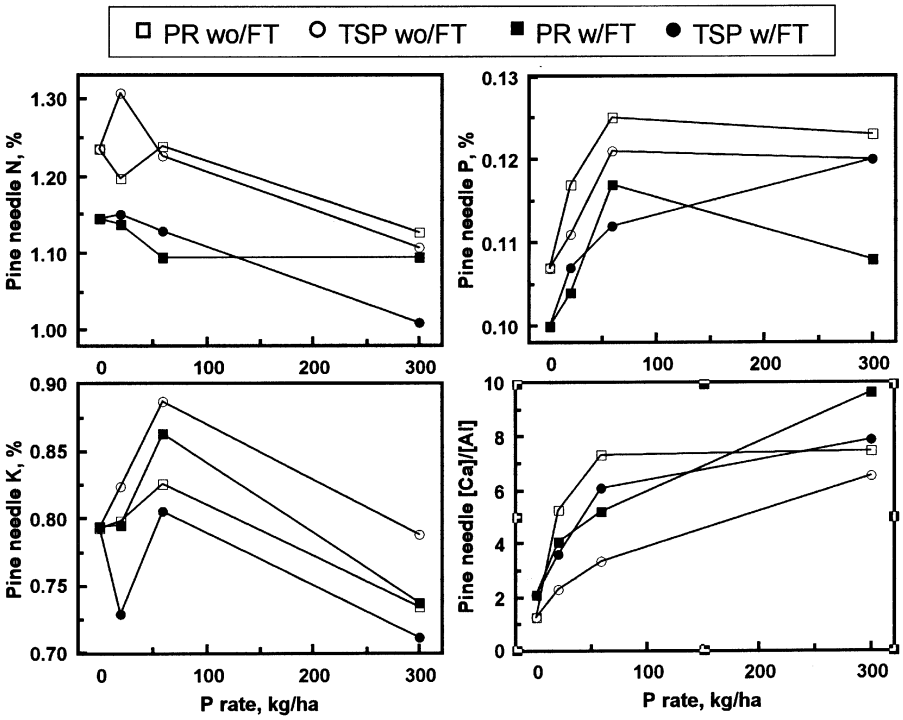

Fig. 9. Chemical composition of loblolly pine needles as affected by various soil application rate of PR and TSP, with or without application of fertilizer tree tablets, at 240 days after site preparation.

A noticeable decrease in 0.01-M $SrCl_2$ extractable Al was observed with increased PR soil application (Fig. 6). The decrease in Al can be explained by a soil pH increase caused by PR decreasing the solubility of Al in soil. The correlation between 0.01-M $SrCl_2$ Al and soil pH is shown in Fig. 7. Although PR may not increase pH greatly, the slight amount it does increase pH may be enough to reduce Al toxicity at very low soil pH levels. Another good indicator for Al toxicity and nutrient stress in forest soils is the molar ratio of Ca:Al in soil solution [3] where a value of 0.2 indicates a 100% likelihood of toxicity stress and a value of 0.5 indicates a 75% likelihood of toxicity stress. The molar ratio of Ca:Al in the 0.01-M $SrCl_2$ extract is shown in Fig. 6. The ratio was much greater in PR compared to TSP. The greater Ca:P weight ratio of 2 in PR compared to 0.67 in TSP and the influence of PO_4^{3-} in PR to increase pH and decrease soluble Al caused the Ca:Al molar ratio to be much higher in PR -amended soils compared to TSP. Phosphate rock greatly decreases the probability of toxicity stress occurring in vegetation grown on extremely acid forest soils.

As expected, Bray P increased with increased soil P application (Fig. 8). The very low Bray P in soils with TSP application after 240 days was probably due to a high fixation capacity of the water-soluble P from TSP in the Copper Basin soil containing high levels of Al. Bray P was much greater in PR amended soils. The acidic Bray extractant was much more effective at solubilizing Ca-phosphates in PR remaining in the soil compared to Al-phosphate formed when water-soluble TSP was applied to soil.

3.3. Loblolly pine needle analyses

Needles from recent growth of loblolly pine were harvested after 240 days for tissue analysis. Phosphorus concentrations increased with increase soil P application rate (Fig. 9). The lower P concentrations in the needles with fertilizer tablets compared to those grown on soil without fertilizer tablets could be a dilution effect from greater tree growth with fertilizer tablets (Fig. 1). Nitrogen concentrations in needles were greatest with trees grown without fertilizer tablets. As with P, the N differences were most probably due to a dilution effect with greater tree growth in soil with fertilizer tablets and at higher soil P application rates. There were little discernible differences in needle K concentrations. Needle Al concentrations decreased with increased soil P application rate (data not shown). The decreased Al was also most likely due to dilution of Al in the trees with improved growth at higher soil P application rate. The Ca:Al molar ratio in needles increased with increasing P rate but little difference was observed between PR and TSP treatments when fertilizer tablets were used. There may have been enough Ca in the fertilizer tablets to increase the Ca:Al ratio in pine needles regardless of the source of P that was surface applied. The TSP treatment did result in lower Ca:Al ratios compared to PR when fertilizer tablets were not used which was probably due to greater Ca application in PR compared to TSP. Cronan and Grigal [3] suggest a Ca:Al molar ratio less than 12.5 indicates a 50% likelihood of toxicity stresses being present. Phosphorus application rates improved the Ca:Al molar ratios but the ratios were still in the low range where the likelihood of toxicity stress was high.

4. CONCLUSIONS

Use of PR in reclaiming extremely acidic soils provides several benefits that water-soluble P fertilizers cannot supply. Phosphate rock improves the growth of legumes due to the acidic rhizosphere of legumes solubilizing apatite in PR and releasing P. Better legume growth in turn enhances the overall sustainability of vegetative growth due to the N input into the ecosystem via atmospheric N fixation. Phosphate rock also decreases soil acidity as observed with increases in soil pH and decreases in soluble Al. This is also confirmed by the increase in the molar ratio of Ca:Al in 0.01-M $SrCl_2$ extracts with increased PR addition. Decrease in soil acidity and improvement of legume growth associated with PR may have been the explanation for improved loblolly pine growth with PR compared to TSP when P was applied at 59 kg/ha without fertilizer tree tablets.

Fertilizer tree tablets provided great benefit in increasing loblolly pine growth when no surface application of P occurred. However, with surface P application of 59 kg/ha as PR, no additional benefit in tree growth was observed with the fertilizer tablets. Some improved tree growth still occurred with the use of fertilizer tablets when P was applied at 59 kg P/ha as TSP. The effect of fertilizer tablets on tree growth with some surface application of P may have been slight, but it was striking on growth of weeping love grass, with much greater ground cover observed with PR compared to TSP. With surface application of P in reclaiming extremely acid soils, fertilizer tree tablets may add more benefit to growth of ground cover grass species than to survival and growth of loblolly pine trees.

The experimental site was only monitored for 960 days. All of the observed effects were in a short time window considering the life expectancy of the developing ecosystem. Observations at longer time periods would be worthwhile to determine long-term effects of PR and fertilizer tablets on soil chemistry and growth of plant species.

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REFERENCES

[1] MUNCY, J.A., A plan for cooperatively completing vegetation of Tennessee's Copper Basin by the year 2000. (1986) TVA/ONRED/LER-86/51, Technical Note B59.

[2] PRITCHETT, W.L., GOODING, J.W., Fertilizer recommendations for pines in the southeastern coastal plain of the United States, (1975) Fla. Agric. Exp. Sta. Bull. No. 774.

[3] CRONAN, C.S., GRIGAL, D.F., Use of calcium/aluminum ratios as indicators of stress in forest ecosystems, J. Environ. Qual. **24** (1995) 209-226.

[4] WHITE, D.P., ELLIS, B.G., Slow-release fertilizers greatly aid tree planting, Crops and Soils (Aug-Sep) (1963) 21-22.

[5] BERRY, C.R., Slit application of fertilizer tablets and sewage sludge improve initial growth of loblolly pine seedlings in the Tennessee Copper Basin, Reclamation Rev. (1979) 33-28.

[6] BERRY, C.R. Growth response of four hardwood tree species to spot fertilization by nutrient tablets in the Tennessee Copper Basin, Reclamation and Revegetation Res. **2** (1983) 167-175.

[7] MURPHY, J., RILEY, J.P., A modified single solution method for the determination of phosphate in natural waters, Anal. Chim. Acta. **27** (1962) 31-36.

[8] BREMNER, J.M., Total nitrogen. In C.A. Black et al. (ed.) Methods of soil analysis, 2nd ed. (1965) ASA, SSSA, CSSA, Madison, WI.

[9] GILLISPIE, A.R., PIPE P.E., A comparison of three rock phosphates for use in forest soils, Fert. Res. **23** (1990) 141-145.

AGRONOMIC EVALUATION OF GUANO SOURCES BY MEANS OF ISOTOPE TECHNIQUES

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Abstract. Many soils of the tropics and subtropics under continuous cultivation are very infertile, thus poor yields are obtained and little crop residues remain to protect the soils from degrading erosion. External nutrient inputs in the form of chemical fertilizers, organic materials and other nutrients sources are essential for developing sustainable agricultural production systems. As chemical fertilizers are costly for developing countries with insufficient foreign currency for their purchase and their supplies are limited and irregular for small landholders, alternative nutrient sources must be sought and evaluated for use in dominant agricultural production systems. Locally available organic materials of different origin are potential sources of nutrients. One such source with high agronomic potential is guano. The present study was carried out to evaluate the agronomic effectiveness of two guano materials of different origin (Zaire and Peru) as sources of nitrogen and phosphorus as compared to chemical fertilizers (ammonium sulfate and triple superphosphate) using isotopic (^{15}N and ^{32}P) techniques. Using the classical method of comparing dry matter weight and P uptake, no significant differences among the tested guano sources were found. The use of the isotopic techniques allowed a quantitative assessment of the N and P supply to crops. Both guano materials were found to be good sources of N but in contrast were poor sources of phosphorus. In addition, from the agronomic evaluation, it was found that the guano of Zaire and the ammonium sulfate were N sources of equivalent efficiency and the guano of Peru even slightly better than the ammonium sulfate. As expected, P in the single superphosphate was as available to the P in the triple superphosphate. However, the substitution ratios for the guano sources were relatively high. Thus, 1 kg P as single superphosphate was equivalent to 9.5 kg P as guano from Zaire or 12.5 kg P as guano from Peru. Further field trials in selected locations (soil, climatic and management factors) are required to validate these findings, in particular their residual effect or their build up effect on soil fertility status with time.

1. INTRODUCTION

Increased intensification of agricultural production in existing cultivated land resources requires the rational utilization of high agricultural inputs, in particular fertilizers to replace the nutrients removed by the harvested portion of crops. Thus, in continuously cropped soils with low organic matter there is a widespread N deficiency and similarly there is a widespread deficiency of P especially in acid soils of the tropics and subtropics. Sources of N and P must be applied for optimum plant growth and production of food and fibre. Chemical fertilizers are costly for many developing countries with insufficient foreign exchange for their purchase. In addition, their supplies are limited and irregular for small land holders [1]. Alternatives nutrient sources must be sought and evaluated for developing sustainable agricultural production systems. Locally available organic materials of different origin are potential sources [2].

Guano materials are natural organic nutrient sources of different animal origin, normally found in deposits. They may be considered as nutrient sources with good agronomic potential. However, their nutrient content (NPK and others including micro-nutrients) is highly variable according to their origin and age. Normally, when fresh and rich in urine, they are mainly a source of nitrogen (12 to 15% N and 8-10 % $P_2 0_5$) and when dry and old, they became a good source of phosphorus (15-20 % P_20_5) [3]. Phosphorus concentration relatively increases upon ageing due to a loss of water and ammonia volatilization. Commercial guano formulations can be prepared adding N and K fertilizers to the old guano sources. A common drawback with most natural organic sources is the relatively slow nutrient release with regard to the plant nutrient requirements in particular at early stages of growth. This is often reported as lack of synchronization between nutrient supply from the organic material and plant nutrient demand [2]. In contrast, guano is an organic fertilizer of immediate action because it contains organic matter at advanced stage of decomposition and thus, undergoes fast nitrification [3]. Currently, commercial guano sources are available for organic agriculture, in particular for horticultural crops.

Guano deposits of variable origin and magnitude are world wide distributed. A well-known guano material is the Peruvian reserve, which consist of deposits from seabird droppings located along the coastline and small islands in the Pacific Ocean. Its fertilizer value was known to ancient cultures of the Andean region. It was extensively used for the fertilization of monoculture crops under intensive agriculture and more recently mainly for horticultural crops and gardening [3]. Other guano deposits of mostly bat droppings can be found in caves in the tropical forests of the African continent. One such sizeable deposit is found in caves from schist-calcareous material with a karstic drainage regime in the lower part of Zaire.

Isotope techniques (^{15}N and ^{32}P) permit the quantitative measurement of the N and P nutrient uptake from nutrient sources. A direct approach is utilized for the labeled fertilizer sources in study whereas an indirect approach would be applied for unlabelled nutrient sources such as natural organic sources [4]. Both approaches were used in a network of ^{15}N isotope-aided field trials to assess the N supply from *Azolla*, an aquatic fern which can be incorporated to rice paddy [5]. These authors found that *Azolla* was equivalent to urea as a source of N to rice, both in terms of N recovery by rice and panicle dry matter yield.

The purpose of this study was, therefore, to carry out the agronomic evaluation of guano materials of different origin (Peru and Zaire) in comparison to chemical fertilizers as sources of nitrogen and phosphorus utilising isotopic (^{15}N and ^{32}P) techniques.

2. MATERIALS AND METHODS

A series of greenhouse experiments was conducted at the FAO/IAEA Agriculture and Biotechnology Laboratory in Seibersdorf, Austria. Barley (*Hordeum sativum*) plants were grown in pots containing 2 kg soil. The soil used was a Typic Eutrocrepts with a pH 7.7 in 1*N* KCl, coarse clay loam textural class, calcareous (14.3% $CaC0_3$), medium to high N content and medium level of available P. Detailed characteristics are described elsewhere [6].

2.1. Experiment I (N experiment)

Three N sources were tested: Guano from Zaire (GZ) with 13.6% N, Guano from Peru (GP) with 4.72 % N and commercial ammonium sulfate (CAS) with 21% N. The N rates of application were 100 mg N/kg soil for the ammonium sulfate, and 210 and 195 mg N/kg soil for the guano from Peru and Zaire, respectively. A standard treatment without N source application but with the ^{15}N labeled fertilizer was included as reference for the isotope indirect method [4]. Unlabelled nitrogen fertilizers were applied to each pot by prior mixing with the soil in a twin blender. At planting, ammonium sulfate labeled with 5% atom ^{15}N excess was added to each pot in quantities equivalent to 50 mg N/kg soil. An unfertilized control treatment (0N), without a N source or ^{15}N fertilizer application was included to gather information on the dry matter yield response to fertilizer N application. Each treatment was replicated four times in a complete randomized block design.

2.2. Experiment II (P experiment)

Three P sources were used, Guano from Zaire with 4.60% total P, Guano from Peru with 6.28% total P, and triple superphosphate with 16.1% total P. These sources were applied in quantities equivalent to 80 mg P/ kg soil for the triple superphosphate, and 280 and 67 mg P/kg soil for the Guano from Peru and Zaire, respectively. A standard treatment without P source was included as reference for the isotopic technique. All the fertilizers were mixed thoroughly with the soil. Also, the ^{32}P labeled single superphosphate with a specific activity of 20 MBq (0.5 mCi) ^{32}P/g P was applied at a rate of 50 mg P/kg soil to all the treatments. Experimental design is similar to that before described for the N experiment.

In both experiments the guano sources were applied at a much higher N or P rates than the chemical fertilizers considering that they are organic materials, which need to be mineralized before they can release N or P available to plants.

Potassium and other nutrients were supplied as nitrogen/phosphorus-free Hoagland nutrient solution at a rate of 30 ml/pot each week. Pots were maintained at a moisture content near field capacity throughout the experiment. Plants were maintained in the greenhouse at a mean day/night temperature of 25/20° C and 50-70% humidity. Harvesting was performed at 11 weeks after planting by cutting the aboveground plant material.

For the N experiment, the harvested plant material was oven-dried at 70° C for 48 hours. Plant samples were finely ground and analyzed for total N and the N isotopic ratio on a 1500 Carlo Erba Automatic Nitrogen Analyzer coupled to a SIRA mass spectrometer [7].

In the P experiment, the harvested plant material was cut into small pieces and oven-dried, ashed and dissolved in HCl for the determination of the ^{32}P activity of the samples by Cerenkov counting using a liquid scintillation analyzer Canberra Packard model 2000. Total P was determined using the vanadomolybdate yellow method [8].

Nutrient uptake was estimated from the N and P nutrients cumulated in the plant. Isotopic parameters were estimated using the isotopic data obtained using ^{15}N and ^{32}P as tracers [4].

The A value is a quantitative measure of the available amount of a soil nutrient in terms of a standard. In practice this is done by using an isotopically labeled fertilizer standard because it gives a direct measurement of the proportion of nutrient that was derived from the standard fertilizer. This technique has been further extended to estimate the available amounts of nutrients in fertilizer sources, which cannot be labeled. In this case the nutrient (N or P) in the plant derived from a labeled fertilizer must be determined in presence and absence of the unlabelled fertilizer source under study. Thus a pair of treatments is needed to make such a quantitative estimate [9].

In the N experiment, the standard treatment involving soil and the ^{15}N labeled ammonium sulfate is used to estimate the A nitrogen value of the experimental soil. In each of the other treatments, besides soil and the ^{15}N labeled ammonium sulfate, the unlabelled N sources in study, i.e.: commercial ammonium sulfate, guano of Peru and guano of Zaire are added respectively. For these treatments the estimated A values represent the combined available amounts of nitrogen from soil and the unlabelled fertilizer source. Finally the A value of nitrogen from the unlabelled source can be obtained by difference [4]. Similar procedure has been applied in the P experiment to assess the available amounts of P from the guano sources.

For the agronomic evaluation, the substitution ratios, i.e. kg N or P as guano sources equivalent to 1 kg N or P of the fertilizer standard used, were estimated. Since the nutrient content (% N or P) of the guano sources and their application rates are known, one can then calculate how many kg. of the guano source would supply the same amount of nutrient (N or P) to the crop as 1 kg of the fertilizer standard (ammonium sulfate or superphosphate) under the experimental conditions [4].

Analysis of variance was performed on the yield and isotopic parameters for each of the experiments and comparisons between means of treatments for the various measured parameters were made by the least significance difference (LSD) test ($P<0.05$).

3. RESULTS AND DISCUSSION

3.1. Guano as a source of nitrogen

Dry matter yield and nitrogen uptake for the N treatments is given in Table I. Both parameters for the fertilized treatments were significantly higher than the unfertilized control (0N). However, there were no significant differences in dry matter yield between the N sources (treatments 2, 3, and 4).

The N uptake increased significantly over the control (0N) with the addition of N fertilizer treatments. These increases were greater for the guano treatments. This is very likely due to both the higher N rates of application and the faster nitrification rates of the N of the guano [3].

TABLE I. SHOOT DRY WEIGHT AND N UPTAKE OF BARLEY FERTILIZED WITH GUANO SOURCES (N EXPERIMENT)

N fertilizer treatment	Shoot dry weight g pot^{-1}	N uptake mg pot^{-1}
^{15}N-labelled ammonium sulfate (^{15}N-AS)	7.28	135
^{15}N-AS + commercial ammonium sulfate	7.62	187
^{15}N-AS + GUANO (Peru)	8.15	247
^{15}N-AS + GUANO (Zaire)	7.99	224
Unfertilized control	5.61	76
LSD (0.05)	1.48	28

In Table II, the values of nitrogen in the plant derived from the ^{15}N labeled fertilizer (Ndff) are reported. A significant decrease of the Ndff values was observed when comparing the standard treatment (29.4%) and the guano treatments (11.3-13.5%). This so-called "dilution" effect is due to the extra N available to the plant in the guano treatments. This is also reflected in the magnitude of the estimated A values (available amounts of nitrogen expressed in ammonium sulfate equivalent units) for the N treatments. The available amount of N from the soil, i.e., 242 mg N pot^{-1} estimated from the standard treatment. For the fertilizer N sources treatment, the estimated A values represent the sum of the available amounts of N from the soil and the added unlabelled N source and were therefore much higher. The A values were 785 and 644 mg N pot^{-1} for the guano from Peru and Zaire, respectively.

TABLE II. NITROGEN IN THE PLANT DERIVED FROM THE LABELLED FERTILIZER AND ESTIMATED A VALUES

N fertilizer treatment	Ndff (%)	A_N values mg N pot^{-1}
^{15}N-labelled ammonium sulfate (^{15}N-AS)	29.4	242
^{15}N-AS + commercial ammonium sulfate	17.8	463
^{15}N-AS + GUANO (Peru)	11.3	785
^{15}N-AS + GUANO (Zaire)	13.5	644
LSD (0.05)	1.9	44

Comparing the guano sources, guano from Peru showed the highest amount of plant available nitrogen, i.e.: 785-242=543 mg N pot^{-1}. This is likely explained by the fact that this source contains several plant nutrients other than nitrogen, which might have influenced a better plant growth and nitrogen uptake by the crop [3]. The guano from Zaire had a lower amount of plant available nitrogen, i.e.,: 644-242 = 402 mg N pot^{-1}.

Table III displays the data from the agronomic evaluation which was based on the estimated substitution ratios, i.e.: kg N as product equivalent to 1 kg N of the fertilizer standard, ammonium sulfate in this case.

TABLE III. AGRONOMIC EVALUATION OF GUANO MATERIALS AS SOURCE OF NITROGEN

Fertilizer N sources	N rate (mg N pot-^{1})	A_N Values (mg N pot^{-1})	Substitution ratio (kg N as material equivalent to 1 kg N as AS
Ammonium sulfate (commercial)	200	221	0.90
Guano (Peru)	420	543	0.77
Guano (Zaire)	390	402	0.97

The substitution ratio for the guano of Zaire is almost similar to that of the commercial ammonium sulfate (a chemical N source). The guano of Peru is even better than both of them, as mentioned above. Some organic materials with low C/N ratios and/or advanced stages of decomposition/composting are reported to be equivalent to inorganic N sources in supplying N to plants [2, 5].

3.2. Guano as a source of phosphorus

The dry matter and P uptake data are presented in Table IV. The application of P fertilizers increased significantly both dry matter and P uptake of plants over the check treatment without P. However, no significant differences in dry matter or P uptake were found among the P fertilizer sources in study.

TABLE IV. SHOOT DRY MATTER AND P UPTAKE OF BARLEY FERTILIZED WITH GUANO SOURCES (P EXPERIMENT)

P fertilizer treatment	Dry matter yield g pot^{-1}	P uptake mg P pot^{-1}
^{32}P labeled Ordinary Superphosphate (P-OSP)	8.10	20
^{32}P-OSP + triple super	7.85	22
^{32}P-OSP + Guano (Peru)	8.46	21
^{32}P-OSP + Guano (Zaire)	8.38	19
Unfertilized control	5.61	12
LSD 0.05	0.95	4

The isotopic data (Pdff values) and derived parameters are shown in Table V. As mentioned before for the N experiment, the magnitude of the decrease in Pdff of the P fertilizer treatment compared to the standard treatment (Pdff = 42%) is an indication of its relative P availability to the plant.

TABLE V. PHOSPHORUS IN THE PLANT DERIVED FROM THE LABELLED FERTILIZER AND A VALUES

P fertilizer treatment	Pdff (%)	A_P values (mg P pot $^{-1}$)
^{32}P-labelled Ordinary Superphosphate (^{32}P-OSP)	42.0	166
^{32}P-OSP + triple superhosphate	27.0	326
^{32}P-OSP + Guano (Peru)	36.2	211
^{32}P-OSP + Guano (Zaire)	40.0	180
LSD 0.05	3.9	43

In this case, the highest decline was observed for the water-soluble P source, i.e., triple superphosphate treatment (Pdff = 27%). The effect of the addition of guano, though significantly different, was smaller indicating that the P forms in the guano were less available. This may be due to inherent characteristics of the guano sources and/or the properties of the soil used (alkaline pH, calcareous, medium content of available P), thus reducing its P availability to plants [10, 11].

The A value of the soil was 166 mg P/pot and it was not significantly different from the A values of the guano treatments (Table V), indicating that very little P was plant-available from the guano sources. The highest A value, i.e.: 326 mg P pot^{-1}, was obtained for the triple superphosphate treatment due to the available P supplied by the TSP.

The agronomic evaluation of these sources is shown in Table VI. The P in the single superphosphate is as available as the P in the triple superphosphate. This is explained by the fact that both are water-soluble P fertilizers and have similar P availability to plants [10]. However, the resulting substitution ratios for the guano sources are 1 kg of P as single superphosphate is equivalent to 9.5 kg P as guano from Zaire or 12.5 kg P as guano from Peru. These values are relatively high, confirming the low P availability from these sources compared to the superphosphate.

TABLE VI. AGRONOMIC EVALUATION OF GUANO MATERIALS AS SOURCES OF PHOSPHORUS

Fertilizer P sources	P rate (mg P pot^{-1})	A_P values (mg P pot^{-1})	Substitution ratio kg P as material equivalent to kg P as OSP
Triple superphosphate	165	160	1.03
Guano (Peru)	558	45	12.40
Guano (Zaire)	133	14	9.50

4. CONCLUSIONS

These preliminary studies were carried out to study the relative agronomic effectiveness of these guano materials as sources of N and P to plants in comparison to chemical fertilizers. This evaluation should be done with organic materials of different origin and composition before their application in agricultural systems. In this case, both guano materials are good sources of N comparable to the chemical fertilizer ammonium sulfate but poor sources of P with respect to TSP. This quantitative assessment has been possible to be made through the use of isotopic (^{15}N or ^{32}P) techniques. Using the classical method of comparing dry matter weight and P uptake, no differences were found among the tested guano source. These results should be further validated in a network of field trials in selected locations reflecting predominant soil, climatic and local management practices, in particular to evaluate their residual effect or their "build-up" effect of the P fertility status with time.

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REFERENCES

[1] BOWEN, G. D., ZAPATA, F., Efficiency in uptake and use of nitrogen by plants. In: Stable Isotopes in Plant Nutrition, Soil Fertility and Environmental Studies.(Proc. Int. Symp., Vienna, (1990). International Atomic Energy Agency, Vienna, Austria, (1991), 349-362.

[2] ZAPATA, F., HERA, C., Enhancing nutrient management through use of isotope techniques. In: Nuclear Techniques in Soil-Plant Studies for Sustainable Agriculture and Environmental Preservation. (Proc. Int. Symp., Vienna, 1995). International Atomic Energy Agency, Vienna, Austria, (1995), 83-105.

[3] GOMERO, O.L., Guano de islas: Recurso olvidado. Medio Ambiente, vol. **47** (1991) 35-39.

[4] ZAPATA, F., Isotope techniques in soil fertility and plant nutrition studies. In: Use of Nuclear Techniques in Studies of Soil-Plant Relationships. Ed. G. Hardarson. International Atomic Energy Agency, Vienna, Austria, (1990), 61-127.

[5] KUMARASINGHE, K.S., ESKEW, D.L., Isotopic studies of *Azolla* and nitrogen fertilization of rice. Developments in Plant and Soil Sciences No. **51**. Kluwer Academic Publishers. Dordrecht, The Netherlands, (1993).

[6] ZAPATA, F., DANSO, S.K.A., HARDARSON, G., FRIED, M., Time course of nitrogen fixation in field-grown soybean using nitrogen-15 methodology. Agr. J. **79** (1987) 172-176.

[7] AXMANN, H., Methods for ^{15}N determination. In: Use of Nuclear Techniques in Studies of Soil-Plant Relationships. Ed. G. Hardarson. International Atomic Energy Agency, Vienna, Austria, (1990), 55-59.

[8] ALLEN, S.A., Chemical Analysis of Ecological Materials. Blackwell Scientific Publication, Oxford, England, (1974).

[9] FRIED, M., Quantitative evaluation of processed and natural phosphates. Agr. Food Chem. **2** (1954) 241-244.

[10] KHASAWNEW, F.E., DOLL, E.C., The use of phosphate rock for direct application to soils. Adv. Agr. **30** (1978) 159-206.

[11] CHIEN, S.H., MENON, R.G., Factors affecting the agronomic effectiveness of phosphate rock for direct application. Fert. Res. **41** (1995) 227-234.

Part III

STUDIES FROM CENTRAL AND SOUTH AMERICA

THE USE OF NUCLEAR AND RELATED TECHNIQUES FOR EVALUATING THE AGRONOMIC EFFECTIVENESS OF PHOSPHATE FERTILIZERS, IN PARTICULAR ROCK PHOSPHATE, IN VENEZUELA:
I. PHOSPHORUS UPTAKE, UTILIZATION AND AGRONOMIC EFFECTIVENESS

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Abstract. Field experiments were conducted to evaluate the efficiency of natural and modified rock phosphate using conventional and isotopic techniques in an acid soil from El Pao, Cojedes state, Venezuela, using maize and sorghum with the application of different phosphate fertilizers to measure dry matter production, P accumulated in plant, efficiency parameters using isotopic techniques or yield. Finally, commercial plots were established with the application of soluble P fertilizers and rock phosphate products to validate the results obtained in the field experiments. The results showed highly significant differences between partially acidulated rock phosphate, natural rock phosphate, and the check plot in dry matter production, and P accumulation in plant and grain yield. When the efficiency parameters were evaluated in microplots with ^{32}P-TSP at 60 days of plant growth, it confirmed results obtained in semi commercial plots where the P in the plant derived from the fertilizer was 46% with partially acidulated rock phosphate (PAR) and 14% with natural Riecito rock phosphate (RR). Utilization coefficients of P by the plants were 34.2 and 8.8% for both treatments, respectively. The Substitution relation parameter showed that just 0.8 kg of P of PAR or 3.1 kg P of RR was required to produce the same yield as 1 kg P of TSP. These results were further validated in 5 ha commercial plots using corn and sorghum.

1. INTRODUCTION

A more rational use of P fertilizers has been proposed in order to counteract the dependency of imported fertilizers, which are very important to maintain and increase agricultural productivity [1]. To achieve more rational use of P fertilizers, the knowledge of P dynamics and availability in tropical soils as well as the evaluation of soil and crop management factors to increase the efficiency of the fertilizers applied need to be known [2].

Previous research conducted in laboratory and greenhouse settings [3] using nuclear and related techniques to evaluate the agronomic effectiveness of phosphate fertilizers showed a high variability in P fixing capacity of the soils (r1/Ro= 0.02 to 0.76) with the same level of available P. This variability was also associated with a range of 10 to 88% of P removed by the Bray solution being available P. Incubation studies showed that the effectiveness of the P sources were related to their reactivity and the soil P fixing properties. Increasing the fixing capacity caused a significant reduction in the E value independent of the P source used. A high positive and significant correlation between P extracted by Bray and the E value (r = 0.95) showed the affinity of the Bray extractant for some forms of available P in soils where rock phosphate was applied. In the greenhouse experiment, crop response was related to the P fixing properties of the soil, the initial availability and solubility of the P source used. The P derived from the fertilizer (%Pdf) and the Utilization Coefficient (UC) decreased significantly withthe increase of P fixing capacity indicating a lower availability for the crop.

The objective of this study was to quantitatively evaluate P uptake and utilization from P fertilizers, in particular rock phosphates, and to enhance their agronomic effectiveness in order to obtain agronomic and economic recommendations on the efficient use of P fertilizers under the soils and climatic conditions of Venezuela. The effect of the P fixing capacity of the soil on P availability parameters in the soil and the efficient use of P fertilizers of different solubility was evaluated. Plant parameters were obtained using conventional and isotopic techniques, in order to calculate the amount of P isotopically exchangeable in the soil, the percentage of P in the plant derived from the fertilizer, the utilization coefficient of P by the plant and the substitution relation in kg of P for each source required to produce dry matter and grain yield similar to a highly soluble source such as triple superphosphate.

2. MATERIALS AND METHODS

The following P sources were evaluated: Riecito Rock Phosphate (RR, 12.7% P), 40% Acidulated Riecito Rock Phosphate (RR40, 10.7% P), 60% Acidulated Riecito Rock Phosphate (RR60, 14% P) and Triple Superphosphate (TSP, 19.7% P). The solubility in ammonium citrate pH 7 was 1.6, 6.5, 8.4, and 13.3% of total P for RR, RR40, RR60, and TSP, respectively.

The percentage of P derived from the fertilizer (%Pdf) was determined experimentally by applying the procedure described by Morel and Fardeau [4], Zapata and Axmann [5], and Salas et al. [2] for evaluating fertilizers that cannot be labeled directly with the ^{32}P radioisotope, where $^{32}PO_4$ is added to soil to label soil-available P. The Utilization Coefficient (UC) was also determined for each of the treatments comparing the P in plant derived from the fertilizer (Pf) with the total amount of P applied using the equation suggested by the International Atomic Energy Agency [6].

The field experiment was conducted in El Pao soil to evaluate the efficiency of the different P fertilizers using conventional and isotopic techniques. The same P fertilizers described earlier were used in addition to a check plot without P. The design was a complete randomized block with 5 replications in a semi commercial area of 2800 m^2 and each experimental plot had an area of 80 m^2. The corn hybrid planted was PB8 with a plant density of 62500 plants/ha. A basic fertilization was applied at 40 kg N/ha and 66 kg K/ha at planting and a side dressing with N at 21 days after planting at 87 kg N/ha. The P treatments were applied at a rate of 44 kg P/ha broadcast for the natural Riecito rock phosphate and banded at 5 cm depth for the 40% and 60% acidulated Riecito rock phosphates. The evaluation of biomass and P accumulation in plant were measured at 20, 31, 45, 60 and 120 days after planting. The method of measuring these variables were similar to the one described for the greenhouse experiment [2]. The variables measured were dry matter (kg/ha), grain yield (kg/ha), and total P accumulation in plant in each sampling (kg P/ha). Efficiency of P fertilizer use was determined by conventional methods, which included: 1. Utilization Coefficient assuming that the quantity of P in plant derived from the fertilizer (Pdf) was the difference between the P accumulated in each treatment and the P in the check plot, 2. Increment of grain yield per unit of P applied, 3. Amount of grain producedper unit of P absorbed by the plant.

The isotopic parameters were calculated using Triple Superphosphate (^{32}P-TSP, 18.5 MBq/g P) in a microplot in each treatment placed in a band at 5 cm depth and at a rate of 9 kg P/ha at planting. The size of the microplot was 6.4 m^2 that was situated in the middle of the 80 m^2 experimental plots. The isotopic parameters (P in plant derived from the fertilizer, Pdf; P utilization by the plant, UC) were measured at 60 days after planting in the microplots in the same way as described for the field experiment. These parameters are measured indirectly because the rock phosphates cannot be tagged with ^{32}P therefore, the method determines the effectiveness of these P sources based on the P uptake difference derived from a traced P fertilizer used as reference (^{32}P-Triple Superphosphate). The procedure has been documented elsewhere [5, 6]. It is based, first in the application of ^{32}P fertilizer to all treatments (microplots) to measure the isotopic parameters and second, to calculate the uptake and efficiency parameters of the rock phosphates following equations described by the authors mentioned before [5, 6].

To validate the results obtained in the experimental field plots, a 5 ha demonstration was conducted in Valle La Pascua and Tigre soils with corn and sorghum where grain yield was measured. Corn was planted in both soils and in the Valle La Pascua soil simple sources of N-P-K were used to apply 120 kg N/ha (Urea), 26 kg P/ha and 50 kg K/ha (potassium chloride) with the difference that the P source was either natural Riecito rock phosphate (RR), 40% acidulated Riecito rock phosphate (RR40), or triple superphosphate (TSP). In the Tigre soil an N-P-K formula (12-24-12 or 14-14-14 where the source of P is triple superphosphate) was compared to the same amount of nutrient applied in simple sources using 40% acidulated Riecito rock phosphate as the P source. The check plot did not receive N, P or K fertilizers. Because of the size of the commercial plots, just one plot per crop-soil was established in each location.

3. RESULTS

The soil properties have been described previously [2,3,7,8]. The dry matter production and P absorption by the corn plants in the semicommercial field experiment as a function of the growing stages of the crop and the sources of P applied are shown in Fig. 1 and 2. Figure 1 shows the increase in dry matter production which was statistically different at 31, 45, 60 and 120 days between the acidulated rock phosphates treatments and the values obtained with the natural Riecito rock phosphate and the check plot. In the case of plant P accumulation (Fig. 2), there was significant differences between the rock phosphate treatments and the check plot. No significant differences were found between the acidulated rock phosphate treatments, thus acidulation at 40 % yielded as much dry matter and accumulated P in the plant as the acidulation at 60 %. This information is very important fromthe industrial point of view, for the commercial production of these P sources.

Table I shows the treatment effects using efficiency parameters obtained by conventional and isotopic techniques in the microplots (^{32}P) at 60 days after planting. Dry matter production and P accumulation confirmed the results explained in Fig. 1 and 2 from the experimental plots. From the 44 kg P/ha applied in each treatment, the Pdf represented 3.9, 15.0, and 12.4 kg P/ha with statistically differences between the acidulated treatments and the natural Riecito rock phosphate. These values represented 14.0, 46.5, and 35.1 as % Pdff and 74.8, 46.5, and 56.4 as % P derived from the soil (%Pds) for RR, RR40, and RR60, respectively. Similarly, the Utilization Coefficient of P changed significantly between the acidulated tretaments and the natural rock phosphate. The use efficiency of P obtained from the field experiment increased with the increase of the solubility of the P sources used. The comparison between the conventional methods with the isotopic techniques to determine the use efficiency of the P applied (Table II) showed an overestimation of the utilization values obtained by the conventional (P uptake difference) method because any increase in P uptake in method is considered derived from the P fertilizer applied not taking in consideration the soil P supply. The values of dry matter production, P accumulation by the corn plants, and efficiency parameters were arranged similar to the grain yield shown in Fig. 3. Even though the yield of the check plot is considered good for El Pao location (4,950 kg/ha), they increased to 5,994 with the natural Riecito rock phosphate, to 6,895 with RR40and to 7,680 kg/ha with RR60 (Table II).

Figures 4, 5, and 6 show the results obtained in the field plots in Valle La Pascua and Tigre soils with corn and sorghum. The results were similar in both locations with very low or no yields (798 and 0) for the check plot (no N-P-K applied). A yield of just 2063 kg/ha for the natural Riecito rock phosphate indicated the low availability of this source for annual crops as was shown in laboratory, greenhouse, and experimental field plots experiments. Corn grain yield increased from 2686 to 3805 kg/ha using TSP as a highly soluble P source. The highest yield (3317 to 3849 kg/ha) was obtained with RR40. The mean values for each Figure were statistically different. These results confirmed the general order of P efficiency for the P sources used. Figure 6 shows a similar experience with sorghum in El Tigre soil under the same methodology explained in Fig. 5. The results were similar to corn, showing the lower yield in the check plot (1965 kg/ha), the yield increase to 3153 kg/ha with the formula where the P source was TSP and the best yield was obtained with RR40 (3546 kg/ha). The mean values were statistically different.

An agronomic and economic efficiency analysis was done to show the advantages of the Riecito partially acidulated rock phosphate (RR40) compared to a high soluble P source (Table III) using the data of sorghum yield in El Tigre (Fig. 6). The increase in agronomic and economic efficiency with RR40 showed that the partially acidulated rock phosphate had agronomic and economic advantages compared to a highly soluble P source (triple superphosphate).

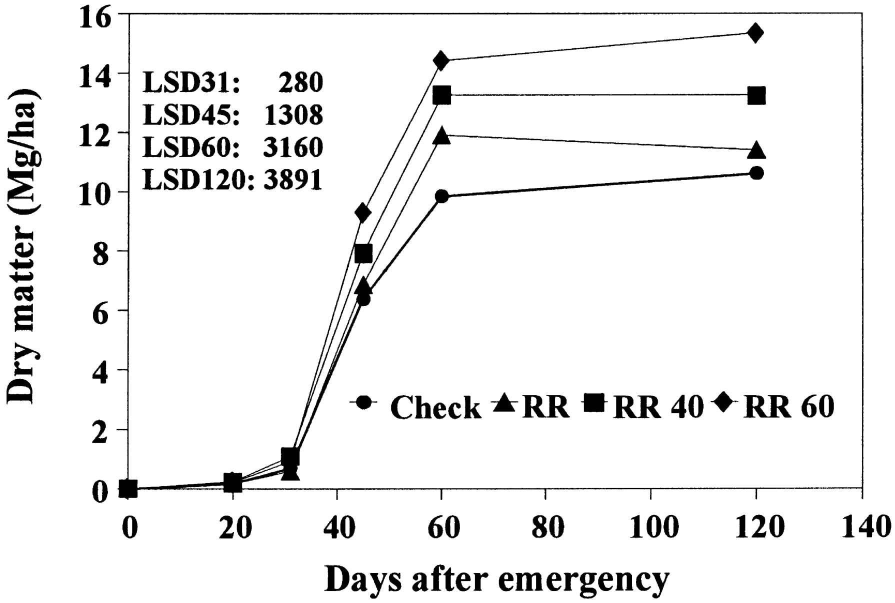

Fig. 1. Effect of the treatments evaluated on total P accumulation at different growth stages of corn.

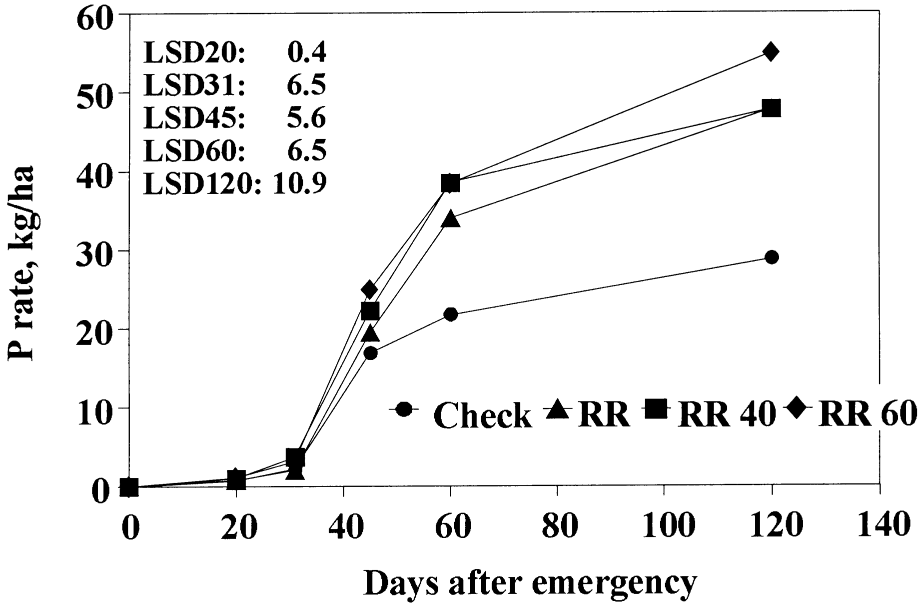

Fig. 2. Effect of treatments evaluated on total P accumulation at different growth stages of corn.

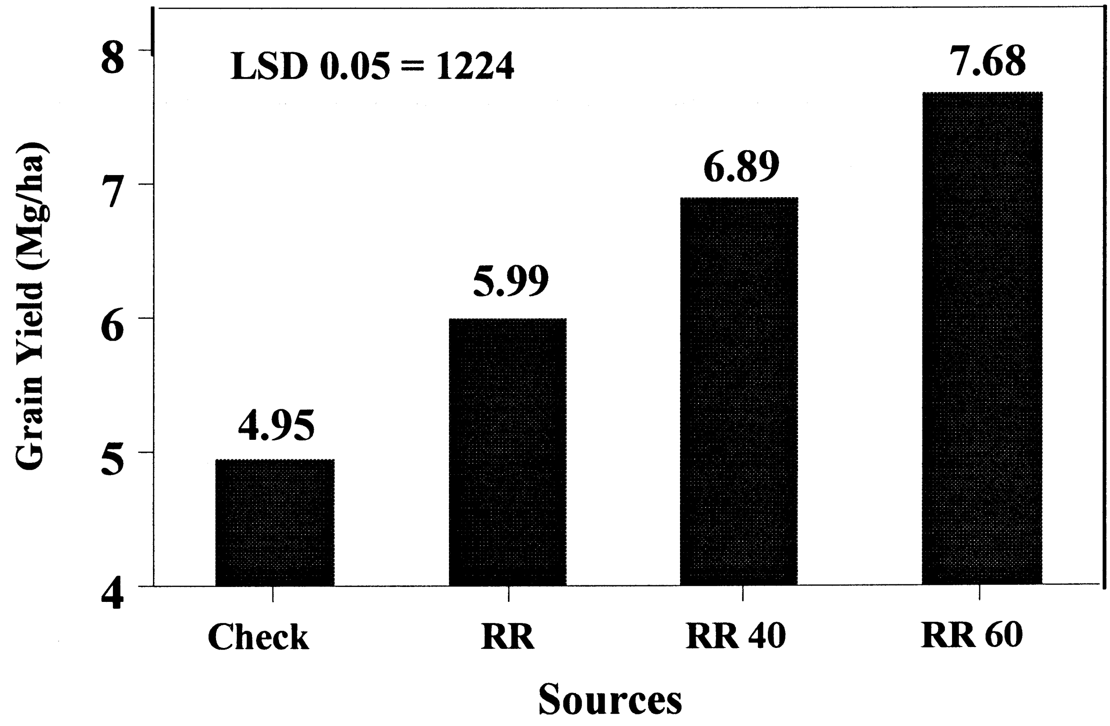

Fig. 3. Effect of treatments on grain yiel of corn (120 days after emergence) from experimental field plots.

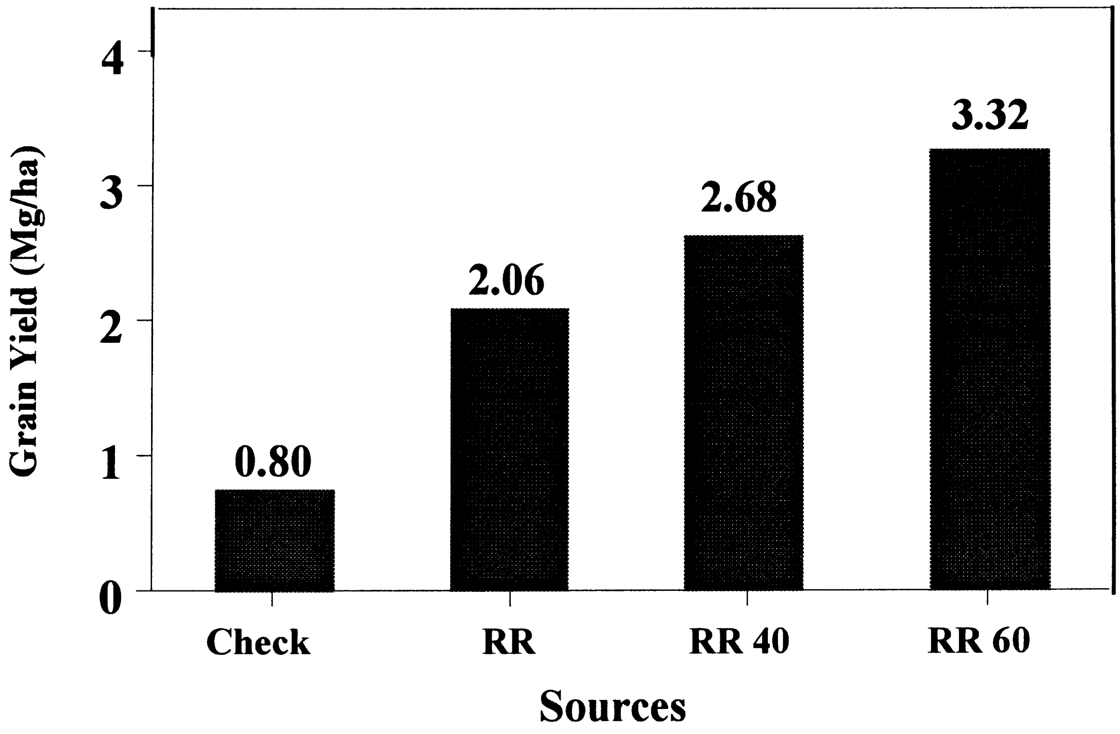

Fig. 4. Effect of P sources on corn yield in Valle La Pascua soil in the commercial experiment in 1997.

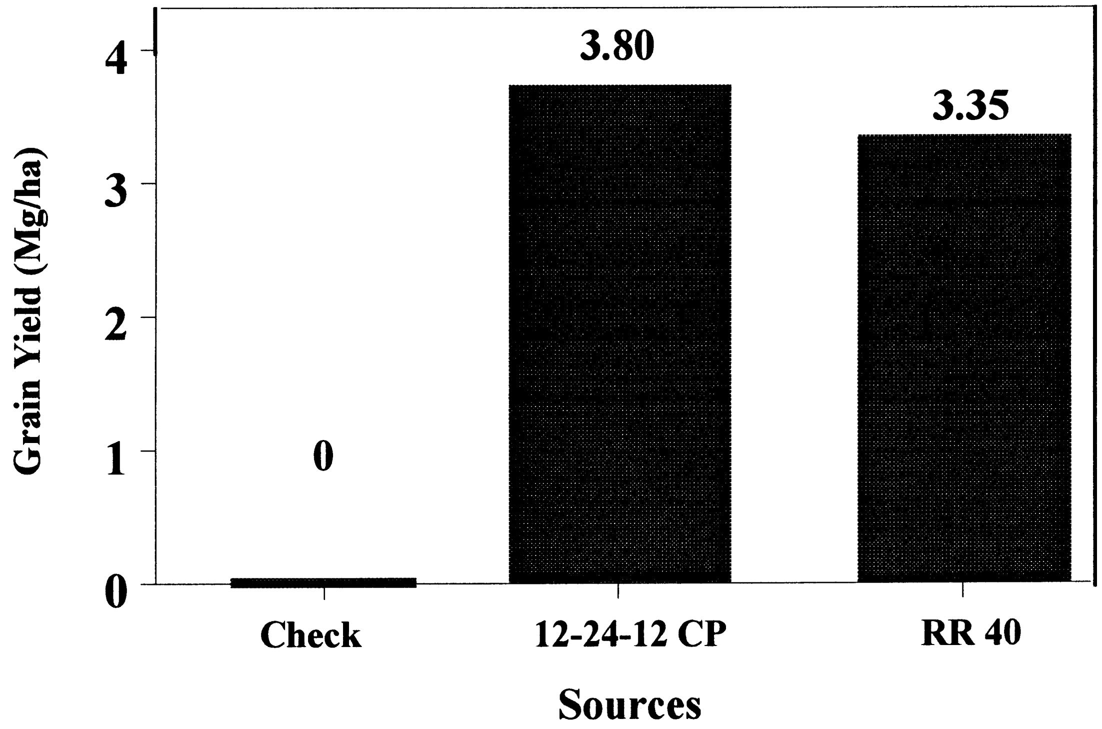

Fig. 5. Effect of P sources on corn yield in El Tigre soil in the commercial experiment in 1997.

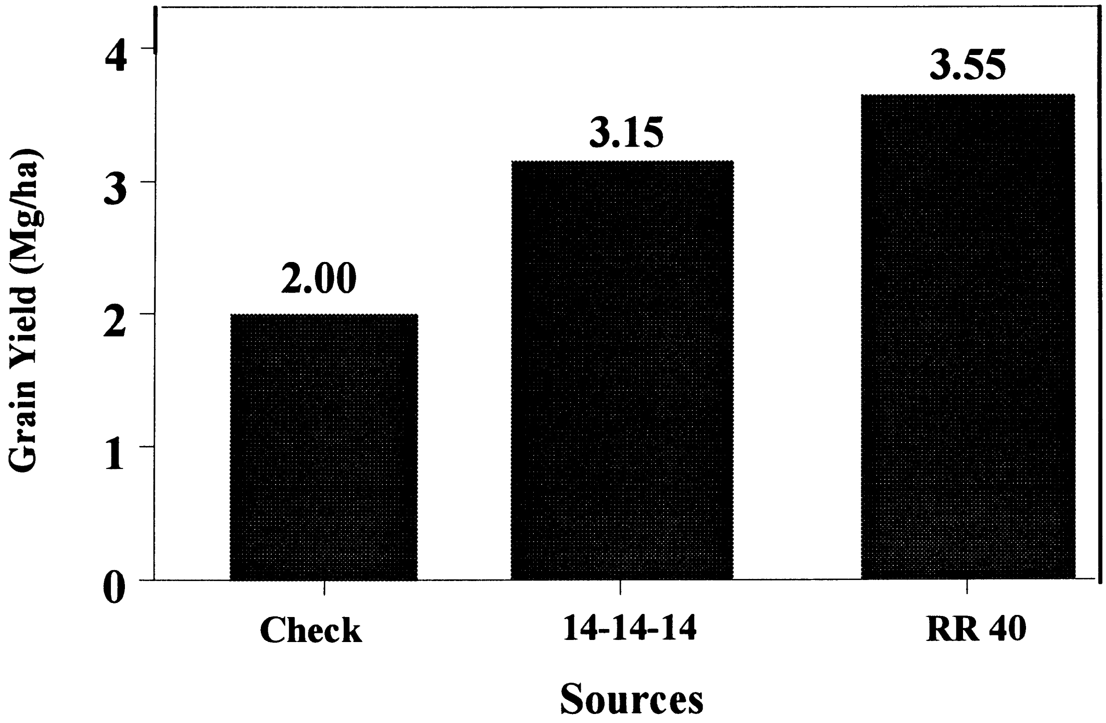

Fig. 6. Effect of P sources on sorghum yield in El Tigre soil in the commercial experiment in 1997.

TABLE I. EFFECT OF TREATMENTS ON EFFICIENCY PARAMETERS OBTAINED BY CONVENTIONAL AND ISOTOPIC TECHNIQUES AT 60 DAYS IN THE MICROPLOT WITH ^{32}P-TSP

Treatments	Dry matter kg/ha	Total P Accum. kg P/ha	AE [1] cpm/mgP	Pdf [2] kgP/ha	Pdf [3] %	Pds[4] %	UC[5] %
Testigo	9792 c	20.6 c	4237 a	---	---	---	---
RR	11230 b	28.0 b	3634 b	3.9 b	14.0 c	74.8 a	8.8 b
RR 40	11260 b	32.3 a	2741 c	15.0 a	46.5 a	46.5 b	34.2 a
RR 60	13980 a	35.1 a	2260 c	12.4 a	35.1 b	56.4 b	28.2 a
LSD (0.05)	8	4.2	395	4.7	11.3	10.3	10.3

[1] Specific Activity in the plant.
[2] P in the plant derived from the fertilizer.
[3] % P in the plant derived from the fertilizer.
[4] % P in the plant derived from the soil.
[5] % of P utilization by the plant.

TABLE II. COMPARISON BETWEEN USE EFFICIENCY PARAMETERS OBTAINED BY CONVENTIONAL AND ISOTOPIC TECHNIQUES IN THE FIELD WITH CORN IN EL PAO

Treatments	Grain yield kg /ha	Total P Accumulated kg P/ha	UC_{iso} [1] %	UC_{conv} [2] %
Check	4950 c	28.8 b	---	---
RR	5994 ab	47.7 a	8.8 b	43.0 b
RR 40	6895 ab	47.9 a	34.2 a	43.4 b
RR 60	7680 a	54.8 a	28.2 a	59.0 a
LSD (0.05)	1224	10.0		

[1] UC_{iso}: % of P utilization of P applied from fertilizer at 60 days, with isotopic techniques.
[2] UC_{conv}: % of P utilization of P applied from fertilizer at 60 days, with conventional techniques obtained by difference in the P absorption, according to the following equation:

$\%UC_{conv} = 100 * (P_{trat} - P_{check})/P_{applied}$, $P_{applied} = 44 kgP/ha$

TABLE III. AGRONOMIC AND ECONOMIC EFFICIENCY OF P FERTILIZERS FOR SORGHUM IN EL TIGRE SOIL IN 1997 IN THE COMMERCIAL EXPERIMENT[1]

Treatments [2]	Grain Yield, kg/ha	Agronomic [3] Efficiency, kg Grain / kg P Applied	Economic [4] Efficiency, \$ Profit / \$ Invested in P fertilizers
CHECK	1996	-	-
TSP	3153	71.66	18.28
RR40	3546	80.59	26.77

[1] P Applied: 44 kg P/ha; Corn Price: 0.25 \$/kg grain; Prices of P Sources: 0.73 \$/kg P (RR40); 0.98 \$/kg P (TSP)
[2] CHECK: No P Applied; RR40: Riecito Rock Phosphate Acidualted at 40 %; TSP: Triple Superphosphate.
[3] Agronomic Efficiency: Grain yield (kg/ha)/P applied (kg/ha).
[4] Economic Efficiency: \$ received for grain yield/\$ invested in P fertilizer.

4. CONCLUSIONS

1. An acidulation higher than 40% of Riecito rock phosphate did not increase significantly the availability and efficiency of P from this fertilizer.
2. The isotopic technique allowed the determination of P absorbed by the plant from the fertilizers, thus obtaining the real use efficiency of the evaluated fertilizers.
3. The increase in agronomic and economic efficiency with RR40 showed that the partially acidulated rock phosphate had agronomic and economic advantages compared to a water-soluble P source like triple superphosphate.
4. The series of laboratory, greenhouse, and field research work conducted during 4 years together with the results of experiments conducted in Venezuela with natural and modified rock phosphate during the last 10 years, have produced a great economic and social impact in the agriculture of the country, up to a point that Riecito rock phosphate is commercialized under the name of "Superfosforita" for use in acid soils and permanent crops. Since October 1998, an industrial plant will be operating to produce 150,000 t of 40 % partially acidulated rock phosphate (Fosfopoder) to cover the local P demand for annual crops in acid soils and for exportation. This approach will allow for the rationalization of phosphate fertilizer use in Venezuela and give local farmers a national product of low cost and of high agronomic and economic efficiency.

ACKNOWLEDGEMENTS

The authors wish to express their acknowledgement to the International Atomic Energy Agency, Vienna, Austria for the financial support of the research project VEN-7507 under the FAO/IAEA Phosphate project. Also, to PEQUIVEN, the company in Venezuela that produces and commercializes national fertilizers, for financial support.

REFERENCES

[1] CASANOVA, E., Las rocas fosfóricas naturales y modificadas y su uso potencial en suelos y cultivos de Venezuela. In: Memorias del Curso sobre Fertilización Balanceada. Palmaven-Impofos (Eds.), Valencia, Venezuela (1992) p.88.

[2] SALAS, A., CASANOVA, E., DUQUE, J., Evaluación de la disponibilidad de fósforo y transformación de fertilizantes fosfatados en suelos de importancia agrícola en Venezuela. II: Parámetros de plantas, Agron. Trop. **45 (2)** (1995) 265-282.

[3] SALAS A., CASANOVA, E., Evaluación de la disponibilidad de fósforo y transformación de fertilizantes fosfatados en suelos de importancia agrícola en Venezuela. I: Parámetros de suelos, Agron. Trop. **45 (2)** (1995) 247-264.

[4] MOREL, C., FARDEAU, J.C., Le phosphore assimilable des sols intertropicaux: ses relations avec le phosphore extrait par deux méthodes chimiques, Agronomie Tropicale **42 (4)** (1987) 248-257.

[5] ZAPATA, F., AXMANN, H., ^{32}P Isotopic techniques for the agronomic evaluation of phosphate rock materials. In: International Symposium on Nuclear and Related Techniques on Soil/Plant studies on Sustainable Agriculture and Environmental Preservation, Vienna, Austria (1994) p.12.

[6] INTERNATIONAL ATOMIC ENERGY AGENCY, Measurement of soil and fertilizer phosphorus availability to plants, In: Tracer Manual on Crops and Soils. Techn. Rep. Series. IAEA, Vienna, Austria (1976) 129-138.

[7] CASANOVA, E., Las rocas fosfóricas y su uso agroindustrial en Venezuela. Apuntes Técnicos Palmaven, Caracas, Venezuela (1993) 128pp.

[8] CASANOVA, E., Agronomic evaluation of fertilizers with special reference to natural and modified phosphate rock, Fertilizer Research **41** (1995) 211-218.

THE USE OF NUCLEAR AND RELATED TECHNIQUES FOR EVALUATING THE AGRONOMIC EFFECTIVENESS OF PHOSPHATE FERTILIZERS, IN PARTICULAR ROCK PHOSPHATE, IN VENEZUELA: II. MONITORING MYCORRHIZAS AND PHOSPHATE SOLUBILIZING MICROORGANISMS

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Abstract. The objectives of the study were to quantify and isolate P solubilizing microorganisms (fungus and bacteria) from corn, sorghum and beans rhizosphere from El Sombrero soil, located in Guarico state, a very important agricultural area in Venezuela. Rhizospheric soil samples were taken from the crops in the field and taken to the laboratory to conduct a serial dilution procedure in specific medium culture to obtain pure cultures and isolate microorganisms according to their function. The spores of arbuscular mycorrhiza (AM) from the soils were reproduced using trap pots in the greenhouse and after 4-6 months a dilute soil sample was wet-sieved and decanted for isolation of AM spores which were used for classification and for obtaining native pure cultures. Finally, the infective potential of AM was determined by setting pots with test crops and determining the AM colonization and efficiency to produce potential infection in the root system. There were no differences in the total microflora in both crop rhizospheres but there was a tendency of higher values in the corn rhizosphere due to the root exudates. Two solubilizing fungi identified were *Aspergillus terreus* and *Aspergillus niger.*

1. INTRODUCTION

Several approaches have been proposed to achieve a sustainable P supply in agro ecosystems and one possibility is the use of rock phosphate and the exploitation of soil microbial activities to solubilize the rock phosphate [1-5]. Recent interest on the topic is based on the demonstrated activities of mycorrhizal fungi, particularly those forming arbuscular mycorrhiza. In such symbiotic association the fungus colonizes biotrophically the root system. The symbiotic fungi also develop an external mycelium, which colonize extensively the soil surrounding the roots. Thereby, the mycorrhizal symbiosis, by linking the biotic and geochemical portions of the ecosystem, can contribute to nutrient capture and supply. The fungi can also improve soil structure and stimulate other beneficial members of soil microbiota. Also some phosphate-solubilizing bacteria, able to solubilize rock phosphate in vitro, have been characterized as rhizobacteria, because of their “aggressiveness” in colonizing the root region of plants, where they can change phosphate bioavailability. Some rhizobacteria can even improve mycorrhiza formation. By manipulating such micro organisms the plant can be provided with an active myco-rhizosphere, which could be specifically tailored to try to improve the use of less available sources, like rock phosphate [6].

Selected micro organisms of the rhizosphere may be used as inoculants to enhance plant growth. These include rhizobacteria, which participate in many ecosystems, and symbiotic microorganisms such as mycorrhizal fungi, which develop an external mycelium acting as a bridge connecting the root with the surrounding soil microhabitats. Particularly, arbuscular mycorrhizal symbiotic associations play a direct role in making available to plants sparingly soil P forms [7-9].

The objective of this paper was to quantify and isolate P solubilizing microorganisms (fungus and bacteria) from corn and bean rhizosphere from El Sombrero soil, located in Guarico state, a very important agricultural area in Venezuela.

2. MATERIALS AND METHODS

In field experiments, where corn and beans were grown in El Sombrero soil, Guarico state, P solubilizing microorganisms (fungus and bacteria) were quantified and isolated. Table I shows that the main properties of the soil. The soil was acid, loam to silty loam, low organic matter content, high in available P, high to medium in available K, low in calcium, high to medium in available magnesium and low in available sodium. The methodology will be described according to the objectives of the paper.

2.1. Reproduction of Arbuscular Mycorrhizal (AM) spores from the native soil

A soil sample of 3 kg from the field was passed through a 0.4 cm sieve and placed in the trap pots in the greenhouse. One seed of corn or black beans were planted in each pot and they growth for about 4 to 6 months. Five replications of each pot were established. Then, a root sample is taken to evaluate the presence of the AM fungus. Also a soil sample is taken for the extraction of the fungus spores and to proceed to their reproduction. Diluted soil samples from the rhizosphere (1:20 soil - water ratio) were wet-sieved (250, 100 and 60 µm mesh sieves) and decanted for isolation of AM spores and were classified for native pure cultures. Figure 1 shows a diagram of the procedure.

2.2. Determining the infective potential of Arbuscular Mycorrhiza (AM)

The infective potential of AM spores obtained in the first objective, was determined in 3 kg soil-pots in the greenhouse by planting sorghum (*Sorghum vulgare)* and common beans *(Phaseolus vulgaris)* as test crops. Fifteen days after planting, 20 ml of the native pure culture of the isolated spores (objective a) in a concentration of 20 spores per g of soil together with mycelium and mycorrhizal root fragments are applied to each pot.

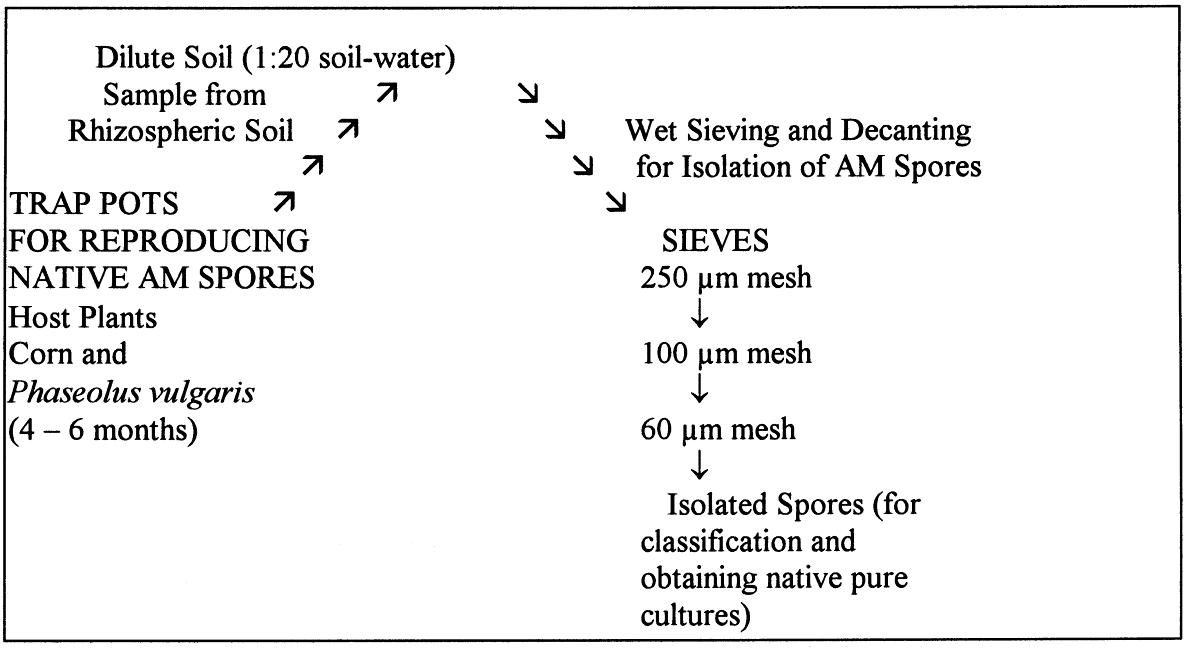

Fig. 1. Reproduction of Arbuscular Mycorrhizal (AM) Spores from Native Soil (Experimental plot in El Sombrero, Venezuela).

The plants were grown in a greenhouse under a day/night cycle of 12/12 h and 25°C and 50 % relative humidity and the pots were weighed and watered to 80% of field capacity daily, following the procedure described by Toro et al. [7]. After 6 weeks, the root system is observed to determine the % AM colonization and number of entry points. Using the most probable number test described by Toro et al. [7] the AM colonization was determined and the efficiency to produce potential infection in the root system. Figure 2 shows a diagram of the process.

2.3. Monitoring soil microorganisms of an agroecosystem and their manipulation for agricultural purposes

In order to identify P solubilizing fungi and bacteria that may have potential to solubilize rock phosphate applied to the soils, rhizospheric soil samples were taken from El Sombrero soil from corn and beans roots. A procedure similar to the one explained in Figure 1 was followed (seriate dilutions) until a pure culture is obtained. Threafter, the isolation of microorganisms according to their function is made and the identification of P solubilizing fungus and bacteria is done following the procedure described by Vassileva et al. [8]. Figure 3 shows a diagram of the procedure.

The total microflora in both rhizospheres was quantified. In addition, fungus and bacteria that solubilize phosphate were isolated and quantified using dicalcium phosphate and Riecito rock phosphate.

3. RESULTS AND DISCUSSION

3.1. Reproduction of Arbuscular Mycorrhizal (AM) spores from the native soil

The spores of fungus that formed AM were reproduced in each one of the soil samples where corn and bean were grown and after six months the quantity and variety of spores in each rhizosphere were measured as shown in Table II.

The corn rhizosphere had a higher quantity and variety of spores than the bean rhizosphere. Corn is known to have a rich-exudate rhizosphere, which could be the reason for the higher results of AM spores observed.

3.2. Determining the infective potential of Arbuscular Mycorrhiza (AM)

Even though no significant differences in the infective potential of AM were found in both crops (Table III), there was a trend for higher values in the bean. This could be explained by the higher affinity of AM for leguminous crops. They are more susceptible to colonization probably due to the particular chemical composition of their root exudates. The results indicate that for every 100 g of soil there is a potential of 2.58 and 3.40 infective spores that could colonize the sorghum and bean crops that are planted in them.

3.3. Monitoring soil microorganisms of an agrosystem and their manipulation for agricultural purposes

The last microbiological experiment isolated and quantified P solubilizing microorganisms from rhizospheres of corn and bean crops grown in El Sombrero soil. The values of total microflora, fungi and bacteria, which solubilize dicalcium phosphate and Riecito rock phosphate are shown in Table IV.

The values did not show significant differences for the total microflora for both rhizospheres but thre is trend for higher values of P solubilizing fungus and bacteria in the corn rhizosphere. The fungi *Aspergillus terreus* and *Aspergillus niger* were identified. They are known for their solubilizing capacity of sparingly P sources. In future studies, these microorganisms will be inoculated in greenhouse and field experiments to evaluate their effectiveness in solubilizing natural and modified rock phosphate using isotopic techniques (^{32}P). The effectiveness of this practice in soil is unknown because of the difficulties related to the translocation of phosphate ions to the root surface, if there is any solubilization of the riock phosphate product. The microbially-solubilised phosphate would be taken up by a mycorrhizal system, thereby developing synergistic microbial interactions [1].

* Natural soil samples from the field is used and passed through a 1 cm sieve

* 3 kg soil – pots are set.

* Setting pots with a test crop: *Sorghum vulgare* and *Phaseolus vulgaris*

* 20 ml of native pure culture of isolated spores (20 spores/g of soil) + mycelium + roots fragments is applied at 15 days after planting.

* After six weeks the root system is observed to determine % AM colonization and/or number of entry points (Most Probable Number Test)

* The infective potential of AM propagules is determined
and the efficiency to produce a potential infection in the root system

Fig. 2. Determining the Infective Potential of Arbuscular Mycorrhizal (AM) in an agroecosystem.

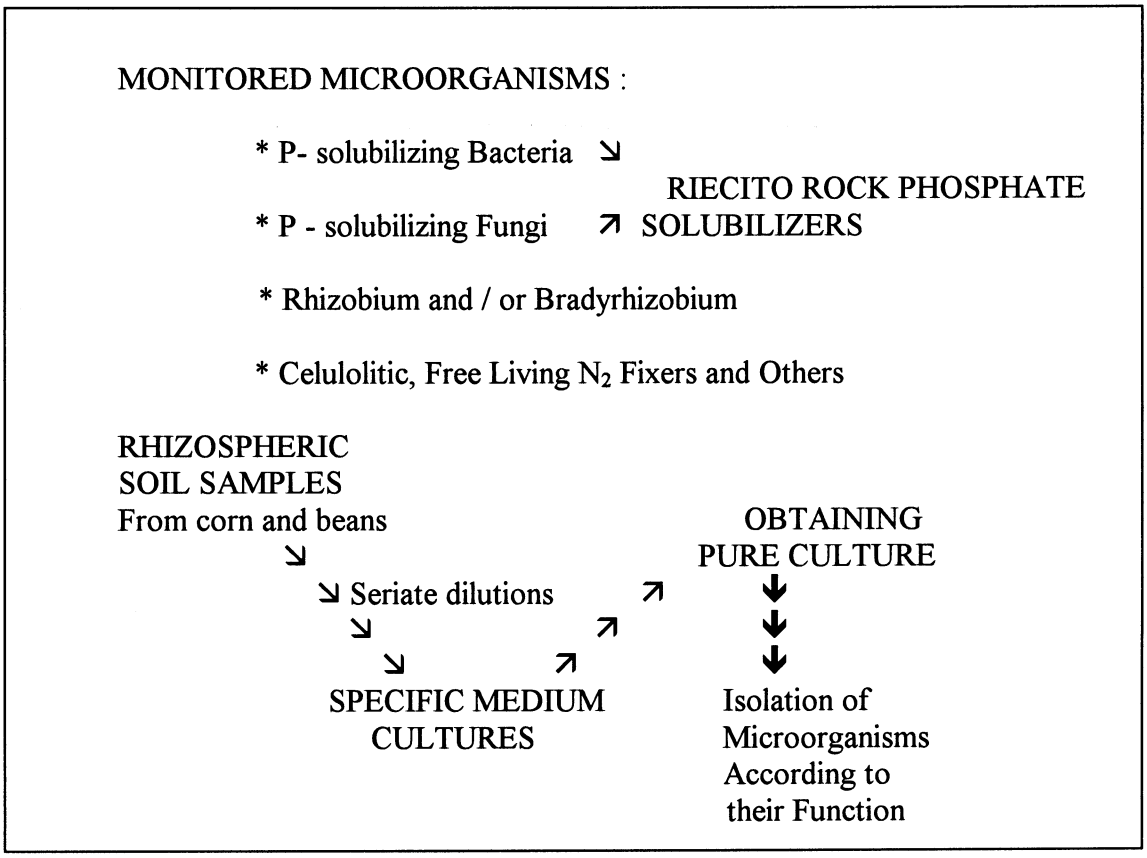

Fig. 3. Monitoring soil microorganisms in an agroecosystem for their manipulation with agricultural purposes.

TABLE I. MAIN PROPERTIES OF EL SOMBRERO SOIL WHERE CORN AND BEANS WERE PLANTED AND SPORES OF ARBUSCULAR MYCORRHIZA (AM) WERE OBTAINED

Crop	%clay	%silt	%sand	Texture	pH (1 :1)	Elect. Cond. S/m	OM %	Avail. P mg/kg	Avail. K mg/kg	Avail. Ca mg/kg	Avail. Mg mg/kg	Avail. Na mg/kg
Bean	20.4	46.8	32.8	Loam	4.62	0.120	2.31	53	101	156	114	43
Corn	16.4	50.8	32.8	Silty loam	4.74	0.090	1.85	85	50	215	74	19

TABLE II. QUANTITY AND VARIETY OF SPORES FROM FUNGUS THAT WILL FORM ARBUSCULAR MYCORRHIZA FROM THE CORN AND BEAN RHIZOSPHERE

	Corn Rhizosphere	Bean Rhizosphere
Spores quantity (# spores/80 g of dry soil)	60 a[1]	25 b
Diversity (types of spore)	6 a	3 b

[1] Different letters within the same line show significant differences according to Duncan Multiple Range Test (P = 0.05).

TABLE III. NUMBER OF INFECTIVE SPORES OF ARBUSCULAR MICORRHIZA PRESENT IN EL SOBRERO SOIL DURING THE RAINY SEASON OF 1997 IN SORGHUM AND BLACK BEANS

	Sorghum	Black bean
No of infective spores /100 g of soil	2.58[1]	3.40[1]

[1]The mean values are not statistically different according to the Duncan Multiple Range Test

TABLE IV. QUANTIFICATION OF TOTAL MICROFLORA, P SOLUBILIZING FUNGUS AND BACTERIA OF DICALCIUM PHOSPHATE AND RIECITO ROCK PHOSPHATE IN SOIL RHIZOSPHERES OF CORN AND BEAN IN EL SOMBRERO SOIL, GUARICO STATE IN THE RAINY SEASON OF 1997

	Corn Rhizosphere (cfu[1]/gr of soil)	Bean Rhizosphere (cfu/g of soil)
Total Microflora	1.7 x 10^7	2 x 10^7
Dicalcium phosphate fungus	1.7 x 10^4	-
Riecito rock phosphate fungus	4 x 10^5	5.6 x 10^4
Dicalcium phosphate (bacteria)	7.2 x 10^5	1.7 x 10^4
Riecito rock phosphate (bacteria)	1.1 x 10^5	4.5 x 10^4

[1] cfu: colony forming units

4. CONCLUSIONS

The isolation of P solubilizing microorganisms from rhizosphere of corn, sorghum and bean crops from El Sombrero soil, quantification of the total microflora, and isolation and quantification of fungus and bacteria that solubilize phosphate using dicalcium phosphate and Riecito rock phosphate showed no significant differences in the total microflora for both rhizospheres and a trend for higher values of P solubilizing fungus and bacteria in the corn rhizosphere. The fungi *Aspergillus terreus* and *Aspergillus niger* were identified. They are known for their solubilizing capacity of insoluble forms of P. In future studies, these microorganisms will be inoculated in greenhouse and field experiments to evaluate their effectiveness in solubilizing natural and modified rock phosphate using (^{32}P) isotopic techniques.

ACKNOWLEDGEMENTS

The authors wish to express their acknowledgement to the International Atomic Energy Agency, Vienna, Austria for the financial support of the research project VEN-7507 in the frame of the FAO/IAEA Phosphate project. Also, to PEQUIVEN, the company in Venezuela that produces and commercializes national fertilizers, for their financial support.

REFERENCES

[1] BAREA, J.M., AZCON-AGUILAR, C., AZCON, R., Interactions between mycorrhizal fungi and rhizosphere microorganisms within the context of sustainable soil-plant-systems. In: Gange, AC and Brown, VK (eds) Multitrophic interactions in terrestrial systems (1977) pp 65-77, Blackwell Science, Cambridge.

[2] ZAPATA, F., AXMANN, H., ^{32}P isotopic techniques for evaluating the agronomic effectiveness of rock phosphate materials, Fert. Res. **41** (1995) 189-195.

[3] MACRAE, R.J., HILL, S.B., MEHUYS, G.R., HENNING, J., Farm-scale agronomic and economic conversion from conventional to sustainable agriculture. In: Brady, N.C. (ed) Advances in Agronomy **43** (1990) 155-198, Academic Press, New York.

[4] KENNEDY, A.C., SMITH, K.L., Soil microbial diversity and the sustainability of agricultural soils, Plant Soil **170** (1995) 75-86.

[5] VANDERMEER, J., The ecological basis of alternative agriculture, Annu. Rev. Ecol. Syst. **26** (1995) 201-224.

[6] TORO, M., AZCON, R., BAREA, J.M., Improvement of arbuscular mycorrhiza development by inoculation of soil with phosphate-solubilizing rhizobacteria to improve rock phosphate bioavailability (^{32}P) and nutrient cycling, Applied and Environmental Microbiology **63-11** (1997) 4408-4412.

[7] TORO, M., AZCON, R., BAREA, J.M., The use of isotopic dilution techniques to evaluate the interactive effects of *Rhizobium* genotype, mycorrhizal fungi, phosphate-solubilizing rhizobacteria and rock phosphate on nitrogen and phosphorus acquisition by *Medicago sativa*, New Phytol. **138** (1998) 265-273.

[8] VASSILEVA, M., AZCON, R., BAREA, J.M., VASSILEV, N., Effect of encapsulated cells of *Enterobacter* sp on plat growth and phosphate uptake, Bioresource Technology **68** (1998) 1-4.

ENHANCEMENT OF THE AGRONOMIC EFFECTIVENESS OF PHOSPHATE ROCK IN A FERRALSOL FROM CUBA

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Abstract. The Ferralsols from Ciego de Avila, Cuba, have a pH near neutrality and very low exchangeable acidity, thus, they are not suitable for direct application of phosphate rock. In laboratory and greenhouse experiments, different P fertilizers were tested in order to assess their agronomic effectiveness through the use of nuclear and conventional methods. The phosphate rocks (PRs) came from different deposits (Higuanojo, La Pimienta and Trinidad de Guedes from Cuba; Riecito, Baja California and North Carolina from other countries). Partial acidulation (PA) of some of these rocks was also evaluated. Trinidad de Guedes PAPRs were found to be highly effective compared to their natural PR when evaluated through dry matter production, P uptake and isotopic parameters. Further field experiments are needed to validate the greenhouse results to enhance the agronomic effectiveness of the local Trinidad de Guedes PR through partial acidulation.

1. INTRODUCTION

One of the major constraints to food production in the central region of Cuba is the poor soil phosphorus fertility. Besides being deficient in total and extractable P, these soils have high P-sorption capacities. Adequate P fertilization is therefore, essential for economic and sustained food production in such soils. Use of conventional, water-soluble phosphorus fertilizers has been limited primarily by the high cost [1]. This factor linked with the rising concern about environmental pollution has led to the evaluation of alternative P inputs, with unknown efficiencies.

Phosphate rock (PR) deposits occur in several regions of Cuba [2]. Some of these PRs have been studied as a substitute for the expensive, water-soluble P fertilizers in acid soils and/or long growing season crops, i.e. sugar cane [3]. Most of these PRs, however, perform poorly, especially when used for crops with short growing seasons and neutral or alkaline soils, which are unfavorable conditions for direct application [4]. A major reason for the low effectiveness of PRs in Ferralsols of Cuba is that only a minor proportion of these products dissolve within several years after application to these soils and thus, much of the applied P remains as PR. This is in marked contrast to soils fertilized with superphosphates, where most fertilizer P dissolves rapidly and is sorbed by soil constituents.

Phosphate rocks can be made more effective by different biological and/or technological processes [5]. One of the technological ways is through preparation of partially acidulated phosphate rocks (PAPRs). The PAPRs are prepared by treating PR with less acid than would be normally needed to convert the entire P content into superphosphates. Only part of the acid used in preparing superphosphate is used on the dissolution of apatite and thus increasing available P; the remaining acid is used to dissolve some carbonate and release Fe and Al [6]. The partial dissolution saves acid, improves the agronomic effectiveness of PR, and could be used in soils with pH higher than 6. Complete solubilization of PR requires large quantities of acid and energy.

For most crops, it is adequate to have 40–60 % of the total P in the water-soluble form, provided that the remainder is available with time, as measured by conventional methods [7]. The PAPRs, which contains both soluble “fast” release and sparingly soluble “slow” release P forms, can be used for annual crops which require high levels of P in soil [8].

Soil properties like pH, exchangeable Ca, P concentration of the soil solution, P sorption capacity, CEC and base saturation, can influence the degree of PR dissolution [5, 9]. Truong and Montange [6] characterized two Ferralsols representative of the Ciego de Avila region, Republic of Cuba, which have been used in our experiments. They concluded that these soils are not suitable for direct application of PR.

An integrated evaluation program of the agronomic effectiveness of PR sources should include a series of studies at several levels. As a first step, a detailed physical, chemical and mineralogical characterization of the soil and PR sources under study is required. Then, greenhouse experiments will follow to obtain preliminary information on the suitability of PR sources for direct application to soil and to study means for enhancing their effectiveness [5].

Thus, the main objective of this study was to assess the agronomic effectiveness of different P fertilizers, including phosphate rock products, through the use of nuclear and conventional methods in laboratory and greenhouse experiments.

2. MATERIALS AND METHODS

The characteristics of the Ciego de Avila soil used were described elsewhere [10]. Briefly, the Ferralsol has the following properties: pH 7.1, CEC 11.79 cmol $^{(+)}$ kg^{-1}, organic matter 2.7%, total P 392 mg kg^{-1}, Olsen P 5.90 mg kg^{-1}.

The comparison of the P fertilizers was carried out through the evaluation of their reactivity in the laboratory, the determination of isotopic parameters in incubation experiments and the performance of a crop in a greenhouse experiment.

2.1. Reactivity of the P fertilizers

Various PR materials with wide range in reactivity and origin (Higuanojo, La Pimienta and Trinidad de Guedes from Cuba; Riecito from Venezuela, Baja California from Mexico and North Carolina from USA) were evaluated. The total P content, the P content soluble in 2% citric acid, 2% formic acid and Neutral ammonium citrate were determined in each of the rocks [11]. A detailed characterization of Trinidad de Guedes PR was presented in another paper [12].

2.2. Effect of various phosphate rock sources on phosphorus bioavailability

With the objective of measuring the effectiveness of various P sources, two incubation studies were conducted.

2.2.1. Experiment 1

The Ferralsol under study was incubated for two months with 100 mg P kg^{-1} using different phosphate rocks of Cuba and overseas. The sources were: Trinidad de Guedes PR (TGPR), Trinidad de Guedes PAPR 30% (TG PAPR), Riecito PR (RPR), Riecito PAPR 60% (R PAPR), North Carolina PR (NCPR) and triple superphosphate (TSP). A check of soil alone and two replications of all treatments were included. Soil bioavailable P was evaluated by determining the E value along with other static and kinetic parameters according to Fardeau et al. [13].

2.2.2. Experiment 2

The Ferralsol soil was incubated with the following Trinidad de Guedes PR (TGPR) products: TGPR, 40% sulfuric acid acidulated TGPR (SA-40), 40% sulfuric acid + monoammonium phosphate acidulated TGPR (MA-40), 60% sulfuric acid acidulated TGPR (SA-60), 60% sulfuric acid + monoammonium phosphate acidulated TGPR (MA-60). TSP and a check without P were included in two replications. After one month of incubation with 100 mg P kg^{-1}, the isotopic parameters were determined according to Fardeau et al. [13].

After an addition of carrier-free ^{32}P ions in a soil solution system in steady-state, the following data was determined in both experiments: the concentration, Cp, of phosphate ions in the soil solution, the fraction r_1/R, of the radioactivity applied, R, that remains in the soil solution after 1 minute of isotopic exchange and a parameter, n, that quantifies, with time t, the decrease of the quantity of radioactivity, r_t, in soil solution. Cp was taken as intensity factor, $E_1 = 10$ Cp R/r_1 as quantity factor and $E_1/Cp = 10\ R/r_1$ as capacity factor, CF. With the experimental values r_1/R, n and Cp, other kinetic parameters were calculated: the mean rate, K_m, of exchange of phosphate ions between the soil and its solution ($K_m = n / [r_1/R]^{1/n}$), the mean sojourn time, T_m, of phosphate ions in soil solution ($T_m = 1/K_m$) and the mean flux, F_m, of exchange between the soil and the solution ($F_m = 10$ Cp K_m) [14]. In addition the determination of the size of P pools, which can move towards soil solution was realized. Pool A corresponds to the quantity of phosphate which can be taken up by a given root zone, which can actively take up P within 1 day. The size of this pool is: A = 10 Cp $[R/r_{1440} - R/r_1]$. Pool B is explored during the time of root functioning of a short cycle crop. Its size is estimated as: B = 10 Cp $[R/r_{129600} - R/r_{1440}]$. Pool C corresponds to the quantity of phosphate ions which can be released from soil into the soil solution in less than 1 year: C = 10 Cp $[R/r_{518400} - R/r_{129600}]$. Pool D corresponds to very slowly exchangeable P, which can be released into the solution over the years under the condition of zero P fertilization. Its size is estimated by: D = 10 Cp $[P_T - R/r_{518400}]$, where P_T is total soil P.

The efficiency of P fertilizers was measured through the P derived from fertilizer (Pdff) in the soil solution for 1 minute of contact between the soil and the fertilizer applied: Pdff % = 100 $[E_{1F} - E_{1C}] / E_{1F}$ where E_{1F} is the value of the isotopically exchangeable P for 1 minute in the soil which received the fertilizer and E_{1C} is the value of the isotopically exchangeable P for 1 minute in the control soil. A coefficient of relative agronomic effectiveness (RAE) was also calculated from the ratio of Pdff of the phosphate rock to the Pdff of the TSP [13].

Radioactivity in soil solution was determined using liquid scintillation counting of the ^{32}P by the Cerenkov effect. Counts were corrected for counting efficiency. Phosphate ion concentration in soil solution was determined using a colorimetric method with malachite green oxalate as dye [15].

2.3. Greenhouse experiment

A greenhouse experiment was conducted in order to obtain preliminary information on the suitability of partial acidulation as a means for enhancing the agronomic effectiveness of TGPR. The same P sources of experiment 2 were used. After mixing the soil with the different fertilizers at a rate of 100 mg P kg^{-1}, 1 kg of soil was placed in individual pots. Four replicates were made for each treatment. *Sorghum vulgare* was sown and thinned to 10 seedlings five days after germination. A nutrient solution free of phosphate was added.

Aerial parts were harvested 6 and 12 weeks after sowing. The harvested plant material was oven-dried at 65° C and shoot dry weight was recorded. Phosphorus concentration in shoots was determined using the phospho-vanado-molybdate method. Total P was calculated as the product of dry matter weight and P concentration.

3. RESULTS

3.1. Reactivity of the P fertilizers

The total and soluble P contents of the phosphate rocks are shown in Table I. The PR samples coming from the Cuban deposits are less reactive than the ones from foreign deposits, with the exception of the Trinidad de Guedes PR. The best phosphate rock appears to be North Carolina PR, while the worst was Higuanojo PR. Chien [16] reported similar results with NCPR.

In view of the low reactivity of the natural Cuban PRs, an evaluation of partially acidulated Trinidad de Guedes PR (TGPR) was carried out (Table II). Partial acidulation greatly increased the solubility of TGPR, as measured by any of the three solubility tests. This increase in soluble P was more pronounced for MA-60, which is not unexpected considering that the monoammonium phosphate reacts with sulfuric acid leading to the formation of phosphoric acid, that itself contains soluble P

(Truong Binh, pers. commun.). This enhancement of P solubility of TGPR shows promising prospects for using Trinidad de Guedes PAPR in the near future when local production would be stable [17].

3.2. Effect of various phosphate rock sources on phosphorus bioavailability

3.2.1. Experiment 1

Soil incubation with different P treatments for two months (Table III) showed that Trinidad de Guedes PR and Riecito PR when applied directly or partially acidulated had little effect on enhancing P fertility either when measured through soil solution P concentration, E_1 value or kinetic parameters. The level of 30% acidulation appears to be insufficient to increase soil P fertility. Moreover, the conditions in which the acidulation process was carried out do not ensure a product with optimal quality. North Carolina PR and TSP increased Cp and E_1 value above 0.02 mg $P \cdot L^{-1}$ and 6.5 mg P kg^{-1}, respectively, considered by Barber [18] and Tran et al [19] critical for P nutrition of crops. Riecito PA at 60% showed intermediate values for P fertility. Casanova [7] reported better results with Riecito PR in acid Venezuelan soils.

The capacity factor (CF) was high, indicating a high P-fixing capacity, being uncommon for this neutral soil. An indicator of the very high P-fixing capacity was the low r_1/R values, which were <0.1. Riecito PAPR, North Carolina PR and TSP had low n values contrasted with the n values closer to 0.5 found in the rest of the treatments. This behavior can be explained by the possible saturation of the P sorption sites due to great availability of P easily soluble in Riecito PAPR, North Carolina PR and TSP treatments. The Pdff value was the highest for TSP. The kinetic exchange constants indicated that Riecito PAPR, North Carolina PR and TSP increased the mobility of P ions (Table IV).

Compartmental analysis (Table IV), showed that the higher the P solubility in the fertilizers, the lower the quantity of P ions which can leave the solid phase and enter into the solution in a mean time of uptake by a root system i.e. between 1 minute and 3 months. The phosphate ions derived from Riecito PAPR, North Carolina PR and TSP entered directly in the less mobile pool i.e. compartment D [20].

The results suggest the need for testing other modifications of the Trinidad de Guedes PR in order to enhance the solubilization of phosphorus coming from the rock. Modifying the acidulation process and increasing the acidulation level was evaluated next.

3.2.2. Experiment 2

The isotopic parameters resulted from the study of different P fertilizer sources in Experiment 2 are shown in Table V. The intensity factor, Cp, was increased by P fertilizer treatments. Nevertheless, only TSP source was able to reach a concentration higher than 0.02 mg P L^{-1}, considered the value above which P will not limit crop yield [18]. This fact can be explained by the low reserves of P in the solid phase of the soil i.e. Total P = 392 mg P kg^{-1} and by the very high fixing capacity of the soil. i.e. $r_1/R < 0.2$ [21]. The quantity factor, E_1, was also increased by P fertilizer treatments, but when TGPR and MA-40 were applied the E_1 values were lower than 3 mg P kg^{-1}, so the available soil P can be a limiting factor for P nutrition of crops [22].

The capacity factor remains high for all the treatments indicating the difficulty in modifying soil solution P concentration without any regard to the type of P fertilizer used. The expected %Pdff was higher than 40% in PAPR and TSP predicting that these P fertilizers will be efficient in supplying P to crops [13].

The kinetic factors (Table VI) showed values that were considered non-limiting for the mobility of P ions in the soil [22]. Compartmental analysis of bioavailable soil P showed that phosphate ions coming from the sources more soluble can enter directly into the less mobile P pool i.e. compartment D, which contains phosphate ions that could be released to the soil solution in a period greater than one year [23].

3.2.3. Greenhouse experiment

This experiment was carried out with the objective of knowing the agronomic effectiveness of Trinidad de Guedes PR with different modifications (partial acidulation with different quantity of acid or acidulating substance) that permitted to choose the best treatments of acidulation to accomplish field experiments with common bean.

The dry matter production of sorghum (Table VII) as well as P uptake (Table VIII) were greater in the second harvest than in the first, due to the establishment of a bigger rooting density that allowed the plants to grow more quickly.

Significant differences were observed between treatments. Lowest values were obtained without phosphorus in both harvests, while the greatest occurred in the treatment with superphosphate in the first harvest. For the treatment where the PR was acidulated to 60 % with sulfuric acid + mono-ammonium phosphate (MA-60) the dry matter production was the highest in the second harvest, showing significant differences with superphosphate application. TGPR did not increase the values of dry matter weight or P uptake in either harvest. This result was expected since the soil pH near neutrality, was not suitable for TGPR solubilization.

The treatments where the PR was modified had an intermediate performance between the control and the superphosphate treatment during the first harvest. However, in the second harvest, modified PRs surpassed the soluble TSP source, though they did not show statistical differences. Evidently, PAPRs have a residual effect greater than that of superphosphate. This behavior can be explained by the form of delivery of P from the modified PRs in relationship to the superphosphate (partial release vs. rapid release) and by the high P fixing capacity of the soil that fixed greater quantity of P of the source water-soluble [24]. It has been suggested that PAPR can be as effective as or sometimes better than superphosphates on soils possessing high P-fixing capacity. This is likely due to the hydrolysis of superphosphates yielding phosphoric acid, and increasing soil acidity. Thus, Fe and Al compounds may be solubilised and react with water-soluble phosphates. The consequence of the soil reactions is that the P availability from superphosphates is decreased because of the P-fixing effect of the Fe-Al compounds. Taking into account that the soil in the pot experiment remained moist most of the time, the hydrolysis reactions originating from the P fertilizers occur at a greater speed and they are therefore, solubilized faster. In the case of PAPR, part of the phosphoric acid produced by the hydrolysis could be neutralized by the un-acidulated fraction of the PR, allowing more P to be released into the water-soluble P pool [25].

The highest total dry matter yield of sorghum was recorded for TSP and PAPRs whereas the lowest values were obtained for the check. The dry matter production of the TSP and PAPRs treatments was significantly higher than the PR and control treatments.

Comparing both methods of acidulation, it can be observed that the best performance occurred with the acidulation using sulfuric acid + monoammonium phosphate. This could be due to the secondary reactions that take places during the process, in which phosphoric acid produced from sulfuric acid and monoammonium phosphate provokes an additional solubilization of PR residues not solubilized.

The total P uptake (Table VIII) of the treatments where P is found in more water-soluble and thus more available to the plants was statistically superior to the control and to Trinidad de Guedes PR. An exception of this response was the treatment SA-40, which in spite of solubilising a significant proportion of P, did not show significant differences with the control. The acidulation with sulfuric acid + monoammonium phosphate resulted in a superior product compared to the acidulation with sulfuric acid only, although differences were not statistically significant. Higher values in P uptake were found for treatments where 60% of acidulation was employed compared to 40% acidulation.

TABLE I. P CONTENT AND REACTIVITY OF THE ROCKS

Phosphate rock	Total P (%, w/w)	P soluble in 2% citric acid (%, w/w)	P soluble in 2% formic acid (%,w/w)
Riecito	12.6	9.5	9.6
Baja California	8.2	6.3	4.0
North Carolina	12.8	10.1	8.5
Trinidad de Guedes	12.1	7.3	7.4
Higuanojo	1.2	0.3	0.1
La Pimienta	5.6	1.7	0.4

TABLE II. REACTIVITY OF DIFFERENT TRINIDAD DE GUEDES PHOSPHATE ROCK PRODUCTS

	Soluble P (%,w/w)		
Phosphate rock	2% Formic acid	2% Citric acid	Neutral Ammonium Citrate
TGPR	7.8	7.7	3.3
SA-60	12.6	14.9	10.4
MA-60	16.3	17.5	13.3

TGPR = Trinidad de Guedes PR
SA-60 = TG partially acidulated (60%) by sulfuric acid
MA-60 = TGPA (60%) by monoammonium phosphate + sulfuric acid

TABLE III. ISOTOPIC PARAMETERS AFTER A SOIL INCUBATION WITH DIFFERENT PHOSPHATE ROCKS AND TSP (EXPERIMENT 1)

Treatment	Cp (mg P L^{-1})	r_1/R	n	E_1 (mgP kg^{-1})	CF (L kg^{-1})	Pdff (%)	RAE (%)
Check	0.010	0.024	0.53	4.4	425	---	---
TGPR	0.013	0.029	0.54	4.5	349	2.2	5
TG PAPR	0.020	0.042	0.59	4.7	239	6.4	14
RPR	0.022	0.046	0.41	4.8	217	8.3	18
R PAPR	0.031	0.068	0.18	4.7	149	6.4	14
NCPR	0.034	0.050	0.15	6.9	200	36.2	78
TSP	0.045	0.055	0.12	8.2	181	46.3	100

TABLE IV. SIZE OF COMPARTMENTS AND KINETIC PARAMETERS OF SOIL P (EXPERIMENT 1)

Treatments	Km (min^{-1})	Tm (min×10^{-3})	Fm (mg P kg^{-1} min^{-1})	A	B	C	D
				(mg P kg^{-1})			
Check	657	1.5	67	134	239	39	45
TGPR	417	2.7	53	149	238	34	37
TG PAPR	127	7.9	25	193	224	21	18
RPR	8371	3.4	1789	93	154	34	176
R PAPR	3x10^{6}	0.001	9.6x10^{5}	12	20	10	416
NCPR	63x10^{6}	0.0001	22x10^{6}	13	18	8	416
TSP	2x10^{11}	0.00001	97x10^{9}	10	12	5	426

TABLE V. ISOTOPIC PARAMETERS AFTER SOIL INCUBATION WITH DIFFERENT PHOSPHATE ROCKS AND TSP (EXPERIMENT 2)

Treatments	Cp (mg P L^{-1})	r_1/R	n	E_1 (mg P kg^{-1})	CF (L kg^{-1})	%Pdff	%RAE
Check	0.0088	0.051	0.39	1.7	193	---	---
TGPR	0.0097	0.052	0.37	1.9	196	10	13
SA-40	0.0120	0.037	0.21	3.2	267	46	60
MA-40	0.0153	0.053	0.28	2.9	190	41	54
SA-60	0.0126	0.041	0.23	3.1	246	45	59
MA-60	0.0187	0.054	0.22	3.5	187	51	67
TSP	0.0541	0.075	0.25	7.2	133	76	100

TGPR = Trinidad de Guedes PR
SA-60 = TG partially acidulated (40 or 60 %) by sulfuric acid
MA-60 = TGPA (40 or 60 %) by monoammonium phosphate + sulfuric acid

TABLE VI. KINETIC PARAMETERS AND P POOLS AFTER A SOIL INCUBATION WITH DIFFERENT PHOSPHATE ROCKS AND TSP (EXPERIMENT 2)

Treatment	Km. (min^{-1})	Tm (min)	Fm (mg P kg^{-1} min^{-1})	A	B	C	D
					(mg P kg^{-1})		
Check	804	1.2 x10^{-3}	71	28	141	124	268
TGPR	1.1 x10^{3}	9.1 x10^{-4}	106	26	118	99	294
SA-40	1.3x10^{6}	7.2 x10^{-7}	1.6 x10^{5}	12	24	13	379
MA-40	10 x10^{3}	9.9 x10^{-5}	1542	19	56	37	355
SA-60	247 x10^{3}	4 x10^{-6}	31151	13	30	18	374
MA-60	4.4 x10^{9}	2.2 x10^{-10}	8.2 x10^{8}	19	50	32	360
TSP	4.7 x10^{6}	2.1 x10^{-7}	2.5 x10^{6}	28	73	45	347

TGPR = Trinidad de Guedes PR
SA-60 = TG partially acidulated (60%) by sulfuric acid
MA-60 = TGPA (60%) by monoammonium phosphate + sulfuric acid

TABLE VII. DRY MATTER PRODUCTION (g/POT) IN TWO SORGHUM HARVESTS

Treatments	Dry matter (1st harvest)	Dry matter (2nd harvest)	Dry matter (Total)	%RAE
Check	0.46 c[1]	1.82 d	2.28 b	-
TG	0.53 c	1.96 cd	2.49 b	12
SA-40	0.98 b	3.02 ab	4.00 a	95
MA-40	1.63 a	3.00 ab	4.63 a	130
SA-60	1.84 a	2.91 abc	4.75 a	137
MA-60	1.82 a	3.43 a	5.25 a	165
TSP	1.94 a	2.14 bcd	4.08 a	100

TGPR = Trinidad de Guedes PR
SA-60 = TG partially acidulated (60%) by sulfuric acid
MA-60 = TGPA (60%) by monoammonium phosphate + sulfuric acid
[1] Means with the same letters in the same column do not differ significantly (p=0.05) according to Duncan´s test.

TABLE VIII. P UPTAKE (mg P/POT) IN TWO SORGHUM HARVESTS

Treatments	P uptake (1st harvest)	P uptake (2nd harvest)	P uptake (Total)
Check	0.72 c[1]	3.54 c	4.26 cd
PR	0.75 c	2.99 c	3.74 d
SA-40	1.52 c	5.00 bc	6.52 bc
MA-40	2.87 b	5.68 ab	8.55 ab
SA-60	3.50 b	6.18 ab	9.68 a
MA-60	3.70 ab	7.41 a	11.11 a
TSP	4.69 a	4.52 bc	9.21 ab

TG - Trinidad de Guedes PR
SA-60 - TG partially acidulated (60%) by sulfuric acid
MA-60 - TGPA (60%) by monoammonium phosphate + sulfuric acid
[1] Means with the same letters in the same column do not differ significantly (p=0.05) according to Duncan´s test.

4. CONCLUSIONS

The results of this study showed that phosphate rocks from Cuba are not suitable for direct application in Ferralsols of pH higher than 6, which are predominant in large agricultural areas of the country. Nevertheless, it is possible to enhance the agronomic effectiveness of Trinidad de Guedes Phosphate Rock through partial acidulation. Trinidad de Guedes PAPRs were found to be highly effective compared to their natural PR, when evaluated through dry matter production, P uptake and isotopic parameters. It should be pointed out, however, that these results were short-term data obtained under greenhouse conditions. Long-term field experiments are needed to validate the greenhouse results.

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REFERENCES

[1] CHIEN, S.H., MENON, R.G., BILLIGHAM K.S., Phosphorus Availability from Phosphate Rock as Enhanced by Water Soluble Phosphorus, Soil Sci. Soc. of Am. J. **60** (1996) 1173 – 1177.

[2] VILLEGAS, R., CABRERA, A., Roca fosfórica: fuente alternativa de fósforo para la caña de azúcar, Terra **12** 1 (1994) 37-42.

[3] PANEQUE, V.M., GONZÁLEZ, P.J., MENA, G., MACHÍN, J.C., Utilización de la caliza fosfatada como fuente de fósforo para la caña cultivada en suelo Ferralítico Cuarcítico (caña planta), Cultivos Tropicales **8** 2 (1986) 13-20.

[4] CHIEN, S.H., MENON, R.G., Factors affecting the agronomic effectiveness of phosphate rock for direct application, Fert. Res. **41** (1995) 227-234.

[5] KATO, N., ZAPATA, F., AXMANN, H., Evaluation of the agronomic effectiveness of natural and partially acidulated phosphate rocks in several soils using ^{32}P isotopic dilution techniques, Fert. Res. **41** (1995) 235-242.

[6] TRUONG, B., MONTANGE, D., Characterization of soils used for experiments by contractors of the RCM. Compared effectiveness of Partially Solubilized Phosphates, PR and SSP on various soils, Presented in the Third Research Coordination Meeting of the FAO/IAEA Phosphate Coordinated Research Program, IAEA, 17-21, March Vienna, Austria, (1997).

[7] CASANOVA, E.F., Agronomic evaluation of fertilizers with special reference to natural and modified phosphate rock. Results from the Latin American Phosphate Rock Network, Fert. Res. **41** (1995) 211-218.

[8] BOLAN, N.S, HEDLEY, M.J., HARRISON, R., BRAITHWAITE, A.C., Influence of manufacturing variables on characteristics and the agronomic value of partially acidulated phosphate fertilizers, Fert. Res. **26** (1990) 119 -138.

[9] KHASAWNEH, F.E., DOLL, E.C., Use of phosphate rock for direct application, Adv. Agron. **30** (1978) 199-206.

[10] MONTANGE, D., Chemical characterization of soils used for experiments by contractors of the RCM. Methods of analysis. Comparison of available P measurements methods. Final Research Coordination Meeting of the FAO/IAEA Coordinate Research Program "The use of nuclear and related techniques for evaluating the agronomic effectiveness of phosphate fertilizers, in particular, rock phosphates", IAEA, 16-20 Nov., Vienna, Austria (1998).

[11] CHIEN, S., Solubility assessment for fertilizer containing phosphate rock, Fert. Res. **35** (1993) 93-99.

[12] TRUONG, B., Standard characterization of phosphate rock samples from the FAO/IAEA Phosphate project, This issue.

[13] FARDEAU, J.C., GUIRAUD, G., MAROL, C., Bioavailable soil P as a key to sustainable agriculture. Functional model determined by isotopic tracers. In: Proceedings of an International Symposium on Nuclear Techniques in Soil-Plant Studies for Sustainable Agriculture and Environmental Preservation, IAEA STI/PUB/947 (1995) 131-141.

[14] FARDEAU, J.C., MOREL, C., BONIFACE, R., Cinétiques de transfert des ions phosphate du sol vers la solution du sol: parametres caractéristiques, Agronomie **11** (1991) 787-797.

[15] NOVOZAMSKI, I., VAN DIJK, D., VAN DER LEE, J.J., HOUBA, V.G.J., Automated determination of traced amounts of phosphate in soil extracts using malachite green. Commun. Soil Sci. Plant Anal. **24** (9, 10) (1993) 1065-1076.

[16] CHIEN, S.H., Chemical, mineralogical and solubility characteristics of phosphate rock for direct application. Communication to the Int. Workshop of Direct Application of phosphate rock and appropriate technology fertilizer in Asia, Feb 20-24 (1995).

[17] CANTERA, V., Producción industrial de fosfato parcialmente acidulado. Presented in: First RCM Phosphorus-Phaseolus-Rhizobium, Havana, October 22-24 (1997).

[18] BARBER, S.A., Soil nutrient bioavailability. A mechanistic approach. Wiley Interscience and Sons. New York. 414 p. (1995).

[19] TRAN, S.T., FARDEAU, J.C., GIROUX, M., Effect of soil properties on plant available phosphorus determined by isotopic dilution phosphorus method, Soil Sci. Soc. Am. J. **52** (1988) 1383-1390.

[20] FARDEAU, J.C., The role of isotopic techniques on the evaluation of the agronomic effectiveness of P fertilizers, Fert. Res. **45** (1996) 101-109.

[21] ZAPATA, F., CASANOVA, E., SALAS, A.M., PINO, I., Dynamics of phosphorus in soils and phosphate fertilizer management in different cropping systems through the use of isotopic techniques. Proc. 15th World Congress of Soil Science, Acapulco, Mexico, pp. 451-466 (1994).

[22] FARDEAU, J.C., Isotopic exchange kinetic. Experimental procedure, interpretation of results and application of the efficiency of P fertilizers. Presented at the Third Research Coordination Meeting of a FAO/IAEA Coordinated Research Program, IAEA, Vienna. Austria, 17-21, March (1997).

[23] FARDEAU, J.C., Le phosphore assimilable des sols: sa représentation par un modèle fonctionnel à plusieurs compartiments, Agronomie **13** (1993) 317-331.

[24] PERALTA, H., Sistemas de fertilización fosfórica de la papa en una secuencia de cultivos papa-maíz en un suelo Ferralítico rojo compactado. Tesis en opción al grado de Dr. en C. Agrícolas, INCA, La Habana (1991).

[25] CHIEN, S.H., MENON, R.G., Agronomic evaluation of modified phosphate rocks products: IFDC´s experience, Fert. Res. **41** (1995) 197-209.

EVALUATION OF METHODS FOR QUANTIFYING BIOAVAILABLE PHOSPHORUS IN A FERRALSOL FROM CUBA

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Abstract. As part of a research program related to enhance the agronomic effectiveness of P fertilizer, in particular phosphate rock, several methods to assess P availability of phosphate fertilizers were evaluated. Soil samples from pot experiments and a long-term field experiment in a Ferralsol from Ciego de Avila, Cuba, were analyzed using ^{32}P isotopic exchange kinetic method and five chemical methods (Oniani, Bray 1, Olsen, Mehlich 2 and resin-P). Oniani and Bray 1 methods were good descriptors of available phosphorus (P) in soil when water-soluble P fertilizers were used. However, they only provided a static estimation of plant-available P. All the chemical methods used in this paper to evaluate P availability in a Ferralsol amended with Trinidad de Guedes phosphate rocks did not perform well because less than 10% of the P extracted was bioavailable. The ^{32}P isotopic exchange kinetic method provided more reliable and accurate information of various parameters describing soil P status better than the soil P testing methods studied.

1. INTRODUCTION

Most of the phosphate fertilizers currently used worldwide are water-soluble, which is a constraint to agricultural production in countries like Cuba, where economic limitations prevent sufficient fertilizer importation. The use of local phosphate rock sources could be an alternative solution. The high level of water-solubility of most phosphate fertilizers currently produced is not essential in tropical soils froman agronomic point of view.

The ratio between the portion of available soil phosphate and the fraction of unavailable soil P extracted by chemical soultions varies with soils and, for a given soil, with its fertilization history. This explains why chemical methods of soil analysis are considered as rough methods to predict P uptake by plants or the crop response to P fertilizers [1].

Common soil extractants do not necessarily remove the actual fraction of P in soil that is bioavailable; they are also destructive due to chemical reactions, and correlations have to be established for individual soil and environmental conditions [2]. The use of radioisotopes such as ^{32}P as tracer enables to measure the amount of soil P present in the labile or exchangeable form without using chemical extractants [3]. Further problems arise in soils amended with phosphate rock due to the presence of high quantities of calcium phosphates and other compounds, that are able to react with acid extractants, such as Oniani´s method (H_2SO_4 0.05 M) commonly used in Cuba.

Quantifying the availability of soils amended with P fertilizers is imperative for making recommendation on the best type and rate of fertilizers to use to obtain maximum agronomic and economic benefits. The ability of routine chemical methods to extract the “available” soil P, whatever the method, can be tested, using the isotopic method as reference. The determination of their ability is based on the fact that isotopically exchangeable soil phosphate is assumed to be the available soil P [4]. The objective of the research was therefore, to evaluate the performance of routine chemical methods and radioisotopic methods to assess available P for utilising them in a research program to assess P availability of phosphate fertilizers, including phosphate rocks using isotopic techniques [2].

2. MATERIALS AND METHODS

2.1. Soil characteristics

The soil used was a Ferralsol from Ciego de Avila, Cuba. The soil was air-dried and screened to 2 mm. The soil had pH 7.1, CEC of 13 cmol(+) kg^{-1}, 5.9 mg Olsen P kg^{-1} and 2.7% organic matter. A complete characterization of the soil is presented elsewhere [5].

2.2. Chemical and radioisotopic methods used

A radiochemical method, i.e. the ^{32}P isotopic exchange kinetic method was used in order to determine the different pools of available phosphate as affected by the application of P fertilizer [4]. A quantity, R, of radioactivity, as carrier free ^{32}P phosphate ions, is injected into a soil-water suspension (ratio 1:10) in a steady state. At selected times, the suspension was filtered on millipore filter. The following data was determined: the concentration, Cp, of phosphate ions in the soil solution, the fraction r_1/R, of the radioactivity applied, R, that remains in the soil solution after 1 minute of isotopic exchange and a parameter, n, that quantifies, with time t, the decrease of the quantity of radioactivity, r_t, in soil solution. Cp was taken as intensity factor, $E_1 = 10\ Cp\ R/r_1$ as quantity factor and $E_1/Cp = 10\ R/r_1$ as capacity factor, CF. With the experimental values r_1/R, n and Cp, other kinetic parameters were calculated: the mean rate, K_m, of exchange of phosphate ions between the soil and its solution ($K_m = n / [r_1/R]^{1/n}$), the mean sojourn time, T_m, of phosphate ions in soil solution ($T_m = 1/K_m$) and the mean flux, F_m, of exchange between the soil and the solution ($F_m = 10\ Cp\ K_m$) [6]. In addition the determination of the size of P pools, which can move towards soil solution was realized. Pool A corresponds to the quantity of phosphate which can be taken up by a given root zone, which can actively take up P within 1 day. The size of this pool is: $A = 10\ Cp\ [R/r_{1440} - R/r_1]$. Pool B is explored during the time of root functioning of a short cycle crop. Its size is estimated as: $B = 10\ Cp\ [R/r_{129600} - R/r_{1440}]$. Pool C corresponds to the quantity of phosphate ions which can be released from soil into the soil solution in less than 1 year: $C = 10\ Cp\ [R/r_{518400} - R/r_{129600}]$. Pool D corresponds to very slowly exchangeable P, which can be released into the solution over the years under the condition of zero P fertilization. Its size is estimated by: $D = 10\ Cp\ [P_T - R/r_{518400}]$, where P_T is total soil P.

Radioactivity in soil solution was determined using Cerenkov counting of the ^{32}P in a liquid scintillation counter. Counts were corrected for counting efficiency. Phosphate ion concentration in soil solution was determined using a colorimetric method with malachite green oxalate as dye [7].

Available P was extracted by the following chemical methods: Oniani (H_2SO_4 0.05 M, 1:25 soil/solution ratio, shaking time 3 minutes), Bray 1, Olsen and Mehlich 2. The Morel and Fardeau [8] method was also used. The soil of the pots coming from an incubation experiment described below, was air-dried and 10 g was shaken with 99 ml of distilled water (1:10 soil:solution ratio) for 24 hours in plastic centrifuge tubes. Then 1 ml of ^{32}P carrier free solution (0.3 MBq/ml) was added to each tube and the tubes were shaken for a time equal to the time recommended for different extraction methods (Oniani, Bray 1, Olsen and Mehlich 2). The tubes were centrifuged and ^{32}P activity (Cerenkov) and total P were determined in the supernatant. The extracting solutions were then added to the corresponding tubes in duplicate; the tubes were shaken, centrifuged and the ^{32}P activity and total P were determined in the supernatant [7]. Specific activities (SA) in soil solution and in the extractants were calculated.

2.3. Evaluation of the bioavailable soil P by both, chemical and isotopic exchange kinetic methods in a long-term field experiment

Soil samples (0-20 cm depth), from a long-term field experiment with different P fertilization and crop rotation systems, were taken by the end of the seventh year of the experiment. The effect of the P fertilizer and crop rotation systems on bioavailable P was evaluated using chemical and radiochemical methods.

In the field experiment four P fertilization systems were evaluated: A) No phosphorus (check), B) P banded at planting of each crop in accordance with current P recommendations in Cuba, C) Application of 100% of the P corresponding to the whole sequence broadcasted before the first crop, and D) Application of 70% of treatment C broadcasted before the first crop. Phosphorus fertilizer was applied as triple superphosphate using the following P rates (Table I). The available P was extracted by Bray 1 and Oniani methods. The ^{32}P isotopic exchange kinetic method, as described by Fardeau was also used [4].

TABLE I. CROP ROTATIONS AND RATES OF P FERTILIZER (kg P_2O_5 ha^{-1})

Crop Rotation 1

Treatment	Potato	Soybean	Plantain	Maize	Total P applied (after 3 cycles)
A	0	0	0	0	0
B	180	100	52	35	1101
C	367	0	0	0	1101
D	257	0	0	0	771

Crop Rotation 2

Treatment	Potato	Maize	Common bean	Plantain	Total P applied (after 3 cycles)
A	0	0	0	0	0
B	180	35	93	52	1080
C	360	0	0	0	1080
D	252	0	0	0	756

Crop Rotation 3

Treatment	Common bean	Maize	Plantain	Total P applied (after 3 cycles)
A	0	0	0	0
B	93	35	52	540
C	180	0	0	540
D	126	0	0	378

2.4. Incubation studies

Several laboratory experiments were carried out. The soil was incubated alone or with an addition of 50-100 mg P kg^{-1} using different natural and modified rock phosphates of Cuba and overseas as phosphate carrier. The sources tested were Trinidad de Guedes PR (TGPR, 12.1% total P), Higuanojo PR (HPR, 1.2% total P), La Pimienta PR (LPPR, 5.6% total P) all of them from Cuba; Baja California PR, Mexico (BCPR, 8.2% total P) Riecito PR, Venezuela (RPR, 12.6% total P), North Carolina PR, USA (NCPR, 12.8% total P). After 1 to 9 months, the determination of available P using different chemical methods was carried out in some experiments, whereas in another the soil from the different treatments was analyzed following the experimental procedure described by Fardeau et al [6] to assess the bioavailable soil P. In one experiment, after one-month incubation period, soil samples were analyzed following the isotopic method of Morel and Fardeau [8].

3. RESULTS

The results from the isotopic characterization of the soil are presented in Table II. The low Cp and E_1 values show the low P fertility of this Ferralsol. The CF values, the different compartments of the model of Fardeau and their kinetic parameters, are related to the high P sorption capacity of this type of soil.

TABLE II. INITIAL ISOTOPIC CHARACTERIZATION OF THE SOIL USED IN THE EXPERIMENTS

Parameter	Value	Parameter	Value
PH	7.1	A (mg P kg^{-1})	46
Cp (mg P L^{-1})	0.014	B (mg P kg^{-1})	159
r_1/R	0.059	C (mg P kg^{-1})	68
N	0.43	D (mg P kg^{-1})	185
E_1 (mg P kg^{-1})	2.4	Km (min^{-1})	310
CF (L kg^{-1})	171	Tm (min)	3×10^{-3}
		Fm (mg P kg^{-1} min^{-1})	43

3.1. Evaluation of the bioavailable soil P by both, chemical and isotopic exchange kinetic methods in a long-term field experiment

After seven years of continuous cropping there is an increase in soil P content of the fertilized treatments, as shown by either Oniani or Bray I methods (Tables III and IV respectively).

The largest increases occurred in crop rotations 1 and 2, where the largest P quantities were applied because a potato crop was included. Generally, higher values are reported for treatment B, which was the one that received fresh-banded P fertilizer before each crop. Oniani and Bray 1 methods were good descriptors of soil available P when water-soluble P fertilizers were used, but only provided a static estimation of plant available P. Both chemical methods had a good behavior in similar conditions [9].

The isotopically exchangeable P content, E_1 (Table V), depended on the method of fertilizer application and, to a lesser extent, on the P rate. Higher E values were obtained when banded P was applied to each crop in the rotation. This may be due to a shorter time in P ageing, showing that a fraction of the applied P remains available after the harvest of the crops, which received fresh fertilizer applications. The correlation coefficient between Bray 1 and E_1 was 0.4755^{**}, and between Oniani and E_1 was 0.6342^{***}.

TABLE III. ONIANI P (mg kg^{-1}) AFTER SEVEN YEARS OF CROPPING

Treatments	Rotation 1	Rotation 2	Rotation 3
A	21.3 b[1]	16.9 c	21.8 b
B	32.2 a	32.7 a	26.7 a
C	35.4 a	31.6 a	22.9 b
D	22.9 b	24.0 b	25.6 a

[1] Means with the same letters do not differ significantly (p=0.05) according to Duncan´s test.

TABLE IV. BRAY 1 P (mg kg^{-1}) AFTER SEVEN YEARS OF CROPPING

Treatment	Rotation 1	Rotation 2	Rotation 3
A	0.7 b[1]	0.7 b	0.9 ab
B	1.1 a	1.1 a	1.0 a
C	1.0 a	1.0 a	1.1 a
D	0.9 ab	0.9 ab	0.8 b

[1] Means with the same letters do not differ significantly (p=0.05) according to Duncan´s test.

TABLE V. E VALUE AFTER 1 MINUTE OF ISOTOPIC EXCHANGE AFFECTED BY P FERTILIZATION TREATMENTS

Total P rate after 3 cycles (kg P_2O_5 ha^{-1})	E_1 (mg P kg^{-1})	
	Banded P	Broadcasted P
378		1.5 d
540	4.2 bc[1]	2.0 cd
756		2.9 cd
771		2.0 cd
1080	6.0 ab	3.4 cd
1101	7.0 a	3.2 cd

[1] Means with the same letters do not differ significantly (p=0.05) according to Duncan´s test.

TABLE VI. SOIL SOLUTION P CONCENTRATION (C_P) AFFECTED BY P FERTILIZATION TREATMENTS

Total P rate after 3 cycles (kg P_2O_5 ha^{-1})	Cp (mg P kg^{-1})	
	Banded P	Broadcasted P
378		0.008 e[1]
540	0.020 cde	0.012 cde
756		0.011 de
771		0.016 cde
1080	0.027 bcd	0.016 cde
1101	0.040 ab	0.020 cde

[1] Means with the same letters do not differ significantly (p=0.05) according to Duncan´s test.

Irrespective of the P fertilization, very low P concentrations were detected for all treatments. This similar behavior of the P concentration in soil solution (Intensity factor, Cp) confirms the high P retention capacity of the Ferralsol (Table VI). Taking into account the criteria of Tran et al [10] and Barber [11] who classified soils with $E_1<5$ mg kg^{-1} and $Cp<0.02$ mg L^{-1}, as P-depleted soils, only fresh P fertilizer treatment is able to maintain adequate levels of P for crop nutrition. The values are lower than those reported for Vietnamese soils [12]. The correlation coefficients between Bray 1 and Cp was 0.4478^{**}, and between Oniani and Cp was 0.6344^{***}.

Banded applications of water-soluble P fertilizer were better than broadcasted ones in these high P-fixing soils. Nevertheless, no specific fertilizer treatment was able to diminish the phosphate fixing capacity (r_1/R) and the capacity factor (E_1/Cp) of the soil (data not shown). The values of these two parameters were always lower than 0.1 and higher than 100, respectively. It has been recently reported that the number of P sinks in soil particles is infinitely greater than the quantity of P that can be applied in soils [13]. Therefore, it is very difficult to modify the P fertility of this Ferralsol using only mineral fertilizers. A potential approach could be the recycling of organic matter residues as much as possible to modify the strength of the bonds of P ions in the soil. The P ions linked to organic matter components with Ca seem more labile than P ions linked by other mechanisms [14].

3.2. Assessment of soil P fertility in soils amended with rock phosphate

In one incubation experiment (Table VII), the Oniani and Bray 1 methods were able to detect differences in available P in the soil amended with different PR sources and TSP. However, the Oniani method overestimated the effect of PR on the level of the available soil P. The overestimation of available P was not apparent with Riecito PR, where P is more readily available. The Oniani extracting solution dissolves considerable amounts of PR residues, which may not be solubilised during a growing season under field conditions. Similar results using adsorption isotherms have been reported [15], which indicates that Oniani´s method overestimates available soil phosphate in soils-amended with rock phosphate.

Comparing these methods with resin-P in soil samples taken after harvest of a field experiment (Table VIII), the Oniani and Bray 1 methods were not able to detect any significant difference between treatments, although the variability was very high.

Higher levels of available P were detected for the TSP treatment with the three methods. An exception was Oniani, which overestimated the available P when TGPR was used. There was no significant correlation between the soil test methods.

TABLE VII. SOIL AVAILABLE P AND pH FOLLOWING INCUBATION FOR ONE MONTH AT 50 mg P kg^{-1}

		Available P (mg/100 g)	
Treatment	pH(H_2O)	Oniani	Bray I
Check	7.68	4.46	1.68
La Pimienta PR	7.71	17.70	1.81
Trinidad de Guedes PR	7.62	16.70	1.91
Baja California PR	7.69	18.20	3.43
North Carolina PR	7.62	19.70	3.22
Riecito PR	7.62	15.27	2.57
Riecito cogranulated	7.60	7.63	2.36
Riecito PAPR	7.62	3.90	3.22
TSP	7.57	8.94	3.22
Standard error	0.01	0.36	0.21

TABLE VIII. AVAILABLE SOIL P BY ONIANI, BRAY I AND RESIN-P METHODS

P source[1]	Oniani P (mg $P.kg^{-1}$)	Bray 1 P (mg $P\ kg^{-1}$)	Resin P (mg P kg^{-1})
Check	21.0	6.95	30 c[2]
TGPR	26.0	6.74	34 b
SA-60	23.0	8.82	33 bc
TSP	25.5	8.91	38 a
Standard error	0.4	0.44	1

[1] TGPR: Trinidad de Guedes Phosphate Rock; SA-60: Trinidad de Guedes partially acidulated (60%) Phosphate Rock; TSP: Triple Superphosphate. All the sources were applied at a rate of 50 kg $P_2O_5\ ha^{-1}$.

[2] Means with the same letters do not differ significantly (p=0.05) according to Duncan´s test.

TABLE IX. ISOTOPIC PARAMETERS AFTER SOIL INCUBATION FOR ONE MONTH WITH HIGUANOJO PHOSPHATE ROCK AND TSP

Parameters	Check	Higuanojo PR	TSP
PH	7.0	7.5	7.1
Cp (mg P L^{-1})	0.011	0.013	0.048
r_1/R	0.045	0.083	0.057
N	0.32	0.29	0.29
E_1 (mg P kg^{-1})	2.4	1.6	6.2
CF (L kg^{-1})	218	123	129
Km (min^{-1})	5174	1548	2005
Tm ($min \times 10^{-4}$)	1.93	6.46	4.98
Fm (mg P $kg^{-1}\ min^{-1}$)	569	201	962
Pdff%	-	0	61

3.3. Isotopic techniques for evaluating P bioavailability in soils amended with PR

In an incubation study, the rock phosphate from Higuanojo (a hard and low reactive ore) promoted an increase in soil pH and a decrease in P fertility (Table IX). Only a small fraction (7.6%, expressed as the ratio ($E_{1[TSP]} - E_{1[Check]}$)/P applied) of the P applied as TSP, remained directly available due to the high P fixing capacity of the soil ($r_1/R<0.2$) [10].

The capacity factor was high, indicating the difficulty for modifying the soil fertility. The mobility of phosphate ions in the soil expressed through the kinetic parameters (Km, Tm and Fm) is not a limiting factor for the P nutrition of crops. The P isotopic exchange kinetic method provides more reliable and accurate information of the soil P dynamics.

In another experiment, testing four chemical methods with a radioisotopic method [8], large differences in specific activities (SA) (Table X) were observed comparing soil solution and the extractant for allthe methods tested. SA in the extractants was lower than SA in the soil solution.

Mehlich 2 soil test extracts almost half the bioavailable P of the check soil. The effectiveness of the different methods in measuring the P availability in the soil amended with rock phosphate is very poor (less than 10% of the P extracted is bioavailable) due to an overestimation of the available P content. Therefore, all the chemical methods tested are inadequate to predict bioavailable soil P when PR is used in this Ferralsol. Other authors [2, 16] have reported that Olsen and Bray 1 performed in a different way for different soils therefore, it is not possible to use a unique P extraction method in all soil types.

TABLE X. COMPARISON OF DIFFERENT EXTRACTION METHODS[1]

Treatment	Method	SAss[2] (µg P g^{-1})	SAe[2] (µg P g^{-1})	Available P in the extractants[3] (%)
Check	Oniani	213.1	9.9	4.8
	Bray 1	69.8	26.0	37.3
	Olsen	38.1	12.4	33.3
	Mehlich 2	91.3	42.7	48.1
TSP	Oniani	102.8	4.7	4.7
	Bray 1	26.5	2.0	7.8
	Olsen	46.4	1.2	3.3
	Mehlich 2	26.6	10.4	39.3
TGPR	Oniani	113.9	0.6	0.5
	Bray 1	40.8	0.4	1.0
	Olsen	35.2	1.9	5.6
	Mehlich 2	39.3	1.1	2.8

[1] Soil samples coming from an incubation experiment with 100 mg P kg^{-1} for two months.

[2] Specific Activity in the soil solution or in the extract.

[3] The percentage of the available P extracted by soil test methods was obtained from the ratio of SAe/Sass.

4. CONCLUSIONS

Broadcasted applications of water-soluble P fertilizers where less effective than banding the fertilizer at planting each crop of the crop rotation, as assessed with chemical or radioisotopic methods. Oniani and Bray 1 methods were good descriptors of the available P in the Ferralsol, when water-soluble P fertilizers were used but only provided a static estimation of the plant-available P. The Oniani method was not suitable to determine available P in Ferralsols amended with phosphate rock. All the chemical methods used in this study to evaluate P availability in soils traditionally fertilized with water-soluble P fertilizers did not perform well when PR was applied. The ^{32}P isotopic exchange kinetic method provided more reliable and accurate information describing various parameters of soil P dynamics.

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REFERENCES

[1] BOLLAND, M.D.A., GILKES, R.J., Evaluation of the Bray I, Calcium Acetate Lactate (CAL), Truog and Colwell soil tests as predictors of triticale grain production on soil fertilized with superphosphate and rock phosphate, Fert Res **31** (1992) 363-372.

[2] ZAPATA, F., CASANOVA, E., SALAS, A.M, PINO, I., Dynamics of phosphorus in soils and phosphate fertilizer management in different cropping systems through the use of isotopic techniques. Proc. 15th World Congress of Soil Science, Acapulco, Mexico, (1994) 451-466.

[3] IAEA, Tracer manual on crops and soils, Technical reports series No. 171. STI/DOC/10/171. International atomic Energy Agency, Vienna, (1976).

[4] FARDEAU, J.C., Dynamics of phosphate in soils. An isotopic outlook, Fert Res **45** (1996) 91-100.

[5] MONTANGE, D., Chemical characterization of soils used for experiments by contractors of the RCM. Methods of analysis. Comparison of available P measurements methods. Final Research Coordination Meeting of the FAO/IAEA Coordinate Research Program "The use of nuclear and related techniques for evaluating the agronomic effectiveness of phosphate fertilizers, in particular, rock phosphates", 16-20 Nov, Vienna (1998).

[6] FARDEAU, J.C., MOREL, C., BONIFACE, R., Cinétiques de transfert des ions phosphate du sol vers la solution du sol: paramètres caractéristiques, Agronomie **11** (1991) 787-797.

[7] NOVOZAMSKI, I., VAN DIJK, D., VAN DER LEE, J.J., HOUBA, V.G.J., Automated determination of traced amounts of phosphate in soil extracts using malachite green, Commun. Soil Sci. Plant Anal. **24** (9, 10), (1993) 1065-1076.

[8] MOREL, C., FARDEAU, J.C., Le phosphore assimilable des sols intertropicaux: ses relations avec le phosphore extrait par deux méthodes chimiques.Agronomie Tropicale **42** (4) (1987) 248-257.

[9] BALLBÉ, A., HERRERA, J.A., PERALTA, H., RODRÍGUEZ, M., Métodos químicos para controlar la fertilización fosfórica de la papa. Centro Agrícola v. XIV. 12 (1987) 82–87.

[10] TRAN, S.T., FARDEAU, J.C., GIROUX, M., Effect of soil properties on plant available phosphorus determined by isotopic dilution phosphorus method, Soil Sci Soc Am J. **52** (1988) 1383-1390.

[11] BARBER, S.A., Soil nutrient bioavailability. A mechanistic approach. Wiley Interscience and Sons. New York. (1995).

[12] DOAN SAT, CONG, Studies of the dynamics of soil phosphorus and agronomic effectiveness of phosphate fertilizers in particular PR in three main soil types of South Viet Nam. Second RCM of a FAO/IAEA CRP, Montpellier, France (1995).

[13] FARDEAU, J.C., Soil P fertility replenishment and liming using phosphate rocks in soils with a low pH and developed under tropical climates. Presented at the Third Research Coordination Meeting of a FAO/IAEA Coordinated Research Program, IAEA, Vienna, Austria, (1997).

[14] OBERSON, A., FARDEAU, J.C., BESSON, J.M., STICHER, H., Soil phosphorus dynamics in cropping systems managed according to conventional and biological agricultural methods, Biol Fertil Soils **16** (1993) 111-117.

[15] Peralta, H., Sistemas de fertilización fosfórica de la papa en una secuencia de cultivos papa-maíz en suelos ferralíticos rojos. Ph.D. Thesis, Cuba, (1991).

[16] FARDEAU, J.C., MOREL, C., BONIFACE, R., Pourquoi choisir la méthode Olsen pour estimer le phosphore assimilable des sols? Agronomie **8** (7) (1988) 577-584.

AVAILABILITY OF P FROM PHOSPHATE ROCK, THERMOPHOSPHATE AND TRIPLE SUPERPHOSPHATE AFTER DIFFERENT INCUBATION PERIODS

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Abstract. Patos phosphate rock, Yoorin thermophosphate and triple phosphate were mixed with a tropical acid soil (Haplic Ferralsol) and incubated for different periods (short term experiment 1: 0, 1 and 30 days, and long term experiment 2: 0, 1, 30, 60, 150 and 300 days). The experiments were started with the longest period in order to have all the periods ending at the same time when rice was sown. Soil samples were taken for available P determination through Bray 1 method. There was clear decrease in extractable P with increasing period of incubation, probably due to reversion reactions to form less soluble forms of P. In addition, the reversion reactions seemed to be a more intensive process than the dissolution process. The Yoorin thermophosphate, probably due to its alkaline nature and Si content, proved to be a superior agronomic P source by maintaining the same extractable P content during the whole incubation period.

1. INTRODUCTION

Brazilian agriculture is responsible for the production of food for 150 million people. At the beginning of the next century, optimal food production should reach 140 million t of grain. Current production estimates are still less than 80 million t in 1998. In spite of recent advances in biotechnology, the main limiting factor for increasing crop yields in the tropics is soil nutrient availability. The fastest way to reach the goal of high food production is by supplying adequate nutrients for maximizing plant growth and increasing yields. Supplying adequate phosphorus is problematic, not only for its low content in the soil, but also for its complex dynamics in the soil. Research carried out using ^{32}P labelled superphosphate showed that utilization efficiency of applied P fertilizer to the soil is less than 10% [1].

In Brazuil the annual P consumption is around 1.5 million t P_2O_5. To achieve the optimal grain production in the beginning of next century, it would be necessary to utilize an extra 500 000 t of P_2O_5 to reach a total of 2 million t. The estimated Brazilian phosphate reserves are approximately 350 million t of P_2O_5. However, to meet total P requirements, a considerable part of the deficit needs to be imported, if this nutrient is not used more efficiently. Therefore, much effort should be given on better management of P fertilizer for increasing P utilization efficiency by crops.

Usually phosphate rocks are recommended as a better economic alternative to correct P deficiency in tropical acid soils, as it is believed that the high soil acidity dissolve the apatite. Sanchez [2] considers that the use of phosphate rock would be economically more efficient than soluble sources in acid soil with high P fixing capacity. Results, however, have been contradictory [3, 4].

Traditionally the most widely used P sources in Brazil are water-soluble fertilizers (Triple and single superphosphate, DAP and MAP), which are also dominant sources in acid soils. Another source, which has been very efficient, is fused magnesium thermophosphate, which also contains Si, Ca and Mg in addition to P. The Ca and Mg have some advantages in ameliorating soil acidity. The Si reduces P fixation, competing for the same fixation sites for P on soil colloids.

Since the information on the availability of P with time of application is still scarce, the objective of this study was to determine P availability in a tropical acid soil amended with different P sources and incubated for variable periods up to 300 days.

2. MATERIAL AND METHODS

Two experiments were carried out consecutively. The first was a short-term experiment conducted with incubation periods of 0, 1, and 30 days. A second, longer-term experiment was conducted with incubations at 0, 1, 30, 60, 150 and 300 days.

The following P fertilizers were used: Patos phosphate rock (24.06% total P_2O_5 and 4% P_2O_5 citric acid (2%) soluble); triple superhosphate (TSP) (48.57% total P_2O_5; 47.88% P_2O_5 neutral ammonium citrate (a.c.) soluble P and 41.54% P_2O_5 water-soluble P) and Yoorin thermophosphate (17.4% total P_2O_5; 17% P_2O_5 citric (2%) acid soluble P; and 5.1% P_2O_5 neutral ammonium citrate (a.c.) soluble P)

Amounts of each P fertilizer equivalent to 50 and 100 mg P kg^{-1} soil for TSP and Yoorin; and 50, 100 and 500 mg P kg^{-1} soil were thoroughly mixed with 4 kg of medium texture Dark Red Latosol or Haplic Ferralsol (Table I). A check soil without P was also included. The incubation started with the longest period (30 days in the first experiment and 300 days in the second) in order to have all the incubation periods ending at the same time.

Prior to seeding samples were taken from each pot for Bray 1 P extraction [5]. After incubation, six rice (IAC 25 cultivar) seeds were sown and a week later the plants were thinned to have 4 plants. Nitrogen and potassium, as urea and KCl were applied at the rate of 100 mg N and K kg^{-1} soil. Plants were harvested 30 days after seeding for total P analysis.

TABLE I. CHEMICAL CHARACTERISTICS OF THE HAPLIC FERRALSOL

pH	C	Al^{3+}	H^+	Ca	Mg	K	P
	%	-------------	-------------	cmol $_c$ 100 dm^{-3}	---------		mg kg^{-1}
5.1	0.9	0.23	0.42	0..86	0..32	0.64	3

3. RESULTS

The soil Bray 1 extractable P measured in the short and long-term experiments are shown in Tables II and III. There was a clear decrease in the Bray 1 extractable P with increasing period of incubation in the soil fertilized with water-soluble P fertilizer (TSP) (Tables II and III). This was also reflected in the dry matter yield and P uptake by rice in both P rates (50 and 100 µg P g^{-1}) (Tables IV and V). Its seems that after dissolution of TSP, the reversion reaction to form less soluble forms of P is a slow process, as there was continuous decrease in Bray 1 extractable P up to the longest period of incubation. The rate of reaction was more intensive within the 30-day period, especially in the first day.

The increase in contact time soil-PR did not influence PR dissolution or, if it happened to occur, the solubilized P was fixed or transformed to insoluble forms. Probably, the fixation reaction is a more intensive process than the dissolution process, because there were slight decreases in dry matter yields and P uptake at the two lower P rates (50 and 100 µg P g^{-1}) with increasing incubation period, although not statistically significant.

The Patos PR gave only slight increase in dry matter yield, even at 500 µg P g^{-1}. The effect of the highest rate of this PR was less than that obtained with 50 µg P g^{-1} of TSP or Yoorin. No statistically significant differences were found between 500 µg P g^{-1} of Patos PR and control treatment.

The Yoorin thermophosphate showed better results in this Ferralsol, probably due to its alkaline nature and the presence of Si which reduces P fixation, maintaining the same Bray 1 extractable P content during the whole incubation period. The effect of Yoorin was similar to that of TSP, in both P rates in the incubation periods of 0 and 1 day. As the incubation period increased, the effect of 50 µg P g^{-1} of thermophosphate on rice growth surpassed the effect of 100 µg P g^{-1} TSP, which occurred at 30 days.

TABLE II. EFFECT OF INCUBATION TIME ON BRAY 1 EXTRACTABLE P (SHORT TERM EXPERIMENT)

		Bray 1 extractableP Incubation period (days)	
P Fertilizer	0	1	30
mg kg^{-1}		µg P g^{-1}	
0 control	2.7	2.8	3.5
50 TSP	28.3 a	12.3b	16.3b
100 TSP	54.0a	25.6b	23.5b
50 Yoorin	9.5a	16.1b	23.6c
100 Yoorin	21.3a	35.4b	33.4b
50 Patos PR	5.6	4.8	4.3
100 Patos PR	9.7	6.6	5.1
500 Patos PR	17.7a	15.0ab	10.4b

The values in the same row followed by the same letter do not differ statistically ($P < 0.05$).

TABLE III. BRAY 1 SOIL EXTRACTABLE P, AFTER INCUBATION (LONG TERM EXPERIMENT)

			Incubation (days)					
Treat Ment	P Fertilizer	P rate µg g^{-1}	0	1	30	60	150	300
			Bray 1 extractable P (µg g^{-1})					
T_1	-	0	3.4 D	3.3 D	2.9 D	3.5 E	3.0 E	3.1 E
T_2	TSP	50	18.0 Ba	14.4 Bb	12.3 Cc	12.0 Dc	10.5 Dc	10.2 Dc
T_3	TSP	100	39.0 Aa	28.3 Ab	25.6 Bb	24.7 Bb	23.4 Bb	22.4 Bb
T_4	Yoorin	50	17.2 B	17.8 B	16.1 C	17.6 C	18.0 C	17.3 C
T_5	Yoorin	100	35.0 A	33.0 A	36.3 A	33.2 A	36.6 A	35.1 A
T_6	Patos PR	50	4.2 D	4.4 D	4.5 D	5.0 E	3.0 E	3.8 E
T_7	Patos PR	100	5.0 D	4.9 D	6.3 D	5.5 E	5.0 E	4.6 E
T_8	Patos PR	500	11.0 C	10.4 C	11.4 C	11.0 D	10.0 D	9.6 D

Values within the rows and columns having the same letter are not significantly different at $P = 0.05$ (capital letter for columns and small letter for rows). Absence of small letter for rows indicates no significant differences for different incubation times.

TABLE IV. DRY MATTER YIELD OF RICE –PLANTS (g/POT)

Treatment	P Fertilizer	P rate $\mu g\ g^{-1}$	Incubation (days)					
			0	1	30	60	150	300
			g/pot					
T_1	-	0	1.12 C	1.04 B	1.30 C	0.98 C	1.17 C	0.88 C
T_2	TSP	50	3.24 AB	3.35 A	2.80 B	2.82 B	2.77 B	2.80 B
T_3	TSP	100	4.56 Aa	4.60 Aa	3.00 Bb	3.22 Bb	3.06 Bb	3.10 Bb
T_4	Yoorin	50	4.13 A	4.21 A	4.42 A	4.60 A	4.70 A	4.64 A
T_5	Yoorin	100	4.65 A	4.55 A	4.81 A	4.92 A	4.96 A	4.92 A
T_6	Patos PR	50	1.21 C	1.18 B	1.34 C	1.19 C	1.22 C	1.00 C
T_7	Patos PR	100	1.44 C	1.23 B	1.32 C	1.25 C	1.20 C	1.16 C
T_8	Patos PR	500	2.20 BC	1.95 B	2.00 BC	2.13 BC	2.16 BC	2.21 BC

Values within the rows and columns, having the same letter are not significantly different at P = 0.05 (capital letter for columns and small letter for rows). Absence of small letter for rows indicates no significant differences for different incubation times.

TABLE V. TOTAL P UPTAKE BY RICE PLANTS (mg/POT)

Treatment	P Fertilizer	P $\mu g\ g^{-1}$	Incubation (days)					
			0	1	30	60	150	300
			mg/pot					
T_1	-	0	1.23 C	1.11 C	1.28 C	1.15 E	1.22 D	0.98 D
T_2	TSP	50	3.89 B	3.91 B	3.18 B	3.20 CD	3.30 BC	3.21 BC
T_3	TSP	100	5.30 Aa	5.36 Aa	3.70 Bb	3.81 BC	3.67 Bb	3.74 Bb
T_4	Yoorin	50	4.97 A	5.01 AB	5.16 A	5.00 AB	5.21 A	5.19 A
T_5	Yoorin	100	5.42 A	5.33 A	5.58 A	5.60 A	5.55 A	5.71 A
T_6	Patos PR	50	1.36 C	1.30 C	1.34 C	1.28 E	1.31 D	1.18 D
T_7	Patos PR	100	1.57 C	1.48 C	1.34 C	1.29 E	1.27 D	1.09 D
T_8	Patos PR	500	2.18 C	2.04 C	1.99 c	2.15 D	2.23 CD	2.33 C

Values within the rows and columns, having the same letter are not significantly different at P = 0.05 (capital letter for columns and small letter for rows). Absence of small letter for rows indicates no significant differences for different incubation times.

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REFERENCES

[1] NEPTUNE, A.M.L., MURAOKA, T., STEWART, J.W.B., Efficiency of fertilizer phosphorus utilization by common bean (*Phaseolus vulgaris* L.) cv. Carioca under different method of applying phosphatic fertilizers. Turrialba **29** (1979) 29-34.

[2] SANCHEZ, P.A., Fósforo, silicio y azufre. In: Suelos del Tropico; características y manejo. San José, IICA, 1981, 234p.

[3] GOEDERT, W.J., LOBATO, E., Avaliação agronômica de fosfatos em solos de Cerrado. Rev. Bras. Ci. Solo **8** (1984) 97-102.

[4] BRAGA, N.R., MASCARENHAS, H.A.A., FEITOSA, C.T., RAIJ, B.VAN, Efeitos de fosfatos sobre o crescimento e produção de soja. Rev. Bras. Ci. Solo **4** (1980) 36-39.

[5] BRAY, R.H., KURTZ, L.T., Determination of total, organic, and available forms of phosphorus in soils. Soil Sci. **59** (1945) 39-45.

AVAILABILITY OF NATIVE AND FERTILIZER P IN BRAZILIAN SOILS

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Abstract. Inorganic forms of phosphorus were determined in two Red-Yellow Latosols, which were incubated with P fertilizers for a month, after equilibration with ^{32}P for 60 hours. The methods used were soil P fractionation combined with the ^{32}P isotopic dilution technique. The fertilizers applied were: H_3PO_4, 10-30-0 suspension, MAP and triple superphosphate, at the rate of 92 mg P kg^{-1} of soil. In both soils, the isotopically exchangeable inorganic phosphorus fractions decreased in the following order: water soluble P > Al bound P > Fe bound P > calcium bound P > occluded-P. The water- soluble and Al bound P were the main source of available P for the newly fertilized soil. The Fe bound phosphate was also an important source of available P in both soils when fertilizer was not applied. The soil P fixing capacity affected the availability of native and added phosphorus.

1. INTRODUCTION

In most Brazilian soils, as in other tropical soils, P deficiency is the main limitation to optimum crop yields due to low natural P fertility and high P retention capacity. The application of phosphate fertilizers in these soils is essential to supply P to crops. Rational utilization of P fertilizer, however, requires a better understanding of the availability of this element to plant roots in the soil. Usually, less than 10% of applied fertilizer P is utilized by an annual crop [1], the rest being fixed in several forms of inorganic P [2]. Information on the fate of fertilizer P remaining in the soil is scarce in Brazil. Dunbar and Backer [3] presented interesting results, evaluating the inorganic phosphate transformations in the soil using ^{32}P. They observed that the increase in the active P of solid phase is associated with greater availability of phosphorus in determined soil types. The objective of this research was to determine, by isotopic dilution, the availability of native and added phosphates in two Latosols with different P fixation capacity.

2. MATERIAL AND METHODS

Two surface (0-20 cm) soils, classified as very clayey Alic Red-yellow Latosol (soil A) and medium texture Red-Yellow Latosol (soil B), with different physical and chemical properties were utilised (Table I). Prior to P fertilizer application, the soil was limed and incubated for 20 days. Then, the soil was transfered to 200 g capacity plastic pots. Four P sources, namely H_3PO_4, 10-30-0 coloidal P suspension (susp.), Mono-ammonium phosphate (MAP), and triple superphosphate (TSP) were applied at a rate of 92 mg P/kg soil. A control without P application was also included. After mixing with fertilizers, the soil was alternatively moistened and air-dried weekly for one month.

TABLE I. PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE SOILS

Soil	Sand	Silt	Clay	pH	P*	P_{fc}**	SiO_2	Al_2O_3	Fe_2O_3	TiO_2
	------------%------------				---µg P cm^{-3}---		----------------%-----------------			
A	36	8	56	4.1	3	1118	19.0	19.2	19.7	6.5
B	86	0	14	4.2	2	525	2.6	4.1	2.1	0.7

* Resin extractable P [10]

Soil	H+Al	Al^{3+}	Ca^{2+}	Mg^{2+}	K^+	OM
	----------------------c_{mol} dm^{-3}----------------------					
A	15	1.4	0.39	0.13	0.11	6.3
B	6.1	0.7	0.25	0.10	0.10	2.9

** P_{fc}: fixing capacity [11]

TABLE II. SOIL PHOSPHORUS CONTENT (TOTAL AND INORGANIC FRACTIONS)

	------------------------------P fraction----------------------------					
P source	P_{H2O}	P_{Al}	P_{Fe}	P_{Ca}	$P_{Occluded}$	Total P
	------------------------------------µg P/g soil------------------------------------					
(Soil A)						
Control	1	47 b*	50 a	18 b	239	386 b
H_3PO_4	1	88 a	74 a	21 b	214	473 a
Susp.	1	84 a	78 bc	22 b	238	458 a
MAP	1	93 a	88 a	21 b	210	481 a
TSP	1	88 a	88 ab	29 ab	218	475 a
CV (%)	17	8	5	9	8	9
(Soil B)						
Control	1 b	42 b	23 c	7 b	52 b	180 b
H_3PO_4	2 a	91 a	29 b	6 b	66 a	267 a
Susp.	1 b	99 a	34 a	10 b	52 b	257 a
MAP	2 a	91 a	28 b	7 b	59 ab	273 c
TSP	2 a	93 a	31 ab	18 a	70 a	236 a
CV (%)	17	6	7	29	10	4

TABLE III. PERCENTAGE OF ISOTOPICALLY EXCHANGEABLE P OF SOIL INORGANIC FRACTIONS AFTER INCUBATION WITH FERTILIZERS

	P fraction					
P source	PH_2O	P_{Al}	P_{Fe}	P_{Ca}	$P_{Occluded}$	Total P
	%					
(Soil A)						
Control	100	21 b	20	6 b	2 a	7 b
H_3PO_4	100	35 a	18	9 a	1 b	10 a
Susp.	100	32 a	17	9 a	1 b	10 a
MAP	100	32 a	16	9 a	1 b	10 a
TSP	100	34 a	16	7 ab	1 b	10 a
CV (%)	-	13	21	16	20	8
(Soil B)						
Control	100	31	30 a	7	0.4	12 b
H_3PO_4	100	41	17 b	7	0.3	16 a
Susp.	100	39	15 b	4	0.4	18 a
MAP	100	35	18 b	6	0.4	15 a
TSP	100	37	16 b	2	0.3	15 a
CV (%)	-	16	10	24	10	7

Soil samples (1.0g) were shaken with 5 mL carrier free ^{32}P solution (206 KBq) for 60 hours for attaining isotopic equilibrium [3]. The suspensions were then centrifugated and the soils were analysed for P fractions by the Chang & Jackson technique [4]. Total P was also determined in each soil sample, by perchloric-nitric-hydrofluoric acid digestion [5].

The ^{32}P activity was determined by counting in a liquid scintillation counter using the Cerenkov effect and total P was analysed by colorimetry. The amount of solid phase P of each P fraction, which equilibrated with ^{32}P was considered as available P.

3. RESULTS

The total soil P contents, which include the native and added P, were higher in soil A than soil B, as a consequence of the higher clay content of soil A (Table II). In both soils, the lowest amount of P was observed in the water-soluble fraction (P_{H2O}). In the soil A, the native phosphates are constituted mainly by the occluded P fraction ($P_{ocluded}$), followed by iron bound P (P_{Fe}) and aluminum bound P (P_{Al}), both in equivalent amounts, and calcium bound P (P_{Ca}). For soil B, the sequence obtained for native P was $P_{occluded} > P_{Al} > P_{Fe} > P_{Ca} > P_{H2O}$. The predominance of $P_{ocluded}$, P_{Fe} and P_{Al} reflect the advanced weathering of these soils, as with the evolution of pedogenesis, the calcium phosphates are converted to aluminum and iron phosphates and finally, as ocluded iron and aluminum phosphates [6, 11].

TABLE IV. AVAILABLE P IN THE SOIL P FRACTIONS, AS DETERMINED WITH ^{32}P

	----------------------------P fraction-----------------------------					
P source	PH_2O	P_{Al}	P_{Fe}	P_{Ca}	$P_{Occluded}$	Total P
	-----------------------------------µg P/g soil------------------------------------					
(Soil A)						
Control	1	10 b*	50 a	18 b	239	386 b
H_3PO_4	1	31 a	74 a	21 b	214	473 a
Susp.	1	27 a	78 bc	22 b	238	458 a
MAP	1	30 a	14 a	21 b	210	481 a
TSP		30 a	13 a	29 ab	218	475 a
CV (%)	17	8	5	9	8	9
(Soil B)						
Control	1 b	42 b	23 c	7 b	52 b	180 b
H_3PO_4	2 a	91 a	29 b	6 b	66 a	267 a
Susp.	1 b	99 a	34 a	10 b	52 b	257 a
MAP	2 a	91 a	28 b	7 b	59 ab	273 c
TSP	2 a	93 a	31 ab	18 a	70 a	236 a
CV (%)	17	6	7	29	10	4

The low calcium bound phosphate content observed even after fertilizer additions could be a consequence of the acid conditions predominant in these Latosols. It is interesting, however, to note that soil B fertilized with TSP presented a significantly higher P_{Ca} fraction than the other sources. Probably part of this fertilizer had not reacted with the soil components, remaining as calcium phosphate.

A considerable fraction of applied fertilizer P was converted to P_{Al} and P_{Fe} fractions, altering the original distribution of P fractions. This was especially the case in soil B, where the P_{Al} fraction became predominant. Yuan et al. [7]; Chang and Chu [8]; and Gonçalves [9] have reported similar results.

The isotopically exchangeable P determined in the P fractions in the soils (A and B) is presented in Table III. The P_{Al} fraction is the most available form. However, in the control, which represents the availability of native P, the contribution of P_{Fe} to available P is comparable to P_{Al} fraction. For both soils, the portion of P fractions which equilibrated with ^{32}P could be ordered as follows: $P_{H2O} > P_{Al} > P_{Fe} > P_{Ca} > P_{ocluded}$. Dunbar and Backer [3] observed the some sequence for soils with contrasting chemical and mineralogical characteristics.

Although the amount of total available P found in both soils were similar, comparing this value with total P content (Table IV), the availability of P in soil A is proportionally lower than soil B. This result corroborates the work from Chang and Chu [8], where soils with high P fixing capacity have P adsorbed in less available form.

4. CONCLUSIONS

The main conclusions from the study were:

The inorganic P fractions which equilibrated with solution ^{32}P followed the sequence: $P_{H2O} > P_{Al} > P_{Fe} > P_{Ca} > P_{occluded}$, in both soils, indicating that the availability of inorganic P in each fraction decreases from P_{H2O} to the $P_{occluded}$ fraction.

The P_{H2O} and P_{Al} fractions constituted the main sources of available P in freshly fertilized soil. In non-fertilized soils, P_{Fe} is another main source, beside P_{H2O} and P_{Al}.

The availability of native and added phosphates was higher in the soil B, with smaller P retention capacity.

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REFERENCES

[1] NEPTUNE, A.M.L.; MURAOKA, T.; STEWART, J.W.B., Efficiency of fertilizer phosphorus utilization by common bean (*Phaseolus vulgaris* L.) cv. Carioca under different methods of aplying phosphatic fertilizer. Turrialba **29** (1979) 29-34.

[2] BARROW, N.J., The description of phosphate adsorption curves. J. Soil Sci. **29** (1978) 447-462.

[3] DUNBAR, A.D. and BACKER, D.E., Use of isotopic dilution in a study of inorganic phosphorus fractions from different soils. Soil Sci. Soc. Am. Proc. **29** (1965) 259-262.

[4] CHANG, S.C. and JACKSON, M.L., Fractionation of soil phosphorus. Soil Sci. **84** (1957) 133-144.

[5] HESSE, P.R., A textbook of soil chemical analysis. Willian Clowes and Sons Ltd. London (1971)

[6] HSU, P.H. & JACKSON, M.L., Inorganic phosphate transformation by chemical weathering, in soils as influenced by pH. Soil Sci. **90** (1960) 16-24.

[7] YUAN, T.L.; ROBERT SUN, W.K.; NELLER, J.R., Forms of newly fixed phosphorus in three sandy soils. Soil Sci. Soc. Am. Proc. **24** (1960) 447-450.

[8] CHANG, S.C. & CHU, W.K., The fate of soluble phosphate applied to soils. J. Soil Sc. **12** (1961) 286-293.

[9] GONÇALVES, J.L.M., Cinetica de transformação do fosforo labil em não labil em amostras de solos de Cerrado. 1988. 62p. (M. Sc. Dissertation Universidade Federal de Viçosa).

[10] RAIJ B. van; QUAGGIO, J.A., Métodos de análises de solos para fins de fertilidade. IAC, Campinas (1983) 31p (IAC Techn. Bulletin, 81).

[11] CATANI, R.A. and BATAGLIA, O.C., Formas de ocorrência do fósforo no solo latossolico Roxo. Anais da Escola Superior de Agricultura “Luiz de Queiroz”- USP **25** (1968) 99-119.

PLANT-AVAILABILITY AND FATE OF P FROM APPLIED PHOSPHATIC FERTILIZERS IN TWO LATOSOLS

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Abstract

The effectiveness of fluid (phosphoric acid, H_3PO_4 and 10-30-00 colloidal suspension, CS) and solid (monoammonium phosphate, MAP and triple superphosphate, TSP) fertilizers and the fate of fertilizer P to inorganic P fractions were evaluated in laboratory and in a greenhouse experiment. Corn plants were grown in pots (8 plants per pot; 3 replicates) containing 1 kg of two red-yellow Latosols with different phosphorus retention capacities, for three successive cycles (30 days each). The fertilizers were applied prior to the first sowing at rates of 0 (control), 70, 140 and 210 mg P_2O_5 kg^{-1} (0, 30.6, 61.2 and 91.8 mg P kg^{-1}). Dry matter yield and total P were determined at each harvest time. Results showed no difference between the effects of fluid and solid phosphate fertilizers on dry matter yield and phosphorus uptake. However, the rates of phosphorus applied were significantly and positively related with dry matter yield and phosphorus uptake. In both soils, the agronomic effectiveness of fluid and solid phosphate fertilizers was equivalent.

A laboratory experiment was carried out to measure the fate of P fertilizers converting into inorganic soil P fractions after incubation over a period of 30 days in both Latosols. Inorganic soil phosphates were fractionated and P derived from fertilizer was determined in each fraction. The larger parts of soil applied phosphates were recovered as aluminum (P_{Al}) and iron bound P (P_{Fe}) fractions. Only small quantities of fertilizer P were found as water soluble P, calcium bound P and occluded P. The P derived from H_3PO_4, MAP and CS was retained in more stable forms than that derived from TSP. The proportion of P_{Al} to P_{Fe} was larger in soil B, which had less P fixing capacity, than in soil A. This result suggests that P_{Al} fractions were more available to plants than P_{Fe}.

1. INTRODUCTION

Since the 1970's research on agronomic evaluation of phosphorus sources has increased considerably in Brazil, due to the rising prices of soluble P fertilizers and the dependency of the country on external P supplies [1]. Therefore, the search for alternative phosphate fertilizers has been a constant concern [2].

The use of fluid fertilizers as an alternative for supplying phosphorus to crops is still very limited in Brazil. However, the perspectives of increasing its consumption are promising, due to the advantages offered in relation to solid fertilizers. Among these, the following can be considered: ease in storage and application, better uniformity in application, reduced losses, versality for formulations, less manual work on the product, and lower cost. Very little is known with respect to agronomic efficiency of fluid fertilizers. Nevertheless, according to Silva et al. [3], fluid and solid fertilizers have similar efficiency when applied at the same rate and conditions of application. The few studies carried out in Brazil have been only made with sugarcane [3,4,5]. Information on other crops is scarce.

Phosphate ions released by dissolution of soluble P fertilizers added to the soil do not remain stable. They are converted into less soluble forms through a series of reactions with the soil components. This phenomenon is known as P retention or fixation. According to [6], P retention is the process by which phosphate ions react with aluminum, iron and calcium ions of soil solution resulting in new phases in the system. These reactions take place in two stages. The first stage is the surface adsorption that is rapid occurring in a matter of minutes or hours. The second stage is slower and involves the migration of P to subsurface layers of adsorbed P, resulting in its occlusion [7].

The complex dynamics of soil phosphorus fixation processes results in a reduction of the P fertilizer utilization by the plants [8]. Therefore, knowledge of soil phosphate transformations is fundamental for establishing rational criteria and better management of phosphate fertilization [9].

The objectives of the present work were a) to evalaute in two Latosols the agronomic efficiency of some fluid and solid P fertilizer, using corn as a test crop in a greenhouse experiment, and b) to determine the fate of the applied P fertilizers into soil inorganic P fractions in the laboratory.

2. MATERIALS AND METHODS

The chemical and physical characteristics of two Latosols are described in Table I. After lime amendment to correct the soil pH to 6.0, using equivalent amounts to 10.8 and 3.9 t/ha of dolomitic lime for soils A and B, respectively, the soils were placed in 1 kg plastic pots. Four P sources were utilized in the study: phosphoric acid, H_3PO_4 (FA); 10-30-0 colloidal suspension in fluid form (CS), monoammonium phosphate (MAP), and triple superphosphate (TSP). The MAP and TSP were applied in powder form. Applied phosphate rates were 0, 70, 140 and 210 mg P_2O_5 per kg soil (0, 30.6, 61.2 and 91.8 mg P kg^{-1} soil). Experimental treatments were replicated 3 times.

Each pot also received additional fertilization consisting of 70 mg N and 120 mg K per kg soil (as ammonium nitrate and KCl) and 1 mL kg^{-1} soil of a mix of micronutrients. The P fertilizers were applied in a band at a 3 cm depth diametrically in the pots. Eight corn seeds were sown in each pot. Corn was grown three consecutive times for 30 days each crop. The two successive crops also received N, K and micronutrients at the same rate applied at seeding. Supplements of N and K (160 mg N and 120 mg K/kg soil as ammonium sulfate and KCl) were applied to all three crops on a weekly basis, four times for N and twice for K. After harvest, plant samples were dried, weighed and ground for P analysis by colorimetry, after nitric-perchloric digestion.

For the soil P transformation study, ^{32}P-labelled TSP, MAP, H_3PO_4 and 10-30-0 colloidal suspension in fluid form (CS) were used. Fertilizers were applied to 200 g of soil at a rate of 91.2 mg P kg^{-1} soil. The fertilizers were labelled with ^{32}P at a specific activity varying between 222 to 296 kBq/mg P. Two Latosols were utilized, a very clayey texture alic Red Yellow Latosol(soil A) and a medium texture alic Red Yellow Latosol (soil B). The soils used were contained in plastic pots and incubated for one month after watering to saturation. During the period the soils were alternatively dried and moistened weekly.

After incubation, soil samples were analyzed for P inorganic fractions, according to [10]: water soluble P (P_{H2O}), Al bound P (P_{Al}), Fe bound P (P_{Fe}), Ca bound P (P_{Ca}) and occluded P. The ^{32}P activity in each fraction was also determined [11] for identifying the fate of fertilizer P converted to various inorganic soil P fractions.

3. RESULTS AND DISCUSSION

Comparing the dry matter yield data over the 3 crops (Table II), the second crop had values smaller than others in the P fertilized treatment, which coincided with the growing period, when the temperature was the lowest. In the control treatment (without P), however, there was increase in dry matter yield from first to third crop, due probably to increasing availability of native P.

TABLE I. PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE SOILS

Soil	Sand	Silt	Clay	pH	P*	P_{fc}**	SiO_2	Al_2O_3	Fe_2O_3	TiO_2
	------------%-----------				--µg P cm^{-3}--		---------------%---------------			
A	36	8	56	4.1	3	1118	19.0	19.2	19.7	6.5
B	86	0	14	4.2	2	525	2.6	4.1	2.1	0.7

* Resin extractable P

Soil	H+Al	Al^{3+}	Ca^{2+}	Mg^{2+}	K^+	OM
	----------------------c_{mol} dm^{-3}--------------------					%
A	15	1.4	0.39	0.13	0.11	6.3
B	6.1	0.7	0.25	0.10	0.10	2.9

** P_{fc}: fixing capacity

The dry matter yield and P uptake were significantly greater in soil B compared to soil A (Tables II and III) probably due to the lower P fixing capacity of soil A. There was no statistical difference amongst the P sources on dry matter yield and P uptake, showing the similarity on P efficiency to corn of the P fertilizers studied in liquid and solid form. The data confirm those obtained by Silva et al.[3], Korndorfer [4], Penatti [5], for sugarcane.

For both soils, fertilizer P was recovered mostly as aluminum and iron bounded P (P_{Al} and P_{Fe}). The contribution of other P fractions such as Ca bound P (P_{Ca}), Al and Fe occluded P (P_{occl}), and water-soluble or weekly soluble P (P_{H2O}) were very small (Table IV). These results could be attributed to the predominance of iron and aluminum oxides with high affinity for phosphate ions in these acid Latosols.

Comparing P_{Al} and P_{Fe}, the aluminum bound phosphate was responsible for a larger part of the fixed P. This fact suggests a higher concentration and solubility of aluminum phosphate containing compounds in soil in relation to iron phosphate compounds. In the course of time, part of the P_{Al} is converted to P_{Fe} due to the lower solubility of iron bound phosphates. Ultimately, P may be converted to occluded iron and aluminum phosphates [12]. These processes explain the small recovery of the applied phosphates in the occluded P fraction, indicating that the period of contact fertilizers: soil was not sufficient for the P retention reactions to be completed. The ratio P_{Al} to P_{Fe} was larger in soil B, which is a less P fixing soil, than in the high P-fixing soil A, suggesting that the P_{Al} fractions are more available to plants than P_{Fe}.

TABLE II. EFFECT OF P SOURCES AND RATES ON CORN DRY MATTER YIELD OF CORN GROWN IN THREE SUCESSIVE CROPS IN TWO LATOSOLS

P source(1)	P rate	I	II	III	Total
		--------------------Crop			------------------------
	mg kg^{-1} P_2O_5	-------------------g pot^{-1}			----------------------
		------------------*Soil A*			------------------------
	0	3.99	4.79	5.27	14.05
FA	70	4.74	4.55	5.20	14.49
	140	6.56	4.78	6.08	17.42
	210	7.55	4.54	6.18	18.27
	0	4.02	4.41	6.21	14.64
CS	70	5.14	4.71	6.51	16.36
	140	6.38	4.50	6.26	17.14
	210	7.58	5.03	6.03	18.64
	0	4.14	4.71	6.11	14.96
MAP	70	5.10	4.30	6.17	15.57
	140	5.75	4.84	7.11	17.70
	210	9.92	4.97	5.96	20.85
	0	4.21	4.44	5.44	14.09
TSP	70	5.32	4.87	5.43	15.62
	140	5.84	5.51	6.03	17.38
	210	6.34	4.94	6.14	17.42
		------------------*Soil B*			------------------------
	0	4.28	4.74	6.00	15.02
H_3PO_4	70	6.44	5.64	6.18	18.26
	140	7.22	6.12	8.02	21.36
	210	8.02	7.10	8.41	23.53
	0	3.99	4.99	5.46	14.44
CS	70	6.79	5.07	6.39	18.25
	140	7.52	6.28	7.88	21.68
	210	8.86	6.53	8.68	24.07
	0	4.49	4.55	5.84	14.88
MAP	70	6.06	5.30	6.82	18.18
	140	7.04	6.01	8.12	21.17
	210	8.04	6.36	8.80	23.20
	0	4.02	4.61	6.21	14.84
TSP	70	6.10	5.46	6.38	17.94
	140	7.24	6.47	8.49	22.20
	210	8.15	7.01	8.51	23.67

FA= H_3PO_4; CS= colloidal suspension (10-30-00); MAP= Monoammonium phosphate; TSP= Triple superphosphate.

TABLE III. EFFECT OF P SOURCES AND RATES ON P UPTAKE BY CORN GROWN IN THREE SUCESSIVE CROPS IN TWO LATOSOLS

		Crop			
P source(1)	P rate	I	II	III	Total
	mg kg^{-1} P_2O_5	mg pot^{-1}			
		Soil A			
FA	0	3.95	4.04	3.76	11.75
	70	5.41	4.30	4.00	13.71
	140	8.49	4.26	5.20	17.95
	210	10.36	4.28	5.16	19.80
CS	0	4.11	3.88	4.61	12.60
	70	5.54	4.50	4.89	14.93
	140	7.84	4.13	4.69	16.66
	210	11.67	4.67	5.19	21.53
MAP	0	3.97	3.81	4.31	12.09
	70	5.50	3.90	4.76	14.16
	140	7.18	4.40	5.32	16.90
	210	9.70	4.82	5.05	19.57
TSP	0	4.13	3.88	3.96	11.97
	70	5.81	4.36	4.27	14.44
	140	7.79	5.09	4.81	17.69
	210	8.83	4.49	4.60	17.92
		Soil B			
H_3PO_4	0	4.39	4.23	4.59	13.21
	70	8.50	5.10	5.27	18.87
	140	11.96	6.02	6.51	24.49
	210	15.58	7.18	7.09	29.85
CS	0	4.15	4.44	4.20	12.79
	70	9.14	4.62	5.23	18.99
	140	13.91	6.03	6.30	26.24
	210	19.44	6.44	7.21	33.09
MAP	0	4.35	3.96	4.24	12.55
	70	7.19	4.98	4.86	17.03
	140	12.20	5.95	6.82	24.97
	210	17.19	6.18	7.59	30.96
TSP	0	4.06	3.97	4.08	12.11
	70	7.83	5.21	5.03	18.07
	140	11.76	6.35	6.95	25.06
	210	14.42	6.99	7.71	29.12

FA = H_3PO_4; CS = Colloidal suspension (10-30-00); MAP= Monoammonium phosphate; TSP = Triple superphosphate.

The data of Table IV also show the significant effect of P sources on the inorganic P fractions. The effect is more pronounced in soil B that probably occurred due to the higher recovery of the applied phosphate in this soil.

The P recovery in all fractions in soil B and in P_{H2O} and P_{Al} in soil A was significantly larger for TSP than the values obtained for other sources. Nevertheless, these differences are small in terms of alterations in soil P fertility levels, and thus, it may be concluded that fluid and solid fertilizer P have similar fate in the Latosols studied.

TABLE IV. PHOSPHORUS DERIVED FROM THE FERTILIZER IN DIFFERENT P INORGANIC FRACTIONS OF TWO LATOSOLS AS AFFECTED BY P SOURCES

	P inorganic fraction*				
P Source	P_{H2O}	P_{Al}	P_{Fe}	P_{Ca}	$P_{occl.}$
	------------------------------μg P g^{-1} soil------------------------------				
Soil A					
TSP	0.8 a	41.4a	17.4	1.1	2.0
H_3PO_4	0.3b	36.3bc	16.2	1.2	2.0
MAP	0.4b	38.6ab	16.2	0.9	1.6
CS	0.3b	32.4c	15.1	1.2	1.7
CV %	27	6	13	20	19
Soil B					
TSP	2.9 a	102.6 a	15.4 a	1.1 a	0.4 a
H_3PO_4	1.5c	51.2c	6.4c	0.4c	0.1b
MAP	2.4b	77.3b	12.0b	0.8b	0.1b
CS	1.7c	50.6c	8.1c	0.4c	0.1b
CV %	11	12	8	23	29

*PH_2O= water soluble P; P_{Al} = Al bound P; P_{Fe}= Fe bound P; P_{Ca}= Calcium bound P; P_{occl}.= Occluded P. The values in the same row followed by the same letter are not significant.

4. CONCLUSIONS

1. No significant differences in dry matter yield and P uptake of corn were found for the fluid and solid P fertilizer sources studied.

2. Corn dry matter yield and P uptake showed a linear response to the increasing P rates. These effects were more pronounced in soil B, due to its lower P-fixing capacity.

3. In both Latosols, the agronomic efficiency of fluid and solid fertilizers was equivalent, demonstrating the potential for the application of fluid P sources for annual crops such as corn.

4. In the one-month incubation experiment, the larger proportion of soil-applied P sources was recovered as aluminum and iron bound P fractions. Only small quantities of P were found as water soluble P, calcium bound P and occluded P. The ratio P_{Al} to P_{Fe} was larger in soil B, with less P-fixing capacity.

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REFERENCES

[1] DEFILIPPE, G., Panorama da rocha fosfática e ácido fosfórico. In: ENCONTRO NACIONAL DE ROCHA FOSFÁTICA, 5., São Paulo, 1990. Anais. São Paulo, IBRAFOS, s.d. p.5-9.

[2] NOGUEIRA, A. V., Eficiência agronômica, como fertilizante, de um lodo de esgoto e de dois resíduos provenientes da indústria siderúrgica. Viçosa, Universidade Federal de Viçosa, 1990. 85p. (MSc. Dissertation).

[3] SILVA, L.C.F., MARAFON JUNIOR, J., BELTRAME, J. A ., ARAGÃO, J. A. , ORLANDO FILHO, J., Adubação fluida na cana-de-açúcar no Estado de São Paulo. Brasil. Açúcar., Rio de Janeiro, **106** (1988) 27-32.

[4] KORNDORFER, G.H., Fertilizantes fosfatados sólidos e fluidos na cana-de-açúcar. Piracicaba, ESALQ/USP, 1990. 91p. (PhD Thesis).

[5] PENATTI, C.P., Uso de ácido fosfórico ou superfosfato triplo como fonte de fósforo para a cana-de-açúcar. Piracicaba. ESALQ/USP, 1991. 72p. (MSc. Dissertation).

[6] HSU, P.H. Fixation of phosphate by aluminum and iron in acidic soils. Soil Sci. **84** (1965) 398-402.

[7] GONÇALVES, J.L., M. Cinéticas de transformação de fósforo lábil em não lábil em amostras de solos de Cerrado. Viçosa, 1988. 62p (MSc. Dissertation, Universidade Federal de Viçosa, MG, Brazil).

[8] YOST, R.S., KAMPRATH, E.J., NADERMAN, G.C., LOBATO, E., Residual effects of phosphorus applications on a high phosphorus adsorbing Oxisol of Central Brasil. Soil Sci. Soc. Am. J. **45** (1981) 540-543.

[9] FASSBENDER, H.W., Fósforo. In: Química de suelos; con enfasis en suelos de America Latina. Turrialba, Instituto Interamericano de Ciências Agrícolas, 1978. p.262-307.

[10] CHANG, S.C., JACKSON, M.L., Fractionation of soil phosphorus. Soil Sci. **84** (1957) 133-33.

[11] AWERBUCH, T., AUNIMELECH, Y., Counting ^{32}P in plant tissues using the Cerenkov effect. Plant and Soil **33** (1970) 260-264.

[12] ROBERTSON, W.K., THOMPSON JR., L.G., HUTTON, C.E., Availability and fractionation of residual phosphorus in soils high in aluminium and iron. Soil Sci. Soc. Am. Proc. **30** (1966) 446-50.

PHOSPHATE FERTILIZERS WITH VARYING WATER-SOLUBILITIES APPLIED TO AMAZONIAN SOILS: I. AGRONOMIC EFFICIENCY OF P SOURCES

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Abstract. The relative agronomic efficiency of four phosphate sources (triple superphosphate, ordinary Yoorin thermophosphate, coarse Yoorin thermophosphate and North Carolina phosphate rock) were evaluated, in a pot experiment carried out under greenhouse conditions, using five soils (medium texture Yellow Latosol, clayey Yellow Latosol, very clayey Yellow Latosol, clayey Red-Yellow Podzolic and very clayey Red-Yellow Podzolic) from Pará State, Brazil. The soils received three rates of phosphorus (40, 80 and 120 mg P/kg of soil) plus the control (0P) treatment. A randomized block design with three replicates was used. Two consecutive crops (cowpea and rice) were used as test plants. The results showed that the best dry matter yield and P uptake for cowpea were obtained in soils fertilized with triple superphosphate. The agronomic efficiency index of ordinary Yoorin was superior to the coarse Yoorin and North Carolina phosphate rock for the cowpea grown as first crop. The indices were similar for all phosphate sources for the subsequent rice crop. The best residual effect was obtained with North Carolina phosphate rock and coarse Yoorin. The larger particle size of coarse thermophosphate resulted in a decreased P efficiency.

1. INTRODUCTION

The phosphate fertilizers most often used in Brazilian agriculture are water-soluble phosphates (single and triple superphosphate, MAP and DAP). Although the water-soluble P fertilizers are more efficient than less soluble sources, they are expensive products, due to high-energy consumption for manufacturing, and the need for sulfur, which is an imported product. Utilization of finely ground phosphate rocks has been suggested as an alternative for alleviating the P deficiency of many Brazilian soils. These materials require a less sophisticated industrial process and therefore, can be sold at a lower cost than water-soluble fertilizers.

Sanchez [1] recommended the application of less soluble phosphates in acid soils with high P-fixing capacity, and considered these sources economically more efficient than water-soluble sources. The Brazilian phosphate rocks, most of them igneous apatites, have presented low agronomic efficiency compared to water-soluble phosphates, in spite of soil acidity [2,3]. North Carolina phosphate rock (NCPR), a fluorapatite, has been reported as highly efficient phosphate rock [4,5,6]. The choice of P source is based on its efficiency in supplying P to the plant demand and its cost. However, other aspects such as source of other nutrients, soil acidity amelioration, and residual effects should be also considered. According to Goedert et al. [7] thermophosphates have shown efficiencies superior to superphosphate in Brazilian soils. These products have been also effective in reducing soil acidity, due to high contents of Si, Ca and Mg [8]. Another important aspect to be considered for P efficiency is the fertilizer granule or particle size [9].

The objective of the current study was to evaluate the agronomic efficiency of four phosphate fertilizers in five tropical acid soils of the Para State in the Amazon region of Brazil.

TABLE I. GENERAL CHEMICAL [18]* AND PHYSICAL [19] CHARACTERISTICS OF SOILS

	Soils				
Characteristics	LAm	LA$_{\text{arg}}$	LA$_{\text{marg.}}$	PV$_{\text{marg.}}$	Pva/$_{\text{marg.}}$
Sand (%)	73	67	17	66	66
Silt (%)	5	9	12	8	7
Clay (%)	22	24	71	26	27
O.M. (%)	2.4	2.4	4.0	2.7	2.5
PH ($CaCl_2$)	4.0	3.5	3.5	3.2	3.8
Ca^{2+} (cmol dm^{-3})	1.0	0.5	1.0	0.4	0.8
Mg^{2+} (cmol dm^{-3})	0.3	0.2	0.8	0.1	0.2
K^+ (cmol dm^{-3})	0.17	0.11	0.11	0.07	0.09
P (mg dm^{-3})	2	5	9	4	4
Al^{3+} (cmol dm^{-3})	0.6	1.2	1.5	2.2	0.8
H^++Al^{3+} (cmol dm^{-3})	4.2	5.8	9.8	12.1	4.7

*Ca, Mg, K and P by resin extraction [18]

2. MATERIALS AND METHODS

Some representative surface (0-20 cm depth) soils were collected from the Amazon region of Brazil. The five soils were: Ipixuna, a medium texture alic yellow Latosol (LAm); Capitão Poço, a clayey texture alic caolinitic yellow Latosol (LA.arg.); Ipixuna, a very clayey alic yellow Latosol (LAm.arg.); Capitão Poço, a medium texture clayey allic caolinitic Red Yellow Podzolic Soil (PVm/arg); and Tailandia, a clayey texture, very clayey alic Red Yellow Podzolic Soil (PVa/m.arg.) (Table I).

Soil samples were passed through a 4 mm sieve. After sieving, 3.5 kg of each of the 5 soils was filled in plastic pots. The soils were amended with dolomitic lime to raise the volume of saturation base V% to 40%, and incubated for 15 days, prior to the application of P sources at 0, 40, 80 and 120 mg P kg^{-1} soil. The following P sources were tested: North Carolina phosphate rock (NCPR); fused magnesium thermophosphate, coarse (Yoorin-c); fused magnesium thermophosphate, ordinary (Yoorin); and Triple superphosphate (TSP) was the standard P source (Table II). The experimental design was a factorial of 5 soils, 4 P rates and 4 P fertilizers. Each treatment was replicated 3 times.

TABLE II. TOTAL P CONTENT AND SOLUBILITY OF P FERTILIZERS [20]

	P content			
Fertilizer*	Total	2% Citric acid sol.	NAC[1]+H_2O sol.	H_2O sol.
	% P			
TSP	20.64	16.89	18.02	15.97
NCPR	13.09	4.76	1.79	-
Yoorin-c	7.59	5.63	2.66	-
Yoorin	7.42	7.42	2.22	-

[1] NAC = neutral ammonium citrate

TSP = Triple Superhosphate; NCPR = North Caroline phosphate rock; Yoorin-c = Coarse Yoorin thermophosphate; Yoorin = ordinary Yoorin thermophosphate

The particle size of thermophosphates was: a) coarse= 100% particles passing through a 0.84 mm sieve; b) ordinary = 75% particles passing through a 0.15 mm sieve. The NCPR was a product commercially used in Brazil, with 64% particles passing through a 0.3 mm sieve.

Two successive crops were grown, using cowpea (CNC 1371 Poty cultivar) and rice (IAC 25 cultivar). Seeds were planted in excess and seedlings were thined to three (cowpea) and eight (rice) per pot. Cowpea seeds were innoculated with Rhizobium (CN-1525, CN-1527 and CN-1545) prior to seeding. Nitrogen, as urea, and K, as KCl (200 and 250 mg of nutrient/pot respectively) were added to all soil growing rice. Cowpea received only K at the same rate. Micronutrients (20 mL/pot of solution containing 1.0; 1.0; 0.1 and 2.5 μg/mL B, Cu, Mo and Zn, respectively) were also applied.

Cowpea plants were harvested 52 days after seeding and rice plants were harvested 46 days after seeding. After harvesting, plants were dried at 70^{O}C and ground. The ground material was analysed for total P content by the vanadate-molybdate method after nitric-percloric acid digestion.

The phosphates were evaluated through the Agronomic Efficiency Index (AEI), according to Goedert et al. [7] on the basis of dry matter yield and P uptake differential to TSP as a reference source using the same total P rate for all sources.

TABLE III. EFFECT OF P FERTILIZERS ON DRY MATTER WEIGHT (g/POT) AND P UPTAKE (mg/POT) OF COWPEA AND RICE GROWN IN DIFFERENT TROPICAL ACID SOILS

		-------------Cowpea-------------		-----------------Rice-------------------	
Soil	Fertilizer	Dry matter	P uptake	Dry matter	P uptake
		(g/pot)	(mg/pot)	(g/pot)	(mg/pot)
$LA_{arg.}$	TSP	8.92 a*	25.16 a	7.11a	15.67 a
	Yoorin	8.52 a	26.71 a	6.58a	13.27 b
	Yoorin-c	5.91 b	13.44 b	6.40a	12.13 b
	NCPR	5.43 b	10.15 c	6.56a	12.93 b
$LA_{marg.}$	TSP	8.28 a	13.57 a	7.68 b	12.11 b
	Yoorin	6.07 b	10.92 a	6.68 c	11.24 bc
	Yoorin-c	3.28 c	5.24 b	7.03 bc	10.36 c
	NCPR	3.85 c	6.07 b	9.62 a	14.48 a
LA_{m}	TSP	9.46 a	28.47 a	5.97a	12.97 a
	Yoorin	9.33 a	26.32 a	6.12a	11.80 a
	Yoorin-c	7.70 b	19.13 b	5.58a	9.80 b
	NCPR	5.60 c	9.90 c	5.34a	9.53 b
$PV_{m/arg.}$	TSP	8.32 a	24.97 a	6.12 a	12.80 a
	Yoorin	7.29 b	18.33 b	5.54 a	10.58 b
	Yoorin-c	4.22 c	9.02 c	5.32 ab	8.73 c
	NCPR	2.11 a	2.67 d	4.52 b	6.35 d
$PV_{arg/m.arg.}$	TSP	9.49 a	23.01 a	6.14a	12.06 a
	Yoorin	6.27 b	13.22 b	5.75a	9.31 b
	Yoorin-c	6.03 b	14.20 b	5.46a	8.84 b
	NCPR	3.84 c	7.40 c	5.64a	9.39 b

*means followed by the same within a soil type letter are not significantly different at 0.05 probability level as determined by Tukey test

3. RESULTS AND DISCUSSION

Considering dry matter yield and P uptake by plants (Table III), there were significant effect and interactions amongst soils, sources, and rates, with exception of the source by rate interaction on dry matter yield. Triple superphosphate gave significantly higher dry matter yield than the other sources in most of the soils. This was likely favoured by the soil lime amendment prior to planting. Next best source was ordinary Yoorin, which performed similarly to TSP except on soils Lam and LAarg. Several studies have reported that thermophosphates were good P sources as water-soluble fertilizers [10, 11].

Yoorin-c and NCPR produced the lowest dry matter yield for cowpea. In case of Yoorin-c, the large particle size was the probable cause of lower yields [12]. For NCPR, the results do not agree with those reported elsewhere, where good plant response was obtained with this product. However, the low efficiency of NCPR on cowpea was probably also related to the particle size of the applied product in this study. Kanabo & Gilkes [9] observed that the particle size affects the efficiency of NCPR, increasing the dissolution with a decrease in particle size.

The results of P taken up by the cowpea plants (Table III), followed the same tendency observed for dry matter weight, except that Yoorin behaved statistically equal to TSP in all Latosols.

TABLE IV. AGRONOMIC EFFICIENCY INDEX OF FERTILIZERS BASED ON DRY MATTER WEIGHT OF COWPEA AND RICE PLANTS

		-------------Cowpea-------------			-----------------Rice----------------		
Soil	Fertilizer Rate	NCRP	Yoorin-c	Yoorin	NCRP	Yoorin-c	Yoorin
	mg P kg^{-1}	--------------------------------------%--------------------------------------					
LA$_{\text{arg.}}$	40	34	34	80	82	72	82
	80	53	65	86	79	75	82
	120	59	66	106	91	97	95
LA$_{\text{marg.}}$	40	30	26	37	115	65	61
	80	40	31	70	123	93	78
	120	44	29	76	313	89	84
LA$_{\text{m}}$	40	39	62	94	92	98	110
	80	50	77	94	78	93	107
	120	56	78	101	79	93	100
PV$_{\text{m/arg.}}$	40	12	21	75	64	82	72
	80	12	32	88	56	80	77
	120	14	42	84	65	76	79
PV$_{\text{arg/m.arg.}}$	40	41	32	47	95	84	125
	80	34	45	44	76	64	77
	120	29	91	80	73	105	85

The rice plants dry matter yield (Table III) presented results different from those observed in cowpea. There were no differences among the P sources for most of soils. One exception was NCPR that gave better results in Lam.arg and worst results in PVm/arg. Some aspects should be considered to explain the behavior of phosphates in this crop: the reduction of TSP efficiency, in second crop, and increase in efficiency of less soluble sources. The effects of P fertilization on successive crops are well known, usually water-soluble P sources provide better results in the first crop and reduced residual effect with time whereas the reverse occurs with less soluble P sources with higher residual effects in subsequent crops compared with P soluble sources [13].

Considering the AEI (Agronomic Efficiency Index) based on cowpea dry matter (Table IV), Yoorin was superior to Yoorin coarse and NCPR, and equal to TSP at the highest rate, in LA.arg and Lam soil. These results agree with those obtained by Braga et al. [2], Yost et al. [8], and Oliveira et al. [14], showing that the high efficiency of this phosphate usually is attributed to its dissolution and soil liming effect.

The values of AEI value of Yoorin-c were much smaller compared with ordinary Yoorin. The NCPR presented the least AEI in cowpea and similar to values reported in other works for Brazilian phosphate rocks [7, 15, 16]. However, Barnes and Kamprath [17] reported that, in organic soils this fertilizer was as efficient as TSP for corn, soybean and wheat.

TABLE V. AGRONOMIC EFFICIENCY INDEX OF FERTILIZER BASED ON P UPTAKE BY COWPEA AND RICE PLANTS.

		------------------------Cowpea---------------------			--------------------Rice-----------------		
Soil	Fertilizer Rate	NCRP	Yoorin-c	Yoorin	NCRP	Yoorin-c	Yoorin
	mg P kg^{-1}	--		%		---	
LA$_{arg.}$	40	39	49	92	85	66	73
	80	42	51	98	73	72	92
	120	26	49	108	76	72	82
LA$_{marg.}$	40	32	28	61	117	70	68
	80	62	44	94	114	87	89
	120	37	33	78	115	80	96
LA$_{m}$	40	27	56	91	86	79	91
	80	30	81	94	72	79	93
	120	94	57	91	56	64	85
PV$_{m/arg.}$	40	13	26	79	66	94	104
	80	7	20	64	40	62	76
	120	6	26	72	39	52	68
PV$_{arg/m.arg}$	40	61	52	84	109	76	147
	80	34	46	49	69	49	53
	120	18	72	51	63	87	64

The AEI results of rice dry matter show that residual effect of NCPR tends to be equal to more soluble sources, such as Yoorin thermophosphate. The results demonstrate further that the index related to Yoorin-c increased considerably in relation to that obtained in the first crop, confirming that the granule size was the determining factor for the slow initial release of phosphorus to the plants, but better supplying power for the subsequent crop.

The AEI of both crops obtained from total absorbed P by cowpea and rice plants (Table V) were of the same order to those presented for dry matter yield.

4. CONCLUSIONS

For the first crop (cowpea), the best results for dry matter yield and P uptake were obtained with TSP application. For the second crop (rice), no differences among the sources were found.

The ordinary Yoorin thermophosphate presented the better Agronomic Efficiency Index for the first crop, while there was increase in efficiency of coarse Yoorin and NCPR in the second crop.

The particle size of Yoorin-c thermophosphate negatively affected its efficiency in the first crop.

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REFERENCES

[1] SANCHEZ, P. A. Fósforo, silicio y azufre. In: SANCHEZ, P.A. Suelos del tropico; características y manejo. San Jose: IICA, 1981. 234p.

[2] BRAGA, N.R.; MASCARENHAS, H.A .A.; FEITOSA, C.T.; RAIJ, B. van. Efeitos de fosfatos sobre o crescimento e produção de soja. Rev. Bras. Ci. Solo **4** (1980) 36-39.

[3] GOEDERT, W.J.; LOBATO, E. Eficiência agronômica de fosfatos em solos de Cerrado. Pesq. Agropec. Bras. **15** (1980) 311-318.

[4] CHIEN, S.H.; HAMMOND, L.L. A comparison of various laboratory methods for predicting the agronomic potential of phosphate rocks for direct application. Soil Sci.Soc. Am. J. **42** (1978) 935-939.

[5] HAMMOND, L.L.; LEON, L. A.; RESTREPO, L.G. Efecto residual de las aplicaciones de 7 fuentes de fósforo sobre el rendimiento de *Brachiaria decumbens* en un Oxisol de Carimagua. Suelos Ecuatoriales, Medellin **12** (1982) 122-128.

[6] HAMMOND, L.L.; CHIEN, S.H.; MOKWUNYE. Agronomic value of unacidulation and partially acidulated phosphate rocks indigenous to the tropics. Advances in Agronomy **40** (1986) 89-140.

[7] GOEDERT, W.J.; SOUZA, D.M.G. de. Avaliação preliminar de fosfatos com acidulação parcial. Rev. Bras. Ci. Solo **10** (1986) 75-80.

[8] YOST, R.S.; NADERMAN, G.C.; KAMPRATH, E.J.; LOBATO, E. Availability of rock phosphate as measured by an acid tolerant pasture grass and extractable phosphorus. Agron. J. **74** (1982) 462-468.

[9] KANABO, I.A .K.; GILKES, R.J. The effect of particle size on North Caroline phosphate rock on its dissolution in soil and on levels of bicarbonate-soluble phosphorus. Fertilizer Research **15** (1988) 137-145.

[10] GOEDERT, W.J.; LOBATO, E. Avaliação agronômica de fosfatos em solo de Cerrado. Rev. Bras. Ci. Solo **8** (1984) 97-102.

[11] GOEDERT, W.J.; SOUZA, D.M.G.; LOBATO, E. Fósforo. In: GOEDERT, W.J. Solos de Cerrado: tecnologias e estratégias de manejo. São Paulo: Nobel, 1987, p.129-166.

[12] STEFANUTTI, R. Efeito da granulometria de um termofosfato magnesiano no aproveitamento do fosforo. 1991. 76p. MSc. Dissertation, Centro de Energia Nuclear na Agricultura, USP).

[13] SOUZA, D.M.G. de; VOLKWEISS, S.J. Rendimento da matéria seca e conteúdo de fósforo da parte aérea do milho influenciados pela adubação com superfosfato triplo em pó e em grânulos. Rev. Bras. Ci. Solo **11** (1987) 127-132.

[14] OLIVEIRA, E.L.; de; MUZILLI, O.; IGUE, K.; TORNERO, M.T.T. Avaliação da eficiência agronômica de fosfatos naturais. Rev. Bras. Ci. Solo **8** (1984) 63-67.

[15] FERREIRA, T.N.; KAMINSKI, J. Eficiência agronômica dos fosfatos naturais de Patos de Minas e Gafsa, puros e modificados por acidulação e calcinação. Rev. Bras. Ci. Solo **3** (1979) 158-162.

[16] GOEDERT, W.J.; REIN, T.A .; SOUZA, D.M.G. de. Eficiência agronômica de fosfatos naturais, fosfatos parcialmente acidulados e termofosfatos em solos de Cerrado. Pesq. Agropec. Bras. **25** (1990) 521-530.

[17] BARNES, J.S.; KAMPRATH, E.J. Availability of North Carolina rock phosphate applied to soils. North Carolina. (1975) 22p. (Tech. Bulletin, 229).

[18] RAIJ, B. van; QUAGGIO, J.A. Métodos de análise de solos para fins de fertilidade. IAC, 1983. 31p. (IAC. Techn. Bulletin, 81).

[19] VETTORI, L. Métodos de análise do solo. Ministério da Agricultura, Equipe de Pedologia e Fertilidade.

[20] BRASIL. Ministério da Agricultura. Análise de corretivos, fertilizantes e inoculantes: métodos oficiais. Rio de Janeiro, 1988. 104p.

PHOSPHATE FERTILIZERS WITH VARYING WATER-SOLUBILITY APPLIED TO AMAZONIAN SOILS: II. SOIL P EXTRACTION METHODS

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Abstract. A pot experiment was carried out under greenhouse conditions at the Centro de Energia Nuclear na Agricultura, Piracicaba (SP, Brazil), to evaluate the phosphorus availability of different phosphate sources in five Amazonian soils. The soils utilized were: medium texture Yellow Latosol, clayey Yellow Latosol, very clayey Yellow Latosol, clayey Red-Yellow Podzolic and very clayey Red-Yellow Podzolic. Four phosphate sources were applied: triple superphosphate, ordinary Yoorin thermophosphate, coarse Yoorin termo-phosphate and North Carolina phosphate rock at P rates of 0, 40, 80 and 120 mg kg^{-1} soil. The dry matter yield and the amount of P taken up by cowpea and rice were correlated with the extractable P by anionic exchangeable resin, Mehlich-1, Mehlich-3 and Bray-I. The results showed that the extractable P by Mehlich-1 was higher in the soils amended with North Carolina rock phosphate. Irrespective of the phosphorus sources used, the Mehlich-3 extractant showed close correlation with plant response. The Mehlich-3 and Bray-I extractants were more sensitive to soil variations. The Mehlich-3 extractant was more suitable in predicting the P availability to plants in the different soils and phosphorus sources studied.

1. INTRODUCTION

The Amazon region presents great geological diversity, where sedimentary, metamorphic and magmatic rocks are encountered. This fact combined to a high geomorphological variation, determine the existence of many types of soils. Among the soil taxonomic units, yellow Latosols and red yellow Podzolics are the predominant soils of the region. Approximately 88% of the Amazon soils are characterized as poor in chemical soil fertility, with very low nutrient contents. Phosphorus (P) is the most limiting element for plant growth (1 to 9 μg g^{-1} available P, by Mehlich 1, and <200 μg g^{-1} total P). To increase crop productivity, the need for P fertilization is imperative. The utilization of phosphatic fertilizers in this region, however, is still restricted, due to high costs of P fertilizer supplies (product and transport) and limited investigations on the subject.

The application of water-soluble phosphate fertilizers, in spite of P being totally available, promotes further acidification in acid soils with consequent dissolution of Al and Fe oxides, accelerating P-fixing processes. An alternative to reduce these processes is the utilization of low-cost P sources, with low acidification capacity, and satisfactory solubility, such as thermophosphate and North Carolina phosphate rock.

Pepper growers have used the thermophosphate in the region. One of its advantages is the acidity correcting effect, which reduces P fixation. Rock phosphates are another alternative that have better efficiency in acid and low P-content soils. The North Carolina rock phosphate, a fluorapatite, has been reported as a highly efficient product [1, 2]. Considering transport costs of the products, the cost ofthis fertilizer is almost the same as PR locally produced in Brazil.

The rational and economical utilization of P fertilizers requires the understanding of P dynamics and its interactions with the soil. In addition, an accurate determination of “available” P is required in order to diagnose the soil P status and consequently to recommend the necessary practices for obtaining maximum yield.

The Mehlich 1 method is routinely utilized to determine available P in approximately 90% of the laboratories in the Amazon region [3]. It was introduced without previous studies to evaluate its efficiency. Paradoxically, this method has been considered not suited for acid soils, because it extracts more soil P bound to Ca, and only small proportions of P bound to Al and Fe. Considering that acid soils are rich in Fe and Al oxides and caolinite, as occurs in the majority of Brazilian soils, the predominant P reaction products in the soil are aluminum and iron phosphates. Therefore, this extractant would not be the correct option for the determination of soil available P. Furthermore, the Mehlich 1 extractant solubilizes unaltered rock phosphate residues, overestimating P availability in soil fertilized with PR.

According to Tomas and Peasle [4], the Bray 1 extractant can be recommended for acid soils and also for the soil fertilized with PR. The extracting reaction occurs by its acidity and complexation of Al-P and Fe-P by fluoride.

Since 1983 in the Sao Paulo State, Brazil, the official method for soil P testing is the resin method [5]. The advantage of this method is that other elements, Ca, Mg and K, are also determined in the same extracts. Several studies carried out during the last 5 years have shown the superiority of this method over the others. Reports about its performance in soils fertilized with PR, however, are scarce.

The objective of this research was to evaluate four chemical extraction methods for assessing P availability in soils from the Amazon region, amended with phosphates of varying water-solubility.

2. MATERIAL AND METHODS

The five soil types, their characterization and the pot experiments run were described in previous work [6].

Soil samples were taken from the pots twice: first prior to cowpea seeding and second, before rice seeding, and analysed for available P, using the following methods: Mehlich 1 [3], Bray-1 [7], Anion + cation exchange resin [5] and Mehlich 3 [8].

To evaluate the P availability, data of soil extracted P were correlated against dry matter yields of cowpea and rice, considering fertilizers and soils separately. The regression curves of the dry matter yields and soil P contents were adjusted for each method, considering all the soils and P sources.

In order to evaluate differences between correlation coefficients obtained as a function of soils, sources and rates, the r-values were transformed to Z and statistically analysed by t test [9]. Linear simple correlations among soil P extracted by different methods were also determined.

3. RESULTS

Correlation results for plant response to different P sources versus P extraction methods are presented in Table I. The correlation with Triple Superphopsphate (TSP) was highly significant with all the extractants for both crops, which indicated that for water-soluble P sources any method gives a satisfactory estimation. With North Carolina phosphate rock (NCPR) fertilizer, the correlation coefficient reflected the specific behaviour of each method. The Mehlich 3 method presented good sensitivity in extracting available P in soils with phosphate residues having an apatite origin. The results confirm Mehlich’s [8] observation that acetic acid is a more moderate agent to solubilize apatite in relation to equivalent mineral acids present in other extractants. The Mehlich 1 extractant did not present good correlation in soils amended with phosphate rocks, due to its high extraction capacity, which gave overestimation of P availability, as observed by Feitosa and Raij [10] and Raij [11].

TABLE I. LINEAR CORRELATIONS BETWEEN P EXTRACTED BY DIFFERENT METHODS AND DRY MATTER AND P PUTAKE OF COWPEA AND RICE PLANTS, FOR EACH APPLIED FERTILIZER

	-------------------Linear Correlation coeficient (r)------------------			
	---------------Cowpea---------------		----------------Rice---------------	
	Dry matter	P uptake	Dry matter	P uptake
	-------------------------------Triple Superphosphate-------------------------------			
Resin	0.742*	0.755*	0.722*	0.898*
Mehlich 1	0.798*	0.758*	0.720*	0.901*
Mehlich 3	0.774*	0.809*	0.714*	0.926*
Bray 1	0.751*	0.844*	0.681*	0.889*
	------------------------North Carolina Phosphate Rock------------------------			
Resin	0.524*	0.467*	0.551*	0.582*
Mehlich 1	0.540*	0.521*	0.653*	0.739*
Mehlich 3	0.736*	0.700*	0.684*	0.797*
Bray 1	0.236$^{n.s.}$	0.201$^{n.s.}$	0.757*	0.871*
	---------------------------Coarse Yoorin Termophosphate-----------------------			
Resin	0.305*	0.256*	0.609*	0.697*
Mehlich 1	0.753*	0.728*	0.683*	0.757*
Mehlich 3	0.705*	0.690*	0.716*	0.797*
Bray 1	0.568*	0.547*	0.679*	0.759*
	------------------------Ordinary Yoorin Termophosphate------------------------			
Resin	0.683*	0.680*	0.627*	0.683*
Mehlich 1	0.790*	0.737*	0.716*	0.836*
Mehlich 3	0.825*	0.828*	0.741*	0.875*
Bray 1	0.826*	0.785*	0.750*	0.867*

* = significant at 5% level. n.s.= not significant.

Surprisingly the Bray 1 extractant did not correlate well with cowpea P uptake and dry matter yield in treatments with phosphate rock. The results disagree with those obtained by Raij and van Diest [12] and Kaminski [13], as they reported that Bray 1 is one of most adequate methods for available P estimation. According to Smith et al. [14], the Bray 1 extractant is able to discriminate soils fertilized with phosphate rock from those with water-soluble phosphates. For the treatments with coarse Yoorin (Yoorin-c), both Mehlich 1 and Mehlich 3 gave good correlation with cowpea plant response.

The resin method did not perform well for cowpea in both NCPR and Yoorin-c treatment. The low efficiency of this method could be due to the capability of resin to extract high amounts of P on higher pH (6.5-7.0). Probably Yoorin-c, which has an alkaline reaction, increased soil pH in the laboratory, favoring the resin extraction, without correspondent increase in P uptake by cowpea.

The residual effect (rice plant response) generally correlated better with extracted P, for the different phosphates studied, mainly in treatments with smaller correlation in the first crop. This indicated that having longer period for fertilizer/soil reaction, the extractants present higher efficiency in extracting P with regard to plant uptake.

For both crops, Mehlich 3 and Bray 1 showed better sensitivity to soil variation (Table II). Lins and Cox [15] evaluated the effect of some chemical properties of seven Cerrado soils, reported the superiority of Mehlich 3 over Bray 1 and resin methods. Piha [16], comparing the Mehlich-3 and resin methods in soil of Zimbabwe, observed that the two methods varied in efficiency depending on soil texture, though Mehlich-3 was considered more adequate for large variations of soil type. Freire et al. [17] observed good sensitivity of Bray 1 extractant to soils with different clay content. The Mehlich-1 was the least correlated method for all soils.

The correlation coeficients obtained as a function of soils, P sources and rates for Mehlich 3 and Bray 1 in cowpea plants were significantly superior to other methods. For rice plants, through the tendency was similar, the values were not significantly different.

The Mehlich-3 method correlated well with Bray 1 (Table IV). Wolf & Baker [18] and Gascho et al. [19] reported similar results. The Mehlich-1, Bray 1 and Resin methods did not correlate well with each other, which was probably due to differences in extracting capabilities of each solvent.

TABLE II. LINEAR CORRELATIONS BETWEEN P EXTRACTED BY DIFFERENT METHODS AND RESPONSE OF COWPEA AND RICE IN DRY MATTER AND P UPTAKE, FOR EACH SOIL

Method	----------------Linear correlation coefficient (r)-------------------			
	---------------Cowpea---------------		----------------Rice-----------------	
	Dry matter	P taken up	Dry matter	P taken up
	--------------------------Clayey Yellow Latosol--------------------------			
Resin	0.877*	0.887*	0.632*	0.688*
Mehlich 1	0.707*	0.675*	0.624*	0.682*
Mehlich 3	0.827*	0.947*	0.795*	0.911*
Bray 1	0.747*	0.835*	0.706*	0.841*
	-----------------------Very Clayey Yellow Latosol----------------------			
Resin	0.374*	0.439*	0.692*	0.729*
Mehlich 1	0.503*	0.553*	0.794*	0.769*
Mehlich 3	0.839*	0.887*	0.765*	0.874*
Bray 1	0.846*	0.859*	0.543*	0.672*
	-------------------Medium Texture Yellow Latosol--------------------			
Resin	0.694*	0.765*	0.592*	0.607*
Mehlich 1	0.566*	0.558*	0.656*	0.702*
Mehlich 3	0.781*	0.890*	0.737*	0.870*
Bray 1	0.663*	0.810*	0.620*	0.792*
	--------------------Clayey Red-Yellow Podzolic Soil-------------------			
Resin	0.682*	0.688*	0.693*	0.666*
Mehlich 1	0.209*	$0.207^{n.s.}$	0.481*	0.430*
Mehlich 3	0.894*	0.879*	0.798*	0.887*
Bray 1	0.883*	0.938*	0.723*	0.884*
	---------------Very Clayey Red-Yellow Podzolic Soil-----------------			
Resin	0.636*	0.636*	0.618*	0.620*
Mehlich 1	0.414*	0.400*	0.631*	0.658*
Mehlich 3	0.713*	0.707*	0.821*	0.899*
Bray 1	0.841*	0.847*	0.707*	0.814*

* = significant at 5% level.

TABLE III. COMPARISON OF CORRELATION COEFFICIENTS OBTAINED BETWEEN DRY MATTER WEIGHT OF COWPEA AND RICE AND SOIL EXTRACTED P, IN FUNCTION OF SOILS, P SOURCES AND RATES (VALUES TRANSFORMED TO Z, T TEST)

Method	---------------Cowpea---------------		----------------Rice-------------------	
	R	Z*	R	Z*
Resin	0.776	1.035A	0.657	0.787A
Mehlich 1	0.756	0.987A	0.553	0.623AB
Mehlich 3	0.659	0.791B	0.554	0.624AB
Bray 1	0.524	0.582C	0.581	0.664^{A}

Z values in the same column followed by the same letter do not differ estatistically (p=0.05)

TABLE IV. LINEAR CORRELATION COEFICIENTS BETWEEN QUANTITY OF EXTRACTED P BY DIFFERENT EXTRACTANTS IN SOIL SAMPLES COLLECTED PRIOR TO COWPEA AND RICE SEEDLING

	-----------------Correlation coefficient (r)-----------------		
Method	Mehlich 1	Mehlich 3	Bray 1
	---------Soil analysed before cowpea seeding------------		
Resin	0.496**	0.623**	0.458**
Mehlich 1	1.000**	0.521**	0.308**
Mehlich 3	0.521**	1.00*	0.850**
	-------------Soil analysed before rice seeding-------------		
Resin	0.529**	0.614**	0.441**
Mehlich 1	1.000**	0.572**	0.328**
Mehlich 3	0.572**	1.000**	0.887**

* = significant at 5% level. n.s.= not significant.

4. CONCLUSIONS

1. The Mehlich-3 extractant presented good correlations with cowpea and rice response, irrespective of the P source utilized.
2. The Mehlich-3 and Bray 1 were the most sensitive to soil variations, and the correlation between the two extractants was highly significant.
3. The Mehlich 1 extractant gave the poorest correlation with both cowpea and rice plant responses.

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REFERENCES

[1] CHIEN, S.H., HAMMOND, L.L., A comparison of various laboratory methods for predicting the agronomic potential of phosphate rocks for direct application. Soil Sci. Soc. Am. J. **42** (1978) 935-9.

[2] LEON, L.A., FENSTER, W.E., HAMMOND, L.L., Agronomic potential of eleven phosphate rocks from Brazil, Colombia, Peru and Venezuela. Soil Sci. Soc. Am. J. **50** (1986) 798-802.

[3] NELSON, W.L., MEHLICH, A., WINTERS, E., The development, evaluation and use of soil tests for phosphorus availability. In: PIERRE, W.H. & NORMAN, A. G. Soil Fertilizer Phosphorus. New York, Academic Press (1953) 153-188. (Agronomy, 14).

[4] THOMAS, G.W., PEASLEE, D.E., Testing soils for phosphorus. In: WALSH, L.W. & BEATON, J.D. ed. Soil testing and plant analysis. Madison, SSSA (1973) 15-29.

[5] RAIJ, B. van, QUAGGIO, J. A., Métodos de análises de solo para fins de fertilidade. Campinas, IAC (1983) 31p. (IAC. Boletim Tecnico, 81).

[6] BRASIL, E.C., MURAOKA, T., SCIVITTARO, W.B., Phosphate fertilizers with varying water-solubility applied to Amazonian soils: I- Agronomy Efficiency of P sources (in this publication, 2001)

[7] BRAY, R.H., KURTZ, L.T., Determination of total, organic and available forms of phosphorus in soil. Soil Sci. **59** (1945) 39-45.

[8] MEHLICH, A., Mehlich-3 soil test extractant: A modification of Mehlich-2 extractant. Comm. Soil Sci. Plant Anal. **15** (1984) 1409-16.

[9] STEEL, R.G.D., TORRIE, J.H., Principles and procedures of statistics: a biometrical approach. New York, McGraw-Hill Book, 1980. 633p.

[10] FEITOSA, C.T., RAIJ, B. van., Influência da natureza de fosfatos aplicados à dois solos no fosfato solúvel em extratores químicos e disponível para trigo e milho. In: CONGRESSO BRASILEIRO DE CIÊNCIA DO SOLO, Campinas, Anais (1975) 215-220.

[11] RAIJ, B. van., Seleção de métodos de laboratório para avaliar a disponibilidade de fósforo em solos. Rev. Bras. de Ci. Solo. **2** (1978) 1-9.

[12] RAIJ, B. van, DIEST, B. van., Phosphate supplying power of rock phosphate in an Oxisol. Plant and Soil **55** (1980) 97-104.

[13] KAMINSKI, J., Efeito de cinco fosfatos pré-, co- e pós aplicados ao calcário no suprimento de fósforo ao sorgo (*Sorghum bicolor* (L) Moench-CV. Conti-Brasil), em três solos ácidos. Piracicaba, 1983. 126p. (PhD Thesis – ESALQ/USP).

[14] SMITH, F.W., ELLIS, B.G., GRAVA, J., Use of acid-fluoride solution for the extraction of available phosphorus in calcareous soil to which rock phosphate has been added. Soil Sci. Soc. Am. Proc. **21** (1957) 400-404.

[15] LINS, I.D.G., COX, F.R., Effect of extractant and selected soil properties on predicting the correct phosphorus fertilization of soybean. Soil Sci. Soc. Am. J. **53** (1989) 813-6.

[16] PIHA, M.I., Evaluation of Mehlich-3 extractant for estimating phosphorus deficiency and phosphorus sorption of Zimbabwean soils. Comm. Soil Sci. Plant Anal. **241** (1993) 397-1408.

[17] FREIRE, F.M., NOVAIS, R.F., BRAGA, J.M., FRANÇA, G.E., SANTOSM H.L., SANTOS, P.R.R.S., Adubação fosfatada para a cultura da soja (*Glycine max* (L) Merrill) baseada no fósforo disponível e no fator "capacidade". Rev. Bras. Ci. Solo **3** (1979) 105-111.

[18] WOLF, A .M., BAKER, D.E., Comparison of soil test phosphorus by Olsen, Bray P1, Mehlich-I and Mehlich-III methods. Comm. Soil Sci. Plant Anal. **16** (1985) 467-84.

[19] GASCHO, G.J., GAINES, T.P., PLANK, C.O., Comparison of extractants for testing Coastal Plain soils. Comm. Soil Sci. Plant Anal. **21** (1990) 1051-77.

COMPARATIVE STUDY OF P UPTAKE AND UTILIZATION FROM P FERTILIZERS BY CHILEAN WHEAT GENOTYPES IN VOLCANIC ASH SOILS

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Abstract. The intensification of the agricultural production in Southern Chile demand the application of P fertilizers to volcanic ash soils for optimum plant growth and crop yields. Due to the high P sorption capacities of these soils, high amounts of water-soluble phosphatic fertilizers need to be applied. Therefore, the direct application of locally available Bahia Inglesa phosphate rock has been utilized to supply P to crops in these acid soils. Phosphate rock is a very efficient P input for crops with long growth cycles or crop rotations nevertheless water-soluble P fertilizers must still be applied to crops of short growth cycle. Combined with these strategic P inputs, the use of acid-tolerant and P-efficient genotypes can further contribute to agricultural sustainability. Greenhouse studies were undertaken to explore and identify genotypic variations in P efficiency of wheat grown in Andisols of Southern Chile. ^{32}P isotopic techniques were utilized to measure the uptake of P from triple superphosphate, a water-soluble P fertilizer and the locally available Bahia Inglesa phosphate rock. Substantial genotypic variations in P use efficiency were found among the Chilean wheat genotypes tested. The utilization of the ^{32}P isotopic techniques enabled to quantify the P taken up from the P fertilizer and the assessment of differences among the genotypes. Significant genotypic differences were obtained in the P uptake from the local phosphate rock Bahia Inglesa. Much higher applications of phosphate rock were required in Santa Barbara soil series (Andisol) due to its high P retention. A sustainable strategy for agricultural production in the Andisols of Chile would therefore, be the combined utilization of those efficient wheat genotypes and the local phosphate rock Bahia Inglesa. As P efficiency is a multi-faceted trait, which interacts with a range of environmental factors, further field-testing and validation is required accompanied by in depth studies to assess the relative importance of the morphological and physiological traits contributing to a better P efficiency.

1. INTRODUCTION

Volcanic ash soils cover extensive areas of land in the southern regions of Chile. Originally forests and permanent pastures were the predominant land use, but they have been progressively converted into arable land and cropped mainly to wheat [1]. These volcanic ash soils, however, show several soil fertility constraints such as low pH, high P retention, and low base saturation. A key factor to secure agricultural productivity is reducing P deficiency. Therefore, P fertilizers have to be applied to obtain optimum plant growth and crop yields [2]. As these soils have very high P sorption capacity, very high rates of water-soluble P fertilizers are required to obtain good crop yields. This practice is, however, not sustainable and also uneconomic. An alternative approach to supply P to these acid soils has been the direct application of phosphate rock coming from local deposits. Several studies have evaluated the agronomic effectiveness of the local phosphate rocks, in particular Bahia Inglesa in these soils. This PR has good reactivity with crops of relatively long growth cycle and also shows long residual effect in a crop rotation of annual crops [3, 4, 5]. Nevertheless, water-soluble P fertilizers are still required for annual crops. Combined with strategic P inputs, the use of acid-tolerant and P-efficient germplasm can further contribute to agricultural sustainability [6]. It should be noted here that the use of P-efficient germplasm is not an alternative to P fertilizer applications. Generally, the factors that contribute to P efficiency by plants are well established [7, 8]. Crops differ widely in their ability to grow in soils of low P status and this has been attributed to several factors [9, 10].

These studies were, therefore, carried out to identify genotypic variation in P efficiency in wheat grown in Andisols of the Southern Chile. Phosphate-32 isotopic techniques were utilized to measure the uptake of P from triple superphosphate, an imported water-soluble P fertilizer and the Bahia Inglesa phosphate rock, coming from Chilean ore.

2. MATERIALS AND METHODS

The greenhouse experiments were conducted at the Nuclear Center La Reina, Santiago, Chile. Several wheat genotypes (*Triticum aestivum, L.* and *Triticum durum*) were chosen from the Chilean wheat collection [11].

2.1. Experiment I

The first study was designed to explore differences in P efficiency between Chilean wheat genotypes. The soil utilized was an Andisol from Pemehue soil series (Typic Hapludand). The soil characteristics have been described elsewhere [12]. Phosphorus fertilizers tested were a water-soluble source, the triple superphosphate (16.2% total P), and the Bahia Inglesa phosphate rock (8% total P). They were applied at rates of 500 and 1000 mg P kg^{-1} soil, respectively. The indirect isotope method was used to assess
the P availability from the phosphate rock. The triple superphosphate was labeled with ^{32}P with a specific activity of 18.5 MBq g P^{-1} [13, 14]. Nineteen cultivars of contrasting characteristics were selected (Table I). The experiment comprised 38 treatments, which included a factorial of 19 genotypes,
and two P fertilizers. Each treatment was replicated 3 times in a completely randomized design.

TABLE I. CHILEAN WHEAT GENOTYPES UTILIZED IN EXPERIMENT I

Cultivar	Growth cycle	Wheat type
1. Cisne	Spring	Bread
2. Lilén	Spring	Bread
3. Nobo	Spring	Bread
4. Reihue	Spring	Bread
5. Talhuén	Spring	Bread
6. Onda	Spring	Bread
7. Saeta	Spring	Bread
8. Canelo	Alternative	Bread
9. Maqui	Alternative	Bread
10. Patagua	Alternative	Bread
11. Perquenco	Alternative	Bread
12. Peumo	Alternative	Bread
13. Quillay	Alternative	Bread
14. Candela	Winter	Bread
15. Laurel	Winter	Bread
16. Lautaro	Winter	Bread
17. Chagual	Spring	Durum
18. Chonta	Spring	Durum
19. Licán	Spring	Durum

The plants were harvested at 12 weeks after planting by cutting the plant material above the ground. After sample preparation the ^{32}P activity was measured using the Cerenkov effect in a Liquid scintillation counter Beckman 5000 TD and total P was determined by colorimetry with a spectrophotometer Spectronic 20.

The calculation of the isotopic parameters was done according to Zapata and Axmann (1991) [14]. Physiological utilization of P efficiency (g dry matter/mg P^{-1}) was also calculated. The agronomic evaluation of genotypes with reference to their P uptake from Bahia Inglesa PR compared to TSP was made using the substitution ratio in terms of kg P as PR equivalent to 1 kg P as TSP [13].

2.2. Experiment II

This experiment was a follow-up study to confirm the results of the first experiment and to get an insight on the rooting characteristics of the genotypes [15, 16].

The soil utilized was Santa Barbara soil series (Typic Haploxerand), which had a higher P retention capacity [17]. The number of genotypes under study was limited to twelve (Table II). The ^{32}P labeled triple superphosphate was applied at a lower rate of 250 mg P kg^{-1} soil. The experiment included 24 treatments comprised of a factorial of 12 genotypes and two P fertilizers. Each treatment was replicated 5 times. Two replicates of each treatment were sown without ^{32}P addition for studies on root biomass and P content.

Harvest was performed at heading stage, which occurred 125 days after planting on average. The precise time was variable for the cultivars, depending on their growth cycle. Other procedures were similar to those described for experiment I.

TABLE II. SELECTED WHEAT CULTIVARS UTILIZED IN EXPERIMENT II

Cultivar	Growth cycle	Wheat type
1. Lilén	Spring, early	Bread
2. Nobo	Spring, early	Bread
3. Reihue	Spring, early	Bread
4. Saeta	Spring, early	Bread
5. Maqui	Alternative, early	Bread
6. Canelo	Alternative, early	Bread
7. Perquenco	Alternative, normal	Bread
8. Peumo	Alternative, normal	Bread
9. Lautaro	Winter, early	Bread
10. Chagual	Spring, normal	Durum
11. Chonta	Spring, early	Durum
12. Licán	Spring, early	Durum

3. RESULTS AND DISCUSSION

3.1. Experiment I

Significant differences among the genotypes were obtained for the agronomic assessments (dry matter yield and total P uptake) and the isotopic parameters [12]. Considering the dry matter and P uptake the spring and alternative flour wheat cultivars were more efficient than the summer and winter wheat ones for both P fertilizer treatments. The PR treatments showed lower dry matter and P uptake data than the TSP treatments (Data not shown).

The isotopic parameter Pdff (Phosphorus in the plant derived from the fertilizer) that is yield-independent was the most sensitive criterion to assess differences among the genotypes. For the treatment with TSP, the Pdff data are shown in Table III. The values ranged from 64.4 to 74.7%. The spring and alternative cultivars showed the highest values while the summer types had the lowest values and the winter ones were intermediate. For the treatment with Bahia Inglesa phosphate rock, the Pdfr (Phosphorus in the plant derived from the rock) showed large differences between genotypes. The values ranged from 9.7 to 42.4% with no particular cultivar type able to predict performance (Fig.1).

TABLE III. PHOSPHORUS IN THE PLANT DERIVED FROM THE ^{32}P-LABELLED TSP (Pdff). (EXPERIMENT I)

Genotype	Pdff (%)
Spring, bread	
1. Cisne	73.0 c
2. Lilén	73.7 c
3. Nobo	74.4 d
4. Reihue	73.7 c
5. Talhuén	69.9 b
6. Onda	74.7 d
Alternative, bread	
7. Saeta	71.3 b
8. Canelo	73.4 c
9. Maqui	74.2 d
10. Patagua	74.1 d
11. Perquenco	68.8 ab
12. Peumo	64.5 a
13. Quillay	66.6 ab
Winter, bread	
14. Candela	67.5 ab
15. Laurel	68.3 ab
16. Lautaro	64.4 a
Spring, hard (durum)	
17. Chagual	64.5 a
18. Chonta	64.5 a
19. Licán	65.6 a

Means followed by the same letter are not significantly different at $P < 0.05$.

These differences can be attributed to several factors including differences in root system morphology and root hair density [10], and more important to the specific rhizhosphere effects such as the root exudates, that may play a role in several mechanisms leading to an increase in P acquisition [9, 18]. These root-soil interactions may have contributed to an enhanced utilization of P from the phosphate rock in the Pemehue soil.

Combining the isotopic data, the agronomic evaluation of the PR compared to superphosphate was calculated (kg P as PR equivalent to 1 kg P as TSP) for the genotypes. The genotypes have been grouped arbitrarily in four efficiency classes based on these values (Table IV). In the Pemehue Andisol, a five-fold difference was found between contrasting genotypes. One kg P as TSP was equivalent to2 kg P as PR for the most efficient genotypes and more than 10 kg P as PR for the less efficient ones.

TABLE IV. AGRONOMIC EFFECTIVENESS OF WHEAT CULTIVARS GENOTYPES GROWN IN THE PEMEHUE ANDISOL (EXPERIMENT I)

Wheat cultivars (Type, name)	Agronomic evaluation kg P as PR equivalent to 1 kg P as TSP	Efficiency class
Spring, bread		
1.Cisne	2.4 a	High
2.Lilén	2.1 a	High
3.Nobo	3.4 b	Medium
4.Reihue	5.0 b	Medium
5.Talhuén	7.4 e	Low
6.Onda	3.9 b	Medium
7.Saeta	5.9 d	Low
Alternative, bread		
8.Canelo	3.7 b	Medium
9.Maqui	4.8 c	Medium
10.Patagua	4.2 c	Medium
11.Perquenco	12.8 f	Very Low
12.Peumo	4.1 c	Medium
13.Quillay	5.6 d	Low
Winter, bread		
14.Candela	6.6 d	Low
15.Laurel	5.5 d	Low
16.Lautaro	3.7 b	Medium
Spring hard (durum)		
17.Chagual	8.7 e	Very Low
18.Chonta	3.8 b	Medium
19.Licán	4.9 c	Medium

Means followed by the same letter are not significantly different at $P< 0.05$.

3.2. Experiment II

In this experiment, the dry matter and P uptake were recorded separately for roots and tops [15]. Although there were some significant differences among the genotypes, the magnitude of the response was lower due to the higher extractable Al [15] and very high P retention of the Santa Barbara Andisol. The spring and summer cultivars were the most efficient in terms of physiological efficiency (g dry matter mg P^{-1}). Besides, the cultivars that showed the highest dry matter yield were not necessarily the most efficient in utilization of the absorbed P. It should be noted that growth cycle of the genotypes contrasted greatly among them varying from 105 to 180 days. Thus, large differences in total P requirements of the cultivars were expected as well as in their demand with time. Differences between wheat cultivars in P acquisition and utilization were related to reduced sensitivity to P deficiency in formation of the yield components such as flower initiation and grain setting [19]. Also, the plants have different mechanisms to access to poorly available soil phosphorus [8, 10].

The Pdff in the TSP treatment are shown in Table V. They were, on the average 70-75 % for most of the genotypes with no significant differences among them. The highest (88.6%) and the lowest (57.9%) values corresponded to two genotypes of the alternative type. The PR showed very low effectiveness as demonstrated by the Pdfr values. They ranged from 0.9 to 19.6% (Fig. 2). These values are much lower than the ones reported in the experiment I, confirming the higher P retention of this soil, thus affecting to a greater extent the availability of P to the plants [17]. Nevertheless, significant differences were observed among the genotypes. The summer cultivars were the best genotypes and the worst werethe alternative ones.

Table VI shows the data from the agronomic evaluation. Much higher values are required in the Santa Barbara Andisol to replace 1 kg P as TSP than the ones previously reported for experiment I, with significant differences for the genotypes under study.

TABLE V. PHOSPHORUS IN THE PLANT DERIVED FROM THE ^{32}P-LABELLED TSP (Pdff). EXPERIMENT II

Genotypes	Pdff (%)
Spring, bread	
1.Lilén	71.1 b
2.Nobo	71.2 b
3.Reihue	73.0 b
4.Saeta	73.1 b
Alternative, bread	
5.Maqui	72.6 b
6.Canelo	88.6 a
7.Perquenco	74.8 b
8.Peumo	57.9 c
Winter, bread	
9.Lautaro	72.8 b
Spring, durum	
10.Chagual	74.7 b
11.Chonta	70.8 b
12.Licán	71.6 b

Means followed by the same letter are not significantly different at P<0.05.

TABLE VI. AGRONOMIC EVALUATION OF WHEAT CULTIVARS GROWN IN THE SANTA BARBARA ANDISOL EXPERIMENT II

Wheat cultivars	Agronomic evaluation kg P as PR equivalent to 1 kg P as TSP	Efficiency class
Spring, bread		
1.Lilén	126.3 a	Very low
2.Nobo	34.8 cd	Low
3.Reihue	108.6 a	Very low
4.Saeta	19.4 d	Medium
Alternative, bread		
5.Maqui	291.6 a	Very low
6.Canelo	99.6 b	Low
7.Perquenco	329.0 a	Very low
8.Peumo	10.2 e	High
Winter, bread		
9. Lautaro	64.3 b	Low
Spring, durum		
10.Chagual	35.5 cd	Low
11.Chonta	15.7 de	Medium
12.Licán	11.8 e	High

Means followed by the same letter are not significantly different at P< 0.05.

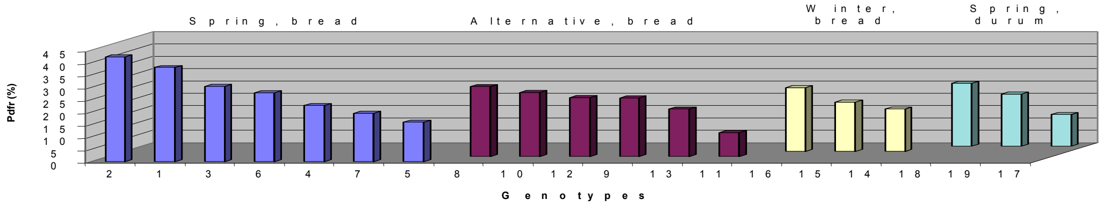

Fig.1. Phosphorus in the plant derived from the rock (Pdfr)in Chilean wheat genotypes. Experiment I

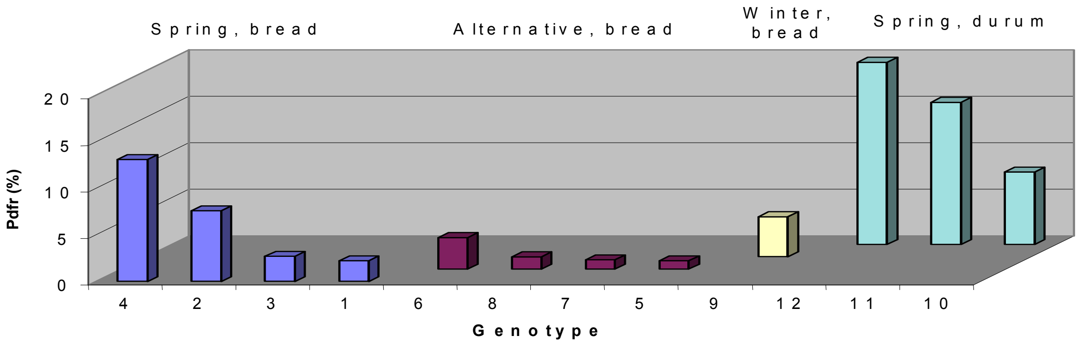

Fig.2. Phosphorus in the plant derived from the rock (Pdfr) in selected wheat genotypes. Experiment II.

4. CONCLUSIONS

From these preliminary studies it was found that there was significant genetic variation in P uptake efficiency in wheat genotypes of Chile. The utilization of the ^{32}P isotopic technique enabled a quantitative measurement of the P taken up from the P fertilizer thus allowing the assessment of differences among the tested genotypes. Significant genotypic differences were obtained in the P uptake from the local phosphate rock Bahia Inglesa. Much higher P applications were required in the high P-fixing Santa Barbara Andisol. A sustainable strategy for agricultural production in the Andisols of Chile would, therefore, be the combined utilization of those P-efficient genotypes and the local phosphate rock Bahia Inglesa. As P efficiency is a multi-faceted trait, which interacts with a range of environmental factors, further field experiments and validation are required accompanied by in depth studies to assess the relative importance of the morphological and physiological traits determining a better P efficiency.

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REFERENCES

[1] TOSSO, J., (Ed.), Suelos volcánicos de Chile. Instituto de Investigaciones Agropecuarias. Ministerio de Agricultura. Santiago, Chile (1985).

[2] CARRASCO, A., OPAZO, J., Predicción de parámetros de respuesta al P de las plantas en función de algunas propiedades químicas en suelos Ultisols y Andisols del Sur de Chile. Agricultura Técnica (Chile) **55** (1995) (3-4): 243-250.

[3] PINO, I., CASAS, L., Evaluación agronómica de la roca fosfórica de Bahía Inglesa con utilización de técnicas isotópicas. II. Efecto de la aplicación de tres suelos derivados de cenizas volcánicas en condiciones de invernadero. Nucleotécnica **9** (16) (1989) 37-40.

[4] PINO, I., BUNEDER, M., PARADA, A.M., Métodos isotópicos en la evaluación de roca fosfórica en condiciones de invernadero. In: Primer Seminario Nacional sobre Uso de Rocas Fosfóricas en Agricultura. Instituto Nacional de Investigaciones Agropecuarias, Serie Carillanca No. **29**, Chile (1992) 191-200.

[5] PINO, I., MONTENEGRO, A., BUNEDER, M., RODRIGUEZ, N. Evaluación agronómica de la fosforita de Bahia Inglesa mediante técnicas isotópicas. Nucleotécnica 14(26) (1994) 53-57.

[6] HELYAR, K.R., Efficiency of nutrient utilization and sustaining soil fertility with particular reference to phosphorus. Field Crops Res. **56** (1998): 187-195.

[7] BALIGAR, V.C., DUNCAN, R.R., Crops as enhancers of nutrient use. Academic Press, Inc. San Diego. USA (1990).

[8] SATTELMACHER, B., HORST, W.J., BECKER, H.C., Factors that contribute to genetic variation for nutrient efficiency of crop plants. Z. Pflanzenernaehr. Bodenk. **157**(1994) 215-224.

[9] HOCKING, P.J., KEERTHISINGHE, G., SMITH, F.W., RANDALL, P.J., Comparison of the ability of different crop species to access poorly available soil phosphorus. In: T. Ando et al. (eds). Plant Nutrition for sustainable food production and environment. Kluwer Academic Publishers, Japan, (1997) 305-308.

[10] RANDALL, P.J., Genotypic differences in phosphate uptake. In: Genetic Manipulation of Crop Plants to Enhance Integrated Nutrient Management in Cropping Systems. I. Phosphorus: Proc. of an FAO/ICRISAT Expert Consultancy Workshop. Eds. C. Johansen, K.K.Lee, K.K. Sharma, G.V. Subbarao, and E.A. Kueneman, (1995), 31-47. International Crops Research Institute for the Semi-Arid Tropics, Patancheru, Andra Pradesh, India.

[11] RAMIREZ, I., CORTAZAR, R., RIVERO, F., MORENO, O., HACKE, E., GRANGER, D., Clasificación de genotipos de trigo. Agricultura Técnica (Chile) **50**(1990) 400-411.

[12] ZAPATA, F., PINO, I., BAHERLE, P., PARADA, A.M., Estudio comparativo de la eficiencia de uso y absorción de fósforo, a partir de fertilizantes fosfóricos, por genotipos chilenos de trigo. Terra **14** (3) (1996) 325-330.

[13] ZAPATA, F., Isotope techniques in soil fertility and plant nutrition studies. In: Hardarson, G. (ed). Use of Nuclear Techniques in Studies of Soil-Plant Relationships. IAEA Training Course Series No.2. IAEA, Vienna, Austria, (1990) 61-128.

[14] ZAPATA, F., AXMANN, H., Agronomic evaluation test of rock phosphate by means of radioisotope techniques. Pedologie XLI-3 (1991) 291-301.

[15] NAVIA, M., PINO, I., LUZIO, W., PARADA, A.M., Eficiencia agronómica de superfosfato triple y roca fosfórica en variedades de trigo utilizando el método de dilución isotópica. I. Parámetros agronómicos. Terra. **15** (1) (1997a) 15-20.

[16] NAVIA, M., PINO, I., LUZIO, W., PARADA, A.M., Eficiencia agronómica de superfosfato triple y roca fosfórica en variedades de trigo utilizando el método de dilución isotópica. II. Parámetros isotópicos. Terra. **15** (1) (1997b) 21-27.

[17] ZAPATA, F., CASANOVA, E., SALAS, A.M., PINO, I., Dynamics of phosphorus in soils and phosphate fertilizer management in different cropping systems through the use of isotope techniques. In: Trans. 15th World Congress of Soil Science, Acapulco, Mexico (1994),Vol. **5a**, Commission IV: Symposia, Int. Soc. Soil Science, Mexico 451-456.

[18] JONES, D.L., Organic acids in the rhizosphere-a critical review. Plant and Soil. **205**(1998), 25- 44.

[19] HORST, W.J., ABDOU, M., WIESLER, F. Differences between wheat cultivars in acquisition and utilization of phosphorus. Z. Pflanzenernaehr. Bodenk. **159**(1996), 155-161.

PHOSPHORUS DYNAMICS OF REPRESENTATIVE VOLCANIC ASH SOILS THROUGH THE USE OF CONVENTIONAL AND ISOTOPIC TECHNIQUES

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Abstract. In Chile, the total extension covered by volcanic ash soils including recent and old volcanic deposits is around 5,244,400 ha. This study was carried out in "La Araucanía and Los Lagos " regions (IX and X Regions of Chile respectively), which cover approximately 2,350,000 ha. The main chemical characteristics of these soils are: very low available P (Olsen); a high P retention capacity and a high quantity of aluminum (Al) associated to a high amount of short-range order minerals. The main objective of this study was the characterization of the P dynamics of representative volcanic soils through the use of conventional and isotopic techniques. In the X Region (Los Lagos) of Chile samples from the arable layer (0-20 cm) of eleven soils (Ultisols and Andisols) were collected. Four entire soil profiles were sampled in the IX Region (Araucanía). The characterization of soils was made utuilising conventional and isotopic analyses. The P retention was over 85% in all soils, except for the Metrenco soil series (Paleudult). Nevertheless, the P retention of this soil, from 72% to 79% can be also considered high for a non-volcanic ash soil. In the same way, the Al+1/2 Fe (ox) in all profiles showed high values for non-volcanic ash soils. These results indicate the great difficulty in increasing the available P in these soils, even when high rates of phosphate fertilizers are applied. The principal P-limiting factor in both regions was the P intensity factor.

1. INTRODUCTION

In Chile the total surface covered by volcanic ash Solís, including recent and old volcanic deposits, is around 5,244,400 ha. This study was carried out in "La Araucanía and Los Lagos" regions with a surface of approximately 2,350,000 ha. Therefore, this study was conducted on land surface representing 45% of the total volcanic ash soils in both Regions.

Crops, pastures and forestry are the main land uses in these volcanic soils for both regions. The principal chemical characteristics of the soils are: very low available P (Olsen); a high P retention capacity and a high quantity of aluminum (Al) associated to a high amount of short-range order minerals.

The farmers apply high rates of water-soluble phosphate such as triple superphosphate (TSP) but more recently the consumption of rock phosphate from a local deposit (Bahía Inglesa) has increased for direct application. It is, therefore, important to gather knowledge on the dynamics of soil P when these soils are treated either with water-soluble and insoluble P sources for providing recommendations of the best management practices of P fertilization.

The main objective of this study was therefore, to perform the characterization of P dynamics of representative volcanic soils through the use of conventional and isotopic techniques.

2. MATERIALS AND METHODS

In the X Region (Los Lagos) of Chile samples from the arable layer (0-20 cm) of eleven soils (Ultisols and Andisols) were collected whereas four entire soil profiles were sampled in the IX Region (Araucanía).

The characterization of soils included conventional analyses such as available P (Olsen, North Carolina and Pi methods), P retention (Blakemore), organic carbon (OC), Total N, pH, C/N, Al, Fe and Si (oxalate acid), micronutrients [1] and biomass N and C [2].

The isotopic analysis was made using Fardeau's methodology [3, 4] in order to describe the soil P status by the quantity, capacity and intensity factors and determine the different P pools and kinetic parameters.

The soils were shaken up to equilibrium and then a labeled solution of ^{32}P was added. The analysis was made at two sampling times, 1 and 10 min [3, 4, 5]. The green malachite method [6] was used to measure the concentration of P in the soil solution and the liquid scintillation method with a Beckman counter LS 5000 was used to measure the initial and the final radioactivity.

The Quantity, Intensity and Capacity factors and also the kinetic parameters Fm, Km and Tm were estimated [7, 3, 5]. Values less than 0.02 mg P L^{-1} for the Intensity factor were considered as limiting for crops. In the same way, the values between 0.07 and 2.4 mg P kg^{-1} obtained for Quantity factor were also considered limiting for crops [7, 5].

TABLE I. CHARACTERIZATION OF SOILS FROM REGION IX OF CHILE

Soil	Depth	*pH*	*pH*	*Db*	*Al*	*Fe*	*Si*	*Al+1/2Fe*
	cm	H_2O	$CaCl_2$	Mgm^{-3}	*%*	*%*	*%*	*%*
Quiripio HAPLUDAND								
H-A1	0- 13	5.3	4.8	0.93	4.4	1.6	1.6	5.2
H-A2	13- 28	5.6	4.9	0.94	4.7	1.7	1.7	5.5
H-B1	28- 48	5.5	5.1	0.65	6.7	2.3	2.6	7.9
H-B2	48-170	5.2	5.1	0.79	7.2	2.2	3.5	8.3
Metrenco PALEUDULT								
H-A1	0- 9	5.7	5.1	1.21	0.7	0.7	0.1	1.0
H-A2	9- 24	5.4	4.7	1.29	0.7	0.9	0.1	1.2
H-B1	24- 52	5.3	4.6	1.39	0.8	1.2	0.1	1.4
H-B2	52- 73	5.3	4.4	1.44	0.6	1.1	0.1	1.2
H-B2T	73-180	5.2	4.3	1.35	0.5	0.6	0.1	0.8
Pto. Dominguez FULVUDAND								
H-A1	0 - 5	5.5	5.1	0.69	3.1	1.4	0.1	3.8
H-A2	5 - 11	5.3	4.6	0.80	3.6	1.5	1.2	4.4
H-A3	11- 24	5.3	4.7	0.88	4.3	2.0	1.7	5.3
H-B1	24- 37	5.2	4.8	0.74	4.8	2.6	2.1	6.1
H-B2	37- 69	5.4	5.1	0.72	5.7	3.0	2.6	7.2
H-B3	69-110	5.7	5.4	0.92	5.2	3.0	2.6	6.7
Los Prados MELANUDAND								
H-A	0- 45	5.3	4.6	0.68	4.6	2.1	1.4	5.6
H-B1	45-106	5.6	5.0	0.56	6.3	2.7	2.3	7.7
H-B2	106-120	5.6	5.0	0.51	6.6	2.8	2.3	8.0

TABLE II. CHARACTERIZATION OF SOILS FROM REGION IX OF CHILE (CONT.)

Soil	*Depth*	OM	*OC*	*Total N*	*C/N*	*Biomas-N*	*Biomas-C*	*C/N*
	cm	*%*	*%*	*%*		*ugN/g soil*	*ugC/g soil*	*biomass*
Quiripio HAPLUDAND								
H-A1	0- 13	36.9	18.5	1.0	19	97	1856	19
H-A2	13- 28	31.1	15.6	0.7	22	94	1878	20
H-B1	28- 48	21.6	10.8	0.2	54	56	1538	28
H-B2	48-170	7.4	3.7	0.3	12	28	526	19
Metrenco PALEUDULT								
H-A1	0- 9	21.4	10.7	0.5	21	75	768	10
H-A2	9- 24	13.3	6.6	0.3	22	-	-	-
H-B1	24- 52	7	3.5	0.2	18	33	607	18
H-B2	52- 73	4.4	2.2	0.1	22	-	-	-
H-B2T	73-180	1.2	0.6	0.1	6	-	-	-
Pto. Dominguez FULVUDAND								
H-A1	0 - 5	39.5	19.8	0.7	28	84	1186	14
H-A2	5 – 11	15.8	7.9	0.5	16	53	1028	19
H-A3	11- 24	8.7	4.4	0.3	15	33	663	20
H-B1	24- 37	7.7	3.9	0.2	20	19	768	40
H-B2	37- 69	9.7	4.9	0.2	25	10	782	78
H-B3	69-110	4.3	2.1	0.2	11	17	655	39
Los Prados MELANUDAND								
H-A	0- 45	38.4	19.2	0.9	21	112	1420	13
H-B1	45-106	25.8	12.9	0.7	18	19	535	28
H-B2	106-120	26.8	13.4	0.6	22	29	832	29

3. RESULTS AND DISCUSSION.

3.1. Soils from the IX Region, La Araucanía

Tables I and II contain some chemical characteristics of soils from Region IX. All soils are acid (pH between 5.2 to 5.7). The Andisols had lower bulk density (*Db*) in comparison with the Ultisols (Metrenco Soil Series). Also, the Al and Fe (oxalate) are higher in Andisols than in Ultisols (Table I).

In most soils, Organic C levels are very high (Table II). Organic C content is especially high in the surface horizons decreasing with depth, except for the soil series Los Prados (Acrudoxic Melanudand). In the soil series Los Prados, the total N was very low and C/N ratio was very high. The same was observed for biomass N and C. It means that the high summer temperatures and showers duringthe sampling time promoted a very high microbial activity and consequently high oxygen consumption.

The characterization of soil P is presented in Table III. The available P (Olsen and Carolina methods) is very low in all soils. P retention was over 85% in all soils, except for soil series Metrenco (Paleudult). Nevertheless, P retention, from 72% to 79% of this soil can be considered very high figures for non-volcanic ash soils. Also, the Al+1/2 Fe (ox) in all profiles showed high values for non-volcanic ash soils. These data confirm the extensive and deep coverage of volcanic ashes that have been gradually added to the soils in this region.

TABLE III. CHARACTERIZATION OF SOILS FROM REGION IX IN CHILE

Soil	Depth	*Olsen P*	*Carolina P*	*P Retention*	*Total P*
	cm	*ppm*	*ppm*	*%*	*ppm*
Quiripio HAPLUDAND					
H-A1	0- 13	<1	2.44	97	1350
H-A2	13- 28	<1	1.34	97	1275
H-B1	28- 48	<1	0.64	99	1163
H-B2	48-170	<1	0.50	99	680
Metrenco PALEUDULT					
H-A1	0- 9	<1	9.45	72	608
H-A2	9- 24	<1	6.33	75	461
H-B1	24- 52	<1	3.67	77	229
H-B2	52- 73	<1	2.61	79	162
H-B2T	73-180	<1	2.55	76	149
Pto. Dominguez FULVUDAND					
H-A1	0 - 5	<1	6.44	91	1155
H-A2	5 - 11	<1	6.13	95	1133
H-A3	11- 24	<1	1.13	98	689
H-B1	24- 37	<1	0.71	98	673
H-B2	37- 69	<1	0.62	98	656
H-B3	69-110	<1	0.54	99	672
Los Prados MELANUDAND					
H-A	0- 45	<1	0.92	97	1610
H-B1	45-106	<1	0.16	99	1801
H-B2	106-120	<1	0.32	99	1871

The soil series Metrenco showed high amounts of Cu and Mn (Table IV). The exchangeable bases (Table V) are higher in the surface horizon of the soil series Quiripio (Hapludand), Metrenco and Puerto Dominguez (Fulvudand) with a highest value in the A_1 horizon of the soil series Puerto Dominguez.

The soil series Los Prados is very poor in exchangeable bases in the whole profile. Therefore, Los Prados have a great limitation in supporting plant growth not only because of high P retention but also its low base saturation.

The Cp values are very low in soil series Los Prados and the E_1 value is low in most of the soils in the surface horizon. Also the values r_i/R are very low indicating high fixation capacity (Table VI).

The pool A (Table VII) is low in the surface horizon and increases with depth. In the first surafe horizon (0-10 cm) the pool D is the greatest but it decreases with depth. If these soils were not P-fertilized, it would be difficult to grow crops or forest trees.

3.2. Soils from the X Region

The surface samples (0-20 cm) collected from ten representative volcanic ash soils of the X Region were classified according to the Soil Taxonomy [8], as shown in Table VIII.

TABLE IV. CHARACTERIZATION OF SOILS FROM REGION IX IN CHILE

Soil	Depth	*Fe*	*Cu*	*Zn*	*Mn*	*Ni*	*Cd*
	cm	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*
Quiripio HAPLUDAND							
H-A1	0- 13	88	1.6	2.4	22	< 0.4	< 0.2
H-A2	13- 28	67	1.6	< 0.1	19	< 0.4	< 0.2
H-B1	28- 48	44	0.4	< 0.1	4.1	< 0.4	< 0.2
H-B2	48-170	19	< 0.2	< 0.1	0.5	< 0.4	< 0.2
Metrenco PALEUDULT							
H-A1	0- 9	55	3.1	< 0.1	47	< 0.4	< 0.2
H-A2	9- 24	54	3.2	< 0.1	44	< 0.4	< 0.2
H-B1	24- 52	34	1.8	< 0.1	26	< 0.4	< 0.2
H-B2	52- 73	17.2	0.5	< 0.1	4.4	< 0.4	< 0.2
H-B2T	73-180	7.4	< 0.2	< 0.1	< 0,2	< 0.4	< 0.2
Pto. Dominguez FULVUDAND							
H-A1	0 - 5	92	1.6	< 0.1	92	< 0.4	< 0.2
H-A2	5 - 11	47	2.0	< 0.1	23	< 0.4	< 0.2
H-A3	11- 24	27	0.4	< 0.1	3.2	< 0.4	< 0.2
H-B1	24- 37	15	< 0.2	< 0.1	0.8	< 0.4	< 0.2
H-B2	37- 69	19	< 0.2	< 0.1	1.0	< 0.4	< 0.2
H-B3	69-110	16	< 0.2	< 0.1	0.9	< 0.4	< 0.2
Los Prados MELANUDAND							
H-A	0- 45	74	3.2	< 0,1	8.6	< 0.4	< 0.2
H-B1	45-106	95	2.6	< 0,1	5.4	< 0.4	< 0.2
H-B2	106-120	86	1.3	< 0,1	5.0	< 0.4	< 0.2

The soils were sampled following a line east-west direction and from 1082 masl to 160 masl, starting with a Vitrandic Udorthent with a very low profile development with clear stratification of volcanic materials.

The Huilma Soil Series was sampled under three different soil management conditions, which included Huilma forest vegetation, wheat crop and fallow systems.

The maximum accumulation of OC (Table IX) was found in the Alerce soil (Duric Placaquand) and the minimum OC accumulation in Antillanca soil (Vitrandic Udorthent).

The Ultisols (Fresia and Huilma fallow) under the same land use showed similar amounts of OC. It should be mentioned that the wheat monoculture in Huilma soil produced a decline in the soil OC. Under *Pinus radiata*, by the effect of the permanent vegetal cover and limited erosion, an effective accumulation of OC is observed at least in the surface horizon.

The lowest accumulation of OC was found in the soils with high volcanic glass content (Antillanca and Ralún). Both vitric soils are coarse textured (mostly sandy and gravelly) with a high leaching potential and low water retention. The reaction is strongly acid (pH 5.0) (Table VIII) and P retention (Blakemore) is relatively low due to the small amounts of short-range order minerals. The available P (Olsen) is lowand the OC is low.

TABLE V. CHARACTERIZATION OF SOILS FROM REGION IX IN CHILE

Soil	*Depth*	CEC	*Na*	*K*	*Ca*	*Mg*	*Exch bases*
	cm	*cmol(+)/kg*	*cmol(+)/kg*	*cmol(+)/kg*	*cmol(+)/kg*	*cmol(+)/kg*	*sum*
Quiripio							
HAPLUDAND							
H-A1	0- 13	72.6	0.15	0.89	14.7	3.70	19.4
H-A2	13- 28	54.1	0.09	0.46	9.86	1.76	12.2
H-B1	28- 48	35.5	0.22	0.94	0.43	1.21	2.8
H-B2	48-170	35.9	0.08	0.07	0.59	0.19	0.9
Metrenco							
PALEUDULT							
H-A1	0- 9	40.8	0.13	1.20	13.0	2.91	17.3
H-A2	9- 24	29.2	0.08	0.82	4.97	1.70	7.6
H-B1	24- 52	24.1	0.13	0.23	0.17	1.47	2.0
H-B2	52- 73	24.1	0.17	0.10	1.47	1.37	3.1
H-B2T	73-180	30.4	0.21	0.05	1.37	1.57	3.2
Pto. Dominguez							
FULVUDAND							
H-A1	0 - 5	55.5	0.47	1.14	14.1	5.02	20.7
H-A2	5 - 11	45.4	0.28	0.59	2.08	1.60	4.6
H-A3	11- 24	32.0	0.23	0.78	0.47	0.81	2.3
H-B1	24- 37	35.0	0.24	1.01	0.42	1.17	2.8
H-B2	37- 69	35.3	0.12	1.17	0.49	1.86	3.6
H-B3	69-110	30.7	0.31	1.93	0.63	1.21	4.1
Los Prados							
MELANUDAND							
H-A	0- 45	64.5	0.12	0.18	0.89	0.44	1.6
H-B1	45-106	58.1	0.10	0.04	0.76	0.16	1.1
H-B2	106-120	67.3	0.11	0.03	0.77	0.19	1.1

Although Corte Alto soil series is considered an Andisol, it seems that the volcanic materials have undergonea more intense weathering to such extent that the mineralogy exhibit the presence of halloysite as a common mineral [9].

The Olsen P gave very low values (Table X), which are normal for Andisols. According to the results, *Pinus radiata* vegetation cover does not produce an important alteration in the soil parameters of pH, Olsen P, P retention (Blackmore), total N, OC and C/N.

The retention index is less than 0.2. The inverse relation of the index retention (r_1/R) is very high [4]. This result indicates the great difficulty in increasing the available P in these soíls, even when high rates of phosphate fertilizers are applied. The principal P limiting factor in both regions is the intensity factor (Table XI).

The Cp values are very low (Table XI) and agree with the index retention. The immediately available pool of P was slightly higher in the Huilma soil under fallow than in the other two management systems (Table XII). The A, B and C pools showed a relatively homogeneous distribution. An increase inthe pool D that represents the P inmobilized from former applications was observed.

In the Huilma soil under pines the unique source of P for plants comes from pool D, which will decrease gradually as it is absorbed by plants. In the Huilma soil with wheat, the major part of P is ound inthe pool A coming from the recent application of fertilizers [4].

TABLE VI. ISOTOPIC PARAMETERS OF SOILS FROM REGION IX OF CHILE

Soil	*Depth*	*Cp*	E_1	E_1/Cp	R_1/R	*Km*	*Tm*	*Fm*
	cm	*mgP/L*	*mgP/kg*	*L/kg*		*L/min*	*min*	*mgP/kg min*
Quiripio HAPLUDAND								
H-A1	0- 13	0.0120	4	339	0.030	6.9E+03	1.4E-04	7.7E+02
H-A2	13- 28	0.0109	7	654	0.015	3.1E+04	3.3E-05	3.2E+03
H-B1	28- 48	0.0064	28	4287	0.002	9.8E+09	1.0E-10	5.7E+08
H-B2	48-170	0.0109	57	5167	0.002	3.3E+06	3.0E-07	4.0E+05
Metrenco PALEUDULT								
H-A1	0- 9	0.0186	7	360	0.028	7.6E+03	1.3E-04	1.4E+03
H-A2	9- 24	0.0213	9	429	0.023	9.6E+04	1.0E-05	2.1E+04
H-B1	24- 52	0.0103	40	3907	0.003	1.1E+16	8.9E-17	1.2E+15
H-B2	52- 73	0.0131	131	7106	0.001	1.2E+09	8.1E-10	1.6E+08
H-B2T	73-180	0.0124	62	6260	0.002	1.1E+11	9.3E-12	1.3E+10
Pto. Dominguez FULVUDAND								
H-A1	0 - 5	0.0193	14	728	0.014	-	-	-
H-A2	5 - 11	0.0127	10	766	0.013	2.4E+03	4.2E-04	3.0E+02
H-A3	11- 24	0.0109	32	2920	0.003	4.9E+03	2.1E-04	5.3E+02
H-B1	24- 37	0.0150	55	5144	0.002	1.1E+04	9.4E-05	1.1E+03
H-B2	37- 69	0.0081	34	4154	0.002	3.0E+03	3.3E-04	2.4E+02
H-B3	69-110	0.0102	51	5993	0.002	7.4E+03	1.4E-04	7.5E+02
Los Prados MELANUDAND								
H-A	0- 45	0.0011	1	918	0.011	9.8E+02	1.0E-03	1.1E+01
H-B1	45-106	0.0022	5	2413	0.004	8.5E+02	1.2E-03	1.9E+01
H-B2	106-120	0.0048	27	5666	0.002	1.1E+05	9.1E-06	5.4E+03

TABLE VII. ISOTOPIC PARAMETERS OF SOILS FROM REGION IX OF CHILE (CONT)

Soil	Depth	*Pool A*	*Pool B*	*Pool C*	*Pool D*
	cm	*mg P/kg*	*mg P/kg*	*mg P/kg*	*mg P/kg*
Quiripio HAPLUDAND					
H-A1	0- 13	49	177	111	1009
H-A2	13- 28	93	295	151	729
H-B1	28- 48	141	230	95	669
H-B2	48-170	333	213	30	47
Metrenco PALEUDULT					
H-A1	0- 9	73	183	76	271
H-A2	9- 24	61	118	47	226
H-B1	24- 52	31	36	12	110
H-B2	52- 73	-	-	-	-
H-B2T	73-180	-	-	-	-
Pto. Dominguez FULVUDAND					
H-A1	0 - 5	-	0.3	0.1	1141
H-A2	5 - 11	285	586	11.0	140
H-A3	11- 24	545	104	5.0	3.3
H-B1	24- 37	545	69	2.7	2.0
H-B2	37- 69	570	50	1.4	0.8
H-B3	69-110	567	51	1.6	1.0
Los Prados MELANUDAND					
H-A	0- 45	79	643	332	555
H-B1	45-106	842	895	38	20
H-B2	106-120	647	924	130	144

TABLE VIII. SOIL CLASSIFICATION (KEYS TO SOIL TAXONOMY, 1996) AND CHEMICAL CHARACTERISTICS OF SOIL FROM REGION X OF CHILE

Series	Classification	*pH*	*Al+1/2Fe*
Depth 0- 20cm		H_2O	%
Alerce	Medial isomésica Duric Placaquand	4.6	3.3
Frutillar	Medial isomésica Typic Placaquand	4.7	4.8
Antillanca	Ashy frígida Vitrandic Udorthent	5.0	0.7
Chanleufu	Medial Humic Udivitrand	4.7	0.9
Ralún	Udivitrand	5.1	1.1
Corte Alto	Medial isomésico Typic Hapludand	4.8	3.3
Puerto Fonk	Medial isomésico Pachic Melanudand	5.0	4.6
Puyehue	Medial isomésico Acrudoxic Hapludand	4.8	2.1
Huilma Fallow	Typic Paleudult	5.1	1.6
Huilma Pine	Typic Paleudult	5.0	1.5
Huilma Wheat	Typic Paleudult	5.1	1.4
Fresia	Typic Hapludult	4.7	2.0

TABLE IX. CHARACTERIZATION OF SOILS FROM REGION X OF CHILE

Soil	*OM*	*OC*	*Total N*	*C/N*	*Biomas-N*	*Biomas-C*	*C/N*
Depth 0- 20 cm	*%*	*%*	*%*		*ugN/g soil*	*ugC/g soil*	*biomass*
Alerce	59.4	29.7	1.1	27	-	1487	-
Frutillar	25.8	12.9	0.8	17	433	12252	28
Antillanca	10.1	5.1	0.3	20	165	1253	8
Chanleufu	20.2	10.1	0.3	36	166	2265	14
Ralún	13.2	6.6	0.5	14	77	962	13
Corte Alto	24.8	12.4	0.8	16	89	1137	13
Puerto Fonk	34.4	17.2	0.8	22	107	1343	13
Puyehue	32.6	16.3	0.8	20	96	1001	10
Huilma Fallow	19.2	9.6	0.5	19	872	1291	2
Huilma Pine	23.4	11.7	0.5	23	247	847	3
Huilma Wheat	11.9	5.9	0.3	22	526	1030	2
Fresia	16.0	8.0	0.4	19	749	1541	2

TABLE X. CHARACTERIZATION OF SOILS FROM REGION X OF CHILE

Soil	*Olsen P*	*Carolina P*	*P Retention*	*Total P*
Depth 0- 20 cm	*ppm*	*ppm*	*%*	*ppm*
Alerce	4.2	5.2	98	1330
Frutillar	9.1	14.6	99	1805
Antillanca	4.4	9.6	56	430
Chanleufu	5.4	7.1	75	477
Ralún	4.6	14	73	766
Corte Alto	5.7	9.2	96	2219
Puerto Fonk	5.4	5.8	95	1648
Puyehue	4.6	7.9	96	1077
Huilma Fallow	5.8	5.6	93	1470
Huilma Pine	25.8	27.4	83	998
Huilma Wheat	19.3	10.0	87	1353
Fresia	1.3	2.3	90	1179

TABLE XI. ISOTOPIC PARAMETERS OF SOILS FROM REGION X OF CHILE

Soil	*Cp*	E_1	E_1/Cp	r_1/R
Depth 0-20 cm	*mg P /L*	*mg P/kg*	*L/kg*	
Alerce	0.0013	0.31	240	0.0417
Frutillar	0.0020	2.40	1176	0.0085
Antillanca	0.0015	0.17	115	0.0869
Chanleufu	0.0011	0.07	68	0.1473
Ralún	0.0017	0.11	63	0.1583
Corte Alto	0.0015	1.26	861	0.0116
Puerto Fonk	0.0018	0.95	530	0.0189
Puyehue	0.0020	0.67	331	0.0302
Huilma Fallow	0.0020	1.23	618	0.0162
Huilma Pine	0.0016	0.34	217	0.0460
Huilma Wheat	0.0018	0.21	121	0.0828
Fresia	0.0019	0.20	102	0.0978

TABLE XII. ISOTOPIC PARAMETERS OF SOILS FROM REGION X OF CHILE (CONT.)

Soil	*Pool A*	*Pool B*	*Pool C*	*Pool D*
Depth 0-20 cm	*mg P/kg*	*mg P/kg*	*mg P/kg*	*Mg P/kg*
Alerce	23	260	227	820
Frutillar	79	458	285	981
Antillanca	16	154	92	168
Chanleufu	8	107	94	268
Ralún	38	471	149	108
Corte Alto	87	736	446	949
Puerto Fonk	46	364	269	968
Puyehue	32	253	180	612
Huilma Fallow	41	268	198	962
Huilma Pine	5	24	19	950
Huilma Wheat	1211	141	0.25	0.02
Fresia	94	857	148	80

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REFERENCES

[1] SADZAWKA, M.A., Métodos de análisis de suelos. Instituto de Investigaciones Agropecuarias (Chile) Est. Exp. La Platina (Santiago). Serie La Platina N° 16. (1990), 130 p.

[2] BROOKES P.C., LANDMAN A., PRUDEN G., JENKINSON D.S., Chloroform Fumigation and the Release of Soil Nitrogen: A Rapid Direct Extraction Method To Measure Microbial Biomass Nitrogen in Soil. Soil Biol. Biol.Biochem. Vol.**17**, N°6, (1985) 837-842.

[3] FARDEAU, J.C., GUIRAUD, G., MAROL, C., Bioavailable soil P as a key to sustainable agriculture. In: Proceedings of a symposium "Nuclear techniques in soil-plant studies for sustainable agriculture and environmental preservation" IAEA. STI/PUB/947(1995),131-144.

[4] FARDEAU, J.C., P-32 isotopic exchange kinetics. Experimental procedure, interpretation of results. Application to the prediction of the efficiency of P fertilizers. Working paper presented at the Third Research Coordination Meeting of the FAO/IAEA Coordinated Research Project "The use of nuclear and related techniques for evaluating the Agronomic Efectiveness of Phosphatic fertilizers, in particular Rock Phosphate" (1997). Report D1-RC-542.3.

[5] FARDEAU, J.C., Dynamics of phosphate in soils. An isotopic outlook. Fertilizer Research **45** (1996), 91-100.

[6] NOVOZAMSKY, I., VAN DIJK, D., LEE, J.J., HOUBA, V.J.G., Automated determination of trace amounts of phosphate in soil extracts using malachite green. Commun. Soil Sci. Plant Anal. **24** (9&10) (1993) 1065-1077.

[7] FARDEAU, J.C., Le phosphore assimilable des sols: sa representation par un modele fonctionnel a plusiers compartiments. Agronomie **13** (1993), 317-331.

[8] SOIL SURVEY STAFF, Keys to Soil Taxonomy. 7th edition. Natural Resources Conservation Service. USDA. (1996). 644 p.

[9] BEINROTH, F H., LUZIO, W., MALDONADO, F., ESWARAN, H., Proceeding of the Sixth International Soil Classification Workshop, Chile and Ecuador. Part II. (1985), 236.

STUDIES ON P AVAILABILITY OF VOLCANIC ASH SOILS FROM CHILE AMENDED WITH VARIOUS P FERTILIZERS

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Abstract. A high P retention capacity and a low P availability to plants characterize the volcanic ash soils from Chile. For this reason, the purpose of this incubation study was to compare different extraction methods, P sorption, and estimations of the agronomic efficiencies of different fertilizers in these soils. In order to study the agronomic effectiveness of rock phosphates and their suitability for direct application, ^{32}P was used for assessing the bioavailability of P and the efficiency in rock phosphate materials. Incubation experiments were carried out to measure the soil parameters of Intensity, Quantity and Capacity. Triple superphosphate (TSP, 20% P) was applied to the soil in granular form, whereas local Bahia Inglesa PR (7.68% P) was added as powder. These Chilean soils have a very high P fixing capacity with maximum P adsorption values greater than 1000 mg P/kg soil. Moreover these soils also exhibit higher fixation strength compared to the Venezuelan soils. In relation to isotopic exchangeable P, (E value), the Chilean soils have a low value of isotopic exchangeable P without added P. There is a progressive increase in E value, under increasing P fertilizer rates, particularly at 500 ppm P and above. The P application as PR or TSP did not reduce the P retention capacity of the Perquenco soil. Nevertheless, it exists a positive effect when the P sources are applied as mixtures, which induces a decrease in the P retention percentage. Available P in this soil increased from 3.6 ppm P for the check to a maximum of 20 ppm P for the highest TSP rates, reaching medium to high values according to the extraction methodology used.

1. INTRODUCTION

A high P retention capacity and low P availability for plants are the main characteristics of the volcanic ash soils from Chile. The rational and economic utilization of P fertilizers requires an accurate determination of the available soil P to assess soil P status and formulate the best P fertilizer recommendations. It is essential to gather knowledge on the changes of available P when amended with P fertilizers. For this reason, the purpose of these incubation studies was to compare different extraction methods to determine available P, P sorption capacity, and to estimate the agronomic efficiencies of different P fertilizers applied to these soils. In order to study the agronomic effectiveness of rock phosphates and their suitability for direct application, ^{32}P was used to measure the soil P parameters of Intensity, Quantity and Capacity for assessing P bioavailability and the efficiency of rock phosphate materials.

2. MATERIALS AND METHODS

2.1. Experiment 1: Comparison of extractable P and P retention methods

Three methodologies were used to determine which protocol provides the best estimation of available P and which is its best correlation coefficient between the extractable P methods. Olsen, North Carolina and Bray 1 methods [1] were used to define the available phosphorus (P) in some Chilean soils (Nueva Braunau, Fresia, Frutillar, Huilma and Osorno from X Region) and Venezuelan soils (El Pao, Chaguaramas, El Tigre and Yaritagua). The soil characteristics are described in Pino, et al [3], and Mella and Kuhne [4]. Also the P adsorption capacity according Langmuir [2] was determined in Nueva Braunau, Frutillar, Osorno and Yaritagua soils. The pH (H_2O, 1:2.5) was also measured in the soils studied.

2.2. Experiment 2: Incubation study

This incubation study was designed to estimate the agronomic efficiency of phosphate rock, triple superphosphate and a mixture of both. In this experiment Triple Superphosphate (TSP) at rates of 100 and 250 ppm P and local Bahia Inglesa Phosphoric Rock at 500 and 1000 ppm P (Table I), were added as fertilizer materials. In addition 100 ppm P TSP + 500 ppm PR and 100 ppm P TSP + 1000 ppm PR were included. The TSP (20 %P) was incorporated to the soil in a granular form, whereas the PR (7.68 %P) was applied as powder**.** A sample (50 g) of the Perquenco soil series was incubated with the P fertilizers for 30 days at 25ºC and at about 70% of field capacity. At the end of the incubation period the following parameters were measured: available P (Olsen), P retention (Blakemore) [1] and isotopic parameters [5-9]. The % Reversible P was calculated according the following equation [9-11]:

$$\% \text{ Rev. P} = \text{E value (ppm)/ Fixed P (ppm)}*100$$

The isotopic parameters were determined according to Fardeau's methodology on isotopic exchange kinetics considering times 10 and 100 minutes. The intensity (Cp), quantity (E_1) and capacity (E_1/Cp) parameters were evaluated as well as the fixation index (r_1/R), [12, 13].

TABLE I. TREATMENTS FOR EXPERIMENT 2

T0 = check
T1 = 100 ppm P as TSP
T2 = 250 ppm P as TSP
T3 = 500 ppm P as PR
T4 = 1000 ppm P as PR
T5 = 100 ppm P as TSP + 500 ppm P as PR
T6 = 100 ppm P as TSP + 1000 ppm P as PR

3. RESULTS AND DISCUSSION

3.1. Experiment 1

The results of available P in the soils studied as measured by the chemical extraction methods are presented
in Table II. The correlation coefficients among the methods were 0.68 for Olsen vs N. Carolina, 0.07 for Olsen vs Bray 1, and 0.49 for N. Carolina vs Bray 1. The N. Carolina method characterized in a better way the status of P in the Chilean and Venezuelan soils, which did not happen with the Bray 1 method.

To quantify the P retention in some soils, the Langmuir adsorption model was used and the adsorption strength (K) and the maximum adsorption capacity (B) were measured (Table III). With regard to these para-meters, 3 soils coming from Chile (N. Braunau, Frutillar and Osorno) and one soil coming from Venezuela (Yaritagua) were compared in relation to phosphorus adsorption characteristics (Table III).

The Chilean soils have a very high P fixing capacity with maximum P adsorption values greater than 1000 mg P/kg soil. The Chilean soils also exhibit higher fixing strength compared to the Venezuelan soil. In relation to isotopic exchangeable P, (E value), the Chilean soils have a low value of isotopic exchangeable P without added P (Table IV). There is a progressive increase in E value, under increasing fertilizer rates, particularly at 500 and 1000 ppm P (Table IV).

TABLE II. AVAILABLE P AS MEASURED BY CHEMICAL EXTRACTION METHODS

		Available Phosphorus (mg/kg)		
Soil	PH	Olsen	N. Carolina	Bray 1
N Braunau	4.15	1.94	4.96	0.47
Fresia	4.48	1.29	2.34	---
Frutillar	4.31	8.90	17.38	---
El Pao	4.48	1.94	8.01	6.65
Chaguaramas	5.06	4.63	13.38	11.81
El Tigre	5.03	3.85	15.90	21.90
Huilma Fallow	4.95	5.79	5.55	0.65
Huilma Conifer	4.99	19.28	26.53	13.15
Huilma Wheat	4.98	7.45	9.97	1.02
Osorno	5.46	3.27	4.13	0.28
Yaritagua	6.43	6.26	19.03	8.77

TABLE III. PHOSPHORUS ADSORPTION PARAMETERS

Soil	B (mg P/kg soil)	*K*
Yaritagua	296	0.032
N. Braunau	1505	43.5
Frutillar	1156	14.7
Osorno	2069	0.39

TABLE IV. "E" VALUE (PPM)

	E_1 VALUE (ppm)			
P rate (ppm)	Venezuela Yaritagua soil	Venezuela N. Braunau soil	Chile Osorno soil	Chile Frutillar soil
100	6.6	---	1.58	0.11
250	13.0	---	1.31	1.77
500	18.3	15.4	248	3.53
1000	24.1	54.8	141	21.3
2000	34.0	24.9	173	70.5

In the Nueva Braunau and Frutillar soils, the reversible P (%) with higher P rates reached 5.5 %, while for the Yaritagua soil the reversible P fluctuated between 8% and 12%, according to the P rates applied (Table V).

The Nueva Braunau and Frutillar soils have a very low percentage of reversible P, due to the high P-fixing capacity, (Table VI) facing the Yaritagua soil, which has a progressive increase as the added P rates increased.

TABLE V. REVERSIBLE P (%)

	Reversible P (%)			
P rate (ppm)	Venezuela Yaritagua Soil	Venezuela N. Braunau Soil	Chile Osorno Soil	Chile Frutillar Soil
100	8.33	---	1.58	0.11
250	9.16	---	0.52	0.71
500	9.81	3.07	50.3	0.71
1000	10.5	5.48	13.1	2.13
2000	12.6	1.25	9.1	3.53

TABLE VI. PHOSPHOROUS FIXED (%)

	Fixing P percentage			
P Rate (ppm)	Venezuela Yaritagua Soil	Venezuela N. Braunau Soil	Chile Osorno Soil	Chile Frutillar Soil
100	79.5	100	100	100
250	56.7	100	100	100
500	37.3	100	100	98.5
1000	23.7	99.8	100	98.3
2000	14.0	99.9	100	95.5

3.2. Experiment 2

Table VII shows the change in available P (Olsen method) according to the different treatments. An important increase of available P-Olsen was shown in relation to the check, due to the application of both sources. The highest results were obtained with TSP at the 250 ppm P and the mixture of 100 ppm P as TSP and 1000 ppm P as PR (Table VII).

TABLE VII. OLSEN P AT 30 DAYS OF INCUBATION

P Treatments	Olsen P (ppm)
T0 = 0 ppm P	3.60
T1 = 100 ppm P (TSP)	6.71
T2 = 250 ppm P (TSP)	19.7
T3 = 500 ppm P (PR)	8.15
T4 = 1000 ppm P (PR)	11.5
T5 = 100 TSP + 500 PR	13.8
T6 = 100 TSP + 1000 PR	17.5

In relation to the water-soluble P source (TSP), there is a response according to the applied increasing P rates. This indicated there was a good solubilization of P and thus an increase of available P as the dosis increases.

It is important to mention that the high P fixing capacity of the soil (higher than 70%) may influence the low response to P applications. It is possible that a great part of liberated P, coming from soluble and less soluble sources, could be quickly fixed by the soil and potentially diminishes the response to P application.

The relevance of this assay has to be found not only in the P enrichment in the soil due to the treatments, but also in the contribution of other nutrients like the calcium present in TSP and PR. Obviously, both nutrient improved the general conditions of soil fertility.

The P retention (Blakemore) confirms even more the low available P values obtained by the Olsen method for each one of the treatments. From Table VIII, we may conclude that the soil has a high P retention capacity, and most of the applied P to the soil is quickly fixed. There is no variation between the values coming fromthe soil without fertilizer and the values coming from the soil with P fertilizers. The values between the soil alone and the higher P rates did not show important variations like the case of available P values by the Olsen method for the same treatments. P retention decreases in treatments T2 (250 ppm of P as TSP) and T5and T6, which are mixtures of TSP and PR.

The intensity factor was low for the check treatment, below the 0.02 mg/L that is considered nornmal for plant growth. The Cp values improved significantly with the increasing P rates of application within each source. An increase of Cp was observed as the applied P rates increases, except for T2 treatment (250 ppm of P as TSP) where Cp decreased (Table IX). In relation to Cp values, it increases a little in T1, T2 and T3with regard to T0. It is important to point out the highest value in the intensity factor (Cp) was obtained in the T6 treatment. This situation means that the mixture of P sources in that treatment showed a higher response to phosphates fertilizers application. A very low retention index (r_1/R) was found for all the treatments, thus confirming the very high P-fixing capacity of the soil. This would imply that the P-sorption capacity strongly controlled P activity in the soil solution. The combination of very low P concentrations in the soil extractand very high P fixation in this soil resulted in very high quantity (E values) and capacity (E_1/Cp) factors. Abnormally very high E values were obtained (Data not reported). Specific protocols for application ofthe isotope exchange method should be developed for these conditions.

TABLE VIII. P RETENTION ACCORDING TO BLAKEMORE [1]

Treatment	P Retention (%)
T0	75.0
T1	75.3
T2	73.2
T3	75.2
T4	75.2
T5	73.4
T6	71.3

TABLE IX. INTENSITY FACTOR (Cp)

Treatment	Cp X10^{-2} mg/L
T0	1.45
T1	7.33
T2	5.56
T3	7.61
T4	10.6
T5	10.7
T6	21.6

TABLE X. PERCENTAGE OF P DERIVED FROM FERTILIZER

Treatments	Pdff%
T0	---
T1	59.4
T2	34.5
T3	56.9
T4	61.9
T5	59.2
T6	77.0

The %P derived from fertilizer [12] showed pronounced differences between the treatments (Table X). The highest percentage of P derived from fertilizer was obtained with 100 ppm P rate as TSP (T1) and 1000 ppm P as PR (T4), [12]. The mixture of TSP and PR is the best treatment as it is shown in Table X. Both the % of Pddf and the Cp values increased with increasing P rates of application. There was also an increase in available soil P-Olsen, as shown in Table VII..

4. CONCLUSIONS

The P retention percentage (Blakemore method) of the Perquenco soil was very high. The P application as PR or TSP did not reduce significantly the P retention of this soil. Nevertheless, it exists a positive effect whenhe P sources are applied as mixtures, resulting in a slight decrease of the P retention percentage.

Available P (Olsen method) in this soil increased from 3.6 ppm P for the check to a maximum of 20 ppm P for the 250 mg P/kg as TSP, reaching medium to high values according to the extraction method utilised.

The intensity factor was low in the check treatment but increased to satifactory levels with the P fertilizer treatments. The fixation index was very high leading to an overestimation of the quantity and capacity factors. Particular care must be taken in utilizing this isotope technique in soils with low P concentration in solution and high P-fixing capacity.

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REFERENCES

[1] SADZAWKA, M.A., Métodos de análisis de suelos. Instituto de Investigaciones Agropecuarias (Chile) Est. Exp. La Platina (Santiago). Serie La Platina N° **16** (1990),130 p.

[2] BARROW, N.J., The description of phosphate adsorption curves. J. Soil Sci. **29** (1978), 447-462.

[3] PINO, I., PARADA, A.M., ZAPATA, F., NAVIA, M., LUZIO, W., Comparative study on P uptake and utilization from P fertilizers by Chilean wheat genotypes in volcanic soils (in this publication, 2001).

[4] MELLA, A., KÜHNE, A., Sistemática y descripción de las familias, asociaciones y series de suelos derivados de materiales piroclásticos de la zona central - sur de Chile. En: Tosso, J. (ed.). Suelos volcánicos de Chile. Instituto de Investigaciones Agropecuarias. Ministerio de Agricultura. Santiago. (1985), 549-716.

[5] FARDEAU, J.C., Le phosphore assimilable des sols: sa représentation par un modèle fonctionnel à plusieurs compartiments. Agronomie **13** (1993) 317-331.

[6] FARDEAU, J.C., GUIRAUD, G., MAROL, C., Bioavailable soil P as a key to sustainable agriculture. In: Proceedings of a symposium “Nuclear techniques in soil- plant studies for sustainable agriculture and environmental preservation” IAEA.STI/PUB/947 (1995) 131-144.

[7] FARDEAU, J.C., Dynamics of phosphate in soils. An isotopic outlook. Fertilizer Research **45** (1996) 91-100.

[8] FARDEAU, J.C., GUIRAUD, G., MAROL, C., The role of isotopic techniques on the evaluation of the agronomic effectiveness of P fertilizers. Fertilizer Research **45** (1996) 101-109.

[9] PINO, I., URBINA, C., LUZIO, W., CASAS, L., Retención de fósforo en dos suelos derivados de cenizas volcánicas. Nucleotécnica**. 3** (4) (1983) 47-50.

[10] PINO, I., VANDERDEELEN, J., BAERT, L., Kinetics of phosphate adsorption in a soil derived from volcanic ash. Turrialba **23** (3)(1973) 291-296.

[11] PINO, I., URBINA, C., CASAS, L., Evaluación de la capacidad de retención de fósforo en suelos derivados de cenizas volcánicas. Nucleotécnica **4** (6) (1984) 43- 47.

[12] FARDEAU, J.C., P-32 isotopic exchange kinetics. Experimental procedure, interpretation of results. Application to the prediction of the efficiency of P fertilizers. Working paper presented at the Third Research Coordination Meeting of the FAO/IAEA Coordinated Research Programmes. “The use of Nuclear and related techniques for evaluating the Agronomic Effectiveness of Phosphate fertilizers, in particular Rock Phosphate”. Report D1-RC-542.3 (1997).

[13] NOVOZAMSKY, I., VAN DIJK, D., LEE, J.J., HOUBA, V.J.G., Automated determination of trace amounts of phosphate in soil extracts using malachite green. Commun. Soil Sci. Plant Anal. **24** (9&10) (1993) 1065-1077.

PART IV

STUDIES FROM AFRICA, ASIA AND AUSTRALIA

EVALUATION OF PHOSPHORUS UPTAKE FROM MINJINGU PHOSPHATE ROCK, GROWTH AND NODULATION OF AGROFORESTRY TREE SPECIES ON AN ACID SOIL FROM KENYA

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Abstract. A series of studies were carried out to study the effect of P application on fast growing multi-purpose trees. A greenhouse experiment was conducted to evaluate availability and uptake of phosphorus (P) from Minjingu phosphate rock (MPR). An acid soil and six agroforestry tree species namely *Leucena leuco-cephala*, *Gliricidia sepium*, *Sesbania sesban*, *Grevillea robusta*, *Cassia siamea* and *Eucalyptus grandis* were used. Phosphorus was applied at 25.8 mg P/ kg soil as Minjingu phosphate rock (MPR) or Triple Superphosphate (TSP). Pregerminated seedlings were transplanted and divided into two sequential harvests at 3 and 6 MAT (months after transplanting). ^{32}P isotope carrier free solution was added to transplanted seedlings at the beginning and when they were 3 months old. The soil was tested for isotopically exchangeable P by incubating the soil with the MPR and TSP. The soil was high in P-fixing capacity. At 3 MAT all the species except *G. robusta* gave a 150 -250% significantly higher stem dry weights where P was added and *L. leuco-cephala*, *S. sesban* and *C. siamea* maintained this up to 6 MAT. The legumes and *E. grandis* where P was applied differed significantly from controls in root dry weight with Minjingu PR being superior with *G.sepium* and *E. grandis*. The legumes and *E. grandis* had significantly higher P uptake where P was applied at 3 MAT. The relative availability of MPR at 3 MAT showed that *L.leucocephala* and *G. sepium* derived 2.93 and 1.06 times more P from Minjingu PR than from TSP respectively. Data obtained from *G. robusta* P uptake showed that this species preferred soil P to externally supplied P in the three sampling periods. Tree species and fertilizer P interactions at 6 MAT were highly significant (P = 0.01). Vesicular arbuscular mycorrhiza (VAM) inoculation improved growth, P uptake from MPR and nodulation of *G. sepium* seedlings. Inoculating *L. leucocephala* seedlings with VAM increased availability of P from MPR.

1. INTRODUCTION

In Kenya the demand for fuelwood, building materials, fodder and green manures by the small-scale farmers is continuously increasing. As a result, there has been a lot of emphasis on fast growing multipurpose trees such as *Leucaena leucocephala*, *Gliricidia sepium* and *Sesbania sesban* (legumes), *Eucalyptus grandis*, *Grevillea robusta* and *Cassia siamea* (non-legumes). Their establishment, especially the legume species in acid soils of Western Kenya is nonetheless poor and P deficiency has been identified as a probable factor inhibiting their adequate growth [1]. Thus, a major problem which hampers establishment of *L. leucocephala* is its initial slow growth is the lack of nodulation for N2 fixation, attributed to the low pH and low soil P [2, 3]. In legumes an adequate P supply is necessary for their optimum growth, survival of rhizobia in the soil, nodule formation and N_2 fixation [4-6].

The magnitude of nutrient mining in the fragile tropical soils is huge [7]. In the sub-Saharan Africa the net loss per-hectare during 30 years is estimated to be 700 kg N, 100 kg P and 450 kg K in about 100 million hectares of cultivated land [5]. The high cost of water-soluble P fertilizers such as triple super phosphate (TSP) has generated considerable interest in the use of alternative sources of P, in particular phosphate rock [8-11] for forestry and agriculture [12]. The use of phosphate rock (PR) offers a possibility for cost savings [13, 11]. In Kenya, Minjingu PR imported from neighboring Tanzania is locally sold at about US $5 per 50 kg bags as compared to about US $20-22 per 50 kg bags of TSP or Single Super Phosphate [9, 14]. Increased yields have been reported where PR has been used as a source of P to crops [10] in low pH soils. There is a lack of information on the ability of tree crops to utilize P from phosphate rock. A series of studies were conducted to assess the effects of the addition of Minjingu phosphate rock (MPR) and TSP on the growth and P uptake of common agroforestry tree species growing in acid soils from Kenya using conventional and ^{32}P isotope techniques.

2. MATERIALS AND METHODS

2.1. Site description

Malava is situated at an altitude of 1595 m above sea level, in the Kakamega district of Western Kenya province. The terrain is gentle to undulating. Climate is described as wet and warm with a bimodal rainfall regime, the first rains averaging 1800 mm to more than 2500 mm and the second rains averaging 700 to 800 mm. The mean monthly temperature is 20.4 to 18.1° C. The soils are moderately drained clayey soils, humic Cambisols with humic Acrisols [1]. In the past a sub-tropical forest composed of indigenous tree species covered the area but the present land use includes smallholder farming with agricultural crops, maize and beans cultivation dominating. Livestock farming and agroforestry practices (hedge row intercropping) are currently being introduced. Gituamba is situated in Thika district of central Kenya province and lies at an altitude of 1603 m above sea level. The area is generally sloppy to undulating. It has a bimodal kind of rainfall totaling 1300-1500 mm per year and distributed as first rains (700-850 mm) and second rains (400-480 mm). Mean monthly temperatures range between 18.0-18.7° C with wet/ cold and dry/warm spells. The soils are described as acid humic topsoils, ando-humic Nitisols with humic Andosols [1]. They are organic soils of volcanic origin with good to moderate drainage. The farming system here is intensive small scale farming on a rotational basis, the main agricultural crops being coffee, tea, and sorghum. The experience from past IAEA's Coordinated Research Projects (CRP) showed that the required information could be obtained through a series of simple experiments than a single complicated experiment [15]. Thus, to achieve the objectives of the project, a series of experiments were carried out.

2.2. Experiment I: Evaluation of availability and uptake of P from rock phosphate by four agroforestry tree species in two acid soils of Kenya

The experiment was conducted in a glasshouse using an Acrisol from Western (Kakamega) and an Andosol from Central (Gituamba) Kenya. Soil samples were collected from the arable layer (0-20 cm) and the main properties of these soils are given in Table I. The trees species used in this study were *Senna siamea, Leucaena leucocephala, Grevillea robusta* and *Eucalyptus grandis.* The seeds of *L. leucocephala, G. robusta, C. siamea* and *E. grandis* obtained from the seed center of the Kenya Forestry Research Institute (KEFRI) were first pregerminated on agar-plates, then sown into sand trays in the glasshouse after two weeks. However *L. leucocephala* and *C. siamea* (legumes) seeds were first pretreated (to soften seed coat) by leaving them overnight in hot water before pregerminating. The seedlings were pricked out into the pots 30 days after sowing into the sand trays.

Minjingu phosphate rock (12.9% P) was applied at three rates: 0 (PR_0), 52 (PR_1) and 77 (PR_2) kg P ha^{-1} equivalent to 0, 25.8 and 38.7 mg P/ kg soil respectively. Two kilograms of air-dried soil were placed into plastic bags (gauge 300, 4" wide x 7" length), the required amount of Minjingu RP was added and mixed thoroughly with the soil. About 200 ml of water was added to bring the soil to field capacity and left for a week to allow for equilibration [16]. The seedlings were pricked out into the pots 30 days after sowing into the sand trays. A basal nutrient solution containing 200 mg N as NH_4NO_3, 400 mg K as $K_2SO_4 \cdot H_2O$ and 100 mg Mg as $MgSO_4.7H_2O$ was also applied to each pot at planting. An amount of water not exceeding 250 ml was added to the pots on a weekly basis to maintain the soils at field water capacity. The pots were laid out in a completely randomized design (CRD) in the glasshouse.

In this experiment, height (ht.) and root collar diameter (rcd.) were recorded on a weekly basis up to 19 weeks after transplanting (19 WAT) using a meter rule and diameter tape respectively. The data at 19 weeks after planting (19 WAT) were subjected to an analysis of variance (ANOVA) and a Tukey's Test ($P< 0.05$) was used to compare the means using SAS software program.

TABLE I. SOME PROPERTIES OF THE SOILS FROM THE ANDOSOL AND ACRISOL

Properties	**Andosol** (Gituamba)	**Acrisol** (Kakamega)
pH (H_2O) 1:1	4.2	4.4
% organic carbon [1]	5.9	2.4
% N [2]	0.6	0.18
P cmol/ kg soil [3]	0.5	$2.05x10^4$
Al “ [4]	2.04	1.03
K “ [5]	13.2	0.11
Ca “	10.4	0.92
Mg “	Trace	0.19
Na “	3.2	0.04
Zn me/100g[6]	0.02	0.01
Fe “	0.64	0.47
Mn “	0.04	0.20
Cu “	0.003	Trace
% Sand [7]	73.0	18.0
% Silt	3.0	8.0
% Clay	24.0	74.0
Texture	Sandy loam	Clay

[1] Walkley-Black method, [2]Kjeldahl method, [3]Olsen’s Method, [4]TSBF titrimetric method, [5] EDTA method, [6]Ammonium acetate extraction method, [7] Hydrometer method

2.3. Experiment II: Response to rock phosphate fertilization and mycorrhizae inoculation by *G. robusta* and *L. leucocephala* in an Acrisol from Kenya

The MPR fertilizer rates were maintained as in Experiment I. Ten kilograms of soil from the Acrisol, Kakamega was weighed into plastic bags (gauge 300, 8"wide x 12" length). 2 g (RP_1) and 3 g (RP_2) of Minjingu RP was then added and mixed thoroughly. Two agroforestry tree species used in the study were *L. leucocephala* and *Grevillea robusta* and the procedures for raising and pricking out of the seedlings was as mentioned in experiment I. Mycorrhizae inoculant were prepared as described by [17]. The infected roots of *Acacia spp.* and freshly collected soils from Kakamega were placed on roots of host plant in this case, maize. A portion of the infected roots of maize and soil with endomycorrhizal associates were then used to inoculate *Acacia tortilis* seedlings. Two grams of the mixture soil and roots was spread halfway down the pots (except pots of treatment I) just before the pre-germinated seedlings were pricked out. The treatments used in this experiment were:

I. RP_0
II. RP_1
III. RP_2
IV. RP_0 + Mycorrhizae (M).
V. RP_1 + M
VI. RP_2 + M

Experiment II was an RCBD replicated four times. Some seedlings were grown and set aside for destructive sampling.

Monthly readings height (ht.) and root collar diameter (rcd.) were recorded for 12 months. Plants in experiment II were harvested at 12 months after transplanting (12 MAT). Parameters assayed were shoot and root dry matter for both tree species and nodule number and fresh weight for *L. leucocephala* only. The data, as indicated above for experiment I were subjected to an analysis of variance (ANOVA) and a Tukey's Test ($P< 0.05$) was used to compare the means using SAS software program.

2.4. Experiment III: Evaluation of P-uptake from Minjingu rock phosphate and TSP by six agroforestry tree species growing in an Acrisol from W. Kenya, using the ^{32}P isotope dilution technique

The study was carried out in the glasshouse at the University of Nairobi. Surface samples (0-20 cm) from an Acrisol, Kakamega were collected randomly from an experimental farm. Samples were bulked and mixed thoroughly from which an amount was set aside for analysis and about 100 g was used for the P dynamic studies. The two phosphate sources were: Minjingu Rock Phosphate (MRP), 12.9%P and Triple Super Phosphate (TSP), 21.0%P

2.4.1. Choice of P fertilizer rates for pot experiments

The rate of 400 kg ha^{-1} MRP was selected based on the results obtained in experiments I and II and an equivalent amount in % P content in the form of TSP. In isotope-aided experiments only one single fertilizer rate of application is normally utilized, namely that recommended for optimum yield [15]. The Andosols from Gituamba showed little or no response to added P fertilizer, therefore only the Acrisol from Kakamega was chosen for experiments III and IV. The methods used were adopted from [18]. The six trees species selected for this study included three legumes: *Sesbania sesban*, *Leucaena leucocephala, Gliricidia sepium* and three non-legumes: *Grevillea robusta, Cassia siamea* and *Eucalyptus grandis.* The seeds were obtained from the seed center of KEFRI. The seedlings were pricked out after 30 days into 5 kilogram air-dried soils, which were already mixed thoroughly with either Minjingu RP or TSP as per the treatments listed in section 4.8. *L. leucocephala*, *S. sesban* and *G. sepium,* were inoculated with appropriate *Rhizobium* strain(s). A basal nutrient solution containing 200 mg N as NH_4NO_3, 400 mg K as K_2SO_4, H_2O and 100 mg Mg as $MgS0_4.7H_2O$ was also applied to each pot at planting. An amount of water not exceeding 250 ml was added on a weekly basis to maintain the soils at field water capacity. A set of six treatments listed below was used in this experiment. However treatments I, II and III received ^{32}P labeled KH_2PO_4 solution (10 ppm of P concentration) with an activity of 185 x 10 Bq ^{32}P /kg soil (50µCi ^{32}P/kg soil) applied as 20 ml aliquots per pot:

i: Soil + $KH_2{}^{32}PO_4$
ii: Soil + Minjingu rock phosphate [MRP (25.8 mg P/kg soil)]+ - $KH_2{}^{32}PO_4$
iii: Soil + Triple superphosphate [TSP (25.8mg P/kg soil)] + -$KH_2{}^{32}PO_4$
iv: Soil + Minjingu rock phosphate [MRP (25.8 mg P/kg soil)]
v: Soil + Triple superphosphate [TSP (25.8mg P/kg soil)].
vi: Soil alone (check treatment)

2.4.2. Experimental design and layout

The experiment was set-up as a Randomized Complete Design with 3 replications and three harvests for each tree species. Harvesting was done at 3 month intervals and the experiment lasted for 9 months. The ^{32}P-labeled solution was applied sequentially, immediately after pricking out of the seedlings into the pots (period 1), then was applied to 3 months-old seedlings for period 2 and this coincided with the first harvest. This was repeated two more times. The harvests were thus referred to as 3 MAT (months after transplanting), 6 MAT and 9 MAT respectively. Height and root collar diameter increase were measured in centimeters (by use of a meter rule) at monthly intervals for up to 9 months. The first destructive harvest was carried out at 3 MAT. The pots with unlabelled plants were harvested first. Roots and shoots were carefully separated. The roots (only from unlabelled plants) were washed out carefully on a 0.5 mm sieve by a water nozzle at low pressure and the nodules (for legume trees) carefully removed. Nodule count and characterization followed immediately. The soils were carefully collected in a bucket per replicate and later transferred to polyethylene sheets for drying. This was later analyzed for micro and macronutrients. The shoots and roots from unlabelled plants were air-dried in an oven at 80°C till a constant weight was attained and shoot and root dry matter in grams (SDW and RDW respectively) were recorded. The shoot samples were then ground for determination of tissue nutrient P, C, N, Na, Ca, K and Mg contents.

At each harvest the shoots were cut at 1cm from the soil surface chopped into small sections (approximately 1 cm), placed in porcelain crucibles and dried at 105°C in a muffle furnace for 24 hours to obtain dry weight. This was followed by subsampling into 2g portions which were then dry-ashed (in a muffle furnace at 250-300°C for 2 hours) and dissolved into 20 ml HCl after cooling. A 5 ml aliquot was then obtained for plant tissue P determination by colorimetric method. The rest of the solution was transferred to vials for measuring the ^{32}P activity of the plant samples in disintegration per-second (dps) in a liquid scintillation counter at National Agricultural Research Laboratories, Kabete, Nairobi. A series of calculations were made to evaluate the relative agronomic effectiveness (RAE) of Minjingu rock phosphate.

2.5. Experiment IV: A glasshouse evaluation of the response of *L. leucocephala* and *G. sepium* to P fertilization and VA-mycorrhizae inoculation

Seedlings of *L. leucocephala* and *G. sepium* were raised the same way as in the previous experiments, whereas VA-mycorrhizae inoculation was done as in experiment II and application of ^{32}P labeled solution as in experiment III. At six months after transplanting nodule number, nodule dry weight, biomass and P uptake were assessed.

3. RESULTS AND DISCUSSION

3.1. Experiment I: Growth response of four agroforestry species to Minjingu PR application in two acid soils of Kenya

The effect of Minjingu PR application on height and root collar diameter of the four tree species growing in two acid soils at 19 WAT (weeks after transplanting) is given in Table II. At 19 WAT *L. leucocephala* growing on the Acrisol, Kakamega showed significant increases in height ($P<0.05$) and diameter in presence of Minjingu PR compared to the control. However, addition of 77 kg P ha^{-1} (RP$_2$) gave the largest height increase, although this was not significantly different from 52 kg P ha^{-1} (RP$_1$). *E. grandis* responded similarly but the means did not differ significantly. In the case of *G. robusta* and *S. siamea* increases in height and root collar diameter were up to 52 kg P ha^{-1} , above which a negative growth response was observed. The highest height of *E. grandis* was recorded at 77 kg P ha^{-1} (RP$_2$). Responses to Minjingu PR fertilization by the four tree species were differential in the Andosol, Gituamba. *L. leucocephala* and *E. grandis* showed increases in height and root collar diameter of 1.80 times and 1.31 times respectively where Minjingu PR was added up to 52 kg P ha^{-1} but declined afterwards. This suggested that the Andosol from Gituamba was probably supplying enough P, hence no response (Zapata, 1994 pers. comm.). This little or no response could also be attributed to lower P fixation capacity as compared to the Acrisol, Kakamega. There was a reduction in height of *S. siamea* at both levels of Minjingu PR but increased in root collar diameter at 77 kg P ha^{-1}. *G. robusta* displayed the opposite trend. This negative effect on *S. siamea* could not be explained in terms of P addition but for *G. robusta* it seemed that the soil was supplying enough P.

3.2. Experiment II: Response to rock phosphate fertilization and mycorrhizae inoculation by *G. robusta* and *L. leucocephala*

3.2.1. Plant height and root collar diameter

Response in height and root collar diameter of *L. leucocephala* and *G. robusta* to Minjingu PR application and mycorrhizae inoculation at 12 MAP (months after planting) are given in Table III. Results of experiment I showed that positive responses with the majority of the tree species were observed in the Acrisol, Kakamega. Thus, this soil was selected in this study. A recurrent attack by the *Leucaena* psyllid from the second month to about the fifth month may have affected the growth of *L. leucocephala.* There was a significant difference in height ($P < 0.001$) and root collar diameter ($P < 0.05$) between *L. leucocephala* seedlings receiving Minjingu PR and Minjingu PR + mycorrhizae combinations and those receiving mycorrhizae alone and the control. Trees receiving Minjingu RP$_1$+M resulted in about 121% growth increases in both height and root collar diameter above the control. VAM inoculation alone did not influence growth of *L. leucocephala.* The initial low levels of P in the soil (Table I) and the high P fixation capacity of the soil (Zapata, 1994, pers. comm.) thus making it unavailable to the mycorrhizae colonization. A minimum soil P level is required to have any significant mycorrhizal infection on the roots. The available soil phosphate (P) status influences the root infection of plant by VAM. Studies in three tropical soils showed that VAM effectiveness was very restricted or altogether unexpressed, irrespective of VAM fungal inoculation, if soil solution P was not optimized for VAM effectiveness. They further observed that, after P optimization, effectiveness was significantly increased by VAM inoculation. Growth depressions due to VAM inoculation have also been observed in sweet potato [19], in maize [20] and in some Kenyan soils [21].

These depressions were attributed to limited carbohydrate availability in the host plant and to competition for photosynthates between roots and VAM [21] suggesting that the VAM inoculant could be partially parasitic. *G. robusta* as in experiment I produced tallest plants, root collar diameter, shoot and root dry weight compared to *L. leucocephala.* This was probably due to better adaptability of *G. robusta* to various soils in the field sites. *G. robusta* had more biomass in the shoots with VAM compared to the roots whereas VAM inoculation improved root biomass production than shoots with *L. leucocephala.* Addition PR_1+M to *G. robusta* gave the lowest response of the measured parameters as opposed to VAM inoculation alone that gave the highest. VA-mycorrhizae inoculation resulted in an 11% growth increase compared to the control. These differences in response to VAM inoculum between *G. robusta* and *L. leucocephala* may be related to the effectiveness or the symbiotic association.

3.2.2. Nodulation of Leucaena leucocephala

Data on nodulation of *L. leucocephala* are presented in Table IV. There was some nodulation, although the seedlings were not inoculated and this was unexpected. Fields with no history of *L. leucocephala* cultivation normally require that *L. leucocephala* be inoculated with specific strains. Nodulation in the pots could however, be attributed to the presence of some native legumes or rhizobia strains belonging to the same cross-inoculation group as *L. leucocephala*. Nodulation significantly improved where Minjingu PR and VAM were added (Table IV). This could be related to improved P supply to the plant. An adequate supply of P to legumes is necessary for both nodule formation and nitrogen-fixation, ensuring the growth of the host and survival of the microsymbiont in the soil. This was shown by low or lack of nodulation in the control of this study. However, nodulation of *L. leucocephala* within the same treatments was variable, which could be due to variability within *L. leucocephala* provenances. Sanginga (1994 pers. comm.) reported this kind of variability while working with *L. leucocephala* in Nigeria.

3.3. Experiment III: Evaluation of P-uptake from Minjingu RP and TSP by six tree species grown in an Acrisol using the ^{32}P isotope dilution technique

3.3.1. Effect of P fertilizer on shoot and root dry weights

Effect of fertilizer P application on the stem and root dry weights at 3, 6 and 9 MAT is shown in Table V. At 3 MAT there were highly significant differences in stem dry weight between P-fertilized and control plants of all the species, except *G. robusta*. Significant increases in stem dry weight over their respective controls was found for P-fertilized *L. leucocephala, S. sesban* and *S. siamea*. Only *E. grandis* showed significant differences in stem dry weight between Minjingu PR and TSP fertilizers. However all species had a superior stem dry weight where P was added compared to the controls. At 6 MAT *L. leucocephala, S. sesban* and *S. siamea* had significant stem dry weight where P fertilization compared to none at all.

During the three periods, stem dry weight was lower for *L. leucocephala* compared to *S. sesban*. *G. sepium* stem dry weight increased rather slowly during the three periods whereas its RDW decreased to nearly 5-10 times at 9 MAT compared to 3 MAT. At 3 MAT *L. leucocephala, S. sesban, G. sepium* and *E. grandis* had a significant difference where P was added compared to their controls. In the latter three species Minjingu PR gave higher stem dry weights compared to TSP and only with *G. robusta* was TSP superior. At 6 MAT *L. leucocephala* and *S. sesban* maintained similar response

TABLE II. EFFECT OF P FERTILIZER ADDED AT TWO RATES AS MINJINGU PR ON HEIGHT AND ROOT COLLAR DIAMETER OF FOUR TREE SPECIES GROWING ON TWO ACID SOILS AT 19 WEEKS AFTER PLANTING

	Species							
Treatment	*L.leucocephala*		*G. robusta*		*E. grandis*^{1}		*C. siamea*	
	Height (cm)	Root collar diameter (cm)	Height (cm)	Root collar diameter (cm)	Height (cm)	Root collar diameter (cm)	Height (cm)	Root collar diameter (cm)
				Acrisols				
PR$_0$	7.3b^{2}	0.39a	36.5a	0.58b	33.0a	ND^{3}	23.3ab	0.47b
PR$_1$	13.2a	0.63a	46.7a	0.90a	44.7a	"	27.0a	0.70a
PR$_2$	20.5a	0.70a	46.3a	0.79a	50.0a	"	22.0b	0.60ab
c.v%	7.3	8.3	6.3	3.4	7.2	"	2.6	2.6
				Andosols				
PR$_0$	7.1a	0.48	46.9a	0.88a	39.4a	"	31.9a	0.73a
PR$_1$	17.1a	0.68	28.1b	0.68b	50.2a	"	24.5ab	0.69a
PR$_2$	11.7a	0.57a	31.9b	0.61b	45.2a	"	19.2b	0.57a
c.v%	10.5	6.8	2.1	2.3	8.7	"	4.1	6.0

[1] *E.grandis* was sown late and the values shown represent growth 11 weeks after planting. [2] Any column values followed by the same letter are not significantly different per species per measured parameter. [3] Not determined.

TABLE III. EFFECTS OF TWO RATES OF MINJINGU PR FERTILIZER APPLICATION AND VA-MYCORRHIZAE INOCULATION ON THE HEIGHT AND ROOT COLLAR DIAMETER OF *Leucaena Leucocephala* AND *Grevillea Robusta* 12 MONTHS AFTER PLANTING

	Species			
Treatment	*Leucaena leucocephala*		*Grevillea robusta*	
	Height (cm)	Root collar diameter (cm)	Height (cm)	Root collar diameter (cm)
Control	12.1 d[1]	0.72 e	66.2 a	1.82 a
PR_1	21.8 bc	1.15 bcd	71.7 a	1.76 a
PR_2	24.8 ab	1.39 ab	70.8 a	1.80 a
VA-mycorrhizae (M)	13.3 bc	0.91 cde	75.0 a	1.93 a
PR^1+M	26.8 a	1.60 a	65.8 a	1.77 a
PR_2+M	24.9 ab	1.24 abc	70.0 a	1.74 a
c.v%	4.2	2.3	2.4	1.4

[1] Any column values followed by the same letter are not significantly different per species per measured parameter.

TABLE IV. EFFECT OF TWO RATES OF MINJINGU PR FERTILIZER APPLICATION AND VA-MYCORRHIZAE INOCULATION ON THE NODULE NUMBER ON UNINOCULATED *Leucaena Lecocephala* AT 12 MONTHS AFTER PLANTING

	Treatment					
	Control	PR_1	PR_2	VA-mycorrhizae	PR_1 + M	PR_2 + M
Nodule number	1 b[1]	20 a	45 a	6 b	36 a	35 a

[1] Any column values followed by the same letter are not significantly different per species per measured parameter.

in stem dry weight as at 3 MAT. Their stem dry weight increased by about 12 and 3 times between 3 and 6 MAT respectively and between 10 and 2 times respectively over the controls in the same period. The same was observed for *E. grandis, G. robusta* and *S. siamea,* which had about 5, 12 and 4 times, increases, respectively, over the same period. P addition also gave significant differences in stem dry weight in *C. siamea.* At 9 MAT only *L. leucocephala* maintained a significant difference between the plants that received P and controls. However the superiority of P addition was still evident in all the species.

At 3 MAT it was evident that root dry weight was higher than stem dry weight in all the species sometimes up to 12 times where PR was to *G. robusta* and TSP to *E. grandis.* Similar observations were made by [22] using *Leucaena* as the test species which be attributed to direct P response by the roots in the early establishment phase. Plants probably allocate a greater proportion of assimilates to roots when nutrients such as nitrogen and phosphorus are limiting. At 6 MAT the trend reversed except with *L. leucocephala* and *G. sepium*. The high root dry weight compared to stem dry weight at 3 MAT suggested initial high response to P fertilization for purposes of maximum exploration of the soil by the roots. P has been reported to be crucial in early root development. At 6 MAT the change in trend where stem dry weight was more could be attributed to secondary growth of the seedlings where shoots developed more to maximize on photosynthesis. Early root growth especially in *L. leucocephala* has been attributed to development of taproots and grows faster than those of *G. sepium* that develop lateral roots [2]. At 6 MAT *L. leucocephala, S. sesban, G. robusta* and *C. siamea* maintained a higher root dry weight. The figures were lower than at 3 MAT because this was a different harvest but the trend was similar. In all of them Minjingu PR and TSP were not significantly different but were superior to the control emphasizing that P addition could show residual effects after 6 months. At 3 MAT and 6 MAT all species had superior root dry weight compared to the control and only *L. leucocephala* maintained this up to 9 MAT. *G. robusta* produced the highest stem and root dry weights. At 9 MAT where TSP gave superior stem and root dry weight for most of the species although not significant.

3.3.2. Effect of added phosphorus fertilizer on P uptake

Table VI shows the effect of added P on P uptake by six agroforestry tree seedlings at 3 and 6 MAT respectively. At 3 MAT there were significant differences in *L. leucocephala, S. sesban, G. sepium* and *E. grandis* where soil was amended with P compared to the controls. Though insignificant *G. robusta* and *S. siamea* still had more P uptake from Minjingu PR and TSP compared to control. At 6 MAT there was a reduction in P uptake and only with *L. leucocephala* did Minjingu PR show superiority to TSP and control. Similarly Amer et al. [23] showed that there were no significant differences in P concentrations of pinnules between VAM inoculated and uninoculated *Leucaena*, that had received phosphate rock at 10 days after planting, however their was a significant reduction in P concentration 15 days after planting in all the treatments. This reduction was probably due to the dilution effect of growth because dry matter usually accumulates faster than P uptake [24]. *E .grandis* maintained its differences as at 3 MAT whereas for *G. sepium* TSP was superior to both control and Minjingu PR. *S. sesban, G. sepium* and *E. grandis* had very high P uptake levels at 3 MAT even where P was not added compared to the rest of the species. This could be attributed to the initial P in the seeds (Fardeau-pers. comm.). The same could also explain the drop in P uptake at 6 MAT. At 9 MAT P uptake of *G. sepium, E. grandis* and *G. robusta* increased with or without P addition but only with *G. sepium* the increase was significant when compared to the controls (data not shown). Phosphorus uptake by all the species was 200-300% more at 3 MAT compared to 6 and 9 MAT.

Thus, addition of Minjingu PR resulted in significant increases in P uptake as confirmed by enhanced tree growth. These observations could assist in explaining the high efficiency of Minjingu PR as a source of P to trees in Acrisols possibly due to residual effects [25]. This was attributed to slower dissolution of PR unlike with soluble P-fertilizers [24]. Less soluble P would therefore, be available for fixation. Some authors [26] have observed that applied P as water-soluble P fertilizers to high fixation soils is quickly converted to forms unavailable to plants. They concluded that under these conditions and where rock phosphate is readily available it is better to utilize less soluble and less expensive P sources [22].

TABLE V. SHOOT AND ROOT DRY WEIGHTS (g pot^{-1}) OF SIX TREE SPECIES AT 3.6 AND 9 MAT AFTER P APPLICATION AS EITHER MINJINGU PHOSPHATE ROCK (MPR) OR TRIPLE SUPERPHOSPHATE (TSP)

	Species											
	G. robusta		*L. leucocephala*		*S. sesban*		*G. sepium*		*C. siamea*		*E. grandis*	
P sources	SDW[1]	RDW[2]	SDW	RDW	SDW	RDW	SDW	RDW	SDW	RDW	SDW	RDW
						3 MAT						
MPR	0.9 a[3]	11.6 a	0.5 a	3.7 a	5.3 a	16.9 a	2.2 a	9.6 a	1.3 a	9.9 a	3.4 a	21.7 a
TSP	1.2 a	11.0 a	0.5 a	5.1 a	4.4 a	23.3 a	1.4 a	9.2 a	1.0 a	4.6 b	1.8 b	24.4 a
Control	0.8 a	4.4 b	0.2 b	1.6 b	1.3 b	8.8 b	1.2 b	5.8 b	0.6 a	3.1 c	0.5 c	2.3 b
						6 MAT						
MPR	15.1 a	7.0 a	6.3 a	9.9 a	14.3 a	4.3 c	2.8 a	4.5 a	7.8 a	2.9 a	13.7 a	4.3 a
TSP	15.8 a	6.7 a	6.1 a	8.3 a	15.3 a	14.3 a	3.0 a	4.6 a	4.6 ab	1.7 a	15.6 a	6.6 a
Control	12.8 a	4.1 b	0.6 b	4.1 b	7.5 b	7.6 b	3.0 a	2.1 b	2.7 b	0.9 b	1.0 b	4.2 a
						9 MAT						
MPR	25.3 a	16.3 a	8.9 a	18.6 a	ND[4]	ND	3.2 a	0.9 a	ND	ND	13.5 a	15.3 a
TSP	20.1 a	21.2 a	7.1 a	19.5 a	“	ND	3.7 a	2.8 a	“	“	23.4 a	15.9 a
Control	26.8 a	17.9 a	4.3 a	7.0 a	“	ND	2.5 a	0.2 a	“	“	16.8 b	8.9 a

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[1] Shoot dry weight, [2] Root dry weight, [3] Any column means per species per harvest followed by the same letter are not significantly different, [4] Not determined.

TABLE VI. P UPTAKE AND OTHER ISOTOPICALLY DETERMINED PARAMETERS OF SIX AGROFORESTRY TREE SPECIES AT 3 AND 6 MAT

	3 MAT				6 MAT			
	Total P[1] uptake	%Pdff[2]	APdff[3]	RAID[4]	P uptake	%Pdff	APdff	RAID
				L. leucocephala				
P source								
Minjingu PR	3.0 a[5]	86	2.58	293	2.8 a	60	1.68	127
TSP	2.6 a	29	0.75	---	1.7 b	48	0.82	---
Control	1.2 b	---	---	---	0.4 c	---	---	---
				S. sesban				
Minjingu PR	14.6 a	N/A[6]	ND[7]	ND	2.2 a	91	2.00	111
TSP	13.3 a	N/A	ND	---	1.9 a	82	1.56	---
Control	3.8 b	---			1.5 a	---	---	---
				G. sepium				
Minjingu PR	12.3 a	93	11.44	106	1.2 b	70	0.84	94
TSP	8.7 a	87	7.57	---	5.3 a	75	3.98	---
Control	3.7 b	---	---	---	1.4 b	---	---	---

TABLE VI (continued). P UPTAKE AND OTHER ISOTOPICALLY DETERMINED PARAMETERS OF SIX AGROFORESTRY TREE SPECIES AT 3 AND 6 MAT

	3 MAT				6 MAT			
P source	Total P uptake	%Pdff	APdff	RAID	P uptake	%Pdff	APdff	RAID
				G. robusta				
Minjingu PR	2.0 a	3	0.06	50	1.0 a	N/A[8]	ND	ND
TSP	3.0 a	6	0.18	---	1.0 a	N/A	ND	---
Control	1.7 a	---	---	---	0.7 a	---	--	---
				C. siamea				
Minjingu PR	6.4 a	97	6.21	104	1.8 a	82	1.48	111
TSP	5.9 a	93	5.49	---	2.6 a	74	1.92	---
Control	3.0 a	---	---	---	2.0 a	---	---	---
				E. grandis				
Minjingu PR	12.3 a	42	5.17	63	1.1 a	88	0.97	98
TSP	9.1 a	67	6.10	---	1.4 a	89	1.24	----
Control	2.4 b	---	---	---	0.3 b	---	---	---

[1] Total amount of P (mg plant^{-1}) in shoots (Soil P + Fertilizer P). [2] Percent P derived from Minjingu RP and TSP fertilizers (%Pdff). [3] Actual amount of P (mg plant^{-1}) in shoots derived from Minjingu RP and TSP fertilizers (Total P uptake x %Pdff). [4] Relative availability of Minjingu RP as determined by isotope dilution (%RAID). [5] Any column values followed by the same letter per species per harvest time are not significantly different. [6] Values found to be more than 100%. [7] Not determined. [8] Values found to be negative %.

TABLE VII. EFFECT OF P ADDITION ON MEAN NODULE NUMBER AND NODULE MASS (mg PLANT^{-1}) AT 3 AND 6 MAT IN AN ACRISOL

	Species					
	L. leucocephala		*S. sesban*		*G. sepium*	
P sources	NN	NDW	NN	NDW	NN	NDW
			3 MAT			
Minjingu PR	3 a	0.03 a	208 a	0.4 a	11 a	0.03 a
TSP	0 b	0 b	168 b	0.3 a	0 b	0 b
Control	0 b	0 b	10 c	0.01 b	0 b	0 b
			6 MAT			
Minjingu PR	93 a	0.3 a	182 a	0.5 b	148 a	0.12 a
TSP	79 a	0.2 a	206 a	0.9 a	34 b	0.09 b
Control	18 b	0.02 b	135 b	0.6 b	0 c	0.02 c

NN = nodule number, NDW = nodule dry weight.

[1] Any column means per species per harvest followed by the same letter are not significantly different (≤0.05).

TABLE VIII. EFFECTS OF VESICULAR ARBUSCULAR MYCORRHIZAL (AM) INOCULATION ON P UPTAKE, SHOOT BIOMASS AND NODULE NUMBER OF SIX MONTH-OLD SEEDLINGS OF *L. Leucocephala* AND *G. Sepium*

	Leucena leucocephala				*Gliricidia sepium*			
Treatments soil	Nodule number	Shoot biomass	P uptake	% Pdff	Nodule number	Shoot biomass	P uptake	% Pdff
		--------- mg pot^{-1} -------				--------- mg pot^{-1} -------		
Soil (control)	8	6.8	3.0	-	0	5.5	3.8	0
Soil + AM	17	7.8	3.1	22	18	5.2	3.9	-1
Soil + MPR	17	7.3	3.0	25	36	8.0	4.1	8
Soil + TSP	13	6.7	2.7	9	16	6.3	2.8	5
Soil + AM + MPR	15	10.3	3.7	42	15	8.5	4.3	30
Soil + AM + TSP	9	7.6	2.5	4	0	5.5	3.3	0

AM = arbuscular mycorrhiza, MPR = Minjingu phosphate rock, TSP = triple superphosphate,
$LSD_{0.05}$ treatments, Biomass = 1.6, P uptake = 0.7, % Pdff = 5.0, Species = 1.3 and 0.4, Nodule = 4.0.

3.3.3. ^{32}P isotopic parameters

Table VI shows the isotopically measured and derived parameters, proportion and amount of P derived from Minjingu PR and TSP fertilizers (%Pdff and Apdff respectively), by the six species, relative availability of PR as determined by isotope dilution (%RAID) at 3, and 6 MAT. At 3 MAT *L. leucocephala*, *G. sepium* and *S. siamea* derived more P from Minjingu PR compared to TSP. *G. robusta* and *E. grandis* exhibited the opposite trend. The RAID values of *L. leucocephala* at 3 MAT indicated that P uptake from Minjingu PR was about 2.93 times higher than from TSP. This meant that Minjingu PR was 2.93 times as effective as TSP for *L. leucocephala*. Similarly, Minjingu PR was 1.06 times as effective as TSP for *G. sepium,* 1.04 times for *S. siamea.* For *G. robusta,* A_L values showed that there was about 834 and 404 mg P/kg soil in terms of Minjingu PR and TSP respectively (data not shown). A similar case also applied to *E. grandis.* At 6 MAT *L. leucocephala, S. sesban* and *S. siamea* had more P derived from PR and was more effective than TSP. However the effectiveness of the Minjingu PR compared to TSP for *G. sepium* and *E. grandis* tended to be equal. At 9 MAT only *G. sepium* and *E. grandis* had their isotopic parameters determined. Both derived more P from Minjingu PR compared to TSP and were as much as 3.8 times that of TSP. The RAID values confirmed the previous observations indicating that Minjingu PR was a better source of P at 9 MAT.

Results of P uptake, %Pdff, and RAID indicate that *L. leucocephala, G. sepium* and *S. siamea* were more efficient in utilizing P from Minjingu PR than from TSP in the Acrisol, Kakamega. The P demand by the above mentioned three species from the fertilizers added as either Minjingu PR or TSP was high as indicated by % Pdff. However, *G. robusta* had low demands whereas *E. grandis* had intermediate demand for added P. The parameter Pdff is a direct measure of how much P is taken up by the plant from the fertilizer whereas the P derived from the soil is obtained by difference [15]. Thus, the P uptake from the soil in the P fertilized treatments may be higher, similar or lower than the P uptake from control plots.

The relative availability of PR as determined by isotope dilution (RAID) to *L. leucocephala, G. sepium* and *S. siamea* was higher compared to *G. robusta* and *E. grandis*. This supports the higher P utilization from Minjingu PR by these three tree species qualifying the Minjingu PR as a possible cheap substitute to the soluble inorganic P fertilizers for some (legume) agroforestry trees in the Acrisol, Kakamega. This is probably due to demand for P by the legumes for N_2-fixation and growth. However, for non-legumes such as *G. robusta* and *E. grandis* PR was 50-63% as effective as TSP, having Pdff (Phosphorus derived from fertilizer) values of 3.2% and 6.3% for Rock-P and TSP respectively and a RAID of 0.51. *S. sesban* AL and Pdff values were not conclusive. There were large differences between the tree species in their A_L values. Of great interest was *G. robusta* where A_L values were 786 and 386 for Minjingu PR and TSP respectively. These values show that *G. robusta* prefers the inherent P derived from soil rather than the external phosphates.

3.3.4. Nodulation

Results of nodule number and nodule dry weight of the three legumes are shown in Table VII. At 3 MAT Minjingu PR gave a significantly higher nodule number than TSP and the control in *L. leucocephala* and *G. sepium*. In *S. sesban* the P sources did not differ significantly but were about 16 to 20 times more compared to the controls. *S. sesban* also has the highest number of nodules compared to the other two. The trend in nodule dry weight was similar to that observed for nodule number. At 6 MAT there was a marked improvement in nodulaltion of *L. leucocephala* and *G. sepium* whereas *S. sesban* maintained nodule numbers as at 3 MAT. Only with *G. sepium* did the two P sources differ significantly in nodule number and dry weight with Minjingu PR being superior. In *L. leucocephala* and *S. sesban* the two P sources were superior to control in both parameters. Although there was a decline in nodule number at 6 MAT the nodule dry weight increased slightly in all the treatments. The above results indicate that added P improved nodulation probably due to direct influence onto the plant or the nitrogen fixing *Rhizobium*. An adequate supply of phosphorus to legumes is necessary, not only for optimum plant growth but also for survival of rhizobia in the soil, nodule formation and N-fixation [27].

3.4. Experiment IV: Response to phosphate application and vesicular arbuscular (VAM) inoculation by *L. leucocephala* and *G. sepium*

Addition of P either as MPR or TSP improved growth of *G. sepium* while with *L. leucocephala,* no advantage over the control (Table VIII). Nodulation of the two legume trees was significantly improved by addition of P-fertilizer. This would confirm the need for P application to acid, low P soils like the Acrisols from Kakamega, if dinitrogen fixation were expected to take place. Inoculating the seedlings with VAM alone improved nodulation, which shows that an improved P supply to these seedlings was achieved as a result of the symbiotic association with VAM, in agreement with some authors [4, 28]. An adequate supply of P to legumes is necessary for growth of the host, survival of rhizobia bacteria, nodule formation and nitrogen fixation [27, 29]. Inoculating *G. sepium* seedlings with VAM before transplanting them in acid soils would be highly beneficial. Inoculating *L. leucocephala* seedlings with VAM was equivalent to addition of 77 kg P ha^{-1} as MPR but when both VAM inoculation and MPR addition were applied together, the % Pdff was doubled. Thus, VAM inoculation is necessary for improved P uptake efficiency from MPR by the *L. leucocephala* seedlings. The need for VAM inoculation to *G. sepium* seedlings is crucial to the successful growth and establishment in the poor acid soils, as it was observed that %Pdff was significantly improved through VAM inoculation. From another experiment in this study, [12] found that, *G. sepium* and *L. leucocephala* were more efficient in utilizing P from MPR than *G. robusta* , *E. grandis* and *S. siamea* as they recorded a 121% increase growth of *L. leucocephala* seedlings using the same Acrisol, Kakamega.

4. CONCLUSION

Some tree species responded significantly to the addition of Minjingu PR at 3 months after transplanting (MAT). In this work it was clearly established that MPR was as readily available as TSP to tree seedlings growing in the acid soils (Acrisol and Andosols) of Kenya. It was also shown that patterns of utilization of P differ between the tree species studied. Different P acquisition mechanisms of the tree species and their P utilization patterns could also contribute to the differences, as demonstrated in *G. robusta* and *E. grandis* and between legumes and non-legumes. *G. robusta* preferred or utilized inherent soil P while the other species especially *L. leucocephala* and *S. sesban* required high amounts of P irrespective of the source (Minjingu PR or TSP). This was a pointer that demand for P for growth and probably N_2-fixation (as seen from the nodulation response to P addition) was higher than the non-legumes. *G. robusta* performed well in the low-P acid soils, exhibited a preference for inherent soil P and formed cluster roots. The fact that there were no significant differences between P addition and the controls and that no signs of nutrient deficiencies were observed in this species warrants more investigations. Investigations need to be conducted to establish why this discrimination and whether cluster root formation is an adaptability mechanism special to this species as reported by Skene et al. [30]. The high efficiency of Minjingu PR in P tree seedling nutrition when compared to TSP in several instances shows that Minjingu PR can be used as substitute to TSP in nursery potting media preparation as well as a cheap source of P for faster establishment of agroforestry tree species. Use of VAM inoculants particularly to the legume trees being established in acid, low-P soils would greatly improve phosphorus nutrition, even in absence of phosphate fertilizers. The ^{32}P isotope dilution technique offers a reliable tool to quantifying uptake of P from P fertilizers in young tree species. Further field studies need to be carried out to confirm these observations made from glasshouse experiments.

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REFERENCES

[1] FAO-UNESCO, Soil Map of the World 1: 5000000 (1974) Vol. 1, legend. UNESCO, Paris.

[2] EZENWA, I.V., ATTA-KRAH, A.N., Early growth and nodulation in *Leucaena* and *Gliricidia* and effects of pruning on biomass productivity (pp 171-178). In: Mulongoy, K., Gueye, M., and Spencer, D.S.C. (eds.) (1992). Biological nitrogen fixation and sustainability of tropical Agriculture. Proceedings of the Fourth International Conference of the African Association for Biological Nitrogen Fixation (AABNF), held at Ibadan, Nigeria, 24-28 Sept. 1990.

[3] AHMAD, N., NG, F.S.P., Growth of *Leucaena leucocephala* in relation to soil pH, nutrient levels and *Rhizobium* concentration. *Leucena* Research **2** (1981) 5-10.

[4] MOSSE, B., POWELL, C. LI, HAYMAN, D.S., Plant growth responses to vesicular-arbuscular mycorrhizae IX. Interactions between VA mycorrhiza, rock phosphate and symbiotic nitrogen fixation. New Phytol. **76** (1976) 331-342.

[5] SMALING, E., An agroecological framework for integrated nutrient management with specific reference to Kenya. Doctoral Thesis (1993) Agricultural University, Wageningen, Netherlands P 290.

[6] TRAN, S.T., FARDEAU, J.C., GIROUX, M., Effects of soil properties on plant-available phosphorus determined by the isotopic dilution phosphorus-32 method. Soil Sci. Soc. Am. J. **52** (1988)1383-1390.

[7] SANCHEZ, P.A., IZAC, A.M., VALENCIA,I., PIERI, I., Soil fertility replenishment in Africa: A concept note. In: Breth. S. A. (ed.) Proceedings of a Workshop 26-30 September 1996, Addis Ababa.

[8] KUGLER, M., The beneficial bonding of plants and fungi. IDRC Reports. January 1986. Laval University, Quebec, Canada.

[9] MINJINGU PHOSPHATE COMPANY LIMITED, Minjingu Phosphate for direct application. Bulletin P4 (1991).

[10] MATHUR, B.S., SURESH, L., Effect graded levels of rock phosphate on plant nutrition of an Alfisol. J. of Indian Soc. of Soil Sci. **37** (1989).

[11] NNANDI, L.A., HAQUE I., Agronomic Effectiveness of Rock Phosphate in an Andept of Ethiopia. Common. Soil Sci. Plant Anal., **19** (1988):79-90.

[12] MWENDWA, A.K., N.K. KARANJA., Evaluation of availability and uptake of P from rock phosphate (RP) with mycorrhizae inoculation by agroforestry tree species growing on two acid soils in Kenya. Paper presented to 2nd Crop Science Conference for Eastern and Southern Africa. University of Malawi, 19-24 February 1995, Blantyre, Malawi.

[13] GREGG, P.E., SYERS, J.K., Phosphate rock: an alternative phosphate fertilizer. New Zealand Agriculture Sc. **16**(2) (1982) 84-86.

[14] WOOMER, P.L., OKALEBO, J.R., SANCHEZ, P.A., Phosphorus replenishment in Western Kenya: From field experiments to an operational strategy. Paper presented to Approaches to replenishing soil fertility in Africa - NGO perspectives workshop. 3-9 June 1997, ICRAF House, Nairobi, Kenya.

[15] ZAPATA, F., Isotope Techniques in Soil Fertility and Plant Nutrition Studies. FAO/IAEA Program In: Use of Nuclear Techniques in Studies of Soil-Plant Relationships. Training series No.2 (1990) IAEA, Vienna, Austria, p 223.

[16] OSUNDE, A.O., SANGINGA, N., Growth and nitrogen fixation of *L. leucocephala* and *Gliricidia sepium* lines grown on an Ultisol from southeastern Nigeria. In: Trees for Development in Sub-Saharan Africa (1989) Stockholm, Sweden, IFS. p 103.

[17] WILSON, J., MUNRO, R.C., INGLEBY, K., MASON, P.A., JEFWA, J., MUTHOKA, P.N., DICK, J. McP., LEAKY, R.R.B., Tree establishment in semi-arid lands of Kenya - Role of mycorrhizal inoculation and water-retaining polymer. For. Ecol. and Management **45** (1991) 153-163.

[18] FARDEAU, J.C., AND JAPPE, J., Nouvelle méthode de détermination du phosphore assimilable du sol par les plantes: Extrapolation des cinétiques de dilution isotopique. C.R. Seances Acad. Sci. Ser. D. **282** (1976) 1137-1140.

[19] MULONGOY, K., CALLENS, A., OKOGUN, J.A., Differences in mycorrhizal infection in P uptake of sweet potato cultivars (*Ipomoea batata* L.) during early growth in three soils. Bio Fert. Soils (1988) 7-10.

[20] SIMPSON, D., DAFT, M.J., Interactions between water stress and mycorrhizal inocula on plant growth and mycorrhizal development in maize and sorghum. Plant and Soil **121** (1990) 179-86.

[21] MUSANDU, A.A.O., GILLER, K.E., Effect of Vesicular-arbuscular mycorrhizae on Kudzu (*Pueraria phaseoloides*) growth in phosphate fixing Kenya soils. Afr. Crop Sci. J. **2** (1) (1994) 79-85.

[22] MANJUNATH, A., HUE, N. V., HABTE, M., Response of *Leucaena leucocephala* to vesicular-arbuscular mycorrhizal colonization and rock phosphate fertilization in an oxisol. Plant and Soil **114** (1989) 127-133.

[23] AMER, F., S. MAHDI, ALRADI. A., Limitations in isotopic measurements of labile phosphate soils. J. Soil Sci. **20** (1969) 91-100.

[24] JARREL, W.M., BEVERLY,R.B., The dilution effect in plant nutrition studies. Adv. Agron. **34** (1981) 97-224.

[25] OSUNDE, A.O., ZAPATA, F., SANGINGA, N., Agronomic evaluation of a rock phosphate as a phosphorus source for *L. leucocephala* grown on an Ultisol (pp. 133-138). In: Mulongoy, K., Gueye, M., and Spencer, D.S.C. (eds.) Biological nitrogen fixation and sustainability of Tropical Agriculture. Proceedings of the Fourth international Conference of the African Association for Biological Nitrogen Fixation (AABNF), held at 11TA, Ibadan, Nigeria, 24-28 Sept. 1990.

[26] FOX, R.L. AND SEARLE, P.G.E., Phosphate adsorption by the soils of the tropics. In: Diversity of Soils of the tropics. M. Drosdrof (ed.), pp 97-119 (1978) Am. Soc. of Agron. Madison, Wisconsin, USA.

[27] AZCON-G DE AQUILAR, C., AZCON, R., BAREA, J.M., Nature, (London) **279 (1979)** 325-327. Endomycorrhizal fungi and *Rhizobium* as biological fertilizers for *Medicago sativa* in normal cultivation.

[28] HAYMAN, D.S., Mycorrhizae of nitrogen-fixing legumes. MIRCEN J. **2** (1986) 121-145.

[29] SMITH, S.E., NICHOLAS, D.J., SMITH, F.A., Effect of early mycorrhizal infection on nodulation and nitrogen fixation in *Trifolium subterraneum* L. Aust. J. Plant Physiol. **6** (1979) 305-316.

[30] SKENE, K.R., SPRENT, J.I., C. ONG. Three steps to heaven: Nutrient acquisition in *Grevillea robusta* A. Cunn. ex. R. Br (Proteaceae). Short communication - Agroforestry Today. **8** (2): (1995) 11-12.

RESPONSE OF SEEDLINGS OF *GREVILLEA ROBUSTA* A. CUNN TO PHOSPHORUS FERTILIZATION IN ACID SOILS FROM KENYA[1]

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Abstract. Three experiments were conducted to assess the response of *G. robusta* to phosphorus fertilization using acid low-P soils from Eastern (Andosols, Gituamba) and Western (Acrisols, Kakamega) Kenya. In the first experiment, P was applied as Minjingu Phosphate rock (MPR, 12.9% total P) at 0, 25.8 and 38.7 kg P/kg soil into pots containing five kg soil. In the second experiment, 2g VAM soil + roots inoculum/5 kg soil was included in addition to the same MPR rates but only to Acrisol, Kakamega. In the third experiment, MPR and TSP were added to 2 kg soil (Acrisols, Kakamega) at a rate of 25.8 mg P kg^{-1} soil and ^{32}P isotope dilution techniques were used to assess P uptake and divided into two destructive shoot harvests at 3 and 6 MAT (months after transplanting). Application of MPR in Andosols significantly ($P < 0.05$) reduced height and root collar diameter of *G. robusta* as compared to the control whereas significant increases ($P<0.05$) in height and root collar diameter were recorded in the Acrisol in the P-fertilized treatments compared to control. Interaction soil with P fertilizer rates was highly significant ($p<0.001$) for both height and root collar diameter growth. The roots were not infected with VA-mycorrhizae after 12 months. At 3 MAT the percentage P derived from the MPR and TSP (%Pdff) was 3% and 6% respectively. P uptake decreased significantly ($p<0.05$) between 3 and 6 months. The results indicate that addition of P fertilizer and inoculation with VA-mycorrhizae to *G. robusta* in the two soils was probably required at the early stages of growth. Further research, especially extensive root studies (nursery and field) are required to explain the above observations.

1. INTRODUCTION

Grevillea robusta A. cunn was introduced in Kenya mainly as a shade tree for coffee and tea and from 1910 as a mixture with *Cupressus lusitanica*. Streets, 1962; Milimo, 1988 [1, 2]. The species is currently well accepted in Western [3] and Central [4] Kenya. *Grevillea robusta* is well established in subtropical and tropical highland environments [6] and in densely populated zones it is an important source of fuelwood and income from sale of construction timber [4]. Harwood and Booth [7] reported that the species is popular with African farmers because it provides viable products, it is easy to propagate and its proteoid roots help it grow in low fertility soils. Further, *G. robusta* does not compete with adjacent crops. Annual growth rates of 2 m in height and 2 cm in diameter over the first 5 years are commonly achieved in a number of countries where climate and soils are suitable [7, 4]. Therefore, this tree is a good candidate in Agroforestry systems. The majority of the areas in Western Kenya and parts of Central Kenya highlands are dominated by acid soils with low levels in phosphorus (P) and nitrogen (N) [8].

P addition up to 500 kg P_2O_5 ha^{-1} as triple super phosphate (TSP) has produced a response in above ground growth of *G. robusta* in experimental farms in Maseno, W. Kenya (Bashir, pers. comm.).

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However TSP and other commercial fertilizers are expensive and unaffordable by the majority of the smallholder farmers who would like to increase their yields on these inherently infertile soils [9]. Use of phosphate rock has been suggested as an alternative [10, 9] in replenishing their low P status.

Vesicular arbuscular mycorrhizal (VAM) associations with plant roots plays an important role in P-nutrition of plants particularly those growing in soil having low available P [11]. Plants infected with VA-mycorrhizae on their roots have been shown to produce greater plant growth and increased P-uptake in P deficient soils by increasing the root surface area [12]. VA-mycorrhizal fungi readily absorb soluble phosphate from the labile pool of phosphorus in soils and improve the use of phosphate rock [13-15]. Tinker 1980 [12] estimated that increased P uptake from VAM-inoculation was equivalent to 100 kg ha^{-1} of fertilizer. Isotopic labeling (^{32}P) experiments have also indicated that both mycorrhizal and non-mycorrhizal plants utilize the same pool of phosphorous in soil [15, 14]. However, limited research has been conducted to investigate the role of P in the establishment of *G. robusta,* hence information is scarce or unavailable. These glasshouse studies were thus initiated to evaluate *G. robusta* growth response and P uptake after application of P fertilizers:Minjingu phosphate rock (MPR) and TSP, with and without VA-mycorrhiza inoculation.

2. MATERIALS AND METHOD

2.1. Characteristics of soil and tree seedlings

Surface soil samples (0-20 cm) were randomly collected from experimental farms. Main properties of the Andosol from Gituamba in E. Kenya were:pH (1:5 soil to H_2O ratio) 4.2, carbon = 5.9%, available P-Olsen = 2.5 mg kg^{-1}, exchangeable Al = 2.1 cmol kg^{-1}, CEC. = 22.3 cmol kg^{-1} . The Acrisol of Kakamega in W. Kenya had the following properties: pH (1:5 soil to H_2O ratio) 4.3, carbon = 1.8%, exchangeable P-Olsen = 2.1 mg kg^{-1}, exchangeable Al =1.0 cmol kg^{-1} and CEC = 3.2 cmol kg^{-1}. Seeds of *G. robusta* were pregerminated on sterile water-agar Petri dishes and after emergence transferred into sterilized sand trays for 3 weeks. Thereafter seedlings were transplanted one per pot (30 cm x 15 cm diameter) containing 5 kg of soil.

2.2. Experiment I and II: Assessing growth of the tree seedlings due to P application and VAM inoculation

In experiment I, Minjingu PR (12.9% P and 40% CaO) was applied at the rates of 0 (PRo), 25.8 (PR1) and 38. 7 (PR2) mg P kg^{-1} (equivalent to 0, 400 and 600 kg Minjingu PR ha^{-1}) and mixed thoroughly with the two soils before transplanting the one-month-old seedlings. The design of the experiment was a randomized complete block replicated three times.

In experiment II, the treatments were PR0, PR1, PR2, PRo + VAM-mycorrhizae, PR1+VA-mycorrhizae and PR2+VA-mycorrhizae using just Kakamega soil. Minjingu PR was applied and mixed thoroughly with the soil. About 200 ml of water was added (to approximately 80% field capacity) and the set-up left for a week to allow for equilibration. The VA-mycorrhizae inoculation method described by [16] was adopted at a rate of 2 g of inoculum per pot. The inoculum consisted of a mixture of roots and soil from *Acacia tortilis* and was added approximately quarter-way down the soil in the pots. A basal nutrient solution containing 200 mg N (NH_4NO_3), 400 mg K ($K_2SO_4.7H_2O$) and 400 mg Mg ($MgSO_4.7H_2O$) was applied to each pot at transplanting. The experiment was replicated four times in a completely randomized design.

In experiment I, height and root collar diameter were recorded at 21 weeks after transplanting (WAT). This age (21 WAT) is normally recommended by Forestry Department in Kenya to transplant tree seedlings to the field. In experiment II, the height and root collar diameter was recorded at 12 months after transplanting (12 MAT), after which the seedlings were harvested. Shoot dry weight was determined after drying the materials at 80° C in an oven for 24 hrs. One-centimeter root sections from experiment II were stained to assess VA-mycorrhiza infection using the methods described by [17, 18]. The grid intercept method of [19] was used to quantify the infection. The remaining portions of roots were oven-dried at 80° C for 24 hrs. for root dry weight determination.

2.3. Experiment III: Procedures for ^{32}P labeling the P fertilized experiment

In experiment III, ^{32}P isotope dilution technique was applied to discriminate between soil and fertilizer derived phosphorus in the plant material. MPR and TSP, were applied at the rate of 25.8 mg P/kg soil equivalent to 52 kg P ha^{-1}, and the Acrisol was used as the test soil. The treatments included:

(a) Soil alone as the control
(b) Soil + Minjingu PR and
(c) Soil + TSP

To all pots, 20 ml of a 10 ppm KH_2PO_4 solution labeled at an activity of 185x104 Bq ^{32}P/kg soil (50µCi ^{32}P per kg soil) were then uniformly applied over the soil surface of all pots immediately after transplanting the 3 week-old seedlings. Small amounts of distilled water were added to each pot to wash down the labeled solution. The soils were constantly watered to approximately field capacity. The experimental design was completely randomized with 3 replications for each of the harvests done at 3 and 6 months after transplanting (3 and 6 MAT). Coinciding with the first destructive harvest of shoots at 3 MAT, a similar amount and activity of ^{32}P labeled solution was again uniformly added onto the soil surface of 3 month old seedlings which constituted the second destructive harvest of shoots that was carried out at 6 MAT. For radiation protection measures, root data were not collected.

In experiment III, P uptake and other isotopically derived parameters were determined. At each harvest the shoots of the seedlings to which ^{32}P was applied were cut into small sections and oven dried at 80°C for 24 hours to obtain dry weight. This was followed by subsampling into 2 g portions and placed into oven dried porcelain dishes. The samples were moistened by a little distilled water and dry ashed in a muffle furnace at 450°C. After cooling, the ash were dissolved using 20 ml of 1 M HCl; 10 ml of this solution was used for plant tissue P determination by colorimetric method. The rest was transferred to vials for Cerenkov counting to assess ^{32}P activity using a liquid scintillation counter Packard Model LSC 2000. The following formulae were used to derive isotopically determined parameters [20].

$$SA = \frac{\text{Disintegration per minute (dpm)}}{(\text{mg P }/2\ )} \tag{1}$$

where SA= specific activity of plant material and mg P/2 because only half the sample was used in the P determination;

$$\%\ \text{Pdfs} = \frac{\text{SA plant (in presence of fertilizer) x 100}}{\text{SA plant (in absence of fertilizer)}} \tag{2}$$

where %Pdfs = The percentage of P in the plant material derived from the soil; the assumption in this method is that the higher the P availability from fertilizer (Minjingu PR or TSP) to the plant, the more it will dilute the SA of the material;

$$\text{Pdff}=\frac{(1\text{-Pdfs})}{(100)} \text{ x } 100 \tag{3}$$

where Pdff = percentage of P in the plant material derived from the respective fertilizers; the assumption made here was that the plant absorbs P in direct proportion to its availability and that the ratio of availability of soil P and labeled carrier ^{32}P was unaffected by the addition of fertilizer.

The actual amount in the plant material derived from the fertilizers was determined as follows:

$$\text{AAPf} = \text{Total P uptake x \%Pdff} \tag{4}$$

Where AAPf = actual amount of P in mg taken up by the seedlings from the fertilizer. The relative availability of Minjingu PR was then determined as follows:

$$\text{RAID} = \frac{\text{AAPf (MPR)}}{\text{AAPf (TSP)}} \qquad (5)$$

Where RAID = relative availability of (Minjingu PR compared to TSP) as determined by isotope dilution, AAPf (MPR) = actual amount of P in plant derived from Minjingu phosphate rock as determined by isotope dilution.

2.4. Statistical analysis

The data at 21 WAT (Experiment I), 12 MAT (Experiment II), 3 and 6 MAT (Experiment III) were subjected to analysis of variance (ANOVA) using the Genstat 3.22 computer software package [21] while least significant differences (l.s.d) at ($P<0.05$) were used to compare the means.

3. RESULTS AND DISCUSSION

3.1. Experiment I: Height and root collar diameter of 21 week-old seedlings

Results for height and root collar diameter for experiment I are shown in Table I. When the soil types and P rates were separated during the data analysis, a significant reduction of up to 1.5 times for both tree height and root collar parameters was observed upon addition of P fertilizer to the Andosol, Gituamba compared to the control. With the Acrisol, Kakamega there was a significant increase in height and root collar diameter of up to 1.5 times when P was applied compared to the control. Soil and P rates interaction were significant ($P<0.001$) confirming that the two soils behaved differently to P application. The mineralization of high organic matter in the Andosol,Gituamba under greenhouse conditions could have contributed to the negative response to P application. Furthermore growth response to P application in the Acrisol, Kakamega still remained lower than that recorded in the Andosol, Gituamba control.

The Andosols, Gituamba are volcanic soils, which typically have amorphous alumino-silicates and humus-Al complexes that have a very high capacity to sorb P [22, 23]. This sorption tends to be essentially irreversible, and even high rates of P application do not satisfy the P sorption capacity [24].

TABLE I. EFFECT OF P FERTILIZATION ON
THE HEIGHT AND ROOT COLLAR DIAMETER INCREASE OF *G. robusta*
AFTER 21 WEEKS WHILE GROWING IN TWO ACIDIC SOILS FROM KENYA

	P rate (kg P_20_5/ha)			
	0	52	77	LSD ($p<0.05$) soil x P rates
Soil		Height (cm)		
Andosol, Gituamba	31.8	15.4	18.3	9.8
Acrisol, Kakamega	15.9	27.6	28.7	
		Root collar diameter (cm)		
Andosol, Gituamba	0.6	0.4	0.4	0.1
Acrisol, Kakamega	0.3	0.6	0.5	

However P fixed by amorphous materials in Gituamba Andosols was probably easily extracted by *G. robusta* through its special root structure [25]. This may have accounted for the poor response to P application. Moreover, the reduction in growth observed with larger P applications might be due to toxic amounts of exchangeable Al^{3+} released from the mineralizing organic matter-Al complexes influenced by the Ca^{2+} ions form Minjingu PR that contains 40% CaO as it solubilized to release nutrients into the soil solution. Such an effect of Ca^{2+} on organic matter-Al complexes in Andosols has also been reported by [26].

The seedlings in the control of Acrisol, Kakamega had poor growth compared to those of Andosol, Gituamba control because of inherently low P level in Acrisols [27]. The positive response to P application was probably due to the low organic matter levels, which were unable to supply sufficient P through mineralization [28]. Buresh et al., 1997 [22] reported that a decrease in soil organic matter is likely to lead to a reduction in supply of plant-available P. However, the low response to P fertilization in the Acrisols, Kakamega could be explained by their high Al content (approx. 37%) when compared to the Andosol, Gituamba control leading to an increase in the sorption of the P released from the applied Minjingu PR or directly affecting the growth of *G. robusta* seedlings.

3.2. Experiment II: Dry matter production, height and root collar diameter of 12 month-old seedlings

Results of experiment II on seedlings growing in the Acrisol, Kakamega are shown in Table II. There were no significant differences in response in terms of height; root collar diameter and root dry weights to P application or VA-mycorrhizae inoculation by *G. robusta*. No VAM infection was detected on the root samples and the seedlings looked healthy without symptoms of nutrient deficiencies. The results though inconclusive, imply that mycorrhizal inoculation may not be necessary when *G. robusta* is grown in this Acrisol. There was however, no trend in Minjingu PR addition and VAM inoculation at 12 MAT.

3.3. Experiment III: Height, root collar diameter and P uptake as estimated through isotope dilution method of 3 month-old and 6 month-old seedlings

Minjingu PR and TSP gave significant improvement on seedling height (for Minjingu PR only), root collar diameter, P uptake above the control (Table III). Addition of phosphate fertilizers to the Acrisol of low fertility probably enhanced root proliferation hence increased P uptake by the fertilized tree seedlings. Although height, root collar diameter and shoot dry weight increased between 3 and 6 MAT, P uptake declined significantly with increase in age of the tree seedlings (Table IV). The reduction of P uptake at 6 MAT was likely due to a dilution effect of P by the increase in tissue biomass. I is reported that there is a dilution effect of P due to additional growth because dry matter usually accumulates faster than P uptake[29]. However, at both 3 and 6 MAT P uptake by *G. robusta* from the two sources were not significantly different (Table V).

At 3 MAT of the total P taken up by the seedlings only 3% (0.09 mg P) was derived from Rock-P and 6% (0.18 mg P) from TSP. This supports observations made in experiments I and II to the effect that *G. robusta* showed a preference for inherent soil derived P. The relative availability of Minjingu PR, as determined by isotope dilution (RAID) value indicated that Minjingu PR was 50% as effective as TSP in supplying P to *G. robusta* seedlings. At 6 MAT the negative results for % Pdff and AAPf could mean that little or almost no P was taken up from either Minjingu PR or TSP between 3 and 6 MAT and thus, it was assumed that all the P in the plant was derived from the inherent soil P. Kato *et al*., 1994 [30] reported that % Pdff in the plant seems to be affected by various soil and/or plant borne factors. However, similar studies conducted with other five fast growing tree species gave consistent % Pdff results [31].

These soils are high P-fixing and it is possible that the P applied as Minjingu PR or TSP was fixed immediately after dissolution in the soil. As the soil retained more strongly newly added cation (anion) than the one it had before [32], the plant had to exploit the P retained in the soil using other mechanisms, such as cluster roots [25]. These structures (roots) cling onto soil clods with nutrient

TABLE II. EFFECT OF MINJINGU PR APPLICATION AND VA-MYCORRHIZAE INOCULATION ON HEIGHT, ROOT COLLAR DIAMETER, STEM AND ROOT DRY WEIGHT OF *G. robusta* AFTER 12 MONTHS GROWING IN THE ACRISOL, KAKAMEGA

Treatments	Height (cm)	Root collar diameter (cm)	Shoot dry weight (g/plant)	Root dry weight (g/plant)
PR_0	66.3	1.8	94.7	34.1
PR_0 + M[1]	75.0	1.9	102.4	36.6
PR_1[2]	77.5	1.8	93.5	44.0
PR_1 + M	76.2	1.8	66.5	38.5
PR_2	70.8	1.8	79.4	35.9
PR_2 + M	72.7	1.7	103.2	36.4
LSD ($p<0.05$)	12.3 ns[3]	0.2 ns	29.9 ns	13.4 ns

[1] VA-mycorrhizae inoculum. [2] Minjingu rock phosphate. [3] ns= not significant.

TABLE III. EFFECT OF TWO P SOURCES ON HEIGHT, ROOT COLLAR DIAMETER, SHOOT DRY WEIGHT AND P UPTAKE OF *G. robusta* AT 6 MONTHS AFTER TRANSPLANTING INTO KAKAMEGA SOIL

P sources	Height (cm)	Root collar diameter (cm)	Shoot dry weight (g/plant)	P uptake (mg P/plant)
Minjingu PR[1]	38.1	0.5	8.0	2.0
TSP[2]	31.2	0.6	8.5	2.0
Control	30.0	0.5	6.8	1.2
LSD ($p<0.05$)	6.1*[3]	0.1*	1.8 ns[4]	0.7*

[1]Minjingu phosphate rock. [2]Triple superphosphate. [3] *= $p<0.05$. [4]ns=not significant.

TABLE IV.EFFECT OF P APPLICATION ON HEIGHT, ROOT COLLAR DIAMETER, SHOOT DRY WEIGHT AND P UPTAKE OF *G. robusta* AT 3 AND 6 MONTHS AFTER TRANSPLANTING INTO THE ACRISOL, KAKAMEGA

	Harvest period		
	3 MAT[1]	6 MAT	LSD ($p<0.05$)
Height (cm)	16.5	49.7	5.0***[2]
Root c.d (cm)[3]	0.3	0.8	0.1***
Shoot dry weight[4]	1.0	14.6	1.5***
mg P/plant	2.6	0.9	0.6***

[1] Months after transplanting. [2] ***= $p<0.001$. [3] Root collar diameter(cm). [4] Shoot dry weight (gm/plant)

patches, and probably exudate citrates, which move in rhizosphere for the mobilization of iron phosphates and acquisition of P [33]. It was observed during this study through low power microscopy that *G. robusta* root had such cluster roots. Skene *et.al.* [25] suggested that these roots occur at fixed distances and provide *G. robusta* with the opportunity of growing in soils of low available phosphate. These roots are specifically designed for nutrient patches exploration, exploitation and exportation. Moreover, Grierson and Attiwell, 1989 [34] showed that cluster roots produce hydrogen ions, reductants and possible chelating agents. These cluster roots in *G. robusta* exude citrate[25]. Some species with cluster roots exude as much as 23% of the total plant dry weight as citrate [35].

TABLE V. EFFECT OF TWO P SOURCES ON THE P UPTAKE, %Pdfs, %Pdff, AAPf AND RAID OF *G. robusta* AT 3 AND 6 MAT

P sources	Total P uptake (mg plant^{-1})	%Pdfs[1]	%Pdff[2]	AAPf (mg)[3]	RAID[4]
		3 MAT			
Minjingu PR	3.1	87	3	0.09	50
TSP[5]	3.0	84	6	0.18	n/a[6]
Control	1.7	n/a	n/a	n/a	n/a
	LSD($p<0.05$-P sources) 1.5				
		6 MAT			
Minjingu PR	1.0	124	-24	-22.8	n/a
TSP	1.0	135	-35	-35.0	n/a
Control	0.7	n/a	n/a	n/a	n/a
	LSD($p<0.05$-P sources) 0.60				

[1] Percent of phosphorus in plant material derived from soil. [2] Percent of phosphorus in plant arterial derived from fertilizer. [3] Actual amount of P taken up by the seedlings (%Pdff x Total P uptake) from fertilizer. [4] Relative availability of Minjingu PR as determined by isotope dilution. [5] Triple super phosphate. [6] n/a = value not applicable, LSD ($p<0.05$) P source * Harvest=0.99***.

4. CONCLUSIONS

The application of Minjingu PR to the Acrisol, Kakamega improved the growth of *G. robusta* seedlings at the early stage. The failure to get a response with the Andosol, Gituamba was attributed to increased availability to *G. robusta* of fixed P in Andosols and to the toxic effect of exchangeable Al^{3+} released by the Ca^{2+} input from the PR application. VAM inoculation may not be necessary with *G. robusta* and none of the seedlings were infected with VAM. Through use of ^{32}P isotope dilution techniques it was observed that availability of P from Minjingu PR was a half of that from water-soluble TSPat 3 MAT. The reduction of P uptake at 6 MAT was probably due to a P dilution effect by increased growth. *G.* robusta was shown to be able to utilize inherent soil P even in the absence of external P sources e.g. Minjingu PR and TSP. The ability of *G.* robusta to perform well in low available P and acidic Andosols is interesting. However, P fertilization might still be necessary in the Acrisols at the early stages of growth of *G. robusta*. Further investigations are needed with this tree species to establish the nature of the uptake discrimination against fertilizer P and whether the formation of cluster roots is an adaptation mechanism.

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REFERENCES

[1] STREETS, R.J., Exotic forest trees in the British Commonwealth, Oxford, UK: Clarendon Press (1962).

[2] MILIMO, P.B., Growth and utilization of *Grevillea robusta* in Kenya, Paper presented at a workshop on the use of Australian trees in China, Guangzhou, China, October 1-4 (1988).

[3] OTIENO, H.J.O., Growth performance of *Grevillea robusta* in various agroecological zones of Siaya District, Western Kenya, In: Harwood CE. *Grevillea* in Agroforestry and Forestry. Proceedings of an International Workshop (1992), p. 81-85. Nairobi, Kenya: ICRAF.

[4] KAMWETI, D.M., Growth and utilization of *G. robusta* around Mt. Kenya. In: Harwood CE. *Grevillea* in agroforestry and forestry, Proceedings of an international workshop (1992), p. 73-80, Nairobi, Kenya: ICRAF

[5] KAMWETI, D.M., Assessment and prediction of wood yield from agroforestry systems in Kenya, Ph.D. Thesis, University of Nairobi, Kenya, (1996) 138 p.

[6] HARWOOD, C.E., *Grevillea robusta*: an annotated bibliography, Nairobi, Kenya: ICRAF (1989) 131 pp.

[7] HARWOOD, C.E., BOOTH, T.H., Status of *Grevillea robusta* in forestry and agroforestry. In: Harwood CE. *Grevillea* in Agroforestry and Forestry, Proceedings of an International Workshop (1992) p. 9-19, Nairobi, Kenya: ICRAF.

[8] FAO, Efficient fertilizer use in acid upland soils of the humid tropics, FAO Fertilizer and Plant Nutrition Bulletin 10. Rome:FAO (1986).

[9] KARI-KEFRI-ICRAF and Government of Kenya, Soil fertility re-capitalization and replenishment project in Western Kenya, Financing research proposal to EU (1997) 32 pp.

[10] CHIEN S.H., MENON, R.G., Factors affecting the agronomic effectiveness of phosphate rock for direct application, Paper presented at FAO/IAEA Consultants Meeting on "Evaluation of Agronomic Effectiveness of Phosphate Fertilizers through the use of nuclear and Related Techniques" (1993) May 10-12, Vienna.

[11] BAREA, J.M., *Vesicular-arbuscular* mycorrhizae as modifiers of soil fertility, Adv. Soil. Sci. **15** (1991) 1-40.

[12] TINKER, P.B., Role of rhizosphere microorganisms in phosphorus uptake by plants. In: Khasawneh, FE. *et.al*. The role of phosphorus in agriculture (1980) pp 617-647, Madison, WI: ASA, CSSA, and SSSA.

[13] BAREA, J.M., AZCON, R., AZCON-G de AQUILAR, C., Interactions between phosphate solubilizing bacteria and VA mycorrhiza to improve the utilization of rock phosphate by plants in non acidic soils, In: 3rd International Congress on Phosphorus Compounds. Brussels: IMPHOS (1983) 127-144.

[14] BOLAN, N.S.A., Critical review on the role of mycorrhiza fungi in the uptake of phosphorus by plants, Plant Soil **134** (1991) 189-207.

[15] GIANINAZZI-PEARSON, V., GIANINAZZI, S., Phosphorus metabolism in mycorrhizas. In: Boddy L., Marchant R., and Read DJ. (Eds.), Nitrogen Phosphorus and Sulfur utilization by Fungi. (1989) p. 227-241, Cambridge UK: Cambrdge University Press.

[16] WILSON, J., MUNRO, R.C., INGLEBY, K., MASON, P.A., JEFWA, J., MUTHOKA, P.N., DICK, J. McP., LEAKEY, R.R.B. Tree establishment in semi-arid lands of Kenya - Role of mycorrhizal inoculation and water-retaining polymer, For. Ecol. and Manage. **45** (1991) 153-163.

[17] PHILIPS, J.M., HAYMAN D.S., Improved procedures for clearing roots and staining parasitic and vesicular-arbuscular mycorrhiza fungi, Trans. Br. Mycol. Soc. **55** (1970) 158-161.

[18] KOSKE R.E., GEMMA J.N., A modified procedure of staining roots to detect VA-mycorrhizae, Mycol. Res. **92** (1989) 486-505.

[19] TENNANT, D., A test of modified line intersect method of estimating root length, J. Ecol. **63** (1975) 995-1001.

[20] ZAPATA, F., AXMANN, H., ^{32}P Isotopic techniques for evaluating the agronomic effectiveness of rock phosphate materials, Fert. Res. **41** (1995) 89-195.

[21] Genstat 5 Committee of the Statistics Department of Rothamsted Experiment Station, Genstat 5 Release 3 Reference Manual, Oxford, UK: Oxford University Press, 796 p. (1993)

[22] BURESH, R.J., SMITHSON, P.C., HELLUMS, D.T., Building soil phosphorus capital in Africa. In: Buresh RJ., Sanchez PA., Calhoun F. Replenishing Soil Fertility in Africa, SSSA Special Publication **51** (1997) 111-149. Madison, WI: SSSA; ASA.

[23] VAN WAMBEKE, A., Sols des tropiques- Proprietes et applications, Huy, Belgique: Trop Asbl, 335 p. (1995)

[24] ESPINOSA, J., Phosphorus diagnosis and recommendations in volcanic ash soils. In: Proc. of tropsoils phosphorus. Decision support system workshop, College Station, TX, 11-12 Mar., (1992) p. 109-115, TropSoils Bull. 92-01. Dept. of Agron. and Soil Sci., College of Trop. Agric. And Human Resources. Univ. Hawaii, Honululu.

[25] SKENE, K.R., SPRENT J.I., ONG C.K., Cluster roots of *Grevillea robusta* - foragers or scavengers, Agroforestry Today **8** 2 (1996) 11-12.

[26] LE MARE, P.H., LEON, A., The effect of lime on adsorption and desorption of phosphates in five Colombian soils, J. Soil Sci. **40** (1989) 59-69.

[27] OKALEBO, J.R., A study of the effect of phosphate fertilizers on maize and sorghum production in some East African soils, Ph.D Thesis, University of Nairobi. (1987) 186 pp.

[28] HARRISON, A.F., Soil organic phosphorus. A review of world literature, Willingford, UK: CAB International, (1987) 256p.

[29] JARREL, W.M.., BEVERLY, R.B., The dilution effect in plant nutrition studies. Adv. Agron. **34** (1981) 197-224.

[30] KATO, N., FARDEAU, J.C., ZAPATA F. Evaluation of the residual effect of P fertilizers on the plant P nutrition using isotopic techniques. In: Nuclear Techniques in Soil-Plant studies for sustainable agriculture and environmental preservation, Proceedings of a Symposium, Vienna, 17-21 October 1994 jointly organized by IAEA and FAO, (1994) 189-196p. Vienna, IAEA.

[31] MWENDWA, K.A., KARANJA, N.K., ZAPATA, F., MAINGI, S.W., Evaluation of P uptake from Minjingu phosphate rock and growth of six agroforestry tree species growing on an acid soil from W. Kenya using ^{32}P isotope dilution technique, International J. of Biochem.Physics Vol. **6-7** (1-2) (1997-1998) 79-85.

[32] DUCHAUFOUR, P., Pédologie. Sol, végétation, environnement. 2nd edition, Paris: Masson 289 p. (1991)

[33] GARDENER, W.K., BARBER, D.A., PARBERRY, D.G., The acquisition of phosphorus by *Lupinus albus* L. III. The probable mechanism by which phosphorus movement in the soil/root interface is enhanced, Plant Soil **70** (1983) 107-124.

[34] GRIERSON, P.F., ATTIWELL, P.M., Chemical characteristics of the proteoid root of *Banksia integrifolia* L.f., Aust. J. Bot. **37** (1989) 137-143.

[35] DINKELAKER, B., ROMHELD, V., MARSCHNER, H., Citric acid excretion and precipitation of calcium in the rhizosphere of white lupine (*Lupinus albus* L.) Plant Cell Env. **12** (1989) 285-292.

EXPLORING PLANT FACTORS FOR INCREASING PHOSPHORUS UTILIZATION FROM ROCK PHOSPHATES AND NATIVE SOIL PHOSPHATES IN ACIDIC SOILS

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Abstract. Six plant species with contrasting capacity in utilizing rock phosphates were compared with regard to their responses to phosphorus starvation in hydroponic cultures. Radish, buckwheat and oil rapeseed are known to have strong ability to use rock phosphates while ryegrass, wheat and sesbania are less efficient. Whereas other plants acidified their culture solution under P starvation (-P), radish plants make alkaline the solution. When neutralizing the pH of the solutions cultured with plants under either -P or + P conditions, solutions with P starved buckwheat, rapeseed, and radish had a higher ability to solubilize Al and Fe phosphates than did those cultured with sesbania, ryegrass and wheat. Characterization of organic ligands in the solutions identified that citrate and malate were the major organic anions exuded by rapeseed and radish. Besides citrate and malate, buckwheat exuded a large amount of tartrate under P starvation. In contrast, ryegrass, wheat and sesbania secreted only a limited amount of oxalic acid, regardless of P status. Changes in activities of phosphoenolpyruvate carboxylase, acid phosphatase, and nitrate reductase in these plants were also compared under P- sufficient or -deficient conditions. The results indicated that plant ability to use rock phosphates or soil phosphates is closely related to their responses toward P starvation. The diversity of P starvation responses was discussed in the context of co-evolution between plants and their environment. Approaches to use plant factors to enhance the effectiveness of rock phosphates were also discussed.

1. INTRODUCTION

The effectiveness of rock phosphates for direct application is determined by an array of factors. These include the characteristics of the rock materials, soil and environmental conditions and last but not the least, plant factors. It has long been recognized that some plants are more efficient in utilizing soil phosphates or rock phosphates than other plants. For example, plants such as buckwheat, radish and oil rapeseed were identified as highly efficient in utilizing Chinese rock phosphates in field and greenhouse experiments [1]. The underlying mechanisms accounted for the high P efficiency in these plants have been speculated to include high Ca uptake, the exudation of protons and secretion of organic acids. However, comprehensive analysis of responses to P deficiency with these high P-efficient crop plants is still not available. It is also not clear why different plants utilize different mechanisms in their adaptation to P deficiency. In the frame of the FAO/IAEA coordinated research project on evaluation of the effectiveness of rock phosphate-based fertilizers, we attempted to explore those plant factors that are expected to contribute significantly to an enhanced utilization of P from rock phosphates or soil native phosphates. The understanding of the adaptation of these high P-efficient plants to P starvation may eventually help us to engineer crop plants with improved ability to use rock phosphates or soil P accumulated from long-time application of P-fertilizers.

2. MATERIALS AND METHODS

2.1. Plants

Six plant species were used in the present study: buckwheat (*Fagopyrum esculentum* Moench), radish (*Raphanus sativus* L.), oil rapeseed (*Brassica napus* L.), sesbania (*Sesbania cannabina* Pers), ryegrass (*Lollium multiflorum* Lam), and wheat (*Triticum aestivum* L.). Except for wheat, these plant species used are commonly cultivated in acidic soils of southern China and they have economic or ecological significance.

2.2. Hydroponic culture

The nutrient solution consisted of the following: 1 mM $NH_4H_2PO_4$, 0.34 mM NH_4NO_3, 4 mM Ca $(NO_3)_2$, 1.31 mM $CaCl_2$, 2mM $MgSO_4.7H_2O$, 5.98 mM KNO_3, 14.3 μM Fe EDTA, 23 μM H_3BO_3, 0.0235 μM $CuCl_2.2H_2O$, 4.55 μM $MnCl_2.4H_2O$, 88 μM $ZnCl_2$, and 0.0123 μM $H_2Mo_4H_2O$. Treatments with phosphorus (+P) did not include NH_4NO_3 and those without phosphorus (-P) did not have $NH_4H_2PO_4$.

2.3. Quantification of H^+ secreted in cultured solutions

The pH of the cultured solution was measured with a Beckman pH meter. The amount of protons excreted by the plants under indicated conditions was quantified by titrating aliquots of the cultured solutions with standard alkaline or acid solution.

2.4. Dissolution of rock phosphate, Fe and Al phosphates by root exudates or organic acids

Each of the following phosphates was extracted at 25°C for 2 hr with 20 ml solution individually cultured with the plant species mentioned above: 0.5 g North Carolina Rock Phosphate (100 mesh), 0.1 g $FePO_4.nH_2O$ (Fe-P) [2] or 0.1 g $AlPO_4.nH_2O$ (Al-P) [3]. A control treatment with distilled water was also run simultaneously. Phosphorus in the solution was determined by molybdate blue method.

2.5. Solubilization of rock phosphate by organic acid

Twenty-five ml of 0.1 M organic acids (adjusted to pH 6.0 or unadjusted) was mixed with 0.5 g of NCPR or 0.1 g $FePO_4.nH_2O$ or $AlPO_4.nH_2O$ and extracted at 25°C for 2 hr. Extracts were filtered and analyzed for P.

2.6. Analysis of organic acids

Hydroponic solutions with plants growing for specific periods of time under -P or +P conditions were collected and passed through cation exchange resin column and 0.25 μM filter. The resulting clear solutions were then condensed on a vacuum rotary evaporator until 1 to 2 ml remained. The solutions analyzed for organic acids by HPLC. Separated organic acids by Bondapak C-18 column were eluted with dilute H_3PO_4 (pH 2.65) and detected at 214 nm against organic acid standards. Organic acids in plant samples were assayed by enzymatic methods following procedures provided by the supplier of the enzyme kits (Boehringer-Mannhein, Germany) [4].

2.7. Assay of enzyme activities

The activity of phosphoenolpyruvate carboxylase (PEPC) was assayed as described in [5]. Acid phosphatase activity was determined using *p*-nitrophenyl phosphate (*p*NPP) as substrate. Nitrate reductase activity (NRA) was determined according to [6].

3. RESULTS

3.1. Excretion of protons in response to phosphorus deficiency

Three plant species were cultured in full strength nutrient solution with P (+P) for 10 days before they were transferred to solution deprived of P (-P). Changes in pH of the -P solution were evident one day following the transfer (Table I). For oil rapeseed and buckwheat, there was a decrease in pH initially, but a gradual restoration to the original value eventually occurred. On the contrary, pH values of solution with radish increased after transferring to P deficient solution (Table I). Clearly, under P deficient condition, acidification of the rhizosphere was not a strategic response adopted by radish.

To quantify the amount of protons excreted or consumed during P starvation, aliquots of solutions from cultures 1 or 5 days after deprivation of P were titrated with standard alkaline solution. Except for radish, all other plant species showed a significant increase in excretion of protons to the medium under -P condition (Table II). Sesbania, wheat and ryegrass all exhibited a high excretion of protons under normal P supply (+P). They also showed an enhanced excretion under P starvation. The background proton excretion with P supplied (+P) may be related to a preferential uptake of NH_4^+ relative to NO_3^- in these plants or a general higher cation uptake than anion uptake. On the other hand, buckwheat, oil rapeseed, and radish excreted very little protons under P-sufficient condition, yet under P starvation, buckwheat and oil rapeseed increased the excretion of protons while there was little increase in proton excretion with radish.

3.2. Solubilization of various forms of phosphates by nutrient solutions cultured with plants

The above results indicated that there were changes in pH in solutions cultured with different plants under -P relative to +P conditions. Thus, it was interesting to study the capacity of these cultured solutions to solubilize different forms of phosphates. Results are presented in Table III.

The data showed that solutions from these plant species had various capacities to solubilize different forms of phosphates. In most cases, solutions from -P treatments had higher capacity to solubilize phosphates than did those cultured with + P plants. Solutions cultured with oil rapeseed, buckwheat, and wheat had high ability to dissolve Fe and Al phosphates regardless of the supply of phosphates. The solutions cultured with rapeseed and buckwheat also showed a higher solubilizing ability to RP with -P treatment compared with +P treatment. On the contrary, radish, sesbania, and ryegrass had enhanced solubilizing ability to these phosphates only under -P condition. Among them, the increase was most significant for radish whose +P-cultured solution had little effect on these phosphates.

3.3. Solubilization of Al-P was enhanced by more alkaline solution

The above extraction of P from various phosphate compounds with cultured solutions was done with the solution without any adjustment in pH. The effect was therefore, a result of combined proton effect (Tables I and II) and other root exudates. Thus the effect of pH adjustment on the solubilization of Al phosphates was investigated. The results indicated that when rising solution pH from 4.5 to 6.0, all cultured solutions increased significantly in the solubilization of P from Al phosphates (Table IV). On the other hand, there was no change in the dissolution of either Fe phosphate and RP (Table V and data not shown).

3.4. Different ability of various organic acids in solubilizing phosphates

Organic acids are the major components in root exudates that enhance the solubilization of phosphates in rhizosphere soils. Several organic acids have been identified in root exudates from plants experiencing P starvation (for review, see Jones, 1998[7]). Nevertheless, data regarding the relative ability of these acids in attacking phosphates are incomplete. Although information from the reaction equilibrium parameters of these organic acids with various phosphates can be obtained, it is more straightforward to compare their ability in a single experiment. Table V presents the results of the assay of P dissolved by organic acids from various forms of phosphates with or without adjustment of solution pH. Tha data indicated that different acids have quite different ability in solubilizing these phosphates. With regard to forms of phosphates, it can be seen that the solubilization of RP was largely dependent on the proton effects of these acids. When adjusting solution pH to 6.0, the amount of phosphate solubilized by these organic acids decreased dramatically, while its effect on Fe phosphate was not very significant, suggesting protons were not the major factor controlling P release from Fe phosphate. Adjustment of the pH to 6.0 resulted in increased solubilization of Al phosphates, as also demonstrated in Table IV. Among all these organic acids, oxalic acid was the strongest in solubilizing Fe phosphate, while oxalic acid, citric acid, and tartaric acid had stronger ability in solubilizing Al phosphate. Oxalate was particularly efficient in solubilizing Al phosphate after adjusting the pH to 6.0 (Table V).

TABLE I. CHANGES IN pH IN -P SOLUTION AT DIFFERENT TIMES AFTER TRANSFERING PLANTS FROM +P TO -P SOLUTION (INITIAL pH=6.2)

Days after Changing Solution	Radish	Buckwheat	Rapeseeds
1	6.16	5.73	5.86
3	6.45	5.78	5.89
5	6.80	5.93	6.07
7	6.81	6.07	6.13
9	7.64	6.15	6.45
13	7.32	6.40	6.70

TABLE II. PROTON EXUDATION 1 OR 5 DAYS AFTER TRANSFERRING PLANTS TO P SOLUTIONS (meq/g FRESH WEIGHT)

Plant Species[1]	Treatment	1 day	5 days
Buckwheat	-P	0.26	0.31
	+P	0.04	0.03
Rapeseed	-P	0.47	0.38
	+P	0.01	0.01
Sesbania	-P	2.14	2.76
	+P	1.26	1.38
Wheat	-P	3.15	3.29
	+P	2.76	2.87
Ryegrass	-P	3.37	3.78
	+P	2.68	2.74

[1] Solution cultured with radish had a higher pH than background control and proton excretion was not determined.

TABLE III. SOLUBILIZATION OF ROCK PHOSPHATE (NCPR) AND SYNTHESIZED PHOSPHATES BY CULTURED SOLUTIONS (μg P/ml)

Plant Species	Fe-P		Al-P		RP	
	-P	+P	-P	+P	-P	+P
Rapeseed	4.70	4.03	4.92	4.06	0.36	0.12
Buckwheat	4.72	4.56	4.89	4.27	0.26	0.11
Radish	5.67	0.77	5.86	1.24	0.45	0.23
Sesbania	3.79	1.02	4.16	1.15	0.21	0.18
Wheat	4.73	4.13	4.82	4.01	0.17	0.16
Ryegrass	3.80	1.41	4.07	1.26	0.23	0.18

TABLE IV. SOLUBILIZATION OF Al PHOSPHATE BY CULTURED SOLUTIONS ADJUSTED TO DIFFERENT pH (μg P/ml)

Plant Species	pH of Solution	P Concentration in Solution (μg/ml)
Rapeseeds	4.5	6.54
	6.0	16.1
Buckwheat	4.5	9.59
	6.0	17.4
Radish	4.5	4.92
	6.0	12.0
Sesbania	4.5	1.85
	6.0	5.92
Wheat	4.5	4.42
	6.0	7.88
Ryegrass	4.5	2.69
	6.0	6.46

TABLE V. PHOSPHORUS SOLUBILIZED BY VARIOUS ORGANIC ACIDS (0.1 M) AT THEIR NATURAL pH OR AT pH 6.0 (0.1 g PHOSPHATES) (μg P in 25 ml)

Organic Acids	pH adjustment	Fe-P	Al-P	RP
Citric	No	31.3	176	1218
	6.0	31.2	870	39.3
Malic	No	30.8	111	2785
	6.0	68.8	514	123
Oxalic	No	529	186	2655
	6.0	141	1233	138
Acetic	No	52.0	25.0	730
	6.0	38.8	196	n.d.
Lactic	No	14.5	179	1757
	6.0	59.5	181	n.d.
Tartaric	No	37.5	257	2940
	Yes	88.3	391	69.5
Succinic	No	n.d	56.2	1500
	Yes	191	n.d.	200

n.d., not determined.

3.5. Characterization of organic acids secreted by plants under P deficient condition

The above studies indicated that in addition to protons, P-components were released in the cultured solution because after adjusting the pH of the solution to neutral, there was still much P-releasing capacity from solution cultured with plants under P deficient conditions. Additional results presented in Table V also demonstrated the ability of various organic acids in solubilizing insoluble phosphates at near-neutral pH. Further experiments were conducted to characterize these components.

Results in Table VI indicated that under P deficient conditions, all plants exhibited enhanced excretion of organic acids, yet the extent and kinds of the acids varied with plant species. Four organic acids were identified, i.e., citric, malic, oxalic and tartaric. Radish and oil rapeseed secreted a large amount of citric acid, while buckwheat showed significant increase in tartaric acid and malic acid secretion. Although wheat excreted malic acid under phosphate deficient condition, only oxalic acid was detected under P sufficient condition. Wheat, sesbania, and ryegrass showed a limited response in oxalic acid excretion under P starvation. This pattern of organic acid excretion matched closely with the ability of these plants in utilizing different forms of soil phosphates and rock phosphates.

3.6. Acid phosphatase activity in plants under phosphate starvation

It is well known that acid phosphatase activity in plants will dramatically increase when plants suffer from P deficiency. However, information on comparison of acid phosphatase activity among plant species under P deficient conditions and how it relates to plant P efficiency is still not available. In this study, we determined acid phosphatase activity in roots and plant leaves at various positions under P starvation (Table VII).

Results indicated that acid phosphatase activity was higher in new leaves than in older leaves, the lowest levels were found in roots (Table VII). It is also noted that radish, oil rapeseed, and buckwheat had higher acid phosphatase activities in leaves than those of wheat, sesbania, and ryegrass.

TABLE VI. SECRETION OF ORGANIC ACIDS (μg)
UNDER P SUFFICIENT AND DEFICIENT CONDITIONS

Plant Species	Treat-ments	Citric Acid	Malate Acid	Oxalic Acid	Tartaric Acid
Radish	-P	547	168	80.2	bd
	+P	87.2	34.7	47.6	bd
Rapeseed	-P	490	147	92.7	bd
	+P	189	99.6	62.4	bd
Buckwheat	-P	128	253	57.4	428
	+P	72.6	46.3	52.6	20.2
Wheat	-P	bd	177	67.6	bd
	+P	bd	bd	62.3	bd
Sesbania	-P	bd	bd	57.8	bd
	+P	bd	bd	55.4	bd
Ryegrass	-P	bd	bd	87.6	bd
	+P	bd	bd	79.5	bd

bd, below determination limit.

TABLE VII. ACID PHOSPHATASE ACTIVITY IN DIFFERENT PARTS OF PLANTS (µmol NPP/g f.w.)

Plant Species	New leaf	2nd Leaf	4th or 5th Leaf	Roots
Radish	13.8	6.32	3.26	0.62
Rapeseeds	12.5	5.27	3.42	0.57
Buckwheat	9.96	4.27	2.78	0.48
Wheat	7.84	2.76	1.56	0.42
Sesbania	2.36	1.07	0.86	0.32
Ryegrass	2.84	1.27	0.91	0.39

To further compare the acid phosphatase activities, as induced by phosphorus deficiency, we choose the first expanded leaf to assay the activity under either +P or -P conditions. Results were presented in Figure 1. Obviously, there are two patterns of responses in acid phosphatase under phosphate deficient condition. Activities of acid phosphatase in buckwheat, oil rapeseed, and radish increased 3.2, 3.9 and 3.8 times under -P than under +P conditions, respectively. On the contrary, there was little change in the activities for ryegrass, sesbania, and wheat (Fig. 1).

The activities of acid phosphatase in root exudates presented a slightly different picture. Wheat, radish, buckwheat and rapeseed showed an obvious increase in secreted acid phosphatase activities in their root exudates under -P condition while the increase in ryegrass and sesbania was to a lesser extent (Fig. 2).

3.7. Secreted acid phosphatase activities, as affected by sparingly soluble phosphates

Acid phosphatase activity and the secretion of the enzyme are mainly regulated by interior inorganic P status in plants. It is of interest to know if any sparingly soluble inorganic P sources in the root environment could regulate the enzyme activities. We tested the effect of RP, synthesized iron phosphate and Al phosphate on acid phosphatase activity in the exudates under -P or +P conditions. The enzyme activity in the exudates was normalized with regard to plant fresh weight. Results in Fig. 2 indicated that except for sesbania and oil rapeseed the addition of RP to culture solution resulted in an elevated acid phosphatase activity compared with -P alone. Iron and Al phosphates also had similar effect albeit the effect was not as strong as with RP.

3.8. Changes in activities of other related enzymes

Increased excretion of organic acids under P starvation may suggest a concurrent increase in the synthesis of organic acids within the plants. One key enzyme in organic acid metabolism is phosphoenolpyruvate carboxylase (PEPC). We assayed the enzyme activity in -P and + P treated roots and shoots. Table VIII showed that whereas there was no obvious increase in PEPC activities in roots of rapeseed and radish, obvious increase in its activity was observed in the shoots. On the other hand, with buckwheat, there was an increase in PEPC activity in both roots and shoots.

TABLE VIII. ACTIVITY OF PEPC IN SHOOTS AND ROOTS
UNDER +P OR -P CONDITIONS (nmol NAD/min/g f.w.)

	Rapeseed		Radish		Buckwheat	
	+P	-P	+P	-P	+P	-P
Shoot	264	548	284	463	148	206
Roots	166	169	181	192	97	123

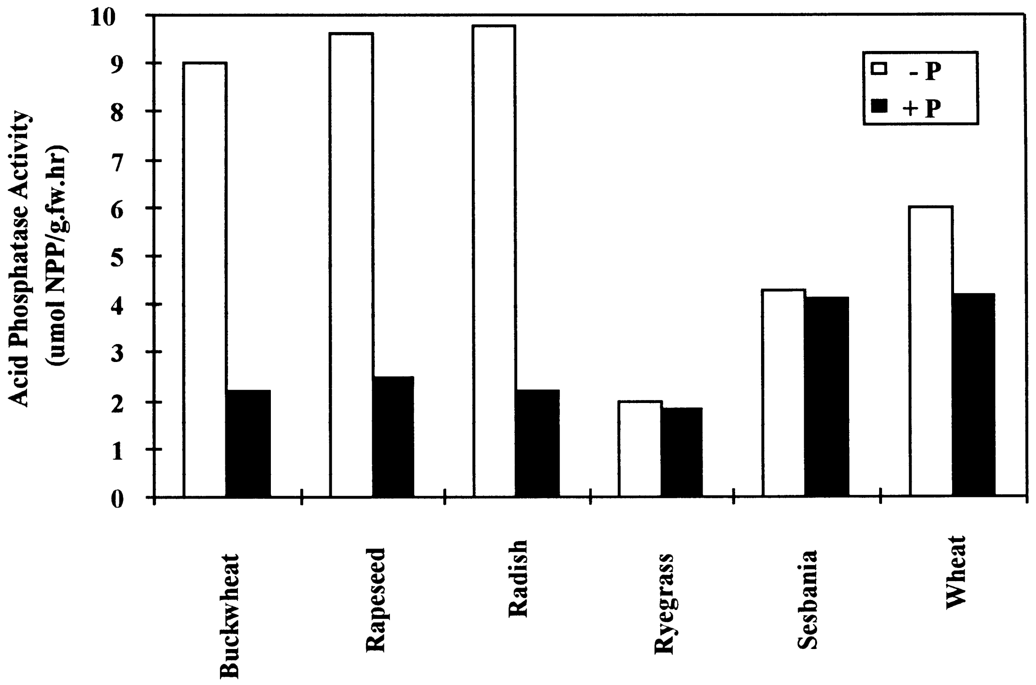

Fig. 1. Acid phosphatase activity (μmol NPP/g fresh weight.hr) in newly expanded leaf under P starvation (-P) *or with phosphorus supply* (+P) *(μmol NPP/g fresh weight.hr). Data are the averages of duplicate determinations.*

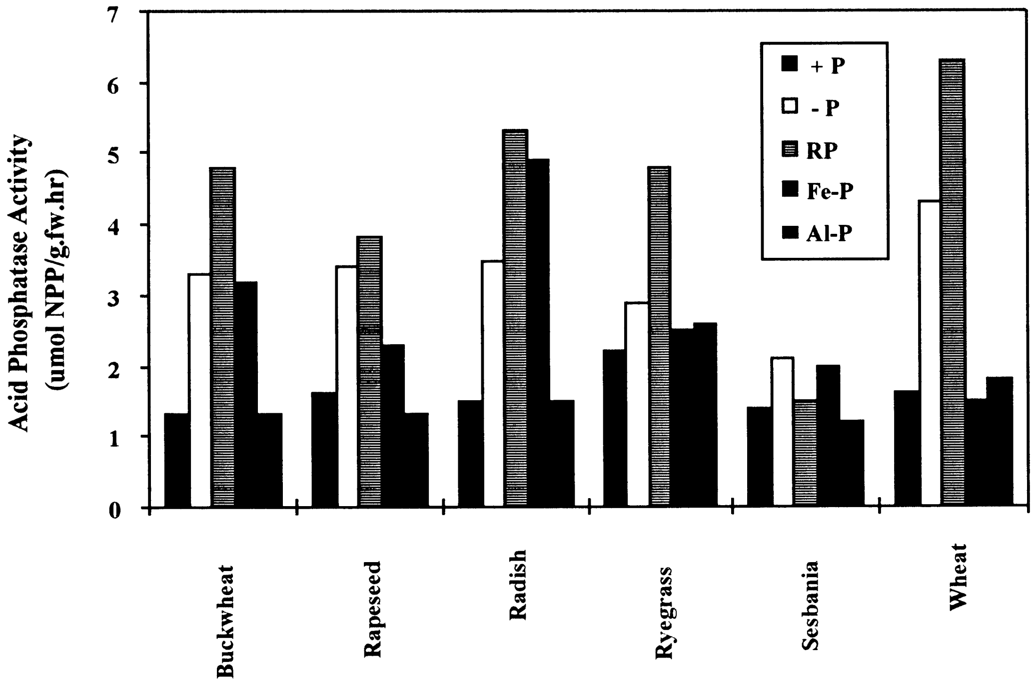

Fig. 2. Acid phosphatase activity (μmol NPP/g fresh weight.hr) in root exudates under P starvation condition as affected by the addition of NCPR (PR, bars with horizontal strips), iron phosphate (Fe-P, bars with down diagonal strips) and aluminum phosphate (Al-P, bars with up diagonal strips). Also shown are -P alone (open bars) and +P treatment (black bars). Data are the averages of duplicate determinations.

Another enzyme that was also affected by P starvation is nitrate reductase (NR) Table IX presented results with NRA in both leaves and roots. Results indicated that while there was a general trend that under phosphorus deficiency condition, NRA decreased, the trend was particularly clear in roots. A higher NRA may associate with higher rhizosphere pH [8]. Reduced NRA may shift the preference from the uptake of NO_3^- to NH_4^+ and decrease rhizosphere pH [9].

TABLE IX. NITRATE REDUCTASE ACTIVITY IN ROOTS AND SHOOTS UNDER -P OR +P CONDITIONS (μg NO_2^--N/g fw/hr)

Plant	*Leaves*		*Roots*	
species	-P	+P	-P	+P
Rapeseed	19.2	40.2	4.6	21.7
Radish	28.7	16.8	3.6	38.4
Buckwheat	32.6	17.5	4.9	41.2
Sesbania	12.4	20.3	2.8	2.5
Ryegrass	8.7	9.6	1.2	1.8
Wheat	20.4	26.3	3.1	10.6

4. DISCUSSION

4.1. Diversity of plant responses to phosphorus deficiency

Under condition of P limitation, plants exhibit a large diversity of responses, which are presumably used to increase P acquisition from the surrounding environment or mobilize internal P resources for use in key processes that are vital for survival. At the molecular level, increased transcription of some genes was observed. These included, for example, genes that encode root-specific phosphate transporters (e.g., [10]). Changes at cellular or morphological levels that are well-documented include alteration of root architectures, excretion of protons, organic ligands, and acid phosphatases. Although it is still not clear whether these responses are adaptation strategies or simply consequences of damage caused by P starvation, these processes are probably of great significance for plants to survive in P-insufficient habitats. Plants may select one or several responses and the choice of these strategies may be related to the natural habitats, which they have long been co-evolved with.

Our study indicates that under P deficiency, wheat and ryegrass had a significant secretion of protons, which acidified the solution. However, cultured solutions with these plants were less efficient in dissolving either Fe or Al phosphates (Table V). Presumably, these plants originated from temperate regions, where the predominant form of phosphorus in soils is calcium phosphates. Fe or Al phosphates are little component fractions of the total P in these soils [11, 12]. A small pH decrease in the rhizosphere would increase significantly the available phosphorus for plants in such a Ca phosphate abundant soil. In natural conditions, these plants also establish symbioses with mycorrhizal fungi and the resulting mycorrhizae are very important for acquisition of phosphorus from bulk soils that extend far away from the otherwise limited rhizosphere.

Other plants in this study that also secreted protons under P starvation were sesbania, buckwheat, and oil rapeseed. When P supply was adequate, these plants did not exude much protons. In acidic soils where these plants are well adapted, increased proton exudation may lead to increased level of toxic Al in their rhizosphere. In contrast to wheat or ryegrass, besides proton secretion, buckwheat and rapeseed also excreted quite large amount of organic ligands under P deficient conditions. On the other hand, radish plants did not acidify their rhizosphere, yet they also secreted a large quantity of organic acids. The organic acid excretion in radish, buckwheat and rapeseed endowed these plants the ability to exploit Al and Fe phosphates which are the major forms of phosphates in acidic soils. Interestingly, unlike cereal and legume plants, rape and radish do not establish any mycorrhizal symbiosis.

4.2. Role of organic ligands in plant acquisition of phosphorus

When experiencing P deficiency, many plants exude increased amounts of organic components to the surrounding environment. A great variety of organic acids have been detected in root exudates [7], however, some major acids seem preferentially to be secreted by plants. Among these are citric and malic acids (or citrate and malate depending on the pH of the environment involved). A striking example of organic acid excretion was found with white lupin. Under P deficient condition, white lupin secreted a large amount of both citric and malic acids through the segment 1 to 3 cm from the tips of their young proteoid roots [13]. The amount of citric acid secreted may account for more than 10 percent of total plant dry weight [14]. Another organic acid detected was piscidic acid, i.e., hydroxybenzyl tartaric acid, which was secreted by pigeon pea under P deficient conditions and contributed to solubilization of iron phosphates in Alfisols [15].

In the present study, citric and malic acids were the major organic acids secreted by oil rapeseed and radish. Ryegrass and sesbania secreted only small amount of oxalic acid under -P or +P conditions. In addition to oxalic acid, wheat also exudated some malate under P starvation, but the quantity was limited. A special case is with buckwheat. Besides some citric acid and malic acid, buckwheat secreted a significant amount of tartaric acid. The induction in tartaric acid excretion was particularly significant under -P condition (Table VI).

It is not known whether the citrate or malate secretion in oil rapeseed and radish is P starvation-specific. While the excretion of oxalic acid in buckwheat (the same cultivar as we used in this study) was reported to be specifically induced by Al [16], which is consistent with the observation that oxalate had the strongest ability to solubilize Al phosphate (Table V), oxalic acid was not induced by -P treatment. Whereas there was not as much increase in the exudation of citric and malic acids, 20 times increase in the exudation of tartaric acid under -P condition was found with buckwheat (Table VI). It was laso observed a more than 3 times increase in the content of tartaric acid in buckwheat shoots under -P condition. In comparison, the increase in citric and malic acids in oil rapeseeds and radish shoots was less than 2 times (data not shown). It is therefore, very likely that the exudation of tartaric acid in buckwheat is P starvation-specific. Detailed characterization of the specificity of organic acid excretion was first made by Delhaize et al. (1993) [17] in the case of Al toxicity. They demonstrated in a series of studies that the excretion of malate from an Al-tolerant ecotype of wheat was specifically induced by Al but not by other related stresses. While induction of the secretion of some organic ligand in our study is probably P starvation-specific, secretion of citrate and malate is likely stimulated by both P starvation and Al toxicity. Both stresses are common in acidic soils. It is, therefore, possible that an interaction between P deficiency and Al toxicity may lead to even higher secretion of organic ligands than that observed in this study, where only P starvation was applied.

Plants do not normally accumulate high amount of free organic acids. Increased excretion of organic acids under -P condition may imply there are profound changes in carbon metabolism within plants. An important enzyme in carbon metabolism, phosphoenolpyruvate carboxylase (PEPC, EC 4.1.1.31) plays an important role in organic acid synthesis. The enzyme catalyzes the carboxylation of PEP using HCO_3^- as a C source to form oxaloacetate and meanwhile releases the Pi from PEP. While it is not known to what extent this process increases cellular Pi supply, increased PEPC did occur under P deficiency condition, and the increased excretion of organic acids may attribute to this elevated activity of PEPC. Several reports have shown that P deficiency stimulated the activity of C_3 PEPC in leaves [18, 19] and nonphotosynthetic PEPC in roots [17,18]. Yet, in most cases, it is not clear where the increased amount of organic acid came from. Hoffland (1992) [18] suggested that shoot PEPC may contribute to increased citrate synthesis in P-deficient rape plants. Results with white lupin demonstrated both roots and shoot contribution to the increased synthesis of organic acid [20]. In this experiment, we did not detect increased activities of PEPC in roots of rapeseed and radish, the increased activity of PEPC was found mainly in the shoots (Table VIII). This may suggest that citrate and malic acids excreted in these plants probably come from the synthesis in the shoots. On the other hand, a concomitant increase in PEPC was observed both in shoot and in roots of buckwheat, suggesting that non-photosynthesis carbon fixation may contribute to the synthesis and excretion of organic acids in buckwheat.

4.3. How did rock phosphate enhance acid phosphatase activity

It has long been known that under nutrient-limited conditions, plants are able to sense and direct their roots toward the location where nutrients are relatively abundant. Once roots reach the nutrient source, a lot of new laterals are initiated to explore the resources. The molecular explanation for this phenomenon is emerging [21]. By analog, we hypothesized that when we supply a limited amount of available P in the form of rock phosphates the plants would show an increased responses in the excretion of organic acids or acid phosphatase.

Our preliminary experiments indicated that indeed, supply of rock phosphate stimulated the activity of acid phosphatase within the plants (Fig. 1) and increased the secreted enzyme activity (Fig. 2). However, it is not clear whether the effect is from a supply of trace amount of phosphate from the rock phosphate or is from the ions existed in rock phosphates which may be solubilized to some extent in the presence of root exudates. Several kinds of protein phosphatases (e.g., PP2B and 2C) depend on binding with Ca or calmodulin to function (e.g., [21, 23]) (for review, see [24]) yet the amount of Ca in plant cells or in the nutrient solution are more than sufficient for this purpose. Although acid phosphatases are not reported to need Ca for their function, evidence indicated that Ca did increase their activity [25]. On the other hand, detailed analysis of acid phosphatases indicated Fe and Zn are cofactors for their activity [26]. Again, the supply of these nutrients in nutrient solution should be sufficient.

Considering these factors, it is more likely that the small amount of phosphate in the solution caused the increase in acid phosphatase. Experiments with low concentration of soluble phosphate should prove this hypothesis. If this is true, one may wonder why orthophosphate ions should be able to stimulate the secretion of acid phosphatases which target organic phosphorus? In the soil environment, organic phosphate molecules would travel around much easier than inorganic phosphates and hence would be more likely to become a candidate signal to signify to the plants the existence of a P resource for consumption. The induction of phosphatase synthesis is in fact induced by Pi deficiency and the signal is internal. Trace amount of phosphate ions in the bulk soil environment as a result of decomposition of organic matter may therefore act together with internal P deficiency signals in plants to exaggerate the secretion of acid phosphatase and/or organic acids.

It should be pointed out that it is not clear whether the detected changes in acid phosphatase activity were due to changes in the amount of proteins or just due to alteration in activities. With *B. nigra* suspension cells or intact roots experiencing a transition from P sufficiency to deficiency, Duff et al. (1991) [27] quantified extracted acid phosphatase protein by immunoblots and found that the amount of total acid phosphatase protein was closely correlated with total enzyme activity. Additional experiments should be conducted to clarify the uncertainties encountered in the present experimental conditions.

4.4. Using plant factors to increase the efficiency of rock phosphate-based fertilizers

As demonstrated in the present experiments and in other studies, plants differ greatly in their responses to P deficiency. Likewise, some plants are more efficient in using soil phosphates or other sparingly soluble sources of P applied as fertilizers. Agronomic practices taking the advantage of this fact in crop rotations have been suggested. For example, it was recommended that legume crops which have stronger ability to utilize rock phosphate and soil phosphates be included in the rotation between double rice, and rock phosphates be applied to these legume crops and not directly to cereal crops [1].

In the Indian subcontinent, incorporation of pigeon pea was also practiced by farmers to increase the exploitation of soil phosphates [15]. Advances in molecular cloning techniques have made transferring of genes across genera border a routine practice. Recently, Herrera-Estrella and co-workers successfully transferred the citrate synthase gene from bacterium *Pseudomonas aeruginosa* to tobacco and papaya. The increased citrate content in plants and secreted citrate contributed to the detoxification of Al in these transgenic plants [28]. Given the great impact of organic acid on plant acquisition of phosphate, these transgenic lines should also be efficient in utilizing rock phosphates or soil phosphates. However, it is not known what other consequences of the heterogeneous genes will have on host plants. Also, the transferred genes may not function the way expected. This concern is particularly important considering that carbon metabolism as the primary metabolism of plants is not very flexible [29] and is recalcitrant to modification. Nevertheless, it is still very optimistic that similar studies should lead to the production of engineered plants with improved ability to use soil phosphates or rock phosphates. For example, modification of plants with enhanced organic acids synthesis and root exudation should increase plant utilization of inorganic phosphates. Over expression of genes encoded secreted acid phosphatases should also increase the possibility of using organic phosphates, although the role of acid phosphatase in plant phosphorus nutrition is still ambiguous [30]. As plant mutants defective in secreted acid phosphatases are being isolated [31], characterization of these mutants should provide insightful knowledge regarding the role of these enzymes in plant P nutrition under various soil conditions.

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REFERENCES

[1] LI, C.K., JIANG, B.F., LU, R.K., Phosphate Rocks for Agriculture Use in China Jiangsu Science and Technology Publishing House, Nanjing (1992) (in Chinese).

[2] CHANG, S.C., JACKSON, M.L., Solubility product of iron phosphate, Soil Sci. Soc. Am. Proc. **21**(1957) 265-269.

[3] OKAZAKI, R., SMITH, H.W., MOUDIE, C.D., Hydrolysis and salt retention errors in conventional cation exchange capacity procedures, Soil Sci. **95**(1963) 205-209.

[4] ANONYMOUS, Methods of biochemical analysis and food analysis using single reagent. Boehringer-Mannhein gebH, Mannheim, Germany

[5] ARNOZIS, P.A., FINDENEGG, G.R., Phosphoenolpyruvate carboxylase activity in plants grown with NO_3^- or NH_4^+ as inorganic nitrogen source, J. Plant Physiol. **32** (1988) 23-27.

[6] TOR, H., KAWMURA, T., IZUI, K., Molecular evolution of phosphoenolpyruvate carboxylase, Plant Cell Environ. **17** (1994) 31-43.

[7] JONES, D.L., Organic acids in the rhizosphere. A critical review, Plant Soil **205** (1998) 25-44.

[8] KLOTZ, F., HORST, W.J., Effect of ammonium- and nitrate- nitrogen nutrition on aluminum tolerance of soybean (*Glycine max* L.), Plant Soil **111**(1988) 59-65.

[9] HAYNES, R.J., Active ion uptake and maintenance of cation-anion balance: A critical examination of their role in regulation rhizosphere pH, Plant Soil **126** (1990) 247-264.

[10] SIMTH, S.W., EALING, P.M., DONG, B., DELHAIZE, E., The cloning of two *Arabidopsis* genes belonging to a phosphate transporter family, Plant J. **11** (1997) 83-92.

[11] XIONG, L.M., LU, R.K., TRUONG, B., An evaluation of the agronomic potential of partially acidulated rock phosphates in calcareous soil, Fert. Res. **38** (1994) 205-212.

[12] XIONG, L.M., ZHOU, Z.G., Magnesium influence on plant uptake of phosphorus in a calcareous soil, J. Plant Nutri. **18** (1995) 1251-1261.

[13] KEERTHISINGHE, G., HOCKING, P.J., RYAN, P.R., DELHAIZE, E., Effect of phosphorus supply on the formation and function of proteoid roots of white lupin (*Lupinus albus L.*), Plant, Cell, Environ. **21** (1998) 467-478.

[14] GARDNER, W.K, BARBER, D.A., PARBERY, D.G., The acquisition of phosphorus by *Lupinus albus* L. III. The probable mechanism by which phosphorus movement in the soil/root interface is enhanced, Plant Soil **70** (1983) 107-124.

[15] AE, N., ARIHARA, J., OKADA, K., YOSHIHARA, T., JOHANSEN, C., Phosphorus uptake by pigeon pea and its role in cropping systems of the Indian subcontinent, Science **248** (1990) 477-480.

[16] MA, J.F., ZHENG, S.J., HIRADATE, S., MATSUMOTO, H., Detoxifying aluminum with buckwheat, Nature **390** (1997) 569-570.

[17] DELHAIZE, E., RYAN, P.R., RANDALL, P.J., Aluminum tolerance in wheat (*Triticum aestivum* L). II. Aluminum-stimulated excretion of malic acid from apices, Plant Physiol. **103** (1993) 695-702.

[18] HOFFLAND, E., VAN DEN BOOGAARD, R., NELEMANS, J., FINDENEGG, G., Biosynthesis and root exudation of citric and malic acids in phosphate-starved rape plants, New Phytol. **122** (1992) 675-680.

[19] PIBEAM, D.J., CAKMAK, I., MARSCHNER, H., KIRKBY, E.A., Effect of withdrawal of phosphorus on nitrate assimilation and PEP carboxylase activity in tomato, Plant Soil **154** (1993) 111-117.

[20] JOHNSON, J.F., ALLAN, D.L., VANCE, C.P., WEIBLEN, G., Root carbon dioxide fixation by phosphorus-deficient *Lupinus albus*. Contribution to organic acid exudation by proteoid roots, Plant Physiol. **112** (1996) 19-31.

[21] ZHANG, H., FORDE, B.G., An Arabidopsis MADS box gene that controls nutrient-induced changes in root architecture, Science **279** (1998) 407-409.

[22] BERTAUCHE, N., LEUNG, J., GIRAUDAT, J., Protein phosphatase activity of abscisic acid insensitive 1 (ABI1) protein from *Arabidopsis thaliana,* Eur. J. Biochem. **241** (1996) 193-200.

[23] LIU, J., ZHU, J.K., A calcium sensor homolog required for plant salt tolerance, Science **280** (1998) 1943-1945.

[24] COHEN, P., The structure and regulation of protein phosphatases, Ann. Rev. Biochem. **58**(1989) 453-508.

[25] GABBRIELLI, R., GROSSI, L.,VERGNANO, O., The effects of nickel, calcium and magnesium on the acid phosphatase activity of two *Alyssum* species, New Phytol. **111** (1989) 631-636.

[26] STRATER, N., KLABUNDE, T., TUCKER, P., WITZEL, H., KREBS, B., Crystal Structure of a purple acid phosphatase containing a dinuclear Fe (III)-Zn (II) active site, Science **268** (1995) 1489-1492.

[27] DUFF, S.M.G., PLAXTON, W.C., LEFEBVRE, D.D., Phosphate-starvation response in plant cells: *De nove* synthesis and degradation of acid phosphatase, Proc. Natl. Acad. Sci. USA **68** (1991) 9839-9842.

[28] DE LA FUENTE, J.M., RAMIREZ-RODRIGUEZ, V., CABRERA-PONCE J.L., HERRERA-ESTRELLA, L., Aluminum tolerance in transgenic plants by alteration of citrate synthesis, Science **276** (1997) 1566-1568.

[29] TAYLOR, C.B., Factories of the future? Metabolic engineering in plant cell, Plant Cell **10** (1998) 641-644.

[30] RICHARDSON, A.E., “Soil Microorganisms and phosphorus availability” Soil Biota-management in Sustainable Farming System, (Pankhurst, C.E., Doupta VVSR, and Grace, P.R eds), CSIRO Editorial and Publishing Unit, Melbourne, Australia (1994) 10-62.

[31] TRULL, M.C., DEIKMAN, J., An Arabidopsis mutant missing one acid phosphatase isoform, Planta **206** (1998) 544-550.

APPLICATIONS OF ISOTOPE TECHNIQUES FOR THE ASSESSMENT OF SOIL PHOSPHORUS STATUS AND EVALUATION OF ROCK PHOSPHATES AS PHOSPHORUS SOURCES FOR PLANTS IN SUBTROPICAL CHINA

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Abstract. In an attempt to assess current soil phosphorus status and evaluate the effectiveness of local rock phosphates in subtropical China, nearly 40 representative soil samples from this region were collected and characterized by using ^{32}P isotope and chemical extraction techniques. Pot experiments, incubation studies and field trials were conducted to investigate the interaction of rock phosphates and water-soluble phosphates as well as the effects of rock phosphate on soil chemical properties in selected soils. Results indicated that these soils were generally low in available phosphorus and high in P-fixing capacity. The soil characteristics dictated that the employed isotope kinetic model was less successful in predicting plant P uptake than the chemical procedures tested. A new chemical extraction method consisting of sodium bicarbonate and ammonium fluoride was proposed to evaluate available P in these Solís. Data on available P generated with the proposed method gave the best prediction of plant uptake amongst all methods compared. In a pot experiment, the combined application of soluble P fertilizer with local rock phosphate significantly enhanced plant growth and increased P uptake. This positive interaction was attributed to the improved soil chemical properties due to the application of low-grade rock phosphates, as demonstrated in incubation studies. These results suggest that rock phosphate-based fertilizers should be good alternative fertilizers for plants in similar acidic soils in southern China.

1. Introduction

Field investigations and laboratory studies in the 1950's and 60's identified that many cultivated soils across southern China were seriously deficient in available phosphorus (P) [1]. During the 1960's, application of phosphate fertilizers was considered one of the most important practices to secure a bumper harvest in this region. During the same period, exploration of phosphate deposits and subsequent tests on direct application of rock phosphates in acid soils received a lot of attention [1]. Nevertheless, the latest investigations in the early 1980's indicated that there were still about 60 percent of the arable land in this area deficient in available phosphorus (Olsen-P less than 5 mg/kg) [2]. Although more recent investigations are not available, it is speculated that with decades of application of phosphate fertilizers, soil P fertility in most areas should have been improved significantly. Thus, the evaluation of the actual P status in soils of this region and accordingly, the formulation of adequate strategies to manage P resources is essential for sustainable development of agriculture in southern China.

The objectives of these studies are multiple. First, an assessment of present phosphorus status in soils across southern China is sorely needed for regional or country scale decision-making on how much P fertilizers should be produced and how much should be imported from the world market. Even though there are still soils deficient in available P according to our estimation from 1993 data, there were 1.9 million tons of surplus P in our cultivated land in that year. This surplus was even higher than our domestic production of phosphate fertilizers in the same year [3]. Total phosphate accumulation from fertilizer application in our cultivated land amounted to 20 million tons of P (our unpublished data). This large surplus P is not only affecting the efficacy of our limited resources but also presenting a serious potential threat to environmental quality. In order to evaluate current available soil P status, a reliable soil test method is needed. In China, the Olsen method with sodium bicarbonate extraction has been traditionally used to assess soil available phosphorus, regardless of soil characteristics. Although this method is applicable for P determination in most soils, the lower amount of P extracted from some soils and the weak buffer capacity of the extractant render the results subject to variation. Results are also susceptible to changes in soil acidity that may not necessarily be associated with P fertility of the soils. A method that would allow extraction of higher amounts of P that facilitates conventional colorimetric assay and extracts sources of phosphates prevailing in acidic soils has been searched by researchers. The recently developed isotopic kinetic approaches to assess soil P status will be tested to study their suitability in the acidic soils of southern China.

Moreover, as there are ample resources of medium to low grade phosphate rock deposits in the area, there is a need to evaluate the effectiveness of these rock phosphates and rock phosphate-based fertilizers in these acidic soils. Although extensive field and laboratory works on rock phosphate application had been conducted in our laboratory [1], a mechanistic study of the interaction between rock phosphates and soil phosphorus as well as water-soluble phosphate is still not available. These investigations can be also done using isotopic approaches. In the frame of the current FAO/IAEA Coordinated Research Project, a series of experiments were carried out to address these issues with the use of recommended isotope methods. Some of the research findings from this project are presented here. Results of other studies in the framework of this project were reported elsewhere [4-7].

2. MATERIALS AND METHODS

2.1. Soils

Thirty-nine soils were collected from 9 Provinces in subtropical China. Although all of them were characterized and used in ^{32}P isotopic kinetic studies, only 34 soils were used in pot experiments. Among these 34 soils, 27 were acidic with pH below 6.5 and 7 were calcareous with pH higher than 7.0. Table I presents major properties of the 39 soils with average, range and standard deviation of the data. In Table I, the cation exchange capacity (CEC) was determined by neutral NH_4OAc method, free Fe_2O_3 was extracted by Na dithionite (pH 7.3), and Al_2O_3 was extracted by 0.5 M NaOH.

2.2. ^{32}P isotopic kinetics

The determination of isotopic kinetic characteristics of soil phosphorus was conducted according to Fardeau et al. [8]. Briefly, 10 grams of soil sample (20 mesh) in 99 ml of double distilled water were shaken overnight. In the following day, 1 ml of carrier-free ^{32}P (with radioactivity around 0.15-0.25 MBq) was introduced into the system while the soil-water mixture was kept stirring at 200 rpm on a magnetic stirrer. Exactly at 1 minute and 10 minutes after introducing the isotope, an aliquot of 15 ml of the mixture was withdrawn from the bottle and immediately passed through a syringe filter (0.2-0.01 μm). ^{32}P radioactivity of the clear solution was recorded on a liquid scintillation counter and the phosphate in the solution was determined spectrophotometrically by the molybdate-blue method [9] using a 10-cm cuvette.

2.3. Modified Olsen method for extraction of soil available phosphorus

The proposed method consisted of using extractants in the Olsen (0.5M $NaHCO_3$) and Bray I (0.03 M NH_4F) methods. The two chemicals were dissolved in double distilled H_2O and the pH of the resulting solution was adjusted to 8.5. In extraction, 2.5 grams of soil were placed in a 100 ml plastic centrifuge tube and 50 ml of fresh-made extraction solution were added and the mixture was shaken at 25 ± 1^oC for 30 min. The mixture was then passed through filter paper and phosphorus in the clear solution was determined by the molybdate blue method [9].

2.4. Other chemical extraction methods for soil available phosphorus

Three soil phosphate extraction methods were chosen for comparison with the proposed modified Olsen extraction method. These are Olsen (0.5 M $NaCO_3$) [10], Mehlich III (0.015 M NH4F + 0.2 M CH_3COOH + 0.25 M NH_4NO_3) [11], and Bray I (0.03 M NH_4F + 0.025 HCl) [12]. These methods are widely used for soil P testing [13].

TABLE I. SUMMARY OF MAJOR PROPERTIES OF THE SOILS USED IN THIS STUDY (n=39)

Properties	Average	Range	Standard Deviation
Soil pH	6.1	4.0 ~ 8.7	1.6
Clay content (%)	26.9	4.3 ~ 55.2	12.6
Organic matter (%)	1.9	0.4 ~ 3.9	0.9
Nitrogen (%)	0.107	0.026 ~ 0.226	0.046
Cation Exchange Capacity (cmol/kg)	8.35	3.11 ~ 17.64	3.57
Exchangeable Cations (cmol/kg)			
Ca	2.67	0.78 ~ 9.75	2.74
Mg	0.58	0.14 ~ 4.37	0.87
K	0.17	0.08 ~ 0.56	0.15
Na	0.39	0.05 ~ 0.82	0.31
Free Fe_2O_3	3.22	0.52 ~ 13.84	3.12
Free Al_2O_3	1.88	0.11 ~ 9.44	2.33

2.5. Determination of isotopic exchangeable phosphate (E values)

E values (soil isotope exchangeable phosphorus) were determined as described by IAEA [14].

2.6. Pot experiment and A values

There were two treatments for each soil which included a no phosphorus control and application of 75 mg P/kg soil in the form of reagent-grade $Ca(H_2PO_4)_2$. The phosphate was added as a solution and was labeled with carrier-free ^{32}P. The radioactivity applied to each pot was 1.85 MBq. One kilogram of soil was placed into each pot and the following amounts of nutrients were added as solution to each pot: 100 mg N as urea, 50 mg K as K_2SO_4, 5 mg Mg as $MgSO_4$, 0.5 mg Zn as $ZnSO_4$ and 0.1 mg B as $Na_2B_4O_7.10H_2O$. Soils were watered to 70 percent of field water holding capacity and were incubated for one week before sowing. There were four replicates for each treatment. The test plant was ryegrass (*Lolium multiflorum* L). Seeds were sown directly on the surface of the pot soils and after germination seedlings were thinned to 30 plants per pot. Plants were left to grow for one month and the above ground portion was cut and the pots were supplied again with the above nutrient solution and a second harvest was made one month later. The harvested plant shoots were oven-dried and ground. Subsamples were dry-ashed and the residues were dissolved in dilute HCl solution and P was assayed with the molybdate blue method. Radioactivity in solution was assayed with a liquid scintillation counter. A values were calculated [15]. Plant uptake of phosphorus for the two separate harvests were combined to report in this study.

2.7. Dissolution of phosphate rocks in acidic soils

Four phosphate rocks were used in the present study. Jinxiang phosphate rock from Hubei, Shimen from Hunan, Kunyang from Yunnan, and North Carolina phosphate rock (NCPR) from the United States of America. Selected properties of the rock phosphates are presented in Table II.

Two acidic red soils sampled from Yingtan, Jiangxi Province were used in the incubation. Soil 1 was a clay soil (clay 43.9%, pH 4.8, CEC 13.2 cmol/kg, and Bray I-P 1.6 mg/kg) and Soil 2 a sandy loam (clay 16.8%, pH 5.0, CEC 6.5 cmol/kg, and Bray I-P 2.5 mg/kg). Both soils were used in previous pot experiments [6].

For incubation, 250 grams of soil was mixed with each of the four rock materials (<100 mesh) at rates equivalent to 0, 50, 100, 200 and 400 mgP/kg soil, respectively. The mixtures were placed in 400-ml plastic beakers and incubated at 80 percent of water holding capacity. At time 0, 1, 3, 6, 10, and 56 weeks after starting the incubation, 40 grams of sample were removed from the beakers without disturbing the rest of the soil. The samples were air-dried and passed through 20 mesh for immediate analysis of 0.5M NaOH extractable P according to the method of Bolan and Hedley [16]. Soil pH (2.5 to 1 of water to soil ratio) and exchangeable Al, Ca, and Mg were also determined by neutral NH_4OAc method.

TABLE II. SELECTED CHEMICAL AND PHYSICAL PROPERTIES OF THE ROCK PHOSPHATES USED IN THE PRESENT STUDY

	Kunyang	Jinxiang	Shimen	NCPR
a axis of apatite (≈)	9.359	9.366	9.370	9.322
Total P_2O_5,%	26.02	19.35	16.86	29.8
Percentage soluble[a]	25.7	8.53	7.40	24.1
CaO, %	39.29	33.0	36.22	5.40
MgO, %	0.20	5.55	8.99	46.0
Fe_2O_3, %	0.83	1.98	0.74	0.40

[a] Percentage of P_2O_5 that is soluble in 2% citric acid.

2.8. Field experiment

Field plot trials to test the effectiveness of Jinxiang rock phosphate and the mixture of this rock powder with single superphosphate were conducted in the Red Soil Ecological Experiment Station at Yingtan, Jiangxi Province. There were four treatments: 1) Control, no P application; 2) RP, Jinxiang rock phosphate; 3) SSP, locally produced single superphosphate; 4) SSP+RP, the mixture of SSP and RP powder. Each treatment had four replicates. The plots measured 4 x 5 m with an area of 20 m^2. Regardless of P forms, the total amount of P applied to a plot was equivalent to 0.225 kg P_2O_5 (112.5 kg P_2O_5 per hectare). The other two major nutrients were applied at the following rates: 0.20 kg N per plot as urea (100 kg N per hectare) and 0.12 kg K_2O per plot as KCl (60 kg K_2O per hectare). The test crops were peanut and buckwheat. Peanut was sown in April, 1996 and harvested in August. Buckwheat was sown immediately after the harvesting of peanut, and was harvested in November, 1996. Yield data were subjected to analysis of variance and comparisons amongst mean values were made by the Newman multiple range test.

3. RESULTS

3.1. Phosphorus fertility in the soils sampled from southern China

Out of the 39 soils used in the study, 32 soils were acidic and collected from southern China and the remaining 7 calcareous soils were from northern China. These soils represent the major soil types in the respective regions. Among the 32 soils of southern China there were several typical paddy soils. Paddy soils are the major kind of soils intensively cultivated and rice-farming probably represents the largest portion of arable land use in the region. Since the current project is mainly intended for the application of rock phosphate-based fertilizers, our attention was thus primarily focused on major upland soil types that represented medium to low P fertility. Therefore, the P fertility of these soil samples may under-represent the actual soil P fertility level in this region.

The results from the analyses of these samples indicated that these soils had in general relatively low soil fertility, in particular low P fertility. Nine soils showed such a low level of available P (< 1 mg P/kg soil) as extracted by conventional Olsen method that there was no color developed with conventional molybdate blue assay.

Another common feature in these soils was a high content of sesquioxides. Aluminum saturation ratio (i.e., percentage of exchangeable Al in the total cation exchange capacity) was high (from 2 to near 100 per cent, average 24 percent), implying a high P fixation capacity of these soils. The average pH value of the 32 soils from southern China was 5.4. Except for the 7 paddy soils, most of the other soils had pH values below 5.5. Thus, from the results on the overall soil properties, a good effectiveness of rock phosphate-based fertilizers would be expected on these acidic soils.

3.2. Isotopic kinetic approaches to characterize P pools and bioavailability in acidic soils

Using the isotope kinetic model (Fardeau, et al., 1985), we analyzed the P characteristics in the 39 tested soils. Due to contrasting soil chemical properties of these soils, we divided them into two groups, one as acidic (32 soils with pH<8) and the other as calcareous (7 soils with pH>8). We present here the results of the 32 acidic soils. Those of the calcareous soils were reported elsewhere [7].

Isotopic kinetic parameters and soil P pools obtained with the kinetic model are summarized in Table III. Respective isotopic kinetic parameters in Table III are Cp (P in soil solution), r_1 (^{32}P in soil solution after initial 1 minute of isotope exchange), R (total ^{32}P introduced into the system), n (parameter in the kinetic model [8] representing the decrease rate of log (r_t/R) with respect to log t where t is the time after introducing the isotope into the system), E_1 (the amount of soil phosphate exchangeable with ^{32}P within 1 minute after introducing the tracer into the system), Km (mean exchange rate), Fm (mean flux rate of phosphate ions between solid and aqueous phases), and Tm (mean sojourn time of phosphate ions in soil solution). With these parameters, different compartments of exchangeable P within different time periods were calculated. The parameters calculated were P_A (P exchangeable with solution P between 1 min and 1 day); P_B (P exchangeable with solution P between 1 day and 3 months); P_C (P exchangeable between 3 months and 1 year); and P_D (P exchangeable over one year to an indefinite time).

Table III presents average results of the 32 acidic soils. For most soils, P in solution (Cp) was well below 0.02 mg/L, a concentration below which most plants growing on the soil would show P deficiency. Besides the lower Cp, these soils also had a higher P-fixing capacity (1-r_1/R). The correlation between Cp and r_1/R was very significant (r = 0.9200**). This implies that the P-adsorbing surfaces of these soils were far undersaturated and strongly controlled P activity in soil solution. From the regression equation ($Cp = -0.0297 + 0.8606\, r_1/R$), the average Cp of these soils when P-adsorbing surfaces were saturated (i.e., $r_1/R = 1$) was 0.83 mg/L. The Cp values also had a negative correlation with clay contents of these soils. The r_1/R values, which are closely related to soil P-fixing ability [17], had a significant correlation with clay and free Al_2O_3 contents (Table IV). However, there was no significant correlation with free Fe_2O_3 contents, which suggested that amorphous Al might play a more important role in P fixation in these soils. If this is true, one may assume that those chemical extraction methods that could extract Al-associated P would likely perform better in predicting soil available P on these soils.

The parameter n (the decrease rate of log (r_1/R) vs. log t) varied from 0.15 to 0.55, which also negatively correlated with Cp (r= -0.6294**). A higher n value indicates a stronger P-fixing capacity of the soil. Therefore, the correlation between n and r_1/R was also very significant (r = - 0.6485**).

The mean exchange rate of phosphate ions in the solid-solution interface (Km) was higher for soils with higher P-fixing capacity, and the mean sojourn time of phosphate ions in solution (Tm) was shorter. The reverse was true for soils with higher P fertility. The Tm also had a significant correlation with Cp (r= 0.9217**) and a negative correlation with clay content (r= - 0.4586). This suggests that phosphate ions would stay in soil solution longer if the soil has a higher content of phosphate in the solution. Both factors would facilitate plant uptake of the ions. Km and Fm, on the other hand, had no significant correlation with soil properties.

Table III also presents the calculated P pools of these soils. As both Cp and r_1/R were very low, the E_1 values obtained were very high. In some soils, the E_1 values were so high that the isotope kinetic

TABLE III. ISOTOPIC PARAMETERS AND VARIOUS P POOLS OF THE 32 ACIDIC SOILS TESTED IN THIS STUDY

Parameters	Average	Range
Cp, mg/L	0.050	0.004 - 0.590
r_1/R	0.092	0.002 - 0.680
n	0.39	0.15 - 0. 55
E_1, mg/kg	9.3	0.5 - 42.4
Km, min^{-1}	570635	2.0 - 170775336
Tm, min	0.028	0 - 0.510
Fm, mg/kg.min	34837	1.6 - 1007445
P pools, mg/kg		
P_A	45	10 - 123
P_B	102	22 - 291
P_C	39	9 - 105
P_D	218	14 - 572

model was unable to differentiate other P compartments. The E_1 values had significant correlation with clay content and free sesquioxide content of the soil (Table IV), which also reflected that they were contingent upon the P-fixing capacity of these soils.

It is interesting to see if the isotopic kinetic parameters in Table III could predict plant uptake of P on these soils. Pot experiments involving treatments with or without application of water-soluble P were conducted. Results (Table V) showed that generally, the P kinetic parameters in the tested soils had no significant correlation with plant P uptake or A values. When 8 soils with abnormal E_1 value (i.e., soils with high P-fixing ability) were excluded in the statistical analysis, E_1 values had a significant correlation with A values, yet there was still no correlation with plant P uptake.

TABLE IV. CORRELATION COEFFICIENTS OF ISOTOPIC KINETIC PARAMETERS WITH SOIL CHEMICAL AND PHYSICAL PROPERTIES (n=32).

	pH	Clay	CEC	Fe_2O_3	Al_2O_3
r_1/R	0.2719	-0.6434**	-0.1932	-0.3271	-0.4353**
n	-0.4740**	0.4531**	-0.0255	0.2229	0.3007
Cp	0.1897	-0.4705**	-0.0526	-0.2170	-0.2927
E_1	-0.2443	0.4940**	0.1523	0.4120*	0.5724**
E_1'	0.0258	0.4743**	0.2504	0.7559**	0.4331
Km	-0.1066	0.0748	-0.1413	-0.0969	0.2055
Tm	0.0103	-0.4586**	-0.1187	-0.2038	-0.2618
Fm	-0.1017	0.0746	-0.1285	-0.0940	-0.2081

E_1', soils of those with abnormally high E_1 values were excluded. See text.

3.3. A modified Olsen extraction method to predict plant uptake of P in acidic upland soils: comparison with isotopic methods

In all 39 soils available P was extracted with Olsen, Bray I, Mehlich III and the proposed $NaHCO_3$-NH_4F method. Despite the difference in maximum values, the average amount of P extracted from the soils was actually very similar. The averages and ranges of P extracted by

TABLE V. RELATION (CORRELATION COEFFICIENTS) BETWEEN ISOTOPIC KINETIC PARAMETERS AND PLANT UPTAKE OF PHOSPHATE AS WELL AS A VALUES IN ACIDIC SOILS FROM SUBTROPICAL CHINA

	All soils (*n*=27)		Excluding abnormal E_1 (*n*=19)	
	Plant P uptake	A value	Plant P uptake	A value
Cp	0.3639	0.4356	0.3057	0.3994
E_1	-0.2272	-0.0871	0.3238	0.5612*
Pa	-0.2194	-0.0977	0.1006	0.2715
Pb	0.3126	0.3858	0.2393	0.3578
E_1/Cp	-0.4236	-0.3224	-0.4094	-0.2728
Km	-0.1246	-0.1888	-0.1968	-0.2420
Tm	0.2973	0.2573	0.2206	0.1986
Fm	-0.1277	-0.1885	-0.1973	-0.2431

individual methods were as follows (in mg P/kg soil): Olsen, 15.5 (0-93. 6); Bray I, 10.9 (0-58.8); Mehlich III, 20.8 (0-125.9); and the proposed $NaHCO_3$-NH_4F method, 16.4 (1.6-64.7). The overall similar P extraction pattern of these methods was also reflected in the relatively high correlation in the amount of P extracted among these extraction procedures (Table VI).

Correlation analysis between plant P uptake and the amount of P extracted by the four methods was made for 34 soils, for which yield and plant P uptake data were available. Among the three established chemical methods commonly used in testing soil P fertility, we found that Bray I method was the best in predicting plant uptake of phosphorus (Table VI). This is in agreement with the assumption made above that Al phosphates are likely the predominant P form in the soil related to plant utilization.

Interestingly, the modified $NaHCO_3$-NH_4F method was actually the best amongst all the chemical extractions and isotopic methods in predicting plant uptake of phosphorus (Table VI), indicating that the proposed $NaHCO_3$-NH_4F method was a promising method of choice for testing available P in acidic as well as in calcareous soils.

Comparison was also made with isotope exchange method (E value) as well as isotope dilution method (A value). Surprisingly, both methods were less effective in predicting plant P uptake (Table VI). They were also highly correlated with each other (r value 0.9941).

TABLE VI. COMPARISON OF PROPOSED METHODS
WITH OTHER CHEMICAL EXTRACTION AND ISOTOPIC METHODS
FOR PREDICTING PLANT UPTAKE OF P (CORRELATION COEFFICIENTS) (n=34)

	Plant P Uptake	Olsen	Bray I	Mehlich III	Proposed Method	E value	A value
Plant P Uptake	1						
Olsen	0.6615	1					
Bray I	0.7562	0.6774	1				
Mehlich III	0.5010	0.8710	0.7831	1			
Proposed Method	0.8409	0.7870	0.8338	0.6632	1		
E value	0.7585	0.8220	0.7366	0.6723	0.8247	1	
A value	0.7387	0.8463	0.7208	0.6943	0.8149	0.9941	1

3.4. Effects of incorporating soluble phosphate with rock phosphate as a P source for plants on acidic soils

Results from the pot experiments using ^{32}P-labeled water-soluble phosphate indicated that there was a significant synergistic effect in promoting plant growth and P uptake by mixing water-soluble P and a low grade rock phosphate [6]. However, isotopic data (e.g., *Pdfssp*, P derived from superphosphate; *Pdfsoil*, P derived from soil; *Pdfrp*, P derived from rock phosphate) did not suggest any specific enhanced utilization of rock phosphate by plants in this combined treatment. Rather, our data suggested that there was proportionally enhanced utilization of all sources of P present in the system and consequently, the relative *Pdf* data did not change among the treatments [6]. It is proposed that a priming effect or a better root system and improved general soil fertility as a result of the combined treatments were responsible for the beneficial effects observed in our experimental conditions. Determination of Ca and Mg in plant tissues also indicated that there was significant increase in contents of both elements [6]. Follow-up experiments were, thus, conducted to determine the kinetics of phosphorus release from rock phosphates, and the effect of rock phosphate application on soil chemical properties and soil P fertility.

Four rock phosphates were incubated with two typical acidic soils low, in available phosphorus for up to 56 weeks. The amount of P released from the rocks was determined by extracting with 0.5M NaOH. Results showed that after 5 weeks, there was no further dissolution of the rock phosphates in both soils. The data obtained with one red soil (Soil 1, [6]) that had been incubated with rock phosphates for 10 weeks, which corresponded approximately to the time period of the pot experiments conducted previously are shown here [6]. Figure 1 showed that the low-grade Jinxiang and Shimen rock phosphates had lower P release rate as compared to Kunyang and NCPR. The P release rates matched well with the citric acid-solubility of P in the rock materials (Table III). After a 10 week incubation, the amounts of P released from the application of 400 mg P/kg of the rock phosphates accounted for 27.1, 23.8, 53.1 and 70.6 percent of the total P applied for Jinxiang, Shimen, Kunyang and NCPR, respectively.

Results in Figure 2 indicated that the soil that received the rock materials showed improved soil fertility over the control treatment (no rock phosphate). After incubating with 400 mg P/kg for 10 weeks, soil pH values increased 0.28, 0.42, 0.12 and 0.11 unit for Jinxiang, Shimen, Kunyang and NCPR, respectively (Fig. 2A). With a decrease in soil acidity and an increase in exchangeable cations, there was a decrease in exchangeable Al (Fig. 2B). Among the four rock phosphates, the most obvious changes in soil exchangeable Al was with the application of Shimen RP which contained the highest amount of carbonates. However, rapid increases in exchangeable Ca were found with application of NCPR and Shimen RP (Fig. 2C). This suggests that in addition to the free carbonates in the materials, the dissolution of apatite also determined the amount of Ca released. On the other hand, increase in exchangeable Mg was mainly due to the dissolution of dolomite presented in the rock materials. Both Jinxiang and Shimen rock phosphates contained higher amount of dolomite and consequently, soil exchangeable Mg increased 209 and 247 percent with the application of Jinxiang and Shimen RP, respectively (Fig. 2D). In comparison, application of Kunyang and NCPR only increased soil exchangeable Mg by about 100 percent over the control treatment (Fig. 2D). Although these low to medium grade rock phosphates are not comparable to reactive rocks in increasing soil available P levels in a short time period, they can significantly improve soil chemical properties. Thus, their application may also greatly promote crop production in highly acidic soils with generally low fertility (Xiong et al., 1996).

Follow up field experiments were carried out to confirm the results obtained in greenhouse experiments on the significant beneficial effect of combining rock phosphates and soluble phosphate in promoting plant growth and P uptake on acidic soils [6]. These experiments were conducted in Jinxian, Jiangxi Province, where both soils used in the pot experiments [6] and in the present incubation studies were sampled. Result with buckwheat (Soil 1) and peanut (Soil 2) are presented in Table VII. The field experiments showed that Jinxiang rock phosphate had very good agronomic effectiveness on acidic P-deficient soil 1. The effectiveness was even superior to that of the soluble

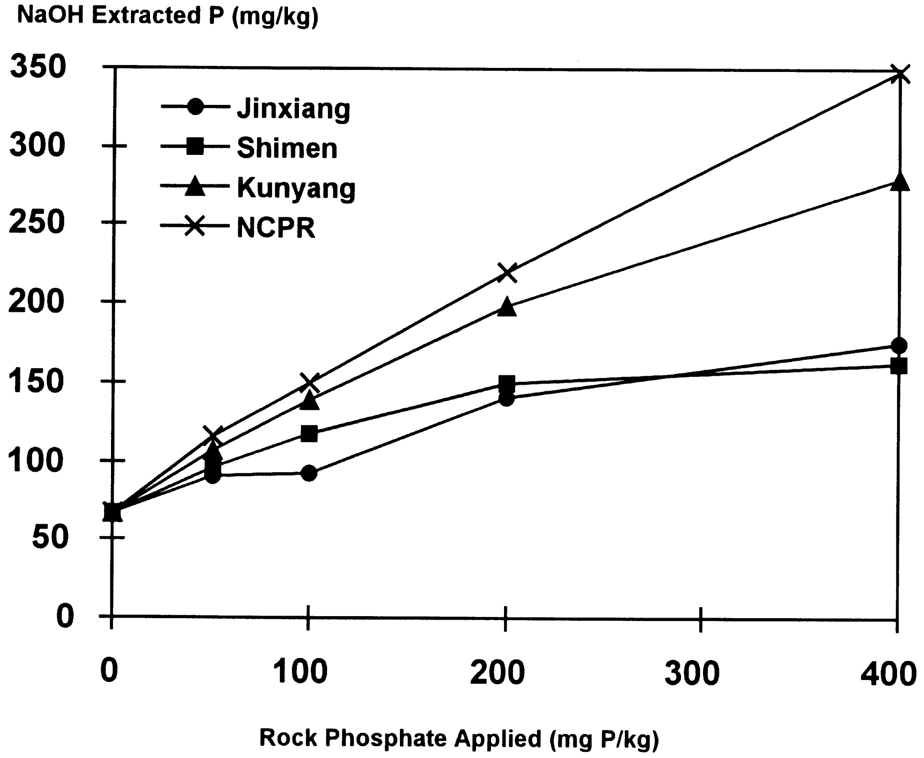

Fig. 1. Dissolution of different rock phosphates in an acid soil after a 10 week incubation.

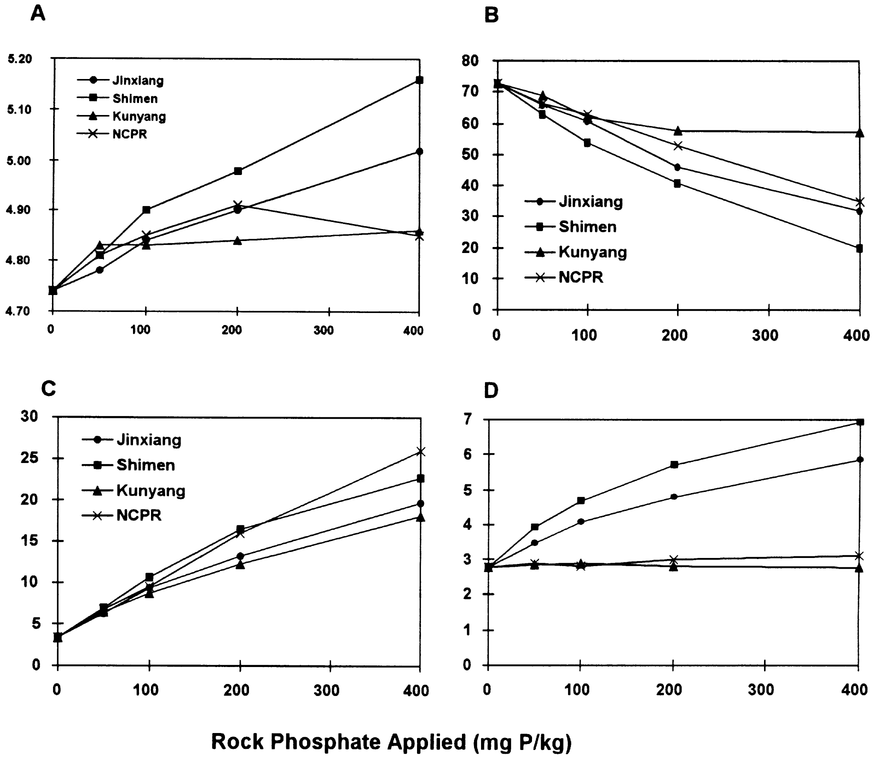

Fig. 2. Changes in soil chemical properties after incubating an acid soil with rock phosphates (400 mg P/kg) for 10 weeks. A. Soil pH values. B. Soil exchangeable Al (cmol/kg). C. Soil exchangeable Ca (cmol/kg). D. Soil exchangeable Mg (cmol/kg). Symbols for RP samples are the same as in A, B, and C.

TABLE VII. EFFECTIVENESS OF FIELD APPLICATION OF ROCK PHOSPHATE AND GRANULATED ROCK PHOSPHATE/SOLUBLE PHOSPHATE MIXTURE IN TWO ACIDIC SOILS IN YINGTAN, JIANGXI PROVINCE (YIELD, kg/ha)

Treatments	Soil 1 (Buckwheat)	Soil 2 (Peanut)
Control (No P)	170 C*	2182 ns
RP	275 A	2255
SSP	220 AB	2537
SSP + RP	265 A	2425

* Means followed with different letter are significantly different at the 0.01 level. ns, not significantly different at the 0.05 level.

single superphosphate (SSP). Nevertheless, in this particular experiment, we did not find a significant interaction on plant growth and P uptake by combining both P sources (Table VII and data not shown). With soil 2, where P was not so deficient, no crop response to application P fertilizers was found (Table VII).

4. DISCUSSION

4.1. Isotopic kinetic approach in characterizing soil P fertility and predicting plant uptake of phosphorus

Compared with routine chemical methods, the isotopic kinetic method as proposed by Fardeau et al. [8] can better describe the soil P status through the intensity factor, Cp, quantity factor, E_1, and capacity factor, E_1/Cp and other parameters such as Km, Fm, and Tm. This method also offers the possibility of distinguishing P pools of varying exchangeability with time. Besides the characterization of soil P pools [18-20], this isotope kinetic method has also been successfully used to predict the effectiveness of phosphate fertilizers including rock phosphates [21, 22].

The method of isotope exchange is based on the Brownian movement of ions between the solid surface and solution phase. This has been considered as an advantage over other extraction methods with which the various extractants alter the ion equilibrium between solid and liquid phases. However, as observed in many other studies and witnessed in the present study, the soil adsorbing surfaces were far undersaturated and the ions absorbed on the surface were strongly held. Thus, it is possible that ^{32}P will not exchange readily with ^{31}P on the absorbing surface and remain there once contacted with the adsorbing sites. This would lead to an imbalance of isotope exchange and would result in an overestimation of soil labile P [23-26].

There is another factor, however, that may be of equal responsibility for the errors of labile P estimation. There existed a close relationship between Cp and r_1/R ($r = 0.9200^{**}$). The lower Cp values are of equal importance in leading to any errors in estimating E_1 values. As the ^{31}P concentration in equilibrium solution was normally at least 4 orders of magnitude higher than that of ^{32}P ions, one would argue that the ^{32}P ions would be impossible to lead to an imbalance of exchange on the absorbing surface. While on the other hand, it is quite reasonable that the lower Cp value determined by conventional method (molybdate blue) may overestimate the actual concentration of phosphate in solution due to an interference from silicates. The overestimated Cp would amplify R/r_1 times in the calculation of E_1 values. To overcome this possible effect, the malachite green method may be used instead to reduce the interference of the silicate in strongly weathered acidic soils.

The E_1 or other P pools, estimated by isotope kinetic method, would bear the same disadvantage as other methods based on the isotope exchange process in that the method is not applicable to high P-fixing soils. Salcedo et al. [25] observed that on oxisols with high P-fixing ability, the E_1 values were not correlated with plant P uptake if r_1/R values were below 0.26. In the present experiment, only 4 soils among the 32 acidic soils had r_1/R above this value. Even for these 4 soils, no obvious correlation between E_1 and plant P uptake existed.

The poor correlation between isotope exchangeable P and plant P uptake in the present study may arise from the inaccurate estimation of E_1 value. Another possible contribution to the poor correlation was that other factors could have existed to limit plant growth and P uptake. On these strongly acidic soils, high Al usually constitutes a stress factor to plant growth. Nevertheless, this may not be important because the conventional chemical extraction can predict plant P uptake much better (Table VI).

Using isotope exchange to estimate soil labile P is a great progress in soil P testing to understand the soil P dynamics. This unique method, however, is quite suitable to weakly weathered soils in temperate regions [7] and to soils with adequate P fertility in tropical and subtropical areas. Like most methodologies, the isotope kinetic method offers several advantages over conventional methods, but it has the limitation of not being suitable in soils with a high P-fixing capacity. Another factor may have also contributed to the failure of isotope exchangeable P in predicting plant P uptake. On these soils, a low amount of P in soil solution (Cp) would induce many plants to adopt a stress response which usually involves the secretion of organic ligands such as citrate and malate [27]. These ligands complex Al and Fe and will exchange with surface-sorbed P or P in phosphate minerals. This process shifts the solid-solution equilibrium upon which the isotope exchange method is based. On the contrary, conventional chemical extractions react in a similar way on soil P as plant roots. Therefore, in soils with a high P-fixation capacity, chemical extraction may perform better in predicting plant P uptake.

4.2. The $NaHCO_3$-NH_4F method to extract soil available phosphorus

As the isotopic kinetic approach was not fully successful in predicting plant available P in the acidic soils tested, other chemical methods should be used to assess bioavailable P in high P-fixing soils. However, the low P fertility in these soils, as extracted by conventional Olsen method did not allow for an accurate determination of the P in the extracts. Correlation analysis suggested that Al-associated P in these soils is likely the major source of plant available P (Table IV). An effective extraction method suitable for these acidic soils should target Al-associated phosphates and therefore, the ammonium fluoride used in Bray methods should be a better choice. Considering the advantages of the established Olsen extraction method (i.e., 0.5 M Na bicarbonate pH 8.5), in this study Olsen and Bray methods were combined to estimate phosphorus availability in these acidic soils.

The results demonstrated that the proposed $NaHCO_3$-NH_4F extraction method gave the best prediction of plant uptake of phosphorus under the present experimental conditions where soils of contrasting chemical properties were evaluated together (Table VI). This extraction also yielded higher amounts of P in acidic soils, which allows for an easier determination with the molybdate blue method. When calcareous soils (n =7) were grouped alone, all the four methods tested performed equally well in predicting plant uptake of P (data not shown). Yet on calcareous soils, $NaHCO_3$-NH_4F extracted less P than $NaHCO_3$ alone. The reason for this is not readily clear. Besides formation of CaF_2 precipitate, the instability of NH_4HCO_3 formed in the extract in the alkaline soil-solution mixture may have contributed to lower extraction of P on these soils. An alternative may be to replace NH_4F with NaF.

The Olsen-Dabin method that is used in France for determination of available P in tropical soils also employs both $NaHCO_3$ and NH_4F (at 0.5 M) in the extraction [28]. However, we found that this method was not as good as the original Olsen method in predicting plant available P in soils from subtropical China (our unpublished data). It seems that a major part of the P released by the high concentration of NH_4F and longer time of extraction (1 hr) was not plant accessible in our subtropical and temperate soils.

4.3. Rock phosphate-based fertilizers for acidic soils in southern China

With long-term application of phosphate fertilizers in southern China, P has accumulated in some soils and the effectiveness of P fertilizers has decreased accordingly. With this new situation, fertilizer formulae that provide some soluble phosphorus for immediate use by the plant and some slowly released P that sustains a long-term supply would be ideal for maintaining soil P fertility. Apparently, rock phosphate-based fertilizers can satisfy this requirement.

Abundant low to medium grade phosphate deposits in subtropical China (which accounts for over 80 percent of total phosphate reserves in the country) and the acid reaction of the soils would favor development and application of rock phosphate-based fertilizers as alternative sources of phosphorus for plants. Results from a collaborative study between our Institute and CIRAD- CA, France demonstrated that partially acidulated rock phosphates had similar agronomic effectiveness as soluble phosphates in acidic soils in southern China [29]. In the present Coordinated Research Project, we also observed the beneficial effect of combined use of rock phosphate and soluble phosphate in enhancing plant productivity and P uptake [6] yet the isotopic data failed to provide evidence that there was an interaction between both P sources. Chien et al. [30] demonstrated in pot experiments that there existed a positive interaction between rock phosphate and soluble phosphate in promoting plant uptake of phosphorus. This enhancement of plant growth and P uptake by combining soluble phosphate with rock phosphate was further studied in field experiments. Although the results from the field trials did show significant effectiveness of rock phosphate in promoting plant growth, an interaction between the two phosphorus sources in increasing crop yield was mnot observed (Table VII).

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REFERENCES

[1] LI, C.K., JIANG, B.F., LU, R.K, Phosphate Rocks for Agriculture Use in China. Jiangsu Science and Technology Publishing House, Nanjing (in Chinese) (1992).

[2] LIN B AND LI J.K., Fertilizer Planning of China. China Agriculture Science Press. Beijing, 90pp. (1986).

[3] XIONG, L.M., Pedosphere and globe phosphorus cycling. In: Zhao, Q.G. (ed) Material Cycling in pedosphere and its relation to agriculture. pp 25-35. Jiangsu Sci and Tech. Publishing House, Nanjing, China (1993).

[4] XIONG, L.M., ZHOU, Z.G., Magnesium influence on plant uptake of phosphorus in a calcareous soil. J Plant Nutri **18** (1995) 1251-1261.

[5] ZHOU, Z.G., XIONG, L.M., Using ^{32}P to study the transformation and bioavailibility of soluble phosphate in calcareous soils. J. Nuclear Agric. Sci. **17** (1996) 129-131 (China)

[6] XIONG, L.M., ZHOU, Z.G., LU, R.K., Enhanced plant growth by uniform placement of superphosphate with rock phosphate in acidic soils. Commun. Soil Sci. Plant Anal. **27** (1996) 2837-2850.

[7] XIONG, L.M., FARDEAU, J.C., ^{32}P kinetic approaches to characterize soil phosphorus pools and bioavailability in some calcareous soils. Acta Agriculturae Boreali-Sinica **11** (1996) 50-55.

[8] FARDEAU, J.C., MOREL, C., JAPPE, J. Cinetique d'Èchange des ions phosphate dans les systemes sol-solution. Verification experimentale de l'Èquation theorique. C.R. Acad. Sci. Paris. t.300. Serie III (1985) 371-376

[9] MURPHY, J., RILEY, J.P., A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta (1962) 31-36.

[10] OLSEN, S.R., COLE, C.V., WATANABE, F.S., DEAN, L.A., Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ. 939. U.S. Gov. Print Office, Washington, D.C. (1954).

[11] MEHLICH, A. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. Commun. Soil Sci. Plant Anal. **15** (1984) 1409-1416.

[12] BRAY, R.H., KURTZ, L.T., Determination of total, organic and available forms of phosphorus in soils. Soil Sci. **59** (1945) 39-45.

[13] FIXEN, P.E., GROVE, J.H., Testing soils for phosphorus. In: Soil Testing and Plant Analysis, 3rd edition. pp 141-180. Soil Science Society of America, Madison, USA (1990).

[14] IAEA, Tracer manual on crops and soils. Technical Report Series No. 171. Vienna, Austria (1996).

[15] ZAPATA, F., Isotope techniques in soil fertility and plant nutrition studies. In: G. Hardarson (ed) Use of nuclear Techniques in Studies of Soil Plant Relationships Training Course Series No. 2. pp. 61-127. International Atomic Energy Agency, Vienna, Austria (1990).

[16] BOLAN, N.S., HEDLEY, M.J., Dissolution of phosphate rocks in soils. 1. Evaluation of extraction methods for the measurement of phosphate rock dissolution. Fertilizer Research. **19** (1989) 65-75.

[17] FROSSARD, E., FELLER, C., TIESSEN, H., STEWART, J.W.B., FARDEAU, J.C., MOREL, J.L., Can an isotope method allow for the determination of the phosphorus-fixing capacity of soils. Comm. Soil Sci. Plant Anal. **24** (1993) 367-377.

[18] SEN TRAN T., FARDEAU, J.C., GIROUX, M., Effect of soil properties on plant available phosphorus determined by isotopic dilution phosphorus method. Soil Sci. Soc. Am. J. **52** (1988) 1388-1390.

[19] LOPEZ-HERNANDEZ, D., LAVELLE, P., FARDEAU, J.C., NINO, M., Phosphorus transformations in two P-sorption contrasting tropical soils during transit through *Pontoscolex corethrurus*. Soil Biol. Biochem. **25** (1993) 789-792.

[20] OBERSON, A., FARDEAU, J.C., BESSON, J.M., STICHER, H., Soil phosphorus dynamics in cropping systems managed according to conventional and biological agricultural methods. Biol. Fertil. Soils. **16** (1993) 111-117.

[21] MOREL, C., FARDEAU,J.C., Phosphorus bioavailability of fertilizers: a predictive laboratory method for its evaluation. Fert. Res. **28** (1991) 1-9

[22] FARDEAU, J.C., GUIRAUD, G., MOREL, C., Bioavailable soil P as a key to sustainable agriculture, functional model determined by isotopic tracers. In: Nuclear Techniques in soil-plant studies for sustainable agriculture and environmental preservation, Proceedings of an international symposium held in Vienna, 17-21 October, 1994. pp 131-144. International Atomic Energy Agency, Vienna, Austra.

[23] AMER, F., MAHDI, S. ALRADI, A., Limitations in isotopic measurements of labile phosphate in soils. J. Soil Sci. **20** (1969) 91-100.

[24] DALAL, R.C., HALLSWORTH, E.G., Measurement of isotopic exchangeable soil phosphorus and interrelationships among parameters of quantity, intensity and capacity factors. Soil Sci. Soc. Am. J. **41** (1977) 81-86.

[25] SALCEDO, I.H., BERTINO, F., SAMPAIO, E.V.S.B., Reactivity of phosphorus in northeastern Brazilian soils assessed by isotopic dilution. Soil Sci. Soc. Am. J. **55** (1990) 140-145

[26] WOLF, A.M., BAKER, D.E., PIONKE, H.B., The measurement of labile phosphorus by the isotopic dilution and anion resin method. Soil Sci. **141** (1986) 60-70.

[27] FENG, G.L., XIONG, L.M., Exploring plant factors for increasing plant utilization of rock phosphates and soil phosphates in acidic soils. In: F. Zapata (ed) The Use of Nuclear and Related Techniques for Evaluating the Agronomic Effectiveness of Phosphate Fertilizers, in Particular Rock Phosphates. IAEA TECDOC, International Atomic Energy Agency, Vienna, Austria (in this publication, 2001)

[28] DABIN, B. Methode Olsen modifie. Cah. OSTOM, Pedologie 5.3 (1965).

[29] XIONG, L.M., LU, R.K., TRUONG, B., Agronomic potential of partially acidulated rock phosphates in acid soils of subtropical China. Pedosphere **5** (1995) 97-105.

[30] CHIEN, S.H., MENON, R.G., BILLINGHAM, K.S., Phosphorus availability from phosphate rock as enhanced by water-soluble phosphorus. Soil Sci Soc Am J. **60** (1996) 1173-1177.

THE USE OF ^{32}P RADIOISOTOPE TECHNIQUES FOR EVALUATING THE RELATIVE AGRONOMIC EFFECTIVENESS OF PHOSPHATE ROCK MATERIALS IN A SOYBEAN-MAIZE CROP ROTATION IN ACID SOILS OF THAILAND

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Abstract

A series of greenhouse experiments was conducted over three years to evaluate the relative agronomic effectiveness (RAE) of phosphate rock materials in a soybean - maize crop sequence, using ^{32}P isotope dilution techniques. For the first two years, the crops were grown in a pot experiment in four acid soils of Thailand. In the first year, four increasing rates of TSP and one rate of four phosphate rocks (PRs) were used. The PRs used were Algerian PR, North Carolina PR, Petchaburi PR, and Ratchaburi PR. Soybean did not respond to P application from TSP, while there was good response in maize which was planted after soybean (1st residual effect). The percent P derived from TSP or PR fertilizer (%Pdff) had the following order: Warin soil > Mae Tang soil > Rangsit soil > Pakchong soil for soybean and Warin soil > Pakchong soil > Rangsit soil > Mae Tang soil for maize.

In the second year, the soybean - maize rotation was replanted to study the residual effect of TSP and PRs, both applied at 180 mg P kg^{-1}. No significant response of soybean and maize to TSP was found in terms of dry matter yield. In terms of %Pdff and %RAE the soils ranked as follows : Rangsit soil > Pakchong soil = Mae Tang soil > Warin soil for soybean and Warin soil > Rangsit soil > Mae Tang > Pakchong soil for maize. Both crops absorbed more P from TSP than from PRs. The %RAE in the 2nd year experiment was higher than %RAE in the 1st year

In the third year, TSP and two PRs were applied at one P rate to Pakchong and Warin soils. The applied PRs were North Carolina PR (NCPR) and Lamphun phosphate rock (LPPR). PRs were applied either alone or in combination with TSP (50:50). Soybean was planted first, followed by maize. The P-response in terms of dry matter yield and %Pdff was highly significant in both soils. The RAE ranked as follows: TSP > NCPR + TSP > LPPR + TSP > NCPR > LPPR. Maize showed the same trend in RAE as soybean in both soils. The RAE for both crops was highest in Warin soil.

1. INTRODUCTION

Ultisols and Oxisols (U.S Soil Taxonomy) represent the largest land area of the world. In southeast Asia, an estimated 212 million hectares or 54% of the land area is covered with acid soils while Thailand has 42 million hectares (82% of the land area) [1]. These soils suffer from one or more of several constraints, including low pH, high exchangeable Al and Mn, low cation exchange capacity, low available P, low organic matter, low water-holding capacity, compaction and erosion. Phosphate rock can improve soil P fertility and contribute to improve productivity of crops grown in these types of soil. Agronomic evaluation experiments were conducted under greenhouse and field conditions to obtain basic information on the ability of these sources to supply phosphorus to crops and crop tolerance to low available P. The agronomic effectiveness of phosphate rock (PR) depends on several factors. One of the inherent rock factors is its reactivity that is related to its mineralogical composition and solubility in chemical reagents.

To increase the P availability of low and medium reactive PR to meet the early P requirements of crops, it has been proposed to add water-soluble P fertilizers to PR in mixtures. This would aid in utilizing PR more effectively than the application of PR alone [2]. The additional P can be supplied by the water-soluble P fertilizer such as triplesuperphosphate (TSP) [3].

Radioactive tracers have been used extensively to measure P uptake in rock phosphate studies [4]. Kucey and Bole [5] also reported that tracer techniques provided more reliable indices of availability than did the conventional method and they were better correlated with chemical extraction measurements. The use of ^{32}P radioisotope dilution techniques allow to assess the relative agronomic effectiveness (RAE) of rock phosphate (RP) materials. The more available the unlabeled PR source, the more it will dilute ^{32}P activity in plant material [5].

The main purpose of these studies was to evaluate the RAE of Thai and foreign phosphate rocks in a soybean-maize crop rotation in acid soils of Thailand using ^{32}P radioisotope dilution techniques. Triple superphosphate (TSP) was used as reference standard of comparison. Also, to improve the RAE of PRs by applying TSP with PR in a 50:50 mixture.

2. MATERIALS AND METHODS

A series of greenhouse experiments were conducted over three years The first and the second year were designed to study the relative agronomic effectiveness (RAE) of TSP and PRs in 4 acid soils utilising a soybean - maize crop rotation. In the third year , the main purpose was to improve the RAE of PR on soybean-maize crop rotation in two acid soils using a mixture of PR:TSP in a 50:50 ratio.

2.1. Soils

The soil series used were Rangsit, Pakchong, Warin, and Mae Tang. The fixation capacities were ranked as follows: Rangsit soil > Mae Tang soil > Pakchong soil > Warin soil [6]. Selected properties of the soils are shown in Table I.

The soil series Pakchong and Warin with different textural class were utilised in the third year experiment. Some properties of these soils are also shown in Table I.

2.2. Experimental design

A Randomized Complete Block (RCB) design with four replications was used for this experiment. Tolerant variety of soybean (Nakhon Sawan 1) was used as first crop with fresh PR application. The subsequent crops for the residual effect study of PR were tolerant hybrid maize (Suwan 3504) in the first and the second years and variety Suwan 5 the third year of the experiment.

2.3. Fertilizer application

2.3.1. The first year experiment

Rangsit, Pakchong, Warin and Mae Tang were the representative acid soils from Thailand utilised.Each pot contained 5 kg soil. The TSP was applied at four levels: 30, 60, 90 and 180 mg P kg^{-1} soil whereas the phosphate rocks North Carolina PR (NCPR) as a standard PR, Algerian PR, (ARPR) Petchaburi PR (PBPR), and Ratchaburi PR (RBPR)) were applied at the rate of 180 mg P kg^{-1} soil. A control with no P application was included for the calculation of P derived from the soils. The ^{32}P isotope was added in the form of a ^{32}P labeled carrier solution of 10 ppm P, as described in section 2.4 . The first crop was soybean and the following one was maize. Only the 30 mg P kg^{-1} as TSP treatment received another application of 30 mg P kg^{-1} as TSP before planting maize. Phosphorus was not added to any other treatment for maize growth.

2.3.2. The second year experiment.

The second year experiment used the same pots as in the first year. Phosphorus was added again at rates of 30, 60, and 90 mg P kg^{-1} TSP before planting soybean. No P was added in the 180 mg P kg^{-1} TSP and PR treatments. Before planting maize, only 30 mg P kg^{-1} TSP was applied in the 30 mg P kg^{-1} TSP treatment. The other treatments did not receive any more P. The maize grown in the PR and 180 mg P kg^{-1} TSP treatment tested the residual effect of these treatments for the 3rd consecutive crop.

TABLE I. GENERAL ANALYSES OF SOILS USED IN THE EXPERIMENTS

Soil series		%	CEC	mg kg^{-1}						Bulk	mg kg^{-1}	
1st and 2nd yr exps.	PH (1:1)	Total C	meq/ 100 g.soil	P (Bray II)	K	Na	Ca	Mg	Texture	Density (g/cm^3)	Fe	Al
Rangsit	4.2	2.0	32.7	5.3	240	230	6118	561	Clay	1.2	42.7	44.0
Pakchong	5.7	0.9	6.3	3.6	102	132	1000	172	Clay loam	1.3	30.4	16.0
Warin	4.6	0.3	1.1	9.3	30	60	90	428	Sandy loam	1.6	13.1	36.0
Mae Tang	4.7	2.0	8.8	5.6	155	67	905	248	Clay	1.1	24.6	50.0

Soil series	pH		% Organic	mg kg^{-1}							CEC	Texture
3rd yr exp.	H_2O (1:1)	KCl (1:1)	Matter	P (Bray 1)	K	Na	Mg	Ca	Al	Fe	meq/100 g.soil	
Pakchong	6.4	5.7	1.61	4.46	70.5	57	101	4441	15.5	13.6	7.2	Clay loam
Warin	4.9	4.0	0.44	2.71	15.5	54	36	102	43.8	7.5	1.5	Sandy loam

2.3.3. The third year experiment

Pakchong and Warin soil series were the representative acid soils in the third year experiment. Analyses of the fertilizers used in the third year experiment are shown in Table II. Each pot contained 5 kg soil. The selected rate of P application was 90 mg P kg^{-1} soil. The P sources were TSP (standard fertilizer), North Carolina Phosphate rock (NCPR), a mixture of NCPR and TSP at the ratio of 50:50, Lamphun phosphate rock (LPPR), and a mixture of LPPR:TSP at a ratio of 50:50. Each fertilizer treatment was applied only for the first crop (soybean) and the residual effect of all P sources was monitored in the following one (maize).

2.4. Soil labelling

The ^{32}P carrier solution contained 10 ppm P (labelled KH_2 PO_4 in dilute HCl) with an activity of 17.8 MBq pot^{-1} (5 kg soil). Five ml of the solution were added onto 200 g of sand mixed until dry. The labelling sand was mixed with the soil already containing basal and P fertilizers (TSP, PRs, and PR + TSP). Basal fertilizer for soybean was 287 mg N kg^{-1} soil and 574 mg K_2O kg^{-1} soil. The soil was moistened to 80% field capacity, (212 ml kg^{-1} soil for Rangsit soil, 126 ml kg^{-1} soil for Pakchong soil, 148 ml kg^{-1} soil for Mac Tang soil and 54 ml kg^{-1} soil for Warin soil) and incubated for 24 hr.

After harvesting soybean, soil samples from each pot were collected for analysing P status before growing maize. N and K were applied as basal fertilizer at the rate of 964 mg N kg^{-1} soil and 964 mg K_2O kg^{-1} soil. The procedure of applying ^{32}P carrier solution was the same as crop 1 (soybean).

TABLE II. P FERTILIZER ANALYSES

		%P				% Particle size (mesh)		
P sources in the 1st and 2nd yr exps.	pH	Total P	2% Formic acid	2% Citric acid	% Ca	80	100	200
TSP	2.8	20.2	-	-	-	-	-	-
Algeria	7.7	12.0	10.8	11.1	35.8	60	31	9
North Carolina	8.4	12.5	10.1	9.0	39.4	79	20	1
Petchaburi	8.0	13.2	10.5	12.4	32.8	55	34	11
Ratchaburi	8.1	9.4	8.2	8.7	25.6	52	40	8

P Sources	%P		
In the 3rd yr exp.	2% Citric acid	2% formic acid	Total
TSP	-	-	20.1
North Carolina	8.10	8.72	12.5
Lumpoon	5.84	5.16	12.3

2.5. Planting

2.5.1. The first and second year experiment

After incubation, the soybean or maize were sown with 3 seeds per pot^{-1} and thinned to one plant after 10 days. Tops and roots of soybean and maize were collected after 4 and 66 weeks, respectively, for plant analysis.

2.5.2. The third year experiment

Seven seeds of soybean or 5 seeds of maize were sown and thinned to 4 and 2 seedlings, respectively. The tops and roots of soybean or maize were harvested in 4 and 6 weeks, respectively, after seed germination.

2.6. Plant analysis

The plants were dried in the oven at 65-70° C and dry weight was recorded. The ground plant samples were incinerated to ash at 500° C for 5 hours. The ash was dissolved in 20 to 30 ml of 2 N HCl. An aliquot of ten ml was pipetted into glass scintillation vials and the ^{32}P activity was counted by the Cerenkov effect using a liquid scintillation counter. The concentration of P in the samples was determined from the same filtrate by the ammonium-vanado-molybdate method. The Bray and Kurtz No. 1 method was used for determining available soil P by ammonium molybdate-ascorbic acid blue color method. Radioactivity counts were corrected by background and for decaying of plant to the date of taking plant samples. Dry matter yield and plant height were measured.

2.7. Calculation

The percentage of P in the plant derived from the fertilizers (PR or TSP) (%Pdff) and P uptake by the plant from soil were calculated by the isotopic dilution concept, where:

$$\%\,\text{Pdff} = 1 - \left(\frac{\text{S.A of } ^{32}\text{P in plant sample treated with test fertilizer P}}{\text{S.A of } ^{32}\text{P in plant samples non treated with test fertilizer P}} \right) \times 100$$

where S.A = the specific activity $= \dfrac{\text{dpm/g plant}}{^{31}\text{P (mg P/g plant)}}$

The relative agronomic effectiveness was determined as:

$$\%\text{RAE} = \frac{\%\text{PdfPR}}{\%\text{PdfTSP}} \times 100$$

where %PdfPR in the percentage of P in plants derived from PR and %PdfTSP is the percentage of P in plants derived from TSP at the P application rate of 180 mg kg^{-1}.

3. RESULTS AND DISCUSSION

3.1. First and second year experiments

3.1.1. Rangsit soil series

Soybean was grown as first crop. Triplesuperphosphate (TSP) was used at various P rates for constructing a response curve for this soil (Table III).

The response curve of soybean on fresh application of phosphate rocks (PRs) and TSP demonstrated no response compared to the control treatment. The lack of response was because of the high P-fixing capacity of the soil and method of applying fertilizer and labelling soil with ^{32}P. P fertilizers and ^{32}P were incorporated with the soil as a basal application in a homogeneous mix, so the soil particles had more chance to contact fertilizer and ^{32}P. Among the phosphate rocks (PRs), Algerian PR gave higher yield than the others. The greater yield with Algerian PR may have been due to its slow release of phosphate ions to the soil from PRs. Kirk and Nye [7] reported that the net rate of dissolution of a sparingly soluble calcium phosphate such as a PR was probably controlled by the rate Ca and P dissolving into the soil. Phosphate rock has a tendency to neutralize soil acidity [8]. This might raise soil pH, so P from the labile pool should move into soil solution.

In the second year experiment (Table III) dry matter yield of soybean showed significant differences among treatments. The additional applications of 30,60 and 90 mg P kg^{-1} TSP were applied in the second year. The maximum yield of 3.4 g pot^{-1} obtained with TSP at the rate of 60 mg P kg^{-1} and the yield at the other rates of TSP were higher than those obtained with phosphate rocks. Petchaburi was the superior PR.

Phosphorus derived from fertilizer (Pdff) in the second year had almost the same pattern as dry matter yield (Table III). The chemical characteristic of Rangsit soil (Table I) seemingly played an important role of releasing available phosphorus for crop demand from the high rate of TSP (180 mg P kg^{-1}) and phosphate rocks. Due to high Fe and Al content, the dissolved phosphorus from TSP in the first year (fresh application) was partially fixed with Fe and Al causing slow release of labile P. In the second year, it was found that the percentage of phosphorus derived from TSP and PRs (%Pdff) were higher than those in the first year. This could have been due to the slow release reaction.

The percentage of the relative agronomic effictiveness (%RAE) (Table III) showed that soybean grown in Rangsit soil could use P from the dissolution of PRs in the first year experiment less than in the 2nd year. For fresh application of PRs, P from these sources could be dissolved. The higher value of %RAE in the 2nd year indicated the residual PR reactivity in soil had provided 60% of the P that TSP could provide.

3.1.2. Pakchong soil series

Dry matter yield of soybean grown in Pakchong soil showed no significant difference (Table III) for fresh application of TSP and phosphate rocks. There was no response to TSP applications.

The phosphate rocks applied to this soil series did not give any difference on yield. The relatively high pH of this soil (near 6.0) may have affected dissolution of PR, thus little or no effect of these sources was observed. The fixation of P is not high in this soil [6]. The plants took up smaller amounts of P from phosphate rock than from TSP (%Pdff), but the dry matter yield obtained with application of various phosphate rocks were not significantly different from those obtained with application of TSP. The North Carolina and Ratchaburi phosphate rock seemed to do better in Pakchong soil series considering % relative agronomic effectiveness (%RAE) which were higher than those of Algerian and Petchaburi phosphate rocks (Table III).

In the second year experiment, the procedure of applying TSP was the same as Rangsit soil. The statistical analysis showed no significant difference on dry matter yield, but yields were higher than that in the first year experiment. The percentage of phosphorus derived from fertilizer (%Pdff) at the rate of 60 and 90 mg P kg^{-1} TSP showed the highest level of 81.2 % and 82.4%, respectively. Phosphorus releasing capability of PRs were somewhat uniform in both years, despite differences in P solubilities in the PRs. The same results were obtained for %RAE.

3.1.3. Warin soil series

Warin soil appeared to have the lowest P-fixing ability among all representative acid soils [6]. The soil characteristies were also poor (Table I). The 1st and 2nd year experiments (Table IV) showed low dry matter yield in all treatments. Even though the percentage of P derived from fertilizers (%Pdff) were the highest among all soils, it might be assumed that this soil was not suitable for soybean plantation. However, the percentage of the relative agronomic effectiveness (%RAE) of P from PR in the 1st year experiment was high. The cation exchange capacity (CEC) was 1.01 meq/100 g soil. This caused low P uptake from every source of P fertilizers (%Pdff) in the following year. The % RAE of ARPR and RBPR were better than those of NCPR and PBPR.

TABLE III. AVERAGE (4 REPS) YIELD, % PDFF AND % RAE OF SOYBEAN IN THE 1ST AND 2ND YEAR OF THE EXPERIMENT IN RANGSIT AND PAKCHONG SOIL

		Rangsit Soil .						Pakchong Soil .					
Source	Treatment	Yield (g/pot)		%Pdff		%RAE		Yield (g/pot)		% Pdff		% RAE	
of P	(mg P kg^{-1})	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
Control	0	1.5 b	1.9 b	-	-	-	-	2.1	2.2	-	-	-	-
TSP	30	1.9 ab	2.6 ab	62.9 c	91.2 a	-	-	2.6	2.9	58.6 bc	59.9 bc	-	-
TSP	60	1.9 ab	3.4 a	68.8 b	86.6 b	-	-	2.7	3.3	50.0 bc	81.2 a	-	-
TSP	90	1.6 ab	3.1 a	74.1 a	91.0 a	-	-	2.5	3.2	72.2 ab	82.4 a	-	-
TSP	180	2.1 a	3.0 a	68.9 b	78.6 d	100	100	2.6	3.2	89.2 ab	67.2 ab	100	100
ARPR	180	2.0 a	2.5 ab	51.8 d	82.0 c	63	89	2.7	3.1	39.3 cd	42.5 c	44	63
NCPR	180	1.9 ab	2.6 ab	55.7 d	78.9 cd	62	88	2.6	2.9	47.9 cd	48.3 bc	54	72
PBPR	180	1.8 ab	3.3 a	33.1 e	79.1 cd	60	81	2.4	3.0	31.4 d	47.7 bc	35	70
RBPR	180	1.8 ab	2.9ab	39.5 e	73.4 c	56	92	2.6	3.0	49.0 cd	47.5 bc	55	71
F-test		*	*	**	**			Ns	ns	**	**		

Means followed by a common letter are not significantly different at the 5% level by DMRT. ns = non significant. * = significantly different. ** = highly significant different.

TABLE IV. EFFECT OF FRESH APPLICATION AND 2ND RESIDUAL EFFECT OF SOYBEAN IN WARIN SOIL AND MAE TANG SOIL ON YIELD %PDFF AND %RAE

		Warin Soil .						Mae Tang Soil .					
Source	Treatment	Yield (g/pot)		%Pdff		%RAE		Yield (g/pot)		% Pdff		% RAE	
Of P	(mg P kg^{-1})	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
Control	0	1.4	1.1	-	-	-	-	2.8	1.8	-	-	-	-
TSP	30	2.0	1.8	73.5 ab	52.9	-	-	3.1	1.7	75.5 ab	81.7 a	-	-
TSP	60	1.9	1.7	75.8 ab	69.7	-	-	3.2	2.1	67.1 b	76.3 ab	-	-
TSP	90	1.7	1.3	86.1 a	63.3	-	-	3.3	2.5	75.6 ab	74.9 ab	-	-
TSP	180	1.5	1.7	85.0 a	67.7	100	100	4.1	1.9	82.5 a	61.0 bcd	100	100
ARPR	180	2.0	1.8	68.5 bc	59.0	80.6	87.2	3.0	1.6	98.6 c	63.2 bc	119.5	103.6
NCPR	180	1.5	2.1	69.0 bc	40.7	75.4	60.1	3.2	1.9	54.7 c	52.5 cd	66.4	86.1
PBPR	180	1.9	1.5	69.6 bc	47.4	81.9	70.0	2.7	2.3	56.0 c	45.5 d	67.9	74.6
RBPR	180	1.6	2.2	57.1 c	51.0	67.7	75.4	3.2	2.4	46.4 c	46.8 cd	56.2	76.7
F-test		ns	ns	**	ns			ns	ns	**	**		

Means followed by a common letter are not significantly different at the 5% level by DMRT. ns = non significant. ** = highly significant different.

ABLE V. AVERAGE (4 REPS) OF DRY MATTER YIELD, %PDFF AND %RAE OF MAIZE IN RANGSIT SOIL AND PAKCHONG SOIL HE FIRST AND THIRD RESIDUAL EFFECT OF P

		Rangsit Soil						Pakchong Soil					
Source	Treatment	Yield (g/pot)		%Pdff		%RAE		Yield (g/pot)		%Pdff		% RAE	
of P	(mg P kg^{-1})	1st	2nd	1st	2nd	1st	2nd	1st	2^{nd}	1^{st}	2nd	1st	2nd
Control	0	2.2	6.0 c	-	-	-	-	4.1	14.0 c	-	-	-	-
TSP	30	7.9	16.3 b	69.0 ab	64.0	-	-	5.1	25.8 a	72.9 a	53.3 bc	-	-
TSP	60	5.8	21.0 ab	58.5 ab	72.1	-	-	5.6	24.7 a	61.5 ab	68.4 ab	-	-
TSP	90	5.7	26.5 a	51.5 b	76.9	-	-	5.5	26.2 a	60.3 ab	73.7 a	-	-
TSP	180	7.0	18.8 ab	68.5 ab	69.0	100	100	6.0	25.9 a	72.5 a	72.4 a	100	100
ARPR	180	6.2	14.9 b	71.7 ab	59.0	104.7	84.8	4.2	22.6 ab	57.0 b	55.2 bc	78.6	76.3
NCPR	180	5.1	15.2 b	65.6 ab	72.4	95.8	105.0	5.2	21.6 ab	56.0 b	48.2 c	77.1	66.7
PBPR	180	6.0	18.3 ab	78.2 a	64.9	114.2	94.0	5.6	18.1 bc	35.2 c	41.7 c	48.5	57.6
RBPR	180	7.0	18.9 ab	69.8 ab	58.8	101.9	85.2	5.0	14.8 c	34.5 c	44.7 c	47.6	61.8
F-test		ns	**	**	ns			ns	**	**	**		

Means followed by a common letter are not significantly different at the 5% level by DMRT.

TABLE VI. YIELD, %PDFF AND % RAE OF MAIZE IN THE 1^{ST} AND 2^{ND} YEAR OF THE EXPERIMENT (1^{ST} AND 3^{RD} RESIDUAL EFFECT P) IN WARIN SOIL AND MAE TANG SOIL

		Warin Soil						Mae Tang Soil					
Source	Treatment	Yield (g/pot)		%Pdff		%RAE		Yield (g/pot)		%Pdff		% RAE	
Of P	(mg P kg^{-1})	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2^{nd}	1st	2nd
Control	0	2.9 bcd	7.9 c	-	-	-	-	5.9	9.4 b	-	-	-	-
TSP	30	3.2 bcd	18.0 ab	72.3 ab	71.5 ab	-	-	8.1	21.0 a	73.1 a	72.9 cd	-	-
TSP	60	4.0 abc	20.9 ab	63.1 bc	73.0 ab	-	-	6.8	17.8 a	25.5 cd	59.2 b	-	-
TSP	90	2.8 cd	20.9 ab	71.4 ab	78.6 a	-	-	8.7	20.1 a	34.4 bc	78.2 a	-	-
TSP	180	2.8 cd	16.4 b	81.2 a	76.2 a	100	100	6.9	19.2 a	60.2 ab	67.0 cd	100	100
ARPR	180	4.2 ab	16.9 ab	76.2 ab	67.1 abc	93.8	88.0	6.9	19.3 a	47.0 abc	70.6 bc	78.1	105.4
NCPR	180	4.7 a	18.2 ab	67.0 bc	53.5 bc	82.5	70.3	6.5	15.9 a	44.1 abc	68.3 bcd	73.3	101.9
PBPR	180	3.7 d	21.1 ab	71.9 ab	61.6 abc	88.5	80.8	7.9	22.1 a	43.8 abc	68.1 bc	72.9	101.6
RBPR	180	2.2 abc	21.9 a	56.9 c	48.5 c	70.0	63.7	7.5	19.0 a	65.5 a	72.8 b	109.0	108.6
F-test		**	**	**	**			ns	*	**	**		

Means followed by a common letter are not significantly different at the 5% level by DMRT.

3.1.4. Mae Tang soi series

This soil had high P fixation [6]. There were no significant differences on yield of soybean in both years of the research (Table IV). The yield did not show any response to P from TSP or PRs. The fresh application of phosphate fertilizers gave the highest yield compared to the other three acid soils (Rangsit , Pakchong and Warin soil). Soil properties for Mae Tang soil (Table I) were considered to be better than those of Pakchong and Warin soil, except for Al which was very high in this soil. Yields in the 2nd were lower than that in the 1st year experiment. The additional application of P in the treatment of TSP at 30, 60 and 90 mg P kg^{-1} did not increase yields in the 2nd year experiment. The treatment at the highest rate of P from TSP (180 mg P kg^{-1}) was designed to look for the residual effect of P. This treatment showed that for fresh application, the %Pdff was the highest (82.5%). In the 2nd year, the %Pdff dropped to 61% (Table IV). The dissolution of P from this treatment could be partially utilized by maize (1st residual effect of P) and fixed by Al and Fe. Split application at the rate of 30 mg P kg^{-1} were recommended. This application gave the highest %Pdff (Table IV). The %RAE of residual P (in the 2nd year) from phosphate rocks on soybean could be ranked as follows: ARPR > NCPR > RBPR = PBPR.

3.1.5. Maize

An additional application of 30 mg P kg^{-1} TSP was applied in the 30 mg P kg^{-1} TSP treatment for maize. The other treatments received no additional P so the residual effect of P could be observed (1st year experiment). In the 2nd year experiment, the same amount of P in the treatments 30, 60 and 90 mg P kg^{-1} was added to soybean (1st crop). In Maize (2nd crop), the procedure of applying P was the same as in the first year. The P treatments for maize are summarized below:

The 1st residual P : Treatment 30 mg P kg^{-1} received P 30 + 30 = 60 mg P kg^{-1}
The 3rd residual P : Treatment 30 mg P kg^{-1} received P 30 + 30 + 30 + 30 = 120 mg P kg^{-1}
: Treatment 60 mg P kg^{-1} received P 60 + 60 = 120 mg P kg^{-1}
: Treatment 90 mg P kg^{-1} received P 90 + 90 = 180 mg P kg^{-1}

Yield of maize in Rangsit and Pakchong soils was not significantly different in the 1st residual P (Table V). Table V distinctly shows higher yield in the 3rd residual P (the 2nd year experiment) than in the 1st residual. They were significantly different from the control. The highest value (3rd residual P) in Rangsit soil was found in 90 mg P kg^{-1} TSP. A high rate of P (180 mg P kg^{-1} TSP) applied only at the beginning of the experiment could produce dry matter yield almost the same as the yield in the 60 mg P kg^{-1} treatment. This could have been due to P remaining in soil solution (3rd residual P) which would be approximately the same as P dissolved from the 60 mg P kg^{-1} treatment. Among the four representative phosphate rocks studied (Table V), Petchaburi phosphate rock (PBPR) and Ratchaburi phosphate rock (RBPR) treatments had the highest biomass production due to their organic origin (guano deposit) with a higher degree of dissolution.

The percentage of phosphorus derived from fertilizer (% Pdff) in Rangsit soil for the 1st and 3rd residual effect of P from TSP and PRs treatments showed highly and non significant differences, respectively (Table V). They have the same trend as dry matter yields.

The percentage of the relative agronomic effectiveness (%RAE) in the 1st year experiment was higher than that in the 2nd year. The phosphate rocks (PRs) which were superior than TSP (same rate of PRs) were ARPR , PBPR and RBPR for the 1st residual P and NCPR for the 3rd residual P. The %RAE of phosphate rock material gave the same trend as %Pdff of PR.

The result of dry matter yield of maize in Pakchong soil series (Table V) was found to be the same as maize grown in Rangsit soil for TSP treatments. For the treatments of phosphate rock (PR), the highest biomass was obtained from Algerian phosphate rock (ARPR) and North Carolina phosphate rock (NCPR). It might be due to more P dissolved from ARPR and NCPR of marine origin. More Ca ion in PR (Table II) might raise pH of soil and increase the solubility of PR. The %Pdff of maize of Pakchong soil series in the second year showed almost the same result as in the first year.

Packong soil series had pH 5.7. Phosphate rock (PR) minerals dissolved slowly in this soil. Phosphate rocks are an important P source for maize because of long term residual P [9, 10]. This was the reason that %RAE from the guano phosphate rock (PBPR and RBPR) was higher in the second year. The reverse reaction was found from ARPR and NCPR which were marine phosphate rocks. The dissolution of P from these PRs in this soil may be higher than that of PBPR and RBPR.

The dry matter yield of maize in Warin soil showed good response of P from TSP (Table VI) in the 1st residual P. The highest yield occurred at 60 mg P kg^{-1} as TSP, NCPR, and ARPR. Biomass in the 3rd residual P (2nd year experiment) was higher than that from the 1st year experiment in every source of P. The lowest dry matter yield was obtained from the 180 mg P kg^{-1} TSP. Split application was better than one application at the beginning (180 mg P kg^{-1} from TSP).

The highest %Pdff of maize was at 180 mg P kg^{-1} TSP in the 1st residual P. The dissolution of P was the same from 30 and 90 mg P kg^{-1} TSP, ARPR and PBPR. In the 2nd year experiment, the % Pdff from TSP treatments gave the same result as Pakchong soil. The %Pdff from PRs gave the same result as in the 1st year experiment where ARPR and PBPR gave the higher value than those of NCPR and RBPR (as well as % RAE).

The yield of maize in Mae Tang soil (Table VI) in both year experiments were the same as the other representative acid soils. Both TSP and PRs showed highly significant differences in %Pdff. In the first year experiment for maize, 30 mg P kg^{-1} TSP was added for the same amount of the rate of application (30 mg P kg^{-1}). This treatment and RBPR were superlative in %Pdff. In the second year experiment (3rd residual P), 90 mg P ha^{-1} TSP which was added at the same amount of rate of application showed superior value of %Pdff than the other TSP and PRs treatments. It could be recommended that split application was the best method for applying P fertilizer.

The relative agronomic effectiveness (RAE) of PR materials on maize for the first residual effect of P could be ranked as follows: RBPR > ARPR > NCPR = PBPR. For the 2nd year experiment (3rd residual P) , the rank of % RAE was the same as %RAE in the 1st residual effect of P.

3.2. The third year experiment

3.2.1. Soybean

Pakchong soil and Warin soils were utilised for evaluating the relative agronomic effectiveness of phosphate rocks from a foreign country (North Carolina, USA, NCPR) and a local P source (Lamphun, LPPR). PR was tested alone and in a 50:50 mixture with TSP.

TABLE VII. EFFECT OF P FERTILIZER ON YIELD , % PDFF
AND % RAE OF SOYBEAN GROWN IN PAKCHONG SOIL AND WARIN SOIL

Sources of P	Treatment (mg P kg^{-1})	Pakchong soil			Warin soil		
		Yield (g pot^{-1})	% Pdff	% RAE	Yield (g pot^{-1})	% Pdff	% RAE
Control	0	7.6 b	-	-	4.4 d	-	-
TSP	90	9.1 a	87.8 a	100	5.4 c	68.2 a	100
NCPR	90	8.0 b	38.0 c	43	6.8 a	58.3 c	85
NCPR+TSP	45 + 45	9.3 a	78.5 b	89	5.9 b	66.0 ab	94
LPPR	90	7.7 b	25.0 c	28	5.8 b	28.4 d	42
LPPR +TSP	45 + 45	9.4 a	82.3 b	94	6.0 b	63.9 b	94
F – test		**	**		**	**	

Means followed by a common letter are not significantly different at the 5 % level by DMRT.
ns = non significant. ** = highly significant different.

Pakchong soil has a clay loam textural class, and Warin soil is a sandy loam. Phosphate fertilizer was assigned as the direct application for PRs and TSP. Dry matter yield, %Pdff and %RAE showed highly significant differences among treatments in both soils (Table VII). The highest dry matter yield of Pakchong soil existed in TSP, NCPR+TSP, and LPPR+TSP. It could be interpreted that TSP was water-soluble P which gave high dissolution of P to plant uptake. Some available P was fixed by Fe and Al (Table I). Even though this reaction occurred, available P was left in sufficient amounts to give maximum yields. The NCPR and LPPR applied solely produced dry matter yield as a control. Because PR disolution released Ca ions, soil with high Ca content (Pakchong soil had high Ca (Table I)) would slow down the dissolution of PR, according to the mass action law [11].

Warin soil (Table VII) showed different results from Pakchong soil. The soil properties are shown in Table I. For many tropical acid soils, exchangable Ca is relatively low, thus providing favorable conditions for PR application [12]. The NCPR promoted the highest yield. The reaction of TSP added to NCPR and LPPR showed the same response on the %RAE increase from 85% with NCPR to 97% with (NCPR + TSP) and 42% with LPPR to 94% with (LPPR + TSP). Plants can uptake P from PR + TSP better than applying PR alone.

3.2.2. Maize

Maize was grown after soybeans to observe the residual effect of P sources after harvesting soybeans. The results in Table VIII showed no difference in dry matter yield. Pakchong soil was found to retain higher residual effect of P in terms of P uptake under TSP. The TSP effect also showed higher %Pdff and %RAE.

The highly significant differences among treatments for %Pdff and %RAE in soil for crop 2 (maize) are shown in Table VIII. All sources of P fertilizer produced higher yield than the control. NCPR + TSP had higher dry matter yields than applying NCPR alone which clearly proved the research of [13]. NCPR + TSP was not different in yield, %Pdff, or %RAE compared to TSP alone.

The NCPR might be in form of soft PR while LPPR was hard PR. NCPR has highly releasable P. The other hypothesis of enhancing the effectiveness of NCPR and LPPR is that plants can excrete acid in the root rhizosphere to dissolve P from NCPR more easily than from LPPR. Maize is one crop that requires high P. Dry matter yield of LPPR and LPPR+TSP were lower than those of NCPR and NCPR+TSP (Table VIII).

In Warin soil (Table VIII), maize showed higher P uptake from fertilizer (%Pdff) than that of maize grown in Pakchong soil. The %RAE values were similar.

TABLE VIII. YIELD, % PDFF AND % RAE BY MAIZE FROM TRIPLESUPERPHOSPHATE (TSP) ALONE, NORTH CAROLINA PHOSPHATE ROCK (NCPR) ALONE, LAMPHUN PHOSPHATE ROCK (LPPR) ALONE AND MIXTURE OF NCPR + TSP AND LPPR + TSP IN PAKCHONG SOIL AND WARIN SOIL

Sources Of P	Treatment (mg P kg^{-1})	Pakchong soil			Warin soil		
		Yield (g pot^{-1})	% Pdff	% RAE	Yield (g pot^{-1})	% Pdff	% RAE
Control	0	58.8 ab	-	-	4.8 d	-	-
TSP	90	66.5 a	61.8 a	100	44.4 ab	87.5 ab	100
NCPR	90	62.4 ab	35.7 d	58	42.3 b	85.7 b	98
NCPR+TSP	45 + 45	62.1 ab	56.0 b	91	46.0 a	87.7 a	100
LPPR	90	57.3 b	8.0 c	13	36.9 c	82.2 c	94
LPPR +TSP	45 + 45	63.3 ab	51.8 c	84	37.6 c	86.0 ab	98
F – test		ns	**		**	**	

Means followed by a common letter are not significantly different at the 5 % level by DMRT.
ns = non significant. ** = highly significant different.

4. CONCLUSIONS

For Rangsit and Pakchong soils, the soybean response in dry matter yield was higher in the second year experiment than that in the first year. There was no yield response of P from TSP in every representative acid soil.

The ranking of %Pdff from TSP and PRs in the first year experiment was in the following order: Warin soil > Mae Tang soil > Rangsit soil > Pakchong soil. For the 2nd year experiment, the order followed: Rangsit soil > Pakchong soil = Mae Tang soil > Warin soil.

The %RAE of PRs compared with TSP in the 2nd year experiment was higher than that in the 1st year. As for maize, the 1st and 3rd residual P gave results on dry matter yield higher in the 3rd residual P than in the 1st residual P which was reverse of the %Pdff and %RAE results, except for the Mae Tang soil series.

In the third year experiment, biomass of maize and soybean was superior in the Pakchong soil compared to Warin soil. The %RAE for the P fertilizers and mixtures was ranked as follows: TSP > NCPR + TSP > LPPR + TSP > NCPR > LPPR.

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REFERENCES

[1] FAO-UNESCO. Soil map of the world. Vol.10. South. East Asia UNESCO, Paris, France, 1979.

[2] CHIEN, S.H., HAMMOND, L.L., Agronomic evaluation of partially acidulated phosphate rock in the tropics. IFDC's experience. Pap. Ser. IFDC-P7. International Fertilizer Development Center, Muscle Shoals, Alabama, 1988.

[3] CHIEN, S.H., SOMPONGSE, D., HENAO, J., HELLUMS, D.T., Greenhouse evaluation of phosphorus availability from compacted phosphate rocks with urea or with urea and triplesuperphosphate. Fert. Res. **14** (1987) 245-256.

[4] FRIED, M., Quantitative evaluation of proceased and natural phosphates. Agric. Food Chem. **2** (1954) 241-244.

[5] KUCEY, R.M.N., BOLE J.B., Availability of phosphorus from 17 rock phosphates in moderately and weakly acidic soils as determined by ^{32}P dilution, A value and total P uptake methods. Soil Sci. **138** (1984) 180-188.

[6] MAHISARAKUL, J., SRITEP, P., Asessment of the relative agronomic effectiveness of phosphate rock materials in a soybean-maize crop rotation using isotope techniques. Paper presented at the FAO/IAEA Research Corrdination Meeting in Montpellier, France, Apr. 24-28, 1995.

[7] KIRK, G.J.D., NYE, P.H. 1986. A sample model for predicting the rates of dissolution of sparingly solution calcium phosphate in soil. l. The basic model. J. Soil Sci. **37** (1986) 529-540.

[8] ROBINSON, J.C., SYERS, J.K., BOLAN, N.S., Importance of proton supply and calcium - sink size in the dissolution of phosphate rock materials of different reactivity in soil. J. of Soil Sci. **43** (1992) 447-459.

[9] ABDEL-MAILK, S.H., Phosphorus application in calcareous soil : II Chemical changes within the soil-plant system due to various forms of phosphorus fertilizers. Fert. Abst. **10** (9) (1979) 282.

[10] GACHON, L. Role of phosphate rocks in the phosphatic fertilization fertilizer of France soils. Fert. Abst. **14** 1 (1981) 27.

[11] HAMMOND, L.L., S.H. CHIEN, MOKWUNYE, A.U., Agronomic value of unacidulated and partially acidulated phosphate rocks indigenous to the tropics. Adv Agron **40** (1986) 89-140.

[12] CHIEN, S.H., MENON, R.G., Factors affecting the agronomic effectiveness of phosphate rock for direct application. Fert. Res. **41** (1995) 227-234.

[13] CHIEN, S.H., MENON, R.G., BILLINGHAM, K.S., Phosphorus availability from phosphate rock as enhanced by water-soluble phosphorus. Reprinted from the Soil Sci. of Am. J. Vol 60, No. 4. July-August, 1996. 1173-1177.

PHOSPHATE FIXATION CAPACITY OF THAI ACID SOILS USING ^{32}P ISOTOPE TECHNIQUES

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Abstract. Five acid soil samples from benchmark sites in Thailand were collected: Rangsit soil, two samples (Sulfic Tropaquepts or acid sulfate soils), Pakchong soil (Oxic Paleustults) Warin soil (Oxic Paleustults), Mae Taeng soil (Typic Paleustults). The soil P status was characterized in the laboratory by the ^{32}P isotope exchange technique using treatemnst with and witout P addition. In another experiment, the P-fixing capacity of the same soils was examined. They were incubated for 30 days with two Thai phosphate rocks Lamphun PR and RP and Ratchaburi PR, and TSP was used as a standard fertilizer. All of them were added at a rate of 50 mg P kg^{-1}. The soils can be ranked according to their P- fixing capacity as follows: Rangsit series (acid sulfate soil) > Mae Tang series (Typic Paleustult) > Pakchong series (Oxic Paleustult) > Warin series (Oxic Paleustult). The P availability from TSP decreased after 30 days incubation with the soils. PR from Ratchaburi was more effective than Lamphun PR.

1. INTRODUCTION

Thailand is a country in Asia with highly wethered, tropical acidic soils. According to FAO-UNESCO [1] the total surface of acid soils in Thailand is 42 million hectares (82% of total land area). Pons and Van der Kevie [2] also reported that Thailand has about one million hectares of acid soil in the central plain and 0.8 million hectares in the northern part.

The main limiting factor for crop production in these acid soils is their phosphorus sorption or fixation by several mineral compounds. This is due to the reaction of the orthophosphate ions with soluble iron and aluminum compounds and possibly with silicate clays. Hence in acid soils, the products of phosphorus fixation are largely complex phosphates of iron and aluminum [3].

The other way P can be fixed by soils is via adsorption of phosphate ions by soil particles. This transfer from soil solution towards soil particles occurs with most of the soil components [4]. Inmediately after a P application, phosphate ions are adsorbed on the surface of soil particles [5]. The fraction of the phosphate applied, which is transferred to soil components depends with soils. The fraction increases when the time of contact between phosphate and soil increases [6] and when the temperature increases [7]. The aim of this study was to assess the changes in the soil P status with time, in particular the reduction of bioavailable soil P and the P fixation capacity of selected acid soils when amended with water-soluble P (triple superphosphate) and Thai phosphate rocks by using isotopic methods.

2. MATERIALS AND METHODS

2.1.Soils

Acid soils collected from different benchmark sites in Thailand are classified according to the Soil Taxonomy as follows:

1. RANGSIT soil series:
Sulfic Tropaquepts, very fine, mixed, acid, isohyperthermic.
2. PAKCHONG soil series:
Oxic Paleustults, clayey, kaolinite, isohyperthermic.
3. WARIN soil series:
Oxic Paleustults, fine-loamy, siliceous, isohyperthermic.
4. MAE TAENG soil series:
Typic Paleustults, clayey, kaolinite, isohyperthermic.

The Rangsit soil is an acid sulfate soil from the central plain of Thailand. Two samples from this series were collected and are indicated as acid sulfate soil No. 1 and No. 2. The Pakchong and Warin soil are from the northeastern part of Thailand. The Maetaeng soil is from the north of Thailand. Chemical and physical characteristics are summarized in Table I.

TABLE I. SOIL CHARACTERISTICS

Soil series	PH (1:1) H_2O	% Total C	C.E.C meq/ 100 g soil	mg kg^{-1}				
				P	K	Na	Ca	Mg
Rangsit	4.2	2.03	32.65	5.25	240	230	6118	561
Pakchong	5.7	0.91	6.25	3.62	102	132	1000	171.7
Warin	4.6	0.29	1.10	9.3	30	60	90	427.6
Mae Taeng	4.64	1.68	8.75	5.6	155	67	905	247.6

Soil series	Texture	Bulk density	mg kg^{-1}	
			Fe	Al
Rangsit	Clay	1.23	42.0	4400
Pakchong	Clay loam	1.26	30.4	1600
Warin	Sandy loam	1.56	13.1	3600
Mae Tang	Clay	1.13	24.6	4960

Method of extractable P = Bray and Kurtz No I; CEC, K, Na, Ca, Mg = NH_4 OAe 1N, pH 7.0; Fe = DTPA; Al (Extractable Al) = NH_4 OAc 1N, pH 4.8

2.2. Fertilizers

The phosphate fertilizers used were: Triplesuperphosphate (TSP) with 46% total P_2O_5, Lamphun phosphate rock (PR_1), about 35% total P_2O_5, and Ratchaburi phosphate rock (PR_2), 25% total P_2O_5. PR_1 is a guano phosphate rock, which has been deposited in the northern part of Thailand whereas PR_2 was deposited in the central part of the country.

In a preliminary laboratory test, the isotopically exchangeable P (E_1 value) of the soils was measured immediately after applying 50 mg P kg^{-1} of triplesuperphosphate (TSP). In another set, each of these soils was treated with 50 mg P kg^{-1} of triplesuperphosphate (TSP) and two Thai phosphate rocks (PR_1 and PR_2) and they were incubated for one month at room temperature (19-23^{o} C) and about 80% field capacity. No P ws added to the check or control treatment and it was incubated in the same way as the P-treated samples.

The isotopic exchange method was used [8]. Ten g of soil was weighed and added to 100 ml distilled water. The soil mixture was shaken for 24 h to make the system homogeneous. Then ^{32}P carrier free solution with known amount of total activity (R) was added. After 1 minute, 10 ml was taken from the suspension and filtered through 0.01 µm. The filtrate was used for ^{32}P count by Cerenkov technique with Liquid Scintillation counter (r_1) and for P analysis in soil solution.

The amount of phosphate exchangeable with ^{32}P within time t was determined as:

$$Et = 10\ Cp\ (R/r_1)\ t^n \tag{1}$$

where Et is the amount of phosphate exchangeable with ^{32}P within time t. Cp is the P concentration in the soil solution, and 10 is the ratio of liquid to soil (100/10 = 10).

To calculate the kinetic factor (n) in Eq. [1], the decrease in radioactivity in soil solution was measured with time. The decrease in radioactivity can be described as:

$$r_t /R = r_1 /R (t + (r_1 /R)^{1/n})^{-n} + r_{eq}/R \tag{2}$$

where r_1/R is the fraction of radioactivity remaining in the solution after one minute of isotopic exchange. The value of r_{eq} /R equals 10 Cp / total P in soil. The value for $(r_1 /R)^{1/n}$ is a very small corrective factor if $r_1 /R < 0.7$ and $n > 0.1$. So, for $1 < t < 1$ day, Eq. [2] becomes

$$r_t /R = (r_1 /R) t^{-n} \tag{3}$$

After taking the logarithm of Eq. [3], the equation becomes

$$\log r_t /R = \log r_1 /R - n \log t \tag{4}$$

The calculation can be plotted in a straight line with log r_t/R vs log t. The kinetic factor, n, was determined from the slope of the plotted line

The pH of soil was measured in a ratio of water:soil = 1:10 after shaking for 17 hr.
Phosphorus remaining reactive from the 50 mg P/kg application was determined from

$$\frac{E_1 \text{ (treated)} - E_1 \text{ (check)}}{50} \times 100 = \%\text{P remaining reactive}$$

Exchangeable cations (K, Ca, Mg and Na) were obtained by extraction of the soil with 1 N NH_4Oac at pH 7 and determination by atomic absorption spectrophotometry.

3. RESULTS AND DISCUSSION

3.1. Isotopic exchangeable P

The results of the preliminany laboratory test are shown in Table II. The data indicate that inmediately after the addition of triple superphosphate (TSP) to the soils, the soil pH did not change or decreased slightly. The P in soil solution (Cp) in the check treatment of the soils series was very low ranging from 0.0086-0.077 mg P L^{-1}, but the Cp was increased when TSP was applied. High P- fixing capacity (r_1/R) was observed in the check treatments of Rangsit (acid sulfate soil no.2), Pakchong and Mae Tang soils. If r_1 /R is below 0.20, 0.2-0.6 or > 0.6 the soil would have a high, medium and low P-fixing ability, respectively. The r_1/R value that is closely related to soil P-fixing capacity [4] had a high relationship with free Al content in soil (Table I).

The linear relationship between log (r_1/R) vs log t was an index of the decrease of the activity with time (n). Lower values indicate low fixation rates and higher values indicated high P fixation rates.

The isotopically exchangeable P at 1 minute (E_1 value) of each acid soil series was very low in the check treatment except for the Acid sulfate soil No. 1, which had a history of heavy P fertilizer application to increase crop yield. This soil without P application showed very high E_1 value, similar to the E_1 value when fresh TSP was applied.

In Table III it is confirmed from the Cp and E_1 values that the Acid sulfate soil No.1 had a very high available soil P. This soil had a history of land use in which it received heavy applications of N

TABLE II. PRELIMINARY LABORATORY TEST OF 5 SOILS (INCUBATED WITH 50 mg P/kg SOIL AS TSP BY THE ^{32}P ISOTOPE EXCHANGE TECHNIQUE)

Soil	Treatment	pH (1:10)	Cp mgP/kg	ri/R	n	E_1 mg P/kg	% P remaining reactive
Acid sulfate soil	check	4.9	8.15	0.43	0.16	190.4	
No.1	TSP	5.0	8.15	0.40	0.15	206.0	31.2
Acid Sulfate soil	check	4.6	0.012	0.025	0.36	4.9	
No.2	TSP	4.6	0.056	0.067	0.23	8.9	8.0
Warin	check	5.3	0.077	0.63	0.11	1.23	
soil series	TSP	4.9	3.37	0.82	0.014	41.2	79.9
Pakchong	check	5.1	0.026	0.097	0.26	2.7	
soil series	TSP	4.8	1.11	0.36	0.088	29.2	53.0
Mae Tang	Check	5.1	0.0086	0.026	0.48	4.2	
Soil series	TSP	5.0	0.038	0.041	0.36	7.5	6.6

and P fertilizers. The main clay mineral of this soil is montmorillonite, pH slightly higher than acid sulfate soil 2. The phosphate from TSP was completely fixed by this soil (% P remaining reactive equals zero). Some P was left reactive in soil when Lamphun pholphate rock (PR_1) and Ratchaburi phosphate rock (PR_2) were added to the soil. The labile P pool (P remaining in soil solution) of this soil, PR_1 and PR_2 were applied at 50 mg P/kg soil was 14% and 30%, respectively. The small pH increase when phosphate rocks were added may be effective in reducing the Fe and Al compared to P application as soluble P.

TABLE III. ISOTOPE KINETIC CHARACTERISTICS OF P IN ACID SULFATE SOIL NO. 1 AND 2 INCUBATED ONE MONTH IN MOIST CONDITION WITH DIFFERENT PHOSPHATE FERTILIZERS

								cation (mg/kg)			
Soil	Treatment	PH (1:10)	Cp mgP/kg	r_1/R	n	E1 mg P/kg soil	% P remaining reactive	K	Ca	Mg	Na
Acid	Check	5.6	5.13	0.38	0.17	135		16	40	6	9.0
Sulfate	TSP	5.5	6.50	0.48	0.17	135	0	14	35	8	8.5
Soil No.1	PR_1	5.7	4.84	0.34	0.19	142	14.0	15	36	7	9.0
	PR_2	5.9	4.78	0.32	0.19	150	30.0	15	35	7	8.5
	Check	5.0	0.015	0.025	0.35	6.0		1.9	2.2	3.5	13.0
Acid	TSP	5.0	0.017	0.042	0.31	4.0	-4.0	1.9	1.4	3.0	13.0
Sulfate	PR_1	5.05	0.048	0.063	0.24	7.1	2.2	2.0	1.7	3.8	13.0
Soil No.2	PR_2	5.1	0.023	0.051	0.28	4.5	-3.0	2.0	1.7	3.3	13.0

Acid sulfate soil No. 2 (Rangsit series) had a pH lower than the acid sulfate soil 1. The PRs were more efficient than TSP. There was no soluble P left in soil solution after treatment with TSP after the incubation period. The P concentration in soil solution (Cp) in the treatment with PR was higher than from the treatment of water- soluble P fertilizer (TSP). This soil has a very high P-fixation or P sorption capacity. In all cases, the r_1/R values were less than 0.2. The slow dissolution of PRs contributed to lower P fixation index of the soil. There were no differences in content of bases (Ca, Mg, K and Na) between treatments.

For Warin soil series (sandy loam) the % P remaining reactive was 36.2% in the TSP treatment and 16.4% with PR1 and 24.0% with PR2 (Table IV). Phosphorus concentration (Cp) in the TSP treatment decreased with time when compared with the TSP treatment in Table II. This result might be due to activity of soil microorganism and soil fixation. Both PR materials showed that they were capable of maintaining a good level of available soil P in the soil. PR_2 seemed to be superior to PR_1. The values of r_1/R were in the range 0.61-0.77. It showed the lowest P fixing capacity among all representative soil samples. The E_1 value for TSP gave the highest value. The other parameter from isotopic kinetics was the n value. It was very low (range of 0.04-0.06) with TSP and both PRs.

In Pakchong soil series the TSP treatment seemed to be more efficient than PR_1 and PR_2, since the P remaining in soil solution was higher with TSP than with PR_1 and PR_2 (Table IV). The same result was shown by the E_1 value. PR_2 seemed to be more efficient than PR_1. This soil had higher fixation capacity than Warin soil series when considering r_1 /R values. The characteristics of the soil were similar to Warin soil. Mae Tang soil series (Table IV) is in the Northern part of Thailand. Soil texture is clay (Table I). It could be seen that P in soil solution (Cp) was very low in every treatment of this soil. The r_1 /R was lower than 0.2. This meant that this soil had a high P fixing capacity. It caused no P to remain reactive to ^{32}P exchange in either the treatment with TSP or PR_1. For PR_2, there was a trace amount of P in the reactive P pool. The PR_2 was superior to PR_1 and TSP.

Cations in acid soil solution (Tables II and IV) were very low. The low Ca could mean Ca could have been a limiting nutrient in addition to P. In Warin soil series, K could also be limiting.

TABLE IV. ISOTOPE KINETIC CHARACTERISTICS OF P IN WARIN, PAKCHONG AND MAE TANG SOIL SERIES INCUBATED IN MOIST CONDITION WITH DIFFERENT PHOSPHATIC FERTILIZERS FOR ONE MONTH

								cation (mg/kg)			
Soil	Treatment	pH (1:10)	Cp mgP/kg	r_1/R	n	E1 mg P/ kg soil	% P re-maining reactive	K	Ca	Mg	Na
Warin Soil series	Check	4.8	0.067	0.61	0.14	1.1		0.6	1.9	1.2	1.2
	TSP	4.9	1.48	0.77	0.04	19.2	36.2	0.7	1.9	1.2	1.2
	PR_1	5.1	0.70	0.75	0.05	9.4	16.6	0.6	2.4	1.2	1.25
	PR_2	5.2	0.96	0.73	0.06	13.1	24.0	0.6	2.6	1.3	1.20
Pakchong soil series	Check	6.3	0.02	0.09	0.32	2.2		0.95	1.3	0.55	1.15
	TSP	6.2	0.29	0.24	0.15	11.7	19.0	1.1	1.4	0.60	1.1
	PR_1	6.4	0.03	0.12	0.33	2.7	1.0	0.95	1.3	0.54	0.9
	PR_2	6.5	0.07	0.15	0.24	4.7	5.0	0.95	1.6	0.58	1.2
Mae Taeng soil series	Check	5.8	0.01	0.01	0.27	6.0		1.8	1.5	0.92	0.9
	TSP	5.7	0.02	0.04	0.31	5.8	-0.4	1.85	2.0	1.2	0.95
	PR_1	5.9	0.02	0.04	0.29	4.9	-2.2	1.8	1.6	0.95	0.95
	PR_2	5.9	0.03	0.04	0.29	6.3	0.6	1.85	2.2	1.25	1.1

4. CONCLUSIONS

Tropical highly weathered, acid soils soils were collected from different benchmark locations in Thailand. The ^{32}P isotopic exchange method was utilized in two sets of soil samples with and without incubation with P fertilizers to describe the changes of soil P status, in particular their P fixation capacity. Acid sulfate soils showed contrasting intensity and quantity factors. Acid sulfate soil 2 had much higher P fixation capacity.

These acid soils can be ranked according to their P fixation capacity as follows: Rangsit series (Acid Sulfate soil) > Mae Tang series(Typic Paleustult) > Pakchong series (Oxic Paleustult) > Warin series (Oxic Paleustult). The P availability from TSP decreased after 30 days incubation with the soils. PR from Ratchaburi was more effective than Lamphun PR. The changes in soil P status when amended with P fertilizers and with time was greatly dependent on their P-fixing capacity of the soils studied.

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REFERENCES

[1] FAO-UNESCO. Soil map of the world Vol. 10. South - East Asia. UNESCO, Paris-France, (1979).

[2] PONS, L.T., KEVIE, W.Van der, Acid sulfate soils in Thailand. Soil survey reports of the Land Development Department. Ministry of Agriculture and Co-operatives (1969).

[3] TISDALE, S.L., NELSON, W.L., Soil fertility and fertilizers. Macmillan Publishing Co., Inc. New York. 3rd ed.: 694 p (1975).

[4] FROSSARD, E., BROSSARD, M., HEDLEY, M.J., METHENELL, A., Reactions controlling the cycling of P in soils. In: Tiessen H (ed) Phosphorus in Global Environment, pp 107-137. John Wiley and Sons Ltd. New York, USA (1995).

[5] FARDEAU, J.C., Dynamics of phosphate in soils. An isotopic outlook. Fertilizer Research **45** (1996) 91-100

[6] BARROW, N.J., Testing a mechanistic model. XI. The effects of time and of level of application on isotopically exchangeable phosphate. J. Soil Sci. **42** (1991) 277-288.

[7] BARROW, N.J., Evaluation and utilization of residual phosphorus in soils. In: Khasawneh FE. Sample EC and Kamprath E.J. (eds). The Role of Phosphorus in Agriculture. Am. Soc. of Agro. Madison, Wisc: USA (1980) 333–361.

[8] FARDEAU, J.C., MOREL, C., JAPPE, J., Cinétique d'échange des ions phosphate dans les systèmes sol-solution. Vérification expérimentale de l'équation théorique. C.R. Séances Acad. Sci. Paris **300** III (1985) 371-376

USE OF RADIOACTIVE ^{32}P TECHNIQUE TO STUDY PHOSPHATE ROCK DISSOLUTION IN ACID SOILS

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Abstract. A laboratory experiment was conducted to evaluate the dissolution of six sources of phosphate rock in two acid soils (Ultisols): a sandy soil and a red clay soil. Labile P was determined using the radioactive ^{32}P technique for Pi extractable P and resin extractable P. Incubations were conducted for 0, 1, 2, 3, 4 and 5 weeks for ^{32}P exchangeable technique, 0 and 5 weeks for Pi technique and 5 weeks for resin technique. Rates of PR were 0 and 400 mgP/ha. The results showed that labile P in the sandy soil decreased from 0-1 weeks for all the PRs except Hahotoe PR and Hazara PR's. Between 1 and 5 weeks labile P remained relatively constant. The ranking of labile P from PRs was: North Carolina = Kouribga > Matam > Hahotoe = Hazara> Patos de Minas. In the red soil, labile P from all PRs appeared to be relatively unchanged during the 0-5 week incubation. Pi extractable P in sandy soil showed no significant differences due to incubation time. In the red clay soil, there was a significant decrease in Pi-P extracted from soil mixtures with PRs after 5 weeks as compared to 0 weeks. Results of the Resin-extractable P in both sandy and red soils were in agreement with labile P as measured by ^{32}P exchange technique.

1. INTRODUCTION

In sustainable agriculture, phosphate rock (PR) is a potential natural resource that can be utilized to supply phosphorus to plants and to increase crop yields. It has been shown that direct application of phosphate rock may be more cost-effective than the use of expensive water-soluble phosphate (P) fertilizers, especially in tropical developing countries, under certain soil, crop and agroclimatic conditions. Major factors affecting the agronomic effectiveness of PR for direct application are PR inherent factors, soil properties, climatic conditions and crop species.

Reactivity of PR varies widely with PR deposits. An understanding of PR reactivity is essential to the selection of proper sources of PR for direct application. Use of the radioactive ^{32}P technique is one means to measure the potential reactivity of PR. The total amount of phosphate ions in the soil (solid phase plus soil solution) that can undergo isotopic exchange is called the "Labile Phosphate" [1, 2]. Labile phosphate (E value of Russell et al. [3]) is often determined by the direct method of equilibrating soil with a solution of ^{32}P labelled orthophosphate. It is assumed the phosphate ions in solution exchange with solid phase phosphate and the added ^{32}P comes in equilibrium with the total exchangeable pool of P in the soil [4]. The P-fixing capacity of the acid soils can be determined at the same time by this technique. The objective of this study was to evaluate the dissolution of various phosphate rocksin acid soils utilizing the ^{32}P exchange technique.

2. MATERIALS AND METHODS

Laboratory studies were conducted at Auburn University, Auburn, Alabama and the International Fertilizer Development Center, Muscle Shoals, Alabama. Six sources of phosphate rock (PR) were incubated with two acid (Ultisols) sandy and red clay soils. The sandy soil was a Trovys loamy sand

and the red clay soil was a Hiwassee clay loam classified as a clayey, kaolinite, humic, rhodic, kanhapludults. A short description of main characteristics of PR and soils is given in Tables I and II.

Ten gram subsamples of soil were weighed in triplicate and mixed well with the Phosphate rock (PR) sources as listed in Table 1 Each source was applied to supply 400 mg P/kg soil. Distilled water was added to bring the soil moisture content to 80% of field capacity (5% for sandy soil and 10% for red clay soil). Soil mixtures were incubated for 0, 1, 2, 3, 4 and 5 weeks at a temperature of 68°F to 78°F

Incubated soil samples were set up for determination of labile P pool using ^{32}P exchange technique, available P determination by resin technique and Pi strip technique, and P fixation. Incubation times were 0-5 weeks for the ^{32}P exchange technique. Incubation time was 5 weeks for the resin method. Incubation times were 0 and 5 weeks for the Pi strip and P fixation methods.

TABLE I. CHEMICAL ANALYSIS OF SIX VARIOUS SOURCES OF PHOSPHATE ROCK

Symbol	PR source		% Total P	NAC - soluble P*
PR_1	North Carolina	(USA)	13.0	2.91
PR_2	Khouribga	(Morocco)	14.5	2.43
PR_3	Matam	(Senegal)	12.5	1.96
PR_4	Hahotoe	(Togo)	15.9	1.56
PR_5	Hazara	(Pakistan)	12.3	1.00
PR_6	Patos de Minas	(Brazil)	9.4	0.70

* NAC - soluble P = Neutral ammonium citrate – soluble P as % of rock.

TABLE II. SELECTED SOIL PROPERTIES (TYPIC ULTISOLS)

						CDR***		
		P*	K*	Mg*	Ca*	Fe_2O_3	Al_2O_3	CEC
Soil	pH	------------------- mg/kg			--------------------	g/kg		meq/100 g soil
Sandy soil	4.7	12	13	17	85	62.0	9.3	3.45
Red clay Soil	5.8	26	140	211	640			8.44

* = Pi extractable P. ** = NaOAc pH 7. *** = Citrate - Dithionite - Bicarbonate extractable.

Labile P attributed to PR alone was determined using the ^{32}P exchange technique without any incubation. The purpose of this step of the experiment was to evaluate labile P from PR dissolution by measuring isotopically exchangeable.

For labile P via ^{32}P for each incubation time, soil mixtures (10 g soil) were equilibrated in 100 ml of ^{32}P solution with 10^{-4} M KH_2PO_4 as a carrier. The activity of ^{32}P in the 100 ml was 1.4 µci/subsample. The soil suspensions were shaken for 24 hr at low speed. A portion of the suspension was centrifuged at 2500 rpm for 1 hr. The supernatant was filtered using 0.2 µm pore filter paper, and 1 ml of supernatant was pippetted into 10 ml of liquid scintillant solution in glass vials. The activity of ^{32}P left in the equilibration solution was measured using a liquid scintillation counter (Beckman model L S 3800).

The total P determinations in the extracts were made colorimetrically using the ammonium molybdate ascorbic acid method. Absorbance was measured at 880 nm.

Labile P was determined from

Labile P = [(Si/Sf - 1) B]

where Si = the initial specific activity, SF = the final specific activity, and B = the amount of P in the solution added to the soil in the ^{32}P exchange technique.

2.1. Phosphorus determination by resin technique

One-half g of soil (soil mixture with phosphate rock at 400 mg P/kg at 5 weeks incubation time) was weighed in a 50 ml centrifuge tube. Resin strip was added to soil together with 30 ml of deionized water, and shaken for 16 h.

Resin was removed and washed are move any adhering soil .The washed resin strips were in 50 ml tubes and extracted with 20 ml 0.5M HCl. After setting 1 h to allow gas to escape, the tubes were capped and shaken in overnight. Phosphorus was determined by the Murphy - Riley method.

2.2. Pi strip technique for ^{31}P determination as labile P pool

Soil with PRs were mixed and incubated for 0 and 5 weeks. One g of soil was to a 100 ml shaking bottle with screw cap. Forty ml of 0.02 M KCl solution was added to the bottle. A Pi strip was placed in the bottle and shaked for 16 h at low speed. The Pi strip was removed and rinsed with distilled water to remove soil particles on the strip. The strip was dried, but it was not necessary to dry completely. The strip was transferred to another bottle and extracted with 40 ml of 0.2 N $H_2 SO_4$ and shaking for1 h. The supernatant was filtered through a 0.2 µm pore filter paper and the filtrate was analysed for total P by the Murphy - Riley method at a wavelength of 880 nm.

2.3. Soil phosphorus fixation capacity

Soil mixtures were incubated for 0 and 5 weeks. After incubation the treated samples (10 g of soil) were transferred into 500 ml plastic bottles. Two hundred ml of 100 ppm P (KH_2PO_4) was added to each sample, and shaken for 6 hr. at low speed. The suspension was centrifuged at 10,000 rpm for 5 min. The supernatent was filtered through millipore (0.02 µm). The total P was determined in the filtrate using the Murphy Riley (1962) procedure.

Phosphorus fixation was calculated as

$$\% \text{ P fixed} = (OPC - c)/OPC \times 100$$

where OPC = original P concentration of 100 ppm P and c = concentration of P found in supernatant.

3. RESULTS AND DISCUSSION

Labile P decreased from incubation at time zero to 1 week for all the PRs except PR (4) [Hahotoe (Togo)] and PR (5) [(Hazara (Pakistan)] in the sandy soil (Fig. 1). Between 1 week and 5 weeks, labile P remained relatively constant. During this period of time, labile P obtained from various PRs followed the order: PR (1) = PR (2) > PR (3) > PR (4) = PR (5) > PR (6), which approximately agreed withthe PR solubility (Table I). A decrease in labile P from 0 week to 5 weeks indicated that isotopically exchangeable P in the surface of PR was initially greater than labile P associated with the surface of reactive products formed after PR dissolution. A relatively unchanged labile P from 1 week to 5 weeks suggests that PR dissolution did not continue after 1 week incubation.

In the red soil, labile P obtained from all PRs appeared to be relatively unchanged during 5 weeks of incubation (Fig. 2). This suggests that only P on the surface of PR use all of the soil mixture exchanged with ^{32}P, but not the P on the surface of reaction products formed from PR dissolution. The fact that labile P at 0 week was about the same as that at 1 week suggests that PR dissolution also occurredat 0 week during the 24 h equilibration for labile P measurement. Again, the order of labile P obtained from various PRs during 5 week incubation followed : PR (1) = PR (2) > PR (3) > PR (4) = PR (6).

Figure 3 shows a significant linear corelation between labile P measured with PR alone and PR's solubility for all the PRs, except PR(1). This indicated that labile P as measured by the radioactive ^{32}P technique confirmed the PR sources varied widely in solubility. It is not known why PR(1), which had the highest solubility, did not have a high correlation between labile P and solubility.

Figure 4 shows that labile P obtained with the various PR sources correlated well with PR solubility at time zero in the sandy soil but not in the red soil. However, average labile P during the 1-5 week incubation correlated well with PR solubility in both the sandy and red soil (Fig.5).

At the end of the 5 week incubation, PR dissolution apparently reduced the P-fixing capacity of the sandy soil (Fig. 6). This suggests that P released from PR dissoluition occupied P-sorption sites and reduced further P adsorption. The effect of PR dissolution on reducing soil P-fixing capacity increased with increasing solubility of PR. However, PR dissolution did not affect the P-fixing capacity of the red soil (Fig. 7). It should be pointed out that the red soil had a higher P-fixing capacity (27.5%) from the sandy soil (12.5%). Thus, the effect of PR dissolution on soil P - fixing capacity was only observed in the sandy soil.

The Pi data in Table III show that no significant PR dissolution occurred after 5 weeks incubation in the sandy soil. The amounts of Pi-P obtained at 0 week and 5 weeks probably reflect P released from PR during the Pi extraction. This appears to contradict to the results as shown in Fig. 1, which suggests
.that PR dissolution occurred in the sandy soil.

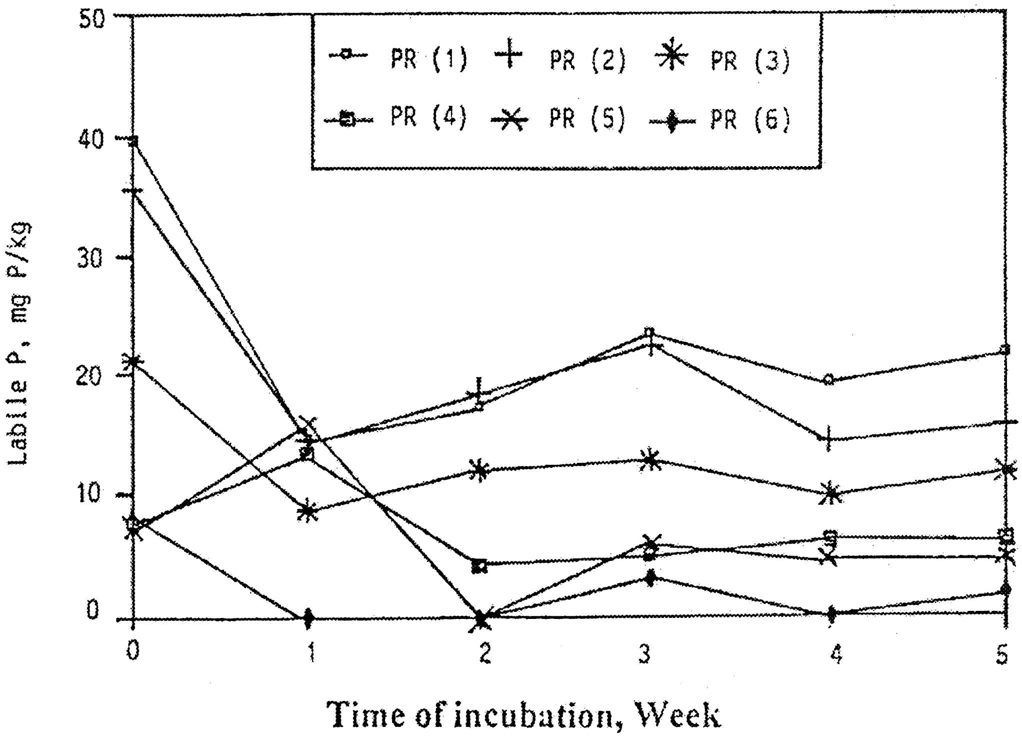

Fig. 1. Labile ^{32}P isotopic exchangeable P after incubating the mixtures of six sources of phosphate rock (PRs) and a sandy soil for 0-5 weeks.

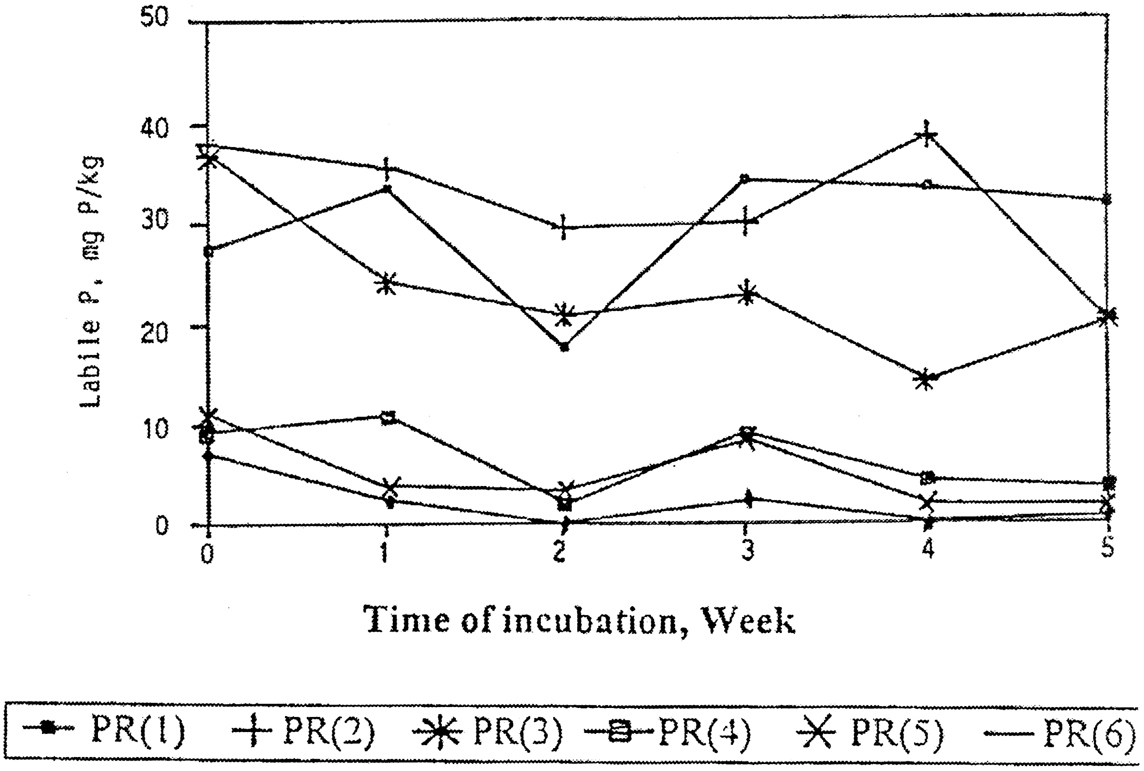

Fig. 2. Labile P (isotopically exchangeable) after incubation the mixtures of six sources of phosphate rock with a red soil.

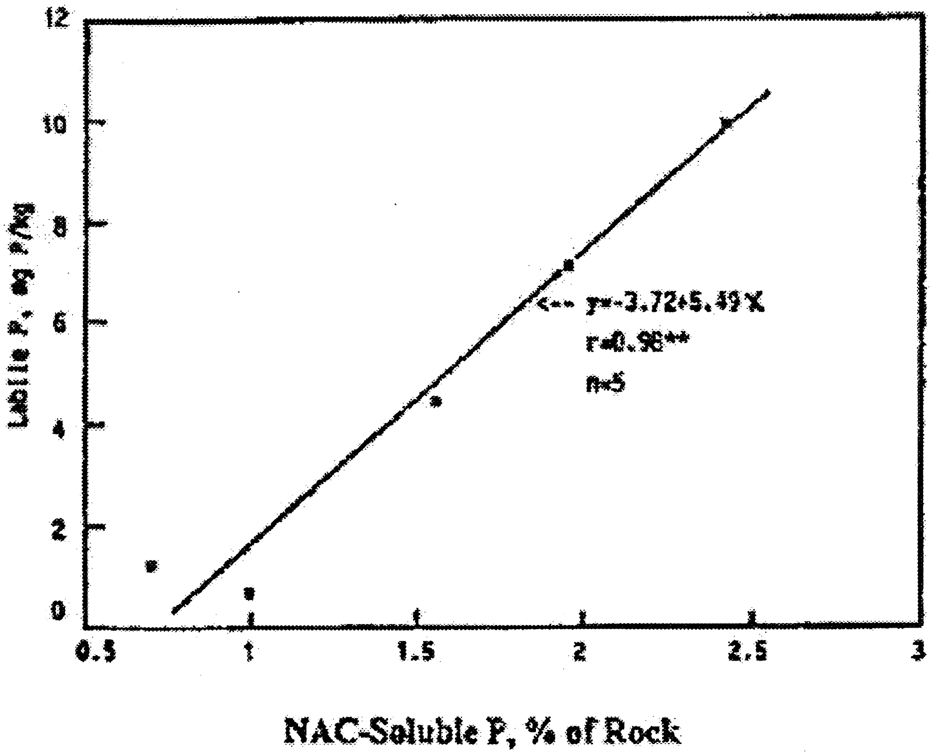

Fig. 3. Labile P (^{32}P technique) from six sources of phosphate rock compared with neutral ammonium citrate-souble P (NAC-soluble P).

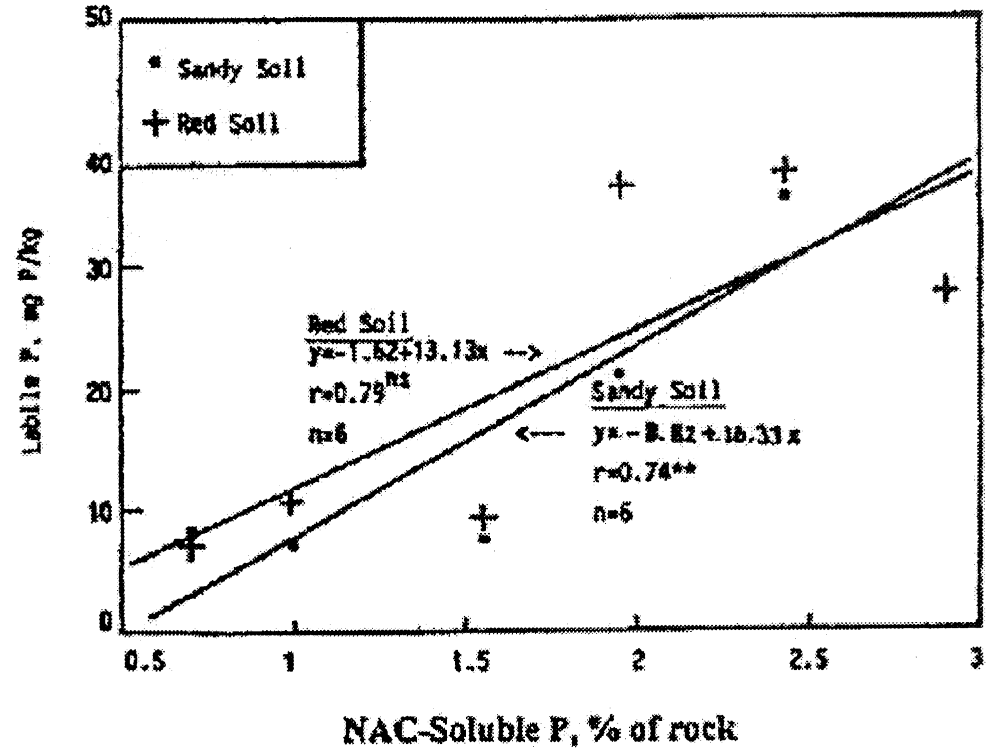

Fig. 4. Labile P (^{32}P technique) at 0 week incubation compared with neutral ammonium citrate soluble P (% of rock).

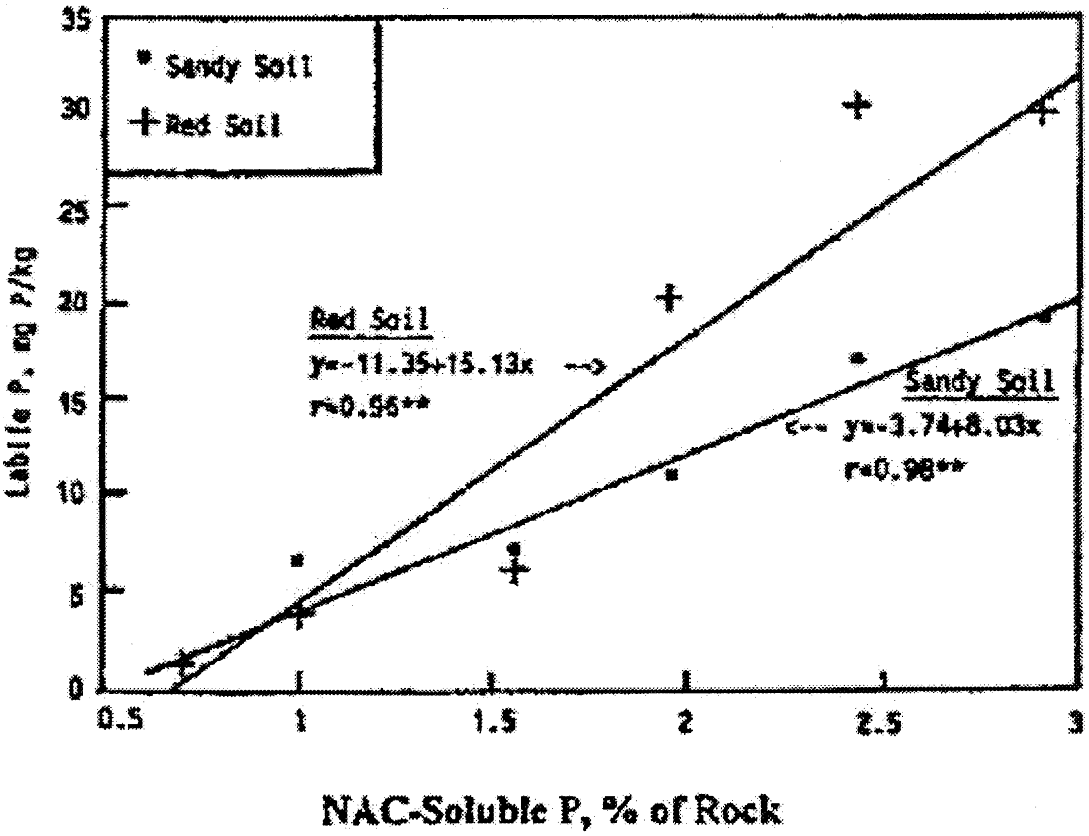

Fig. 5. Comparison of labile P (^{32}P technique) with NAC-soluble P determined on mixtures of various sources of phosphate rock with a sandy and a red soil.

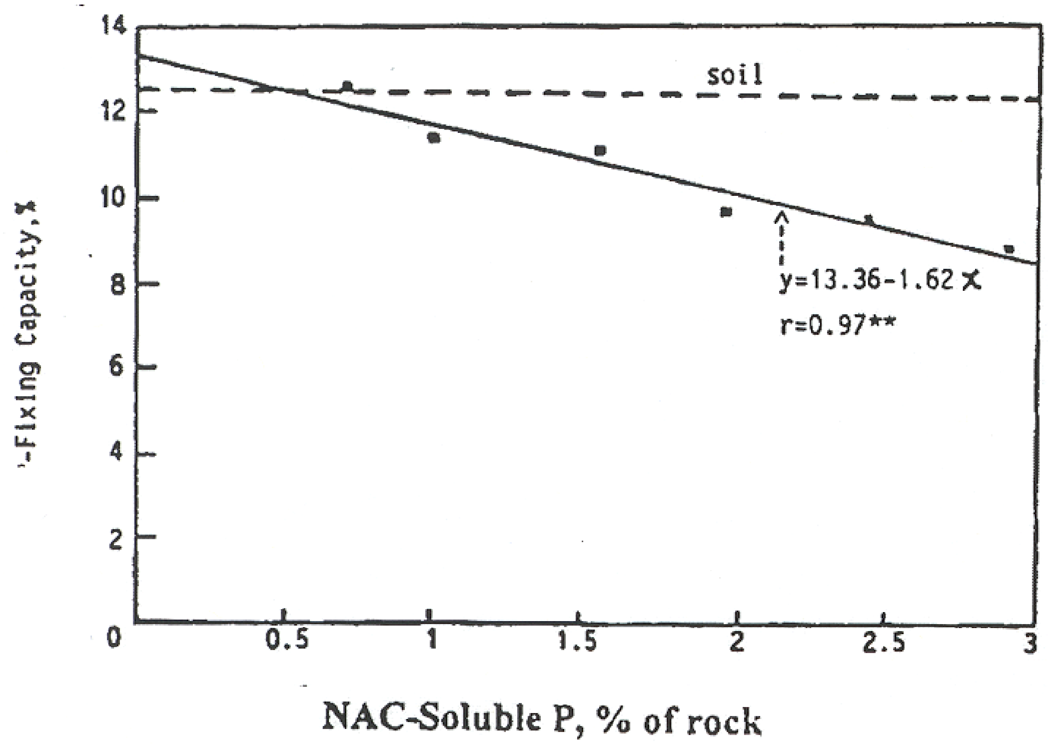

Fig. 6. Comparison of soil P-fixing capacity and phosphate rock solubility after 5 weeks incubation in a sandy soil.

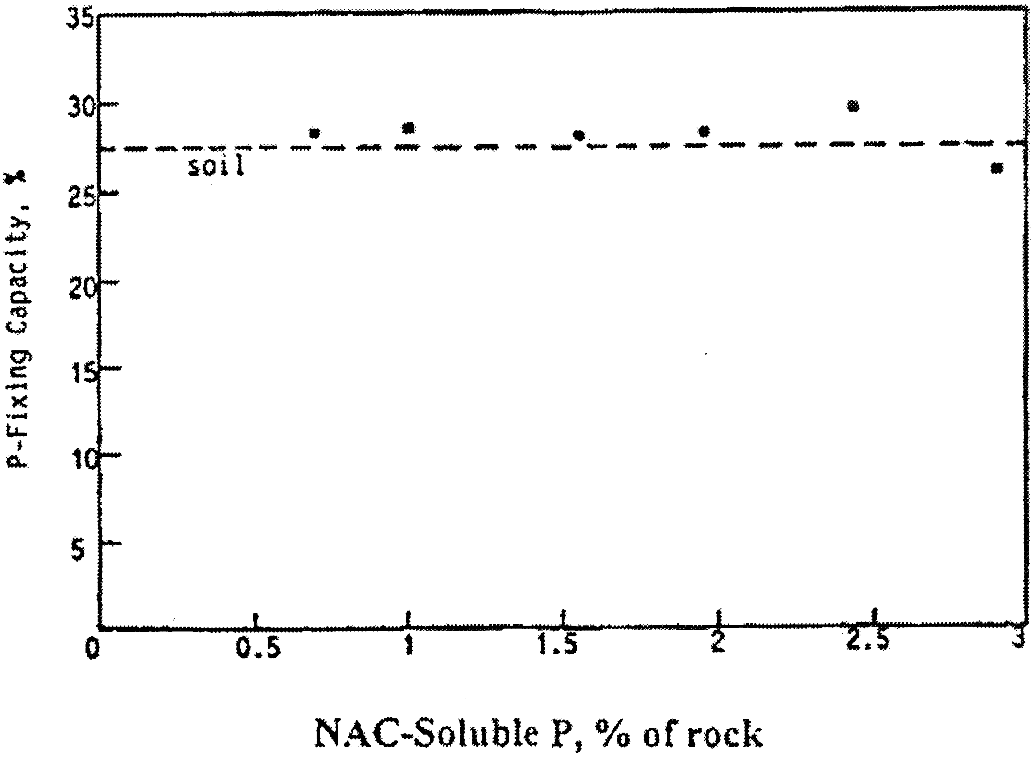

Fig. 7. Comparison of soil P-fixing capacity with phosphate rock solubility after 5 weeks incubation in a red soil.

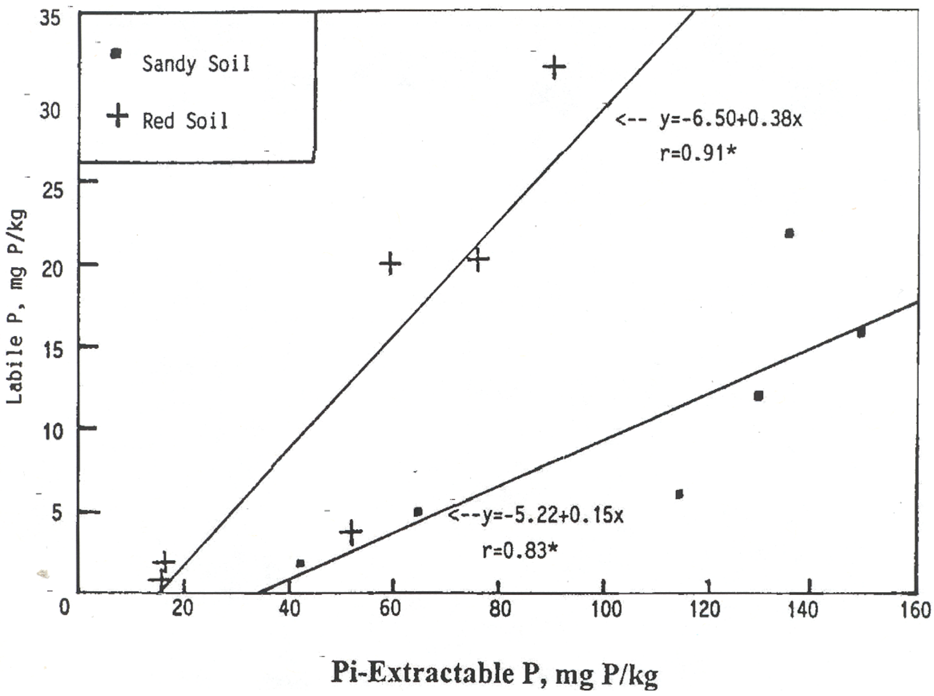

Fig. 8. Comparison of labile P from the ^{32}P isotopic exchangeable P technique with Pi-extractable P after 5 weeks incubation in a sandy soil and a red soil.

TABLE III. Pi SOIL PHOSPHORUS TEST IN SANDY SOIL AND RED CLAYEY SOIL MIXED WITH PRs AT RATE OF 400 mg P/kg AT 0 AND 5 WEEKS

Source of P	Sandy soil Pi (mg P/kg)		Red clayey soil Pi (mg P/kg)	
	0 weeks	5 weeks	0 weeks	5 weeks
Control (just soil)	1.9	1.9	4.1	4.1
North Carolina (USA)	142	136	102	80
Khouribga (Morocco)	154	149	104	76
Matam (Senegal)	130	130	100	59
Hahotoe (Togo)	110	115	61	52
Hazara (Pakistan)	50	65	35	16
Patos de Minas (Brazil)	42	49	23	15

TABLE IV. RESIN-EXTRACTABLE P IN SANDY SOIL AND RED CLAYEY SOIL MIXED WITH VARIOUS PRs AT 400 mg P/kg AFTER 5 WEEKS OF INCUBATION

PR	% P	
	Sandy soil	Red soil
North Carolina	28.6	30.2
Khouribga	27.0	41.0
Matam	16.7	19.0
Hahotoe	12.3	11.1
Hazara	4.8	8.4
Patos de Minas	7.8	7.3

Alternatively, PR dissolution could have occured in the sandy soil and Pi strip was able to extract all of the P from the reaction products formed after PR dissolution. In the red soil, a significant decrease was observed for Pi-P extracted from soil mixtures with PRs after 5 weeks compared to the amounts of Pi-P extracted at week 0 (Table III). Our results suggest that Pi strips extracted less P from the reaction products formed from PR dissolution in the red soil than the P extracted by Pi strips from PRs. This is probably due to the very strong P adsorption by the red soil.

Data of resin-extractable P obtained with various PR sources in the sandy and red soils after 5 weeks incubation are shown in Table IV. In general, resin-extractable P followed the same trend of PR solubility. Many researchers have used resin-P as labile P in P modeling work.

Labile P from the ^{32}P technique was compared with Pi - strips extractable P in sandy soil and red soil incubation for 5 weeks (Fig. 8). There was a significant corelation in the sandy soil and red soil ($r = 0.83$ and 0.91 respectively). It could be suggested that the ^{32}P isotopic technique can be used as another technique to study the dissolution of PRs in acid soils.

4. CONCLUSIONS

The results of labile P as measured by the ^{32}P isotopic exchange technique agree well with the results obtained with conventional techniques Pi – strip and P-resin utilized in this study to measure available P released from PR dissolution during a 5 week incubation in two acid Ultisols. The labile P from PR alone also correlated well with the PR's solubility as measured by neutral ammonium citrate (NAC). Thus the ^{32}P isotopic exchange technique provides another tool that can be used as reference to study the dissolution of PR in acid soils and evaluating their reactivity.

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REFERENCES

[1] TALIBUDEN, O., Isotopically exchangeable phosphorus in soils 1. Factors influencing the estimation of labile phosphorus. J. Soil Sci. **8** (1957) 86-96.
[2] OLSEN, S.R., WATANABE, F.S., Diffusion of phosphorus as related to soil texture and plant uptake. Proc. Soil. Sci. Soc. Am. **27** (1963) 648-653.
[3] RUSSELL R.S., RICKSON J.B., ADAMS, S.N., Isotopic equilibria between phosphates in soil and their significance in the assessment of fertility by tracer methods. J. Soil Sci. Soc. **5** (1954) 85-105.
[4] WHITE, R.E., Concepts and methods in the measurement of isotopically exchangeable phosphate in soil. Phosphorus in Agriculture No. 57, March 1976: 9-16.

FIELD ASSESSMENT OF THE RELATIVE AGRONOMIC EFFECTIVENESS OF PHOSPHATE ROCK MATERIALS IN A SOYBEAN — MAIZE CROP ROTATION USING ^{32}P ISOTOPE TECHNIQUES

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Abstract. Field experiments were conducted at Phrabudhabart Field Crop Research Station, Lopbur Province during the period 1995-1997 to determine the relative agronomic effectiveness (RAE) in a soybean- maize crop rotation using ^{32}P isotope techniques. The soil of the experimental site was the Pakchong soil series (Oxic Paleustults). Four PRs were applied at 120 kg P ha$^{-1,}$ namely Algerian PR (ARPR), North Carolina PR from USA (NCPR), Petchaburi PR from Thailand (PBPR) and Ratchaburi PR from Thailand (RBPR) and TSP was added at three rates (40, 60, 120 kg P ha^{-1}). For the first year harvest, soybeans absorbed more P from TSP fertilizer (% FPU) applied at 40 kg P ha^{-1} than maize, but there was no yield response. Among four PRs, North Carolina phosphate rock (NCPR) gave the highest % Pdff as well as the highest RAE. Maize was planted after soybean to study the residual effect of TSP and PRs. The results were the same as in soybean. In the second year (1996) the grain yield of soybean was higher than in the first year (1995), and there was significant response to P from TSP. The RAE of NCPR was very high. Maize showed the opposite results. In this case Algerian PR (ARPR) had the highest RAE. In 1997, TSP and six PRs (same four used in 1995 and 1996, Morocco PR (MCPR), and Lumphun PR (LPPR)) were applied at 60 kg P ha^{-1}. Phosphate rocks were applied either alone or in combination with TSP (50:50). Application of TSP resulted in high yields of soybean. In terms of RAE the P sources ranked as follows: LPPR+TSP>ARPR>LPPR> MCPR>NCPR+TSP>NCPR. The residual effect of P on the following maize crop resulted in a high RAE for MCPR and LPPR. It was concluded that TSP should be applied to every crop. The reactivity of PRs in the first and the second year experiments were: ARPR>NCPR>RBPR>PBPR. Morocco PR and LPPR were also reactive PRs in the third experiment. The combination of PR and TSP resulted in better P uptake (%Pdff).

1. INTRODUCTION

Low available phosphorus and high P-fixation are important factors limiting plant growth in acid Solís of Thailand. The effective use of phosphorus fertilizers, in particular the application of natural rock phosphates should be considered for sustainable crop production in acid environments [1-3]. The use of local rock phosphate is becoming increasingly important for direct application as an alterative phosphate fertilizer in agriculture. Deposits of rock phosphate were discovered in some parts of the Thailand, particularly in the North and Northeastern regions of the country. Reactivity of PR varies widely because of the origin of the geological deposits and the structure of the phosphate minerals. Several ways exist to enhance the effectiveness of low and medium reactivity PR. Recently it has been proposed to supplement the PR with water-soluble P fertilizers. Thus, the utilization of mixtures of PR and water-soluble P such as TSP can improve the efficacy of PR compared to the application of PR alone [4, 5]. Research on the PR reactivity as well as agronomic evaluation methods should take into account not only the immediate effect of P availability in PR but also their residual effects. ^{32}P isotope dilution techniques can be used for the agronomic evaluation of phosphate fertilizers to assess the plant available amount of phosphorus supplied by rock phosphate to crop [6, 7]. The objective of these field experiments was to evaluate the relative agronomic effectiveness of Thai and foreign sources of phosphate rock in a crop rotation soybean-maize grown in Pakchong soil. PRs, and TSP were applied alone and in mixture PRs + TSP.

2. MATERIALS AND METHODS

2.1. Location, soil and fertilizers

Field experiments were carried out at the Phrabudhabart Field Crop Research Station, Lopburi Province, in the central region of Thailand during the years 1995,1996, and 1997. The soil of the experimental site was Pakchong soil series classified as Oxic Paleustults. The main characteristics of the soil, PRs and TSP are shown in Tables I and II. The experimental design was RCB with four replications. The details of the experimental treatments are shown in tables III and IV.

In 1995 the TSP treatments consisted of application rates: 40, 60 and 120 kg P ha^{-1}. The phosphate rocks used were North Carolina phosphate rock (NCPR), Algerian phosphate rock (ARPR), Ratchaburi phosphate rock (RBPR) and Petchaburi phosphate rock (PBPR). All PRs were applied at 120 kg P ha^{-1}. All treatments were applied before planting soybeans (1st crop). Maize was the crop selected for testing the residual effect of P.

In 1996 (the 2nd year experiment), soybean was planted and received additional fertilizer P from TSP at the rate 40 and 60 kg P ha^{-1}. Maize was used as the second crop in the crop rotation to assess the residual effect of P.

TABLE I. MAIN CHARACTERISTICS OF THE PAKCHONG SOIL (1995-1997)

Depth (cm)	pH H_2O (1:1)	pH KCl (1:1)	Total C 1)	P 2)	K 3)	Na 3)	Ca 3)	Mg 3)	Al 4)	Fe 5)
0-15	6.35	5.73	0.89	4.46	70.5	57	4441	101	15.5	13.6

CEC meq/ l00 g soil	Texture 6)
7.25	Clay loam

1) = Generic combustion by CHNS/O. 2) = Bray and Kurt No.1. 3) = NH_4OAC. 4) = NH_4OAC pH 4.6-4.8. 5) = DTPA method. 6) = Hydrometer.

TABLE II. CHEMICAL ANALYSIS OF PHOSPHATE ROCKS AND TSP (1995-1997)

P Sources	pH	% P						%Ca
		Total	Water Soluble	Citrate insoluble	Available	2% formic acid	2% citric acid	
TSP	2.8	20.1	-	-	-	-	-	-
Algeria	7.7	12.1	0.009	11.1	1.8	7.2	4.7	35.8
Morocco	8.0	10.5	-	-	-	7.4	5.4	-
N.Carolina	8.4	13.0	0.009	6.3	2.8	8.7	8.1	39.5
Petchaburi	8.0	11.8	0.009	11.4	0.4	-	-	32.8
Ratchaburi	8.1	9.4	0.03	4.8	4.6	-	-	25.7
Lamphun	8.0	12.3	-	-	-	5.2	5.8	-

TABLE III. TREATMENTS OF P APPLICATION IN THE EXPERIMENTS PERFORMED IN 1995 AND 1996

Crop	Treatment (kg P ha^{-1})							
	---------	---------	TSP	---------	NCPR	ARPR	RBPR	PBPR
	0	40	60	120	120	120	120	120
1995								
Soybean	R	X	X	X	X	X	X	X
Maize	R	R	R	R	R	R	R	R
1996								
Soybean	R	X	X	R	R	R	R	R
Maize	R	R	R	R	R	R	R	R

Remarks: X = Applying P fertilizer, R = Residual effect of P, TSP = Triplesuperphosphate,
NCPR = North Carolina phosphate rock, ARPR = Algerian phosphate rock,
RBPR = Ratchaburi phosphate rock, PBPR = Petchaburi phosphate rock.

TABLE IV. TREATMENTS OF THE EXPERIMENTS PERFORMED IN 1997

Treatment	Soybean	Maize
	kg P ha^{-1}	kg P ha^{-1}
Control	0	0
TSP	60	-
Algeria phosphate rock (APPR)	60	-
Morocco phosphate rock (MCPR)	60	-
North Carolina phosphate rock (NCPR)	60	-
NCPR+TSP	30+30	-
Lumphun phosphate (LPPR)	60	-
LPPR+TSP	30+30	-

The P treatments and rates of application in the 3rd year experiment are shown in Table IV. The treatments included TSP and PRs alone. The PRs alone included Algerian phosphate rock (ARPR), Morocco phosphate rock (MCPR), North Carolina phosphate rock (NCPR) and Lamphun phosphate rock (LPPR). The ocombined treatments were the mixtures NCPR and LPPR and TSP at the ratio of 50:50. Phosphate rocks were surface broadcasted and triple superphosphate was applied by banding.

2.2. Laid-down procedure

Mian plot size was 9 x 3 m from which the central 4.5 x 2 m was harvested for yield and a separate 1.5 x 1.5 m microplot was used for ^{32}P isotope studies. Each treatment had 2 replications which were treated the same. The total yield was taken as the yields from both the isotope and yield plots. Seeds of soybean variety, Nakhon Sawan 1, was inoculated with *Rhizobium* and planted at the spacing of 50 x 20 cm. A basal fertilization of 20 kg N ha^{-1} and 40 kg K_2O ha^{-1} was applied. After harvesting soybean, the maize hybrid (Suwan 3504) (1995-1996) or variety Suwan 5 (1997) was sown under no tillage condition in both plots at the spacing of 75 x 25 cm. Basal fertilization of 80 kg N ha^{-1} and 80 kg K_2O ha^{-1} was applied. The ^{32}P labelling of the soil was made in the plot, which was formerly the soybean yield area. Weed control and pesticide was done whenever was necessary. Soil available P was measured before and after the experiment. For yield detemination grain, stem and leaf were separared. Total P content and ^{32}P activity was determined for both crops at maturity. Plant height was measured at time of harvest. Rainfall was recorded at a nearby weather station

2.3. ^{32}P labelling in the microplot

The microplot area (1.5 x 1.5m) was surrounded with zinc plate and buried to a depth 15 cm in soil and projected above the soil 15 cm to prevent ^{32}P contamination. The ^{32}P solution, with a carrier of 50 mg P L^{-1} and total activity of 7.5 GBq $plot^{-1}$ was spread homogeneously on the soil surface after sowing the seeds. The area of ^{32}P was covered with a plastic sheet. This was done at the same time as applying the P treatment for incubation and also to prevent dust contamination during the experiment.

2.4. Plant harvesting, analysis and calculations

In soybeans, the microplot was divided into 2 parts. Five whole plants from one part of the microplot were taken at flowering stage and the other five whole plants were taken at maturity stage. These plants were taken for ^{32}P and total P analysis. The plants were dried in an oven at 65-70°C. The total dry weight was determined. The ground plant was ashed at 500°C for 5 hours. The ash was dissolved in 20-30 ml of 2 N HCl. An aliquot of ten ml. was pipetted into glass scintillation vials and the ^{32}P activity was counted by the Cerenkov technique using a Liquid Scintillation Counter. The concentration of total P in the samples was determined by an Ammonium-vanadomolybdate method. The Bray and KurtzNo.-1 method was used for determining available soil P by the Ammonium molybdate ascorbic acid blue color methods. Radioactivity counts were corrected for background and for decay of plant tothe date of taking plant samples.

The percentage of P in the plant derived from fertilizers (PR, TSP, or PR + TSP) (%Pdff) and P uptake by the plant from soil were calculated by the isotope dilution concept, where:

$$\% \text{ Pdff} = \left(1 - \frac{\text{SA of } ^{32}\text{P in plant treated with test fertilizer P}}{\text{SA of } ^{32}\text{P in plant not treated with test fertilizer P}} \right) \times 100$$

$$\text{where SA} = \text{specific activity} = \frac{\text{dpm/ g plant}}{\text{mg P/g plant}}$$

The fertilizer P utilization (%FPU) was determined as:

$$\%\text{FPU} = \frac{\text{Fertilizer P} \times 100}{\text{Rate of P application}}$$

where

$$\text{Fert. P} = \text{P yield} \times \frac{\%\text{ PdfF}}{100}$$

and

$$\text{P yield} = \frac{\%\text{ P} \times \text{yield}}{100}$$

The relative agronomic efficiency (%RAE) was determined as:

$$\%\text{RAE} = \frac{\%\text{Pdf PR}}{\%\text{Pdf TSP}} \times 100$$

3. RESULTS AND DISCUSSION

During the first year non-significantly different soybean yields were found for the fresh application of phosphate fertilizers in the middle of the rainy season (Table V). However, grain yield in the second year (1996) was higher than in the first year (1995). Control yield was rather high compared to other treatments. This result may have been due to (1) soybean variety used was tolerant to low P condition (2) adequate rainfall and (3) good field management with furrows able to drain excess water. It is reported that the fertilizer efficiency of PR increased with increasing rainfall [8]. The renewal of the

Ca sink during leaching was the main reason for the continued dissolution of PR under leaching conditions. It is important not only for annual fertilization but also for basal fertilizer. In general, response to PR is more erratic under low-rainfall conditions [9]. Chien et al [10] reported that temperature was found to have no significant effect on the dissolution of PR in soil. There seems to be a likely agreement between treatment of phosphate rocks (Algerian rock, North Carolina rock, Petchaburi rock and Ratchaburi rock) and the control with regard to dry matter yield.

Table V shows %Pdff and %FPU at flowering stage had the highest uptake of plant elements. The results in 1995 for %Pdff showed significant differences where there was fresh PR application. The highest %Pdff was in the treatment of TSP at 60 kg P ha^{-1} and the lowest value was RBPR at the rate of 120 kg P ha^{-1} (60% and 32%, respectively). The ARPR and NCPR had %Pdff not different from the treatments of TSP at 60 and 120 kg P ha^{-1}, respectively. Phosphorus was split in the treatment of TSP at 40 and 60 kg P ha^{-1} in the second year. The % Pdff was not significantly different, but the value of % Pdff was higher than % Pdff in 1995. The highest value was in TSP at the rate of 120 kg P ha^{-1}.
A similar value in % FPU occurred.

At maturity stage (Table V) % Pdff in 1995 and in 1996 and % FPU in 1995 and 1996 showed the same trend. The %Pdff and %FPU for NCPR had the highest value among PRs in both year experiments. In 1995, the value of %Pdff was increased with increased rate of application. The %Pdff at the rate of TSP 120 kg P ha^{-1} in 1996, which was applied one time at the beginning of the experiment, gave the same result as the treatment of 60 kg P ha^{-1}. The %FPU in 1995 and 1996 showed that the treatment of TSP at 40 kg P ha^{-1} had the highest value of %FPU. This could be interpreted that soybean used sufficient P at the rate of 40 kg P ha^{-1}. Applying P at a high rate of TSP for long term availability would not be a suitable recommendation. The percentage of relative agronomic effectiveness (%RAE) at the flowering and maturity stages (Table VI) had the same trend. The highest %RAE among PRs was NCPR.

Yield of maize hybrid Suwan 3504 (Table VII) showed a higher value in the first residual effect of P (1995) than in third residual effect to PRs (1996). This hybrid was tolerant to low P condition. This caused high yield in the control treatments. Yield in the first residual effect of P showed response to P in the treatment of TSP. In 1996, yields for maize were lower than yields in the first year (1995)

The %Pdff (Table VII) at flowering stage was lower than at maturity stage in both years. The %FPU (Table VII) had higher value at the maturity stage than at the flowering stage. Longer times caused more fertilizer to be utilized by maize.

The relative agronomic effectiveness (RAE) (Table VIII) from fertilizer in the second year of the experiment when compared with TSP at the same rate was higher than in the first year in both growth stages. The agronomic effectiveness of P in phosphate rocks were close to %Pdff of TSP applied at the same rate as phosphate rocks (120 kg P ha^{-1}). The highest %RAE among all PRs occurs with ARPR. It could be interpreted that this PR could dissolve available P to plants close to the third residual P from TSP.

The experiment in 1997 had the direct application of TSP and PRs for soybean. The flowering stage is the stage of high efficiency use of P for the reproductive stage [11].

Yield, %Pdff, %FPU, and %RAE of soybean variety Nakorn Sawan1 (tolerant variety) was shown in Table IX. Soybean yields were higher with TSP applied alone. The TSP showed highest significant differences when compared with the control treatment. Among PRs treatment, NCPR had the highest yield. At flowering stage, Morocco phosphate rock applied alone had the best result in %Pdff. The TSP treatment had the highest value of %FPU in both stages. The treatments with PR added with TSP, gave very reasonable results.

TABLE V. MEAN GRAIN YIELD, %PDFF, %FPU OF SOYBEAN IN 1995 AND 1996 AT FLOWERING AND MATURITY STAGES

				Flowering stage				Maturity stage			
Source	Treatment	Yield		%Pdff		%FPU		%Pdff		%FPU	
of P	(kg P/ha)	1995	1996	1995	1996	1995	1996	1995	1996	1995	1996
Control	0	1.7	2.4	-	-	-	-	-	-	-	-
TSP	40	1.8	2.3	44.4	38.1	3.2 a	0.9 a	51.7 ab	67.8 a	9.2 a	2.8 a
TSP	60	1.8	2.4	60.0	64.4	3.2 a	0.4 cde	61.0 ab	63.9 ab	7.8 ab	2.2 a
TSP	120	1.6	2.3	56.0	76.1	1.6 ab	0.5 b	73.0 ab	63.1 ab	5.1 bc	1.1 b
ARPR	120	1.7	2.4	51.0	61.9	0.9 b	0.3 e	54.0 ab	49.0 b	3.1 bc	0.7 b
NCPR	120	1.6	2.3	52.5	77.6	1.0 b	0.5 bc	66.5 a	61.9 ab	3.7 bc	0.8 b
PBPR	120	1.6	2.3	43.6	63.6	0.8 b	0.4 bcd	36.5 b	48.3 b	2.1 c	0.6 b
PBPR	120	1.7	2.1	32.2	59.0	0.6 b	0.3 de	42.0 b	49.7 b	2.4 c	0.7 b
F-test		ns	Ns	**	ns	**	**	**	**	**	**

Means followed by a common letter are not significantly different at the 5% level by DMRT.

TABLE VII. MEANS (%PDFF AND %FPU) OF YIELD OF MAIZE IN 1995 AND 1996 AT FLOWERING AND MATURITY STAGES

				Flowering stage				Maturity stage			
Source	Treatment	Yield		%Pdff		%FPU		%Pdff		%FPU	
of P	(kg P/ha)	1995	1996	1995	1996	1995	1996	1995	1996	1995	1996
Control	0	1.7	2.4	-	-	-	-	-	-	-	-
TSP	40	6.1	3.6	27.0 ab	46.3 bcd	0.58 a	0.6 a	40.4 ab	40.4 cd	5.24 a	2.40 b
TSP	60	6.2	3.4	25.6 a	49.1 abc	0.32 c	0.47 b	46.9 ab	59.4 a	4.53 b	4.26 a
TSP	120	6.6	3.9	59.0 b	55.0 a	0.43 ab	0.46 b	45.6 ab	50.8 b	2.53 c	2.69 b
ARPR	120	5.2	3.9	39.3 c	53.0 ab	0.26 bc	0.42 b	42.3 ab	46.8 bc	2.55 c	2.35 b
NCPR	120	5.2	3.6	28.4 ab	45.1 bcd	0.21 bc	0.41 b	49.9 a	40.3 cd	1.68 d	1.63 c
PBPR	120	5.6	4.0	30.1 b	41.6 cd	0.16 d	0.33 c	28.7 b	37.5 d	1.43 de	2.51 b
PBPR	120	5.4	3.8	25.2 a	40.0 d	0.17 d	0.35 c	25.4 b	37.8 d	1.21 e	1.77 c
F-test		ns	Ns	Ns	ns	**	**	**	**	**	**

Means followed by a common letter are not significantly different at the 5% level by DMRT.

TABLE VI. %RAE OF SOYBEAN (IN 1995-1996) AT FLOWERING AND MATURITY STAGES

Source of P	Treatment (kg ha^{-1})	Flowering stage		Maturity stage	
		1995	1996	1995	1996
ARPR	120	91.1	81.2	74.0	77.7
NCPR	120	93.8	102	91.1	98.0
PBPR	120	77.9	83.3	50.0	76.6
RBPR	120	57.6	77.5	57.5	78.9
TSP	120	100	100	100	100

TABLE VIII. %RAE OF MAIZE AT FLOWERING AND MATURITY STAGES IN 1995-1996

Source of P	Treatment kg P ha^{-1}	Flowering stage		Maturity stage	
		1995	1996	1995	1996
ARPR	120	88.6	97.6	93.0	92.0
NCPR	120	88.4	93.4	110	80.1
PBPR	120	65.5	80.2	63.0	73.8
PBPR	120	40.8	77.3	55.8	74.4
TSP	120	100	100	100	100

They gave higher values than PRs applied alone in every parameter at flowering and maturity stages. At harvest, the agronomic effectiveness of phosphate rocks from foreign countries and local phosphate rock (Thailand) followed the order: LPPR+TSP > ARPR = LPPR = MCPR > NCPR+TSP > TSP > NCPR.

3.1. Maize

Maize grown in 1997 assessed the residual effect of P sources. Yield, %Pdff, %FPU, and %RAE of maize at flowering and maturity stages are shown in table X. There were non-significant differences in yield when compared with the control treatment. However, there was a high yield for the TSP Treatment. At flowering stage, the highest percentage of P derived from fertilizer (%Pdff) and fertilizer P utilization (%FPU) of maize were obtained from NCPR+TSP and LPPR+TSP. The results may have been due to dissolution of P from NCPR and LPPR and addition of the dissolved P from TSP. Another explanation may be P released from Fe fixation which might have been an effect with higher pH bythe reaction of Ca ion from the dissolution of PRs. Therefore, plants could uptake more P in these treatments. The %RAE at flowering stage of maize showed the same result as %Pdff and %FPU.

There were highly significant differences at the 1% level in the case of %Pdff and %FPU of maize at maturity stage (Table X). The P response was obtained from the TSP application. The %FPU of the MCPR at maturity stage showed high efficiency among the treatments of PR applied alone (Table X). These results indicate MCPR was a very reactive phosphate rock and was more suitable to acid soil than other PRs. For %FPU, the TSP and LPPR+TSP gave the best plant P utilization at maturity stage. The % phosphorus derived for fertilizer (%Pdff) at flowering stage was higher than at maturity stage for both soybean and maize (Table X), which clearly agreed with the work of Ishizuka [11]. The addition of TSP to PR increased the utilization of P from PR in terms of direct application and residualeffects.

TABLE IX. AVERAGE (4 REPS) YIELD, %PDFF, %FPU AND %RAE OF SOYBEAN AT FLOWERING AND MATURITY STAGE IN 1997

Sources	Treatments	Yield	Flowering stage			Maturity stage		
of P	(kg P/ha)	(T/ha)	%Pdff	%FPU	%RAE	%Pdff	%FPU	%RAE
Control	0	351.56 d	-	-	-	-	-	-
TSP	60	520.94 a	72.2 c	1.9 a	100	47.5 d	2.2 a	100
ARPR	60	376.87 cd	71.3 c	1.0 d	99	65.3 b	0.8 cd	137
MCPR	60	413.31 bc	83.6 b	1.3 c	116	62.3 b	1.1 bc	131
NCPR	60	460.81 b	72.2 c	1.0 c	100	42.5 d	0.1 b	89
NCPR + TSP	30+30	419.87 bc	92.7 a	1.6 b	128	54.9 c	1.5 c	116
LPPR	60	409.69 bc	79.4 b	1.2 cd	110	63.1 b	1.0 b	133
LPPR+TSP	30+30	416.56 bc	82.9 b	1.8 ad	115	81.4 a	2.1 a	171
F – test		**	**	**		**	**	

Means followed by a common letter are not significantly different at the 5% level by DMRT.

TABLE X. YIELD, %PDFF, %FPU AND %RAE OF MAIZE AT FLOWERING AND MATURITY STAGE

Sources	Treatments	Yield	Flowering stage			Maturity stage		
of P	(kg P/ha)	(T/ha)	%Pdff	%FPU	%RAE	%Pdff	%FPU	%RAE
Control	0	4.92	-	-	-	-	-	-
TSP	60	6.31	47.6 b	0.08 cd	100	49.6 a	4.04 a	100
ARPR	60	5.62	31.5 c	0.05 d	66	23.6 ef	1.76 bc	48
MCPR	60	5.43	46.9 b	0.02 a	98	28.4 d	2.13 bc	57
NCPR	60	5.26	52.6 b	0.11 b	110	21.6 f	1.57 cd	44
NCPR+TSP	30+30	5.67	58.7 a	0.10 b	123	34.8 c	2.45 b	70
LPPR	60	5.99	36.8 c	0.07 cd	77	27.2 de	1.53 d	55
LPPR + TSP	30+30	5.48	59.7 a	0.11 b	125	43.4 b	3.57 a	88
F – test		ns	**	**		**	**	

Means followed by a common letter are not significantly different at the 5% level by DMRT.

4. CONCLUSIONS

Grain yield of soybean variety Nakorn Sawan 1 in the second year (1996) was higher than in the first year (1995). There was no response of P from TSP in terms of grain yield. The %Pdff, %FPU, and %RAE at flowering and maturity stages followed the same trend. North Carolina phosphate rock had a very good agronomic effectiveness for soybean.

Yield of maize variety Suwas 3504 (hybrid) in the second year was lower than in the first year (1995). The %Pdff did not have any change from the first year in both flowering and maturity stages. The fertilizer phosphorus utilization (%FPU) in both stages was higher than in the first year. Algerian phosphate rock showed the highest %RAE among all represented phosphate rocks.

High soybean yield at harvesting resulted from TSP application. The ranking of treatments acoording to %RAE was LPPR+TSP > ARPR = LPPR = MCPR >NCPR+TSP > NCPR. MCPR and LPPR had good agronomic effectiveness for maize at maturity stage. The combination of PR and TSP resulted in better P utilization.

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REFERENCES

[1] CHIEN, S.H., Direct application of phosphate rocks in some tropical soils of South America: A status report. pp 519-529. Phosphorus and Potassium in the Tropics. The Malaysian Society of Soil Science (1982)

[2] COOKE, G.W., The value of rock phosphate for direct application. Empire J Exp Agric **24** (1956) 195-306.

[3] KHASAWNEH, F.E., DOLL E.C., The use of phosphate rock for direct application to soils. Adv. Agron. **30** (1978) 159-205.

[4] CHIEN, S.H., HAMMOND. L.L., Agronomic evaluation of partially acidulated phosphate rock in the tropics. IFDC's experience. Pap. Ser. IFDC-P7. International Fertilizer Development Center, Muscle Shoals, AL (1988)

[5] CHIEN, S.H., SOMPONGSE, D., HENAO, J., HELLUMS, D.T., Greenhouse evaluation of phosphorus availability from compacted phosphate rocks with urea or with urea and triple superphosphate. Fert. Res. **14** (1987) 245-256.

[6] ZAPATA, F., AXMAN. H., ^{32}P isotope techniques for evaluating the agronomic effectiveness of rock phosphate materials. Fert. Res. **41** (1995) 189-195.

[7] KUCEY, R.M.N., BOLE J.B., Availability of phosphorus from 17 rock phosphates in moderately and weakly acidic soils as determined by ^{32}P dilution, A value and total P uptake methods. Soil Sci. **138** (1984) 180-188.

[8] C.N.R.A., BAMBEY. Rapport d'activités du CNRA de Bambey, (1956).

[9] HAMMOND, L.L., CHIEN, S.H., MOKWUNYE U., Agronomic value of unacidulated and partially acidulated phosphate rocks indigenous to the tropics. Academic Press. Inc.: 140-289 (1986).

[10] CHIEN, S.H., CLAYTON, W.R., MCCLELLAN, G.H., Kinetics of dissolution of phosphate rocks in soils. Soil Sci. Soc. Am. J. **44** (1980) 260-264.

[11] ISHIZUKA, Y., Nutrient uptake at different stages of growth. Paper presented in "The Mineral nutrition of the rice plant "Proceedings of a Symposium at The International Rice Research Institute. Feb., 1964. Pub. for The International Rice Research Institute by the John Hopkins Press, Baltimore, Maryland: 199-217 (1964)

[12] CHIEN, S.H., HAMMOND L.L., A simple chemical method to evaluating the agronomic potential of phosphate rock for direct application. Soil Sci. Am. Soc J. **42** (1978) 615-617.

DIRECT USE OF PHOSPHATE ROCK TO IMPROVE CROP PRODUCTION IN INDONESIA

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Abstract. In Indonesia most of the areas left for producing crops have soils such as Ultisols and Oxisols that are highly weathered, acid and of low fertility. One of the main constraints is their low available P to support food crop production. P inputs such as inorganic fertilizers, organic matter, and phosphate rock (PR) must be applied. Phosphate rock is one of the options for farmers to use as a P-source for food crops. In the frame of the coordinated research program three pot and five field experiments were conducted to determine the agronomic effectiveness of PR for food crops using ^{32}P isotopic techniques. Crops used in the pot experiments were lowland rice, soybean, and mungbean. One of the pot experiments was a crop rotation simulation where upland rice, soybean, and mungbean were grown in sequence. Two of the field experiments were a crop rotation of upland rice, soybean, and mungbean. In the field experiments, ^{32}P was used to determine the agronomic effectiveness, whenever possible. In general, the direct application of PR was able to increase plant growth in the pot experiments and crop production in the field experiments. Use of ^{32}P was a good tool to determine the agronomic effectiveness of PR in the pot and field experiments.

1. INTRODUCTION

According to Hammond *et al* [1], the direct application of phosphate rock (PR) may be more cost-effective than the use of water-soluble phosphate fertilizer such as SSP (single superphosphate) or TSP (triple superphosphate). An additional benefit of PR is its residual effect, which could improve the status of soil P [2]. It is also reported that PR was significantly superior to SSP in building the residual P status in certain soils [3].

In Indonesia, the direct use of PR for food crops was only recently recommended for acid soils due to the increased price of water-soluble fertilizers, such as TSP or SP-36 (SSP). Besides the attractive side of being less expensive than TSP or SP-36, Indonesia has local PR deposits [4].

With the development of sustainable land management, an important aspect is concerned with the long-term preservation of the resource base, including improving marginal soils. To meet the ever-growing need for food, Indonesia will have to enlarge its production base by improving the productivity of the large underutilized areas in a sustainable way [5]. Such areas are dominated by highly wheathered acid soils, namely Ultisols and Oxisols, of low inherent fertility and productive capacity.

In some case studies related to P, Syers and Myers [6] reported that on an acid ultisol area in South Kalimantan, Indonesia, fertilizer P slightly increased available P in the soil and 10 tons of farmyard manure ha^{-1} produced a similar increase. Adiningsih and Fairhurst [7] stated that phosphorus (P) plays a main role in improving fertility of areas presently designated as rainfed areas dominated by *Imperata cylindrica* in Indonesia.

Phosphorus fertilizer prices are continuously increasing due to the reduction in the fertilizer subsidies by the government. This policy results in low levels of fertilizer application and decreased crop productivity and in the long run it is leading to soil degradation. In Indonesia, PR is the chaepest P fertilizer and is recommended in acid soil with low fertility [7]. It is expected from the direct application of PR to have a P-residual effect that could increase production of succeeding crops. The tracer method with ^{32}P utilised to follow phosphorus in the soil-plant system is one method to determine the effectiveness of phosphorus fertilizer [8].

A series of pot- and field experiments were carried out to determine the agronomic effectiveness of various PRs and their potential to increase plant production in Indonesia.

2. MATERIALS AND METHODS

For four consecutive years, 3 pot experiments and 5 field experiments were conducted. The methods used for the experiments are outlined below.

2.1. Greenhouse experiments

2.1.1. Greenhouse experiment I

Soybean varieties Tengger (V1) and Willis (V2) were grown on Red Yellow Podsolic soil. The soil had the following characteristics: total N of 0.15%; Bray I extractable P of 15.2 ppm; organic carbon of 1.92%; pH (in water) of 5.2 and pH KCl (10 g dry soil/10 ml KCl 1 N) of 4.2. Three days prior to planting, the P fertilizers PR, TSP, and ^{32}P-TSP were applied. A basal application of urea and KCl was made at planting time. The plants were harvested one month after planting [9]. The P rates applied as PRs were 1290 mg P and 2580 mg P per pot. The P rates applied as TSP were 300 mg P and 600 mg P per pot.

2.1.2. Greenhouse experiment II

Lowland rice varieties, Atomita-4 (V1) and var. IR-64 (V2) were used. The soil used was a Latosol lowland soil. The soil had the following characteristics: total N of 0.2%, Bray I extractable P of 16.6 ppm, organic carbon of 3.82%, water pH of 6.4, and pH KCl (10 g dry soil/10 ml KCl 1 N) of 5.4. Three week-old rice seedlings were transplanted into pots at planting time and at the same time PR, TSP, N as urea, K as KCl, and ^{32}P-TSP were applied. Plants were harvested one month after seedlings were transplanted [9]. The P rates applied as PRs were 258 mg and 387 mg P per pot. The P rates applied as TSP were 129 mg and 194 mg P per pot.

2.1.3. Greenhouse experiment III

A rotation cropping system was simulated using the same Red Yellow Podzolic soil as used in greenhouse experiment I. The crops used were upland rice (var. Danau Tempe), soybean (var. Tengger), and mungbean (var. Camar). The soil was mixed homogenously with ^{32}P-labelled KH_2PO_4 in a carrier-free solution. The P fertilizers were PR and TSP. Nitrogen and K were added at a rate of 60 kg N (as urea) ha^{-1} for upland rice, 20 kg N (as urea) ha^{-1} for soybean and mungbean and 90 kg K_2O (as KCl) for all three crops. For the last crop, mungbean, no P fertilizers were applied. The purpose of the mungbean crop was to study the residual availabilities of the P fertilizers used [10]. The plants were harvested
one month after transplanting. The P rates applied as PR were 1500 and 3000 mg P per pot. The P rates applied as TSP were 150 mg P and 300 mg P per pot.

2.2. Field experiments

2.2.1. Field experiment I

The experiment was conducted in the lowland rice production area, in the North Coast of West Java. The soil was the same as used in greenhouse Experiment II. Phosphorus fertilizers used were one local PR (at rates of 30, 45 and 90 kg P_2O_5 ha^{-1}) and TSP (at rates of 30 and 45 kg P_2O_5 ha^{-1}). Applications of ^{32}P-TSP were made at the time of transplanting three-week old rice seedlings from the seedbed. Nitrogen as urea and K as KCl were applied on the same day as the P fertilizers at a rate of 90 kg N ha^{-1} and 90 kg K_2O ha^{-1}. One month after transplanting, harvest was carried out to determine the agronomic effectiveness. The second harvest was done at grain maturity [9].

2.2.2. Field experiment II

In this experiment, a Hybrid CP-2 corn was used and planted in an Oxisol (Latosol) soil located at Jakarta. The soil characteristics were total N of 0.14%, extractable Olsen P of 9 ppm, organic carbon of 1.25%, water pH of 5.4, and pH KCl (10 g dry soil/10 ml KCl 1 N) of 4.3. Top soil of the isotope plots were mixed with ^{32}P-KH_2PO_4 carrier free solution. Phosphorus fertilizers used were local and imported PR (at rates of 90 kg P_2O_5 ha^{-1}) and SP36 (at rates of 90 kg P_2O_5 ha^{-1}). Phosphorus, N, K were applied at planting time. The first harvest was performed 1 month after planting and the second harvest was performed at grain maturity [10].

2.2.3. Field experiment III

Field experiment III involved a rotation cropping system as in Greenhouse experiment III. For rice, N as urea was applied at 90 kg N ha^{-1} in two split treatments. One-third was applied at planting and the rest was applied one month after planting. The rate of N as urea for soybean and mungbean was 20 kg N ha^{-1}. Potassium was applied as KCl at the rate of 90 kg K_2O ha^{-1} for all three crops. Phosphorus was not given for the last crop, mungbean, and the plants were assumed to use the residual P applied for rice and soybean. In this experiment, no ^{32}P was used [10, 11]. The P rates applied as PR were 100 and 200 kg P ha $^{-1}$. The P rate applied was 10 kg P_2O_5 ha^{-1} as TSP. The soil and its characteristics were the same as used in field experiment I.

2.2.4. Field experiment IV

Field experiment IV involved a crop rotation sequence as in Field Expriment III. In this experiment, a crop rotation of upland rice, soybean, and mungbean was used. Nitrogen as urea and K as KCl were applied as done in Experiment III. Besides TSP, only one imported PR was used. As in Experiment III, ^{32}P was not used in this experiment [11]. The P rates applied as PR were 100 kg P and 200 kg P ha $^{-1}$. The P rates applied as TSP were 10 kg and 20 kg P ha^{-1}. The soil and its characteristics were the same as used in field experiment III.

2.2.5. Field experiment V

Upland rice was used in this experiment. Nitrogen as urea, K as KCl, and P as imported PR and TSP were applied as in field experiment IV for upland rice. The ^{32}P-TSP was applied at planting time. Two harvests were performed at 1 month after planting and at grain maturity.

2.2.6. Calculations

For field experiments I, II, and V, ^{32}P was used to evaluate the agronomic effectiveness of PR and TSP. The following parameters were determined % P fertilizer use efficiency (%FUE), %P derived from fertilizer (%Pdff), %P derived from soil (%Pdfs), and agronomic effectiveness (AE) as shown by Zapata [12].

3. RESULTS AND DISCUSSION

3.1. Greenhouse experiments

3.1.1. Greenhouse experiment I

Phosphate rock had the same ability as TSP in increasing dry weight above the control (Table I). There were also significant differences between the two soybean varieties used. From the plant –P partitioning, the %Pdff from PR or TSP was much higher than the %Pdff from soil for both varieties.

On the other hand, the % P-ultilization of PR (%FUE) was low at < 1%. This result was apparently due to the high rates of PR applied.

3.1.2. Greenhouse experiment II

Phosphate rock had no influence on the dry weight of two lowland varieties (Table II). Different data was obtained from field experiment V as will be shown later. The %Pdff showed that %^{32}P was quite high. In greenhouse experiment I the value was less than 6%. In this experiment, the value was greater than 10%. This may have influenced the %P from PR. This was also shown for the partitioning of P-yield, where ^{32}P-yield showed high values. These values were nearly as large as P-soil yield. In this experiment, the P-utilization (%FUE) was quite high. This was caused by the low rates of PR used.

3.1.3. Greenhouse experiment III

In this experiment where a rotation crop sequence was simulated, all 4 PRs applied had the ability to increase dry weight (Table III). Combination of PR+TSP did not result in significantly higher dry weight compared to when PR or TSP were applied alone. The % total P data showed that for upland rice and mungbean, the plants receiving PR or TSP had higher values than the controls. Some crops that responded to P not only showed an increase in dry weight, but also in % total P. Phosphorus uptake for plants applied with P also showed a significant increase above the controls. This was observed for all3 crops. For mungbean where only the residual PR was tested, most all of the dry weight and most of the P uptake for plant receiving PR were higher than plants, which received the TSP residues. The %Pdff for PR or TSP was quite high for the first crop (upland rice) and decreased for the second crop (soybean). For the third crop (mungbean), the %Pdff for PR or TSP residues in the soil was not performed. It was assumed that the rate of two applications was the same as the first application for upland rice. This resulted in data of %Pdff for PR and TSP showing not much difference from soybean (second crop) values.

The %FUE showed decreasing values for the second crop (soybean) compared to the first crop (upland rice). In the second crop, there must be some residual of PR-P from the first crop. Also, the different crops may respond differently to P. For the third crop, it becomes more complicated because the P residual had to be known.

3.2. Field experiments

3.2.1. Field experiment I

Data from the first harvest (one month after transplanting – Table IV) showed that although not significant, PR at 90 kg P_2O_5 ha^{-1} could increase dry weight of lowland rice above the control. For the partitioning of P, the %P from PR or TSP was quite high (>50%). According to Partohardjono and Sri Adiningsih [13], the soil where this experiment was carried out had received P fertilization for three decades. Assuming that there was a large amount of residual P, this P residue was used by crops even when low rates of P fertilizer were applied. But data from this experiment showed that for the two different lowland rice varieties, P as PR or TSP must still be applied to increase yield above that ofthe control. This is shown by the P-partitioning data where %P from soil was much lower than %P from PR or TSP.

The P-utilization (%FUE) of TSP was higher than that of PR. This must be due to the solubility of P-TSP compared to P-PR. But, for the 45 kg P_2O_5 ha^{-1} rate, the %FUE of PR showed little difference to %FUE of TSP. This could be the point where P-PR could be used directly to lowland rice instead of TSP.

TABLE I. GREENHOUSE EXPERIMENT I: DRY WEIGHT YIELD, PARTITIONING OF P-PLANT (%), P-YIELD (Mg P/POT), AND P-UTILIZATION (%FUE) OF 2 SOYBEAN VARIETIES

Treatments	Dry weight (g pot^{-1})	Partitioning of P-plant (%)			Partitioning of P-Yield (mg P pot^{-1})			FUE (%)
		^{32}P	PR or TSP	Soil	^{32}P	PR or TSP	Soil	PR or TSP
V1								
Control 0 P	1.71	12.06	--	87.94	0.555	--	4.00	--
PR1 1290 mg P pot^{-1}	2.37	5.78	57.56	36.69	0.372	3.28	2.29	0.254
PR2 2580 mg P pot^{-1}	1.99	4.44	65.98	29.58	0.233	3.47	1.54	0.119
TSP1 300 mg P pot^{-1}	1.98	4.60	63.96	31.45	0.269	4.05	1.96	1.349
TSP2 600 mg P pot^{-1}	1.98	2.68	79.93	17.39	0.186	5.54	1.20	0.923
V2								
Control 0 P	1.61	15.79	--	84.21	0.952	--	3.69	--
PR1 1290 mg P pot^{-1}	1.88	4.57	69.18	26.26	0.337	3.64	1.56	0.282
PR2 2580 mg P pot^{-1}	1.83	2.03	86.34	11.63	0.090	3.08	0.41	0.119
TSP1 300 mg P pot^{-1}	1.97	4.09	72.43	23.49	0.259	4.52	1.48	1.509
TSP2 600 mg P pot^{-1}	1.83	2.37	84.01	13.62	0.146	5.20	0.84	0.866
Average V1	2.01	5.91	66.86	40.61	0.323	3.27	2.20	0.648
Average V2	1.82	5.77	77.99	31.84	0.293	3.29	1.63	0.693
Average : C	1.66	13.93	--	86.07	0.653	--	3.94	--
PR1	2.12	5.17	63.37	31.46	0.307	3.46	1.93	0.268
PR2	1.91	3.23	76.16	20.61	0.153	3.28	0.98	0.126
TSP1	1.97	4.34	68.19	27.47	0.263	4.28	1.72	1.428
TSP2	1.90	2.53	81.97	15.51	0.166	5.37	1.03	0.895
LSD (5% level)								
Variety (V)	0.14	ns	4.24	ns	ns	ns	0.35	ns
Fertilizer (F)	0.21	1.43	6.00	15.31	0.112	0.66	0.55	0.150
Interaction (V x F)	ns	2.725	Ns	ns	0.158	ns	ns	ns

Notes: ^{32}P-TSP applied was 30 mg P pot^{-1}. PR = local PR (powder form) with a 27% P_2O_5. Each value is an average of 4 replicates. Planting: 29-8-1994, V1 = Var. Wilis, V2 = Var. Tengger. ns = not significant. Harvesting: 30-9-1994. CV = Coefficient of variation. PR, TSP, and ^{32}P-TSP application: 26-8-1994. N, P application: 29-8-1994 at a rate of 20 kg N ha^{-1} and 90 kg K_2O ha^{-1}.

TABLE II. GREENHOUSE EXPERIMENT II: DRY WEIGHT YIELD, PARTITIONING OF P-PERCENTAGE (%), P-YIELD (mg P POT^{-1}), AND P-UTILIZATION (% FUE) OF 2 LOWLAND RICE VARIETIES

Treatments	Dry weight (g pot^{-1})	Partitioning of P-percentage (%)			Partitioning of P-Yield (mg P pot^{-1})			FUE (%)
		^{32}P	PR or TSP	Soil	^{32}P	PR or TSP	Soil	PR or TSP
V1								
Control 0 P	9.09	46.70	--	53.29	9.21	--	10.65	--
PR1 258 mg P pot^{-1}	9.13	34.60	25.28	40.13	6.58	5.51	7.64	2.21
PR2 387 mg P pot^{-1}	1.90	32.60	29.59	37.77	5.46	4.87	6.33	1.26
TSP1 129 mg P pot^{-1}	10.85	21.39	53.80	24.77	5.54	13.99	6.42	10.84
TSP2 194 mg P pot^{-1}	11.30	29.79	26.51	37.66	8.08	7.27	9.17	3.75
V2								
Control 0 P	9.01	29.69	--	73.29	5.41	--	13.75	--
PR1 258 mg P pot^{-1}	8.76	19.21	27.74	53.06	3.03	4.71	8.44	1.83
PR2 387 mg P pot^{-1}	8.24	13.17	51.52	35.31	1.99	7.80	5.33	2.02
TSP1 129 mg P pot^{-1}	10.11	21.32	21.50	57.18	4.31	4.87	11.57	3.77
TSP2 194 mg P pot^{-1}	9.86	17.37	36.05	46.37	3.86	8.40	10.29	4.33
Average V1	9.65	33.01	33.79	38.72	6.97	7.96	8.04	33.79
Average V2	9.19	20.15	34.20	53.04	3.72	6.45	9.88	34.20
Average : C	9.03	38.20	--	63.29	7.31	--	12.20	--
PR1	8.94	26.91	26.51	46.60	4.81	5.21	8.04	2.02
PR2	8.07	22.88	40.55	36.54	3.72	6.34	5.83	1.64
TSP1	10.48	21.35	37.65	40.97	4.92	9.43	8.99	7.31
TSP2	10.58	23.58	31.28	42.02	5.97	7.83	9.73	4.04
LSD (5% level)								
Variety (V)	ns	3.44	ns	5.54	0.58	ns	1.24	1.27
Fertilizer (F)	1.45	5.44	ns	8.76	0.91	ns	1.97	1.79
Interaction (V x F)	ns	7.69	4.95	12.38	2.30	4.95	2.78	2.53

Notes: ^{32}P-TSP applied was 30 mg P pot^{-1}. PR = local PR (powder form) with a 27% PO_5. Each value is an average of 4 replicates. V1 = Var. Atomita-4, V2 = Var. IR-64. ns = not significant. Planting of 3 week old seedlings = 1-10-1994. CV = Coefficient of variation. Harvesting: 3-11-1994. P, N, K, ^{32}P-TSP application: 3-10-1994.

TABLE III. GREENHOUSE EXPERIMENT III: DRY WEIGHT, TOTAL-P PERCENTAGE, P YIELD, %PDFF, AND P-UTILIZATION (%FUE) OF A RICE-SOYBEAN-MUNGBEAN ROTATION

Crop/ treatments		P (mg pot^{-1}) PR	TSP	Dry weight (g)	Total P %	Total P uptake (mg P pot^{-1})	% Pdff PR or TSP	FUE (%) PR or TSP
Upland rice								
Control		0	0	8.80	0.189	16.52	--	--
PR 1	a	1500	0	12.04	0.236	28.39	83.62	1.58
	b	3000	0	11.07	0.213	23.61	86.58	0.68
	c	1500	150	10.65	0.231	24.80	87.90	1.33
PR 2	a	1500	0	11.15	0.250	27.86	89.38	1.66
	b	3000	0	11.01	0.223	24.54	87.26	0.72
	c	1500	150	11.10	0.254	27.98	87.64	1.48
PR 3	a	1500	0	9.43	0.207	19.47	57.03	0.74
	b	3000	0	9.49	0.230	21.65	39.85	0.44
	c	1500	150	10.47	0.220	23.04	81.99	1.14
PR 4	a	1500	0	9.36	0.237	22.27	78.29	1.17
	b	3000	0	10.40	0.236	24.56	83.76	0.44
	c	1500	150	8.85	0.257	25.28	87.55	1.34
TSP	a	0	150	8.67	0.222	19.05	80.59	10.27
	b	0	300	10.37	0.257	26.68	86.14	7.65
LSD 5%				1.33	0.031	3.61	4.46	0.38
Soybean								
Control		0	0	3.17	0.201	6.40	--	--
PR 1	a	1500	0	8.24	0.203	16.84	36.03	0.41
	b	3000	0	8.71	0.236	22.16	53.42	0.39
	c	1500	150	9.93	0.220	21.93	58.00	0.76
PR 2	a	1500	0	10.92	0.239	26.19	51.17	1.02
	b	3000	0	9.13	0.259	23.61	61.32	0.48
	c	1500	150	10.17	0.216	22.16	60.59	0.82
PR 3	a	1500	0	8.10	0.200	16.11	34.63	0.38
	b	3000	0	9.15	0.246	22.47	44.48	0.34
	c	1500	150	10.26	0.207	22.93	55.45	0.75
PR 4	a	1500	0	7.91	0.212	16.78	38.85	0.40
	b	3000	0	6.84	0.218	14.95	51.73	0.26
	c	1500	150	10.36	0.226	23.58	60.94	0.88
TSP	a	0	150	11.59	0.237	27.50	65.79	12.08
	b	0	300	10.43	0.236	24.30	84.43	6.86
LSD 5%				2.17	0.025	5.99	11.12	0.75

TABLE III CONTINUED

Crop/ treatments		P (mg pot^{-1})		Dry weight (g)	Total P %	Total P uptake (mg P pot^{-1})	%Pdff	FUE (%)
		PR	TSP				PR or TSP	PR or TSP
Mungbean								
Control		0	0	1.90	0.17	3.43	--	--
PR 1	a	1500	0	4.51	0.212	9.80	53.06	0.366
	b	3000	0	5.38	0.228	12.24	68.15	0.280
	c	1500	150	6.46	0.214	14.52	71.55	0.629
PR 2	a	1500	0	4.46	0.243	10.95	75.56	0.547
	b	3000	0	5.22	0.252	13.19	69.44	0.309
	c	1500	150	4.49	0.206	8.99	56.39	0.307
PR 3	a	1500	0	4.01	0.214	8.74	26.84	0.148
	b	3000	0	5.75	0.212	12.17	61.59	0.252
	c	1500	150	6.16	0.213	13.65	47.61	0.391
PR 4	a	1500	0	4.45	0.221	9.95	29.27	0.189
	b	3000	0	5.04	0.223	11.11	47.78	0.167
	c	1500	150	6.31	0.222	13.84	50.52	0.447
TSP	a	0	150	1.74	0.249	11.65	23.13	1.339
	b	0	300	2.33	0.239	10.93	16.09	0.572
LSD 5%				1.74	0.041	4.00	10.84	0.193

Each value in table is an average of four replicates. PR1 and PR2 were an imported PR. PR1 was used in powder form. PR2 was used in granular form. The P2O5 content was 27%. PR3 and PR4 were a local PR. PR3 was used in powder form. PR4 was used in granular form. The P2O5 content was 26%.

TABLE IV. FIELD EXPERIMENT I: DRY WEIGHT, PARTITIONING OF P-PERCENTAGE (%) AND P-YIELD (μg P OR mg P 2 HILLS^{-1}), AND P-UTILIZATION (% FUE) OF PR FOR TWO LOWLAND RICE VARIETIES ONE MONTH AFTER TRANSPLANTING

Crops / treatments	Dry weight (kg ha^{-1})	Partitioning of P-percentage (%)			Partitioning of P-Yield (kg P ha^{-1})			FUE (%)
		^{32}P	PR or TSP	Soil	^{32}P	PR or TSP	Soil	PR or TSP
V1 - Atomita-4								
Control 0 P	1016	0.382	--	99.61	0.0098	--	2.66	--
30 kg P_2O_5 ha^{-1} - TSP1	1254	0.125	65.89	33.99	0.0043	2.30	1.15	17.42
45 kg P_2O_5 ha^{-1} - TSP2	1280	0.090	75.09	24.82	0.0034	3.01	0.91	15.33
30 kg P_2O_5 ha^{-1} - PR1	1008	0.102	71.50	28.39	0.0027	2.00	0.76	15.16
45 kg P_2O_5 ha^{-1} - PR2	1000	0.122	66.58	33.30	0.0029	1.83	0.78	9.39
90 kg P_2O_5 ha^{-1} - PR3	1222	0.087	74.78	25.13	0.0032	2.93	0.91	6.87
V1 - IR 64								
Control 0 P	984	0.322	--	99.68	0.0082	--	2.58	--
30 kg P_2O_5 ha^{-1} - TSP1	948	0.162	47.19	52.65	0.0042	1.17	1.34	8.87
45 kg P_2O_5 ha^{-1} - TSP2	1030	0.137	55.58	44.28	0.0035	1.59	1.14	8.11
30 kg P_2O_5 ha^{-1} - PR1	1182	0.103	66.97	32.92	0.0029	1.96	0.94	14.84
45 kg P_2O_5 ha^{-1} - PR2	1264	0.122	60.54	39.34	0.0039	2.05	1.26	10.43
90 kg P_2O_5 ha^{-1} - PR3	1352	0.090	70.42	29.49	0.0030	2.38	0.98	6.06
Average V1	1130	0.151	58.97	40.87	0.0044	1.97	1.19	12.83
Average V2	1127	0.156	50.12	49.73	0.0043	1.52	1.37	9.66
Average : C	1000	0.352	--	99.65	0.0090	--	2.60	--
TSP1	1102	0.144	56.54	43.32	0.0043	1.74	1.25	13.15
TSP2	1155	0.114	65.34	34.55	0.0035	2.30	1.02	11.72
PR1	1095	0.103	69.24	30.66	0.0028	1.99	0.35	15.00
PR2	1132	0.122	63.56	36.32	0.0034	1.94	1.02	9.91
PR3	1287	0.089	72.60	27.31	0.0031	2.54	0.94	6.47
LSD (5% level)								
Variety (V)	ns	ns	8.35	5.86	ns	ns	0.20	ns
Fertilizer (F)	ns	0.038	10.57	9.26	0.0078	ns	0.28	3.81
Interaction (V x F)	ns	ns	ns	ns	ns	ns	ns	ns

Notes: All the values are an average of 4 replicates, PR used = local PR-P_2O_5 = 26.52%, TSP = 45% P_2O_5, ^{32}P-TSP applied = 1.5 g plot^{-1}. Isotope plots = 1 m x 1 m, yield plots = 6 m x 5 m. Seeding: 30-5-1995, transplanting: 24-6-1995 + basal fertilization = 45 kg N ha^{-1} (urea tablets) and 50 kg K_2O ha^{-1}. Harvest of isotope plot: 25-6-1995. Harvest of isotope plot: 19-9-1995 (grain maturity).

The second harvest at grain maturity (Table V) showed that PR was able to increase grain and straw dry weight. Due to grain being the most important plant part, the discussion on yield will emphasize grain dry weight. Phosphate rock applied at the highest rate (90 kg P_2O_5 ha^{-1}) also resulted in the highest yield, although the value did not differ significantly from TSP at the 45 kg P_2O_5 ha^{-1} rate. Comparing PR and TSP at the same rate of 30 and 45 kg P_2O_5 ha^{-1}, TSP was superior to increasing grain dry weight compared to PR. Regardless of the superiority of TSP, PR still had good ability to increase grain dry weight above the control.

3.2.2. Field experiment II

Although not significant, PR increased the dry matter of corn harvest 1 month after planting (Table VI). However, SP-36 resulted in the highest dry weight. Although not significant, PR as well as SP-36 increased the % total-P. The highest plant dry weight also caused the highest P uptake as shown for SP-36. The highest P-ultization (%FUE) was shown to be SP-36 followed by PR1, PR2 and PR3.

TABLE V. FIELD EXPERIMENT I: DRY WEIGHT OF TWO LOWLAND RICE VARIETIES AT GRAIN MATURITY

Crop / treatments	Dry weight ($kg\ ha^{-1}$) Grain	Dry weight ($kg\ ha^{-1}$) Straw
V1 - Atomita-4		
Control 0 P	4617	4239
30 kg P_2O_5 ha^{-1} - TSP1	5782	5144
45 kg P_2O_5 ha^{-1} - TSP2	5810	5169
30 kg P_2O_5 ha^{-1} - PR1	5117	4338
45 kg P_2O_5 ha^{-1} - PR2	5690	4800
90 kg P_2O_5 ha^{-1} - PR3	5672	4701
V2 - IR 64		
Control 0 P	5020	4074
30 kg P_2O_5 ha^{-1} - TSP1	5652	4327
45 kg P_2O_5 ha^{-1} - TSP2	6447	5071
30 kg P_2O_5 ha^{-1} - PR1	6137	4027
45 kg P_2O_5 ha^{-1} - PR2	6307	5076
90 kg P_2O_5 ha^{-1} - PR3	6857	5018
Average V1	5448	4732
Average V2	6070	4599
Average : C	4819	4156
TSP1	5717	4736
TSP2	6129	5120
PR1	5672	4183
PR2	5999	4938
PR3	6265	4860
LSD 5%		
Variety (V)	326	ns
Fertilizer (F)	430	596
Interaction (V x F)	ns	ns

TABLE VI. FIELD EXPERIMENT II: DRY WEIGHT, % TOTAL-P, P-YIELD, %PDFF, AND P ULTILIZATION (% FUE) FOR GRAIN AND STOVER OF CORN APPLIED WITH PR AND TSP

Treatments	PR	SP-36	Vegetative growth					Grain maturity	
	kg P_2O_5/ha	kg P_2O_5/ha	Dry weight (kg ha $^{-1}$)	Total-P (%)	Total P Uptake (kg P ha $^{-1}$)	Pdff PR or SP-36 (%)	FUE (%)	Grain yield (t ha^{-1})	Stover yield (t ha^{-1})
Control	0	0	1224	0.182	2.25	--	--	5.88	5.65
PR1	90	0	2080	0.223	4.61	30.31	3.39	8.58	10.05
PR2	90	0	2006	0.207	4.03	32.32	3.31	11.34	9.75
PR3	90	0	1733	0.210	3.61	25.52	2.31	9.03	11.51
SP-36	0	90	3070	0.223	6.86	39.97	6.76	13.48	13.33
LSD (5% level)			629	ns	1.73	16.94	2.85	2.66	20.50

Each value in an average of 4 replicates. PR1 and PR2 were local PR powder obtained from Lumajang and Bojonegoro (East Java). PR3 was an imported PR in granular form. ^{32}P applied in the form of liquid KH_2PO_4 carrier free; 100 ml $KH_2{}^{32}PO_4$/0.8 m^2 (total specific activity = 0.4 mCi). Isotope plots = 0.8 m^2, yield plots = 2 m x 1.6 m. Basal fertilization: Urea:90 kg N ha^{-1} and 100 kg KCl ha^{-1}. P_2O_5 content of the two local-PR, imported-PR and fertilizer P were 26%, 27% and 36%.
Application of 100 ml $KH_2{}^{32}PO_4$: 16-1-1996. Basal fertilization: 23-1-1996. Planting: 30-1-1996. Harvest I: 6-3-1996. Harvest II: grain maturity: 20-4-1996 (yield plot).

Harvest at grain maturity showed that PR, as well as SP-36, could increase grain yield and stover yield. The highest grain yield, as expected, was produced with SP-36, which is a high water-soluble P fertilizer. The PR2 also gave quite high grain yield, while PR1 and PR3 produced lower grain yields. The grain yield of corn applied with PR1 and PR3 were still above the control grain yield. For the P-ultilization (%FUE), the highest value was obtained with SP-36, while PR showed lower %FUE values.

3.2.3. Field experiment III

Phosphate rock was able to increase grain and straw dry weight for all of the three crops implemented in the crop rotation system including upland rice, soybean, and mungbean (Table VII). For mungbean, which only used the residual P from PR and TSP that was applied for upland rice and soybean, the grain yield increase was quite high. Upland rice and soybean did not show significant difference in %P in grain between the control and the PR treatments. Differences in %P in grain were only found in mungbean between the control and PR teatments.

The P grain uptake followed the dry weight, showing higher P grain uptake for the PR treatments compared to the controls. The TSP treatment caused higher grain yields than PR treatments for upland rice and soybean, except for PR1b. For the residual test with mungbeans, PR treatments gave higher grain yield compared to TSP. The same trend for TSP was found for the P grain uptake.

3.2.4. Field experiment IV

For this experiment, where only one PR was used for upland rice followed by soybean in a rotation cropping, the same trend as in field experiment III was shown (Table VIII). Here too, PR was able to increase upland rice and soybean grain yields above the control. For soybean, a tremendous increase in grain yield was shown for the PR treatments. As in previous experiments, TSP gave the highest grain yield above the control. Total P uptake increased in the same fashion as grain, straw or stover dry weight, showing high increases for PR and TSP treatments above the controls.

3.2.5. Field experiment V

For the first harvest 44 days after planting, PR, PR+TSP, and TSP all increased the plant dry weight of upland rice above the control (Table IX). The lowest increase in dry weight was found for PRa, PR with the lowest P rate, while the highest dry weight increase was for TSPb, TSP with the highest P rate. Partitioning of P showed most of the P was derived from the soil. However, PR or TSP had the ability to increase dry weight of plants. The %FUE was low for PR but high for TSP. This was obviously due to the higher solubility of TSP compared to PR.

High grain yields for PR, PR+TSP and TSP were shown at the second harvest at grain maturity (Table X). The grain yields were above 3 t ha^{-1} for PR and around 4 t ha^{-1} for TSP. These yields are considered good for upland rice. The total P grain uptake showed the same trend as the grain yield.

In Indonesia, the main problems faced with P fertilizer use are the determination of appropiate fertilizer rate and application method, time of application, most efficient fertilizer form and economic factors [5]. The field texperiments conducted address some of these problems. For lowland rice soils, the practice of using 100 kg P_2O_5 ha^{-1} as TSP per crop, with two crops per year for more than 30 years, certainly has led to a great P accumulation in those soils [13]. Therefore, it has been suggested that in such soils the P fertilizer rate should be decreased. From the lowland rice experiment carried out in field experiment I (Tables IV and V) it was shown that 30 kg P_2O_5 ha^{-1} as PR can already increase the grain yield abovethe control. Similar results were found in India where PR was as effective as TSP in soil with pH around 7 in lowland soils [3].The cost of PR and TSP when applied to lowland rice is another consideration.

TABLE VII. FIELD EXPERIMENT III:
DRY WEIGHT, TOTAL-P PERCENTAGE, AND TOTAL-P YIELD OF
A CROP ROTATION SYSTEM: UPLAND RICE-SOYBEAN-MUNGBEAN, FIRST YEAR

Crop / treatments	P (kg ha^{-1})		Dry weight (kg ha^{-1})		% total-P		Total-P uptake (kg P ha^{-1})	
	PR	TSP	St or Sv	Grain	Grain	St or Sv	Grain	St or Sv
<u>Upland rice</u>								
Control	0	0	1324	1767.7	0.227	0.090	4.04	1.20
PR 1 a	100	0	2617	2616.3	0.217	0.085	5.66	2.20
b	200	0	2459	2840.8	0.226	0.087	6.44	2.13
PR 2 a	100	0	2217	2568.0	0.231	0.083	5.07	1.83
b	200	0	1966	2735.0	0.198	0.076	5.88	1.49
PR 3 a	100	0	1974	2593.0	0.213	0.107	5.50	2.08
b	200	0	2067	2619.0	0.203	0.080	5.31	1.75
TSP	0	10	2286	2793.0	0.224	0.096	6.40	2.16
LSD 5%			465.9	419.2	ns	ns	1.08	0.51
<u>Soybean</u>								
Control	0	0	705	365.5	0.645	0.123	2.30	0.83
PR 1 a	100	0	1539	881.0	0.655	0.130	5.79	1.97
b	200	0	1477	808.3	0.678	0.118	5.47	1.73
PR 2 a	100	0	1499	800.8	0.673	0.123	5.38	1.86
b	200	0	1459	822.0	0.645	0.100	5.27	1.44
PR 3 a	100	0	1635	896.8	0.625	0.095	5.65	1.53
b	200	0	1806	929.8	0.650	0.115	6.01	2.06
TSP	0	10	1629	1096.5	0.713	0.172	7.87	2.76
LSD 5%			358.9	270.8	ns	ns	1.96	0.57

TABLE VII CONTINUED

Crop / treatments	P (kg ha^{-1})		Dry weight (kg ha^{-1})		% total-P		Total-P uptake (kg P ha^{-1})	
	PR	TSP	St or Sv	Grain	Grain	St or Sv	Grain	St or Sv
Mungbean								
Control	0	0	583.3	437.5	0.328	0.170	1.41	0.92
PR 1 a	100	0	946.8	935.8	0.360	0.238	3.31	2.23
b	200	0	945.8	929.5	0.380	0.283	3.52	2.58
PR 2 a	100	0	1141.8	798.5	0.408	0.233	3.26	2.61
b	200	0	845.5	1003.0	0.420	0.243	4.19	2.06
PR 3 a	100	0	1021.8	1093.8	0.385	0.233	4.21	2.39
b	200	0	827.8	1024.3	0.390	0.245	3.99	2.00
TSP	0	10	1218.0	984	0.408	0.253	4.02	3.07
LSD 5%			266.3	341.8	0.036	0.034	1.24	0.71

Notes :PR1 = imported PR (Tunisia); PR2 and PR3 = local PR; all three are in powdered form. St = straw; Sv = stover; for soybean and mungbean includes the pod-shells. CV = coefficient of variation; ns = not significant. No P was applied for mungbean. N applied for upland rice was 67.5 kg N ha^{-1} in 2 splits, 1/3 at planting and the rest one month after planting. N applied for soybean and mungbean was 20 kg N ha^{-1} applied at planting. K applied for all crops was 90 kg P_2O_5 ha^{-1}.

TABLE VIII. FIELD EXPERIMENT IV: DRY WEIGHT, TOTAL-P PERCENTAGE, AND TOTAL-P YIELD OF A CROP ROTATION SYSTEM: UPLAND RICE-SOYBEAN-MUNGBEAN, SECOND YEAR

Crop/ treatments	P (kg ha^{-1})		Dry weight (kg ha^{-1})		% total-P		Total-P yield (kg P ha^{-1})	
	PR	TSP	Grain	St or Sv	Grain	St or Sv	Grain	St or Sv
<u>Upland rice</u>								
Control	0	0	1088	1325	0.189	0.090	2.05	1.19
PR a	100	0	2235	2160	0.236	0.093	5.26	2.00
b	200	0	2141	2550	0.214	0.083	4.58	2.09
PR + TSP	100	10	2322	2869	0.230	0.087	5.36	2.50
TSP a	0	10	2306	3103	0.222	0.089	5.08	2.77
b	0	20	2685	3281	0.230	0.098	6.16	3.22
LSD 5%			215	438	ns	ns	0.74	0.50
<u>Soybean</u>								
Control	0	0	299	388	0.603	0.110	1.81	0.42
PR a	100	0	724	887	0.693	0.113	4.99	1.00
b	200	0	899	1101	0.718	0.113	6.46	1.22
PR + TSP	100	10	780	954	0.690	0.098	5.39	0.94
TSP a	0	10	879	829	0.705	0.113	6.16	0.93
b	0	20	964	1035	0.705	0.115	6.81	1.21
LSD 5%			158	248	0.073	ns	1.23	0.38
<u>Mungbean*</u>	no harvest due to severe drought							

St = straw, Sv = stover.

PR = imported (Christmas Island).

N, P, and K were applied at a rate at a time as in Exp. III.

TABLE IX. FIELD EXPERIMENT V: DRY WEIGHT, PARTITIONING OF TOTAL-P PERCENTAGE, PARTITIONING OF TOTAL-P YIELD (kg P ha^{-1}) AND P-UTILIZATION (%FUE) OF UPLAND RICE 42 DAYS AFTER PLANTING, THIRD YEAR

Treatments	P (kg P ha^{-1})		Dry weight (kg ha^{-1})	Partitioning of percentage of total-P (%)			Partitioning of total-P yield (kg P ha^{-1})			FUE (%)
	PR	TSP		^{32}P	PR or TSP	Soil	^{32}P	PR or TSP	Soil	PR or TSP
Control	0	0	897.5	1.010	--	99.00	0.0134	--	1.45	--
PR a	100	0	1293.8	0.200	2.42	97.71	0.0054	4.06	2.57	4.07
b	200	0	2085.0	0.101	2.67	97.25	0.0057	8.08	4.63	4.05
PR + TSP	100	10	2375.0	0.164	2.52	97.31	0.0079	7.90	4.76	7.18
TSP a	0	10	1753.8	0.318	2.09	97.59	0.0109	5.08	3.62	50.75
b	0	20	2093.8	0.314	2.09	96.74	0.0122	5.60	4.05	27.99
LSD 5%			595.0		0.34	0.859	0.0037	2.65	1.33	17.69

Notes: PR imported. N, P, and K were applied at a rate and at a time as in Exp. III.

TABLE X. FIELD EXPERIMENT V: DRY WEIGHT, TOTAL-P PERCENTAGE, AND TOTAL-P YIELD OF UPLAND RICE AT GRAIN MATURITY, THIRD YEAR

Crop/ treatments	P (kg ha^{-1})		Dry weight (kg ha^{-1})		% total-P		Total-P uptake (kg P ha^{-1})	
	PR	TSP	Grain	Straw	Grain	Straw	Grain	Straw
Control	0	0	2416	3237	0.180	0.098	4.36	3.18
PR a	100	0	3158	3667	0.200	0.090	6.31	3.25
b	200	0	3497	4068	0.212	0.103	7.41	4.96
PR + TSP	100	10	3528	4287	0.208	0.102	7.35	4.37
TSP a	0	10	4090	4820	0.202	0.099	8.27	4.77
b	0	20	4253	4468	0.208	0.101	8.87	4.53
LSD 5%			548.8	549.0	0.015	0.018	1.54	1.43

TABLE XI. DATES OF PLANTING, FERTILIZERS APPLICATION, AND HARVEST OF CROPS IN A CROPPING SYSTEM, CONDUCTED AT BATUMARTA, SOUTH SUMATERA

	Field Experiment III			Field Experiment IV			Field Experiment V
	Upland rice (var. Danau Tempe)	Soybean (var. Willis)	Mungbean (Local Variety)	Upland rice (var. Danau Tempe)	Soybean (var. Willis)	Mungbean (Local Variety)	Upland Rice (var. Danau Tempe)
Planting	1995, Nov., 2	1996,March, 6	1996, June, 16	1996, Nov., 12	1997, March, 14	1997, June, 13	1997, Dec., 22
Fert. Appl. (N, P, K)	1995, Nov., 2	1996, March, 5	1996, June, 15	1996, Nov., 11	1997, March, 13	1997, June, 12	1997, Dec., 22
^{32}P Appl.	--	--	--	--	--	--	1997, Dec., 22
Harvest	1996, March, 15	1996, June, 12	1996, Sep, 14	1997, March, 12	1997, June, 11	*	1. 1998, Feb ,5** 2. 1998, Apr, 12
Rainfall mm season^{-1}	485	674	244	376	802	25	2885

N (urea) was applied in 2 splits, 1/3 at planting and 2/3 one month after planting at a total of 67.5 kg N ha^{-1} for upland rice; 30 kg N ha^{-1} was applied for soybean and mungbean. K (KCl) was applied 90 kg K_2O ha $^{-1}$. P (PR andTSP) was applied at levels as determined in the treatments.

* No harvest, all plants were destroyed due to drought

** 1. Plants were harvested for ^{32}P analysis. 2. plants were harvested at grain maturity

Experiments in slightly acid and acid upland soils showed that grain yield increases of several food crops above the controls were obtained with PR application. The P rates used for PR were the same as TSP except for the last 3 trials where the rates were 10 to 20 times higher than those of TSP. These high PR-P rates were applied with the purpose to improve soil P status and have P residual effect for the subsequent crops in a crop rotation of upland rice, soybean, and mungbean. The residual effect was clearly shown in one of the experiments (field experiment VI, Table VII). Another factor to be considered in upland soils is the availability of water, depending on the rainfall distribution. Crops responded to P with increasing water availability [1]. In the field trials (field experiments II, IV, V) it was clearly shown that crop yield increased when water availability increased (Table XI). This was especially the case for upland rice in field experiments III, IV, V and soybean in field experiments III and IV.

4. CONCLUSIONS

1. In pot experiments, PR application did not show significant crop yield increases.
2. In the field experiments, PR applied at high rates had the same effectiveness as TSP to increase crop yield
3. The residual effect of PR applied from 2 previous crops was clearly shown for the third crop
4. Water availability in rainfed upland areas is a very important factor affecting the effectiveness of PR and crop yields.
5. The use of ^{32}P in pot and field experiments has an added value to determine the relative agronomic effectiveness of PR, in the sense that PR could be evaluated against the water-soluble P fertilizers.

From the experiments carried out, especially the field experiments, the direct use of PR or PR+TSP for food crops could be recommended for acid upland soil. The ^{32}P technique as used in the experiments can be used to answer the main questions of P fertilizer use in Indonesia such as the determination of the appropiate fertilizer application method, time of application, and most efficient fertilizer form.

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REFERENCES

[1] HAMMOND, L.L., CHIEN, S.H., MOKWUNJE, A.U., Agronomic value of unacidulated and partially acidulated phosphate rocks indigenous to the tropics. Advances in Agronomy **40** (1986) 89-140.

[2] Van der PAAUW, F., Factors controlling the effiency of rock phosphate for potatoes and rye on humic sandy soils, Plant and Soil **126** (1965) 81-98.

[3] DEV, G., Use of rock phosphate in food grain productions under irrigated and rainfed conditions in India, Paper presented at IMPHOS -AARD /CSAR International Conference in Asia and IFA-FADINAP Regional Meeting, “Nutrient Management for Sustainable Food Production in Asia”, Bali, Indonesia, December 1-12, 1996. Preprints papers and Posters (11 pages).

[4] BISRI, U., PERMANA, D., Fosfat. Bahan Galian Industri (Phosphate and Industrial Mining), Center for the Development of Mineral Technology, Bandung (1991).

[5] SANTOSO, D., Development of phosporus fertilizer use on acid soil in Indonesia, Paper presented at IMPHOS-AARD/CSAR International Conference in Asia and IFA-FADINAP Regional Meeting, “Nutrient Management for Sustainable Food Production in Asia”, Bali, Indonesia, December 1-12, 1996. Preprints papers and Posters (12 pages).

[6] SYERS, J.K., MYERS, J.K., Phosphorus in sustainable agriculture in Asia, Paper presented at IMPHOS-AARD/CSAR International Conference in Asia and IFA-FADINAP Regional Meeting, "Nutrient Management for Sustainable Food Production in Asia", Bali, Indonesia, December 1-12, 1996. Preprints papers and Posters (16 pages).

[7] J. SRI ADININGSIH, FAIRHURST, T., The use of reactive phosphate rock for the rehabilitation of antrophic savanah in Indonesia, Paper presented at IMPHOS -AARD /CSAR International Conference in Asia and IFA-ADINAP Regional Meeting, "Nutrient Management for Sustainable Food Production in Asia", Bali, Indonesia, December 1-12, 1996. Preprints papers and Posters (25 pages).

[8] FARDEAU, J.C., GUIRAUD, G., MAROL, C., The role of isotopic techniques effectiveness of P fertilizers, IAEA-CT-112.

[9] SISWORO, E.L., RASJID, H., SISWORO, W.H., HARYANTO, The use of isotopic techniques to determine the availability of P-phosphate rock and P-TSP to food crops, Paper presented at the 2nd RC meeting, 25-29 April 1995, Montpellier, France (unpublished).

[10] SISWORO, E. L., RASJID, H., SISWORO, W.H., IDRIS, K., The use of ^{32}P for the agronomic effectiveness of phosphate rock, Paper presented at the 3th RC Meeting, 17-21 March 1997, Vienna, Austria.

[11] SISWORO, E. L., RASJID, H., SISWORO, W.H., HARYANTO, IDRIS, K., The use of pohsphate rock to improve crop production of a cropping system in acid soil, Paper presented at the 4th RC Meeting, 16-20 Nopember 1998, Vienna, Austria.

[12] ZAPATA, F., Isotope techniques in soil fertility and plant nutrition studies. In: " Use of Nuclear Techniquesin Studies of Soil-Plant Relationships" (Ed. G. HARDARSON) IAEA (1990), 61-128.

[13] PARTOHARDJONO, S. and J. SRI ADININGSIH, Response of food crop to phosphate rocks, Indonesian Agriculture Research and Development Journal **13** (3 & 4), (1991) 45-67.

PHOSPHORUS AVAILABILITY IN AN ACID TROPICAL SOIL AMENDED WITH PHOSPHATE ROCKS

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Abstract

The fate of P from phosphate rocks applied to Malaysian soils has not been studied in detail. Since the plantation sector is the major consumer of phosphate rock (PR) in Malaysia, studies on the dissolution and agronomic effectiveness of PR are of great interest to the country. Thus a series of greenhouse and laboratory experiments involving conventional chemical extractants and ^{32}P isotopic techniques was carried out to evaluate the agronomic effectiveness of PR sources of different reactivity.

Phosphorus and other chemical properties of the soil and PRs studied were determined. The P solubility tests by 2% formic acid, 2% citric acid and neutral ammonium citrate gave positive correlation with P uptake by one-year old oil palm seedlings. Neutral ammonium citrate proved to be a better indicator of PR solubility and its correlation coefficient with P uptake improved by expressing citrate solubility as a percentage of the rock rather than as a percentage of total P_20_5 content.

The agronomic effectiveness of TSP and 6 PR sources was evaluated in glasshouse conditions with oil palm seedlings for one year-period. The percentage of PR dissolution varied greatly among PR sources. The PR dissolution was assessed by 0.5 M NaOH, Pi strip, L-value and 1 M ammonium citrate-dissolved Ca. Irrespective of the methods used, the more reactive PR such as North Carolina and Tunisia dissolved more P than the lower reactive sources such as Christmas Island and China PR. All the four methods used gave positive correlation with plant P uptake, with 0.5M NaOH being the best indirect method for determining PR dissolution. Less than 30% of the applied P was dissolved during the one-year period, with only about 15 to 40% of the dissolved P being taken up by the oil palm seedlings.

A laboratory ^{32}P isotopic exchange method was also carried out in this acid soil to assess the soil P status parameters. A low water soluble P concentration (Cp) was found for all PRs used. The ratio of the specific activity of ^{32}P remaining at one minute over initial radioactivity (r_1/R) was less than 0.2 in all sources of PR used, thus showing the very high P fixing capacity of this soil. This isotopic technique also demonstrated that PR from North Carolina and Tunisia were more readily available to plants than the less reactive PR from Jordan, Morocco, Christmas Island and China.

1. INTRODUCTION

Malaysian soils are deficient in available P due to very low orthophosphate ion concentrations in the soil solution. The abundance of variable charge colloids in these soils together with low pH and low CEC has led to the presence of high amounts of oxides and hydroxides of Fe and Al. The oxides and hydroxides fix large amounts of soluble P leading to low concentrations of available P in soil solution [1]. Thus, large amounts of phosphate fertilizers are required to attain high yields from crops. Phosphate rocks (PR) have been long used in Malaysian agriculture since 1930 when Gafsa PR from Tunisia was introduced. Around 1950, the use of Christmas Island PR became more prominent because of its closer proximity to Malaysia until 1987 when its production diminished. From this time on, more PR sources are being imported into the Malaysian fertilizer market. Phosphate rock has been popular because they are cheaper than the water-soluble P fertilizers. The agronomic effectiveness (AE) of these various PR sources, however, has never been evaluated in detail. This study was conducted to evaluate the AE of 6 sources of PR commonly found in Malaysia (North Carolina, Tunisia, Jordan, Morocco, Christmas Island and China) and triple superphosphate using oil palm seedlings. In addition a dissolution study of these PRs using 0.5M NaOH, 2% citric acid, 2% formic acid, 0.5M ammonium citrate, and ^{32}P isotopic techniques was carried out in the same Ultisol.

2. MATERIALS AND METHODS

A topsoil (0-30 cm) bulk sample of the Rengam series soil (Typic Paleudult) having the following physical and chemical properties was collected. The particle size distribution consisted of clay

(0-2 μm) at 47.2%, fine silt (2-20 μm) at 4.1%, course silt (20-50 μm) at 3.3%, fine sand (50-200 μm) at 11.1%, and course sand (200 – 2000 μm) at 34.3%. The soil had 2.51% organic matter, 1.46% organic carbon, 1.16% total N and a C:N ratio of 12.6. Its total P content was 80.5 mg kg^{-1}, Olsen-P of 3.45 mg kg^{-1} and Bray-2 P of 12.6 mg kg^{-1}. Its exchangeable Ca, Mg, K, Na, Mn, Al and H were 0.24, 0.17, 0.14, 0.03, 0.01, 1.24 and 0.15 cmol (+) kg^{-1} soil, respectively. The soil pH measured in water and 1M KCl solution in a 1:2.5 soil to solution ratio were 4.60 and 4.00, respectively. Fifteen kg of air-dried soil sieved through 2 mm sieve were weighed and placed in black polyethylene bags. Four sets of each treatment were harvested at 3, 6, 9 and 12 months after treatments. All the soil was labeled with 300 μCi ^{32}P solution containing 5 mg P as carrier using 3 L distilled water per bag. The first set that was harvested at 3 months was labeled at the beginning of the experiment. The second set was labeled at the third month and harvested at 6 months. The third set was labeled at the 6th month and harvested at 9 months. The fourth set was labeled at the 9th month and harvested at 12 months after planting. The treatments used were: control (^{32}P only), Triple superphosphate (TSP), and phosphate rocks from North Carolina, USA (NCPR), Gafsa from Tunisia (TPR), Jordan (JPR), Morocco (MPR), Christmas Island (CIPR) and China (CPR). The chemical and physical characteristics of the fertilizers tested are given in Table 1. A total of 4 g P kg^{-1} soil was added for each of the P sources tested and each treatment was replicated four times. Uniform 3 month-old Dura x Pesifera oil palm seedlings were planted into each of the pots. The initial P content of the oil palm seedlings was determined.

After each 3-month interval, the first set of palms were destructively sampled, oven-dried at 70°C, and weighed out. The dry weights were recorded, the tissues were cut into small pieces and the different plant parts were sub-sampled, incinerated at 450°C, and dissolved in 2M HCl solution. Phosphorus-32 activity in the samples were counted using Packard 2300 liquid scintillation counter and inorganic P present in the plant tissues were determined colorimetrically using the method of Scheel [2]. L values were calculated using the formula of Larsen [3] and P derived from the fertilizers by the plants (PdfF) was calculated using the isotope dilution formula described by Zapata and Axmann [4].

To determine P dissolution from PR with time , another complete set of soils was set up without ^{32}P addition and without planting palms. The soils were air-dried, ground to pass 2 mm sieve and P was extracted with 0.5M NaOH [5] and Pi-strip [6]. Calcium was extracted with 1 M ammonium acetate at pH 7.0. The parameters describing the P status of the original soil was determined according to the method described by Morel and Fardeau [7]. Measurements were made at 3,6,9 and 12 months after the start of the experiment.

The data collected were analyzed using analysis of variance (ANOVA) and the differences in the means were analyzed using the least significant difference (LSD) value. These statistical analyses were carried out using the SAS package [8].

3. RESULTS AND DISCUSSION

3.1. Chemical and mineralogical characteristics of phosphate rocks

The highest total P content was found in CPR and the lowest was in NCPR (Table I). However, total P content is not an indication of PR agronomic effectiveness [9]. The Ca concentration varied from 31% in NCPR to 33% in CPR. Heavy metals content (Zn, Mn, Pb, Cd, and Cu) ranged between 144-407 mg/kg for Zn, 21-505 mg/kg for Mn, 21-505 mg/kg for Pb, 3-54 mg/kg Cd and 15-56 mg/kg Cu. Besides the heavy metals, Al and Fe were present in substantial amounts in some PRs. The forms in which Fe and Al are present in PR (either bound to P or present as oxides) may play a significant role in the release of inorganic P from these rocks. Mineralogical properties have been identified using X-ray diffraction. In general, these PRs contain apatite as the primary mineral with quartz as the impurity mineral (Fig. 1).

The Ca:P ratio ranged from 1.29 for CIPR to 1.84 for TPR (Table I). It has been shown that when neutral ammonium citrate-soluble P (expressed as percentage of rock and as percentage of total P_2O_5) was plotted against the molar ratio of Ca:P of apatite in PR, the solubility of PR increased as the Ca:P ratio increased. The substitution of CO_3^{2-} for PO_4^{-3} in the apatite structure causes a decrease in unit cell a-axis that results in a decrease in crystalline size of apatite, thus increasing the chemical reactivity of apatite mineral [10]. The PR reactivity ranked according to Ca:P molar ratio was in the order of NCPR>TPR>JPR> MPR>CPR>CIPR (Table I).

3.2. Solubility characteristics of phosphate rocks

The magnitude of PR solubility in 2% citric acid and 2% formic acid and neutral ammonium citrate as percentage of rock and total P_2O_5 (Table II) showed that all PR can be ranked in the same order as the Ca:P molar ratio, i.e. NCPR > TPR > JPR > MPR > CIPR > CPR. Correlation coefficients of P extracted by these three methods to total P taken up by one-year old oil palm plants showed that neutral ammonium acetate gave the highest r^2 value as compared to 2% formic acid or 2% citric acid The r^2 also improved when the solubility of the PRs were expressed as percentage of the rock rather than total P_2O_5 content (Table IV).

3.3. Dissolution of PR in the soil

Phosphorus dissolution measured by the methods of Pi-strip, 0.5M NaOH, L-value method, and dissolved Ca method by leaching with 1 M NH_4OAc showed marked differences in the extent of dissolution of PR with time.

3.4. Availability of P from PR added to soil using E-value determination

The water-soluble P concentration (Cp) in untreated soil was 0.04 mg/L (Table V). This value increased with the addition of P fertilizers used. The highest increase was with the addition of TSP. The ratio of radioactivity remaining at 1 minute to the initial radioactivity (r_1/R) in PR treated soil was found to be < 0.2. This indicated the soil had a high P fixing capacity [11, 12]. The E1 values for each treatment were calculated using the equation $E1= 10Cp/(r_1/R)$. This is a good approximation of the quantity of free phosphate ions in a soil-solution system that is available to plants [11, 13]. The E1 value was highest in the soil amended with TPR and NCPR, while soil amended with MPR, JPR, CIPR and CPR showed lower E1 values indicating the low P availability in soil amended with P from these sources. The E1 values of soils at 3, 6, 9 and 12 months after PR addition were also found to follow the same pattern as the E1 values.

3.5. Oil palm dry matter yield and P uptake

The dry matter yield and total P yield of oil palm seedlings harvested at 3, 6, 9 and 12 months after planting showed great variability with the fertilizer treatments (Table VI). The P uptake in the first 3 months was almost similar among the PRs tested. The uptake increased with time for NCPR and TPR showing higher P uptake compared to CIPR and CPR. More than 80% of the total P in the plant was derived from the fertilizers added (Table VII), with TSP being the highest contributor of P towards plant P (> 96%). Triple superphosphate supplied the highest amount of P to the palms at 601 mg P for a 12 month-period of growth (Table VII). This corresponded to 15% of the total amount of P added at the beginning of the experiment. Among the PRs tested, NCPR had the highest PdfF at 208 mg P/palm followed by GPR at 160 mg/palm. The PRs, JPR, MPR and CIPR, had equivalent PdfF values, while CPR showed the lowest value of 101 mg P/palm. Fertilizer use efficiency of the PRs ranged between 5.21% for NCPR to 2.15% for CPR (data not shown).

3.6. Relationship between PR solubility to plant P uptake

The magnitude of PR solubility in formic acid, citric acid, and neutral ammonium citrate as a percent of rock has been shown by Chien [14] to be more appropriate since values expressed as percent of total P content may give misleading comparisons, especially for PRs with low total P content [15]. Correlation coefficients obtained when the three methods of PR solubility tests were compared to plant P uptake showed that neutral ammonium citrate gave the best r^2 value (Table IV).

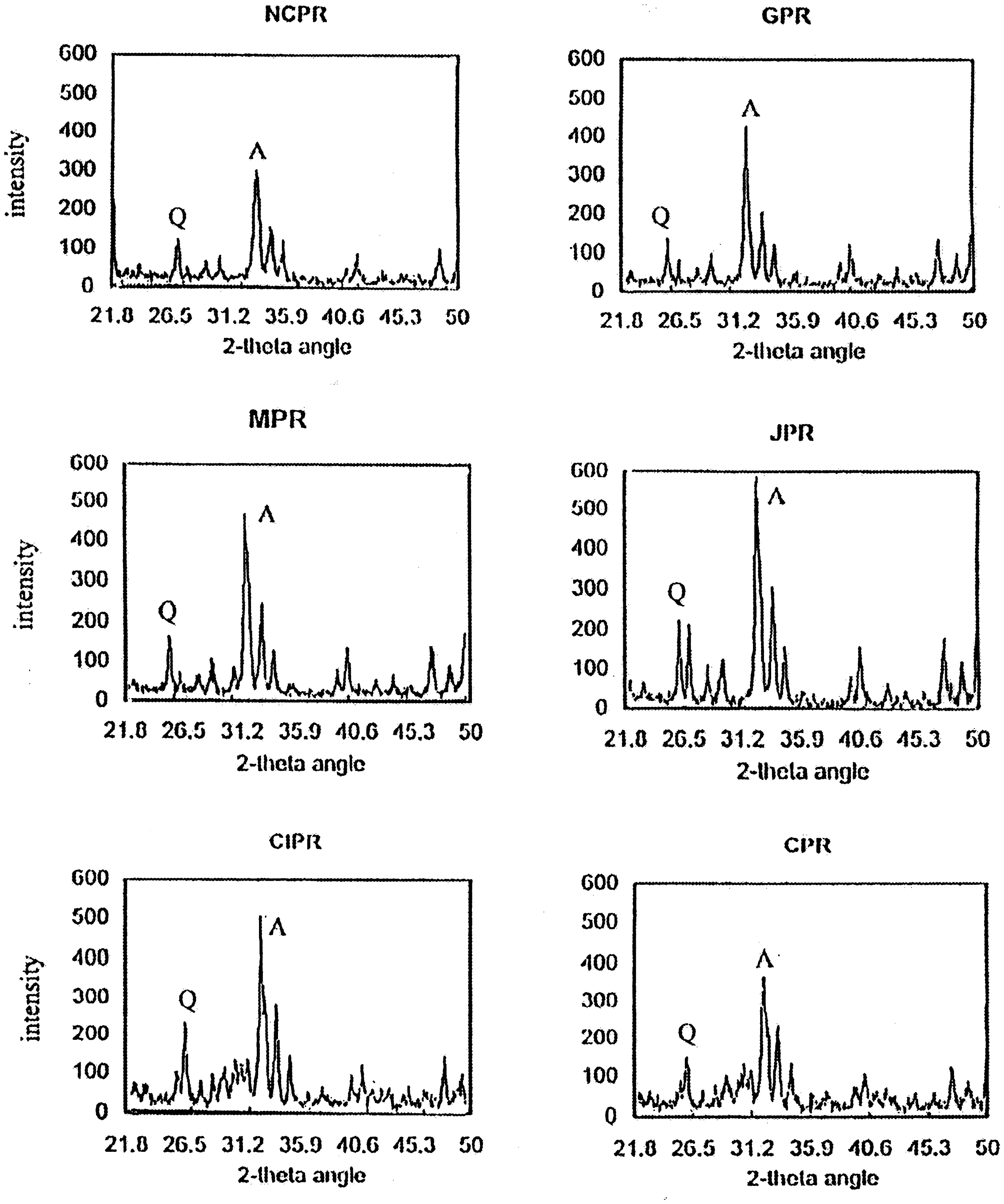
TABLE I. CHEMICAL CHARACTERISTICS OF PHOSPHATE FERTILIZERS TESTED

P Source	P (%)	Ca:P[1]	P_2O_5	Ca	CaO	Fe	Cd	Cu	Zn	Mn	Pb
			(mg kg^{-1})								
NCPR	13.1	1.83	30.1	31.0	43.4	4080	54	18	407	21	54
TPR	13.4	1.84	30.7	31.8	44.5	1560	35	15	358	36	55
JPR	14.1	1.79	32.3	32.6	45.6	1570	9	17	224	21	56
MPR	14.4	1.79	33.0	33.4	46.7	1640	23	40	309	38	55
CIPR	14.5	1.29	33.2	24.2	33.9	28700	5	56	407	443	70
CPR	14.7	1.54	33.7	29.2	40.9	9240	21	21	144	505	207
TSP	20.4	0.62	46.7	11.6	16.2	10380	3	18	379	99	213

[1] mole ratio.

TABLE II. SOLUBILITY OF PHOSPHATE FERTILIZERS TESTED

P Sources	Total P_2O_5	Formic Acid soluble P		Citric Acid soluble P		Neutral Ammonium Acetate soluble P	
		% of Rock	% of Total P_2O_5	% of Rock	% of Total P_2O_5	% of Rock	% of Total P_2O_5
NCPR	30.1	24.7	82.2	12.1	40.4	5.83	19.4
TPR	30.7	20.8	67.9	11.7	38.2	4.97	16.2
JPR	32.3	20.4	63.1	10.8	33.4	4.52	14.0
MPR	33.0	17.9	54.2	10.6	32.0	4.42	13.4
CIPR	33.2	11.6	34.9	9.3	28.0	3.59	10.8
CPR	33.7	8.0	23.8	7.5	22.3	2.73	8.1
TSP	46.7	43.3	92.6	41.9	89.7	40.3	86.2



Note: d spacing for apatite (A) - 0.269 nm
d spacing for quartz (Q) - 0.426 nm

Fig. 1. X-ray diffraction patterns of P rocks studied.

TABLE III. PHOSPHORUS AND Ca DISSOLVED FROM SOIL TREATED WITH P FERTILIZER SOURCES AND PLANTED WITH OIL PALM

		Dissolved P (mg/kg)			
Time	P sources	0.5M NaOH	Pi-strip	L-value	Dissolved Ca (mg/kg)
3 months	NCPR	406 b	246 b	890 b	634 c
	TPR	400 b	227 bc	689 c	926 a
	JPR	305 c	235 bc	578 d	607 c
	MPR	263 d	157 d	661 d	584 c
	CIPR	238 d	146 c	578 cd	303 d
	CPR	258 d	148 d	432 e	188 e
	TSP	3577 a	711 a	1177 a	686 b
	Control	37 e	24 e	40 f	56 f
6 months	NCPR	624 b	281 b	536 c	634 c
	TPR	525 bc	261 b	667 b	2353 a
	JPR	468 c	209 c	379 d	2326 a
	MPR	472 c	210 c	377 d	2010 b
	CIPR	305 d	135 e	302 d	740 d
	CPR	343 d	176 d	287 d	593 d
	TSP	3711 a	742 a	1442 a	1078 c
	Control	37 e	12 f	41 e	43 e
9 months	NCPR	767 b	385 b	1066 b	1955 b
	TPR	650 c	292 c	1074 b	2280 a
	JPR	327 e	220 d	714 c	1906 b
	MPR	462 d	209 d	733 c	1640 c
	CIPR	343 e	209 d	466 d	1046 d
	CPR	319 e	180 e	481 d	906 d
	TSP	3306 a	811 a	3565 a	1876 b
	Control	28 f	10 f	27 e	42 e
12 months	NCPR	858 b	404 b	1254 b	2113 ab
	TPR	632 c	368 b	975 c	2180 a
	JPR	338 d	280 cd	662 d	1953 c
	MPR	408 d	313 c	625 de	1460 d
	CIPR	294 d	255 d	417 f	1113 e
	CPR	291 d	180 e	506 ef	853 f
	TSP	3234 a	727 a	3155 a	1935 bc
	Control	27 e	4 f	20 g	41 g

Values in the same column for each time period that are followed by the same letters are not significantly different at P=0.05.

TABLE IV. CORRELATION COEFFICIENT (r^2 VALUES) OF SOLUBILITY TESTS WITH P UPTAKE BY OIL PALM SEEDLINGS GROWN FOR 12 MONTHS

	r^2 value	
Variable	% of Rock	% of Total P_2O_5
2% formic acid (% of rock)	0.88*	0.88*
2% citric acid (% of rock)	0.90*	0.88*
Neutral ammonium citrate (% of rock)	0.92**	0.91*

* significant at $P \leq 0.10$. ** significant at $P \leq 0.05$

TABLE V. ISOTOPICALLY EXCHANGEABLE P PARAMETERS OF THE SOIL WITH THE ADDITION OF 4 mg P/g OF SOIL

Parameters	Soil *Alone*	Soil + *NCPR*	Soil + *TPR*	Soil + *JPR*	Soil + *MPR*	Soil + *CIPR*	Soil + *CPR*	Soil + *TSP*
Cp (mg P/L)	0.04 e[1]	0.57 b	2.12 a	0.28 cd	0.41 bc	0.19 de	0.39 bc	165
E1 (1 min, mg/kg)	3.2 d	58 b	150 a	26 c	32 c	9.1 d	35 c	3840
Capacity factor (ml/g)	91 ab	101 a	70 c	90 ab	78 bc	48 d	86 abc	23
n	0.149	0.146	0.097	0.174	0.123	0.115	0.109	0.016
E-1 day (mg/kg)	10 d	161 b	281 a	85 c	77 c	18 d	75 c	2086
E-3 mths (mg/kg)	0.34 c	11 a	9.9 a	6.0 b	12 a	0.93 c	0.34 c	1583
E-6 mths (mg/kg)	0.12 d	23 a	17 b	14 bc	11 c	3.2 d	3.2 d	1732
E- 9 mths (mg/kg)	0.5 c	46 b	91 a	43 b	34 b	6.7 c	6.0 c	614
Pool A (mg/kg)	9.6 d	160 b	279 a	84 c	76 c	18 d	75 c	1920
Pool B (mg/kg)	7.3 d	138 a	137 a	96 b	55 c	12 d	46 c	73
Pool C (mg/kg)	3 d	61 a	53 ab	46 b	24 c	5.3 d	19 c	22
Pool D (mg/kg)	63 e	3724 c	3610 d	3855 b	3927 b	4046 a	3942 b	1901
%Pdff (1-day)	0	86.2 b	93.5 a	68.6 c	76.1 c	17 d	75 c	99.8
%Pdff (3-months)	0	89.9 a	91.5 a	83.9 ab	77.9 b	18 d	73 c	98.7
%Pdff (6-months)	0	90.2 a	91.4 a	84.7 b	78.3 b	19 d	73 c	98.6
%Pdff (9-months)	0	90.7 a	91.7 a	85.7 b	79.3 bc	23 d	74 c	98.6
%Pdff (12-months)	0	90.4 a	91.4 a	85.5 b	78.7 bc	20 d	73 c	98.5

[1] Means in a row followed by the same letters are not significantly different at P=0.05.

TABLE VI. DRY MATTER YIELD (DMY) AND TOTAL P (TP) OF OIL PALM SEEDLINGS ACCUMULATED DURING 0-3, 3-6, 6-9 AND 9-12 MONTHS OF GROWTH

P sources	0-3 months		3-6 months		6-9 months		9-12 months		Total	
	DMY	TP	DMY	TP	DMY	TP	DMY	TP	DMY	TP
TSP	2.0	31.6	19.6	159	17.9	209	31.6	214	71.1	614
NCPR	2.6	13.0	19.1	56	9.6	21.4	40.8	128	72.1	218
TPR	2.1	10.3	18.9	58	11.1	13.0	38.4	81.9	70.5	163
JPR	2.3	11.0	18.1	51	14.1	21.1	30.9	87.4	65.4	179
MPR	1.6	10.0	21.5	59	10.9	3.3	29.0	91.8	63.0	177
CIPR	1.0	6.6	21.3	62	14.2	3.5	31.1	95.1	67.5	177
CPR	1.4	7.1	19.9	44	13.0	1.7	21.3	54.8	55.8	106
LSD P=0.05	1.8	4.7	10.7	28	12.8	45.0	10.3	45.2	-	-
	n.s	*	n.s	**	n.s	**	**	**	-	-

TABLE VII. P DERIVED FROM FERTILIZERS (PERCENTAGE AND mg/PLANT) IN OIL PALM SEEDLINGS AT DIFFERENT TIMES OF HARVEST

	----------------- PdfF (%) --------------------				---------------------- PdfF (mg/plant) ------------------------				
P sources	3 months	6 months	9 months	12 months	3 months	6 months	9 months	12 months	Total
TSP	94.8	96.1	98.7	99.0	30.0	153.4	206.0	211.9	601
NCPR	93.1	89.2	96.3	98.2	12.1	50.5	20.6	125.8	209
GPR	92.3	87.7	96.4	97.4	9.5	50.4	12.6	79.8	152
JPR	93.1	86.6	95.6	96.9	10.2	43.9	20.5	84.8	168
MPR	91.2	84.8	94.4	96.3	9.1	50.1	3.7	88.4	163
CIPR	91.9	83.8	92.3	93.7	6.1	51.7	3.1	89.3	159
CPR	89.4	81.2	88.6	95.5	6.3	35.2	2.0	52.4	101
LSD	25.0	35.0	16.7	16.5	4.6	24.6	42.0	43.8	36
P=0.05	n.s	n.s	n.s	n.s	**	**	**	**	**

4. CONCLUSIONS

Chemical and mineralogical properties played an important role in the solubility and dissolution of PR. The extractant used for measuring PR dissolution tends to remove some of the undissolved PR during the extraction process. The extent of this ‘induced dissolution” depends on the nature of the extractant and PR. The use of 0.5 N NaOH was found to be a better extractant for determining the extent of PR dissolution in soil while neutral ammonium citrate was the better extractant for determining the solubility of PRs. However, irrespective of the chemical extractants used, PR dissolution in the soil was higher for PR from North Carolina and Tunisia compared to the sources from China and Christmas Island. The dissolution of PR from Morocco and Jordan was in the intermediate range.

The ^{32}P isotopic exchange technique could be applied to determine and explain the immediate and residual effectiveness of various sources of PR. This technique gave the most complete analysis of soil P status, in particular available P, and provided information on the P dissolution and retention from PR sources. In this study P applied as NCPR and TPR was more readily available than JPR, MPR, CIPR and CPR. This method can be also used to predict the %PdfF value and the RAE of any P fertilizer added at a given rate in a given time. This method has an advantage over the chemical extractant methods because it does not disturb the soil components.

The E-value or L-values obtained from the isotopic technique showed that NCPR and TPR showed the highest P utilization as compared to all the other PRs from Morocco, Jordan, Christmas Island and China.

The effectiveness of these P sources used for oil palm seedlings can be ranked as follows: NCPR>GPR>JPR>MPR>CIPR>CPR. This ranking is similar to the ranking made from the solubility of these PRs in 2% formic acid, 2% citric acid or neutral ammonium citrate expressed as a percentage of the rock. Correlation coefficients obtained when these three solubility tests were compared with plant P uptake showed that ammonium citrate correlated best to plant P uptake when compared with the formic and citric acid extractants.

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REFERENCES

[1] OWEN, G., Determination of available nutrients in Malayan soils, J Rub Res Inst Malaya **14** (1953) 109-120.

[2] SCHEEL, K.C., Calorimetric determination of phosphoric acid in fertilizers with the Pulfrich photometer, Zeitschrift fur Analytische Chemie **105** (1936) 256-269.

[3] LARSEN, S., The use of ^{32}P in studies on the uptake of phosphorus by plant, Plant and Soil **4** (1952) 1-10.

[4] ZAPATA, F., AXMANN, H., ^{32}P isotopic techniques for evaluating the agronomic effectiveness of rock phosphate materials, Fert. Res. **41** (1995) 189-195.

[5] MACKAY, A.D., SYERS, J.K., TILLMAN, R.W., GREGG, P.E.H., A simple method to describe the dissolution of phosphate rock in soil, Soil Sci. Soc. Am. J. **50** (1986) 291-296.

[6] MENON, R.G., CHIEN, S.H., HAMMOND L.L., HENAO, J., Modified technique for preparing paper strips for the new Pi soil test for phosphorus, Fert. Res. **19** (1989) 85-91.

[7] MOREL, C., FARDEAU, J.C., Phosphorus bioavailability of fertilizers: A predictive laboratory method for its evaluation, Fert. Res. **28** (1991) 1-9.

[8] SAS, SAS User’s Guide: Statistics (5th ed.) SAS Institute, North Carolina, USA (1985).

[9] CHIEN, S.H., Chemical, mineralogical and solubility characteristics of phosphate rocks for direct application. In: Dahanayake K et al (eds) Proc Inter Workshop on Direct Application of Phosphate Rock and Appropriate Technology Fertilizers in Asia: What Hinders Acceptance

and Growth, pp 49-58 Inst Fundamental Studies, Sri Lanka and Inter Fert Devt Centre, Muscle Shoal, Alabama, USA (1995).

[10] LEHR, J.R., MCCLELLAN, G.H., A revised reactivity scale for evaluating PR for direct application. Bull Y-43, TVA National Fertilizer Development, Muscle Shoals, Alabama, USA (1972).

[11] TRAN, S.T., FARDEAU, J.C., GIROX, M., Effect of soil properties on plant-available phosphorus determined by isotopic dilution phosphorus-32 method, Soil Sci. Soc. Am. J. **52** (1988) 1383-1390.

[12] MOREL, C., FARDEAU, J.C., Native soil and fresh fertilizer phosphorus uptake as affected by rate of application and P fertilizers, Plant and Soil **115** (1989) 123-128.

[13] SALCEDO, I.H., BERTINO, F., SAMPAIO, E.V.S.B., Reactivity of phosphorus in Northeastern Brazilian soils assessed by isotopic dilution, Soil Sci. Soc. Am. J. **55** (1991) 140-145.

[14] CHIEN, S.H., MENON, R.G., Factors affecting the agronomic effectiveness of phosphate rock for direct application, Fert. Res. **41** (1995) 227-234.

[15] CHIEN, S.H., HAMMOND, L.L., A comparison of various laboratory methods for predicting the agronomic potential of phosphate rocks for direct application, Soil Sci. Soc. Am. J. **42** (1978) 935-939.

THE AUSTRALIAN NATIONAL REACTIVE PHOSPHATE ROCK PROJECT — AIMS, EXPERIMENTAL APPROACH, AND SITE CHARACTERISTICS

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Abstract

Field-based cutting trials were established across Australia in a range of environments to evaluate the agronomic effectiveness of 5 phosphate rocks, and 1 partially acidulated phosphate rock, relative to either single superphosphate or triple superphosphate. The phosphate rocks differed in reactivity, as determined by the degree of carbonate substitution for phosphate in the apatite structure and solubility of phosphorus present in the fertilizers in 2% formic acid, 2% citric acid and neutral ammonium citrate. Sechura (Bayovar) and North Carolina phosphate rocks were highly reactive (>70% solubility in 2% formic acid), whilst Khouribja (Moroccan) and Hamrawein (Egypt) phosphate rock were moderately reactive. Duchess phosphate rock from Queensland was relatively unreactive (< 45% solubility in 2% formic acid). The partially acidulated phosphate rock was made by 50% acidulation of North Carolina phosphate rock with sulfuric acid. Phosphate rock effectiveness was assessed by measuring pasture production over a range of phosphorus levels, and by monitoring the bicarbonate-soluble phosphorus extracted from soil samples collected prior to the start of each growing season. Other treatments included single large applications of triple superphosphate, partially acidulated phosphate rock and North Carolina phosphate rock applied at 2 rates, and the application of monocalcium phosphate and North Carolina phosphate rock sources without sulfur to evaluate the importance of sulfur in the potential use of phosphate rock fertilizers.

A broad range of environments was represented over the 30 sites, which were based on pastures using annual and/or perennial legumes and perennial grasses. Rainfall across the network of sites ranged from 560 to 4320 mm, soil pH-$CaCl_2$, from 4.0 to 5.1, and Colwell extractable phosphorus ranged from 3 to 47 µg/g prior to fertilizer application. Two core experiments were established at each site. The first measured the effects of phosphate rock reactivity on agronomic effectiveness, while the second core experiment measured the effects of the degree of water solubility of the phosphorus source on agronomic effectiveness.

The National Reactive Phosphate Rock Project trials provided the opportunity to confirm the suitability of accepted procedures to model fertilizer response and to develop new approaches for comparing different fertilizer responses. The Project also provided the framework for subsidiary studies such as the effect of fertilizer source on soil phosphorus extractability; cadmium and fluorine concentrations in herbage; evaluation of soil phosphorus tests; and the influence of particle size on phosphate rock effectiveness. The National Reactive Phosphate Rock Project presents a valuable model for a large, Australia-wide, collaborative team approach to an important agricultural issue. The use of standard and consistent experimental methodologies at every site ensured that maximum benefit was obtained from data generated. The aims, rationale and methods used for the experiments across the network are presented and discussed.

1. INTRODUCTION

Briefly, the aims of the National Reactive Phosphate Rock (RPR) Program were:

1. to determine those soil, climate and pasture conditions under which RPR products are effective substitutes for water soluble P sources e.g. single superphosphate (SSP), on pastures [1, 2];
2. to determine what the required level of PR reactivity would be for RPRs to be effective in different pasture environments [3-5];
3. to develop a decision-support system to identify pasture environments where RPRs or derived products would be cost-effective substitutes for SSP [6];
4. to determine the role of sulfur (S) in the viability of RPR use [7].

This paper has been modified from the original article “The national reactive phosphate rock project — aims, experimental approach, and site characteristics” by Simpson, P.G., Sale, P.W.G., Hepworth, G., Gilbert, M., Blair, G.J., Garden, D., Dann, P.R., Hamilton, L., Stewart, J., Hunter, J., Cayley, J., Ward, G., Johnson, D., Lewis, D., Fleming, N., Bolland, M.D.A., Gilkes, R.J., and McLaughlin, M.J. published in Aust. J. Expt. Agric. **37** (1997) 885-904 by permission of CSIRO Publishing.

In addition to these aims, other aspects of the use of RPRs and derived products were also investigated. The other aspects included a comparison of application strategies (annual vs capital) for WSP and RPR fertilizers [8], changes in the effectiveness of RPR during the growing season [9]; the effect of PR on soil pH [10]; the effect of RPR products on soil P concentrations [11]; the effect of fertilizer type on cadmium and fluorine concentrations in clover herbage [12]; a comparison of the range of soil P tests for situations where RPR products are used [13]; identification of pasture environments potentially suitable for RPR use through the use of GIS technology [14]; and the economic analysis of the field performance of North Carolina RPR compared with single superphosphate [15].

2. MATERIALS AND METHODS

2.1. Sites

Thirty sites were established (Fig. 1 and Table I) over a wide range of soil/pasture/ climate environments in 6 States across Australia - Queensland, New South Wales (NSW), Victoria, Tasmania, South Australia and Western Australia.

Sites were selected to cover regions that were representative of the major permanent pasture zones in each State where phosphatic fertilizers were regularly applied to pasture. Within regions, sites were situated on the common soil types, which were acidic (pH-$CaCl_2 < 5.5$). Soil profiles at each site were described according to the Australian Soil and Land Survey Field Handbook, and are described in detail by Simpson et al. [16].

Sites were located on a wide range of soils and covered a wide range of environments. Long-term average annual rainfall varied between 560 mm at Jericho in central Tasmania, to 4320 mm at Tully in northern Queensland. Soil pH-$CaCl_2$ (0-10 cm) ranged from 4.0 on the southern tablelands of NSW, up to 5.1 on the Atherton Tablelands in northern Queensland. All sites had an acidic surface layer although some showed a trend in increasing pH with depth. Initial soil P concentrations (0-10 cm) prior to the application of any fertilizer treatments ranged from 3 µg/g Colwell P at Mackay in Queensland to 47 µg/g at Malanda in far northern Queensland indicating that some sites would be more P responsive than others (Table II). Sites were located where there was an adequate legume content in existing pasture, or in some cases oversown with high rates of seed to ensure that an adequate legume component was achieved. Major pasture species present at each site are detailed in Simpson *et al.* [16].

2.2. Fertilizers

Fertilizer treatments used in the National RPR Project trials were chosen to address two basic areas of concern. First, the question of how soluble the P source needs to be in order to be agronomically effective under particular soil, climatic and pasture conditions, and secondly how reactive does the PR need to be in order to be agronomically effective. Both these questions were addressed by comparing PRs with water-soluble P (WSP) sources.

Five apatite PRs covering a range of reactivity (degree of carbonate substitution) were chosen for the comparisons and included Sechura PR (Bayovar, S PR), North Carolina PR (USA, NC PR), Hamrawein PR (Egypt, E PR), Khouribja PR (Morocco, M PR), and Duchess PR (Queensland, D PR). A partially acidulated PR (PAPR) made by 50% acidulation of North Carolina PR with sulfuric acid was also used. Two WSP sources used were single superphosphate (SSP), and triple superphosphate (TSP). Total P content, origin, and solubility in 2% citric acid, 2% formic acid, and neutral ammonium citrate of WSP, PAPR and PR fertilizers are presented in Table III. Major and minor elements present in each fertilizer (analyzed by XRF fusion technique) are shown in Table IV and V, respectively. XRD analysis of the apatite PRs showed that all of the PRs contained moderate levels of quartz and traces of illite were contained in the Sechura and Duchess PRs. Khouribja PR and Hamrawein PR both contained trace and moderate levels of dolomite, respectively. Duchess PR also contained trace levels of kaolinite and calcite.

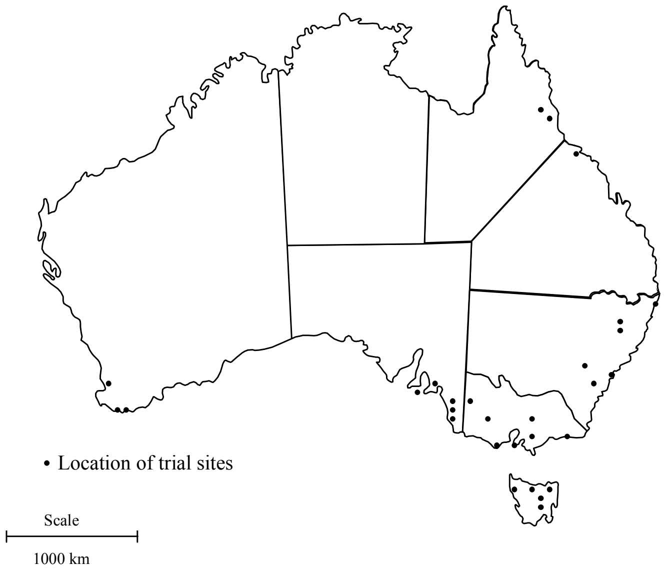

Fig. 1. Location of trial sites for National Reactive Phosphate Rock project (reproduced with permission of CSIRO Publishing [16]).

2.3. Treatments and experimental designs

Two core experiments were established at each trial site. Core Experiment 1 (CE1) was designed to examine the issue of PR reactivity, while Core Experiment 2 (CE2) was designed to address the issue of water solubility of the P source. All trials were field-based small plot experiments. Plot size was 3 x 5 m, except for Tasmania, which used a 2 x 2 m plot size.

2.3.1. Core experiment 1

In Core Experiment 1 (CE1), the treatments consisted of a nil P treatment (control), 5 PRs and SSP applied annually at 3 levels of P i.e. 2X, 4X, and 8X kg/ha (see below for explanation of 'X') replicated 4 times. The 5 PRs were, Sechura PR (Bayover in Peru), North Carolina PR (USA), Hamrawein PR (Egypt), Khouribja PR (Morocco), and Duchess PR (Queensland). In addition, North Carolina PR and monocalcium phosphate (MCP) were applied once only at a single P level (4X or 8X in the case of the Qld. sites) without S to evaluate the role of S in the use of RPR fertilizers. The phosphate rock (PR) fertilizers used in CE1 were selected to cover a range of PR reactivity (Table III).

2.3.2. Core experiment 2

Core Experiment 2 (CE2) consisted of a nil P treatment, TSP, PAPR and North Carolina PR. These P sources were applied (i) at 2 levels of P (8X and 16X) once only at the start of the experiment in 1992 to examine the response to capital applications of P, and (ii) at 5 P rates (X, 1.5X, 2X, 4X, 8X) annually for TSP and PAPR and at 6 P rates (X, 1.5X, 2X, 4X, 8X and 16X) annually for North Carolina PR. All treatments were replicated 3 times except at sites N7 and N8 where 4 replicates were used. North Carolina PR was used in CE2 because it was a highly reactive PR and has been used widely in other research.

2.3.3. Determining the P rate of application (X)

The P levels (kg/ha) used in the National RPR Project trials varied from site to site and were based on the anticipated response to applied P at each site. The levels of fertilizer required were estimated in each region by experienced research agronomists and extension staff.

TABLE I. LOCATION AND ENTERPRISE DETAILS OF SITES USED IN THE NATIONAL RPR PROJECT (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

Site ID	Region	Area	Pasture species	Regional enterprises	Annual P rate used (kg/ha)
Q1	Nth Qld	Malanda	*Brachiaria decumbens.*	Dairy/beef	10.0
Q2	Nth Qld	Tully	*Brachiaria decumbens.*	Beef	7.5
Q3	Central Nth Qld	Mackay	*Aeschynomene americana.*	Beef	5.0
N4	NSW Nth Tbls.	Armidale	*T. repens*, *T subterraneum*, *Festuca arundinacea.*	Sheep/beef/ dairy	10.0/2.5[1]
N5	NSW north coast	Grafton	*T. repens*, *T subterraneum*, *Lotononis* spp.	Beef/dairy	10.0/5.0[1]
N6	NSW Nth Tbls.	Armidale	*T. repens*, *T subterraneum*, *Festuca arundinacea*	Sheep/beef	10.0/2.5[1]
N7	NSW Sth Tbls	Yass	*T. subterraneum*	Sheep	7.5
N8	NSW Sth Tbls	Tarago	*T. subterraneum*	Sheep/beef	7.5
N9	NSW Sth coast	Berry	*T. repens*, *Axonopus*, *Pennisetum clandestinum, Paspalum* spp.	Dairy	10.0
V10	Vic E Gippsland	Bairnsdale	*Dactyls glomerata, T subterraneum*	Sheep/wool	10.0
V11	Vic W Gippsland	Ellinbank	*T. repens*, *Dactyls glomerata*, *Lolium perenne.*	Dairy	9.0
V12	Vic Nth-east	Benalla	*T. subterraneum*, *Holcus spp.*	Sheep/beef	8.0
V13	Vic Sth west	Warrnambool	*T. repens*, *T subterraneum*, *Lolium perenne.*	Dairy	7.5/5.0[1]
V14	Vic west	Edenhope	*T. subterraneum*, *Lolium perenne*, *Phalaris aquatica.*	Sheep	10.0
V15	Vic west	Hamilton	*T. subterraneum*, *Lolium perenne*, *Phalaris aquatica.*	Wool/beef	10.0
V29	Vic Sth	Frankston	*T. repens*, *T subterraneum*, *Lolium perenne*, *Festuca arundinacea.*	Beef/sheep	10.0
T16	Tasa Nth W	Smithton	*T. repens* , *T subterraneum*, *T. fragiferum*, *Lolium perenne*, *Festuca arundinacea.*	Beef/dairy	8.5
T17	Tas Central	Jericho	*T. repens* , *T subterranuem*, *Lolium perenne*, *Dactyls glomerata*, *Festuca arundinacea.*	Wool	2.9
T18	Tas Nth east	Gladstone	*T. subterranuem*, *Lolium perenne*, *Holcus spp.*	Sheep/beef/ dairy	2.9
T19	Tas Cent'l Nth	Elliot	*T. repens*, *Lolium perenne*, *Dactylis glomerata.*	Dairy	5.7
T20	Tas Nth	Cressy	*T. repens*, *T. subterraneum*, *Lolium perenne.*	Sheep	5.7
S21	SA Sth east	Willalooka	*T. subterraneum.*	Beef/dairy	7.5
S22	SA Sth east	Wattle Range	*T. subterraneum.*	Lambs/wool/ beef/dairy	7.5
S23	SA Sth east	Nangwarry	*T. subterraneum.*	Beef/lambs/ dairy	7.5
S24	SA south	Mt Jaggard	*T. subterraneum*cv, *Dactyls glomerata*, *Phalaris aquatica.*	Dairy/lambs/ wool	5.0
S25	SA south	Kangaroo Isl	*T. subterraneum*cv, *Lolium perenne.*	Lambs/wool	5.0
W26	Sth-W WA	Busselton	*T. subterraneum.*	Wool/beef/ dairy	5.0
W27	Sth-W WA	Karridale	*T. subterraneum.*	Beef/lambs/ wool/dairy	7.5
W28	Sth-W WA	Karridale	*T. subterraneum.*	Beef/lambs /wool/dairy	2.5
W30	Sth-W WA	Nornalup	*T. subterraneum.*	Beef/lambs/ wool	10.0

[1] Indicates that this rate was used in the second and subsequent years as it was considered that the initial rate was too high.

TABLE II. SOIL P, K, ELECTRICAL CONDUCTIVITY (EC), pH (WATER AND $CaCl_2$), ORGANIC CARBON AND REACTIVE IRON (Fe) FOR 0-10 CM SOIL LAYER AT SITES USED IN THE NATIONAL RPR PROJECT PRIOR TO FERTILIZER APPLICATION (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

SITE ID	Average Rainfall	Soil type[1]	P	K	E.C.	pH	pH	Organic carbon	Fe
	(mm)		(ppm)	(ppm)	(ds/m)	(H_2O)	($CaCl_2$)	%	(ppm)
Q1	1690	Gn 3.11	47	256.9	0.110	6.07	5.06	3.68	2622
Q2	4321	Gn 2.11	5	36.4	0.045	5.56	4.33	1.80	687
Q3	1474	Dy 3.43	3	48.3	0.090	5.50	4.56	1.03	725
N4	760		14	124.1	0.069	5.74	4.56	2.30	1017
N5	882		22	81.9	0.063	5.51	4.38	1.68	777
N6	760		19	232.1	0.063	5.86	4.79	3.41	1637
N7	664	Dr 2.21	10	120.9	0.059	5.02	4.67	1.60	1489
N8	700	Dy 3.42	10	109.9	0.102	4.87	4.00	2.13	1087
N9	1500		27	140.2	0.065	6.00	5.00	2.00	1812
V10	650	Dy 3.42	11	64.0	0.065	5.70	4.41	2.42	878
V11	1100	Gn 4.11	41	222.4	0.080	5.42	4.54	4.06	6037
V12	800	Db 2.31	18	221.4	0.074	5.00	4.03	3.53	1336
V13	900	Dy 3.21	17	109.4	0.078	5.20	4.17	3.66	431
V14	550	Dy 3.42	20	151.3	0.071	5.52	4.50	1.97	1340
V15	710	Dy 3.21	15	110.7	0.084	5.64	4.68	3.88	4941
V29	787		33	210.0	0.080	6.12	4.91	1.34	289
T16	1100	Uc 4.24	7	80	0.093	5.10	4.06	3.84	234
T17	560	Dy 5.11	19	248	0.157	5.42	4.60	2.74	1565
T18	750	Dy 5.41	21	82	0.095	5.41	4.33	3.92	1076
T19	1200	Gn 4.11	36	236	0.093	5.58	4.72	5.13	3217
T20	640	Uc 5.11	46	231	0.038	5.46	4.35	1.16	746
S21	1650	Dy 5.21	8	66	0.079	5.81	4.65	1.27	167
S22	600	Dy 5.21	11	57	0.093	5.23	4.16	2.05	162
S23	600	Dy 5.21	15	107	0.086	5.56	4.44	2.03	249
S24	750	Dy 3.41	11	244	0.090	5.67	4.61	3.27	601
S25	600	Dy 3.41	12	462	0.099	6.11	4.99	3.08	2261
W26	855		7	128	0.208	5.44	4.33	2.41	995
W27	1000		17	80	0.068	5.75	4.70	2.22	811
W28	1000		7	121	0.147	5.50	4.39	3.12	133
W30	1392		8.5	134	0.197	5.30	4.30	-	-

[1] Northcote (1966) classification.

TABLE III. SOURCE, TOTAL P CONTENT, TYPE AND REACTIVITY OF FERTILIZERS USED IN THE NATIONAL RPR PROJECT (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

Fertilizer	Source	Total P (%)	Type[1]	Reactivity[2]	Solubility in 2% citric acid[3] (1st extraction)	Solubility in 2% formic acid[4] (1st extraction)	Solubility in neutral ammonium citrate[5] (2nd extraction)
					% of total P		
Single superphosphate (SSP)	N/A	9.5	Sol	Extremely high	87	105	59
Triple super phosphate (TSP)	N/A	20.2	Sol	Extremely high	99	93	58
Partly acidulated phosphate Rock –North Carolina (PAPR)	N/A	9.7	Partly Sol	Very high	68	71	33
Mo no calcium phosphate 'Aerophos'	N/A	24.0	Sol	Extremely high			
Sechura PR	Peru	12.9	RPR	high	40	70	9
North Carolina PR	USA	12.7	RPR	mod. High	36	74	8
Egyptian PR	Egypt	12.7	RPR	mod.	31	49	8
Moroccan (Khouribja) PR	Morocco	14.2	RPR	low - mod.	28	56	7
Duchess PR	Queensland	10.5	PR	low	30	45	5

[1] Sol = soluble; the fertilizer is a primarily water soluble source of P. RPR = reactive phosphate rock; indicates the rock has undergone some degree of carbonate substitution and will tend to dissolve in acid soil conditions. PR = a phosphate rock that has undergone little carbonate substitution and will be only slightly soluble in acid soil conditions.

[2] Reactivity here refers to the degree (% of total P) to which the PR dissolves in a 2% formic acid solution; N/A = not applicable.

[3] Analyzed using procedure of the Association of Official Analytical chemists (1960) [17].

[4] Analyzed using procedure of Hoffman and Mager (1953) [18].

[5] Analyzed using procedure of Association of Official Analytical chemists (1990) [19].

TABLE IV. MAJOR MINERAL COMPOSITION OF FERTILIZERS USED IN THE NATIONAL RPR PROJECT (XRF — FUSION TECHNIQUE) (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

	Al_2O_3 (%)	SiO_3 (%)	TiO_2 (%)	Fe_2O_3 (%)	MnO (%)	CaO (%)	K_2O (%)	MgO (%)	P_2O_5 (%)	SO_3 (%)	Na_2O (%)	LOI (%)
SSP	1.0	2.1	0.2	0.6	0.0	33.8	0.1	0.2	22.9	33.2	0.4	30.3
TSP	1.6	2.4	0.2	2.0	0.1	21.6	0.3	0.7	49.4	4.2	0.6	18.7
PAPR	0.5	3.9	0.1	0.6	0.0	38.8	0.5	0.4	24.8	20.3	0.8	21.5
S PR	1.6	8.0	0.1	0.5	0.0	46.2	0.3	0.4	29.8	3.1	1.8	6.6
NC PR	0.5	3.5	0.2	0.8	0.0	48.6	0.2	0.5	29.6	2.9	1.1	9.7
E PR	0.5	4.4	0.0	0.9	0.1	47.5	0.1	2.2	28.7	2.2	1.3	9.5
M PR	0.5	2.0	0.1	0.2	0.0	52.5	0.1	0.3	32.7	1.8	1.0	6.3
D PR	6.5	27.2	0.3	2.1	0.1	33.1	0.7	0.8	22.8	0.4	0.6	5.4
Detection	0.05	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.10	0.01	0.05	0.01

SSP = Single Superphosphate
TSP = Triple
PAPR = Partially Acidulated Phosphate Rock
Superphosphate S PR = Sechura Rock Phosphate

NC PR = North Carolina Rock Phosphate
E PR = Egyptian Rock Phosphate
M PR = Moroccan Rock Phosphate
D PR = Duchess Rock Phosphate

TABLE V. MINOR ELEMENT CONTENT OF FERTILIZERS USED IN THE NATIONAL RPR PROJECT (XRF — FUSION TECHNIQUE) (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

	Element												
	V (ppm)	Cr (ppm)	Mn (ppm)	Fe (%)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Cd (ppm)	Hg (ppm)	Pb (ppm)	Bi (ppm)
SSP	39	47	123	0.5	5	16	<5	188	6	15.1	0.09	7.35	<0.1
TSP	120	83	364	1.4	6	22	<5	371	9	4.08	0.054	13.9	<0.1
PAPR	21	114	79	0.7	<5	22	13	319	10	32	2.36	3.77	<0.1
S PR	53	130	77	0.3	<5	15	<5	47	23	34.7	0.018	8.14	<0.1
NC PR	23	169	48	0.5	<5	28	<5	381	13	40.3	0.071	3.6	<0.1
E PR	71	78	322	0.6	5	32	<5	163	7	5.32	0.036	7.91	<0.1
M PR	157	188	<15	0.2	<5	41	16	258	14	11.4	0.036	1.99	<0.1
D PR	94	67	829	1.4	18	36	98	301	7	1.38	0.036	41.4	0.2
Detection	2	10	15	0	5	10	5	5	1	0.1	0.005	1	0.1

SSP = Single Superphosphate
TSP = Triple
PAPR = Partially Acidulated Phosphate Rock
Superphosphate S PR = Sechura Rock Phosphate

NC PR = North Carolina Rock Phosphate
E PR = Egyptian Rock Phosphate
M PR = Moroccan Rock Phosphate
D PR = Duchess Rock Phosphate

Their estimates of P requirements were based on previous fertilizer field trials and regional experience. The X rate was based on the premise that 4X should achieve 90% of maximum yield response to WSP fertilizer under optimum conditions, for a pasture with a satisfactory legume component. It was envisaged that determining X in this way would result in a series of data points occurring on the rising portion of a P response curve. This outcome would enable the P response for different products to be accurately defined. All fertilizer treatment and rate combinations are shown in Table VI.

2.3.4. Experimental design

A randomized complete block design was used for both core experiments at all sites except those located in Victoria, where the two core experiments were combined into one larger trial. An incomplete block design, including treatments from both core experiments plus 6 no P treatments, was used at the Victorian sites. Because of the small overlap (North Carolina PR 2X, 4X, 6X, and control), the total number of treatments used in Victoria was 40.

The complete block designs at sites other than in Victoria meant that blocks consisted of 21 or 24 plots for CE1 and CE2, respectively. In Victoria, blocks consisted of between 6 and 12 plots, depending on site heterogeneity. For the incomplete block design, treatments were allocated to plots so that comparisons between any pair of treatments had as much precision as possible. The allocation was performed using "DESIGNER", a statistical package developed by Agriculture Victoria for trials with unequal replication of treatments and/or unequal sized blocks. Incomplete block designs can produce considerable gains in precision when estimating treatment effects [20]. The disadvantages of such designs were recognized: there were treatment effects that could not be estimated by simple calculation, and remote site operators could have difficulty in analyzing the results without biometrical assistance. Gains in precision have almost certainly been made but inconvenience did occur. The mixing of the two core experiments at the Victorian sites made sorting, separation and collation of samples and results tedious and time consuming, and simple treatment comparisons were more difficult to obtain compared with the comparisons from a randomized complete block design.

2.3.5. Management of experimental sites

The P fertilizers were applied to the soil surface close to the start of the growing season in each year (around October for Queensland sites and April to May at other sites). Basal nutrients were applied to eliminate other nutrient deficiencies apart from P. At sites where nutrient leaching was anticipated, K and S were applied as a split application at the break of season and again at the height of the growing season (August to September at sites in southern Australia). The frequency and rates of application and forms of basal nutrients are shown in Table VII. Basal S dressings were not applied to the minus-S treatments. The experiments were not grazed.

At sites N7, N8, V12, S22, S23, S25, W26, W27, W28, herbicides were used to maintain legume dominance by removing grass and weed species. Mixtures of perennial grass and subterranean and/or white clover were grown at sites N4, N6, T16-T20, V11-V15 and S24. Site Q3 involved the establishment of the tropical legume *Aeschynomene americana* in the first growing season.

Rainfall was recorded at each site, and was supported with records of the landholder where sites were not located on agricultural research stations. Additional meteorological data was obtained from the nearest weather station.

2.3.6. Plant measurements

2.3.6.1. Pasture production

Pasture production was determined at regular intervals during the growing season, when the high P treatments had formed a dense canopy. Cutting and weighing of pasture material was used to measure pasture production except at the Western Australian sites where a rising-plate-meter was used.

TABLE VI. FERTILIZER TREATMENT COMBINATIONS FOR RANDOMIZED COMPLETE BLOCK DESIGN USED IN ALL EXCEPT THE VICTORIAN SITES (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

Treatment No.	Treatment	Total P rate	Treatment No.	Treatment	Total P rate
	Core Experiment 1			Core Experiment 2	
1	Control	nil	22	Control	nil
			23	Control	nil
2	SSP Superphosphate	2X[1]			
3	SSP Superphosphate	4X	24	Annual soluble P(as TSP)	X
4	SSP Superphosphate	8X	25	Annual soluble P(as TSP)	1.5X
			26	Annual soluble P(as TSP)	2X
5	Sechura PR 'As Recvd'[2]	2X	27	Annual soluble P(as TSP)	4X
6	Sechura PR 'As Recvd'	4X	28	Annual soluble P(as TSP)	8X
7	Sechura PR 'As Recvd'	8X			
			29	Annual PAPR(N.Carolina)	X
8	North Carolina PR 'As Recvd'	2X	30	Annual PAPR(N.Carolina)	1.5X
9	North Carolina PR 'As Recvd'	4X	31	Annual PAPR(N.Carolina)	2X
10	North Carolina PR 'As Recvd'	8X	32	Annual PAPR(N.Carolina)	4X
			33	Annual PAPR(N.Carolina)	8X
11	Egyptian PR 'As Recvd 92'	2X			
12	Egyptian PR 'As Recvd 92'	4X	34	Annual RPR (N.Carolina)	X
13	Egyptian PR 'As Recvd 92'	8X	35	Annual RPR (N.Carolina)	1.5X
			36	Annual RPR (N.Carolina)	2X
14	Moroccan PR 'As Recvd'	2X	37	Annual RPR (N.Carolina)	4X
15	Moroccan PR 'As Recvd'	4X	38	Annual RPR (N.Carolina)	8X
16	Moroccan PR 'As Recvd'	8X	39	Annual RPR (N.Carolina)	16X
17	Duchess(fine) PR 'As Recvd'	2X	40	Year one soluble P(as TSP)	8X
18	Duchess(fine) PR 'As Recvd'	4X	41	Year one soluble P(as TSP)	16X
19	Duchess(fine) PR 'As Recvd'	8X			
			42	Year one PAPR(N.Carolina)	8X
20	Aerophos (MCP)-S	4X	43	Year one PAPR(N.Carolina)	16X
21	RPR(North Carolina)-S	4X			
			44	Year one RPR(N.Carolina)	8X
			45	Year one RPR(N.Carolina)	16X

Total plots/rep.	= 21	Total plots/rep	= 24
No. reps	= 4	No. reps	= 3
Total plot No.	= 84	Total plot No.	= 72

GRAND TOTAL NO. PLOTS = 156

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[1] The rates of X indicated above are on the basis of 4X being at 90% of maximum water soluble P fertilizer yield *response* under optimum conditions with a good clover component.

[2] As received.

TABLE VII. TYPE, FREQUENCY, SUGGESTED RATES, AND FORM OF BASAL NUTRIENTS APPLIED TO NATIONAL RPR PROJECT SITES (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16]).

Nutrient	Application frequency	Rate kg/ha	Form
K	Annual (1/1)[1]	60 kg K/ha as KCl	Muriate of potash
S	split annual(2/1)	30 kg S/ha	Gypsum
Mg	1/2	15 kg Mg/ha	Magnesium sulfate
Zn	1/2	2 kg Zn/ha	Zinc sulfate
Cu	1/2	1 kg Cu/ha	Copper Sulfate
Mo	1/4	75 g Mo/ha	Sodium molybdate
B	1/4	1 kg B/ha	Ulexite (slow release B)
For -S plots			
Mg	1/2	15 kg Mg/ha	Magnesium chloride
Zn	1/2	2 kg Zn/ha	Zinc chloride
Cu	1/2	1 kg Cu/ha	Copper chloride

[1] 1/1 indicates the nutrient should be applied every year (ie once every one year), 1/2 indicates the nutrient should be applied once every two years, 1/4 indicates application once every four years. 2/1 indicates an application twice per year.

Where cutting was carried out, lawn mowers fitted with catchers were used to collect pasture material. At the Queensland sites sickle bar mowers were used due to the height and density of the tropical pasture species. Plant material was collected from the central portion of the plots after the borders had been cut and discarded. Plant material was then weighed wet and sub-sampled for moisture content determination (oven dried at ~ 60^0 C before weighing). Plant material equal to approximately 50% of that harvested from the total plot area was then returned to the plots, evenly spread over the plot area, and mulched back into the plot using Bolans (Masport) mulching mowers. These mowers finely chopped the returned plant material and directed it down toward the soil surface. This recycling of clippings was considered important in an attempt to simulate some return of nutrients to the pasture as would occur in a paddock grazing system. McLaughlin et al. [21] highlighted the importance of returning clippings in obtaining P responses in their work with WSP and RPR fertilizers. Any regrowth on plots (such as annual grasses or summer weeds) after the end of a growing season and prior to the beginning of the next was mowed off and discarded.

2.3.6.2. Botanical composition.

For the majority of sites, botanical composition was visually assessed for each plot in the spring of each year where a mixed pasture sward existed. Many sites were maintained at 100% legume with the control of annual grasses, or were 100% grass as in case sites Q1 and Q2.

2.3.6.3. Tissue analysis.

Plant material from the first control (treatment 22 in the randomized complete block design (Table VI) and from the 3 control replicates at Victorian sites) and from the X, 2X, and 8X rates of North Carolina PR, PAPR and TSP in Core Experiment 2 was collected for determining P uptake. The sample used for determining P content was a composite sample made up of material from each harvest. At the end of each growing season dried and ground plant material from each plot at each harvest was proportionally combined, on the basis of pasture yields at each harvest. Phosphorus content was measured by Incitec Analysis Systems at the Port Kembla laboratory.

Plant material was dried (80^0 C) ground and digested by the Kjeldahl method (concentrated H_2SO_4 and selenium catalyst) and measured colorimetrically in a segmented flow analyzer.

Analyses for macro- and micro-nutrients including N, S, P, K, Ca, Mg, Na, Cl, Cu, Zn, Fe, B, Mo, and Al, were carried out annually by Incitec Analysis Systems to check that no nutrient deficiencies were present. Samples were collected each year from the first control and the highest rates of North Carolina PR (16X) and TSP (8X) in Core Experiment 2 in the spring in southern Australia and in the middle of the growing season in northern Australia. Except for sites Q1 and Q2, where the pasture was 100% grass, legume material collected for these analyses consisted of the terminal and last 2-3 leaflets from stolons or runners, for white (*Trifolium repens*) and subterranean (*T. subterraneum*) clover, respectively. At site Q3 where Lee Joint Vetch (*Aeschynomene americana* cv Lee) was grown, the last 2 leaflets and growing tip of stems were collected. Except for P on the control plots at some sites, no major nutrient deficiencies for either macro or trace elements were detected (data not presented) based on critical levels for nutrients in pasture tissue [22].

On two occasions, plant samples from various North Carolina PR, PAPR, and SSP treatments were collected to study the effects of fertilizer cadmium content on the cadmium concentration of pasture. Collection and preparation of these samples are described further below in Section 4.

2.3.7. Soil measurements

Prior to fertilizer application in each year, soil from all plots was sampled to monitor the changes in extractable P concentrations and soil pH over time. This involved taking 10 soil cores (100 mm depth and 20 mm diameter) from the central portion of each plot and bulking the 10 cores together. Soil samples were air dried and forwarded to the CSBP laboratory in Western Australia where they were crushed and sieved (<2 mm) prior to routine analysis. Analyses for extractable P, K, organic carbon, electrical conductivity, and pH (water and $CaCl_2$) were carried out using methods 9B (bicarbonate extractable P- 'Colwell'), 18A1 (bicarbonate extractable K), 6A1 (Walkley & Black), 3A1, 4A1 and 4B1 respectively, from Rayment and Higginson [23]. Oxalate extractable 'reactive' iron was also measured in the first year (method 13A1 [17]), except that a 1 hr shaking period was used. Sub-samples of soil taken from the minus-S treatments were prepared and forwarded to the University of New England, where they were analyzed for extractable S. Procedures used and the results of these analyses are presented in Blair et al. [7]. Sub-samples of the annual plot soil samples for 1993 and 1995 were also used in work that investigated the efficacy of different soil P tests for situations where RPR and WSP fertilizers have been used [13]. Site soil profiles were sampled to characterize the site and results are presented in Simpson et al. [16] and in Sale *et al.* [1]. Studies of the PR dissolution process, and measures of P sorption capacity and titrateable acidity were also conducted on the 0-2 cm fraction [4]. The effect of particle size on the effectiveness of a moderately reactive RPR was also examined [4].

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REFERENCES

[1] SALE, P.W.G., SIMPSON, P.G., LEWIS, D.C., BOLLAND, M.D.A., GILKES, R., RATKOWSKY, D.A., GILBERT, M.A., GARDEN, D., CAYLEY, J.W.D., JOHNSON, D., The agronomic effectiveness of reactive phosphate rock fertilizers: 1. Effects of the pasture environment, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 921-936.

[2] LEWIS, D.C., SALE, P.W.G., JOHNSON, D., Agronomic effectiveness of a partially acidulated reactive phosphate rock fertilizer, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 985-993.

[3] BOLLAND, M.D.A., GILKES, R.J., The agronomic performance of reactive phosphate rocks: II Effect of phosphate rock reactivity, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 937-945.

[4] BABARE, A.M., GILKES, R.J., SALE, P.W.G., The effect of phosphate buffering capacity and other soil properties on North Carolina phosphate rock dissolution, availability of dissolved phosphorus and relative agronomic effectiveness, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 1037-1049.

[5] BABARE, A.M., GILKES, R.J., SALE, P.W.G., The agronomic effectiveness of reactive phosphate rocks: 5. The effect of particle size on the effectiveness of a moderately reactive RPR, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 969-984.

[6] GILLARD, P., SALE, P.W.G., TENNAKOON, S.B., Building an expert system to advise on the use of reactive phosphate rock on Australian pastures, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 1077-1084.

[7] BLAIR, G.J., ANDERSON, G.C., CRESTANI, M., LEWIS, D.C., Soil sulfur status, sulfur fertilizer responses and rainfall sulfur accessions at trial sites in the National Reactive Phosphate Rock project, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 995-1001.

[8] GARDEN, D.L., WARD, G.N., SALE, P.W.G., TENNAKOON, S.B., HINDELL, R.P., GARDINER, B., The agronomic effectiveness of reactive phosphate rocks: 3. A comparison of application strategies for soluble phosphorus and reactive phosphate rock fertilizers, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 947-956.

[9] JOHNSON, D., SALE, P.W.G., SIMPSON, P.G., CAYLEY, J.W.D., The agronomic effectiveness of reactive phosphate rocks: 4. Early season lag in herbage production when reactive phosphate rock is used as a pasture fertilizer, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 957-968.

[10] LEWIS, D.C., HINDELL, R.P., HUNTER, J., Effect of phosphate rock products on soil pH, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 1003-1008.

[11] FLEMING, N.K., BOLLAND, M.D.A., GILBERT, M.A., Effect of reactive phosphate rocks and water soluble P fertilizers on extractable phosphorus concentrations in soil, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 1009-1017.

[12] MCLAUGHLIN M.J., SIMPSON, P.G., FLEMING, N.K., STEVENS, D.P., COZENS, G., SMART, M., Effect of fertilizer type on cadmium and fluorine concentrations in clover herbage, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 1019-1026.

[13] SIMPSON, P.G., WEATHERLEY, A.J., MCLAUGHLIN, M.J., HOY, V., LANCASTER, P., Assessment of soil phosphorus tests for situations in Australia where reactive phosphate rock and water so soluble fertilizers are used, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 1027-1035.

[14] SALE, P.W.G., BROWN, A., MACLAREN, G., DERBYSHIRE, P.K., VEITCH, A.M., Pasture environments in Australia where reactive phosphate rock will be an effective fertilizer, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 1051-1060.

[15] SIMPSON, P.G., SALE, P.W.G., TENNAKOON, S.B., An economic analysis of the field performance of North Carolina reactive phosphate rock compared with single superphosphate for selected sites from the National Reactive Phosphate Rock Project, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 1077-1084.

[16] SIMPSON, P.G., SALE, P.W.G., HEPWORTH, G., GILBERT, M., BLAIR, G.J., GARDEN, D., DANN, P.R., HAMILTON, L., STEWART, J., HUNTER, J., CAYLEY, J., WARD, G., JOHNSON, D., LEWIS, D., FLEMING, N., BOLLAND, M.D.A., GILKES, R.J., MCLAUGHLIN, M.J., The national reactive phosphate rock project – aims, experimental approach, and site characteristics, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 885-895.

[17] AOAC Official Methods of Analysis, 9th Edn. The Association of Official Analytical Chemists, Washington, USA, (1960), Section 2013b.

[18] HOFFMAN, E., MAGER, D., Solubility of phosphoric acid and phosphate rocks, Pflanzen. Bodenk. **62** (1953) 262-264.

[19] AOAC Official Methods of Analysis, 15th Edn. The Association of Official Analytical Chemists, Washington, USA, (1990), Section 963.03 and 960.01.

[20] MEAD, R., The Design of Experiments, Cambridge University Press (1988).

[21] MCLAUGHLIN, M.J., DANN, P.R., JAMES, T.R., GARDEN, D.L., Glasshouse comparison of North Carolina phosphate rock, alkali-treated Christmas Island phosphate rock and single superphosphate as P fertilizer on an acidic soil, Aust. J. Agric. Res. **43** 7 (1992) 1667-1681.

[22] REUTER, D.J., ROBINSON, J.B., Plant Analysis: an Interpretation Manual, Inkarta Press, Melbourne, (1986).

[23] RAYMENT, G.E., HIGGINSON, F.R., Australian laboratory handbook of soil and water chemical methods, Inkarta Press, Melbourne (1992).

ASSESSMENT OF SOIL PHOSPHORUS TESTS FOR SITUATIONS IN AUSTRALIA WHERE REACTIVE PHOSPHATE ROCK AND WATER-SOLUBLE FERTILIZERS ARE USED

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Abstract. A selection of commonly used soil P tests, which included anion and cation exchange resin membranes, were compared in a glasshouse experiment using subterranean clover, and evaluated in the field at 19 sites from the National Reactive Phosphate Rock Project in 1993 and at 6 sites in 1995. The ability of the soil P tests to predict plant response was used to evaluate the tests. In the glasshouse experiment, the resin test was less effective than the Bray and Colwell tests in its ability to assess the level of plant available P from the different fertilizer treatments. Seventy one percent of the variation in total P content of the subterranean clover tops was explained by resin extractable P values, whereas the Colwell procedure accounted for 81% and the Bray 1 procedure accounted for 78%. Water and $CaCl_2$ extracts were poor predictors of P content. In the field experiments, all tests evaluated performed poorly in describing the relationship between soil test P and the level of P applied and relative yield and soil test P over a wide range of soil types and environments. The best performing test was the Bray 1 test, though the relationship was poor.

1. INTRODUCTION

The existence of first year only applications of fertilizer in one of the core experiments [1] established at each site in the National RPR Project provided the opportunity to compare different soil P testing procedures. This was done by relating soil P test values in soil samples collected at the beginning of the growing season to the pasture yields measured in that growing season. The treatments included large applications of triple superphosphate, North Carolina phosphate rock (NCPR), and a partially acidulated NCPR.

The soil testing procedures used were the Bray 1, Colwell, water, $CaCl_2$ and mixed CER/AER exchange resins. The comparisons were made in a glasshouse pot experiment undertaken in 1993 using subterranean clover and a soil collected from one of the field sites, and 19 field experiments in 1993 and 6 field experiments in 1995.

2. MATERIALS AND METHODS

2.1. Soil P tests

The soil P tests evaluated were anion and cation exchange membrane (AER-CER) [2], 0.01 M $CaCl_2$, water, Colwell [4], and Bray1 [5]. For AER-CER, a soil solution ratio of 1:40 was used with a 16 hr shaking time. The cation and anion exchange resin membranes (BDH products) were prepared using 1 mol/L NH_4Cl. Phosphate ions were eluted from the AER with 40 mL of a 0.25 mol/L $BaCl_2$ and 0.1 mol/L HCl solution using a 0.5 hr shaking time. Phosphorus in the eluent was determined with a spectrophotomer using a $SnCl_2$ reduced ammonium molybdate — HCl solution. The 0.01M $CaCl_2$ and water methods used a soil solution ratio of 1:10 with a 16 hr shaking time. The suspension was centrifuged for 15 min. at 7000 rpm and the supernatant was passed through a Whatman No. 42 filter paper. The first few drops of the filtrate were discarded. The concentration of P in the supernatant was determined with a spectrophotometer using the Malachite green method [3].

This paper has been modified from the original article “Assessment of soil phosphorus tests for situations in Australia where reactive phosphate rock and water soluble fertilizers are used” by Simpson, P.G., Weatherley, A.J., Sale, P.W.G., McLaughlin, M.J., Hoy, V. and Lancaster, P. published in in Aust. J. Expt. Agric. 37 (1998) 1027-1035 by permission of CSIRO Publishing.

For all of the soil P tests the <2 mm fraction of the top 10 cm of soil (pot and field experiments) was used. Soil samples from the pot trial were taken from the full depth of the pot. In the field experiments, soil samples (0-10 cm) were collected by bulking 6 to 10 2-cm soil core samples taken from the central portion of each plot before the start of the growing season in 1993 and 1995. The start of the growing season occurred in the autumn in southern Australia, and the spring in northern Australia.

2.2. Glasshouse pot trial

2.2.1. Treatments and experimental design

Triple superphosphate (TSP), North Carolina PR (NCPR), and a partially acidulated PR (PAPR) made by 50% acidulation of North Carolina PR with sulfuric acid, were applied at levels to produce a range of soil P levels. Some properties of the fertilizers are provided by Simpson *et al.* elsewhere [1]. A soil with pH of 4.0 (0.01 mol/L $CaCl_2$) and a Colwell P of 29 µg/g collected from Upper Ryans Creek, near Benalla, Victoria, was used for the experiment. Soil, taken from the top 10 cm of an established pasture, was sieved (<2 mm) and weighed out into 6.4 kg lots and placed into plastic bags. After the addition of basal nutrients (equivalent kg/ha: 5 of N, 40 of K, 10 of Mg, 2 of Zn, 1 of Cu, 0,1 of Mo, and 1 of B), the P fertilizers were added at equivalent levels of 10, 20, 30, 40, 50, 60, 70, and 80 kg/ha of P for the TSP and PAPR and 10, 20, 30, 40, 50, 60, 80, and 160 kg/ha of P for the NCPR. A nil P treatment was included as a control. All fertilizers were ground to pass a 0.25-mm sieve to achieve an even distribution of fertilizer through the soil. The fertilizers and soil were mixed thoroughly in the plastic bags and placed in 30-cm diameter pots in the plastic bags and so were not free draining. After wetting to 90% field capacity, the soils were allowed to incubate at glasshouse temperature (25^{o}C) for 8 weeks. Pots were then sown with inoculated subterranean clover (*Trifolium subterranean* cv. Trikkala) seeds, with plants later being thinned to 12 per pot. Pots were arranged in a randomized complete block design, were regularly watered to weight and re-randomized at each watering.

2.2.2. Measurements and data analysis

After incubation, a soil sample was collected to measure soil test P using the procedures described above. Soil test P was then related to level of P application. Three harvests were taken of plant tops up to seed set. Plant tops were dried, weighed and analyzed for P concentration to determine the P content (P concentration multiplied by yield).

Linear regression was used to examine (i) the relationship between level of applied P and soil test and (ii) soil test P and P content.

2.2.3. Field evaluation of soil tests

Soil tests were undertaken in the field using soil samples and pasture dry matter yields from sites included in the National Reactive Phosphate Rock project [1]. This project was established to evaluate the agronomic effectiveness of reactive phosphate rocks in a range of Australian environment [6]. Site locations and information, soil physical and chemical descriptions, and comprehensive details of the experimental design and layout are given in Simpson *et al.* [1]. In summary, the sites were located in the high-rainfall permanent pasture zones across Australia. Soils were acidic (pH < 6.5 water), and representative of major soil types in each region. Soils ranged in texture and included, clay loams, loams, sandy clay loams, sandy loams and acid peaty sands. A comprehensive description of soil chemical and physical properties and site characteristics are presented in Simpson *et al.* [1]. Site identification in the National RPR project was made using the first letter in the name of the state in which they were located, and a number representing an arbitrary position in the series of 30 experiments. e.g. Q2 was a site in Queensland and was the second in the series of 30 sites.

2.2.4. Treatments

Treatments from the National RPR Project used for the field evaluation were those receiving applications of TSP, North Carolina PR, and PAPR applied in the first year only of the trials (1992), and the control (nil P) treatment. Fertilizers were applied at 8X and 16X levels determined for each sites, where the 4X P level was expected to produce 90% of the maximum yield response to TSP fertilizer under optimum conditions. For a more detailed description of how the 'X' level was determined see Simpson *et al.* [1]. The level of application depended upon the environment in which the site was located, and differences between environments meant that there was a wide range of P application levels ranging from 23.2 to 160 kg P/ha. Fertilizers for all treatments were applied in 'as received' form to small field plots (3 m x 5 m or 2 m x 2 m in Tasmania) at the start of the growing season in 1992 only (autumn in southern Australia, and spring in tropical northern Australia). Basal nutrients including sulfur were also applied to each plot [1]. Treatments were laid out in a randomized complete block design. One exception was the sites located in Victoria, where an unbalanced incomplete block design was used. Treatments were replicated 3 times [1].

2.2.5. Measurements and data analysis

Soil samples were collected and processed as previously described. In 1993, soil samples from the control treatments were not analyzed.

Pasture dry matter yields were determined in each growing season by regular harvesting of plots with mowers or rising plate meters [1]. The dry matter yield for each plot was expressed as a % of the maximum (relative) yield at each site. The treatment with the highest mean yield for the experiment, which included the year-1 only treatment, was used as the maximum yield.

Linear regression analysis was used to examine the relationship between soil test P and level of P applied. The relationship between relative yield and soil test P was fitted to a Mitscherlich equation. The goodness of the fit of the non-linear relationship between relative yield and soil test P was assessed from the magnitude of the square root of the residual mean square (RMSE). For reasons presented by Kvålseth [7] and Ratkowsky [8], R^2 was not used as it is considered unsuitable for use in multiple or simple non-linear regression. The smaller the RMSE, the better the agreement was between model and data. In this paper, where relative yield (%) is used, a RMSE of 5% or less was considered to be acceptable variation or error in the fitted Mitscherlich model [9].

3. RESULTS

3.1. Glasshouse experiment

There was a good linear relationship between resin, Colwell and Bray 1 soil test values and the level of P applied (Fig. 1). The Colwell and resin procedures extracted more P from the fertilized soil than the Bray 1 procedure, which may simply reflect the increased extraction time. The Colwell soil test showed some differentiation between fertilizer sources, (Fig. 1b) with the regression line for TSP having a significantly greater slope ($P < 0.05$) than the common line fitted to NCPR and PAPR. There was only a fair correlation between water extractable P and the level of P applied ($R^2 = 0.59$), while the relationship between $CaCl_2$ extractable P and the level of P applied was poor ($R^2 = 0.21$) (data not presented).

Both the water and $CaCl_2$ procedures were poor in describing the relationship between extractable P and plant response (P content), and are not considered further. There were no significant dry matter yield responses to fertilizer P application ($P > 0.05$). However, P content responses to applied P were significant ($P > 0.05$) so P content was used. P content increased linearly with level of fertilizer P applied (Fig. 2). The relationship between P content and the level of P applied was similar for all 3 fertilizers (Fig. 2).

Good relationships were found between P content and soil test P (Fig. 3). The Colwell procedure accounted for 81% of the variation in P content, the Bray 1 accounted for 79%, and the AER/CER resin accounted for 71%.

3.2. Field experiment - 1993

For all sites and fertilizers, all tests were poor in describing the linear relationship between soil test P and level of P applied P ($R^2 < 0.11$) (data not presented). Only when each site was considered separately did any of the tests give a good account of the relationship. Values for R^2 for the separate sites were all greater than 0.6 and ranged from 0.64 to 0.98 ($n = 9$). Resin, Colwell and Bray 1 performed equally well at most sites (data not presented).

A multiple linear regression was used to examine the variation in soil test P, across all sites for each soil test, as a function of site, level of P applied, and fertilizer type effects. There was a major site effect ($P < 0.05$) where differences in sites accounted for a significant proportion of the variation in soil test P, and lines of best fit for sites would have significantly different intercepts. This was not surprising given the range (between 3 and 46 µg/g 0-10 cm Colwell, [1]) in pre-fertilizer extractable P concentrations measured in soil samples collected from each site before the experiment began. All tests, except the resin test, showed a fertilizer type effect, indicating that the resin test was the only one that did not discriminate between the fertilizer types. Dry matter results from the field trial for 1993 indicated that there was generally no statistically significant difference in dry matter production between the TSP, PAPR, and RPR treatments used (data not presented). These findings are therefore consistent with the resin test result, which indicated that there was no difference between fertilizers.

None of the soil P tests showed a close relationship between relative yield and soil test P for all sites (Fig. 4). The root mean square error (RMSE) value was lowest for the Bray 1 test (16.5%), followed by the Colwell (16.8%), and resin (18.0%) (Table I). The units of RMSE are the same as relative dry matter yield (ie. %) and represent the average variation observed from predicted values. All the RMSE values were larger than that considered acceptable (5%) for non-linear regression.

There was no improvement in the relationship between relative yield and soil test P when each fertilizer was considered separately (Table I). The best relationship occurred for RPR, with RMSE values of 14.2 for the resin, 13.6 for the Colwell procedure, and 13.8, Bray 1 procedure (Table I).

The majority of relative yield data was greater than 80% of maximum (68% of observations), with very few points at the lower end of the scale. This would contribute to the poor relationship between relative yield and soil test P. High relative yields were due to the two high levels of fertilizer applied in 1992 at each site.

3.3. Field experiment 1995

Over the 6 sites used in 1995 and all fertilizer types, all tests showed a poor linear relationship between soil test P and level of applied P. The Bray 1 test gave the best relationship ($R^2 = 0.48$, $n = 54$), followed by Colwell procedure ($R^2 = 0.39$), and resin test ($R^2 = 0.27$) (data not presented). Multiple linear regression including site, fertilizer type, and level of P applied effects, showed a fertilizer type effect with a significantly different intercept ($P < 0.05$) for different fertilizer types, for all tests except resin. However, R^2 values for any test and fertilizer type were still poor with Bray 1 having the best relationship for RPR ($R^2 = 0.51$ $n = 9$).

Although the sites used for the 1995 evaluation were responsive to P ($P < 0.05$) and a range of soil P values and relative yield responses were represented, none of the tests adequately described the relationship between relative yield and soil test P (Fig. 5). All tests had similar RMSE values (23 for Bray 1, 24 for resin, and 25 for Colwell).

There was no improvement in the fit of the curves when each fertilizer was considered separately, with RMSE values ranging from 22 to 25 (Table II). Only when sites were considered separately, with or without considering each fertilizer type, was there any significant improvement. In general the Bray 1 test had the lowest RMSE values, particularly for the sites in southern Australia (V15, S24, and S25), which supported temperate legume and/or grass pastures. For the tropical sites, the resin test provided the best relationship for PAPR, while the Bray 1 test gave the best relationship for RPR.

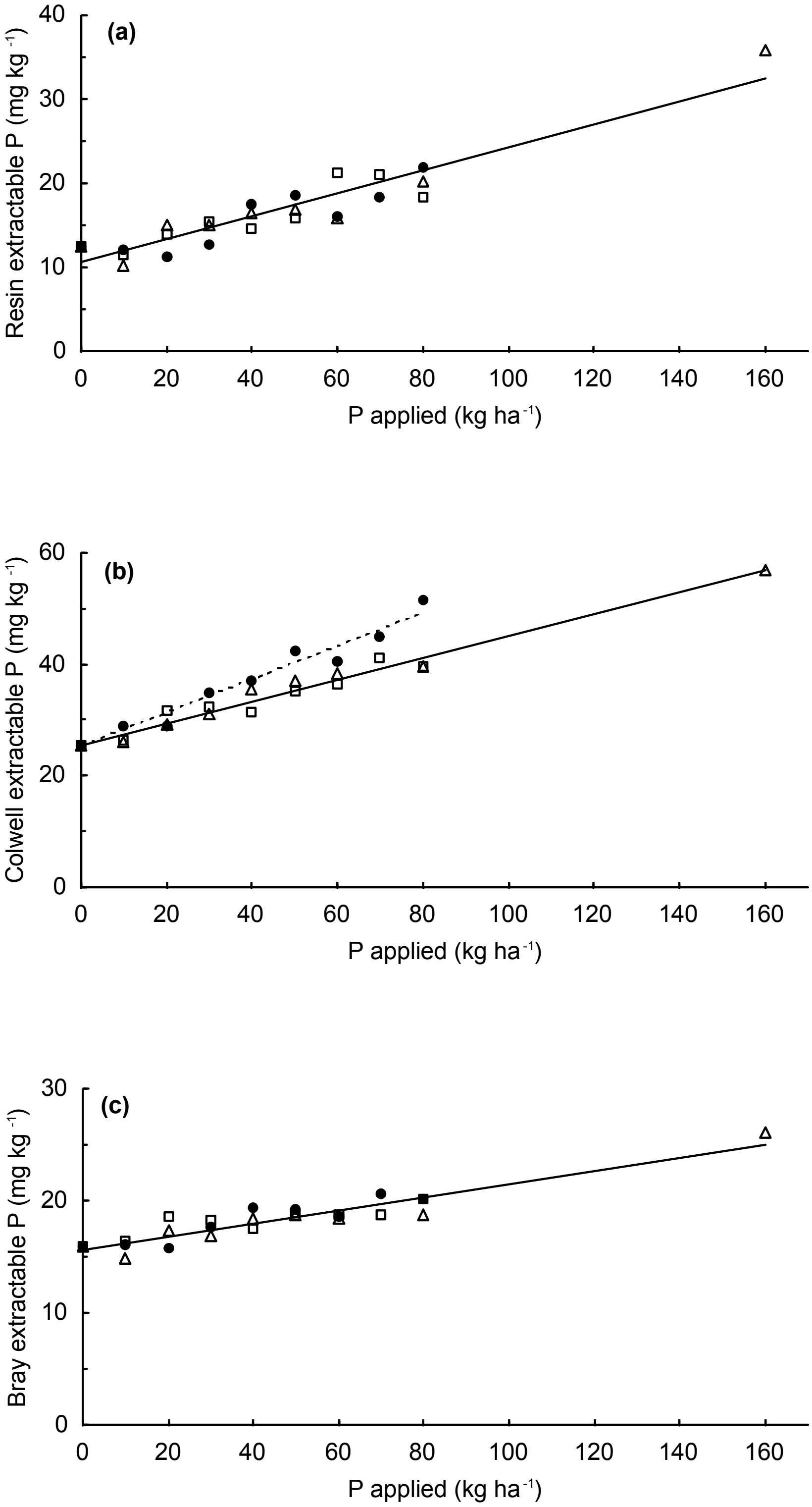

Fig. 1. The relationship between soil test P and the amount of fertilizer applied as TSP (●), PAPR (□), and North Carolina PR (Δ) in the glasshouse experiment for (a) the resin P: $Y = 10.53 + 0.137\ X$ ($R^2 = 0.87$); (b) the Colwell reagent: $Y = 25.5 + 0.296\ X$ ($R^2 = 0.96$) for TSP (-----), and $Y = 25.5 + 0.196\ X$ ($R^2 = 0.96$) for PAPR and North Carolina PR (——————), and (c) the Bray 1 reagent: $Y = 15.7 + 0.058\ X$ ($R^2 = 0.86$) (reproduced with permission of CSIRO Publishing [10]).

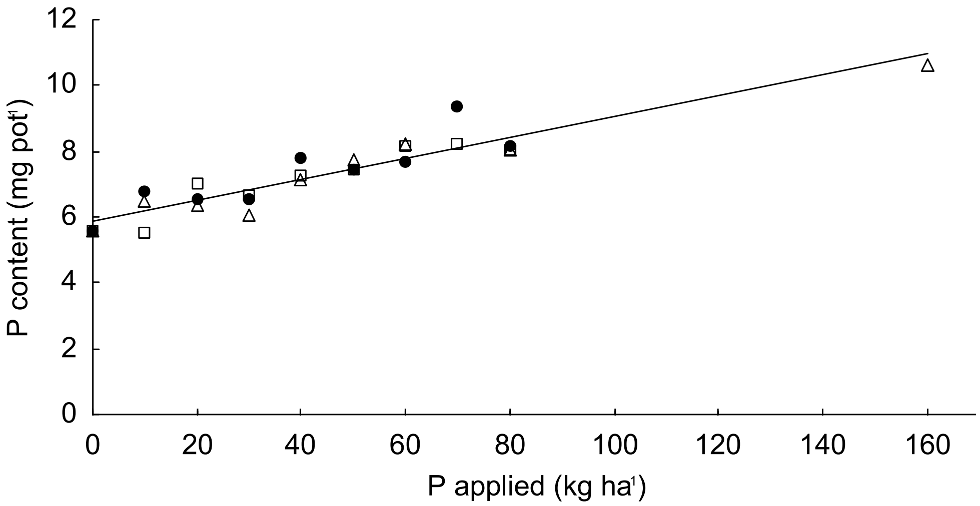

Fig. 2. The relationship between P content of Trikkala subterranean clover and the level of fertilizer applied as TSP (●), PAPR (□), and North Carolina PR (Δ) in the glasshouse experiment. The equation for the fitted line is: Y= 5.89 + 0.032 X (r^2 = 0.72) (reproduced with permission of CSIRO Publishing [10]).

TABLE I. SQUARE ROOT OF THE ERROR MEAN SQUARE (RMSE) VALUES[1] FOR FITTED MITSCHERLICH MODELS FOR THE RELATIONSHIP BETWEEN RELATIVE YIELD AND SOIL TEST P FOR RESIN, COLWELL REAGENT, AND BRAY REAGENT, OVER ALL FIELD SITES FOR TSP, PAPR, AND RPR IN 1993 (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [10]).

Fertilizer	Soil test Resin	Colwell	Bray 1
All fertilizers	19.0	16.8	16.5
TSP	21.9	21.9	17.8
PAPR	17.2	15.8	15.8
RPR	14.2	13.6	13.8

[1] The 'goodness' of fit for the relationship is indicated by a small RMSE. The range for the relative yield is 0-120%. The bigger the RMSE, the poorer the quality of the relationship between soil test P and relative yield.

4. DISCUSSION

All tests used in the field evaluation in 1993 and 1995 performed poorly when examined over a range of soil types and environments with very poor relationships between relative yields and soil test P (Figs. 4 and 5). In soil testing, it is assumed that the use of the relationship between relative yield (instead of absolute yield) and soil test P values minimizes seasonal variation. Our findings suggest that this is not so for the diverse soils and environments used in this study (Table I). The relationship between plant yield and soil test P are usually good where only one or a limited range of soils are used in glasshouse or field experiments [11-14]. Where evaluation of soil P tests has been performed at several sites under field conditions, relationships are often poorer than under glasshouse conditions, and the relationship between relative yield and soil test P differs depending on soil type, plant species or seasonal conditions [15-19].

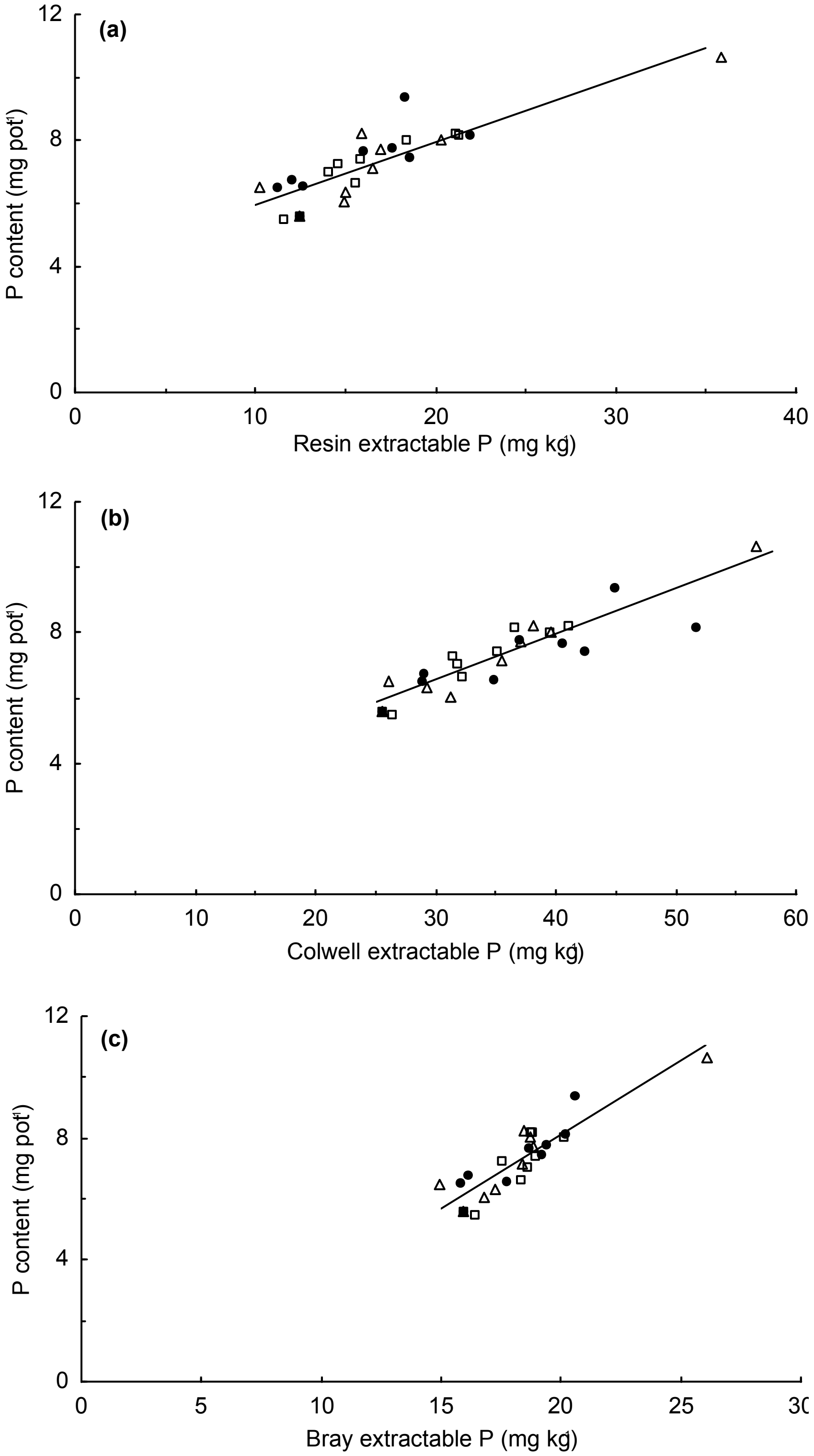

Fig. 3. The relationship for the glasshouse experiment between P content of Trikkala subterranean clover and the amount of (a) resin extractable P: $Y = 3.96 + 2.0\ X$ ($R^2 = 0.72$); (b) Colwell extractable P: $Y = 2.38 + 0.14\ X$ ($R^2 = 0.82$) and (c) Bray 1 extractable P: $Y = -1.65 + 0.49\ X$ ($R^2 = 0.78$). TSP (●), PAPR (□), North Carolina PR (Δ) (reproduced with permission of CSIRO Publishing [10]).

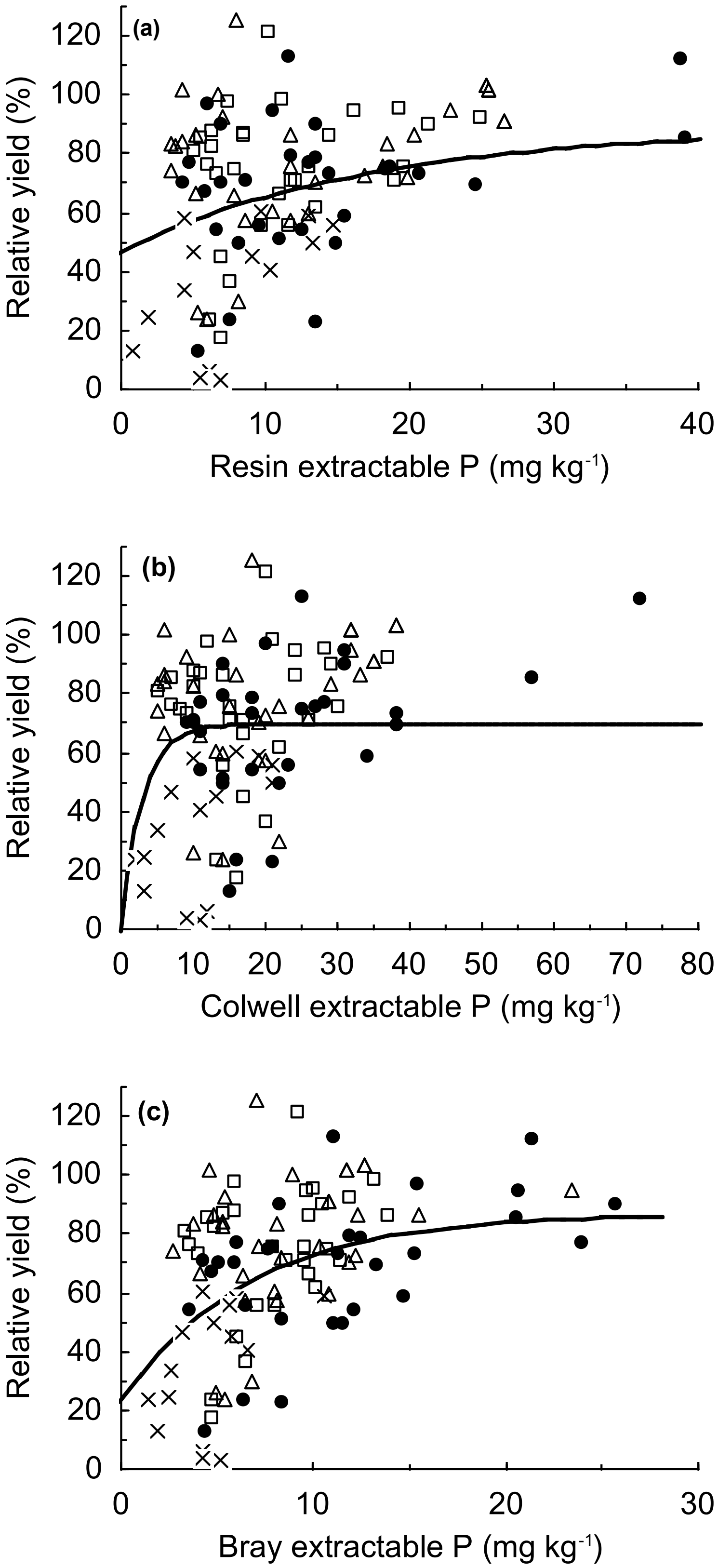

Fig. 4. The relationship between relative yield and soil test P for the 1993 field trial for (a) resin, (b) Colwell, and (c) Bray 1 with fitted Mitscherlich curves. TSP (●), PAPR (□), North Carolina PR (Δ) (reproduced with permission of CSIRO Publishing [10]).

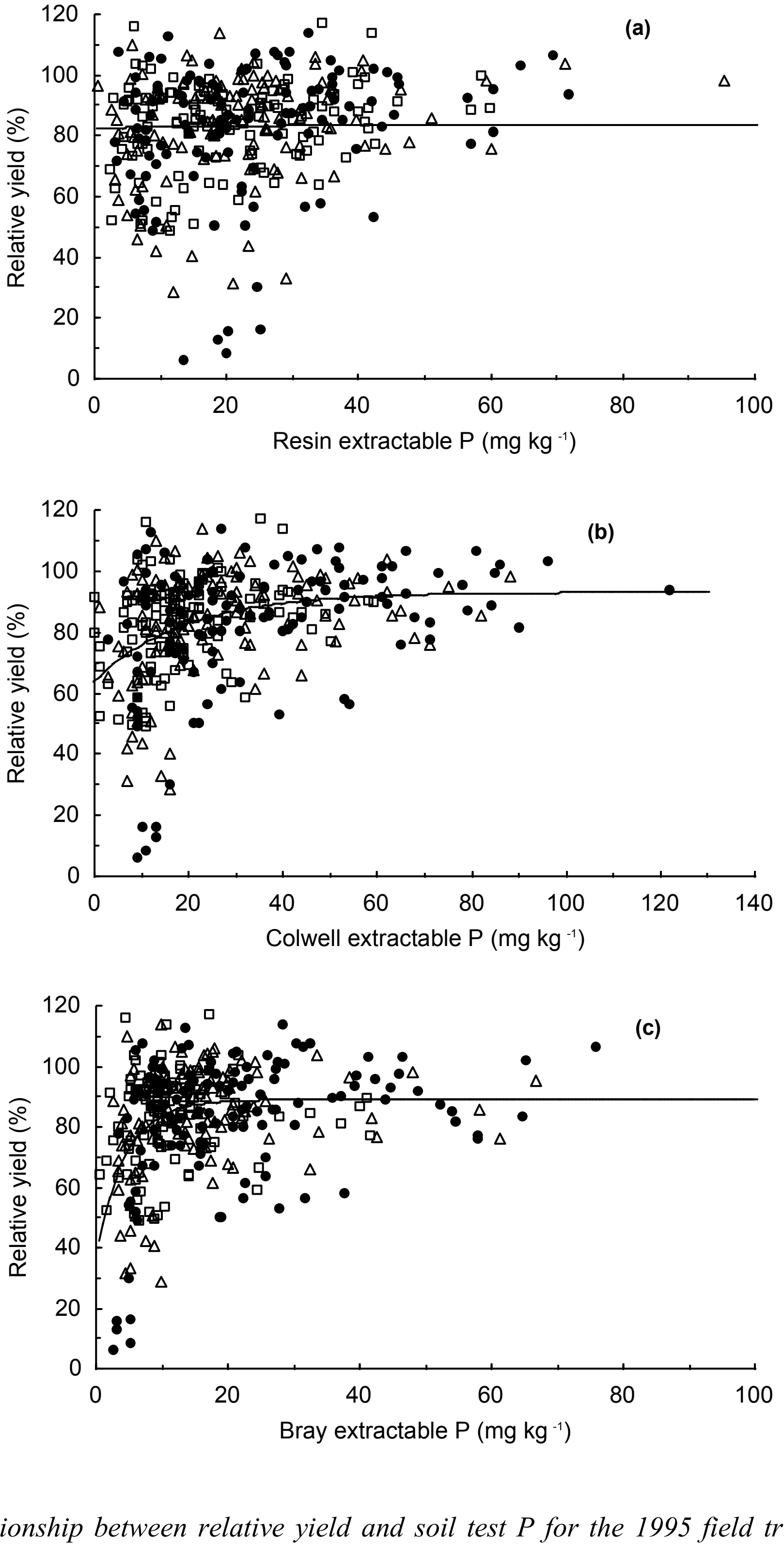

Fig. 5. The relationship between relative yield and soil test P for the 1995 field trial for (a) resin, (b) Colwell, and (c) Bray 1 soil P tests, with fitted Mitscherlich curves. TSP (●), PAPR (□), North Carolina PR (Δ) control (×) (reproduced with permission of CSIRO Publishing [10]).

TABLE II. SQUARE ROOT OF THE ERROR MEAN SQUARE (RMSE) VALUES[1] FOR FITTED MITSCHERLICH MODELS FOR THE RELATIONSHIP BETWEEN RELATIVE YIELD AND SOIL P TEST FOR RESIN, COLWELL REAGENT, AND BRAY REAGENT FOR TSP, PAPR, AND RPR FOR FIELD SITES IN 1995 (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [10])

Site=	Q1 (Malanda)	Q2 (Tully)	Q3 (Mackay)	V15 (Hamilton)	S24 (Victor Harbour)	S25 (Kangaroo Island)	All sites
Fertilizer			RMSE				
				Resin			
All fertilizers	17.0	16.0	17.0	12.0	10.0	34.0	24.0
TSP	11.6	19.4	17.0	11.5	14.7	34.7	23.0
PAPR	16.2	15.3	13.7	14.9	9.6	36.8	22.0
RPR	16.2	19.9	18.9	10.9	9.5	40.4	24.0
				Colwell			
All fertilizers	23.0	12.0	19.0	13.0	12.0	34.0	25.0
TSP	18.4	9.4	13.7	12.5	15.8	34.8	22.0
PAPR	16.4	15.5	17.7	15.4	10.5	37.8	22.0
RPR	24.9	13.6	20.3	13.4	9.7	39.7	25.0
				Bray			
All fertilizers	16.0	11.0	18.0	11.0	10.0	32.0	23.0
TSP	12.2	10.6	16.7	10.9	11.5	31.7	23.0
PAPR	16.5	16.4	21.8	9.06	9.5	33.4	22.0
RPR	14.4	13.5	15.6	7.6	8.3	38.8	23.0

[1] The ‘goodness’ of fit for the relationship is indicated by a small RMSE. The range for the relative yield is 0-120%. As such the bigger the RMSE, the poorer the quality of the relationship between soil test P and relative yield.

There are a number of possible reasons why the relationship between relative yield and soil test P was not constant across the different sites in the present study. The first is that different seasonal conditions result in different relationships between relative yield and soil test values, even for the same species in the same soil, topdressed with the same P fertilizer [15, 20]. The second reason is the wide range of soil types that were used for this study, from a peat sand to a medium clay krasnozem soil [1]. Reuter *et al.* [19] were able to show that soil test P values related to 90% relative yield (critical values) for cereals changed with soil texture. The P sorption capacity of soils from sites in this national project was found to change with soil texture [21]. The third possible reason was the difference in botanical composition of the pastures across the sites. The sites contained tropical grass (site Q2), tropical legume (Q3), mixed perennial grass and clover (e.g. sites V15, and S24) and subterranean clover dominant sites at the remaining locations [1]. Bolland and Gilkes [20] and Reuter *et al.* [19] have shown how critical soil test values differ for different species. Different sites used for this study generally had different species present, and may subsequently have had different soil P levels for similar relative yields.

A fourth possible reason is due to the effect of the different types of P fertilizer. We were not able to show any differences in the Mitscherlich calibration curves for the field data in 1993 and 1995 between the different fertilizer forms because of the variable results in the data. However, differences in calibration relationships between WSP and RPR forms have been previously reported [22, 23]. The extent of RPR dissolution during a growing season, the P nutrition of the pasture, the ability of an empirical soil test to predict P availability, and the extent of RPR dissolution that occurs post-sampling all determines the efficacy of a soil test for RPR and the likelihood that there will be different calibration relationships for WSP and RPR fertilizer. The dissolution of RPR, and the availability of the dissolved P, depends on edaphic and climatic factors [21], which cannot be ascertained across sites by a single soil test. It is not surprising therefore that soil testing for RPR is being developed in conjunction with mechanistic models to describe RPR dissolution during the growing season [24, 25].

The results from the glasshouse and field experiments show that the resin test was not superior to either the Colwell or Bray 1 tests. On the contrary, the Bray 1 and to a lesser extent the Colwell test, were both slightly better than the resin test in the glasshouse study (Fig. 3). Similarly, there was a closer fit of relative yield data in the 1993 growing season to Bray 1 and Colwell extractable P than to the resin extractable P (Table I, Fig. 3), though all tests performed poorly. All soil tests were generally similar in their ability to predict relative yields from the P already present in the soil (Table II, Fig. 5).

The soil used for the glasshouse study was collected from site V12 in the National RPR Project. This soil was non-responsive to P in terms of clover yields, necessitating the use of P content data. The soil also had high levels of titrateable acidity [21]. These two factors meant there were limited dry matter responses to soil P test values, and conditions were very favorable for RPR dissolution, such that all soil tests were able to detect increases in available P in the RPR treatments (Fig. 1) and no fertilizer type was agronomically superior. These conditions contrast to those reported by Saggar *et al* [24] who found the resin test to be superior to the Olsen bicarbonate test where yield responses by perennial ryegrass to added P were recorded for all 4 soils used, and the WSP fertilizer was generally more effective than PR.

Only 2 levels of P were used in the field studies. A wider range of P levels would have provided a better defined soil P test calibration to evaluate the various soil tests procedures.

The resin test extracts many other elements simultaneously so it is a multi-element test. The test therefore has advantages in saving time and cost and when the analysis of other elements is considered [26]. The other soil P tests examined in this study were for P only.

5. CONCLUSION

In the glasshouse experiment, all soil P tests were reasonably effective in predicting P content responses to soil test P values for soils previously fertilized with 3 different fertilizer types. However, under field conditions all tests performed poorly when examined over a range of soil types and environments. On an individual site basis however, there were improved relationships between P applied and soil test P, and between relative yield and soil test P at some sites. This highlights the potential problems that all soil test procedures face when used over a wide range of soil types and environments.

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REFERENCES

[1] SIMPSON, P.G., SALE, P.W.G., HEPWORTH, G., GILBERT, M., BLAIR, G.J., GARDEN, D., DANN, P.R., HAMILTON, L., STEWART, J., HUNTER, J., CAYLEY, J., WARD, G., JOHNSON, D., LEWIS, D., FLEMING, N., BOLLAND, M.D.A., GILKES, R.J., McLAUGHLIN, M.J., The national reactive phosphate rock project – aims, experimental approach, and site characteristics, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 885-895.

[2] McLAUGHLIN, M.J., LANCASTER, P.A., SALE, P.W.G., UREN, N.C., PEVERILL, K.I., Comparison of cation/anion exchange resin methods for multi-element testing of acid soils, Aust. J. Soil. Res. **23** (1994) 229-240.

[3] IRVING, G.C.J., MCLAUGHLIN, M.J., A rapid and simple test for phosphorus in Olsen and Bray No.1 extracts of soil, Commun. Soil Sci. Plant Anal. **21** (1990) 2245-2255.

[4] COLWELL, J.D., The estimation of the phosphorus fertilizer requirements of wheat in southern New South Wales by soil analysis, Aust. J. Exp. Agric. Anim. Husb. **3** (1963) 190-197.

[5] BRAY, R.H., KURTZ, L.T., Determination of total, organic and available forms of phosphorus in soils, Soil Sci. **59** (1945) 39-45.

[6] SALE, P.W.G., SIMPSON, P.G., LEWIS, D.C., BOLLAND, M.D.A., GILKES, R., RATKOWSKY, D.A., GILBERT, M.A., GARDEN, D., CLAYLEY, J.W.D., JOHNSON, D., The agronomic effectiveness of reactive phosphate rock fertilzers: 1. Effects of the pasture environment, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 921-936.

[7] KVÅLSETH, T.O., Cautionary note about R^2, Amer. Statist. **39** (1985) 279- 285.

[8] RATKOWSKY, D.A., Handbook of Nonlinear Regression Models, Marcel Dekker Inc., New York and Basel, (1990), 44-45.

[9] RATKOWSKY, D.A., Personal communication. Department of Agricultural Science, University of Tasmania, Australia, (1997).

[10] SIMPSON, P.G., WEATHERLEY, A.J., McLAUGHLIN, M.J., HOY, V., LANCASTER, P., Assessment of soil phosphorus tests for situations in Australia where reactive phosphate rock and water soluble fertilizers are used, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 1027-1035.

[11] BENBI, D.K., GILKES, R.J., BOLLAND, M.D.A., An assessment of soil tests for phosphate for the prediction of cereal yields on a sandy soil in Western Australia, Fert. Res. **16** (1988) 137-155.

[12] MOODY, P.W., AITKEN, R.L., COMPTON, B.L., HUNT, S., Soil phosphorus parameters affecting phosphorus availability to, and fertilizer requirements of, maize. Aust. J. Soil. Res. **26** (1988) 611-622.

[13] NAIDU, R., SYERS, J.K., TILLMAN, R.W., KIRKMAN, J.H., Assessment of plant available phosphate in limed, acid soils using several soil-testing procedures, Fert. Res. **30** (1991) 47-53.

[14] SAGGAR, S., HEDLEY, M.J., WHITE, R.E., Development and evaluation of an improved soil test for phosphorus: 2. Comparison of the Olsen and mixed cation-anion exchange resin tests for predicting the yield of ryegrass grown in pots, Fert. Res. **33** (1992) 135-144.

[15] BOLLAND, M.D.A., ALLEN, D.G., GILKES, R.J., The influence of seasonal conditions, plant species and fertilizer type on the prediction of plant yield using the Colwell bicarbonate soil test for phosphate, Fert. Res. **19** (1989) 143-158.

[16] HOLFORD, I.C.R., CULLIS, B.R., An evaluation of eight soil phosphate extractants on acid wheat-growing soils, Aust. J. Soil Res. **3** (1985) 647-653.

[17] HOLFORD, I.C.R., CROCKER, G.J., Efficacy of various soil phosphate tests for predicting phosphate responsiveness and requirements of clover pastures on acidic tableland soils, Aust. J. Soil Res. **26** (1988) 479-488.

[18] MAIER, N.A., POTOCKY-PACAY, K.A., JACKA, J.M., WILLIAMS, C.M.J., Effect of phosphorus fertilizer on the yield of potato tubers (Solanum tuberosum L.) and the prediction of tuber yield response by soil analysis, Aust. J. Exp. Agric. **29** (1989) 419-432.

[19] REUTER, K.J., DYSON, C.B., ELLIOT, D.E., LEWIS, D.C., RUDD, C.L., An appraisal of soil phosphorus testing data for crops and pastures in South Australia, Aust. J. Exp. Agric. **35** (1995) 979-995.

[20] BOLLAND, M.D.A., GILKES, R.J., Predicting plant yields using soil testing for phosphorus: effects of error in the estimation of the maximum yield on interseasonal comparisons of yield prediction, Fert. Res. **33** (1992) 145-153.

[21] BABARE, A.M., GILKES, R.J., SALE, P.W.G., The agronomic effectiveness of reactive phosphate rocks: 5. The effect of particle size on the effectiveness of a moderately reactive RPR, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 969-984.

[22] BOLLAND, M.D.A., Summary of research on soil testing for rock phosphate in Western Australia, Fert. Res. **35** (1993) 83-91.

[23] PERROTT, K.W., SAGGAR, S., MENON, R.G., Evaluation of soil phosphorus status where phosphate rock based fertilizers have been used, Fert. Res. **35** (1993) 67-82.

[24] SINCLAIR, A.G., JOHNSTONE, P.D., SMITH, L.C., O'CONNOR, M.B., NGUYEN, L., Agronomy, modeling and economics of reactive phosphate rocks as slow-release phosphate fertilizers for grasslands, Fert. Res. **36** (1993) 229-238.

[25] RAJAN, S.S.S., WATKINSON, J.H., SINCLAIR, A.G., Phosphate rocks for direct application to soils, Advan. Agron. **57** (1996) 77-159.

[26] McLAUGHLIN, M.J., LANCASTER, P.A., SALE, P.W.G., UREN, N.C., PEVERILL, K.I., Comparison of cation/anion exchange resin methods for multi-element testing of acid soils, Aust. J. Soil. Res. **32** (1993) 229-240.

MEASURING P AVAILABILITY IN SOILS FERTILIZED WITH WATER-SOLUBLE P FERTILIZERS USING ^{32}P METHODOLOGIES

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Abstract

Isotope exchange kinetics was used in conjunction with standard procedures for assessing soil P status in soils fertilized with soluble phosphatic fertilizers. Soil samples were collected before fertilizer application in year 1 (one) from 23 of the 30 sites of the National Reactive Phosphate Rock project. Soil phosphorus test values were plotted against indices of pasture response to applied fertilizer, to assess the effectiveness of the various soil tests to predict site responsiveness to applied fertilizer. Isotopically exchangeable P was only weakly related to other measures of available P, with resin P having the best relationship with E values. In some samples, very large values for isotopically exchangeable P (E values) were determined in relation to P extractable by all reagents. Examination of the data however, revealed that all the samples with large E values in relation to extractable P had very low equilibrium concentrations of solution P and high buffering capacities. The best soil test, Bray 1, could account for only 50% of the variation in plant responsiveness to applied fertilizer, with Olsen and Resin tests slightly worse at 41% and the isotopic procedure at 39%.

1. INTRODUCTION

Use of ^{32}P to determine plant-available soil P has advantages over extractants such as Bray1 and Olsen since the method is not based on dissolving soil P forms assumed to be plant-available. Rather, the ^{32}P methodology is non-destructive and involves the exchange of ^{32}P with labile P forms in soil considered to be plant-available. The non-destructive nature of the ^{32}P method should provide good assessment of plant-available P across a wide spectrum of soil types, whereas utility of soil test extractants are limited to major soil groups. The National Reactive Phosphate Rock project involved many sites across Australia assessing the response of pasture species to P fertilizer. The soils used in the project were tested with ^{32}P methodology to assess the utility of using ^{32}P to determine plant-available P compared to the other common soil test methods.

2. MATERIALS AND METHODS

2.1. Soil sampling

Soil samples were collected before fertilizer application in year 1 from 23 of the 30 sites of the National Reactive Phosphate Rock project. All plots were sampled to 10 cm depth prior to fertilizer application, as the aim was to develop soil tests to predict fertilizer responsiveness of the pasture, and hence fertilizer requirement. At approximately the same time (in the autumn in the south and in the spring in Qld), a composite of 10 soil cores (10 cm depth and 2 cm diameter) were taken from each plot and air-dried. Samples were taken from the central strip (within the buffered pasture zone) of each plot. Samples were air-dried (or force dried at 40-50°C) and crushed to pass a 2 mm sieve.

2.2. Chemical analyses

Soils were analyzed by the following procedures:

1) Colwell bicarbonate method [1]
2) Olsen bicarbonate method [2]
3) Resin membranes — as outlined in previous paper
4) Bray 1 acid fluoride method [3]
5) Lactate method [4]
6) Water extractable P - Five grams of soil was shaken for 16 h with 50 ml distilled deionized water. The suspension was centrifuged for 15 min at 7000 rpm and the supernatant filtered through a Whatman No. 42 filter paper, discarding the first few drops of filtrate. Phosphorus in the solution was determined using the Malachite Green method [5].

7) $CaCl_2$-extractable P - Five grams of soil was shaken for 16 h with 50 ml 0.01 M $CaCl_2$ solution. The suspension was filtered through a Whatman No. 42 filter paper, discarding the first few drops of filtrate. Phosphorus in the solution was determined using the Malachite Green method [5].
8) ^{32}P E values and kinetic parameters — methods are described in Fardeau [6]. Isotopically exchangeable P was also determined by the method of Wolf et al. [7], in 0.002M $CaCl_2$ solutions with 5µmol ^{31}P/L.

2.3. Pasture yield: response to applied P and indices of site responsiveness or productivity

Fertilizer treatments and pasture yield data have been summarized in a report of results for the 1992 season of the National RPR Project. For some sites a linear model adequately described the data,

$$y = a + bx \quad (1)$$

where y = shoot yield and x = P applied, while others were fitted to a modified Mitscherlich form;

$$y = a - b\exp(-c^{x}) \quad (2)$$

where $a-b$ is the yield without added fertilizer, a is the maximum yield and c is a curvature coefficient. Four indices of responsiveness were derived from the fitted yield response model for each site which include:

1) Index 1 — yield responsiveness as a fraction of yield without fertilizer - $b/(a-b)$.
2) Index 2 — yield responsiveness as a fraction of maximum yield - b/a.
3) Index 3 — actual yield without fertilizer expressed as a fraction of the actual maximum yield at the greatest rate of fertilizer applied at each site.
4) Index 4 — actual yield without fertilizer expressed as a fraction of the calculated maximum yield (using the appropriate response function) at the greatest rate of fertilizer applied at each site.

Soil test values were plotted against these indices to assess the effectiveness of the various soil tests to predict site responsiveness to applied fertilizer (Indices 1 and 2), or site productivity without fertilizer (Indices 3 and 4).

3. RESULTS

3.1. ^{32}P Isotope data

Kinetics of isotope reaction with the soils are shown in Table I. Isotopically exchangeable P was only weakly related to other measures of available P, with resin P having the best relationship with E values (Olsen and Resin P shown in Figs 1 and 2).

Relationships did not improve if E values, determined at longer equilibration times, were used. Indeed, it appeared that two relationships were evident using the 24-hour equilibration period (Fig. 3). In some samples, very large values for isotopically exchangeable P (E values) were determined in relation to P extractable by all reagents. Examination of the data however, revealed that all the samples with large E values in relation to extractable P, had very low equilibrium concentrations of solution P and high buffering capacities. Excluding these data from the data set, and one value having a very high solution P value (>3 mg/L) subject to errors through dilution (T16), revealed a good 1:1 relationship between resin-extractable P and E value.

To investigate the errors in E values associated with determination of low concentrations of solution P, isotopically exchangeable P was also determined using a carrier procedure [7]. Results in Figure 4 show that E values determined by the two procedures agreed well. The exceptions were where solution P concentrations were low (<0.02 mg/L) and errors in solution P determination probably lead to erroneously large estimates of E. A better representation of this error is shown in Fig. 5.

TABLE I. CONCENTRATION OF ^{31}P AT EQUILIBRIUM (C_P), P BUFFER CAPACITY (C) AND ISOTOPICALLY EXCHANGEABLE P AT 1 MINUTE (E_1), 10 MINUTES (E_{10}) AND 24 HOURS (E_{24}) FOR SOILS AT THE 23 SITES STUDIED

Site	Cp mg/L	C L/kg	E_1 mg/kg	E_{10} mg/kg	E_{24} mg/kg
Q2	0.029	47.53	1.39	4.45	55.06
Q3	0.012	25.30	0.30	0.62	2.88
N4	0.563	12.66	7.12	8.07	10.57
N6	0.402	16.85	6.76	9.61	20.51
N7	0.043	17.90	0.76	1.30	4.08
N8	0.113	14.66	1.66	2.60	6.82
V10	0.269	12.41	3.34	3.96	5.73
V11	0.043	130.13	5.65	14.80	118.24
V12	0.067	21.14	1.43	2.58	9.24
V14	0.215	13.38	2.88	3.49	5.29
V15	0.080	44.25	3.55	9.01	67.04
T17	0.239	15.09	3.61	5.44	13.19
T18	1.425	11.05	15.74	16.76	19.20
T19	0.051	207.24	10.67	27.97	224.10
T20	0.890	12.93	11.50	14.97	26.44
S21	0.372	11.62	4.33	4.29	4.23
S22	1.495	11.50	17.18	16.65	15.57
S24	0.631	11.98	7.56	8.67	11.67
S25	0.031	47.88	1.50	4.71	55.84
W26	0.068	17.34	1.18	1.74	3.99
Q1	0.119	57.96	6.89	20.25	207.30
V13	1.558	11.30	17.60	17.70	17.91
T16	3.089	11.15	34.46	33.65	31.98
S23	1.153	11.47	13.22	13.33	13.57
Mean	0.540	33.114	7.51	10.28	39.60
Median	0.227	14.879	4.99	8.37	14.57
Minimum	0.012	11.049	0.30	0.62	2.88
Maximum	3.089	207.241	34.46	33.65	224.10

3.2. Relationship of soil test methods to pasture response to P fertilizer

Indices 2 and 4 were considered the most appropriate to use to assess the soil test methods. Relationships between soil test values and Index 2 for the sites are shown in Figs. 6-10.

A summary of the correlation coefficients between the test and the two indices is shown in Table II. These data indicate that the Bray-1 test was superior to the other tests irrespective of the index used to describe the sites responsiveness or productivity. The resin test had similar predictive capability to the Olsen test. However, it is evident that all the tests are poor predictors of pasture response to P fertilizer across this wide range of soil and climatic environments.

The shorter-term isotopic techniques (E values determined at 1 and 10 minutes) relate better to pasture response to fertilizer than the 24 hour equilibration (Fig. 11).

TABLE II. CORRELATION COEFFICIENTS BETWEEN SOIL TEST VALUES AND INDICES OF SITE RESPONSIVENESS TO FERTILIZER (INDEX 2) AND SITE PRODUCTIVITY WITHOUT FERTILIZER (INDEX 4)

Soil test method	Index 2 Correlation coefficient (R^2)	Index 4
Colwell	0.22	0.30
Olsen	0.35	0.40
Resin	0.35	0.41
Bray	0.50	0.51
Lactate	0.41	0.41
Water	0.24	0.26
$CaCl_2$	nd	nd
$E_{1\ min.}$	0.39	nd
$E_{10\ min.}$	0.29	nd
$E_{24\ hour}$	0.07	nd

nd = not determined.

4. DISCUSSION

The behaviour of all test procedures was disappointing. The best soil test, Bray 1, could account for only 50% of the variation in plant responsiveness to applied fertilizer, with Olsen and Resin tests slightly worse at 41% and the isotopic procedure at 39%. The performance of the resin test was disappointing, but given the multi-element nature of the test it may offer advantages over the other procedures in terms of laboratory speed and costs. The mild action of this extractant may preclude extraction of Al-bound P in acidic soils. Modifications to the resin procedure, such as acidification using some mole fraction of H^+ ions on the cation exchange resin, or use of a mole fraction of F^- on the anion resin could improve the utility of the procedure. However, modifications such as these reduce the similarity the procedure has to the action of plant roots.

Several studies in Australia have investigated the relationship between soil P test values and response of pastures to applied P [8-11]. McLachlan [8] found that the Colwell procedure was superior to Bray 1. Spencer *et al.* [9] found both Bray and Colwell procedures to be equally effective in predicting responsiveness of pastures to P. Both these studies were on a limited series of soils from the southern Tablelands and south-western slopes of NSW**.** Holford and Crocker [10] investigated soil test procedures on data from 41 sites having acidic soils in northern NSW. They concluded the Bray 1 method was the best correlated with site productivity without fertilizer (relative yield as a % of maximum). Dear *et al.* [11] found on a limited series of soils (10 sites) that P extracted by 0.01 M $CaCl_2$ gave an excellent relationship (r^2 = 0.84) with relative yield of pasture. The Bray 1 test was found to be superior in the group of soils tested here. This supports the general view that the Bray 1 test is a superior test on acidic soils, where the F^- in the reagent promotes release of P from Al oxide/hydroxide surfaces [12].

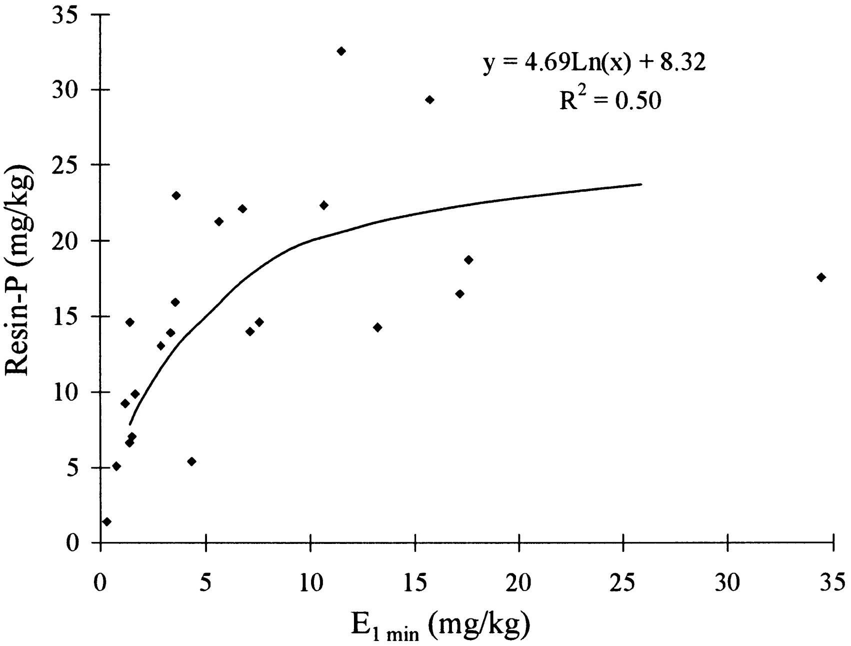

Fig. 1. Relationship between resin-extractable P and isotopically-exchangeable P (after 1 minute equilibration).

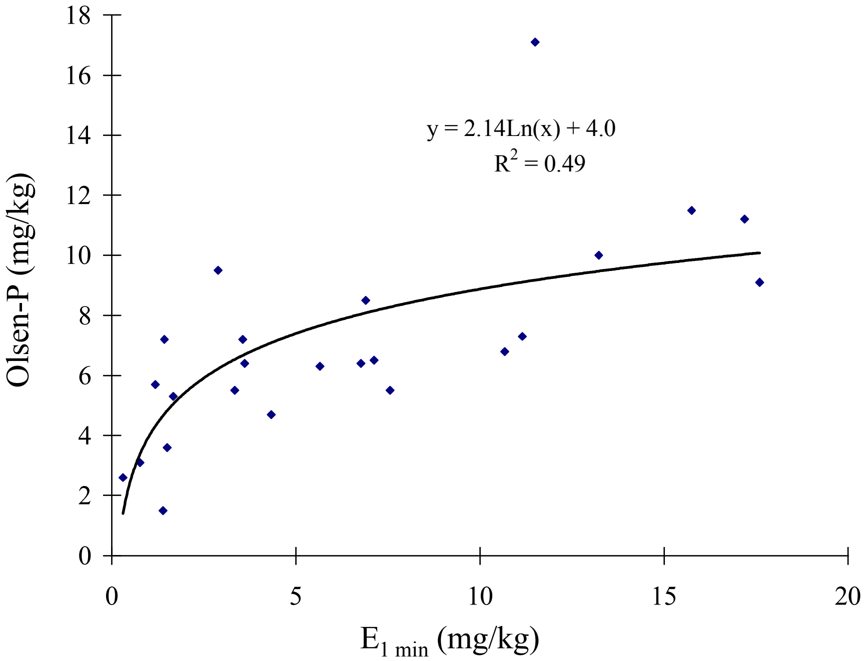

Fig. 2. Relationship between Olsen-extractable P and isotopically-exchangeable P (after 1 minute equilibration).

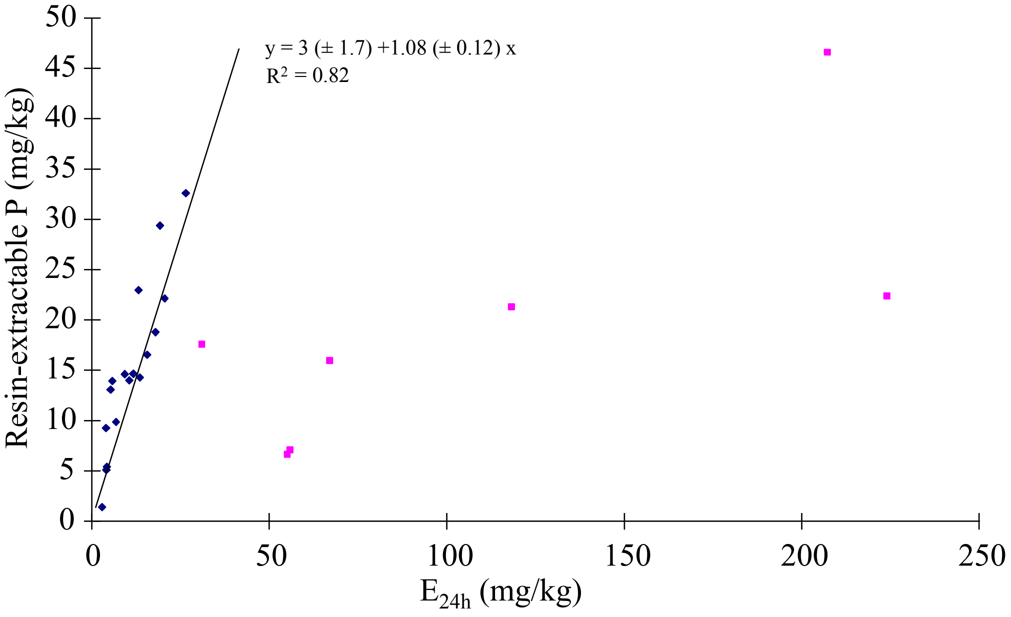

Fig. 3. Relationship between resin-extractable P and E value (24 hour equilibration). Samples marked (■) were excluded from the relationship and had equilibrium P concentrations less than 0.02 mg/L and one sample had a very high solution P concentration (>3 mg/L).

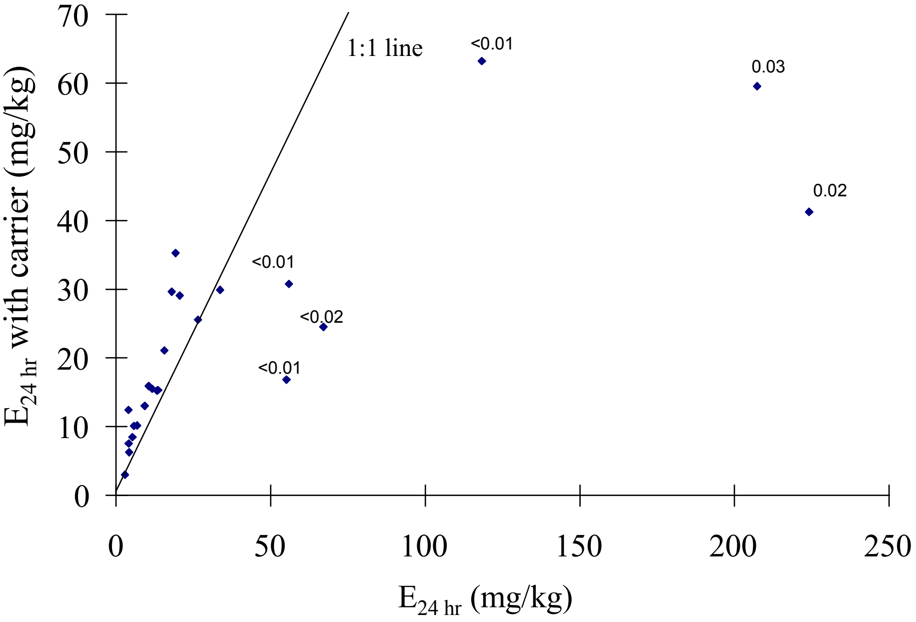

Fig. 4. Relation between E values determined with and without carrier ^{31}P. Text on graph indicates samples with equilibrium solution ^{31}P concentrations (mg/L) in the absence of carrier ^{31}P.

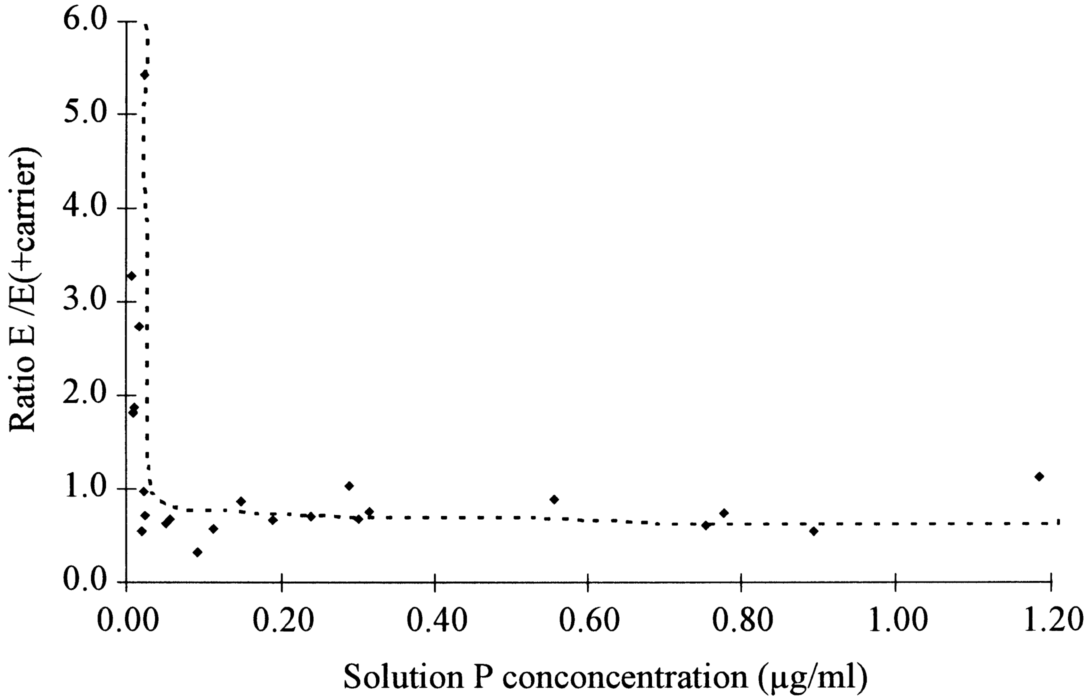

Fig. 5. Relation between E values determined with and without carrier ^{31}P in relation to equilibrium solution ^{31}P concentration (mg/L) in the absence of carrier ^{31}P. Line is hand drawn.

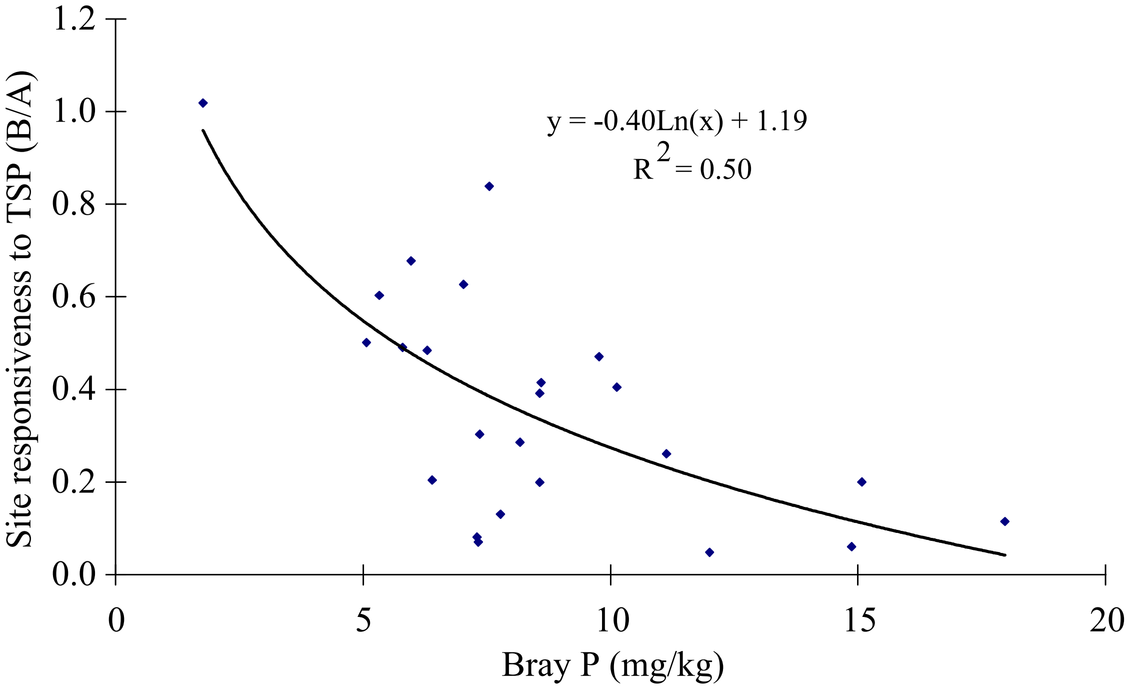

Fig. 6. Relation between Bray P values in unfertilized soil and subsequent response of pasture to addition of triple superphosphate (TSP).

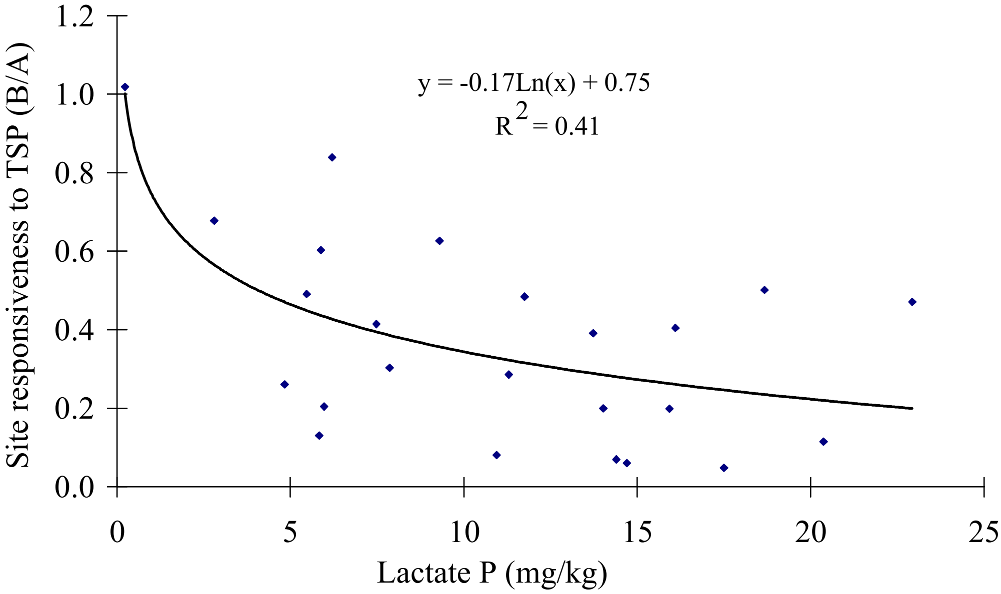

Fig. 7. Relation between Lactate P values in unfertilized soil and subsequent response of pasture to addition of triple superphosphate (TSP).

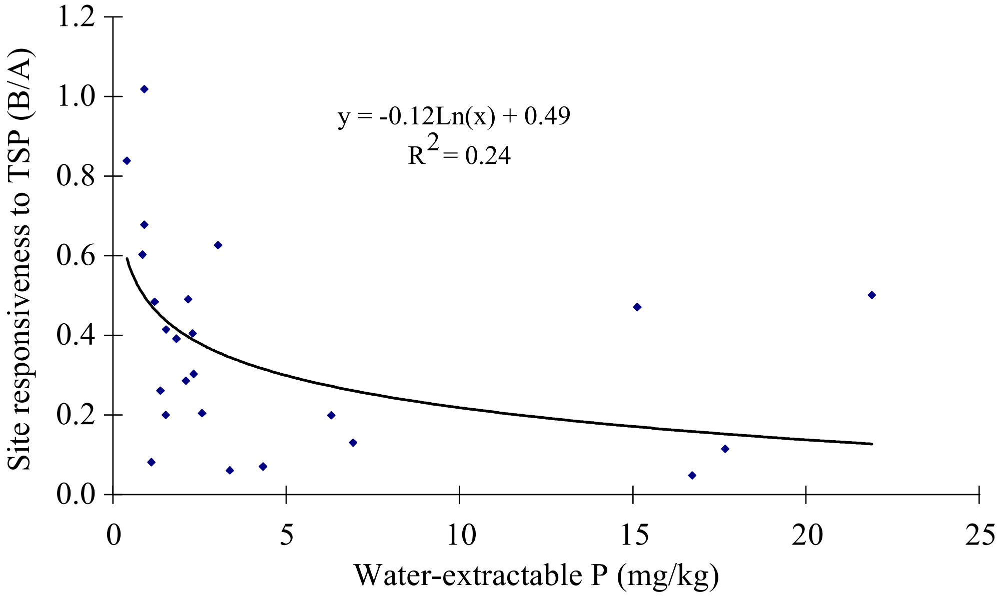

Fig. 8. Relation between water-extractable P values in unfertilized soil and subsequent response of pasture to addition of triple superphosphate (TSP).

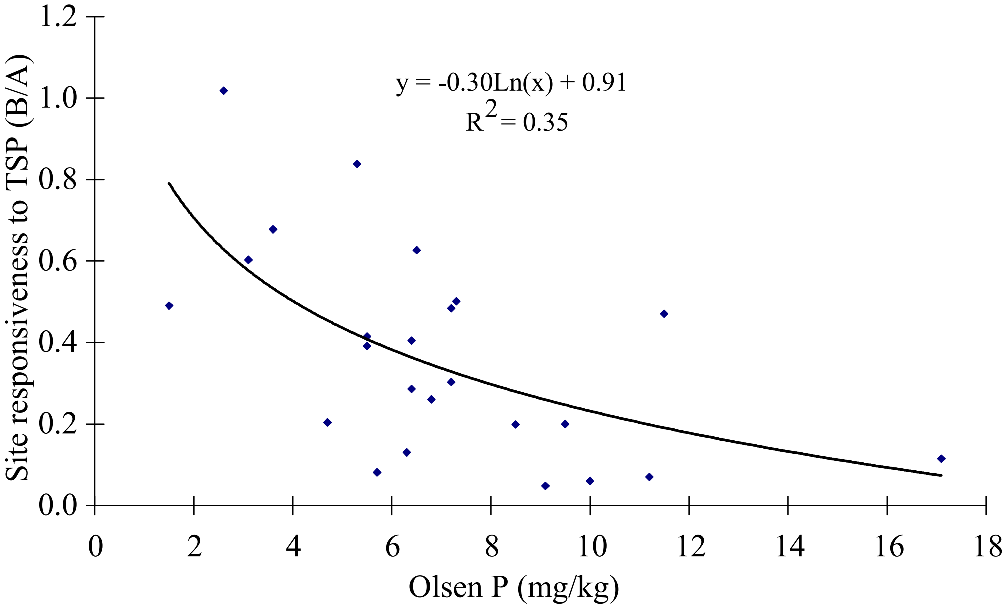

Fig. 9. Relation between Olsen P values in unfertilized soil and subsequent response of pasture to addition of triple superphosphate (TSP).

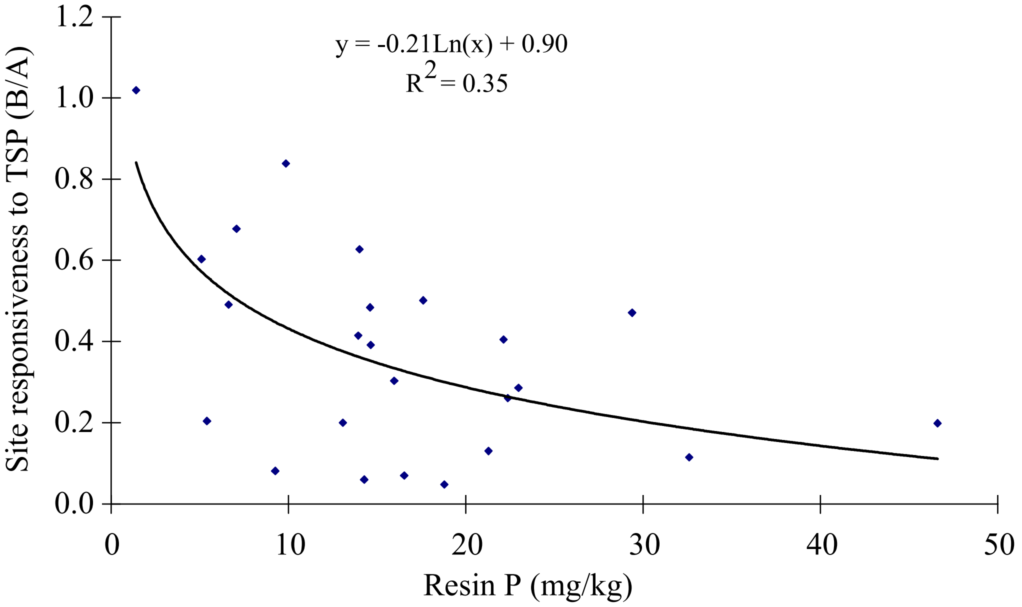

Fig. 10. Relation between Resin P values in unfertilized soil and subsequent response of pasture to addition of triple superphosphate (TSP).

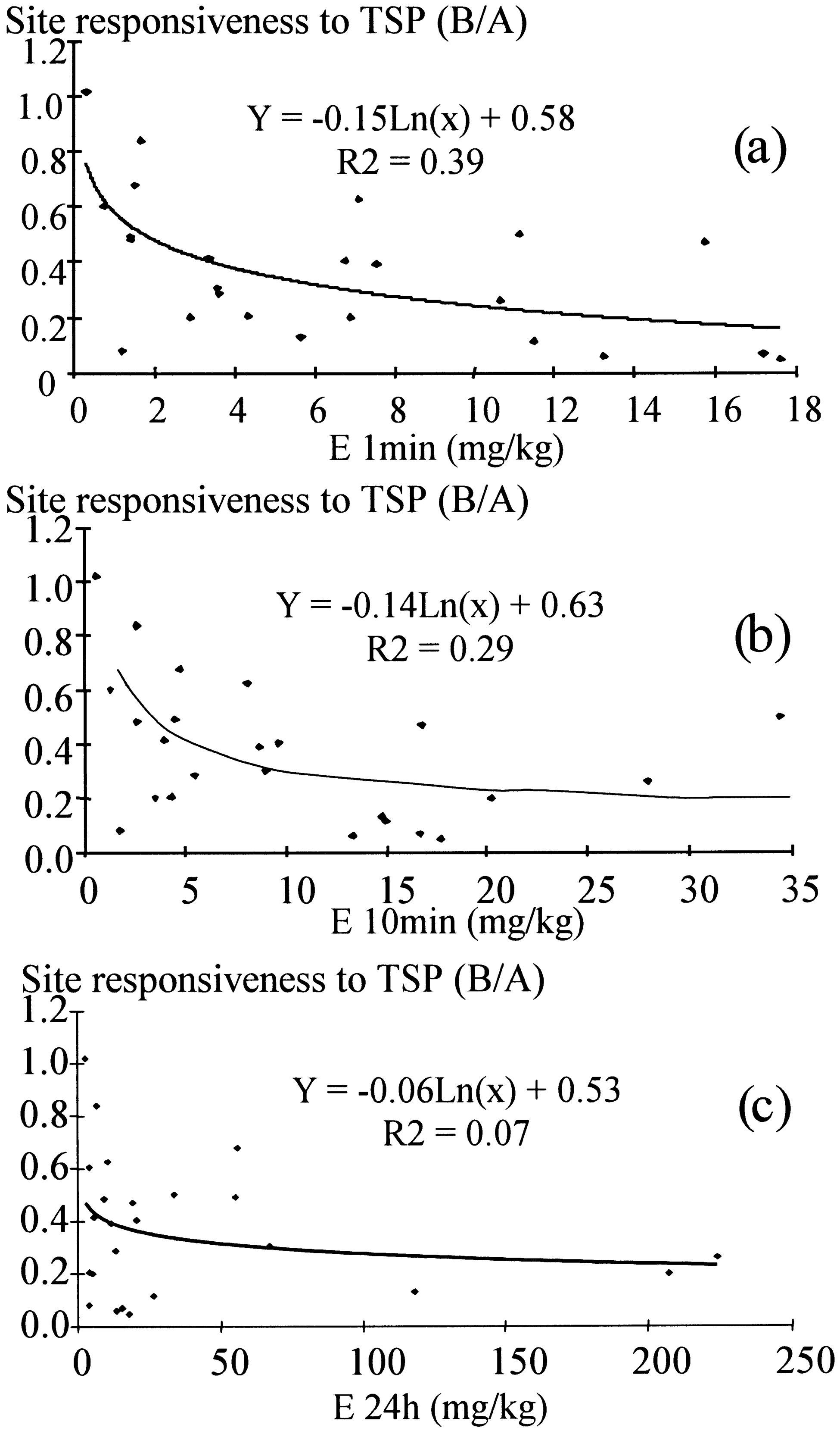

Fig. 11. Relation between isotopically-exchangeable P determined in unfertilized soil after 1 minute(a), 10 minutes (b), and 24 hours (c) equilibration and subsequent response of pasture to soluble P fertilizer addition.

REFERENCES

[1] COLWELL, J.D., The estimation of the phosphorus fertilizer requirements of wheat in southern New South Wales by soil analysis, Aust. J. Exp. Agric. Anim. Husb. **3** (1963) 190-197.

[2] OLSEN, S.R., COLA, C.V., WANTANABE, F.S., DEAN, L.A., Estimation of available phosphorus in soils by extraction with sodium bicarbonate, Circ. US Dep. Agric. (1954) No. 939.

[3] BRAY, R.H., KURTZ, L.T., Determination of total, organic and available forms of phosphorus in soils, Soil Sci. **59** (1945) 39-45.

[4] EGNER, The Lactate Method, (1963).

[5] IRVING, G.C.J., MCLAUGHLIN, M.J., A rapid and simple test for phosphorus in Olsen and Bray No.1 extracts of soil, Commun. Soil Sci. Plant Anal. **21** (1990) 2245-2255.

[6] FARDEAU, J.C., Le phosphore assimilable des sols: sa représentation par un modèle fonctionnel à plusieurs compartiments, Agronomie **13** (1993) 317-331.

[7] WOLF, A.M., BAKER, D.E., PIONKE, H.B., The measurement of labile phosphorus by the isotopic dilution and anion resin methods, Soil Sci. **141** (1986) 60-70.

[8] MCLACHLAN, K.D., The nature of available phosphorus in some acid pasture soils and a comparison of estimating procedures, Aust. J. Exp. Agric. Anim. Husb. **5** (1965) 125-132.

[9] SPENCER, K., BOUMA, D., MOYE, D.V., Assessment of the phosphorus and sulfur status of subterranean clover pastures, 2. Soil tests. Aust. J. Exp. Agric. Anim. Husb. **9** (1969) 320-328.

[10] HOLFORD, I.C.R., CROCKER, G.J., Efficacy of various soil phosphate tests for predicting phosphate responsiveness and requirements of clover pastures on acidic tableland soils, Aust. J. Soil Res. **26** (1988) 479-488.

[11] DEAR, B.S., HELYAR, K.R., MULLER, W.J., LOVELAND, B., The P fertilizer requirements of subterranean clover, and the soil P status, sorption and buffering capacities from two P analyses, Aust. J. Soil. Res. **30** (1992) 27-44.

[12] FIXEN, P.E., GROVE, J.H., Testing soils for phosphorus. In: R.L. Westermann (ed.), Soil Testing and Plant Analysis, Soil Science Society of America, Madison, (1990), 141-179.

EFFECT OF FERTILIZER TYPE ON CADMIUM AND FLUORINE CONCENTRATIONS IN CLOVER HERBAGE

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Abstract

This study investigated whether changing phosphatic fertilizer type affects the accumulation of cadmium (Cd) and fluorine (F) in pasture herbage. North Carolina phosphate rock and partially acidulated fertilizers derived from this rock generally have higher Cd and F concentrations compared to single superphosphate currently manufactured in Australia.

Clover herbage from sites of the National Reactive Phosphate Rock (RPR) trial was collected and analysed for concentrations of Cd (11 sites) and F (4 sites). A comparison was made between pastures fertilized with 4 rates of single superphosphate, North Carolina phosphate rock, and partially acidulated phosphate rock having Cd concentrations of 283, 481, and 420 mg Cd/kg P respectively, and 170, 271, and 274 g F/kg P respectively. One site used Hemrawein (Egypt) phosphate rock (HRP) having a Cd and F concentration of 78 mg Cd/kg P and 256 g F/kg P respectively. To help identify differences in herbage Cd concentrations between sites, unfertilised soils from each site were analyzed for total and extractable Cd contents. At one site Cd concentrations in bulk herbage (clover, grasses and weeds) were related to infestation of the pasture by capeweed (*Arctotheca calendula* L. Levyns).

There were no significant differences between F in herbage from plots fertilized with single superphosphate, partially acidulated phosphate rock or North Carolina phosphate rock, or between sites. Concentrations of F in herbage were low, generally less than 10 mg F /kg. However, there were large differences in Cd concentrations in herbage between sites, while differences between fertilizer treatments were small in comparison. The site differences were only weakly related to total or extractable (0.01 mol/L $CaCl_2$) Cd concentrations in soil.

Significant differences in Cd concentrations in clover due to fertilizer type were found at 5 sites. North Carolina phosphate rock treatments had significantly higher Cd concentrations in clover compared to single superphosphate at 2 sites. Partially acidulated phosphate rock treatments had significantly higher Cd concentrations in clover compared to single superphosphate at 4 sites. At the site where Hemrawein was tested, this treatment had significantly lower Cd concentrations in clover compared to both single superphosphate and North Carolina phosphate rock treatments.

1. INTRODUCTION

The use of phosphatic fertilizers on pastures has been demonstrated to increase Cd concentrations in soil [1-3]. In a national survey of “native” (non-agricultural) and pastoral (fertilised) soils in New Zealand, Roberts et al. [3] found that Cd concentrations were 0.20 mg/kg in the native soils and 0.44 mg/kg in the pastoral soils. They attributed the increase in soil Cd concentrations to the use of phosphatic fertilizers, principally single superphosphate (SSP), which contains high concentrations of Cd as an impurity. The elevated Cd concentrations in soil were not clearly reflected in herbage Cd concentrations, except in weed species.

Cadmium concentrations in SSP, reactive phosphate rock (RPR) and partially acidulated phosphate rock (PAPR) are primarily a function of the Cd concentration in the feed rock used in manufacture [4], with generally little Cd contributed from the sulfuric acid used for acidulation. Cadmium concentrations in RPRs may be different to that of the parent rock material, depending on the degree of physical treatment (washing, size sorting, etc.) prior to dispatch. Cadmium concentrations in SSP in Australia have declined over the last 20 years [4, 5], due presumably to changes in the source of rock raw materials used in manufacturing. Furthermore, limits on Cd concentrations in phosphatic fertilizers are being introduced in Australia. The State of Victoria recently adopted a limit of 350 mg Cd/kg P in phosphatic fertilizers [6], while other countries have already imposed much stricter limits [7].

This paper has been modified from the original article “Effect of fertilizer type on cadmium and fluorine concentrations in clover herbage” by McLaughlin, M.J., Simpson, P., Fleming, N., Stevens, D.P., Cozens, G. and Smart, M.K. in Aust. J. Expt. Agric. **37** 7 (1997) 1017-1026 by permission of CSIRO Publishing.

This Australian limit could prohibit the use of some RPRs, which have Cd concentrations exceeding this value.

Most RPRs also have high concentrations of F, often exceeding 3% by weight (250g F/kg P), while concentrations of F in SSP are lower due to losses of F during acidulation in the manufacturing plant [7]. Fluorine is a strongly sorbed element in most soils [8]. However, in extremely sandy or acidic soils F is more soluble [8, 9], and would potentially be available for plant uptake in conditions where RPR use is often regarded to be agronomically beneficial compared to soluble P fertilizers. Fluorine has been implicated in a number of incidents of injury to grazing stock through fluorosis [10].

Few data are available to determine if phosphatic fertilizer type plays any role in moderating or enhancing Cd or F uptake by herbage in grazed pastures. The aim of this study therefore, was to determine if use of SSP, RPR or PAPR has any significant effect on Cd and F concentrations in herbage.

2. MATERIALS AND METHODS

Eleven sites were used from the national RPR project evaluating RPRs in the high rainfall Mediterranean pasture environment of Australia [11]. These covered a wide range of soil/pasture/climate environments in 5 states across Australia; NSW (Armidale-N4 and N6, Yass-N7, Tarago-N8), Victoria (Benalla-V12, Warnambool-V13), Tasmania (Smithton-T16), South Australia (Wattle Range-S22, Nangwarry-S23, Kangaroo Island-S25) and Western Australia (Nornalup-W30). These sites were chosen on the basis that they represented the lighter-textured and more acidic soils, characteristics known to enhance Cd transfer from soil to plants [12]. Soils (0-100 mm) were acidic with pH (water) varying from 5.0 to 6.1, extractable P concentrations [13] varied from 7 to 19 mg/kg, organic C ranged from 1.6 to 3.8%. Fertilizers were applied to the trial sites from 1992 to 1995 at rates, which varied from site to site, being determined on the basis of plant response to P at each site. A scaling factor (X), was used, on the basis that a rate of 4X at each site should achieve 90% of maximum yield response to water-soluble P fertilizer under optimum conditions with a good clover component in the pasture sward. The scaling factor varied from 5 to 10 kg P/ha per annum across the sites. Treatments sampled were control (unfertilized) plots, and from plots treated with SSP, NCPR and PAPR at P rates of 2X, 4X and 8X, with total P applied to these plots varying from 40 to 320 kg/ha between 1992 and 1995. A more detailed description of soil characteristics, trial treatments and experimental design is given in Simpson *et al.* [11].

2.1. Fertilizer analyses

Samples of SSP, North Carolina phosphate rock (NCPR), PAPR (an experimental batch manufactured by 50% acidulation of NCPR with sulfuric acid) and Hemrawein PR (Egypt) (used at site W30) were analysed for total Cd concentration by X-ray fluoresence spectroscopy [14]. Full chemical characteristics of the fertilizers are presented in Simpson *et al.* [11].

Fluorine concentrations were determined by boiling 1 g fertilizer for 10 min with 140 ml of 2.5 M HCl in the presence of 5% (w/v) aluminium potassium sulfate. The solution was then made to volume and the F^-concentration in an aliquot determined by ion selective potentiometry using neutral (pH 7.0) ammonium citrate buffer.

2.2. Herbage sampling and preparation

Preliminary analysis of Cd concentrations in mixed herbage from four sites indicated a large variability in Cd concentrations between replicate plots (data not shown). This was assumed to be due to a mixed composition of pasture between plots, with varying weed composition leading to variable Cd data. Hence, a single species was chosen for comparisons between fertilizer treatments.

Clover herbage was sampled from selected treatments at sites N4, N6, N7, N8, S22, S23, S25, T16, V12, V13 and W30.

Clover plants were sampled by collecting the terminal and last 2 to 3 sets of leaflets of a stolon from approximately 40 to 50 stolons in the sward. Collection was carried out wearing rubber or surgical gloves to prevent contamination of the plant surfaces by dust or soil. Plants with any noticeable soil contamination were avoided. All plant material was washed in deionized water after collection. Plant material was dried at 40-60°C before dispatch to the laboratory for analysis.

Mixed samples of herbage (grasses, legumes and weeds) were also collected from one site (S25) as part of the normal herbage harvest for dry matter determinations as described by Simpson *et al.* [11]. This herbage was also analyzed for Cd as described below. A visual rating of the degree of infestation of the pasture on each plot by capeweed (*Arctotheca calendula* L. Levyns) was also taken.

All herbage samples were transported in sealed plastic bags and analyzed at the laboratories of the CSIRO Division of Soils in Adelaide. Dried clover material was ground to pass a 250μm stainless steel sieve prior to Cd and F analyses.

2.3. Cadmium analysis

A subsample (0.5g) of the ground dried herbage material was digested by boiling for 2 hours at 130°C with 7 mL concentrated Aristar® HNO_3 acid. The solution was then made up to volume with dilute (1% w/v) HNO_3 acid and Cd concentration in the solution determined by graphite furnace atomic absorption spectrophotometry (GFAAS). Analysis of standard reference materials gave Cd concentrations not significantly different from certified values [6]. All herbage Cd concentrations are expressed on a dry weight basis. The limit of reporting for Cd in herbage material was 0.004 mg/kg.

2.4. Fluorine analysis

Concentrations of acid-labile F in herbage were determined as described by Stevens *et al* [15]. Briefly, dried herbage material (0.1g) was digested with concentrated HNO_3 acid in sealed containers using microwave heating. Fluoride concentrations in the digest solutions were determined using ion selective potentiometry. This method does not solubilize all F in plant material, particularly F retained in crystalline silicates [15] that is unlikely to be solubilized in the rumen after ingestion by grazing animals.

2.5. Soil analyses

Simpson *et al.* determined the general chemical characteristics of the sites [11]. Total Cd concentrations in soil were determined by digesting 0.5 g sample with 8 mL concentrated nitric and hydrochloric acids (3:1) on a steam bath for 2 h. Cadmium was also extracted from soils using 0.01 mol/L $CaCl_2$ solution. Soil (5 g) was shaken for 4 h with 25 mL extracting solution at 20°C. In preliminary experiments, 4 h was found to be a sufficiently long extraction time to allow all desorbable Cd to be released to solution. The suspensions were then centrifuged (20 min at 4000 RCF) and filtered through a 0.45 μm filter. Concentrations of Cd in extracts or digest solutions were determined using GFAAS.

2.6. Data analysis

To examine differences between fertilizers, the relationship between the concentration of Cd or F in the clover tops and fertilizer type and rate was analysed using a factorial design ANOVA for each individual site, excluding data for control (unfertilized plots). To examine the effect of fertilization on Cd concentrations, a separate completely randomized design ANOVA was performed for each fertilizer type at each site, including data for control plots. Differences in Cd concentrations between sites were determined by examining the relationship between Cd concentrations in clover from control (unfertilized) plots and soil (0-100mm) characteristics using a factorial ANOVA and step-wise forward multiple regression analyses. To normalize the skewed distribution of the data sets, data were transformed (square root or logarithm) where appropriate.

3. RESULTS

Cadmium and F concentrations in the fertilizers are shown in Table I. Hamrawein PR had the lowest Cd concentration and Cd/P ratio, while NCPR and PAPR (manufactured with NCPR) had the highest.

TABLE I. CONCENTRATIONS OF Cd AND F IN THE FERTILIZERS USED. SSP, SINGLE SUPERPHOSPHATE; NCPR, NORTH CAROLINA PHOSPHATE ROCK; PAPR, PARTIALLY ACIDULATED PHOSPHATE ROCK; HPR, HEMRAWEIN PHOSPHATE ROCK
(REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

Fertilizer	Cd (mg/kg)	F (%)	P (%)	Cd/P (mg Cd/kg P)	F/P (g F/kg P)
SSP	15.1	1.7	10.0	151	170
NCPR	40.3	3.5	12.9	312	271
PAPR	32.0	2.9	10.8	296	274
HPR	5.3	3.2	12.5	42	256

3.1 Herbage Cd concentrations

Data for treatment means are shown in Table II. Cadmium concentrations (treatment means) in the clover herbage ranged from 0.019 (site T16) to 0.405 mg/kg (site V13), with overall mean and median values of 0.189 and 0.187 mg/kg, respectively. Site mean Cd concentrations ranged from 0.027 mg/kg at T16 to 0.372 mg/kg at V13.

There was considerable variation between replicate plots for mean Cd concentrations in clover at most of the sites (data not shown), with the coefficient of variation (CV) for treatment mean values varying from 0.3% to 107%, with an overall mean CV across all sites and treatments of 20%. Site V13 had the least variability (mean CV 9%) and T16 the greatest (mean CV 35%).

Results from the ANOVA examining fertilizers and rate effects at each site are shown in Table III. At 4 of the 11 sites, rate of fertilizer applied had a significant effect on clover Cd concentrations, although variability between replicate plots was often high (>20%) (Fig. 1).

While higher rates of fertilizer addition resulted in higher Cd concentrations in clover at 3 sites (N6, N8, V12), at site N4 higher rates of fertilizer addition reduced clover Cd concentrations (Table III). Significant differences in Cd concentrations in clover due to fertilizer type were found at 5 sites. NCPR treatments had significantly higher Cd concentrations in clover compared to SSP at sites N6 and S25. PAPR treatments had significantly higher Cd concentrations in clover compared to SSP at sites N6, N7, S23, and S25. At site W30, Hemrawein PR treatments had significantly lower Cd concentrations in clover compared to both SSP and NCPR treatments (Table III).

Effects due to site accounted for the most variation in herbage Cd concentrations (Table IV). The relationship between the visual assessment of capeweed infestation and herbage Cd concentrations is shown in Fig. 2.

3.2. Herbage F concentrations

A National Instituite of Standards Testing (NIST) certified reference material (NIST SRM 2695h) analysed by the acid digestion technique used here gave a value of 181±7 mg/kg, while the certified value is 277±27 mg/kg. The low recovery using acid digestion is similar to the result found by [15], and is probably due to the presence of insoluble fluorosilicates in the NIST standard. We preferred the acid digestion technique for this study as the acid-labile fraction is likely to be the fraction most readily bioavailable for grazing animals.

Herbage F concentrations were extremely low (<10 mg/kg), often near the detection limit for the analysis technique (1 mg/kg). There were no consistent effects due to either fertilizer type or rate (data not shown).

3.3. Relationships between herbage Cd concentrations and soil characteristics

Total and extractable Cd concentrations are shown in Table V. Clover Cd concentrations were unrelated to all soil chemical characteristics, except total (data not shown) and extractable Cd concentrations (Fig. 3), but this relationship was poor ($R^2<0.31$, $P = 0.12$).

4. DISCUSSION

The concentrations of Cd in the NCPR and PAPR fertilizers were high in comparison to the SSP and Hemrawein PR fertilizers. The Cd/P ratio in these fertilizers approached the current regulatory standard of 350 mg Cd/kg P in Victoria for phosphatic fertilizers [6]. The Cd concentration for NCPR found here is slightly lower than those found previously [5] and those reported in the literature [17]. Further Cd and P analyses for NCPR were undertaken at 1 and 2 other commercial laboratories, respectively, yielding Cd and P concentrations of 40.6 mg/kg and 11.9 and 10.2%, respectively. These data result in calculated Cd/P ratios for NCPR of 312 to 545 mg Cd/kg P. Some standardization of laboratory methods is needed to ensure Cd and P concentrations in fertilizers are accurately determined since legislation may prohibit certain products from the market based on Cd/P ratios. It is evident that the Cd/P ratio of NCPR falls close to the current Victorian regulations. Other States are in the process of adopting regulations for Cd in fertilizers, which are likely to be similar to the Victorian levels.

Fertilizer type had a significant effect on clover Cd concentrations at 5 sites, with SSP-treated plots (or Hemrawein PR-treated plots at site W30) having lower Cd concentrations in clover than NCPR- and PAPR-treated plots. However, the significant differences between fertilizers were small and variability between replicate plots was high. Where present, differences between treatments were generally in line with Cd concentrations in the fertilizers, SSP treatments having lower Cd concentrations in clover than PAPR or NCPR treatments.

The treatments sampled represented the upper end of the fertilizer rates commonly used by most grazers (up to 8 times maintenance), yet only small differences in Cd concentrations in clover herbage resulted. Hence it can be concluded that a switch from SSP, containing approximately 150 mg Cd/kg P, to NCPR or PAPR (which contain twice this Cd concentration), will only have a small impact on clover Cd concentrations in the short and medium term. In the long-term however, the higher Cd fertilizers will obviously allow Cd concentrations in soil to increase more rapidly with time with an associated greater risk of increasing Cd concentrations in the herbage and in grazing animals.

As fertilizer type was not independent of fertilizer Cd concentration, no conclusions can be drawn regarding the effect of fertilizer type *per se* on Cd uptake by clover. For example, the availability of Cd present in NCPR or PAPR cannot be assessed relative to Cd present in SSP in these experiments. There are few other data to assess the effect of fertilizer type on plant Cd concentrations. McLaughlin *et al.* [18] examined the effect of 4 types of phosphatic fertilizer (SSP, RPR, diammonium phosphate and monoammonium phosphate) having similar Cd/P ratios on Cd uptake by irrigated potatoes, and found no significant effects. The chemical form of Cd in SSP, RPRs or PAPRs has not yet been clearly identified. Williams and David [1] found granules of SSP in moist soil lost all of their water-soluble P content and still retained 60% of their original Cd content. Williams and David [1] found that concentrations of Cd in the water extracts of the soil were approximately proportional to the soil Ca concentrations, indicating Cd was associated with Ca in both the phosphate and sulfate components of the fertilizer. While there is no evidence to indicate the form of Cd in RPRs, Cd in the rock is presumably substituted for Ca in the crystal lattice (Cd has a similar ionic radius and charge to Ca). The alkaline nature of RPRs [19] may reduce Cd dissolution from the crystal lattice and increase Cd sorption close to the dissolving RPR granule, as Cd sorption to soil is strongly increased as solution pH increases [20]. Further experimentation is needed to determine if Cd in RPR fertilizers is less available to crops than Cd in water-soluble fertilizers.

Fluorine concentrations in all herbage samples were within the range (2-20 mg F/kg) generally considered as background for non-accumulator plants grown in soil free from anthropogenic F

TABLE II. CONCENTRATIONS OF CADMIUM (mg/KG DRY WEIGHT) IN CLOVER SHOOT MATERIAL AT THE SITES. N4, N6, ARMIDALE; N7, YASS; N7, TARAGO; V12, BENALLA; V13, WARNAMBOOL; T16, SMITHTON; S22, WATTLE RANGE; S23, NANGWARRY; S25, KANGAROO ISLAND; W30, NORNALUP. VALUES ARE TREATMENT MEANS (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16]).

Treatment	Rate	N4	N6	N7	N8	S22	S23	S25	T16	V12	V13	W30
Control		0.124	0.074	0.215	0.158	0.253	0.281	0.237		0.257	0.404	0.061
SSP	2X	0.154	0.066	0.190	0.096	0.186	0.271	0.187	0.024	0.232	0.330	0.084
SSP	4X	0.165	0.068	0.214	0.103	0.154	0.221	0.177	0.020	0.273	0.346	0.123
SSP	8X	0.172	0.081	0.255	0.112	0.187	0.256	0.188	0.057	0.291	0.393	0.148
NCPR	2X	0.185	0.084	0.195	0.108	0.194	0.264	0.313	0.021	0.240	0.400	0.112
NCPR	4X	0.167	0.084	0.214	0.076	0.207	0.225	0.266	0.020	0.217	0.405	0.111
NCPR	8X	0.143	0.109	0.208	0.126	0.262	0.240	0.303	0.021	0.304	0.356	0.146
PAPR	2X	0.174	0.078	0.271	0.091	0.170	0.277	0.303	0.019	0.239	0.381	0.079
PAPR	4X	0.207	0.092	0.240	0.127	0.176	0.296	0.241	0.031	0.271	0.356	0.078
PAPR	8X	0.129	0.078	0.288	0.151	0.192	0.329	0.222	0.035	0.302	0.352	0.072
Site means		0.162	0.081	0.229	0.115	0.198	0.266	0.244	0.027	0.263	0.372	0.101

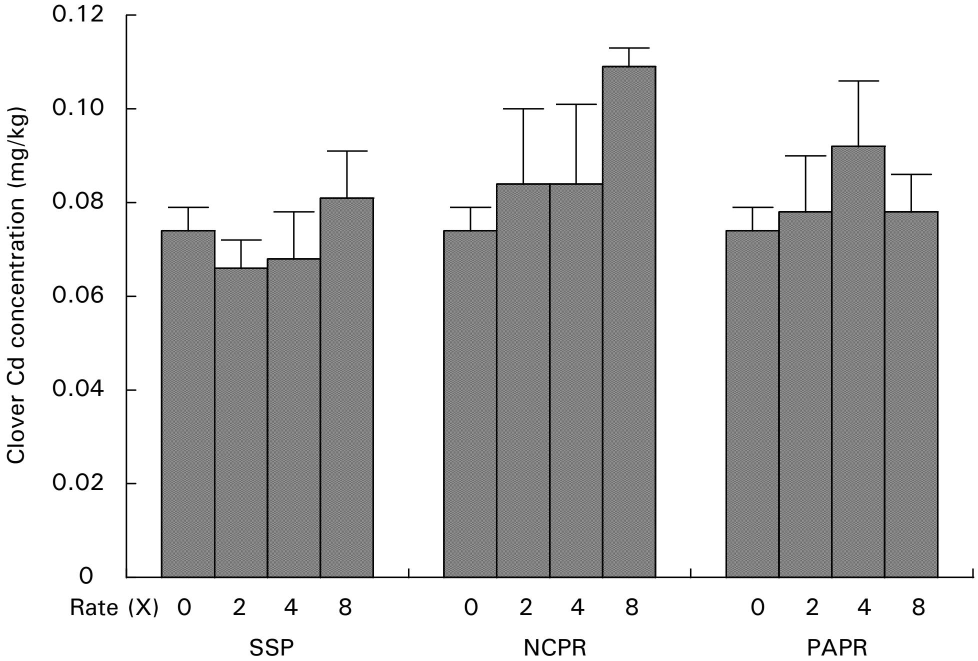

Fig. 1. Effect of addition of SSP, NCPR, and HPR on Cd concentrations in clover shoots at site N6 (Reprinted with the permission of CSIRO Publishing, [16]).

TABLE III. SUMMARY OF ANOVA RESULTS FOR EACH SITE ANALYSED USING A FACTORIAL DESIGN (RATE*FERTILIZER) (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

	ANOVA[1]		
Site	Rate	Fertilizer	Rate*Fert.
N4	**	n.s.	n.s.
N6	*	***	*
N7	n.s.	**	n.s.
N8	*	n.s.	n.s.
V12	**	n.s.	n.s.
V13	n.s	n.s.	n.s.
T16	n.s.	n.s.	n.s.
S22	n.s.	n.s.	n.s.
S23	n.s.	*	n.s.
S25	n.s.	**	n.s.
W30[2]	n.s.	*	n.s.

[1] n.s., not significant, * $p<0.05$, ** $p<0.01$, *** $p<0.001$.

[2] no PAPR at site W30, data for Hemrawein used.

TABLE IV. RELATIONSHIP OF SOIL CHARACTERISTICS (0-100 mm STRATUM) TO CLOVER Cd CONCENTRATIONS ACROSS ALL SITES (CONTROL TREATMENTS ONLY) (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

Source	Degrees of Freedom	Sum of Squares	Mean Square	F value	Probability[1]
Rate (A)	2	0.047	0.023	2.12	ns
Fertilizer (B)	2	0.134	0.067	6.09	**
Site (C)	7	23.683	3.383	306.95	***
Block (D)	2	0.033	0.017	1.51	ns
A*B	4	0.070	0.018	1.59	ns
A*C	14	0.198	0.014	1.59	ns
B*C	14	0.264	0.019	1.28	ns
A*B*C	28	0.240	0.009	1.71	ns
Residual	134	1.477	0.011	0.78	
Total	207	26.147			

[1] n.s., not significant, * $p<0.05$, ** $p<0.01$, *** $p<0.001$.

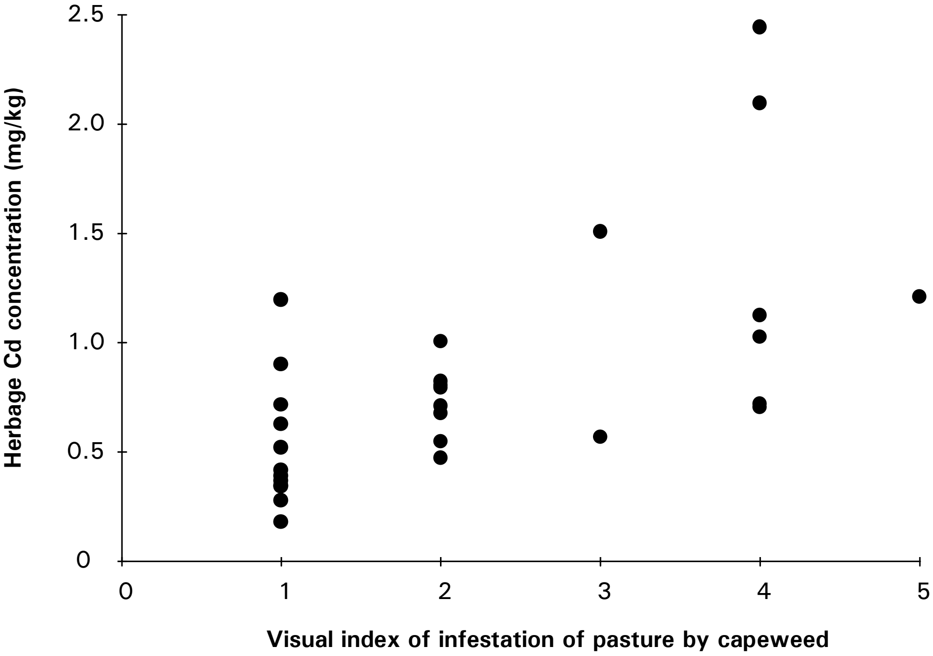

Fig. 2. Relationship between herbage Cd concentration and visual index of infestation of pasture by capeweed (Arctotheca calendula L. Levyns) at site S25 (Reprinted with the permission of CSIRO Publishing [16]).

TABLE V. TOTAL AND EXTRACTABLE (0.01 mol/L $CaCl_2$) Cd CONCENTRATIONS IN UNFERTILIZED SOILS (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

Site	Extractable-Cd (µg/kg)	Total-Cd (µg/kg)
N4	5.3	59
N6	2.8	65
N7	10.7	46
N8	10.5	42
S22	13.5	n.d.[1]
S23	12.5	58
S25	4.0	52
T16	1.2	n.d.
V12	15.0	96
V13	10.2	227
W30	n.d.	n.d.

[1] n.d., not determined.

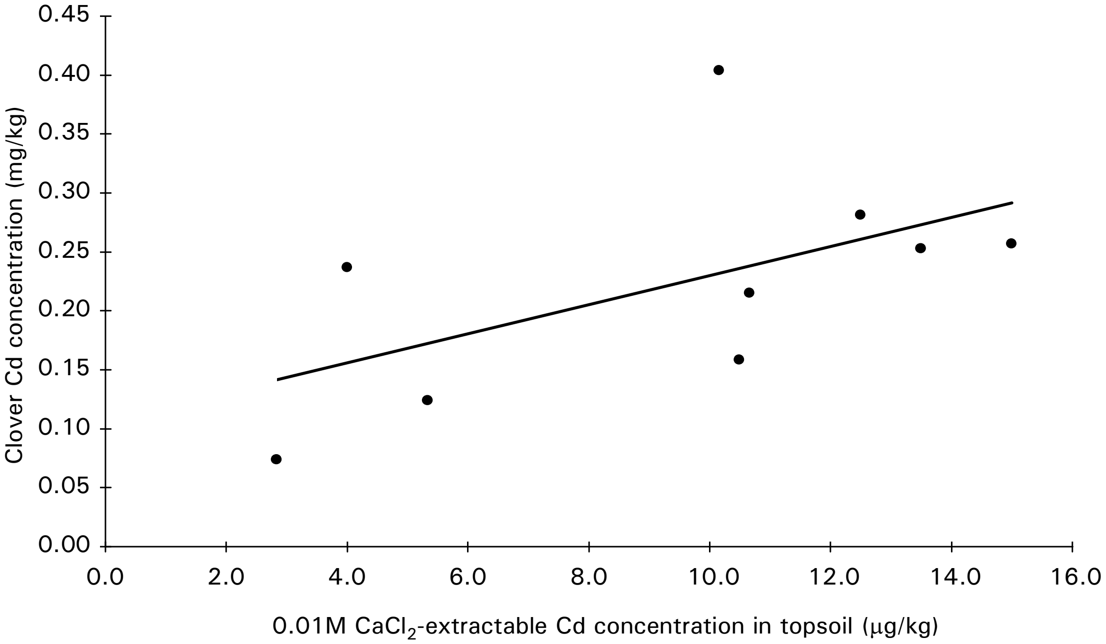

Fig. 3. Relationship between herbage Cd concentration and visual index of infestation of pasture by capeweed (Arctotheca calendula L. Levyns) at site S25 (Reprinted with the permission of CSIRO Publishing [16]).

contamination [21], and were unaffected by fertilizer type or rate. Plant uptake of this element is unlikely to lead to problems for grazing animals in most soils [22]. It has been suggested that the maximum level for F in herbage to protect livestock health should be 35 mg/kg or less [23], with the concentrations found in this study being well below this level. However, ingestion of soil by animals or ingestion of fertilizer material remaining on herbage after heavy topdressing could affect animal health depending on soil and fertilizer F concentrations [24], so that F in fertilizers may require more careful management in the long term. For every kg P applied up to 250 g F are applied per hectare in phosphatic fertilizers [8], with RPRs generally having higher F concentrations than SSP or high analysis P fertilizers. This F does not readily leach and, like Cd, is therefore slowly accumulating in all fertilized agricultural soils [25]. Ingestion of soil may not be a problem currently in terms of F intake by grazing animals, but as F concentrations in the top few centimetres of soil increase due to fertilization, this could pose problems in the future. With a fertilization regime of 10 kg P/ha every 2 years, a F content in fertilizer of 250 g F/kg P, a F concentration in soil of 200 mg/kg [25], and a soil bulk density (0-2 cm) of 1000 kg/m^3, F concentrations would double in 30 years in the top 2 cm of soil. Negative impacts on animal health are difficult to predict and depend to a large extent on patterns of soil ingestion, which is affected by ground cover. Soil ingestion may be significant over dry summer periods in southern Australia, at high stocking rates, and where drought or other stresses (e.g. acidity, salinity, nutrient deficiencies) reduce ground cover. As far as we are aware, there are no data on soil ingestion in southern Australia under field conditions representative of commercial properties. However, data from New Zealand [26] indicate soil ingestion by sheep grazing perennial pastures ranged from 11 to 275 g/day, peaking in winter, presumably due to soil splash, while soil ingestion by dairy cattle may be over 600 g/day [27]. In the Mediterranean climate of southern Australia, it soil ingestion is most likely during summer and autumn when pasture cover is at a minimum, and amounts of soil ingestion may be greater than those reported by [26]. Using a soil intake figure for 1 year old sheep of 250 g/day [26], F concentrations in herbage and soil of 10 and 300 mg/kg, and a DM intake of 1000 g/day [26], ingestion of soil and pasture would provide 75 and 10 mg F/day, respectively. Soil F concentrations are therefore critical in determining F intake by grazing animals, and the continued accumulation of F in grazing soils may pose some concern from an animal health viewpoint where significant ingestion of soil is likely to occur.

It is unknown if the solubility of F in RPR and SSP differs, but it is likely that the F present in SSP is present as CaF_2, which is likely to be more soluble in soil than the F in phosphate rocks. It is therefore possible that with continued use of RPRs the amount of (water-insoluble) F remaining on herbage or at the soil surface may be greater than with SSP, where F may more readily penetrate into the soil. If undissolved RPR remaining on the soil surface is ingested in significant quantities by animals, fluorosis problems could result. However, there is little information available on the bioavailability of F compounds found in SSP and phosphate rock once ingested. Zipkins and Likins [28] and Tsunoda *et al.* [29] found that gastrointestinal absorption of F by rats and humans depended on the forms of F ingested (i.e. CaF_2, NaF, KPF_6).

Clover was chosen as the indicator species in this study as clover is the most desirable component of a mixed pasture sward and grazers generally manage their pastures to maximize (within limits) the percentage clover component in the pasture. The clover Cd concentrations found in this study fall within the range reported by Roberts *et al.* [3] for Cd in mixed legume herbage at 398 sites in New Zealand. Grasses tend to have lower Cd concentrations than legumes, while weed species usually have higher Cd concentrations than both grasses or legumes [2, 3]. As expected, there appeared to be some relationship between the visual assessment of capeweed infestation of the pasture and herbage Cd concentrations at site S25 (Fig. 2), which confirms earlier findings with this weed species [2,30]. Hence, infestation of pastures by capeweed will also lead to higher concentrations of Cd in the herbage ingested by the grazing animals. Thus, the impact of fertilizer type and grazing management on pasture composition is likely to have a much greater effect, in the short and medium term (up to 10 years), on Cd ingested by grazing animals rather than the Cd concentration in the fertilizer. Hence, management of Cd accumulation in grazing systems in Australia needs to be a combination of measures, which includes control of pasture composition to reduce Cd uptake by animals in the short-term, and use of low Cd fertilizers to control Cd accumulation in the long term.

REFERENCES

[1] WILLIAMS, C.H., DAVID, D.J., The effect of superphosphate on the cadmium content of soils and plants, Aust. J. Soil Res. **11** (1977) 43-56.

[2] MERRY, R.H., Investigations on cadmium in South Australia: Rainfall, soils, cereals, pastures and soil-plant interactions, In: J. Simpson, B. Curnow (eds.), Cadmium Accumulations in Australian Agriculture: National Symposium, Canberra. Australian Government Publication Service, Canberra (1988), 62-79.

[3] ROBERTS, A.H.C., LONGHURST, R.D., BROWN, M.W., Cadmium status of soils, plants, and grazing animals in New Zealand. NZ, J. Exp. Agric. **37** (1994) 119-129.

[4] WILLIAMS, C.H., Trace metals and superphosphate: toxicity problems, J. Aust. Inst. Agric. **3-4** (1977) 99-109.

[5] CORRY, H., BERG, G., SHELLEY, B., PEVERILL, K., Survey of heavy metal contaminants in fertilizers and soil amendments, In: Victorian Department of Agriculture Research Report, Agriculture Victoria, Melbourne, (1993), Series 147, 17.

[6] ANON, Agricultural and Veterinary Chemicals. Fertilizer Regulations 1995, Government Printer, Victoria, (1995).

[7] McLAUGHLIN, M.J., TILLER, K.G., NAIDU, R., STEVENS, D.P., Review: The behavior and environmental impact of contaminants in fertilizers, Aust. J. Soil Res. **34** (1996) 1-54.

[8] BARROW, N.J., ELLIS, A.S., Testing a mechanistic model. III. The effects of pH on fluoride retention by a soil, J. Soil Sci. **37** (1986) 287-293.

[9] OMUETI, J.A.I., JONES, R.L., Fluoride adsorption by Illinois soils, J. Soil Sci. **28** (1977) 564-572.

[10] JUBB, T.F., ANNAND, T.E., MAIN, D.C., MURPHY, G.M., Phosphorus supplements and fluorosis in cattle — a northern Australian experience, Aust. Vet. J. **70** (1993) 379-383.

[11] SIMPSON, P.G., SALE, P.W.G., HEPWORTH, G., GILBERT, M., BLAIR, G.J., GARDEN, D., DANN, P.R., HAMILTON, L., STEWART, J., HUNTER, J., CAYLEY, J., WARD, G., JOHNSON, D., LEWIS, D., FLEMING, N., BOLLAND, M.D.A., GILKES, R.J., McLAUGHLIN, M.J., The national reactive phosphate rock project – aims, experimental approach, and site characteristics, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 885-895.

[12] CHANEY, R.L., HORNICK, S.B., Accumulation and effects of cadmium on crops. In: Proceedings of the First International Cadmium Conference, San Francisco, Metals Bulletin Ltd, London, (1978), 125-140.

[13] COLWELL, J.D., The estimation of the phosphorus fertilizer requirements of wheat in southern New South Wales by soil analysis, Aust. J. Exp. Agric. Anim. Husb. **3** (1963) 100-107.

[14] NORRISH, K., HUTTON, J.T., Plant analyses by X-ray spectrometry. I. Low atomic number elements, sodium to calcium, X-ray Spect. **6** (1977) 6-11.

[15] STEVENS, D.P., McLAUGHLIN, M.J., ALSTON, A.M., Limitations of acid digestion techniques for the determination of fluoride in plant material, Commun. Soil Sci. Plant Anal. **26** (1995) 1823-1842.

[16] McLAUGHLIN, M.J., SIMPSON, P., FLEMING, N., STEVENS, D.P., COZENS, G. AND SMART, M.K., Effect of fertilizer type on cadmium and fluorine concentrations in clover herbage, Aust. J. Expt. Agric. **37** (1997) 1017-1026.

[17] SYERS, J.K., MACKAY, A.D., BROWN. M.W., CURRIE, L.D., Chemical and physical characteristics of phosphate rock materials of varying reactivity, J. Sci. Food Agric. **37** (1986) 1057-1064.

[18] McLAUGHLIN, M.J., MAIER, N.A., FREEMAN, K., TILLER, K.G., WILLIAMS, C.M.J., SMART, M.K., Effect of potassium and phosphatic fertilizer type, phosphatic fertilizer Cd content and additions of zinc on cadmium uptake by commercial potato crops, Fert. Res. **40** (1995) 63-70.

[19] LEWIS, D.C., HINDELL, R.P., HUNTER, J., Effect of phosphate rock products on soil pH, In: P. Sale, P. Simpson, C. Anderson, L. Muir (eds.), The Role of Reactive Phosphate Rock Fertilizers for Pastures in Australia. CSIRO Publishing, Melbourne, (1997), 1003-1008.

[20] GARCIA-MIRAGAYA, J., PAGE, A.L., Influence of ionic strength and inorganic complex formation on sorption of trace amounts of cadmium by montmorillonite, Soil Sci. Soc. Am. J. **40** (1976) 658-663.

[21] WEINSTEIN, L.H., Fluoride and Plant Life, J. Occupa. Med. **19** (1977) 49-78.

[22] STEVENS, D.P., McLAUGHLIN, M.J., ALSTON, A.M., Uptake of fluoride by plants from fluoride-polluted soils, in: First International Conference on Contaminants in the Soil Environment in the Australasia-Pacific Region (Proceedings), Adelaide, (1996), 63-64.

[23] NATIONAL RESEARCH COUNCIL, Effects of fluorides on animals. In: Committee on biological effects of atmospheric pollution. Division of Medical Science, Washington DC, National Academy of Sciences, (1974).

[24] STEWART, D.J., MANLEY, T.R., WHITE, D.A., HARRISON, D.L., Fluorine residues on pasture, in soil, and in sheep urine, resulting from topdressing with superphosphate, NZ J. Exp. Agric. **2** 2 (1974) 129-133.

[25] McLAUGHLIN, M.J., Unpublished results, Commonwealth Scientific and Industrial Research Organization, Division of Land and Water, Adelaide.

[26] LEE, J., ROUNCE, J.R., MACKAY, A.D., GRACE, N.D., Accumulation of cadmium with time in Romney sheep grazing ryegrass-white clover pasture: effect of cadmium from pasture and soil intake, Aust. J. Soil Res. **47** (1996) 877-894.

[27] HEALY, W.B., Ingestion of soil by dairy cows, NZ J. Agric. Res. (1968) 487-499.

[28] ZIPKIN, I., LIKINS, R.C., Absorption of various fluorine compounds from the gastrointestinal tract of the rat, Amer. J. Physiol. **191** (1957) 549-550.

[29] TSUNODA, N., SAKURAI, S., TSUNODA, H., Gastrointestinal absorption of fluoride in Humans – a comparative study of NaF and CaF_2. In: H. Tsunoda, M.H. Yu (eds.), Studies in Environmental Science 27: Fluoride Research. Elsevier Science Publishers B.V., Amsterdam, Netherlands, (1985), 389-393.

[30] BRAMLEY, R.G.V., BARROW, N.J., Differences in the cadmium content of some Western Australian pasture plants, Fert. Res. **39** (1995) 113-122.

LONG TERM CHANGES IN CADMIUM BIOAVAILABILITY IN SOIL

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Abstract. A study was conducted to examine changes in total and phytoavailable Cd in a soil, which had received inputs of Cd due to fertilization with single superphosphate (SSP) at various rates since 1948. Accumulation of Cd in the soil was highly correlated to application rate of SSP. No evidence was found to indicate offsite movement of Cd, either through horizontal transfer or via leaching through the profile. Increases in soil Cd led to an increase in the Cd content of wheat, which was grown in the soil. However, using a radioisotope dilution technique, a significant proportion of the added Cd was found to exist in a non-bioavailable pool in the soil. A model was developed which estimated that Cd was being fixed in this soil at a rate of 1 to 1.5 % of total Cd added per year.

1. INTRODUCTION

Applications of phosphate fertilizers, which contain Cd as an impurity, are largely responsible for the increasing Cd load in agricultural soils worldwide [1]. The long-term sustainability of this practice is limited by the strict maximum permissible concentrations (MPC) of Cd allowed in crops for human consumption (eg. 0.1 mg kg^{-1} for staple crops in Australia [2]). While total concentrations of Cd are steadily increasing in soils, it is unknown whether this will lead to a proportionate increase in concentrations of Cd in crops as total concentrations of Cd in soils are often a poor indicator of Cd phytoavailability [3, 4].

One factor, which may reduce Cd phytoavailability, is fixation of Cd in soil pools that are inaccessible to plants. Significant reductions in the long-term plant availability of Zn, a metal considered to have similar chemical behavior in soils to Cd, are recognized [5]. The mechanisms responsible for declines in Zn availability have not been conclusively established, but may involve migration into micropores [6] or movement of Zn into the soil matrix through other solid phase diffusion processes [7]. Soil aging has also been demonstrated to lead to increased Cd sorption to soils [8,9,10] but the direct effect of this on Cd phytoavailability was not ascertained in these studies.

The aim of this study was to determine whether the phytoavailability of Cd could decline with time due to fixation of Cd in the soil.

2. MATERIALS AND METHODS

2.1. Soil

Soil (clay loam, Plinthic Paleustalf) from experimental field plots at Armidale NSW (Upper Kirwans Sites [11]) was sampled in 1995 to a depth of 10 cm using a stainless steel auger. Since 1948 the plots have received different application rates of single superphosphate (SSP) and hence the soil from these plots was expected to contain different concentrations of Cd. Specifically; plots used in the current experiment had annual applications equivalent to 62.5, 125, 250 kg SSP/ha. In 1975 the plots were split such that fertilizer applications were terminated on one half (rundown (R) plots) while the same application rates of fertilizers were maintained on the other half of each plot until the present time (continuous (C) plots). Pasture species are established on the plots, which have also been individually grazed by sheep since 1952 [12]. The air-dried soil was sieved to less than 2 mm using a stainless steel sieve. The sieved soil was spiked with a solution of carrier free ^{109}Cd to give a final mean soil activity of 245 (s.d.= 21) kBq/kg, and thoroughly mixed. Moist soil (equivalent to 240 g dry weight) was then

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placed into acid-washed plastic pots and the moisture content increased to 50% of the water holding capacity. The pots were covered, and left to incubate in the dark in a controlled environment growth chamber (15/20°C, 8/16 hr), for two weeks until seeds were sown. Three replicates of the R and C soils receiving 62.5 or 250 kg SSP/ha were potted and six replicates of the intermediate (125 kg/ha) SSP treatments were potted. Samples of soil (0.25 g) from each of the treatments were digested in hot concentrated $HNO_3/HClO_4$ (3:1 v/v) and Cd concentrations determined as described below.

2.2. Plants

Seeds of wheat (*Triticum turgidum* cv. Yallaroi) were sown in the spiked soil and thinned following seedling development to remove late germinating or unhealthy seedlings. Plants were grown in a controlled environment growth chamber (15/20 °C, 8 hr dark/ 16 hr light). The moisture content was maintained at 50% of the water holding capacity by watering daily with deionized H_2O. The amount of water lost through transpiration was calculated by deducting the amount lost by evaporation (measured by weighing two unplanted control pots of soil) from the daily weight loss of the planted pots. Nutrients (AR grade) were provided in the water replenishing that lost through transpiration. The nutrients added in this solution were: KNO_3 (6.5 mM), NH_4NO_3 (7.5 mM), $MgSO_4$ (2 mM), KH_2PO_4 (0.2 mM).

Plant shoots were harvested 28 days after sowing, at which time there was sufficient material for analysis. Plants were rinsed in deionized H_2O and then dried at 80°C for 16 hours, the dry weights were recorded and the plants were then ground using an agate mortar and pestle. Samples of ground plant material (0.5-1 g) were then digested in hot, concentrated HNO_3 (5 mL).

2.3. Analyses

Following acid digestion, plant and soil samples were made up to 20 mL using acidified, deionized H_2O and stored at 4°C until analysis. Inclusion of plant and soil certified reference material with each of the digests ensured reliability of the final results. The Cd concentrations in the digest solutions were determined using a graphite furnace atomic absorption spectrophotometer (GFAAS) with deuterium background correction and orthophosphoric acid as a modifier. The activity of ^{109}Cd soil and plant digests was assessed by γ- spectroscopy.

2.4. Labile Cd

The amount of soil Cd available for uptake by the plants (labile Cd) (*L*) was calculated according to the method of Larsen [14] as follows:

$$\% L = [\text{specific activity of } Cd_{soil} \text{ (Bq/ug)/specific activity of } Cd_{plant} \text{ (Bq/ug)}] \times 100 \quad (1)$$

This approach assumes that the added ^{109}Cd equilibrates with the immediately phytoavailable Cd in the soil, which in soils with $pH < 7$ is composed primarily of aqueous and easily exchangeable forms of the metal [14]. Hence, the radioisotope is diluted by the phytoavailable unlabelled soil Cd with the end result being the larger the phytoavailable pool of soil Cd, the lower the specific activity of Cd in the plant with respect to the specific activity of Cd in the spiked soil. The method also requires that the contribution of seed Cd to the final total plant concentration of Cd be minimal. In the present experiment, Cd in the seed contributed less than 5% to the total amount of Cd taken up by the plant.

3. RESULTS AND DISCUSSION

3.1. Soils

Application of superphosphate at different rates appeared to have no effect on soil pH with the mean value (± std. error) for all the plots found to be 5.95 ± 0.08. The total cadmium concentration of soils from the R and C series ranged from 0.05 to 0.20 and 0.10 to 0.35 mg Cd kg^{-1} soil respectively (Table I). A nominal background concentration of Cd of 0.026 mg kg^{-1} was determined in soil collected adjacent to the plots which had not received any direct inputs of phosphatic fertilizer.

When this background concentration was subtracted from the total Cd concentration in soil from each of the plots, a linear correlation was found between soil Cd and rate of application of SSP (Fig. 1).

The approximate annual Cd input rates were calculated by dividing the background corrected total soil concentrations of Cd by the number of years of SSP application (27 or 47 years, R and C plots respectively) (Table I). Visual inspection of the plots at the time of sampling the soil indicated that different plant species dominated on different fertilizer treatments. However neither plant composition differences, nor the fact that sheep grazed the plots appear to have had any effect on the total content of Cd in individual plots, as evidenced by the excellent linear fit obtained in Fig. 1. Moreover the linearity of the data in Fig. 1 provides a strong indication that the concentration of Cd in the SSP applied to these plots did not change significantly during the last 20 years of application. If Cd concentrations in the fertilizer had decreased, then the slope of the relationship for the C plots data would have been lower than the slope for the R plots data. Similarly, there appears to have been no movement of Cd down the soil profile or off-site for at least the last 20 years. The calculated annual increase of soil Cd at a given rate of SSP was not significantly lower ($P > 0.7$) in R plots compared to C plots (Table I). This suggest there was no movement of Cd down the soil profile or off-site for at least the last 20 years.

Assuming a bulk density of 1.4 Mg/m^3 for this soil, and no significant movement of Cd from the 10 cm surface layer, an estimation of the concentration of Cd in the applied SSP of 40 mg/kg was obtained. This value falls in the middle of the range of Cd concentrations (25-50) reported for SSP in use in Australia [15]. The absence of significant loss of Cd from the soil surface due to leaching or removal of crops is consistent with data from several studies. For example, Chang et al. [16] observed no decrease in Cd concentration from sludge-amended soils up to 9 years after termination of sludge treatment. Loganathan and Hedley [17] found that even on highly fertilized pasture in highly acidic soils and in a high rainfall environment, Cd applied over 10 years in phosphate fertilizers was retained in the top 12 cm of the soil profile. Calculations by McGrath [18] have estimated that the residence time for Cd in soils is in the order of thousands of years.

3.2. Plants

Plant growth was different between soils, with increased yields noted in soils from plots, which had received the highest rates of SSP application (Table I). The total concentration of Cd in the wheat increased with increasing concentration of Cd in the soil. Cadmium concentrations in the wheat ranged from 0.19 mg/kg (plot 62.5 R) to 1.40 mg/kg (plot 250 C). A curvilinear relationship between concentration of Cd in the plants and concentration of Cd in the soil gave the best fit to the data ($r^2 = 0.81$) (Fig. 2) however this relationship was strongly influenced by the high values for Cd concentration in the plants growing in the 250 C soil. Exclusion of these latter values resulted in a poorer ($r^2 = 0.35$), but still positive, linear correlation.

TABLE I. INFLUENCE OF THE APPLICATION RATE OF SINGLE SUPER PHOSPHATE ON Cd CONTENT IN SOILS AND YIELDS OF WHEAT SHOOTS (REPRINTED WITH PERMISSION OF THE AMERICAN CHEMICAL SOCIETY, 1998).

Plot	Total soil Cd (mg kg^{-1}) (s.e. in brackets)	Increase in soil Cd (mg $kg^{-1}y^{-1}$)	Shoot dry weight (g) (s.e. in brackets)
nil SSP	0.026 (0.008)	Nil	-
62.5 R	0.070 (0.006)	0.0016	0.061 (0.003)
62.5 C	0.115 (0.003)	0.0019	0.084 (0.006)
125 R	0.147 (0.005)	0.0045	0.081 (0.006)
125 C	0.198 (0.005)	0.0037	0.149 (0.009)
250 R	0.195 (0.002)	0.0063	0.097 (0.009)
250 C	0.339 (0.014)	0.0067	0.179 (0.012)

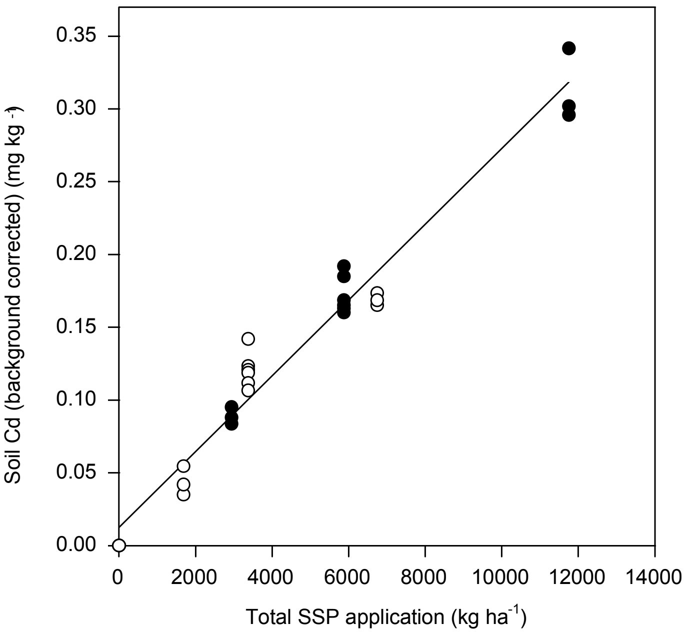

Fig. 1. Background corrected concentration of Cd in the soil versus total cumulative application of single super phosphate (hollow symbols = data from R plots, filled symbols = data from C plots) (Reprinted with permission of the American Chemical Society, 1998).

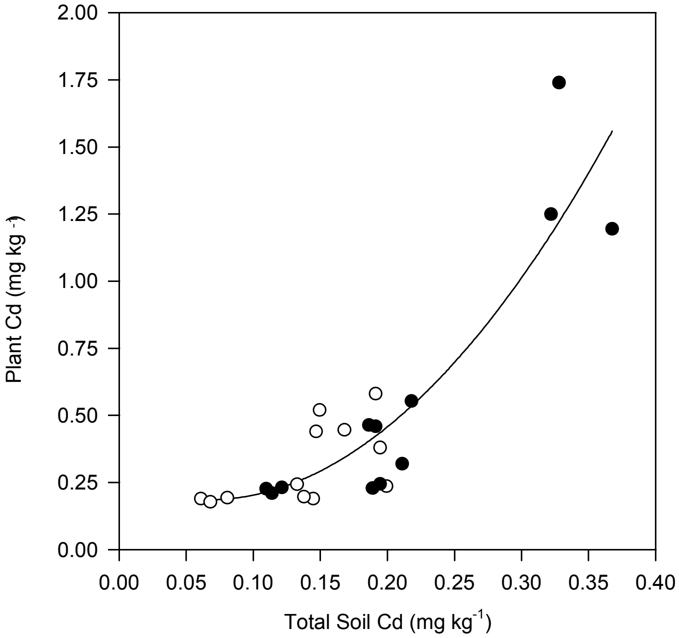

Fig. 2. Relationship between the concentration of Cd in wheat and the total concentration of Cd in the soil (hollow symbols = data from R plots, filled symbols = data from C plots) (Reprinted with permission of the American Chemical Society, 1998).

The positive trend between concentration of Cd in the soil and the Cd content of plants contrasts with results of several authors [9, 20, 21]. These authors that there was no evidence to suggest that Cd concentrations in herbage increased due to long-term applications of phosphatic fertilizers, which contain Cd as an impurity. However, such statements should be treated with caution. In these studies, comparisons were made between plants growing in unfertilized (control) soil and plants growing in soil in which there was either no observable increase in soil Cd following long-term use of phosphatic fertilizers, or addition of fertilizers also led to a significant increase in plant yield. Hence, a possibly large confounding factor, acknowledged by these authors, was 'dilution' of Cd in herbage due to the higher yield [22]. Therefore, in order to conclude that the use of phosphatic fertilizers does not increase Cd concentration in crops, it would be necessary to periodically measure the concentrations of Cd in crops growing in a regularly fertilized soil. Or to use soils in which equivalent amounts of P, but not Cd, have been applied, as controls.

3.3. Labile Cd

Evaluation of the percentage of total soil Cd that was available for uptake by the plants (% *L*) showed that in soil from the R plots approximately 40% of the Cd was in a plant unavailable form (Fig. 3). Cadmium was generally more phytoavailable in the C plot soils with a mean of 72% of the total Cd in a plant available form (Fig. 3). It should be noted that a distinct advantage of using % *L* values to assess the availability of elements is that differences in relative growth rates of plants are cancelled out in the calculation, so available Cd could be determined in spite of the yield differences obtained in this experiment. Moreover, given the relatively small pot size used in these experiments, it is likely that the values reported for % L Cd are, if anything, overestimated in this experiment compared to a field setting. In the confined space of a pot, the extraction power of roots per unit of soil is much greater (i.e. more roots per unit soil resulting in higher concentration gradients) than in a non-confined field setting. Hence, pools of Cd, which may be unavailable except in the presence of high concentration gradients will now form part of the labile pool.

For both types of plots the total concentration of Cd in the soil had little or no effect on the % *L* Cd as indicated by slopes of the lines of best fit approaching zero (Fig. 3). In light of the fact that additions of SSP did not affect soil pH, this result is not entirely unexpected. For example, a it can be assumed a specific set of soil physico-chemical reactions could facilitate metal fixation and the amount of metal fixed would be proportional to the concentration of metal (hence percent metal reacted is independent of concentration). This is providing the metal is not added to the soil at concentrations high enough to lead to non-specific sorption processes dominating exchange equilibria [23,3] or changes in pH [24]. If the reactions responsible for metal fixation became saturated with excess metal, these latter processes would cause % labile metal to increase as a function of the total soil concentration.

This result therefore provides evidence that a) pools of non-phytoavailable Cd can exist in the soil, which supports our previous findings with a different soil [25] and b) that at low concentrations of Cd in the soil, the amount of Cd fixed is proportional to the concentration of soil Cd. While Cd sorption to the solid phase may be increased in the presence of phosphate [26], the effect of phosphate on Cd fixation was minimal as % *L* Cd was independent of the total concentration of P in the soil (data not shown). Since SSP is highly water soluble, it is also unlikely that Cd locked inside recently applied SSP contributed significantly to the non-phytoavailable pool of Cd in either the R or C plots. It is possible that diffusion of Cd into the soil matrix [8,27] was the process responsible for the reduction in the phytoavailability of the added Cd.

For a given concentration of Cd in the soil, Cd was significantly less phytoavailable ($P< 0.001$) in plots which had received their last input of Cd in 1975 (R plots) compared to those still subject to Cd inputs (C plots) (Fig. 3). Providing the sward composition differences associated with the different rates of P application did not affect Cd fixation in the soil, this segregation in % *L* Cd between R and C plots (Fig. 3) further implies that there is a time-dependent component associated with declines in Cd phytoavailability.

From this data it was possible to calculate an approximate annual rate of Cd fixation in the soil using a model derived as follows.

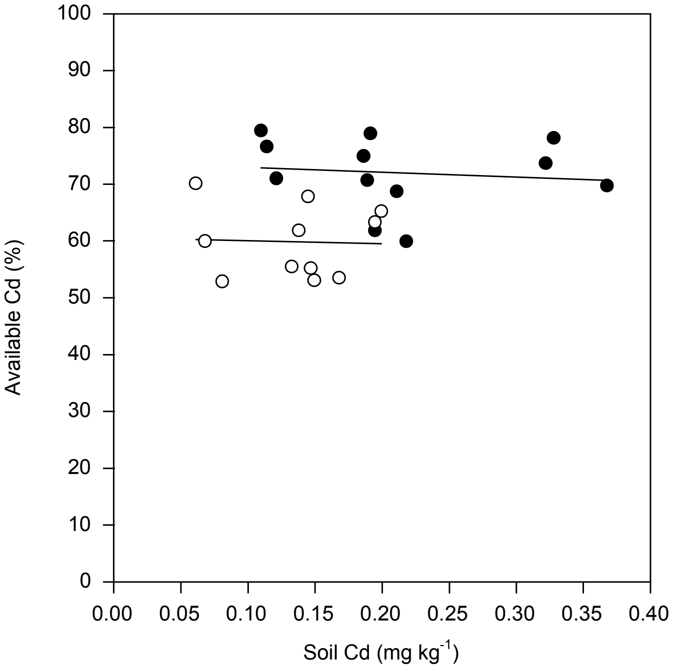

Fig. 3. Percent of total soil Cd which is available for plant uptake versus the concentration of Cd in the soil (hollow symbols = data from R plots, filled symbols = data from C plots) (Reprinted with permission of the American Chemical Society, 1998).

Given an application of *a* units of available Cd, and assuming a constant rate *k* of fixation of Cd in the soil, the amount of Cd which is available (labile Cd) (*L*) at time *t* is:

$$L_t = ae^{-kt} \tag{2}$$

This is a first order reaction that concurs with the observation that the amount of Cd fixed in the soil was concentration limited and not process limited (*i.e.* there was no saturation of the mechanism responsible for Cd fixation in the soil). The percentage of Cd that is available is then:

$$\% L = (ae^{-kt} / a) \text{ x } 100 = \mathrm{e}^{-\mathrm{kt}} \text{ x } 100 \tag{3}$$

Assuming a constant addition rate of available Cd, after *t* years of applications the amount of Cd that remains available in the soil (*T*) will be the sum of the contributions from 0, 1, 2, ... *t* years i.e.:

$$T = a + ae^{-k} + ae^{-2k} + ... + ae^{-kt} \tag{4}$$

Summing the geometric series in equation 3 gives:

$$T = \mathrm{a}\,(1 - e^{-kt} / 1 - e^{-k}) \tag{5}$$

After *t* years of additions, a total of (*a* x *t*) units of Cd would have been applied. The percent of Cd available at that stage would then be:

$$\% L_1 = (T / at) \text{ x } 100 = (1 - e^{-kt}) / t\,(1 - e^{-k}) \tag{6}$$

If there are no further additions of Cd for the next *n* years, the percent available Cd will decrease according to equation 1 giving:

$$\% L_2 = [e^{-kn}\,(1 - e^{-kt}) / t\,(1 - e^{-k})] \text{ x } 100 \tag{7}$$

Values for % L were derived experimentally, hence the annual rate of Cd fixation in the C and R soils could be estimated by determining the value for k in equations 5 and 6, respectively. No explicit solution is possible for equations 5 and 6, but they can be solved by simple iteration. The model for fixation of Cd relies on the assumptions that; 1) during the years when SSP was applied, Cd was added to the soil at a constant rate; 2) there was no movement of Cd away from the surface horizon in each plot; 3) Cd added to the soil was initially all available; 4) the rate of fixation was constant over time.

Using this model, the values obtained for k in each plot are shown in Table II. Assuming that the original background concentration of Cd in the soil was 0, approximately 1.5 % of the total available Cd, was estimated to be fixed per year. Assuming that the original background concentration of Cd was 0.026 mg/kg, and that none of this Cd was available at the onset of SSP applications, approximately 1% of the total available Cd was fixed per year in the plots receiving the 2 highest application rates of SSP. Incongruous values for plots receiving 62.5 kg SSP y^{-1} (Table II) are probably the result of the assumed background concentration of Cd being very close in value to the amount of unavailable Cd in the soil in these plots.

TABLE II. ANNUAL RATE OF FIXATION (k) OF Cd AS A PERCENT OF EITHER TOTAL Cd IN THE SOIL (UNADJUSTED) OR BACKGROUND CORRECTED SOIL Cd (REPRINTED WITH PERMISSION OF THE AMERICAN CHEMICAL SOCIETY, 1998)

	Fertilizer Treatment		
	62.5 kg SSP y^{-1}	125 kg SSP y^{-1}	250 kg SSP y^{-1}
Rundown — unadjusted	1.52	1.69	1.36
Rundown — background corrected	0.06	1.08	0.92
Continuous — unadjusted	1.30	1.72	1.39
Continuous — background corrected	0.18	1.03	0.97

A similar study [28] using the L-value technique to examine Cd lability in soils sourced from house foundations, which had remained sealed for at least 200 years, concluded that there was no change in Cd lability during this time. However in order to reach this conclusion, the authors were forced to make the assumption that at least 30% of the Cd in each of the plants was derived through foliar uptake from an unknown atmospheric source, in spite of the plants being grown in the laboratory. Without this assumption, the calculated size of the labile pools of Cd would be 120 to 150% of total soil Cd. Apart from creating a huge potential source of error, this assumption is theoretically unjustified since there is no reason why the amount of Cd deposited on the leaves should be consistently related to the internal plant Cd concentration when a majority of the plant Cd is soil derived. Studies with solution cultured plants [29] have shown that the specific activity of Cd in plants was equal to that in the culture solutions, verifying that at least in our facilities, there are no significant atmospheric sources of Cd. A more plausible explanation for the results obtained in the above study [28] is that the ^{109}Cd spike was not mixed homogeneously throughout the soil and was physically less available to plant roots than the non-radioactive, native soil Cd.

In the only other study we are aware of where the L-value technique has been used to assess Cd lability, 10 to 20% of Cd in soils contaminated with very high concentrations of Cd from long-term sludge utilization farms was found to exist in non-labile pools [30]. The total length of incubation of Cd in the soil in this study is, however, unclear. Other studies, which have assessed Cd availability through an examination of changes in total Cd uptake by plants, were reviewed by McLaughlin et al. [1] and found to conflict, with Cd phytoavailability being reported both to decrease and remain constant over time. Lack of evidence for decline in Cd phytoavailability with time may be a function of individual soil types, with the constituents responsible for the slow reactions that fix Cd not existent in all soils, or due to the presence of agents, which may inhibit fixation [27]. However, the inability to discern decreases in Cd phytoavailability with time may also be the result of shortcomings in experimental design. For example the short-term nature of many studies and/or relatively high concentrations of Cd being applied to the soil so that any decreases in plant concentrations with time are analytically non-significant when compared to the total plant concentration of Cd. The sensitivity of the L-value should overcome problems associated with this latter aspect.

Though only 1 to 1.5% of the total Cd was being immobilized in this soil per year, in the long-term this may lead to a significant proportion of the total soil Cd being excluded from the equilibrium reactions between the solid and solution phase, important determinants of plant uptake. The fact that Cd can exist in non-phytoavailable pools in soils adds further impetus to arguments that the totals-based approach, which is widely in use for delimiting maximum allowable concentrations of metals in soil [31], is inappropriate. Moreover, evidence that Cd and other metals can be fixed in soils suggests that it is unnecessary to achieve huge reductions in total Cd concentrations to alleviate potential health risks of contaminated soils. Providing remediation treatments to significantly deplete the labile pool of the metal (or other contaminant) is a process we have termed ‘bioavailable contaminant stripping’ (BCS). Risks to human health may be mitigated with this process even without a significant reduction in the total soil content of metal.

REFERENCES

[1] MCLAUGHLIN, M.J., TILLER, K.G., NAIDU, R., STEVENS, D.P., Review: The behavior and environmental impact of contaminants in fertilizers, Aust. J. Soil Res. **34** (1996) 1-54.

[2] ANON, Food Standards Code Ammendment P144, National Food Authority, Australian Government Printing Service, Canberra, (1998).

[3] MCBRIDE, M.B., Reactions controlling heavy metal solubility in soil, Adv. Soil Sci. **10** (1989) 1-56.

[4] JUNG, J., LOGAN, T.J., Environ. Qual. **21** (1992) 73-81.

[5] BRENNAN, R.F., Aust. J. Soil Res. **28** (1990) 293-302.

[6] FISCHER, L., ZUR MUHLEN, E., BRUMMER, G.W., NIEHUS, H., Atomic force microscopy (AFM) investigations of the surface topography of a multidomain porous geothite, Eur. J. Soil Sci. **47** (1996) 329-334.

[7] BARROW, N.J., GERTH, J., BRUMMER, G.W., J. Soil Sci. **40** (1989) 437-450.

[8] BRUMMER, G.W., GERTH, J., TILLER, K.G., J. Soil Sci. **39** (1988) 37-52.

[9] GERTH, J., BRUMMER, G.W., TILLER, K.G., Retention of Ni, Zn and Cd by Si-associated geothite. Pflanzen. Bodenk. **156** (1993) 123-129.

[10] NAKAHONE, L.N., YOUNG, S.D., The significance of (radio-) labile cadmium pools in soil, Environ. Poll. **82** (1993) 73-77.

[11] SCHAFER, B., A Description of the Soils on the CSIRO Pastoral Research Laboratory Property, Chiswick, Armidale, NSW. In: Animal Research Laboratories Technical Paper No. 8, CSIRO Australia, (1980).

[12] KING, K., Personal communication, Commonwealth Scientific Research Organisation, Chiswick, (1995).

[13] LARSEN, S., Plant Soil **4** (1952) 1-10.

[14] TILLER, K.G., HONEYSETT, J.L., DE VRIES, M.P.C., Soil zinc and its uptake by plants. 1. Isotopic exchange equilibria and the application of tracer techniques, Aust. J. Soil. Res. **10** (1972) 151-164.

[15] DAVID, D.J., PINKERTON, A., WILLIAMS, C.H., Aust. Inst., Agric. Sci. **44** (1978) 132-135.

[16] CHANG, A.C., HYUN, H., PAGE, A.L., Cadmium uptake for swiss chard grown on composted sewage sludge treated field plots: plateau or time bomb?, J. Environ. Qual. **26** (1997) 11-19.

[17] LOGANATHAN, P., HEDLEY, M.J., Downward movement of cadmium and phosphorus from phosphatic fertilizers in a pasture soil in New Zealand, Environ. Poll. **95**(3) (1997) 319-324.

[18] MCGRATH, S.P., Pollutant Transport and Fate in Ecosystems, Blackwell Scientific Publications, Oxford, (1987), 301-317.

[19] MULLA, D.J., PAGE, A.L., GANJE, T.J., Cadmium accumulations and bioavailability in soil from long-term phosphorus fertilization, Environ. Qual. **9** (1980) 408-412.

[20] MORTVEDT, J.J., Cadmium levels in soil and plants from some long-term soil fertility experiments in the United States of America, Environ. Qual. **16** (1987) 137-142.

[21] JONES, K.C., JOHNSTON, A.E., Cadmium in cereal grain and herbage from long-term experimental plots at Rothamsted, UK. Environ. Poll. **57** (1989) 199-216.

[22] LOGANATHAN, P., HEDLEY, M.J., GREGG, P.E.H., CURRIE, L.D., Effect of phosphate fertilizer type on the accumulation and plant availability of cadmium in grassland soils, Nutr. Cycl. Agr. **47** (1997) 169-178.

[23] HENDRICKSON, L.L., COREY, R.B., Effect of equilibrium metal concentrations on apparent selectivity coefficients of soil complexes, Soil Sci. **131** (1981) 163-171.

[24] ANDERSON, P.R., CHRISTENSEN, T.H., Distribution coefficients of Cd, Co, Ni, and Zn in soils, J. Soil Sci. **39** (1988) 15-22.

[25] HAMON, R., WUNDKE, J., MCLAUGHLIN, M., NAIDU, R., Availability of zinc and cadmium to different plant species, Aust. J. Soil Res. **35** (1997) 1267-1277.

[26] BARROW, N.J., J. Soil Sci. **38** (1987) 453-460.

[27] COUGHLIN, B.R., STONE, A.T., Environ. Sci. Technol. **29** (1995) 2445-2455.

[28] JENSEN, H., MOSBAEK, H., Relative availability of 200 years old cadmium from soil to lettuce, Chemosphere. **20** (1990) 693-702.

[29] SMOLDERS, E., MCLAUGHLIN, M.J., Unpublished results, Commonwealth Scientific and Industrial Research Organization, Division of Land and Water, Adelaide.

[30] CHANEY, R., Personal communication, U.S. Dept. Agriculture, Beltsville, (1997).

[31] MCGRATH, S.P., CHANG, A.C., PAGE, A.L., WITTER, A., Land application of sewage sludge: scientific perspectives of heavy metal loading limits in Europe and the United States, Environ. Rev. **2** (1994) 108-118.

PART V

STUDIES FROM EASTERN EUROPE AND RUSSIA

THE EFFECT OF ROCK PHOSPHATES ON THE CONTENT OF MINERAL PHOSPHATE FORMS IN SOD-PODZOLIC SOILS

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Abstract. The dynamics of content and changes in the mineral forms of phosphates as a result from the application of rock phosphates (RP) from the Polpino deposit to a Sod-podzolic soil was studied. Thirty days after phosphate rock application to soil, up to 59.2% of all phosphates were in the form of sparingly soluble Ca phosphates. After 200 days, only 36.5% of local RP remained in the original form. The process of P conversion from RP was accompanied by the formation of Ca, Mg, Fe, and Al phosphates. The extent, to which phosphate was mobile, was determined by RP dissolution rates and time of contact with soil. Significant differences in the available soil P values determined by chemical, radiochemical and greenhouse methods were found.

1. INTRODUCTION

One of the main reasons for poor yields of farm crops in the Russian Federation is an insufficient application of mineral fertilizers [1]. Currently, because of the difficult economic situation in the country, the amount of mineral fertilizers applied to agricultural land continues to decrease. In this situation, more attention needs to be drawn to the use of many small- and medium-size deposits of local phosphate ores. Studies carried out have shown a high agronomic effectiveness of rock phosphates (RP) from different deposits [2]. At the same time, studies have shown differences in the content of P, as well as chemical impurities, sand, and clay in the RPs. It is, therefore, necessary to make a comprehensive assessment of the RPs prior to their application.

When a phosphate fertilizer is applied to a soil, fertilizer phosphorus is converted to different chemical compounds unequally available to plants, which significantly influence the effectiveness of phosphorus fertilizers. The most available form of P to plants in acid soils is Ca phosphate followed by Al phosphates and to a lesser extent Fe phosphates [3, 4]. The conversion of P from RP is determined by soil acidity and the time of soil contact. After long-term application of P fertilizers, phosphates are accumulated in soil in forms typical for a given soil [5,6].

The purpose of this study was to evaluate the dynamics of changes in mineral P forms when a sod podzolic soil was amended with a RP from the Polpino deposit located at the interface of the Kaluga and Bryansk regions.

2. MATERIALS AND METHODS

Prior to the experiment, the sod podzolic soil had the following agrochemical characteristics: pH_{KCl} = 4.45; organic matter = 2.58%; exchangeable Ca = 4.61 cmol/kg; exchangeable Mg = 0.99 cmol/kg; exchangeable K = 0.32 cmol/kg; exchangeable Al = 0.06 cmol/kg; P by the Kirsanov method = 11.3 mg/kg; Cation Exchange Capacity = 5.96 cmol/kg [7]. A one kg air-dried soil samples were used.

The treatments consisted of the application of local RP at the rates of 21.8, 43.6 and 87.2 mg P/kg soil. The phosphorus fertilizers included finely grounded phosphorite ore (RP) and granulated superphosphate (Ps) with total P content of 6.7 and 9.6%, respectively.

During seven months, soil moisture in pots was maintained at the 60% level of field capacity. Mineral forms of soil P were evaluated after 30 and 200 days after the application of RP to soil. Prior to the chemical analysis, the soil in the pot was thoroughly mixed, and then an average sample weighing 100 g was collected, dried, and passed through a 1 mm sieve and again thoroughly mixed. A small soil sample (1 g) was collected for the analysis, which was sequentially treated by reagents in accordance with the methodology outlined by Ginzburg [7].

To evaluate the content of P mineral forms in soil, the Chang and Jackson method modified by Ginzburg and Lebedeva was used [8-10]. This method selectively isolates fractions of Ca, Al and Fe phosphates. When soil is treated by different solvents, the fraction of the most soluble forms of phosphates of alkaline and alkaline earth element (Ca-P_1) is initially determined, then the fraction of less soluble forms of Ca and Mg phosphates, as well as phosphates of FeO forms (Ca-P_2). Thereafter, Al-P and Fe-P fractions are isolated followed by the fraction of the most sparingly soluble Ca phosphates (Ca-P_3).

The dynamics of changes in P mineral forms in soil while applying RP availability for plants was estimated in parallel with a greenhouse experiment described elsewhere. The greenhouse experiment was conducted to assess the agronomic effectiveness of local RP using the isotope dilution method. Radioactive ^{32}P was applied to the soil of each pot in the form of $NaH_2{}^{32}PO_4$ solution with a total activity of 920.3 kBq/kg air-dried soil free from isotope carrier. In the experiment we used pots with a capacity of 5 kg. The experimental treatments were replicated 4 times. The experimental crop was barley (Zazersky-85 variety).

The greenhouse experiment and laboratory investigations to study the dynamics of changes in the P mineral forms of phosphorus under P fertilization followed a common scheme. The pot soil was treated with KNO_3 and NH_4NO_3 as background fertilizers, with N and K amounts of 150 and 85 mg/kg dry soil, respectively. In the greenhouse experiment the plants were allowed to grow until biological maturity. In the greenhouse experiment, the control (without the application of P fertilizers) was used to determine both the accumulation of phosphorus in the crop yield from soil and total amount of biologically available phosphorus in soil. The ^{32}P activity in soil, plants and solutions was measured by a radiometric method.

The greenhouse experiments have revealed significant differences in the values of available P supply in soil determined by the chemical (Kirsanov) method in 0.2 N HCl extract [7] and the amount of P assimilated by plants during the growing season. Thus, a modified radiochemical method was utilised using ^{32}P as a tracer. For this purpose, a certain amount of carrier-free ^{32}P was applied to the soil under study. The ^{32}P activity was determined radiometrically in soil and 0.2 N HCl extract.

When the soil phosphorus was determined by the modified Kirsanov method, the total ^{32}P amount in soil was insignificant compared to stable ^{31}P, and soluble P supplied in accordance with the theory of isotope dilution was determined by:

$$M = A_0/a \tag{1}$$

where M is the content of soluble P fraction in soil, A_0 is the overall activity of ^{32}P (Bq), and a is the specific activity of ^{32}P (Bq/mg P).

In the control treatment of the greenhouse experiment, the total availability of soil phosphate was estimated after the calculation of the coefficient of ^{32}P available for plants from soil by the following equation:

$$K = \frac{A_1}{A_2} \times 100 \tag{2}$$

where K is the coefficient of ^{32}P availability for plants (%); A_1 is the ^{32}P content in plant yield, (Bq), and A_2 is the total activity of ^{32}P in soil (Bq). The total content of the available phosphate in soil was calculated as follows:

$$P_\Sigma = \frac{P_1}{K} \times 100 \tag{3}$$

where P_Σ is the total content of available P in soil (mg), P_1 is the amount of P assimilated by plants, and K is the coefficient of P availability for plants (%).

To characterize the phosphate status of soil, it is very important to assess the level of phosphate mobility in soil (the intensity factor). Mobile P determinations were made after 30 and 200 days application of P fertilizers to soil by extracting orthophosphates from soil with 0.02 N $CaCl_2$ at a 1:5 ratio (Schofield method).

3. RESULTS AND DISCUSSION

The process of P transformation from local RP into other forms is lengthy. After 30 days of their application to soil, the major amount of P (up to 59.2%) was in the original form of RP as sparingly soluble Ca phosphates (Ca-P_3). After 200 days only 35.87% of P from local RP remained in the original form (Tables I and II).

The process of transformation of P from local RP is accompanied by the formation of Ca, Mg and FeO phosphates (Ca-P_1 + Ca-P_2) as well as P forms bonded to Fe (Fe-P) and Al (Al-P). The formation of P forms more readily available to plants (Ca-P_1 + Ca-P_2) occurred in greater amounts than P forms bonded to Fe and Al. Thus, the availability for plants of P from local RP increases with time due largely to the formation of phosphates of fractions 1 and 2 and their subsequent partial transfer to phosphates of Fe and Al oxides.

To have an idea of the fractional composition of mineral forms of P from local RP, their chemical analysis was carried out by the Chang and Jackson method modified by Ginzburg and Lebedeva (Table III). The analysis has revealed that more than 91% of P from local RP is represented by the fraction of acid-soluble Ca phosphates (Ca-P_3). The fractions with Ca (Ca-P_1 + Ca-P_2), most readily available for plants, account for 8.0%. The number of fractions bonded to Al and Fe was insignificant.

The values for the level of phosphate mobility in soil were well correlated with the amount of mobile phosphates in soil, as estimated by the Kirsanov method, as well as the dynamics of changes in the most available P forms in soil, estimated by the Chang and Jackson method modified by Ginzburg and Lebedeva (Table IV). The level of RP phosphate mobility in soil increased with the time of contact with the soil.

TABLE I. FRACTIONS OF P MINERAL FORMS IN SOIL (mg/kg)

Fraction	Treatment			
	Background control	RP=21.8 mg P/ kg	RP=46.3 mg P /kg	RP=87.2 mg P/kg
		30 days		
Ca – P_1	14.2	15.6	17.0	21.2
Ca – P_2	56.4	59.2	60.3	66.3
Al –P	21.8	23.8	26.3	31.0
Fe –P	51.9	54.7	58.8	63.5
Ca – P_3	24.4	37.5	47.9	71.9
Total P	169	192	210	254
		200 days		
Ca – P_1	13.3	16.9	21.2	27.7
Ca – P_2	59.0	63.4	67.9	79.6
Al –P	21.1	24.0	27.7	31.0
Fe –P	51.2	55.4	56.6	61.9
Ca – P_3	23.7	30.6	38.2	54.7
Total P	168	190	211	255

TABLE II. NEWLY FORMED MINERAL FORMS OF P IN SOIL (mg/kg)

Fraction	Treatment		
	RP=21.8 mg P/kg	RP=43.6 mg P/kg	RP=87.2 mg P/kg
		30 days	
Ca - P_1	1.44 * 6.51 **	2.83 6.81	7.06 8.28
Ca - P_2	2.74 12.4	3.88 9.32	9.90 11.6
Al –P	2.01 9.07	4.53 10.9	9.20 10.8
Fe –P	2.84 12.8	6.94 16.6	11.6 13.6
Ca - P_3	13.1 59.2	23.4 56.3	47.5 55.7
Total P	22.2 100	41.6 100	85.3 100
		200 days	
Ca – P_1	3.53 16.1	7.81 18.1	14.4 16.6
Ca – P_2	4.45 20.3	8.90 20.6	20.6 23.8
Al –P	2.92 13.3	6.62 15.4	9.89 11.4
Fe –P	4.14 18.9	5.32 12.3	10.7 12.3
Ca – P_3	6.9 31.4	14.5 33.6	31.0 35.9
Total P	21.9 100	43.1 100	86.6 100

* The top number is the P content of the P form in soil as mg/kg soil.
** The bottom number is the % of the total amount of the phosphates.

TABLE III. FRACTIONAL COMPOSITION OF MINERAL FORMS OF P FROM LOCAL RP

Fraction	mg P/g	% of total
Ca – P_1	1.71	2.31
Ca – P_2	4.21	5.69
Al – P	0.55	0.74
Fe – P	0.13	0.19
Ca – P_3	67.4	91.1

TABLE IV. MOBILE SOIL P FOR DIFFERENT P TREATMENTS BY THE SCHOFIELD METHOD (mg/L)

	Time after application of fertilizers to soil, days	
Treatment	30	200
Background control	0.015	0.017
SP=21.8 mg P/ kg	0.037	0.033
SP=43.6 mg P / kg	0.065	0.059
SP=87.2 mg P/ kg	0.100	0.100
RP=21.8 mg P/ kg	0.017	0.028
RP=43.6 mg P / kg	0.026	0.039
RP=87.2 mg P / kg	0.035	0.052

Values for K and P_1 were found to be 8.07% and 26.52 mg, respectively. The content of available P (P_Σ) in soil of the control pots in a greenhouse experiment was 65.7 mg P/kg soil using ^{32}P methods (Table V). The differences found between the three methods (chemical, chemical using ^{32}P, greenhouse experiment using ^{32}P) showed that the most reliable method in evaluating soil available P was the greenhouse method. The results from the chemical method were rather relative and incompletely characterized the phosphate potential of the soil being studied.

When isolating mobile phosphates from soil with various solvents (aqueous, acid and other extracts) one not only dissolves soil phosphates, but secondary sedimentation also occurs during extraction. Therefore, the addition to the solvent of an insignificant amount of ^{32}P, which does not influence the sedimentation reactions and dissolution of soil phosphates, allows one to determine the amount of phosphates taking part in the exchange between liquid and solid phases.

The evaluation of the amount of available P in soil through the use of ^{32}P makes it possible to estimate values close to the amounts of assimilable P resulting from the greenhouse experiment. At the same time, chemical methods do not completely characterize the phosphate potential of soils.

TABLE V. CONTENT OF MOBILE PHOSPHORUS IN SOIL EVALUATED BY DIFFERENT METHODS (mg/kg)

Treatment	Method of evaluation		
	Kirsanov (0.2 N HCl)	Kirsanov + ^{32}P (0.2 N HCl + ^{32}P)	Greenhouse (by ^{32}P), P_Σ
Background control	11.3	57.6	65.7
SP=21.8 mg P/ kg	29.6	80.7	-
SP=43.6 mg P/ kg	46.6	101	-
SP=87.2 mg P / kg	78.6	140	-
RP=21.8 mg P / kg	21.8	71.9	-
RP=43.6 mg P / kg	36.2	92.0	-
RP=87.2 mg P / kg	71.9	133	-

4. CONCLUSIONS

During the incubation of local RP with soil, the transformation of P from RP into other forms occurred for a long period of time. Thirty days after the application to soil, the main fraction of P from local RP (up to 59.2%) was in the original form as sparingly soluble Ca phosphates (Ca-P_3). After 200 days, only 35.9% of P was retained in the original form. The transformation process was accompanied by the formation of Ca, Mg and FeO phosphates (Ca-P_1 + Ca-P_2), as well as P forms bonded to Fe (Fe-P) and Al (Al - P). In this case, the formation of P forms more available for plants (Ca-P_1 + Ca-P_2) was greater in number than P forms bound to Al and Fe. About 91% of P from local RP appeared in the fraction of acid-soluble Ca phosphate (Ca - P_3). The P fractions with Ca (Ca-P_1 + Ca-P_2), which are more readily available for plants, account for 8%. The number of P fractions with Fe and Al is insignificant.

The level of phosphate mobility in soil is well correlated with the supply of mobile phosphates in soil, as estimated by the Kirsanov method. Phosphate mobility is also well correlated with the dynamics of changes in the most available P mineral forms in soil, as estimated by the Chang-Jackson method modified by Ginzburg and Lebedeva [3]. In treatments with local RP, the level of phosphate mobility in soil increases with the increase in time of their contact with soil.

The greenhouse experiment established significant differences in the values of P supplies in soil, estimated by chemical, radiochemical and greenhouse methods. In studies with ^{32}P as a tracer, the amount of soil P available for plants was established by the greenhouse experiment. The Kirsanov method does not completely characterize the available phosphate of soils.

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REFERENCES

[1] MILASCHCHENKO, N.Z., Expanded reproduction of soil fertility in the intensive farming in the Non-Chernozemic area of Russia, Moskow: Nauka (in russian) (1993).

[2] YANISHEVSKY, F.V., ANGELOV, A.I., DUBININ, V.G., Working out of a universal indicator of the effectiveness of rock phosphates, Agrochimiya **7** (1989) 8-17 (in russian)

[3] KHLYSTOVSKY, A.D., KNYAZEVA, K.P., Transformation of different forms of P fertilizers and their effectiveness on soddy-podzolic heavy sandy loam soil, Agrochimiya **11** (1976) 24-36 (in russian).

[4] YAGODIN, B.A., SMIRNOV, P.M., PETERBURGSKY, A.V., AGROCHIMIYA, 2nd ed., Moskow: Nauka, (in russian) (1989).

[5] POKHLEBKINA, I.P., GLAZUNOVA, N.M., Residual phosphates in acid soils and their uptake by plants, Agrochimiya **2** (1988) 105-119.

[6] KHATSIEVA, N.M., PROKOSHEV, V.V., Changes in the content of readily soluble phosphates during the application of P fertilizers to soddy - podzolic light sandy loam soil, Agrochimiya **9** (1979) 25-29 (in russian).

[7] GINZBURG, K.E., Methods of phosphorus determination in soil. pp 106-191, In: Sokolov AV (ed), Agrochemical methods for soil research, Moskow: Nauka, (in russian) (1975).

[8] CHANG, S.C., JACKSON, M.L., Fractionation of soil phosphorus, Soil Sci. **84** (1957) 45-49.

[9] GINZBURG, K.E., LEBEDEVA, L.S., Methodology for evaluating mineral forms of soil phosphates, Agrochimiya **1** (1971) 43-54 (in russian).

[10] JACKSON, M.L., Soil chemical analysis, Madison, Wisconsin (1958).

EVALUATION OF THE AGRONOMIC EFFECTIVENESS OF ROCK PHOSPHATES FROM THE POLPINO DEPOSIT IN THE RUSSIAN FEDERATION AND THEIR POTENTIAL TO REDUCE ^{137}Cs ACCUMULATION IN PLANTS

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Abstract. The ability to supply P to plants (agronomic effectiveness) of local rock phosphates (RP) from the Polpino deposit in the Bryansk region was determined in a sod-podzolic acid soil. In addition, the effectiveness of using the RP to reduce ^{137}Cs accumulation in barley was also studied. A series of greenhouse experiments were carried out using ^{32}P and ^{137}Cs as tracers. Standard methods for soil analysis and evaluation of chemical status of RP in soil were employed. The grain yield increased by 17.7, 44.3 and 57.5% compared to the control at rates of 21.8, 43.6 and 87.2 mg P/kg soil, respectively. The relative availability of phosphorus from RP applied at a rate of 21.8 P mg/kg soil was 56.1% compared to superphosphate and reached 74.5 and 81.3% at rates of 43.6 and 87.2 mg P/kg soil. The uptake of P by plants was increased with the increase in the rates of the fertilizers applied, but the percent of P fertilizer utilization decreased. The amount of P used by plants from fertilizers depended on the type and rates of P fertilizers. With an increase in SP rates from 21.8 to 87.2 mg/kg soil, the use of fertilizer P by plants dropped from 32.6 to 21.9%. For local RP, these differences were less pronounced with the percent of the total amount of P used by plants 2.1 times less than that from SP. The application of local RP at rates of 43.6 and 87.2 mg P/ kg soil resulted in a 1.3-fold decrease in ^{137}Cs accumulation in grain and straw of crops. At a rate of 21.8 mg P/kg soil, the differences in ^{137}Cs accumulation between grain and straw were insignificant compared to the control.

1. INTRODUCTION

In Russia low levels of chemical fertilizers are applied on cultivated land resulting not only in poor yields but also in a substantial decrease of soil fertility. In 1996, the average doses of applied mineral fertilizers amounted to 10 kg/ha of major nutrients. Currently, this amount is continuously decreasing. One of the main limiting factors of farm crop production is the low level of mobile forms of phosphorus in soil. For 65% of arable lands in Russia, the P content in soil is low and does not exceed 50 mg/kg extracted with 0.2 N HCl [1]. The application of phosphorus fertilizers has been greatly reduced due to the difficult economic situation and the soil phosphorus status constantly tends to decrease.

About 70% of arable lands in the Non-Chernozemic area of the Russian Federation are acidic (pH<5.5). This condition results in the possibility of a widespread use of ground rock phosphates since dissolution of phosphate rocks in the soil begins at a potential acidity of 2.5 meq/100 g of soil and greater [2].

Following the accident at the Chernobyl NPP, 19 regions of the Russian Federation were affected by radioactive contamination. One of the most effective ways to reduce radionuclide (^{137}Cs and ^{90}Sr) uptake and transfer from soil to plant products is the application of higher doses of phosphorous and potassium fertilizers. However, the difficult economic situation in Russia prevents the application of phosphorous and potassium fertilizers on arable lands at recommended rates resulting in elevated levels of radioactive contamination of products and extra irradiation of local population due to consumption of these products. The exploitation of local deposits of rock phosphate and their utilization as fertilizers is a promising way to solve the problem. They have the potential to improve soil fertility, increase productivity of farm crops, and improve quality of products reducing their content of radionuclides in areas affected by radioactive contamination.

Some 250 deposits of rock phosphates have been explored on the Russian Federation territory. Of these, 35 are suitable for immediate development with overall ore reserves reaching 483 million tons. The largest RP deposits are located in a central part of the Russian Federation, including regions subjected to radioactive contamination and where acid soils are widespread [3]. Previous studies have shown high agronomic effectiveness of RP from several different deposits with different P content and chemical composition.

The major challenge nowadays is to find those local rock phosphates, which are highly effective on acid soils and contribute to improve the soil fertility and increase crop yields. The most effective way for an agronomic evaluation of phosphorus fertilizers and P availability for plants are through the use of isotopic tracers. For this purpose, the fertilizer being tested is labelled during manufacture with the radioactive isotopes ^{32}P or ^{33}P without changing its physical and chemical properties. The labelled fertilizer can then be applied to the soil. The labelling of natural rock phosphates with radioactive phosphorus isotopes is impossible without severe chemical treatment resulting in significant alteration of RP physical and chemical properties and an incorrect evaluation of the availability of RP phosphorus to plants. In this context, a radioisotope technique has been suggested by a number of researchers to assess RP phosphorus available to plants without direct incorporation of radioactive phosphorus into rock phosphates [4-7]. This technique is an extension of a direct isotope method and consists of estimating P uptake by plants from ^{32}P or ^{33}P-labelled source in the presence or absence of unlabelled source.

The purpose of this work was to evaluate the ability to supply P to plants (agronomic effectiveness) of local rock phosphates (RP) from the Polpino deposit in the Bryansk region was determined in a sod-podzolic acid soil. In addition, the effectiveness of using the RP to reduce ^{137}Cs accumulation in barley was also studied.

2. MATERIALS AND METHODS

A series of studies on the evaluation of the effectiveness of local rock phosphates were conducted under greenhouse conditions in the laboratory of Radioecology, Russian Institute of Agricultural Radiology and Agroecology using commonly established methodologies for soil/plant studies [8]. The phosphorus fertilizers included finely ground apatite ore (RP) and granulated superphosphate (TSP) with total P content of 6.7 and 9.6%, respectively.

For the experiments, pots measuring 20 × 30 cm with a capacity of 5 kg soil were utilised. A sod-podzolic light loamy soil sampled in spring from a homogeneous virgin plot was employed.

Two series of experiments were prepared using a similar scheme. The first series studied the agronomic effectiveness of rock phosphates from the Polpino deposit by means of ^{32}P.isotope dilution technique. The second series evaluated the effectiveness of the Polpino rock phosphate in reducing ^{137}Cs accumulation in plant yield. The treatments consisted of RP and TSP applied at three P rates: 21.8, 43.6 and 87.2 mg P/kg soil plus a control (no P) treatment. The experimental design was a completely randomised of 7 treatments with 4 replications. Barley variety “Zazersky-85” was grown as a test crop.

In the first experiment ^{32}P was applied to the pot soil in the form of a readily soluble salt $NaH_2{}^{32}PO_4$ with a total activity of 920.26 kBq/kg of air-dry soil. The content of stable phosphorus (^{31}P) in the water solution of $NaH_2{}^{32}PO_4$ amounted to 30 $\mu g/cm^3$ or 300 μg/kg soil. In the second experiment ^{137}Cs in the form of a readily soluble salt $^{137}CsCl$ was applied to the soil in pots. The ^{137}Cs activity was 7.4 kBq/kg soil. During the experiment, soil moisture was maintained at a level of 60% of the field capacity. The salts KNO_3 and NH_4NO_3 were added as background fertilizers with a total rate of N and K being 150 and 85 mg / kg of air-dry soil, respectively.

The plants were harvested at maturity. The above- ground plant material was harvested and oven-dried at 60°C. Sample dry weight was recorded and ^{32}P activity was determined in grain and straw using the radiometric device “Nuclear Chicago”. The ^{32}P activity was corrected on the date the experiment was established in accordance with the half-life period of ^{32}P. The total P was determined in grain, straw and chaff following dry ashing and subsequent analysis of P in solution by the method of Truog-Meyer [9]. The specific activity of ^{32}P (S.A.) was measured and expressed in Bq/mg P.

When ^{32}P carrier-free solution is added to the soil of each pot, the S.A. of plant material in the absence of RP is a measure of the S.A. of the soil bioavailable P. In this case, the % of P taken up by plants from the soil bioavailable P in the presence of fertilizer is defined by the equation:

$$\% \text{ PdfL} = \frac{\text{S.A. plant in presence of F}}{\text{S.A. plant in absence of F}} \times 100 \quad (1)$$

where F refers to RP or SP. Percent of P taken up from fertilizers is calculated as:

$$\% \text{ PdfF} = \left(1 - \frac{\text{S.A. plant in presence of F}}{\text{S.A. plant in absence of F}}\right) \times 100 \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Phosphorus availability

There was a tendency for an accelerated ripeness of plants with the increased P rates as superphosphate compared to the control. This tendency was insignificant for various P rates of rock phosphates. It is essential to note that application of the high P rate (87.2 mg/kg) as superphosphate resulted in a decrease in the mean height of plants by 4-5 cm compared to the control (Table I). However, the plants fertilized with PR at different rates did not show change in stem height. Seed weight was the main indicator of plant yield. Plant yield was considerably dependent on the level of P availability in soil. The maximum increase in yield by 68.4% compared to the control was registered at a rate of 87.2 mg/kg soil of superphosphate (Tables I and II).

TABLE I. YIELD OF BARLEY PLANTS IN GREENHOUSE EXPERIMENT

Treatment	Mean height, cm	Total weight, g	Seed weight, g	Straw weight, g	Chaff Weight, g	Weight of 1000 Seeds, g
Background control	73.5±1.7	18.6±1.1	6.5±0.5	10.1±0.7	2.2±0.1	41.7±1.2
SP=21.8 mg P /kg	73.8±0.4	25.9±2.0	9.0±0.8	14.5±1.7	2.4±0.4	46.3±1.5
SP=43.6 mg P /kg	71.5±2.4	27.2±2.0	9.5±1.4	14.9±1.4	2.8±0.2	45.5±2.3
SP=87.2 mg P /kg	67.3±2.2	34.4±0.3	10.9±1.2	15.5±0.6	2.8±0.2	49.3±2.7
RP=21.8 mg P /kg	70.3±3.3	22.0±2.3	7.6±0.9	12.0±1.9	2.5±0.3	45.7±3.7
RP=43.6 mg P /kg	70.8±3.4	25.3±1.9	9.3±1.2	13.4±1.0	2.6±0.7	45.8±4.2
RP=87.2 mg P /kg	71.0±1.6	27.5±2.7	10.2±1.1	14.9±1.6	2.4±0.2	46.9±4.9

TABLE II. INCREASE IN YIELD AS A RESULT OF APPLICATION OF P FERTILIZERS

Treatment	Grain yield, g/pot	Increase compared to the control, %	Straw yield, g/pot	Increase compared to the control, %
Background control	6.45±0.52	-	10.1±0.7	-
SP=21.8 mg P /kg	8.97±0.75	39.1	14.5±1.7	43.9
SP=43.6 mg P /kg	9.52±1.36	47.6	15.0±1.4	48.0
SP=87.2 mg P /kg	10.9 ±1.2	68.4	15.5±0.6	53.5
RP=21.8 mg P /kg	7.59±0.90	17.7	12.0±1.9	18.8
RP=43.6 mg P /kg	9.31±1.17	44.3	13.4±0.9	32.3
RP=87.2 mg P /kg	10.2 ±1.1	57.5	14.9±1.6	47.5

Rates of superphosphate such as 43.6 and 21.8 mg P / kg soil resulted in an increase in seed yield by 47.6 and 39.1% compared to the control. The application of different rates of local RP caused an increase in seed yield as well. However, treatment at 21.8 mg P / kg soil was less pronounced compared to the equivalent superphosphate rate and amounted to 17.7% increase in grain yield. At the same time application of RP at rates of 43.6 and 87.2 mg P / kg soil resulted in seed yield increase approaching those for superphosphate.

A pronounced yield increase of barley plants as a result of application of various rates of P fertilizers is most likely explained by a very low P availability in the soil used for the greenhouse experiment. The same trend towards yield increasing was also noted for the straw weight when various rates of P fertilizers were applied.

The application of superphosphate, at a rate of 87.2 mg P/kg soil, increased the weight of 1000 seeds by 7.6 g. The application of both superphosphate and local RP, at doses of 21.8 and 43.6 mg P/kg soil, had approximately the same effect on the increase in weight of 1000 seeds by an average of 3.8 to 5.2 g.

Total P content and S.A. in plant are given in Table III. The data demonstrated the relative availability of P derived from RP applied at a rate of 21.8 mg P/kg soil was 56.2% compared to SP (those for rates 43.6 and 87.2 mg/kg reach 74.5 and 81.3%, respectively) (Table IV). These results agree with the previously established finding that the comparison of different sources is independent of the amount of fertilizers applied at rates from 50 to 100 mg P/kg soil [7]. At the same time, the results from treatments with very low rates of P fertilizers (21.8 mg P/kg) may not coincide with those from treatments with the high fertilizer rates. The differences are most likely due to the changes in the P uptake and utilisation by plants at the low and high P fertilizer rates.

Based on the results of %PdfL and %PdfF (Table IV), and the values of the total P accumulation in yield of plants, the amount of P taken up by plants from soil and fertilizers, and the P availability derived from local RP and SP was calculated (Table V). The calculations performed have shown that uptake of P by plants is increased with the P rates of the application and the percent of P utilization from fertilizers decreased. The amount of P taken up by plants from soil is not a constant value and tends to decrease with the increase in the rate of fertilizers. When local RP are applied to soil at a rate 21.8 mg/kg, the amount of P taken up by plants from soil is equal to the corresponding P values in the control. With the increase in RP rates up to 43.6 and 87.2 mg/kg, the amount of P taken up by plants from soil is reduced compared to the control by 4.15 and 6.76 mg, respectively. The type and rates of P fertilizers define phosphorus supply to plants from fertilizers. With the increase in SP rates from 21.8 to 87.2 mg/kg, the availability of P from SP was reduced from 32.6 to 19.3%. For local RP the differences are less pronounced, from 14 to 10.5%. The percentage of the total amount of P taken up by plants from local RP is on average 2.1 times less compared to SP.

3.2. Potential reduction of ^{137}Cs plant uptake

One of the most effective ways to reduce radionuclide uptake to plant products is the application of high doses of P and K fertilizers [10-12]. However, the difficult economic situation in the Russian Federation prevents the application of fertilizers on arable lands at recommended doses resulting in low yields and elevated levels of radioactive contamination of products and extra irradiation of local population due to consuming these products. The application of local rock phosphates as fertilizers is a most promising way to solve the problem.

Results from the second experiment showed that increasing rates of local RP influenced ^{137}Cs transfer from soil to barley yield (Table VI). For the treatment at 21.8 mg P/kg soil, the differences in ^{137}Cs accumulation in grain and straw were insignificant compared to the control. Treatments at 43.6 mg P/kg soil resulted in 1.2- and 1.3-fold decrease in ^{137}Cs accumulation in grain and straw, respectively. Treatments at 87.2 mg P/kg soil caused further decrease in ^{137}Cs accumulation in grain and straw.

TABLE III. CONTENT OF P IN PLANTS

Treatment	Content of P in plants, mg/g			Total P	S.A.,
	Grain	Straw	Chaff	Content, mg	kBq /mg P
Background control	2.69±0.13	0.90±0.06	0.92±0.02	28.4±2.9	27.1±3.3
SP=21.8 mg P / kg	3.40±0.18	1.43±0.17	1.40±0.10	54.6±5.5	9.48±0.68
SP=43.6 mg P / kg	3.73±0.20	2.40±0.20	2.29±0.27	77.6±8.8	6.07±0.54
SP=87.2 mg P / kg	4.52±0.34	2.66±0.08	2.67±0.04	111.0 ±5	3.79±0.32
RP=21.8 mg P / kg	3.06±0.10	1.13±0.05	1.06±0.06	41.7±5.8	17.2±1.2
RP=43.6 mg P / kg	3.45±0.08	1.33±0.10	1.28±0.07	52.9±4.0	11.4±1.0
RP=87.2 mg P / kg	3.69±0.12	1.51±0.12	1.53±0.09	65.6± 7.3	8.15±0.46

TABLE IV. MEAN VALUES OF %PdfL AND %Pdf F

Treatment	%PdfL	%Pdf F	RAiD
SP=21.8 mg P / kg	35.0	65.0	-
SP=43.6 mg P/ kg	22.4	77.6	-
SP=87.2 mg P / kg	14.0	86.0	-
RP=21.8 mg P / kg	63.5	36.5	56.2
RP=43.6 mg P / kg	42.2	57.8	74.5
RP=87.2 mg P / kg	30.1	69.9	81.3

TABLE V. MEAN VALUES OF P TAKEN UP BY PLANTS FROM SOIL AND FERTILIZERS

Treatment	Total amount of P in plants (mg)	Amount of P taken up by plants from soil[1] (mg)	Amount of P taken up by plants from fertilizers (mg)	Use of P from fertilizers (%)
Background control	28.4	26.5	-	-
SP=21.8 mg P /kg	54.6	19.1	35.5	32.6
SP=43.6 mg P / kg	77.6	17.4	60.2	27.6
SP=87.2 mg P / kg	97.8	13.7	84.2	19.3
RP=21.8 mg P / kg	41.7	26.5	15.2	14.0
RP=43.6 mg P / kg	52.9	22.3	30.6	14.0
RP=87.2 mg P / kg	65.6	19.7	45.8	10.5

[1] without taking into account P in seeds.

TABLE VI. ^{137}CS CONTENT IN YIELD OF BARLEY, Bq/kg

	Yield, g		^{137}Cs content, Bq/kg	
Treatment	Grain	Straw	Grain	Straw
Background control	5.99±0.70	9.69±0.38	44±7	89±5
RP=21.8 mg P /kg	7.07±0.49	12.40±0.86	51±5	86±3
RP=43.6 mg P / kg	8.58±0.47	13.70±0.85	36±3	69±4
RP=87.2 mg P / kg	9.54±0.57	13.79±1.19	32±3	63±4

The observed reduction in ^{137}Cs accumulation in yield of plants may be a result of an increase in yield capacity of plants and decrease in ^{137}Cs concentration per unit plant mass. The application of RP may favor the formation of different chemical compounds in the soil with ^{137}Cs that changes their availability to plants. The application of local RP to soil has a long residual effect on the soil agrochemical characteristics, which in turn can significantly influence the behavior of radionuclides in the soil-plant system. In this context, field experiments need to be conducted for several years to assess the effects of RP application on variations in ^{137}Cs uptake by plants.

4. CONCLUSIONS

The application of local Polpino rock phosphates on poorly cultivated acid sod-podzolic soil increased the yield of barley. Treatments at rates of 21.8, 43.6 and 87.2 mg P/kg soil as RP resulted in an increase in grain yield by 17.7, 44.3 and 57.5%, respectively, compared to the control. The highest increases of grain yield were obtained with 43.6 and 87.2 mg P/kg soil as PR and approached those of treatments with superphospate.

The relative availability of P derived from RP, applied at 21.8 P mg/kg soil, was 56.1% compared to SP. The values for rates of 43.6 and 87.2 mg P/ kg soil were, respectively, 74.5 and 81.3%. The uptake of P by plants increased with the P rate of application of the fertilizers studied, and the percent of P derived from the fertilizers decreased. The amount of P taken up by plants from soil is not a constant value and tended to decrease with an increase in the rate of fertilizers applied. The amount of P available for plants from fertilizers depends on the type and rate of P fertilizers. With the increase in SP rates from 21.8 to 87.2 mg/kg soil, the P utilisation of SP by plants decreased from 32.6 to 21.9%. For the local Polpino RP, the decrease was less pronounced, from 14 to 10.4%. The percent of the total amount of P contained in local RP and used by plants is on average 2.1 times less compared to SP.

Different rates of local RP have been found to produce different effect on ^{137}Cs transfer from soil to yield of barley. In treatments at 21.8 mg P/kg soil, the differences in ^{137}Cs accumulation in grain and straw were insignificant compared to the control. However, at rates of 43.6 and 87.2 mg P/kg soil the reduction in ^{137}Cs accumulation in grain and straw was on average 1.2 to 1.4 times less than the control without P.

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REFERENCES

[1] MILASCHCHENKO, N.Z., Expanded reproduction of soil fertility in the intensive farming in the non-Chernozemic area of Russia, 864 pp., Moskow: Nauka (in russian) (1993).

[2] YAGODIN, B.A., SMIRNOV, P.M., PETERBURGSKY, A.V., Agrochimiya. Moskow: Nauka (in russian) (1989).

[3] CHUMACHENKO, I.N., RUKAVICHKO, V.G., CHUMACHENKO, E.S., The application of local deposits of rock phosphates. Chimiya v selskom hoseystve **3** (1991) 28-29 (in russian).

[4] FRIED, M., "E", "L" and "A" values. In: Trans. 8th. Int. Congr. Soil Sci. Vol **4** (1964) 29-41. Bucharest, Romania.

[5] IAEA, Measurement of soil and fertilizer phosphorus availability to plants, In: Tracer Manual on Crops and Soils. Tech. Rep. Series 171, pp. 129-138, IAEA, Vienna, Austria (1976).

[6] ZAPATA, F., AXMANN, H., ^{32}P isotopic techniques for evaluating the agronomic effectiveness of rock phosphate materials. Fert. Res. **41** (1995) 189-195.

[7] MOREL, C., FARDEAU, J.C., Phosphorus bioavailability of fertilizers: a predictive laboratory method for its evaluation, Fert. Res. **28** (1991) 1-9.

[8] ZHURBITSKY, Z.I., Theory and practice of a greenhouse experiment. Moskow: Nauka (in russian) (1968).

[9] TRUOG, E., The determination of the readily available phosphorus of soils, J. Amer. Soc. Agron. **10** (1930) 22-27.

[10] ALEXAKHIN, R.M., MOISEYEV, I.T., TIKHOMIROV, F.A., The behavior of ^{137}Cs in the soil-plant system and the influence of fertilizers on the radionuclide accumulation in yield, Agrochimiya **8** (1992) 127-138 (in russian).

[11] JUDINTSEVA, E.V., PAVLENKO, L.I., ZYULIKOVA, A.G., Soil properties and ^{137}Cs accumulation in crop yields, Agrochimiya **8** (1981) 86-93 (in russian).

[12] MOISEYEV, I.T., TIKHOMIROV, F.A., MARTYUSHOV, V.S., On the evaluation of the effect of mineral fertilizers on the dynamics of exchangeable ^{137}Cs in soils and its availability for vegetable crops, Agrochimiya **5** (1988) 86-92 (in russian).

COMPARATIVE EVALUATION OF THE EFFECT OF ROCK PHOSPHATE AND MONOAMMONIUM PHOSPHATE ON PLANT P: NUTRITION IN SOD-PODZOLIC AND PEAT SOILS

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Abstract

The direct application of finely ground rock phosphate (RP) imported from Russia has been suggested as an alternative to the almost twice more expensive water-soluble monoammonium phosphate (MAP) on acid (moderately limed) sod-podzolic and peat soils. A pot experiment was conducted in 1997-1998 for a comparative evaluation of P availability from RP and MAP using the ^{32}P isotope dilution technique. The lupine was grown on sod-podzolic silty clay loam soil with pH 6.0 and a medium level of available P. Ryegrass plants were grown on peat soil with pH 4.9 and a low level of native soil P fertility.

Application of RP and MAP at a rate of 40 mg P/kg soil supplied similar moderate mount of P to lupine plants. The Pdff values, i.e. the fractions of P in the plants derived from the applied RP and MAP, were 7.4 and 8.4%, respectively. The application of the same P fertilizers to the peat soil had different effects on P nutrition of ryegrass plants. The Pdff values were 14.9% for RP and 22.1% for MAP. It may be concluded that for most annual crops water-soluble P forms such as MAP should be preferred. Direct application of RP is recommended for plants with an adequate rhizosphere ability to utilize P, such as lupine on acid sod-podzolic silty clay loam soils (pH<6.0). Considering cost differences of the P fertilizers, RP application on acid peat soil (pH<5.0) may be reasonable for major improvement of radionuclide-contaminated grassland.

The results of the second pot experiment suggested that direct application of RP may be more effective than the use of water-soluble P fertilizers in reducing the plant uptake of ^{137}Cs on contaminated, moderately limed sod-podzolic silty clay loam and peat soils. These soils are widely spread in the radioactive contaminated area of Belarus after the Chernobyl accident. Direct application of RP may be one of the effective countermeasures for the decrease of ^{137}Cs transfer from the contaminated acid soils to crop production.

1. INTRODUCTION

From 1965 to 1990, as a result of large-scale water engineering, liming and the intensive use of organic and mineral fertilizers, the productivity of arable land in Belarus has risen from 1.5 to 4.3 t/ha in grain equivalents. Significant improvement of soil fertility status was also achieved. However, the fertilizer consumption and productivity of agricultural land has been strongly declining over the last decade during the transition to a market economy. This decrease in available phosphorus and other nutrients was revealed by the results of soil testing. The available soil phosphate content has gone down from 1990 to 1997 to levels of 2 to 4 mg P/kg soil. Of a total of 118 districts in Belarus 50 districts showed a negative balance of phosphorus on arable land.

The main types of P-fertilizers produced in Belarus are monoammonium phosphate (MAP) and single ammonium superphosphate, which are water-soluble fertilizers and very expensive. During the period from 1991 to 1995 its consumption has decreased from 194 to 27 thousands tons of P per year. In 1997-1998 the application of P fertilizers has increased again up to 53 thousands tons of P per year. However, there is still evidence of a poor P balance in agriculture and a possible depletion of soil fertility in the future.

Field experiments carried out with various crops on sod-podzolic soils in the former USSR found that cheap rock phosphate with the correct choice and application might be an effective and valuable P fertilizer. The response to rock phosphate for crops grown on acid soils with low phosphorus reserve was larger than for those on limed soils that were better supplied with phosphorus [1-3].

Direct application of rock phosphate has been practiced in Belarus in the 1960s. Field and pot experiments (using the ^{32}P isotope technique) were carried out to study the comparative effectiveness of RP and superphosphate. It was found that there is a considerable scope for effective direct application of RP as a P fertilizer in the cultivation of legumes and other crops on acid soils [4, 5]. After intensive liming of acid soils in Belarus, the consumption of RP for direct application has declined rapidly. During the last 20 years, RP has not been used as a P fertilizer. Currently all imported RP into Belarus is used for the production of compound fertilizers. A significant RP deposit was found in Belarus, which also needs studied in forthcoming years.

Therefore, it is important to study the possibility of a profitable application of finely ground RP imported from Russia, which is sufficiently cheaper than locally produced water-soluble P fertilizers. There is a potential for a direct application of suitable kinds of RP to acid, moderately limed sod-podzolic and peat soils, which comprise about 30% of agricultural land in Belarus.

The aims of these studies were: 1) to determine the P fraction in plants derived from P fertilizers (rock phosphate and monoammonium phosphate) by means of ^{32}P isotopic techniques, 2) to make a comparative evaluation of availability of phosphorus rock phosphate and monoammonium phosphate for lupine and ryegrass, 3) to determine the effect of P fertilizers on the reduction of the root uptake of radionuclide ^{137}Cs in sod-podzolic and peat soils, and 4) to evaluate the possibility of direct application of a cheaper ground RP as an alternative to water soluble P fertilizer.

2. MATERIALS AND METHODS

Pot experiments were set up in the greenhouse of the Belorussian Research Institute for Soil Science and Agrochemistry in Minsk, using sod-podzolic silty clay loam soil (1997) and peat soil (1998). The soil characteristics are shown in Table I.

The sod-podzolic silty clay loam soil with medium content of extractable and available phosphorus and medium level of acidity was suitable for testing the effectiveness of RP. The peat soil had a higher level of acidity and low level of extractable and available P content. Both soils are typical for the area contaminated with radionuclide ^{137}Cs after the Chernobyl accident.

2.1. Pot experiment A: using the ^{32}P isotopic dilution method

A rock phosphate of the Briansk deposit in Russia was used in this study. The RP contained 8.3% total P, 0.04% water-soluble P and 2.9% citric acid-soluble P. Another tested fertilizer was the monoammonium phosphate which contained 21.8% total P and 20.4% water-soluble P.

Samples of the sod-podzolic soil untreated and amended with fertilizers studied were sent to Jean-Claude Fardeau, Centre de Cadarache, France, to determine the soil P status using the ^{32}P isotopic exchange kinetics method [6].

Evaluation of RP in comparison with MAP was made using the ^{32}P-isotope dilution technique [7]. A solution of NaH_2PO_4 labeled with ^{32}P used at low concentration (3.7×10^6 Bq ^{32}P diluted in 200 ml of distilled water per 5 kg of soil) was added to soil and thoroughly mixed. The soil was placed in plastic pots (5 kg per 1 pot) and it was allowed to reach equilibrium for a week. After that, the unlabelled fertilizers were applied according to the following treatments on sod-podzolic soil with lupine as a test crop:

1. Control
2. Rock phosphate (40 mg P/kg soil)
3. Monoammonium phosphate (40 mg P/kg soil)

Potassium was used in all treatments as muriate of potash at a rate of 140 mg K/kg soil. There was no need in applying N fertilizer for the experimental lupine crop. A minimal rate of 22 mg N/kg soil was applied as NH_4NO_3 in treatments 1 and 2 to equalize the amount of N applied with P in treatment 3.

TABLE I. SELECTED PROPERTIES OF THE SOD-PODZOLIC AND PEAT SOILS USED IN THE STUDY

Characteristics	Method used[1]	Value	
		Sod-podzolic soil	Peat soil
(pH H_2O)	1:2.5-25 (soil: water)	6.00	4.90
(pH KCl)	1:2.5-25 (soil: KCl)	5.00	4.15
Organic matter, %	$K_2Cr_2O_7$ oxidation	1.34	-
Extractable P (mg/kg)	0.2M HCl	67.0	30.3
Available P (mg/l)	0.01M $CaCl_2$	0.14	0.12
Cation exchange capacity (cmol(+)/kg)	Buffer solution $BaCl_2$	18.1	70.0
Exchangeable cations (cmol(+)/kg)			
Ca	1M KCl	5.20	25.0
Mg	1M KCl	1.30	12.8
K	1M NH_4OAc, pH 7.0	0.23	0.60
Texture, %	Pipette method		
Clay		24.7	-
Silt		55.7	-
Sand		19.6	-

[1] Ratio soil: water for the peat soil is 10 times lower than for sod-podzolic soil.

On peat soil with ryegrass as a test crop, fertilizers were applied according to the treatments:

1. Control
2. Rock phosphate (40 mg P/kg soil)
3. Monoammonium phosphate (40 mg P/kg soil)

Potassium and nitrogen were used in all treatments as muriate of potash and applied at 170 mg K/kg soil. Nitrogen was applied at 80 mg N/kg soil with ammonium nitrate. Since some N was applied with P in treatment 3, only 58 mg N/kg as ammonium nitrate was needed for this treatment. The fertilizers were mixed with the soil and the soil was placed in plastic pots. There were four replications per treatment.

The pregerminated seeds of yellow lupine (cultivar Pava) were sown in each pot in early June 1997 and seeds of ryegrass (cultivar Avante) in 1998. Pots were arranged in a randomized design. The soil moisture was adjusted to 40 to 60% of the field capacity with distilled water. The tested plants were grown for two months.

The plants of lupine and ryegrass were harvested, cut into small pieces and oven dried at 65°C until a constant weight achieved. Dry matter yield was calculated. Two-gram plant samples from each pot were ashed at 450°C, dissolved in 20 ml of 1 M HCl and filtered. The ^{32}P activity in the samples was measured using Cerenkov counting in a liquid scintillation counter. After dry ashing, the total P content in the plants was also measured by the molybdate blue method. The amount of P derived from the soil and from the tested fertilizers was calculated using the isotope dilution procedure [7, 8].

Since the specific activity (S.A.) of labeled soil = S.A. of the plant in treatment 1, the fraction of P in the plant which was derived from the tested fertilizers (or % Pdff) was calculated from the following equations:

$$\% \text{ Pdff RP} = (1 - (\text{S.A. plant treatment 2/ S.A. plant treatment 1})) \times 100 \quad (1)$$
$$\% \text{ Pdff MAP} = (1 - (\text{S.A. plant of treatment 3/ S.A. plant of treatment 1})) \times 100 \quad (2)$$

The relative availability as determined by isotope dilution (RAID) for comparing the availability of RP with MAP was calculated from the following:

$$\text{RAID} = \%\text{Pdff RP} / \%\text{Pdff MAP} \times 100 \quad (3)$$

2.2. Pot experiment B: with ^{137}Cs contaminated soil

The effect of P-fertilizers on the reduction of the root uptake of radionuclide ^{137}Cs was studied on the same soils with a parallel set of above-mentioned treatments.

A solution of $CsCl_2$ labelled with ^{137}Cs (900 Bq ^{137}Cs diluted in 200 ml of distilled water per 1 kg of soil) was added to soil and thoroughly mixed. After that, the soil was placed in plastic pots (5 kg per 1 pot) and it was allowed to reach equilibrium for a week. Then, unlabelled fertilizers were applied according to the treatments on sod-podzolic soil with lupine as the test crop.

1. Control
2. Rock phosphate (40 mg P/kg soil)
3. Monoammonium phosphate (40 mg P/kg soil)

On peat soil with ryegrass as the test crop, fertilizers were applied according to the treatments:

1. Control
2. Rock phosphate (40 mg P/kg soil)
3. Monoammonium phosphate (40 mg P/kg soil)

Nitrogen and K were applied as described for pot experiment A. The fertilizers were mixed with the soil and the soil was placed in plastic pots. There were four replications per treatment. The seeds of lupine and ryegrass were sown in each pot and were grown. When the plants were harvested, they were cut into small pieces and oven dried at 65° C. The ^{137}Cs activity was determined by a Gamma-spectrometer.

3. RESULTS AND DISCUSSION

3.1. Prediction of the effectiveness of P fertilizer application on sod-podzolic soil

The experimental results obtained in the laboratory of Dr. Fardeau using the ^{32}P-isotope exchange kinetic method are presented in Tables II and III. The fixing capacity of this soil (r_1/R) remained low to medium after 40 days of incubation in moist conditions at a temperature from 25 to 28° C. The C_p value (intensity factor) of the control treatment was slightly lower than 0.2 mg/L and directly available P (E_1) was medium at 4.4 mg P/kg. Therefore, the native soil P fertility is medium and P was not a main limiting factor for crop production.

After application of RP at the rate 50 mg P/kg soil, the directly available P (E_1) and other more mobile pools (A, B, and C) did not increase (Tables II and III). After harvesting, the available P content of the soil (E_1 values as high as 20 mg P/kg) was significantly increased for MAP treatment. Since the fixing capacity was low to medium, a large part of the P applied as MAP remained directly available. The kinetic exchange constants (Table III) indicated the mobility of the P ions was not significantly increased by RP application.

TABLE II. BIOAVAILABLE SOIL P PARAMETERS FOR THE SOD-PODZOLIC SOIL (AFTER AN INCUBATION PERIOD OF 40 DAYS)

Treatment	PH (H_2O)	C_p (mg P/L)	r_1/R	n	E_1 (mg P/kg)	E_1/C_p (L/kg)	Total P (mg P/kg)
Control	6.2	0.15	0.34	0.30	4.4	29.3	473
RP 50 mg P/kg soil	6.2	0.20	0.36	0.25	5.5	27.5	523
MAP 50 mg P/kg soil	6.0	1.10	0.54	0.14	20.0	18.2	523

TABLE III. COMPARTMENTAL ANALYSIS AND KINETIC PARAMETERS OF SOIL P (AFTER AN INCUBATION PERIOD OF 40 DAYS)

	P pools (mg P/kg soil)				K_m	T_m	F_m
Treatment	A	B	C	D	min^{-1}	$min \cdot 10^{-2}$	$mg \cdot min^{-1}$
Control	32	78	50	319	11.0	9	16.4
RP 50 mg P/kg soil	27	56	28	407	15.0	7	30.0
MAP 50 mg P/kg soil	31	38	15	420	11.0	9	125.0

3.2. Experiment A

The shoot dry-weights, P concentrations and P uptake values are shown in Table IV. The shoot yields of lupine and ryegrass were highest in the treatment with MAP, followed by the treatment with RP. Plants of the treatment with RP grew significantly better than did plants of the control treatment, but worse than the MAP treatment. Lupine shoots supplied with P from RP and MAP took up 2.6 and 4.3 mg P/pot more than did plants with no P treatment. The yields of dry mass of lupine shoots were also increased 9 and 15% compared to the control treatment. The highest difference between RP and MAP was observed on peat soil. The shoots of ryegrass took up 2.7 and 9.4 mg P/pot more than did plants on the control treatment.

The data on specific activity (S.A.) of cultivated plants determined at harvest time are shown in Table V. In comparison to the treatment without P, S.A. of the plants decreased as a result of an extra supply of P from RP and MAP added to the soil-plant system.

The Pdff values for lupine (the fraction of P in the plants derived from the applied RP and MAP) were almost the same at 7.4 and 8.4%, respectively. Phosphorus fertilizer recovery values for RP and MAP were only about 1% because of the relative high content of available soil native P. It is evident that for lupine plants 1 kg P as MAP is nearly equivalent to 1 kg P as RP. The high relative availability of RP compared with MAP (RAID = 88%) was due to a high root ability of lupine to utilize P from insoluble forms.

For ryegrass on peat soil, the Pdff values were 14.9 for RP and 22.1% for MAP. Phosphorus fertilizer recovery values for RP and MAP were 1.5 and 2.9%. The higher P uptake efficiency of ryegrass from MAP was due to the water-soluble source of phosphorus in this fertilizer. For the ryegrass plant, 1 kg P as MAP was equivalent to 1.48 kg of RP. The application of MAP proved to have a better agronomic effect on ryegrass than RP application (RAID = 67%) on acid peat soil. However, the application of RP on the peat soil with rather low level of the native P fertility provided a statistically significant increase in ryegrass shoot yield compared to the control treatment without P.

TABLE IV. SHOOT DRY WEIGHT OF LUPINE AND RYEGRASS AND P UPTAKE BY PLANTS

Treatment	Shoot dry weight (g/pot)	P concentration (%)	Total P uptake (mg P/pot)
Lupine (sod-podzolic soil)			
Without P fertilizer	12.8	0.188	24.1
RP 40 mg P/kg soil	14.0	0.191	26.7
MAP 40 mg P/kg soil	14.7	0.193	28.4
LSD_{05}	0.3	0.01	0.7
Ryegrass (peat soil)			
Without P fertilizer	15.4	0.110	16.9
RP 40 mg P/kg soil	16.3	0.120	19.6
MAP 40 mg P/kg soil	18.8	0.140	26.3
LSD_{05}	0.6	0.01	0.9

TABLE V. SPECIFIC ACTIVITY OF LUPINE AND RYEGRASS AND P UPTAKE BY PLANTS FROM FERTILIZERS

Treatment	Specific activities (Bq/mg P)	Pdf soil (%)	Pdff (%)	P fertilizer recovery (%)
Lupine (sod-podzolic soil)				
Without P	22.9	100.0	-	-
RP 40 mg P/kg soil	21.2	92.6	7.4	1.0
MAP 40 mg P/kg soil	20.9	91.6	8.4	1.2
Ryegrass (peat soil)				
Without P	73.4	100.0	-	-
RP 40 mg P/kg soil	62.5	85.1	14.9	1.5
MAP 40 mg P/kg soil	57.2	77.9	22.1	2.9

The effect of RP and MAP on soil fertility properties after harvesting the test crops is shown in Table VI. No significant differences were observed between pH value for the treatments without P and the treatments with MAP and RP application. It is known that most of the native phosphorus in soil is fixed in unavailable forms. Also the fertilizer phosphorus becomes more insoluble in soils with time. Even the amounts classified as “available” by most chemical soil testing methods are not directly soluble and available to plants. For example, the P fertility of sod-podzolic soil was signify-cantly increased to the same level after RP and MAP application when tested using the standard Belorussian method (0.2 M HCl extracting). But, there was only a modest increase in available P tested in 0.01 M $CaCl_2$ solution after RP application. After MAP application, there was a 3-fold greater available P as determined by 0.01 M $CaCl_2$. The 0.01 M $CaCl_2$ extracting method was able to detect difference in available P in sod-podzolic soil amended with RP and MAP relatively close to the ^{32}P-isotope exchange kinetic method of Fardeau (Table II). The local standard method (0.2 M HCl) overestimated the availability of P in natural RP.

The peat soil P fertility was also significantly increased to nearly the same level after application of RP and MAP. The determination of P fertility by the standard method (0.2 M HCl) and 0.01M $CaCl_2$ extracting method did not show the significant superiority of the latter test method for peat soil.

Phosphorus applications on sod-podzolic soils with medium level of available phosphorus have to be mainly for soil fertility maintenance in the rates close to the P output from harvested yields. For most of the crops, there is a preferable application of water-soluble P forms as MAP. But for plants with a high root ability to utilize P such as lupine, buckwheat, and rapeseed, RP may be used for direct application as well as water-soluble P fertilizers on acid soils (pH_{H2O} <6.0, pH_{KCl} <5.0).

The effect of water-soluble P fertilizer MAP on ryegrass was much higher than that of RP on acid peat soil in spite of comparatively low levels of the native soil P fertility. The cost of the fertilizers has to be taken into consideration. The cost of 1 ton of P in the form of MAP delivered to Belorussian market in June 1997 was 773 US$. The cost of 1 ton of P in RP was 481 US$. Therefore, the direct application of finely grounded RP on acid peat soil (pH_{H2O} <5.0), especially for radical improvement of grassland on the radionuclide-contaminated area may be reasonable. Field experiments are needed for the development of economically sound practical recommendations.

TABLE VI. EFFECT OF THE TESTED FERTILIZERS ON AVAILABLE P CONTENT IN SOD-PODZOLIC AND PEAT SOIL EVALUATED BY CHEMICAL METHODS

Treatment	pH (KCl)	Extractable P (0.2M HCl) mg/kg	Available P (0.01M $CaCl_2$) mg/L
Sod-podzolic soil			
Without P	5.00	64	0.14
RP 40 mg P/kg soil	5.20	101	0.19
MAP 40 mg P/kg soil	4.90	111	0.43
LSD (P=0.05)	0.20	16	0.09
Peat soil			
Without P	4.15	30	0.12
RP 40 mg P/kg soil	4.20	62	0.23
MAP 40 mg P/kg soil	4.15	59	0.27
LSD (P=0.05)	0.20	2	0.03

3.3. Experiment B

Phosphorus and K fertilizers applied to radioactive contaminated soil may significantly decrease the radionuclide consumption by plants, as well as increase crop yields. Therefore, the effect of RP and MAP on the root uptake of radionuclide ^{137}Cs was studied on the same soils with a parallel set of pot experiment treatments.

The shoot dry weight of lupine and ryegrass and its ^{137}Cs activity was determined for the same treatments with P fertilizers as in experiment A, but the soils were contaminated with ^{137}Cs (Table VII).

The yields of tested plants in all treatments were close to those in experiment A. There was significant reduction of the root uptake of ^{137}Cs by lupine on RP treated (16% decrease) and MAP (8% decrease) treated soils in comparison with plant activity of the control treatment. The ^{137}Cs activity of ryegrass plants on peat soil decreased 27% after application of RP, but only a 7% decrease was observed with MAP application. A stronger effect of RP on the plant root uptake of ^{137}Cs may be explained from the higher Ca content of RP compared with MAP.

The results of pot experiments suggest that direct application of RP may be more effective than use of water-soluble P fertilizers in reducing the plant uptake of ^{137}Cs on the acid sod-podzolic and peat soils. These data are very important because the tested soils are widely spread in the radioactive contaminated area. It is necessary to continue the comparative evaluation of RP and MAP effectiveness in field trials. Direct application of RP may be one of the effective countermeasures for decreasing ^{137}Cs transfer from the contaminated acid soils to crop production.

TABLE VII. INFLUENCE OF P FERTILIZERS ON THE ^{137}Cs CONTAMINATION OF LUPINE SHOOTS ON SOD-PODZOLIC SOIL AND RYEGRASS ON PEAT SOIL

Treatments		Shoot dry weight (g/pot)	^{137}Cs activity of shoots Bq/kg
Lupine			
Without P		13.0	109
RP 40 mg P/kg		14.1	91
MAP 40 mg P/kg		14.5	101
	LSD (P=0.05)	0.5	5.0
Ryegrass			
Without P		15.1	1156
RP 40 mg P/kg		16.3	847
MAP 40 mg P/kg		18.7	1084
	LSD (P=0.05)	0.5	65

4. CONCLUSIONS

Direct application of RP and MAP, at a rate of 40 mg P/kg soil, made almost the same moderate contribution to P nutrition of lupine grown on a typical Belarus moderately limed sod-podzolic silty clay loam soil with pH_{H2O} 6.0 and medium level of directly available P. The Pdff values for the RP and MAP applied fertilizers were 7.4 and 8.4%, respectively. It is evident that P applications have to be mainly for soil fertility maintenance in the rates close to the P output by harvested yields. For most of the crops there is a preferable application of water-soluble P forms as MAP. But for the plants with a better rizosphere ability to utilize P such as lupine, buckwheat, rapeseed, RP may be used for direct application as well as water-soluble P fertilizers on acid soils ($pH_{H2O} <6.0$, $pH_{KCl} <5.0$).

The effect of water-soluble P fertilizer MAP on ryegrass was much higher than that of RP on acid peat soil (pH_{H2O} 4.9, pH_{KCl} 4.1) with a comparatively low level of the native soil P fertility. The Pdff values for tested RP and MAP were respectively 14.9 and 22.1%. The native peat soil P fertility is one of the main limiting factors for crop production and higher rates of P fertilizers are needed. In general, peat soils prefer application of water-soluble P fertilizers. But, differences in costs of fertilizers have to be considered. The cost of 1 ton of P in form of MAP delivered to Belorussian market in June 1997 was 773 US$, but the cost of 1 ton of P in RP was 481 US$. So the direct application of finely grounded RP on acid peat soil ($pH_{H2O} <5.0$), especially for major improvement of grassland located in the radionuclide contaminated area may be reasonable.

The results of a second pot experiment suggests that direct application of RP may be more effective than use of water-soluble P fertilizers in reducing the plant uptake of ^{137}Cs on acid sod-podzolic and peat soils. There was a noticeable reduction of the root uptake of ^{137}Cs by lupine on RP-treatment (16% decrease) and MAP (8% decrease) in comparison with plant activity of the control treatment. The activity of ryegrass plants on peat soil decreased by 27% after application of RP, but after MAP application there was only a 7% decrease. The tested soils are widely spread in the radioactive contaminated area. It is necessary to continue the comparative evaluation of RP and MAP effectiveness in field trials for development of economically sound practical recommendation. Direct application of RP may be one of the effective countermeasures for decreasing ^{137}Cs transfer from the contaminated acid soils to crop production.

The studies showed that 0.01 M $CaCl_2$ extracting method was able to detect difference in available P in sod-podzolic soil amended with RP and MAP relatively close to the ^{32}P-isotope exchange kinetic method of Dr. Fardeau. The Belorussian standard soil testing method using 0.2 M HCl overestimated the effect of natural RP on soil available P.

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REFERENCES

[1] BEZUGLAYA, Y.M., BULANCEV, Y.V., RYABISINA, T.E., Comparative valuation of rock phosphate efficiency from various deposits, Agrochemistry **1** (1990) 19-25.

[2] KIRPICHNIKOV, N.A., POHLEBKINA, L.P., Influence of high dozes of lime on rock phosphate efficiency in sod-podzolic soil, Agrochemistry **6** (1990) 18-24.

[3] SIROTIN, Y.P., Problems of rock phosphate use in agriculture of USSR, Perspectives of fertilizer assortment expansion (Proc. Conf. Moscow, 1987), VIUA, Moscow (1987) 39-41.

[4] IVANOV, S.N., KRUGLOV, L.V., Comparative study of P availability from superphosphate and rock phosphate to fodder beans by means of ^{32}P techniques, Reports of Belarussian Academy of Sciences **10** (1966) 50-52.

[5] SEMENENKO, N.N., Efficiency of superphosphate and rock phosphate on potato on peat soils, Soil Science and Agrochemistry **10** (1973) 130-137.

[6] FARDEAU, J.C., GUIRAUD, G., MAROL, C., Bioavailable soil P as a key to sustainable agriculture. Nuclear Techniques in Soil-Plant Studies for Sustainable Agriculture and Environmental Preservation (Proc. Symp. Vienna, 1994). IAEA, Vienna (1995), pp.131-144.

[7] ZAPATA, F., Isotope techniques in soil fertility and plant nutrition, In: G. Hardarson (ed.). Use of nuclear techniques in studies of soil-plant relationships, IAEA Training Course Series 2. IAEA, Vienna (1990) 61-128.

[8] ZAPATA, F., AXMANN, H., ^{32}P isotopic techniques for evaluating the agronomic effectiveness of rock phosphate materials, Fertilizer Research **41** (1995) 189-195.

CONDITIONS PROMOTING AND RESTRAINING AGRONOMIC EFFECTIVENESS OF WATER-INSOLUBLE PHOSPHATE SOURCES, IN PARTICULAR PHOSPHATE ROCK (PR): I. INDICES OF PHOSPHATE ROCK USE OPPORTUNITY (PRUOIS) AND OF PHOSPHATE ROCK SUITABILITY FOR DIRECT USE (PRSIDU)

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Abstract. Several issues of phosphate rock (PR) use are discussed in this paper. Maize for green fodder (*Zea mays* L) and ryegrass (*Lolium multiflorum* Lam.) were grown in 7 kg of dry soil and in small pots of 1.25 kg dry soil capacity, respectively, on several base unsaturated soils belonging to Hapludoll and Hapludalf soil groups. The amount of phosphate rock (PR) to apply was based on experimental data considering soil adsorbed acidity (Ah), humus content (H^2), cation exchange capacity (T), sum of exchangeable bases (SEB) and mobile (easily soluble) phosphate content (P_{AL}) in the soil. The factors were combined in a rock phosphate use, opportunity index of the soil (PRUOIS):

$$PRUOIS = \frac{A_h * H^2 * T * 100}{SEB * 10^{0.0245 * P_{AL}}}$$

Rock phosphate suitability for direct use was evaluated by means of the rate of PR-P dissolution (PRPRS) in a 0.6% ammonium heptamolybdate in 0.01M calcium chloride solution (ppm P) and by carbonate content (%$CaCO_3$) in PR. Both of these parameters combined provided a phosphate rock suitability index for direct use (PRSIDU):

$$PRSIDU[ppmP/\min] = PRPRS * (1 - 0.03 * CaCO_3)$$

Water insoluble P sources studied were PR from Kola-Russia, Morocco, Kneifiss-Siria, El Hassa-Jordan, Gafsa-Tunisia, North-Carolina (USA), and Arad-Israel. All PRs were compared with TSP applied at the same rate of P. Neither PRUOIS or PRSIDU considered separately could satisfactorily explain the variance of PR efficiency. An index obtained by multiplicative combination of PRUOIS x PRSIDU did correlate significantly with indices on the agronomic efficiency of PR.

1. INTRODUCTION

The famous Russian scientist Mendeleev (1834-1907), discoverer of the periodic law in chemistry, was actively engaged in coordinating a network of field trials throughout famine affected Russia in the early sixties of the previous century. The experimental results recorded at that time could not be understood and explained with reference to soil and PR intrinsic properties.

Contemporary soil-plant-PR interaction studies and their understanding could probably be traced from a couple innovative activities and publications [1, 2]. Physico-chemical interactions of phosphates in soils as understood at the beginning of thirties of this century were summarised by Buehrer [3].

An important turning point in plant-PR-soil interaction was the introduction of X ray diffraction technology in studies on crystal lattice of apatite minerals in PR of various geographical areas. Advances from this technology were especially significant after the precision of measurements by x ray diffraction was raised to 10^{-11} cm [4-6], permitting accurate measurements of the length of the a axis of apatite crystal lattice. Such an advancement in crystallographic studies on apatites permitted establishment of an inverse relationship between the length of the axis and CO_3:PO_4 molar substitution ratio in PR apatites. The PO_4 substitution for CO_3 in apatite lattice proved to be positively correlated with dissolution of PR-P in neutral ammonium citrate and in 2% formic acid and also with PR agronomic efficiency [7, 8].

Plant-soil-PR interaction studies conducted by means of old classical methods of field trials and chemical soil and plant testing have been summarized [9] by pointing to the role of base saturation (V value) and cation exchange capacity (T value) of the soils in the mobilization of PR-P for crops. Klecikovsky [10] synthesized these studies to show the role of adsorbed acidity in addition to V and T. Golubev and Klecikovsky [9, 10] both established the importance of soil V, T and Ah values to establish whether PR of unspecified P content and solubility were inferior, equal, or superior to soluble P fertilizer sources.

2. PROCEDURES AND METHODS BASED ON CLASSICAL METHODS OF ASSESSING EFFICIENCY OF PHOSPHATE ROOK (PR)

Five double crossed maize plants (*Zea mays* L, CVR DKH 120) were grown until the 10 to 12 leaf stage on 7 kg dry soil in Mitscherlich type pots on three hapludalf soils dressed with 1.25 g of P_2O_5 per pot from all studied P sources. One g of N from ammonium nitrate and 1.0 g K_2O from potassium sulfate were also studied per pot. Four successive crops of maize were grown in this system on 3 soils (Ilişeşti, Suceava and Ițcani) using 5 PR sources of P (TSP; Kola — Russia FA; Morocco; El Hasa — Jordan, and Kneifiss — Siria Prs) and water-soluble TSP.

Chemical properties of the soils suspected of being relevant to PR dissolution were adsorbed acidity (Ah), capacity for cation adsorbtion as a sum of Ah and of exchangeable bases (T), degree of base saturation (V), humus content (H), and mobile P extractable with ammonium lactate-acetic acid (P_{AL}). These parameters were analyzed by official and standardized Romanian methods (STAS 7184/12-88 for determination of Ah, T, SEB and V; STAS 7184/19-82 for P_{AL} and STAS 7184/21-82 for Humus content) are recorded in Table I.

Some of the chemical properties of the phosphate rocks influencing their P bioavailability were established in concordance with Rom. Patent nr.75241/1980 and are recorded in Table II.

After about 7 weeks of growth the plants were harvested by cutting at the soil surface, fixed at 105°C for 30 minutes and dried at 70°C, milled in fine powder and analyzed for total P. Plant material was digested with 9 H_2SO_4 + 1 $HClO_4$. Phosphorus was determined by the molybdo-vanadate yellow method [11, 12]. Variance of analyses was applied on all plant pot experimental analytical data [13].

TABLE I. SOME OF THE CHEMICAL PROPERTIES OF THE SOILS BELONGING TO HAPLUDALF GREAT SOIL GROUP (PLOUGHED LAYER 0–25 cm) USED IN PR STUDIES WITH MAIZE

Soils	PH of 1:2.5 soil water suspension	Clay content < 0.002 mm (%)	Ah (meq/ 100 g soil)	SEB (meq/ 100 g soil)	V (%)	H (%)	P_{AL} (ppm)	PRUOIS[1]
Ilişeşti	5.5	19.0	4.5	10.5	70.0	2.0	10.0	14.7
Suceava	5.6	35.0	5.0	17.0	77.5	3.0	12.0	29.8
Ițcani	7.5	29.0	0.3	25.5	99.0	2.5	45.0	0.2

[1] PRUOIS = Phosphate rock use opportunity index of the soil=$(Ah \times H^2 \times 100)/(V \times 10^{0.0245 \times P_{AL}})$.

TABLE II. SOME OF THE CHEMICAL PROPERTIES OF THE PRs
USED IN THE STUDY WITH MAIZE

P sources	Total P content (%)	Rate of PR-P[1] solubilization (ppm P/min)	Free $CaCO_3$[2] content (%)	PRSIDU[3] (ppm P/min)
Fluorapatite (FA), Kola, Russia	16.6	1.0	3.5	0.89
Morocco PR	14.3	4.5	4.5	3.90
El Hasa Jordan PR	13.9	8.5	5.0	4.25
Kneifiss Siria PR	14.5	9.0	5.2	4.39

[1] Rate of PR-P solubilization = P_{120}-P_{60} / 60. [2] $CaCO_3$ content in PR determined as loss weight when PR was treated with 2NHCl in an aeration device. [3] PRSIDU, ppm P = (P_{120} - P_{60}) x (1 - 0.03 x $CaCO_3$) / 60

3. RESULTS AND DISCUSSION

3.1. Phosphate rock use opportunity index of the soil (PRUOIS)

The mobilization of PR-P for crops is strictly dependent on soil agrochemical properties and without exception has occurred only as a result of PR interaction with the soil. Also, the effect of PR as a source of P for plants cannot be explained by considering only a single soil or PR chemical property.

Graphical schemes, proposed by Golubev [9] and by Klecikovsky [10], have shown adsorbed acidity (Ah), degree of base saturation (V) and cation exchange capacity (T) as important soil properties involved in PR solubilization. At that time no algorithms or formulas were proposed to substantiate relationships. Combining the relevant soil and PR chemical properties in a synthetic index to predict PR efficiency in a soil was not proposed in Eastern Europe at the time of Golubev [9] and Klecikovsky [10].

In the course of studies for working out a PRUOIS, humus (H) and easily soluble phosphate contents in the soil ploughed layer were considered to be parameters that should be included with Ah, V and T soil values considered by Golubev [9] and Klecikovsky [10]. Introduction of humus content in the PRUOIS formula has been encouraged by experimental data with maize for green fodder (Table III). The consideration of easily soluble phosphate (P_{AL}) has its background in chemistry of common ion effects due to orthophosphate anions whose activity in the solution is directly related to easily soluble soil P content. Apart from the humus contribution to CEC of the soil (about 1.5 meq per 100 g of soil for each percent of humus content increase), humus content influences mobilization of PR-P in the soil by complex physico-chemical and biological processes.

Soil CEC (cation exchange capacity) effect on PR-P mobilization is explained by the activity of calcium ions being lower in the soil solution at higher CEC. The lower Ca activity favors the dissolution of PR and mobilization of its P in the soil. Variation of ion binding strength with CEC of soil colloids may be made evident and quantified by a methodology described by Barber [14]. Some of these aspects benefit from an explicit presentation of the formula as shown below:

$$PRUOIS = \frac{Ah*H^2*100}{\frac{SEB}{SEB+Ah}*100*10^{0.0245*P_{AL}}} = \frac{Ah*H^2*\left(SEB+Ah\right)}{SEB*10^{0.0245*P_{AL}}} = \frac{\left(Ah^2+Ah*SEB\right)*H^2}{SEB*10^{0.0245*P_{AL}}} \quad (1)$$

The presence of the T value (CEC = (SEB + Ah)) in its interaction with adsorbed acidity (Ah) and humus content (H^2) in the numerator of the PRUOIS formula indicates agronomic effectiveness of PR with increased P is due to interactions of adsorbed acidity, CEC and humus content in the plow layer of the soil. The interaction of the sum of exchangeable bases (SEB) with mobile phosphorus (P_{AL}) placed in the denominator of the PRUOIS formula reflects the negative influence of these soil properties on PR dissolution in the soil and on PR-P mobilization for crops.

TABLE III. CORRELATION COEFFICIENTS (R) OF PR EFFICIENCY IN MAIZE FOR GREEN FODDER (Y_1 = DRY MATTER YIELD FORMATION; Y_2 = P UPTAKE IN EPIGEIC PARTS OF PLANTS) WITH PRUOIS X PRSIDU SYNTHETIC INDICES[1]

PRUOIS x PRSIDU	y_1	y_2
PRUOIS without humus (H)	0.885	0.889
PRUOIS with humus (H)	0.884	0.862
PRUOIS with humus (H^2)	0.956	0.963
PRUOIS with humus (H^3)	0.961	0.965

[1] 4 successive crops of maize (DKH 120) on 3 soils (Ilişeşti, Suceava and Ițcani) dressed with equal rates of P from TSP, Kola, Morocco, Jordan and Siria PR. Number of correlated pairs were 10.

3.2. Phosphate rock suitability index for direct use (PRSIDU)

The PR-P solubility rate was determined in a 0.6% solution of ammonium heptamolybdate in 0.01 M calcium chloride solution (MoCa 0.6 solution) at ambient temperature (20°C) after 60 and 120 minutes incubation at 1:200 PR: MoCa 0.6 solution ratio. From these two extractions, PR-P solubility rate was determined as ppm P/min by dividing the difference of P at 120 and 60 minutes by 60. Due to the formation of complex phosphate-coordinated dodeca-molybdenum hetero polyions, the equilibrium of P extraction is continuously shifted to the right so that PR-P solubilization-rate is actually an average for the time period from 60 to 120 minutes. The PR-P solubilization rate is inversely related to the length of the a-axis of apatite mineral in PR and directly related to PR solubility. In the course of preliminary research on PRSIDU, it was considered proper to adjust the PR-P rate of solubility in MoCa 0.6 according to free carbonate content of PR:

$$PRSIDU[ppmP/\min] = PRPRS * (1 - 0.03 * CaCO_3) \tag{2}$$

This adjustment was thought necessary because any significant mobilization of PR-P in the soil may start only after removal of alkaline earth carbonates from PR particles. The solubility of basic alkaline earth phosphates is hampered by the presence of calcium carbonates in PR particles through the common-ion effect.

According to Chien and Menon [8] and Lehr and McClellan [7], solubility of P-PR in different conventionally chosen reagents, such as 2% formic acid, is in an inverse relationship with the CO_3:PO_4 molar substitution ratio in the crystal lattice of the apatite mineral of PR. The CO_3:PO_4 molar substitution ratio is inversely related to the length of the crystal lattice a axis according to the following equation:

$$\frac{CO_3}{PO_4} \cong 0.36431 - 0.0049906 * a \tag{3}$$

For an a axis of 10^{-11} cm and x substituted for $CO_3:PO_4$ molar ratio in PR apatite mineral, then Eq. 3 becomes:

$$P_{AF}^{PR} = 86.15 * x - 9.2 \quad (4)$$

It has also been estimated that PR-P solubility in 2% formic acid is in direct relationship with PRSIDU according to the following equation:

$$\text{PR-P solubility in 2\% formic acid} \approx 3.15 * \text{PRSIDU} \quad (5)$$

3.3. Synthetic index of PR reactivity in the soil and of agronomic effectiveness of PR as resulted from multiplicative combination of PRSIDU and PRUOIS

From numerous pot and field experiments it has been noticed that high reactive PR (like North Carolina-USA, Gafsa-Tunisia and others) could be satisfactory sources of P for plants even on soils having less favorable conditions for PR-P mobilization. Less reactive PR under comparable conditions proved to be adequate sources of P for plants only on soils with favorable PR-P mobilization properties. It has also been noticed that no single chemical property of soil or of PR was able to explain the variation of PR efficiency as a source of plant available P.

There is some mutual compensation between soil and PR chemical properties involved in P mobilization processes to such an extent that less reactive PR might be satisfactory sources of P on soils with soil chemical properties favorable for dissolution and PR-P mobilization. Linear correlation coefficients (r) of maize dry matter yields and phosphorus absorption versus PR-PRSIDU, soil-PRUOIS and PRSIDU x PRUOIS are given in Table IV. Values for dry matter and P absorption relative to TSP (triple superphosphate) in three successive maize crops as dependent on PR-PRSIDU x soil-PRUOIS indices are depicted in Figs. 1 and 2 (first two crops) and in Fig. 3 (the last crop of maize for green fodder). The Mitscherlich-type pot experiments with maize were performed using old, classical difference methodology.

TABLE IV. CORRELATION COEFFICIENTS OF MAIZE DRY MATTER YIELD WITH PR-PRSIDU, SOIL PRUOIS AND PRSIDU x PRUOIS

	Independent variables (x) [2]		
Dependent variables (y) [1]	PRSIDU	PRUOIS	PRSIDU x PRUOIS
Maize for green fodder, first cut			
y_1	0.465	0.739	0.859
y_2	0.473	0.759	0.883
Second cut			
y_1	0.465	0.872	0.898
y_2	0.413	0.783	0.873
Third cut			
y_1	0.459	0.811	0.925
y_2	0.459	0.810	0.924
Fourth cut			
y_1	0.526	0.725	0.885
y_2	0.490	0.768	0.902

[1] y_1 = dry matter yield of maize for green fodder, y_2 = P uptake in maize plant (mg of P / pot).
[2] number of correlated pairs was 10.

From the correlation data displayed in Table V and from graphical presentations relative to TSP dry matter yield and P absorption in plants displayed in Figs. 1 and 2, it follows that multiplicative combination of PRSIDU and PRUOIS gave rise to significant improvement of plant-soil and PR correlations. The determination of variation in PR efficiency in maize for green fodder was raised up to 86% with the use of PRSIDUxPRUOIS. This improvement of PR efficiency correlation with combined PRSIDU and PRUOIS indices is certainly due to mutual compensations, which have intervened between PR and soil chemical properties [3]. The mutual compensation substantially enlarges the area of agronomic effectiveness of an increased number of suitable areas for direct use of PR. Also, regularities of relative TSP and PR effects on maize dry matter yield and on P absorption in maize plants, as displayed in Fig. 3, are subject to laws of statistical distribution and should be evaluated by means of their resultant averages. These need to be further substantiated by means of accurate pot and field plant trials, both by classical non-isotope methodology and by ^{32}P isotope dilution techniques.

3.4. Using PRSIDU and PRUOIS synthetic indices as aids in solving aspects of soil fertilization with TSP and PR

The significance of the PRSIDU x PRUOIS synthetic index for PR direct use in soil P fertilization can be used to assess the probability of P use efficiency according to the values outlined in Table VI. The PRSIDU x PRUOIS index can also be used to evaluate PR application rate to use instead of soluble P fertilizers. In order to reach the highest probability of PR being efficient as a P source, the rates of P from PR should be increased so to compensate for their water insoluble P and for their slow or retarded interaction in the soil. It was considered proper to recommend the PR-P rate increase as a complex function of the PRSIDU index of PR and PRUOIS of the soil subject to PR direct use:

$$X = A \times \left(0.55 + \frac{19.0}{PRSIDU \times PRUOIS} \right) \times C \tag{6}$$

where X = rate of P_2O_5 from PR, A = economically sound rates of P_2O_5 from soluble P fertilizers, and C = degree of soluble P fertilizer substitution with PR.

The formula presented above implies the possibility of natural PR and soil compensation to such an extent that PR with favorable reactivity may compensate for less favorable PR mobilization soil chemical properties. The rate of P_2O_5 from water-soluble P fertilizers (D) is:

$$D = A - (1 - C) \tag{7}$$

As far as the economical aspect of using PR as direct P sources is concerned, one should first consider the ratio of water soluble P fertilizer and PR cost per unit of P_2O_5.and the physical efficiency of the P fertilizer in each soil. The cost per unit of P_2O_5 has averaged around 2.22. The physical efficiency may be estimated from plant response to P curve parameters, considering also the state of soil mobile P supply, the efficient amount of P supplied by soil and the degree of growth factors favored for a given crop in a certain soil climate situation. If C is considered to be 0.67 (represents two thirds of the economically sound P rate, application costs being considered equal), one may arrive to the conclusion that combining PR with TSP fertilization amounts fertilization costs at 70 to 85% of using TSP alone. Combining PR (0.67 parts) with TSP (0.33 parts) does not significantly differ from full fertilization with TSP. This is especially true when following the official technological recommendations to incorporate two thirds of P rate into soil by plowing as a basal dressing and to apply the remaining one third of P as "starter NP fertilizer" at planting time. From such an economical estimation, one discovers that within the range of 70 to 85% the higher the PRSIDU and PRUOIS the lower the cost of combined PR and TSP fertilization. In fact, the economical evaluation of PR use for partial or complete substitution of water-soluble P fertilizers may be more complicated due to differences in mobile soil P dynamics under the influence of TSP and PR P sources.

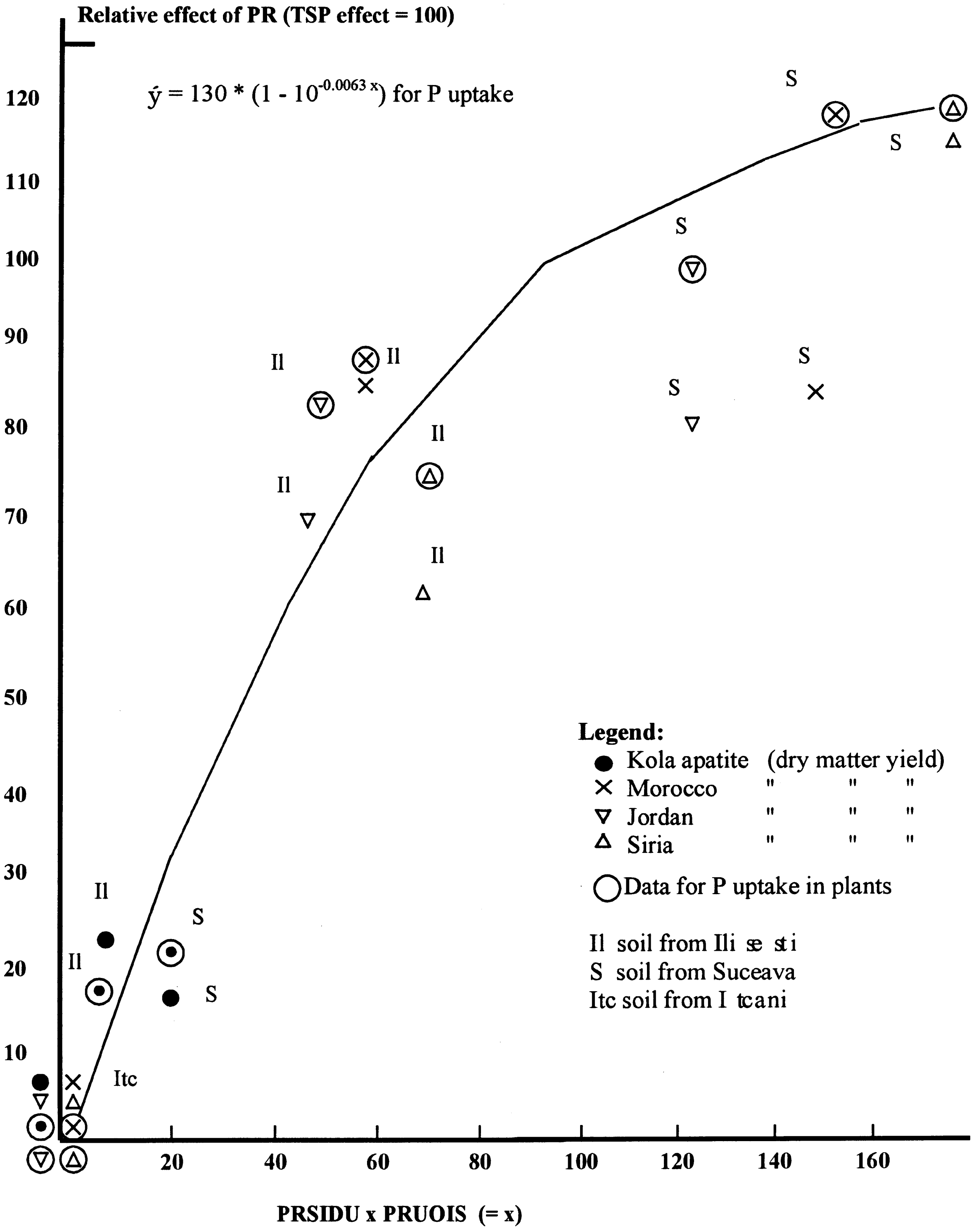

Fig. 1. Relative effect of PR on maize (DKH 120) dry matter yield and on plant P uptake in 1-st year, 2-nd crop versus the composite synthetic index obtained by multiplying PRSIDU x PRUOIS (7 kg dry soil pot experiment on 3 soils).

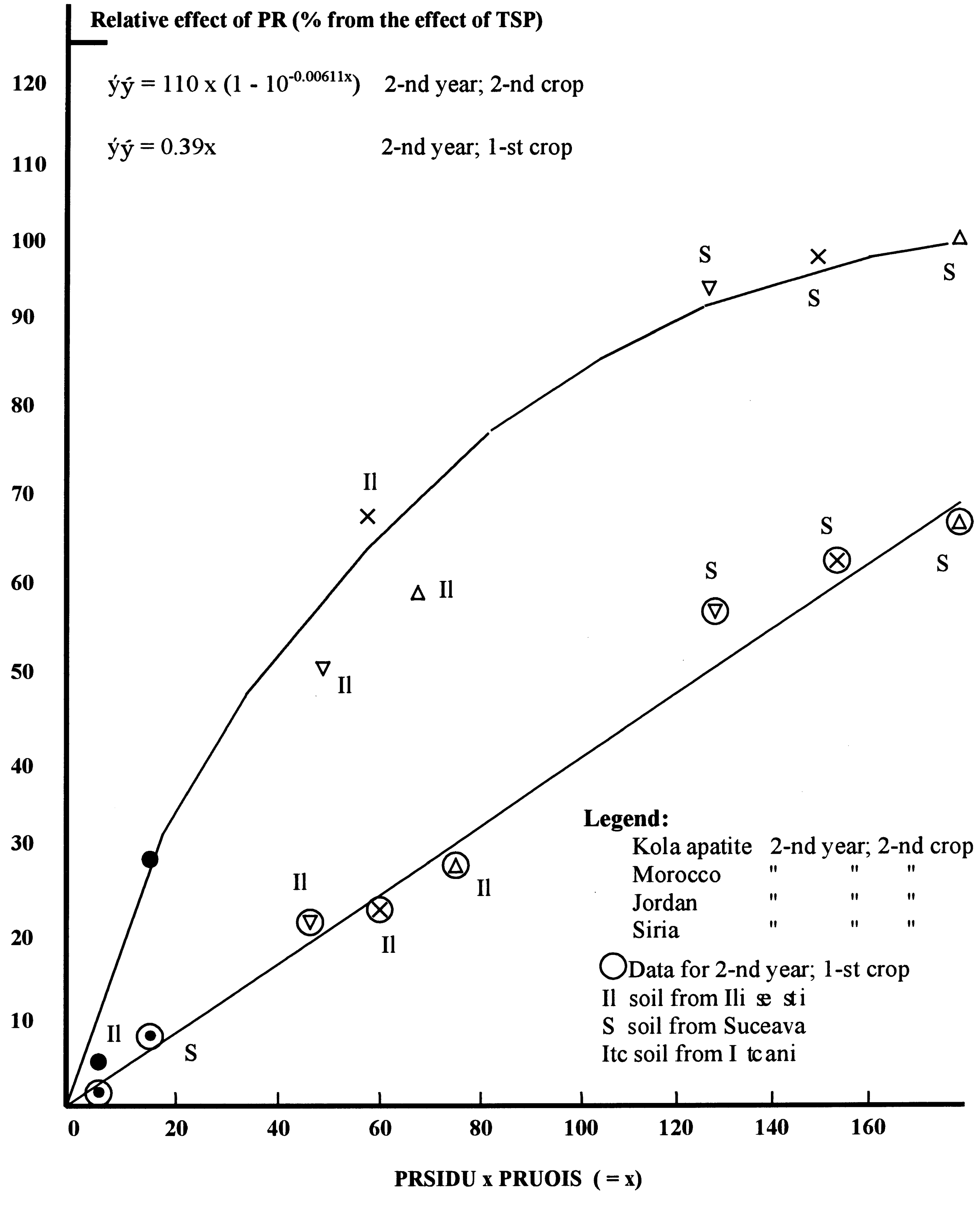

Fig. 2. Relative effect of PR on maize (DKH 120) dry matter yield versus a composite synthetic index obtained by multiplying PRSIDU x PRUOIS (the later calculated with H^3) (7 kg soil pot experiment). Symbols for PR same as used in Fig. 1.

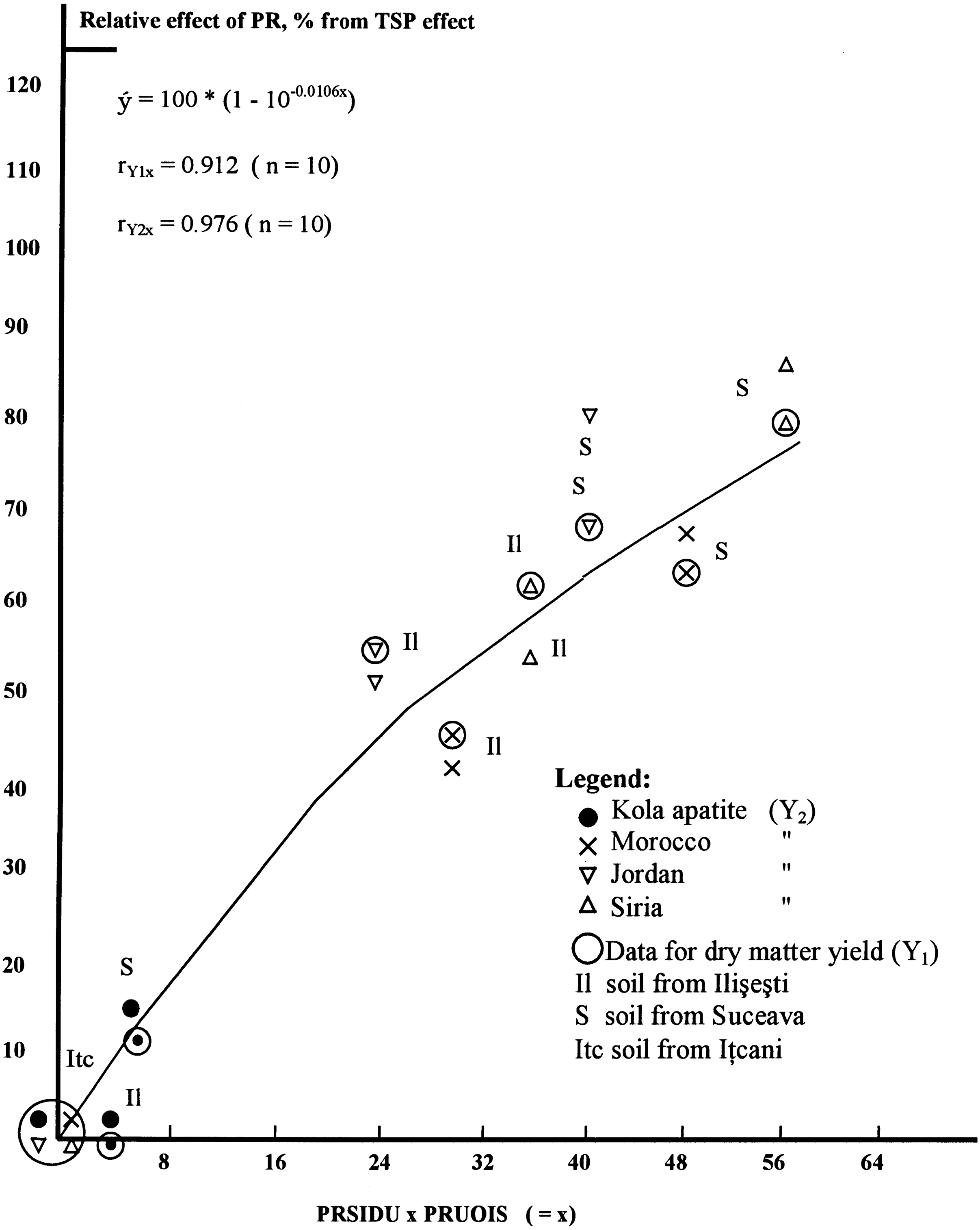

Fig. 3. Relative effect of PR on dry matter yield and on plant P uptake in maize (DKH 120), versus PRSIDU x PRUOIS composite synthetic index. (7 kg soil pot experiment).

TABLE V. SOIL, PR AND PLANT (RYEGRASS) CORRELATION STUDIES
INCLUDING ALSO A COMPARISON OF ^{32}P ISOTOPE DILUTION TECHNIQUE WITH NON-ISOTOPE DIFFERENCE METHOD

Independent variables (X)	Dependent variables (Y)			
	Y_1=PdfPR as % from total plant P	Y_2=PdfPR/PdfCSP[1]	Y_3=PdfPR/PdfCSP[2]	Y_4=(PuPR-PuCheck)/ (PuCSP-PuCheck)[3]
X_1=PRUOISxPRSIDU	0.9311	0.8903	0.7956	0.6317
X_2=PRUOISxPRSIDUxRBCIS	0.9312	0.8909	0.8332	0.6544
	Statistical significance of correlation ratios			
YX_2 compared with YX_1	n.s.	n.s.	n.s.	n.s.
X_3=PRSIDU alone	0.5729	0.6431	0.7105	0.7530
YX_3 compared with YX_1 and YX_2	ooo	ooo	n.s.	n.s.
X_4=PRUOIS alone	0.7089	0.6080	0.3625	0.2351
YX_4 compared with YX_1 and YX_2	ooo	ooo	ooo	o
X_5=RBCIS alone	0.6250	0.5655	0.4503	0.2800
YX_5 compared with YX_1 and YX_2	ooo	ooo	ooo	o
YX_5 compared with YX_4	n.s.	n.s.		
X_6=RBCISxPRSIDU	0.7521	0.7976	0.9696	0.8104
YX_6 compared with YX_1 and YX_2	ooo	n.s.	n.s.	x
YX_6 compared with YX_3	n.s.	n.s.	xx	n.s.
YX_6 compared with YX_4 and YX5		n.s.	xxx	xxx

[1] Pdf P sources as % from total plant P.

[2] Pdf P sources as mg of P per pot.

[3] P uptake in P treatments -P uptake in no P check, established by non-isotope, difference method.

[4] In all cases, number of correlated pairs was 60.

n.s. = non significant; x and o = significant; xx and oo distinctly significant; xxx and ooo very significant positive and negative, respectively.

TABLE VI. PROBABLE MEANING OF (PRSIDU * PRUOIS) SYNTHETIC INDEX IN TERMS RELATIVE TO TSP EFFICIENCY

PRSIDU x PRUOIS	Probability of PR being efficient as P sources in field crops	Probable efficiency[1] (relative to TSP) in field crops %
Below 10	very small	Below 20
10-20	small	20-60
20-40	medium	40-80
40-80	considerable	70-90
Over 80	high	Over 80

[1] subject to considerable variation from crop species to another, depending on their physiological peculiarities of mineral nutrition.

4. CONCLUSIONS

Several aspects of theoretical and practical interest of PR use as a P source on low P and base unsaturated soils have been tackled in the course of our participation in the IAEA Co-ordinated research program on phosphorus: "The use of nuclear and related techniques for evaluating the agronomic effectiveness of phosphate fertilizers in particular rock phosphates".

1. Opportunity of using PR, of adequate quality, directly as a P source depending on adsorbed acidity (Ah), humus (H), degree of base saturation (V) and easily soluble (mobile) P content in the upper layer of soils (PRSIDU).

2. Characterization of PR reactivity in view of its direct use by means of PR-P rate of solubility in 0.6% ammonium molybdate in 0.01 M calcium chloride solution (PRSIDU).

3. A multiplicative combination of PR reactivity index with the opportunity of PR use index of soil in a synthetic index of phosphate rock reactivity and opportunity of PR use (PRSIDU x PRUOIS). Such a combination implies a mutual compensation of PR and of soil properties involved in PR-P mobilization. It also implies a new understanding of PR-P mobilization occurring in the soil as a result of prolonged contact and chemical interaction of PR and soil particles. Some results obtained in plant soil correlation studies when working out PRUOIS and PRUOIS x PRSIDU synthetic indices are recorded in Tables III to V while the regression of P absorption in plants and PR relative efficiency on synthetic PRUOIS * PRSIDU synthetic indices are given in Figs. 1-3.

4. A tentative procedure of interpretation of PRUOIS * PRSIDU from a practical view point so as to predict the probability of PR being efficient as P sources on a particular soil and the necessary rate of PR-P at any given degree of TSP (soluble P fertilizers) replacement with PR.

5. A tentative evaluation of economical aspects of PR direct use as the only P source for partial replacement of water-soluble P fertilizers. This evaluation has pointed out the higher the PRUOIS * PRSIDU the better the economical outcome of PR use.

6. In all these aspects the authors have arrived at sound conclusions and recommendations of practical interest, which certainly may support the use of reactive PR as sources of P for field crops on about one-third of the arable land in Romania.

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REFERENCES

[1] GAITHER, E.W., J. Ind. Eng. Chem. **2** (1910) 315-316.

[2] GHEDROITZ, K.K., Izbranîe Socinenia, ton. I. Selhozghiz, **1955** (1911). Moskva.

[3] BUEHRER, T.F, Arizona Agric. Sta. Techn. Bull. **42** (1932).

[4] EWALD, P.P., Herman, Struktur bericht 1913-1928, Erganizungsland, Akaddemische Verlagsgesch sch. M.B.H Leipzig (1931).

[5] MEHMEL, M., Űber die Struktur des Apatites, I., Zeitsch. Kristall, **75**, heft. 3/4. (1930) 323-331.

[6] NARAY SZABO, S., The structure of apatite $(CaF)Ca_4(PO_4)_3$, Zeitsch. Kristall, **75**, 5/6 (1930) 387-398.

[7] LEHRER, J.R., MCCLELLAN, G.H., A revised laboratory scale for evaluating phosphate rock for direct application, TVA Bull (1972).

[8] CHIEN, S.H., MENON, R.G., BILLINGHAM, K.S., Estimation of phosphorus availability from phosphate rock as enhanced by water-soluble phosphorus, Scil. Sci. Soc. Amer. J. **60** (1996) 1973-1177.

[9] GOLUBEV, B.A., Kislîie pocivî iih ulucisenien (teoreticeskie osnovî), Selhozghiv, Moskva (1954).

[10] KLECIKOVSKY, V.M., Agrochimia. Izd.-vo Kolos, Moskva (1964).

[11] MISSON, G., Colorimetrishe Phosphorbestimmung in stahl Ztg. 32.633 - Chem. Abstr. **1908** (1908) 2527.

[12] QUINLAN, K.P., DE SESA M.A., Spectrophotometric determination of molybdo-vanado-phosphoric acid, Anal. Chem., **27** (1955) 1266-1629.

[13] FISHER, R.A., Statistical method for Research Workers, 7th ed.. Oliver and Bozd, Ltd., Edinburgh (1938).

[14] BORLAN, Z., NEBUNELEA DOBRIȚA, Activitatea aparentă a cationilor adsorbiți în sol. Contribuții la metodologia determinării coeficienților de activitate aparentă şi la stabilirea semnificației acestora - Analele ICPA LI, (1992) 45-67.

CONDITIONS PROMOTING AND RESTRAINING AGRONOMIC EFFECTIVENESS OF WATER-INSOLUBLE PHOSPHATE SOURCES IN PARTICULAR PHOSPHATE ROCK (PR): II. CONFIRMATION AND VALIDATION OF PRUOIS AND PRSIDU USING ^{32}P DILUTION METHODOLOGY AS RECOMMENDED BY IAEA

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Abstract. In view of its importance for practical use of water insoluble phosphate sources, this studies objective was to confirm the PRUOIS and PRSIDU index established with the old difference methodology using ^{32}P dilution methods. Mineral phosphates on the surface of colloids of several hapludalf soils were labeled with carrier-free ^{32}P so that P in plants derived from PR (PdfPR) could be compared with water-soluble P sources (TSP). Experimental and laboratory research with ^{32}P dilution techniques have confirmed the usefulness of an index as obtained by multiplicative combination of PRSIDU and PRUOIS for the assessment of PR use opportunity and for optimal rate of PR-P on a given soil.

1. INTRODUCTION

Advent of radioisotope dilution methodology in the late forties of this century and of E, L, X and A values [1-7] have given important momentums to soil-plant PR interaction studies by permitting a more precise determination of P derived from soil and from P sources labeled with ^{32}P phosphate sources. Dependent plant variables determined by means of ^{32}P dilution methodology have proved to correlate to a significantly greater extent with soil and PR physico-chemical properties as compared with plant variables determined by means of the old difference methodology. The old difference method should be maintained in use as a first aid in assessing the opportunity of PR sources especially due to its low cost and simplicity. When the problem of using PR instead of superphosphates was posed, it was first tackled by using the old difference approach subject to being confirmed with a more precise isotope dilution methodology. Such a confirmation is outlined in this paper.

2. PROCEDURES AND METHODS

Plants were grown on Hapludalf and Hapludol soils (base unsaturated low P soil) having their surface mineral phosphates labeled with carrier-free ^{32}P. Such experiments were carried out with ryegrass (*Lolium multiflorum* Lam. cvr. Arina) in small cubic form pots with perforated bottom. The pots were filled with 1.25 kg of air dry soil dressed with 125 ppm from TSP and studied PR and with 100 ppm N from ammonium nitrate and 100 ppm K from sulfate. For the second harvest the N and K rates were supplemented (50.0 ppm N and 140 ppm K per pot from K nitrate). During the whole duration of the experiments the plants were watered with distilled water by capillary rise from a saturated silica sand bed. Cubic form plastic boxes used in the experiments had their bottoms, with 5 perforations of 1.5 mm diameter each, located in the center and on the corners of the vessel. Mineral phosphates on the surface of soil particles were labeled with 0.05 mCi/pot. The ^{32}P label was first diluted in 120 cm^3 distilled water and then added in 6 separate equal increments delivering 0.0083 mCi each on 200 g dry soil layers. Finally, the pots were seeded with 0.6 g of ryegrass seeds per pot covered with a uniform layer of 50 g of dry soil per pot. At least three harvests were taken at 30 to 32 day intervals. Harvested grass was "fixed" at 105°C for half an hour and subsequently dried at 70°C. The material was then milled in fine powder. Counting ^{32}P beta particles was performed on 1 g of powdered dried material uniformly spread on 28.0 cm^2 surface of a metal counting disk by means of a methane gas flow proportional counter coupled to a beta counting equipment. This procedure assured a counting efficiency of 40% made by Romanian Research Institute of Nuclear Physics. Total P content in plant samples was done in $9H_2SO_4$:$1HClO_4$ digest as molybdenum-phosphate-vanadate yellow [8, 9]. All experimental treatments had three replicates. Accuracy was established with Fisher' s (1928) analysis of variance. Some of the chemical properties thought to be involved in PR-P mobilization in soils are recorded in Table I. These were carried out according to official standardized Romanian procedures of soil analysis as described in STAS nr. 12/1988; 19/1982 and 21/1982. Analytical data used for chemical characterization of PR and for their PRSIDU determination used in ^{32}P studies are recorded in Table II. PRSIDU based on PR-P solubility in 0.6% ammonium molybdate in 0.01 M $CaCl_2$ solution (MoCa 0.6) was used from ROM. Patent nr. 75241/1980.

3. RESULTS AND DISCUSSIONS

3.1. Regression of plant variables established by means of ^{32}P dilution method and by the difference method, on PRUOIS, PRSIDU and PRUOIS x PRSIDU

Correlation matrix of ^{32}P plant variables (y_1 = PdfPR as % from total P and y_2 = PdfPR/PdfCSP) and of dependent plant variables established by the difference method (y_3 and y_4) is recorded in Table III. Plant dependent variables (y_1 = PdfPR as % from total plant P and y_2 = ratio of PdfPR/PdfCSP, both established by means of ^{32}P dilution methodology) did correlate significantly better with soil and PR independent variables than plant dependent variables, Y_3 and Y_4, established by means of difference methods. This correlation matrix also confirmed that no soil nor PR chemical composition data taken separately could explain the variance of plant development variables while multiplicative combination of PRSIDU and PRUOIS explained up to 86% of the considered plant variables. Neither PRSIDU nor PRUOIS taken apart could explain more than 50% of the plant variance in the experiment. The correlation data recorded in Table III also shows that combining PRSIDU and RBCIS (reaction buffering capacity of soil) with PRUOIS gave little to no improvement as compared with PRUOIS x PRSIDU.

3.2. Formal equivalence of tested PR with TSP based on ^{32}P dilution data and on PdfPR/PdfCSP regressions on PRSIDU x PRUOIS synthetic index

Attempts to formally equate the effect of PR in relation to TSP are complicated by continuous change of soil particle external surface per unit of PR applied, provided all other conditions (such as PR and soil fragmentation, soil moisture and others) are comparable. Phosphate rock-P mobilization for plants may take place only as a result of physical contact and chemical interaction with soil. Correspondingly, the surface of PR particles exposed to soil diminishes in pace with the rate of PR application. Therefore, the formal equivalence of PR with soluble P sources has little practical consequences. However, such equivalence is often determined [6] for the sake of quantitative comparison. An interesting possibility arises from good correlation of plant dependent variables by the old difference methodology and with ^{32}P isotope dilution technique [(PdfPR/PdfTSP) x 100], with combined synthetic indices in soil and PR chemical properties (PRSIDU x PRUOIS) as displayed in Figs. 1-3. It is evident that the regression of plant variables on combined soil and PR chemical properties could be described by inverse exponential equations (also called Mitscherlich-Baule type equations) extensively used in describing plant response to soil by means of fertilization. Formal equivalence with TSP or concentrated superphosphate (CSP) of any given PR tested in this system on any given soil may be estimated by means of such inverse exponential equations provided that the synthetic index, PRSIDU x PRUOIS, is known:

$$\frac{PdfPR}{PdfTSP} = 1 - 10^{-0,002(PRSIDU \cdot PRUOIS)} \tag{1}$$

For the sake of improved precision, the above equation should be multiplied by the ratio of the P contents of TSP and PR:

$$\frac{PdfPR}{PdfTSP} = \left[1 - 10^{-0,002(PRSIDU \cdot PRUOIS)} \cdot \frac{P_{TSP}}{P_{PR}}\right]$$

TABLE I. SOME OF THE CHEMICAL PROPERTIES OF SOILS USED IN SMALL POT EXPERIMENT, IN PR STUDIES USING BOTH CLASSICAL DIFFERENCE AND ^{32}P ISOTOPE DILUTION METHODOLOGIES AND RYEGRASS AS TEST-PLANT, CARRIED OUT IN 1994 THROUGH 1997

Soil samples 0-25 cm plowlayer[1]	pH	Clay %	H %	Ah me/100 g of soil	SEB me/100 g of soil	T(CEC) me/100 g of soil	V_{Ah} %	RBCIS[2]	P_{AL} ppm	K_{AL} ppm	PRUOIS
Typludalf from Sânandrei-Timiş	5.6	35.0	2.0	3.8	20.4	24.2	84.2	3.25	8.0	156	11.6
Glosudalf from Timişoara-Timiş	5.1	18.0	1.5	5.3	7.8	13.1	59.5	2.93	145.0	103	0.1
Psamic hapludoll from Suceava	5.8	12.0	1.2	2.9	6.2	9.1	68.1	2.62	40.0	54	0.7
Glosudalf from Caransebeş-Caraş Severin	5.8	19.0	2.6	3.3	10.4	13.7	76.0	3.17	10.0	148	16.2
Agrudalf from Albota-Argeş	6.0	20.0	2.0	2.8	15.4	18.2	84.6	2.98	6.0	160	9.5
Hapludoll from Fundulea-Călăraşi	5.8	28.0	3.2	3.9	22.8	26.7	85.4	3.15	45.0	180	3.6
Fraglossudalf from Caransebeş-Caraş	6.0	19.0	2.0	1.2	11.7	13.9	84.2	3.47	137	137	0.1
Typic Hapludoll from Fundulea-Călăraşi[1]	5.5	28.2	3.3	4.1	22.7	26.8	84.8	4.46	39.0	175	6.1
Typic Hapludoll from Fundulea-Călăraşi[1]	5.0	28.2	3.3	5.3	20.6	25.9	79.5	3.92	39.0	170	8.6
Vertic Hapludalf from Albota-Argeş[1]	5.1	19.5	2.2	5.1	11.1	16.2	68.5	3.75	5.0	105	31.9
Vertic Hapludalf from Albota-Argeş[1]	4.8	19.5	2.2	6.3	10.5	16.8	62.5	3.27	7.0	95	34.7

[1] samples brought from long duration field fertilizer experiments, started in 1967.

[2] RBCIS = reaction buffering capacity index of soils established as ratio between capacity and intensity (Borlan et. al., 1995).

$$\text{RBCIS} = \frac{[T \cdot kg^{-1} \cdot 0.4 \cdot equivalents]}{\left(H^{+}\right) \cdot liter^{-1} moles}$$

TABLE II. CHEMICAL PROPERTIES OF P SOURCES USED IN SMALL POT EXPERIMENT WITH RAZGRASS (LOLIUM MULTIFLORUM LAM. CVR. ARINA), CONSIDERED TO BE RELEVANT TO P MOBILIZATION FROM THESE SOURCES INTO THE SOILS

P sources	Total P content %	Total Cd content ppm	Rate of PR-P solubilization ppm P/minute[1]	Free $CaCO_3$ content[2] %	PRSIDU ppm P/minute[3]
Concentrated superphosphate (CSP)	14.3	12	-	-	-
Kola Fluorapatite Russia	16.6	3	1.00	5.66	0.83
Morocco, PR	14.3	17	4.00	2.50	3.70
Gafsa, Tunisia, PR	12.2	10	16.8	7.50	12.9
North Carolina (USA) PR	13.3	38	16.1	6.35	13.1
Arad, Israel, PR	14.3	13	9.12	2.59	8.40

[1] Rate of PR-P dissolution in MoCa 0.6% solution; 1:200; at ordinary temperature [ppm P/minute] = $(P_{120} - P_{60})$ /60.

[2] Free $CaCO_3$ (calcite) content [%] = determined as loss of weight when PR was treated with 2 N HCl in an aeration device to expel CO_2.

[3] PRSIDU = Phosphate rock suitability index for direct use [ppm P/minute] = $[(P_{120} - P_{60}) \times (1 - 0.03 \times CaCO_3)]/60$ [10].

Regressions of PdfPR/PdfTSP as established with the old "difference" methodology and with ^{32}P isotope dilution techniques are exhibited in Figs. 4 and 5. Such regression curves can be used for appraisal of PR efficiency in terms of TSP using the table below.

Values of synthetic index on regression curve	TSP equivalence (kg of PR to equal to 1 kg of TSP)
500	1.0
400	1.2
300	1.33
200	2.85
100	4.4

Such a formal attempt to equate different efficiencies of PR with TSP has lead to the results recorded in Table IV. For each soil, the equivalence figures differ inversely with PRSIDU of PR while the equivalence data of PR are also in an inverse relationship with PRUOIS of soils. Similar results were obtained when using PdfPR as % total plant P regressed on PRUOIS x PRSIDU synthetic index.

TABLE IV. AMOUNT OF PR EQUAL TO 1 kg OF TSP BASED ON ^{32}P ISOTOPE DILUTION DATA AND PdfPR/PdfTSP REGRESSION ON PRUOIS x PRSIDU[1]

P sources applied at the same rate (100 ppm P)	kg of PR equal to the effect of 1 kg of TSP in ryegrass Soils			
	Fundulea (1)	Fundulea (2)	Albota (1)	Albota (2)
TSP	1	1	1	1
Kola FA	86.0	56.0	17.0	14.0
Morocco PR	17.0	14.0	4.5	3.0
Gafsa PR	7.3	4.9	1.4	1.3
N.Carolina PR	6.7	4.7	1.2	1.2
Arad PR	10.0	7.2	1.9	1.7

TABLE III. SOIL, PR AND PLANT (RYEGRASS) CORRELATION STUDIES INCLUDING A COMPARISON OF ^{32}P ISOTOPE DILUTION TECHNIQUE WITH NON-ISOTOPE DIFFERENCE METHOD.

Independent variables (X)	Dependent variables (Y)			
	Y_1=PdfPR as % from total plant P	Y_2=PdfPR/PdfCSP[1]	Y_3=PdfPR/PdfCSP[2]	Y_4=(PuPR-PuCheck)/ (PuCSP-PuCheck)[3]
X_1=PRUOISxPRSIDU	0.9311	0.8903	0.7956	0.6317
X_2=PRUOISxPRSIDUxRBCIS	0.9312	0.8909	0.8332	0.6544
	Statistical significance of correlation ratios			
YX_2 compared with YX_1	n.s.	n.s.	n.s.	n.s.
X_3=PRSIDU alone	0.5729	0.6431	0.7105	0.7530
YX_3 compared with YX_1 and YX_2	ooo	ooo	n.s.	n.s.
X_4=PRUOIS alone	0.7089	0.6080	0.3625	0.2351
YX_4 compared with YX_1 and YX_2	ooo	ooo	ooo	o
X_5=RBCIS alone	0.6250	0.5655	0.4503	0.2800
YX_5 compared with YX_1 and YX_2	ooo	ooo	ooo	o
YX_5 compared with YX_4	n.s.	n.s.		
X_6=RBCISxPRSIDU	0.7521	0.7976	0.9696	0.8104
YX_6 compared with YX_1 and YX_2	ooo	n.s.	n.s.	x
YX_6 compared with YX_3	n.s.	n.s.	xx	n.s.
YX_6 compared with YX_4 and YX_5		n.s.	xxx	xxx

[1] Pdf P sources as % from total plant P.

[2] Pdf P sources as mg of P per pot.

[3] P uptake in P treatments -P uptake in no P check, established by non-isotope, difference method.

n.s. = non significant; x and o = significant; xx and oo distinctly significant; xxx and ooo very significant positive and negative, respectively.

[4] In all cases, number of correlated pairs was 60.

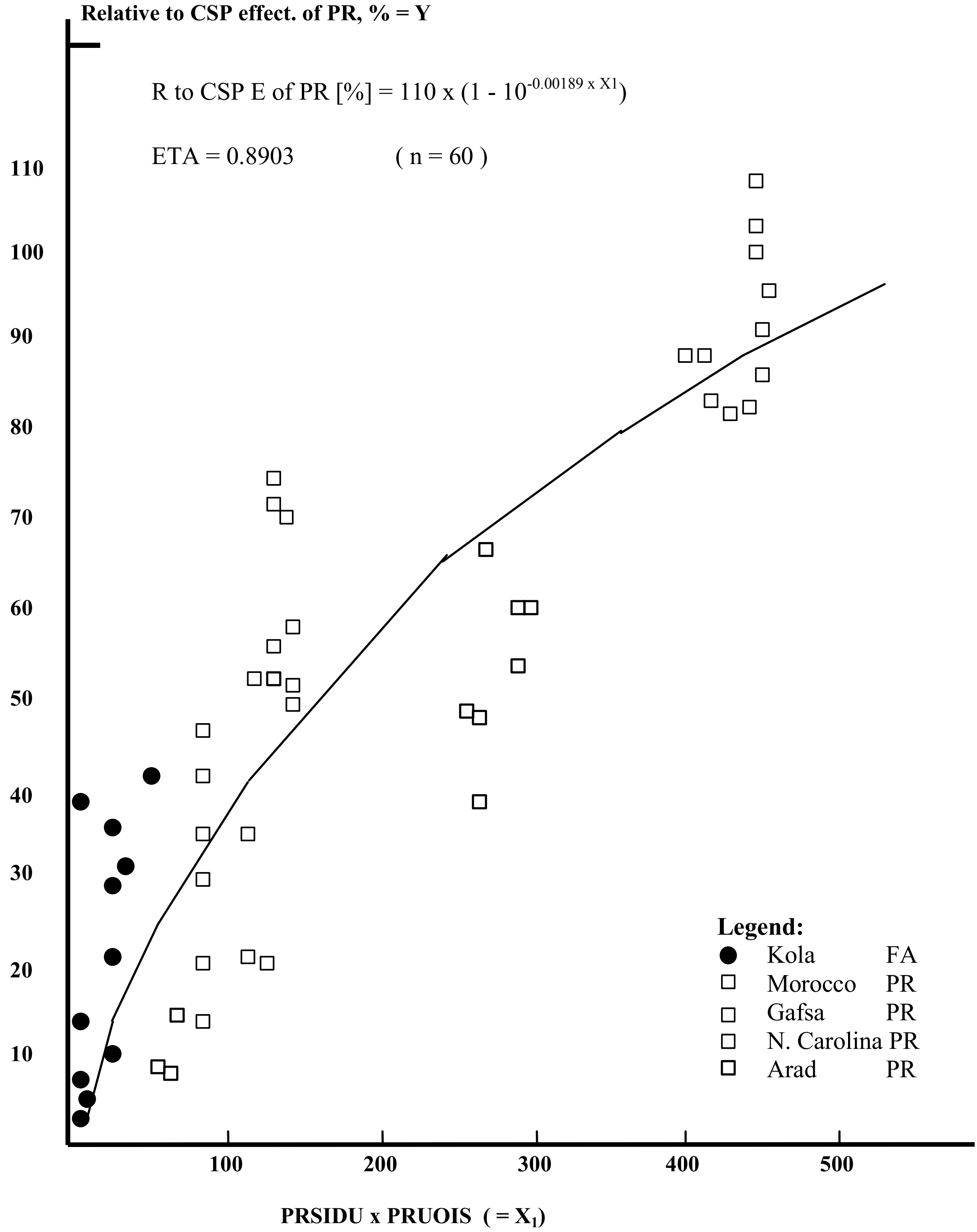

Fig. 1. Regression of relative CSP effectiveness of PR as P sources (PdfPR / PdfCSP x 100) on PRUOIS x PRSIDU synthetic index (pot experiment with Lolium multiflorum *Lam). On.*

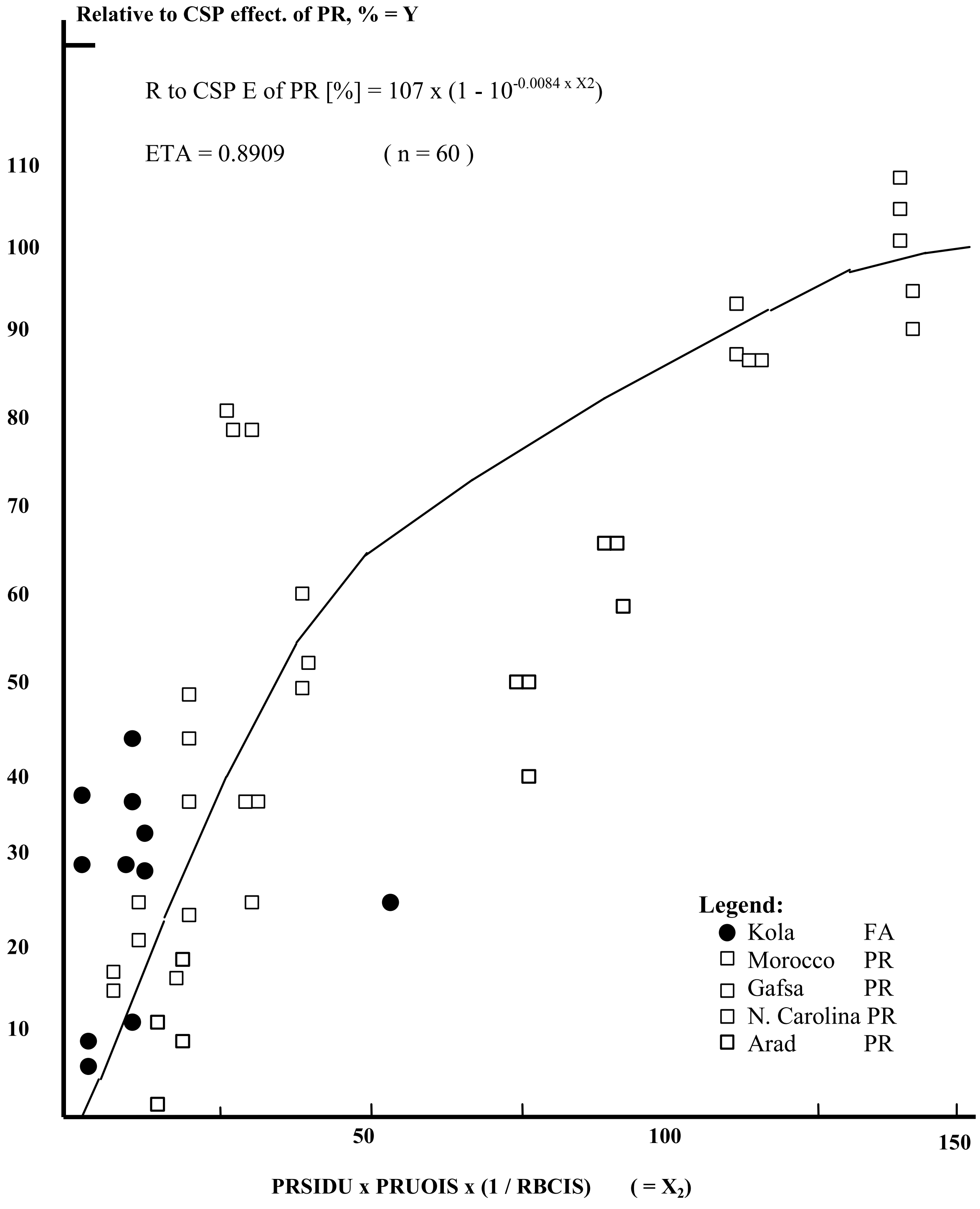

Fig. 2. Regression of relative to CSP effectiveness of PR as P sources (PdfPR/PdfCSP x 100) on PRUOIS x PRSIDU x (1/RBCIS) synthetic index (pot experiment with Lolium multiflorum *Lam. on 4 soils, summer 1994; first cut).*

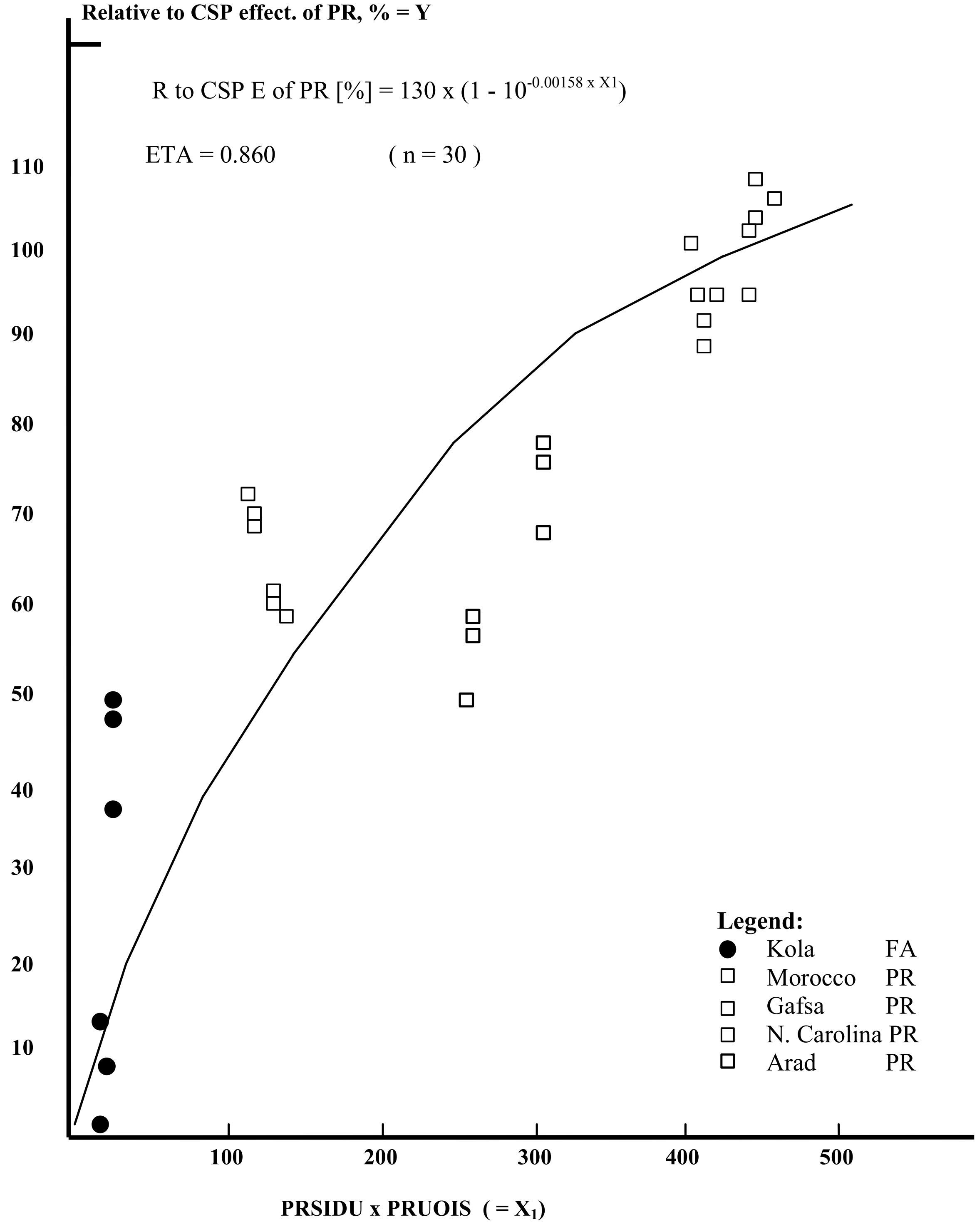

Fig. 3. Regression of relative CSP effectiveness of PR as P sources (PdfPR / PdfCSP x 100) versus PRUOIS x PRSIDU synthetic index (pot experiment with Lolium multiflorum *Lam. On.*

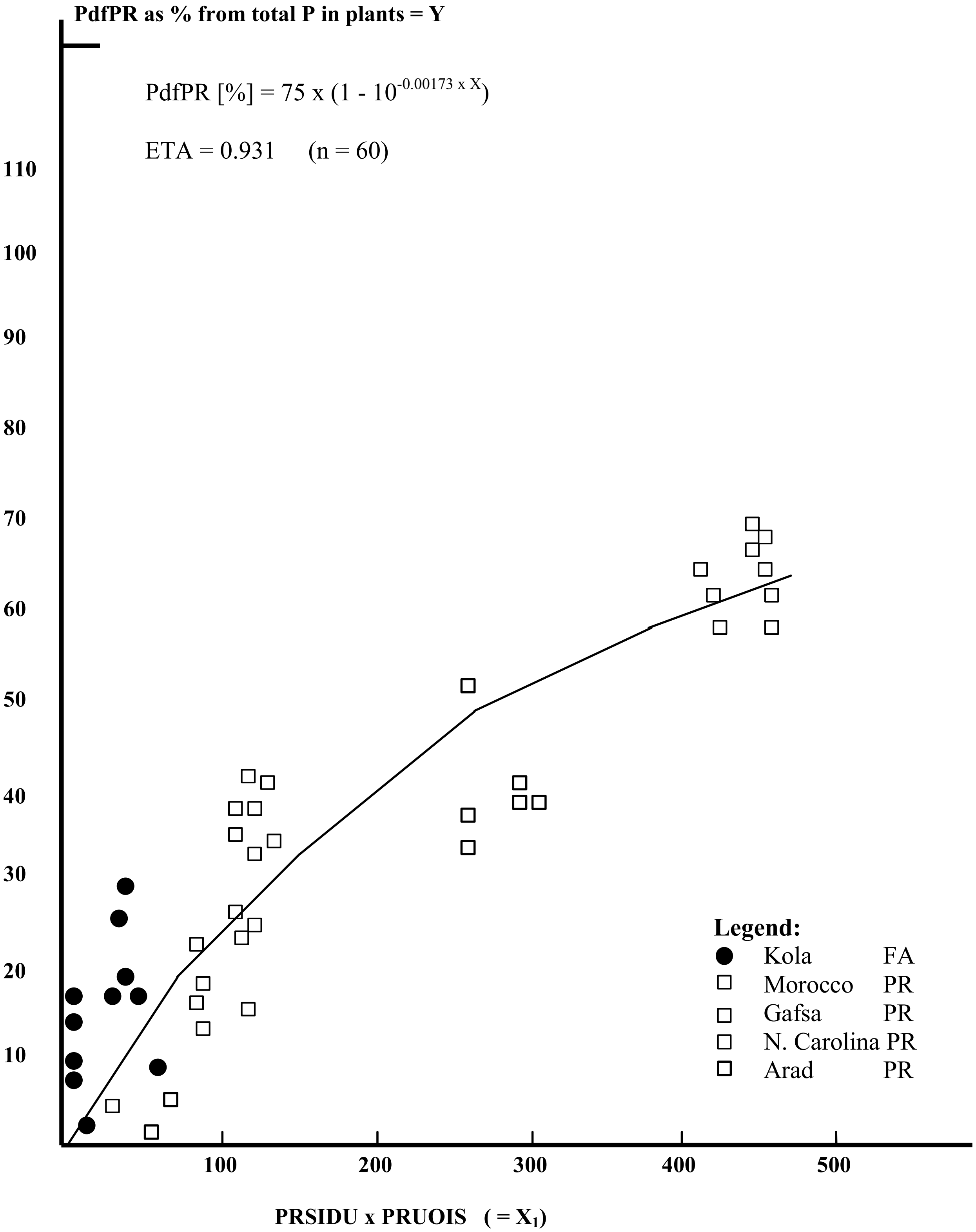

Fig. 4. Regression of PdfPR in Lolium multiflorum *Lam. plants (as % of total P content in plants) on PRUOIS x PRSIDU synthetic index.*

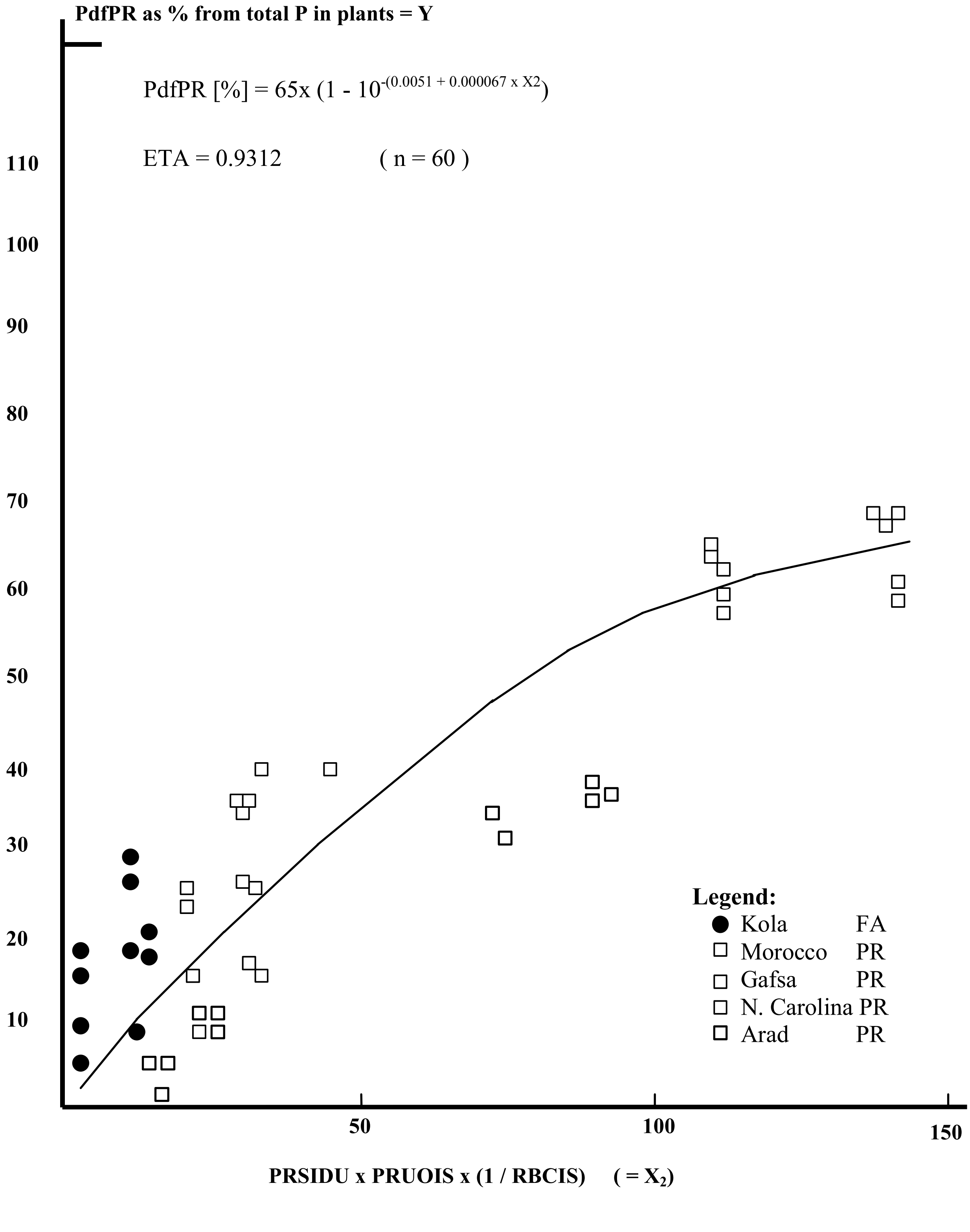

Fig. 5. Regression of PdfPR in Lolium multiflorum Lam. plants (as % from total P content in plants) on PRUOIS x PRSIDU x (1 / RBCIS) synthetic index.

4. CONCLUSIONS

Formerly established indices of phosphate rock suitability index for direct use (PRSIDU) phosphate rock opportunity of the soil (PRUOIS) and PRSIDU x PRUOIS developed from the old difference methodology have been confirmed and validated by means of ^{32}P dilution techniques. The concept that PR mobilization for plants takes place as a result of prolonged chemical and biological interactions of PR with soil chemical and soil microbial life was also confirmed and validated. Within this interaction a mutual compensation of chemical PR and soil properties are taking place to such an extent that less reactive PR became satisfactory sources of P in soils with favourable P mobilization chemical properties. The phenomenon of mutual compensation between PR and soil chemical properties enlarges the area of low P and base unsaturated soils with a high probability of achieving good agronomic efficiency from PR. Due to this phenomenon of mutual compensation between PR and soil chemical properties, substitution of expensive soluble P fertilizers with PR becomes a tangible possibility with greater PRSIDU.

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REFERENCES

[1] FRIED, M., A, E and L values — Trans. 8th Intern. Cong. Soil Sci. IV. (1964) 29-39, Bucureşti.

[2] FRIED M., DEAN L.A., A concept concerning the measurement of available soil nutrients, Soil Sci. **73** (1982) 263-271.

[3] LARSEN, S., The use of ^{32}P in studies on the uptake of P by plants, Plant and soil **4**. (1952) 1-10.

[4] MC AULLIFE, C.D. HALL, N.S., DEAN, L.A., HENDRICKS, S.B., Exchange reactions between phosphates and soils: hydroxyl surfaces of soil minerals, Soil Sci. Soc. Amer. Proc. **12** (1947), 119-123.

[5] RUSSELL, R.S., RICKSON, J.B., ADAMS, S.N., Isotopic equilibria between phosphates in soil and their significance in the assessment of fertility by tracer methods, J. Soil Sci. **5** (1954) 85-105.

[6] ZAPATA, F., AXMANN, H., Agronomic evaluation test of rock phosphate materials by means of a radioisotope technique (1994).

[7] SOKOLOV, A.V., Determination of the availability soil phosphates in fertilizers with the aid of radioactive isotopes of phosphorus - Proc. Intern. Conf. Peaceful uses Atomic Energy, Geneva. (1955) 118-122 UN. New York

[8] MISSON, G., Colorimetrishe Phosphorbestimmung in stahl Ztg. 32.633, Chem. Abstr.**1908** (1908) 2527.

[9] QUINLAN, K.P., DE SESA, M.A., Spectrophotometric determination of molybdo-vanado-phosphoric acid - Anal. Chem. **27** (1955), 1266-1629.

[10] BORLAN, Z., HERA, C.R., BUNESCU, O.V., Agrochimia fosforului. Aspecte actuale de interes practic şi ştiinţific, Ed.Ceres, Bucureşti (1990).

CONDITIONS PROMOTING AND RESTRAINING AGRONOMIC EFFECTIVENESS OF WATER-INSOLUBLE PHOSPHATE SOURCES, IN PARTICULAR PHOSPHATE ROCK (PR): III. ^{32}P-AIDED SOIL-PR INTERACTION STUDIES AIMED AT ENHANCING P BIOAVAILABILITY FROM PR

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Abstract. Mobilization of PR and bioavailability of PR-P for plants takes place through complex chemical and biochemical processes that occurs during prolonged soil interaction with PR. There is a high probability that certain processes of a biochemical nature are also involved through proteinaceous ion carriers whose concentration and physiological activity in plant roots may be influenced by means of specially formulated foliar fertilizer compositions. ^{32}P-aided studies have contributed to identify possibilities of enhancing PR-P bioavailability through foliar fertilizer application.

1. INTRODUCTION

There are several ways to enhancing PR-P bioavailability. Some authors reported the positive influence of nitrogen and potassium fertilizers on P absorption in plants. There is also a positive role of water-soluble sources of P enhancing PR-P bioavailability [1]. Results showed a positive effect of PR acidulation on Cd and PR-P availability in upland rice [2]. There is a significant positive influence of ammonium ions at pH 6.5 and 7.5 on absorption of phosphate ion in sunflower from foliar applied-fertilizers [3]. There are also some indications of ammonium salts enhancing P bioavailability from soil and different phosphate fertilizer sources [4-7]. A series of ^{32}P-aided studies was carried out to explore several ways to enhance the PR-P bioavailability.

2. ESSENTIAL METHODOLOGICAL ASPECTS OF ^{32}P AIDED STUDIES AIMED AT ENHANCEMENT OF PR-P BIOAVAILABILITY IN PLANTS

^{32}P aided studies aimed at enhancing PR-P bioavailability were carried out with ryegrass (*Lolium multiflorum* Lam. cv. Arina) on a soil sample taken from plow-layer of Albota Hapludalf soil in small cubic form pots of 1250 g dry soil capacity. Surface mineral phosphates of the soils used in these studies were labeled with 0.05 mCi of carrier - free ^{32}P supplied by Amersham UK laboratories. Total amount of ^{32}P label (0.05 mCi/pot) contained in 120 cm^3 was divided in 6 separate increments each of these (0.00833 mCi) applied successively on 200 g dry soil with 20 cm^3 solution. Pots were seeded with 0.6 g of seeds and covered with 50 g of soil. The plants were continuously watered with distilled water raised by capillarity from a silica sand water saturated bed. The plastic pots had 5 circular holes on their bottom (perforations) that were 2 mm in diameter. For the first harvest, the soil in pots received 100 ppm of N and K from ammonium nitrate and potassium sulfate. For the second harvest, N and K were supplemented with 50 ppm of N and 140 ppm of K from KNO_3. Radioactive measurements of β particles were performed as described in the second paper of this series. The AS (specific activity as counts per minute/mg of P in plants) as well as total P determinations in plants were performed as described in the first and second paper of this series. Specific activities (SA) and their use have been calculated and used in a way to address the situation of labeling the non-occluded surface mineral soil phosphates with ^{32}P. Some other procedural details are mentioned in the tables along with results presented.

3. RESULTS AND DISCUSSIONS

3.1. Enhancement of PR-P bioavailability by means of water-soluble P sources

Chien et al. [1] have explained effects of enhanced PR-P bioavailability with water-soluble P sources with reference to the positive influence soluble fertilizer sources have on development of branched root system able to explore the soil and make use of less available P sources. As a result of this, availability of PR-P is increased. We also found similar results (Tables I, II, and III).

3.2. Influence of aminoacid and ureide complex (AAUC) applied on ryegrass plants on PdfPR

Enhancement of PR-P bioavailability has also been tried by using amino acid ureide (AAUC) applied on ryegrass plants as 0.25% solution 2 times, each time with 30 cm^3 of diluted solution per pot, 10 days before grass harvest. The AAUC was prepared by hydrolysis of collagen with 2.5 N nitric acid (one part of collagen with 3 volumetric parts of acid at 95 - 100°C for 3 h). The results are recorded in Tables IV and V. The data show that AAUC applied as 0.25% diluted solution had a statistically significant positive effect on enhancing PR-P bioavailability for ryegrass plants. A tentative explanation of these findings may be due to the role of proteinaceous ion-carriers on PR-P uptake in plants. Collagen used to produce AAUC contained a trace amount of P (~ 0.25% P).

3.3. Influence of N chemical form and of solution pH on P absorption and translocation in sunflower plant from leaf applied complex foliar fertilizer solution (CFFS)

A 1% diluted solution of a Complex foliar fertilizer solution (CFFS) labeled with ^{32}P was foliar applied to study the influence of chemical form of N (nitrate, ammonium, and ureic) and pH (4.5; 6.5 and 7.5) on the P absorption and translocation in sunflower plants (*Helianthus annuus*, L, cv. Select). The CFFS was prepared by diluting by 100 times (1%) a solution containing 1000 ppm N, P and K along with equal concentrations of minor nutrients in chelated forms. The P in CFFS was labeled with 0.2 mCi of ^{32}P. Sunflower plants were grown till head formation in Mitscherlich type pots of 8.0 kg dry soil capacity uniformly dressed with N, P, and K and watered to 60% of soil water holding capacity. The solutions were applied 3 times at 3 day time intervals starting on 22 of June 1995 on pieces of cheese cloth firmly attached to leaves utilizing 0.5 cc pipettes with special Brand dispensers. The pH of CFFS was adjusted to pH 4.5, 6.5, and 7.5 with sulfuric acid and sodium hydroxide. Radiometric measurements were taken from representative samples from plants (leaves, stems, tops-inflorescences to be), which were not in contact with labeled CFFS solution in the course of solution application on plants. Effects of N chemical forms and solution pH were determined by means of specific activities of P. The data are recorded in Tables VI, VII, VIII (cv. Select) and IX (cv. Romsun 59).

There were statistically significant effects of tested N chemical forms and of solution pH on P absorption through leaves and on P translocation in sunflower plants. Further systematic and comprehensive experimental work is needed.

TABLE I. THE INFLUENCE OF APPLYING TOGETHER EQUAL RATES OF P FROM TSP AND PR IN ALBOTA[1] AGRUDALF SOIL ON P PRODUCTIVE USE FROM BOTH THESE SOURCES IN RYEGRASS (FIRST CUT-27 JULY 1995)

Treatments: P sources and P rates in mg of P/pot[2]	SA of P in plants, cpm/mg of P	P uptake in plants, mg of P/pot	P in plant derived from applied sources, %
Check: NK+^{32}P	15718	17.4	-
NK+125 mg P (N.Carolina PR)+ ^{32}P	11852	21.0	24.6
NK+125 mg P (Gafsa PR)+ ^{32}P	11258	24.0	28.4
NK+62.5 mg P (TSP)+125 mg P (N.C. PR)+ ^{32}P	9832	31.1	37.4
NK+62.5 mg P (TSP)+62.5 mg P (Gafsa PR)+ ^{32}P	9981	33.2	36.5
LSD for X% level of probability			
X = 5	1475	2.9	
X = 1	2045	3.9	
X = 0.1	2836	5.3	

[1] Some of relevant to PR-P mobilization chemical properties are recorded in Table I from the first paper.

[2] Incorporation of TSP and PR sources in the soil was prior to ^{32}P labeling of soil phosphates.

^{32}P was carrier free.

TABLE II. THE INFLUENCE OF APPLYING TOGETHER EQUAL RATES OF P FROM TSP AND PR IN ALBOTA AGRUDALF SOIL ON P PRODUCTIVE USE FROM BOTH THESE SOURCES IN RYEGRASS (SECOND CUT-14 AUGUST 1995)

Treatments: P sources and P rates in mg of P/pot[1]	SA of P in plants, cpm/mg of P	P uptake in plants, mg of P/pot	P in plant derived from applied sources, %[2]
Check: NK+^{32}P	3861	1.83	-
NK+125 mg P (N.Carolina PR)+^{32}P	3052	2.29	21.0
NK+125 mg P (Gafsa PR)+^{32}P	2894	3.07	25.0
NK+62.5 mg P (TSP)+125 mg P (N.C. PR)+^{32}P	2623	2.73	32.1
NK+62.5 mg P (TSP)+62.5 mg P (Gafsa PR)+^{32}P	2508	2.99	35.0
LSD for X% level of probability			
X = 5	160	0.25	
X = 1	223	0.34	
X = 0.1	309	0.47	

[1] ^{32}P was carrier free.

[2] Data in Tables I and II have shown that water-soluble source of P had a statistically highly significant effect of enhancing PR-P bioavailability.

TABLE III. THE INFLUENCE OF APPLYING TOGETHER EQUAL RATES OF P FROM TSP AND PR IN ALBOTA AGRUDALF SOIL ON P PRODUCTIVE USE FROM BOTH THESE SOURCES IN RYEGRASS (THIRD CUT-20 SEPTEMBER 1995)

Treatments: P sources and P rates in mg of P/pot[1]	SA of P in plants, cpm/mg of P	P uptake in plants, mg of P/pot	P in plant derived from applied sources, %
Check: NK+^{32}P	1414	7.22	-
NK+125 mg P (N.Carolina PR)+^{32}P	1317	9.33	6.9
NK+125 mg P (Gafsa PR)+^{32}P	1136	10.18	19.7
NK+62.5 mg P (TSP)+125 mg P (N.C. PR)+^{32}P	1072	10.51	24.2
NK+62.5 mg P (TSP)+62.5 mg P (Gafsa PR)+^{32}P	1179	8.58	16.6
LSD for X% level of probability			
X = 5	95	0.72	
X = 1	132	0.98	
X = 0.1	183	1.35	

[1] ^{32}P was carrier free.

TABLE IV. THE INFLUENCE OF FOLIAR APPLIED AMINOACID UREIDE COMPLEX (AAUC) ON P DERIVED IN RYEGRASS FROM ROCK PHOSPHATES APPLIED IN ALBOTA AGRUDALF SOIL (FIRST CUT)

Treatments applied[1]		SA[2] of P in plants, cpm/mg	P uptake in plants, mg of P	P in plant derived from PR, % from
in soil	in plants	of P in plants	per pot	total plant P
No P, NK + ^{32}P	distilled w.	15719	17.4	-
No P, NK + ^{32}P	AAUC 0.25%	16542	17.8	-
NK+125ppmP from N.C. PR+^{32}P	distilled w.	11857	21.0	24.6
NK+125ppmP from N.C. PR+^{32}P	AAUC 0.25%	11258	26.8	32.0
NK+125ppmP from Gafsa PR+^{32}P	distilled w.	10982	24.0	31.1
NK+125ppmP from Gafsa PR+^{32}P	AAUC 0.25%	10681	33.5	35.4
DL for X% level of probability				
X = 5		545	2.70	
X = 1		758	3.65	
X = 0.1		1052	5.04	

[1] ^{32}P was carrier free.

[2] SA = P specific activity in plants = counts per minute (cpm) per mg of P in plants.

TABLE V. THE INFLUENCE OF FOLIAR APPLIED AMINOACID UREIDE COMPLEX (AAUC) ON P DERIVED IN RYEGRASS FROM ROCK PHOSPHATES APPLIED IN ALBOTA AGRUDALF SOIL (SECOND CUT)

Treatments applied[1]		SA[2] of P in plants, cpm/mg	P uptake in plants, mg of P	P in plant derived from PR, % from
in soil	on plants	of P in plants	per pot	total plant P
No P, NK + ^{32}P	distilled w.	3861	1.83	-
No P, NK + ^{32}P	AAUC 0.25%	3980	1.83	-
NK+125ppmP from N.C. PR + ^{32}P	distilled w.	3052	2.29	21.0
NK+125ppmP from N.C. PR + ^{32}P	AAUC 0.25%	2661	2.65	33.1
NK+125ppmP from Gafsa PR + ^{32}P	distilled w.	2894	2.07	25.0
NK+125ppmP from Gafsa PR + ^{32}P	AAUC 0.25%	2654	2.41	33.3
DL for X% level of probability				
X = 5		159	0.25	
X = 1		221	0.34	
X = 0.1		307	0.47	

[1] ^{32}P was carrier free.

[2] SA = P specific activity in plants = counts per minute (cpm) per mg of P in plants.

TABLE VI. INFLUENCE OF NITROGEN CHEMICAL FORMS (A) IN COMPLEX FOLIAR FERTILIZER SOLUTIONS AND OF THEIR REACTION (B) ON P UPTAKE AND TRANSLOCATION IN SUNFLOWER PLANTS (CROSSED CVR. SELECT) AS DISCLOSED BY SA (SPECIFIC ACTIVITY OF P IN LEAVES OPPOSITE TO THOSE ON WHICH ^{32}P LABELLED DILUTED COMPLEX FOLIAR FERTILIZER SOLUTIONS WERE APPLIED)

Chemical form and concentration of N in CFF (A)	pH of diluted 1% CFF solutions (B)			Average
	4.5	6.5	7.5	
No nitrogen	430	235	239	301
N-NH_4 nitrogen (1000 ppm N)	367	231	236	278
$(NH_2)_2CO$ nitrogen " " "	350	510	949	603
NH_4NO_3 nitrogen " " "	278	271	376	308
Average=	356	312	450	
LSD for X % level of probability	A (up-down)		B (left-right)	A x B
X = 5.0	67		58	116
X = 1.0	91		79	158
X = 0.1	123		106	213

TABLE VII. INFLUENCE OF NITROGEN CHEMICAL FORMS (A) IN COMPLEX FOLIAR FERTILIZER SOLUTIONS AND OF THEIR REACTION (B) ON P UPTAKE AND TRANSLOCATION IN SUNFLOWER PLANTS (CROSSED CVR. SELECT) AS DISCLOSED BY SA (SPECIFIC ACTIVITY OF P IN INFLORESCENCES (TOPS)

Chemical form and concentration of N in CFF (A)	pH of diluted 1% CFF solutions (B)			Average
	4.5	6.5	7.5	
No nitrogen	670	543	554	622
N-NH_4 nitrogen (1000 ppm N)	860	932	944	912
$(NH_2)_2CO$ nitrogen " " "	791	836	716	813
NH_4NO_3 nitrogen " " "	1242	1098	1143	1161
Average=	891	902	839	
LSD for X % level of probability	A (up-down)		B (left-right)	A x B
X = 5.0	139		120	240
X = 1.0	189		163	327
X = 0.1	254		220	439

TABLE VIII. INFLUENCE OF NITROGEN CHEMICAL FORMS (A) IN COMPLEX FOLIAR FERTILIZER SOLUTIONS AND OF THEIR REACTION (B) ON P UPTAKE AND TRANSLOCATION IN SUNFLOWER PLANTS (CROSSED CVR. SELECT) AS DISCLOSED BY SA (SPECIFIC ACTIVITY OF P IN STEMS BENEATH THE TOUCHED LEAVES WITH ^{32}P LABELLED DILUTED CFF SOLUTIONS)

Chemical form and concentration of N in CFF (A)	pH of diluted 1% CFF solutions (B)			Average
	4.5	6.5	7.5	
No nitrogen	535	576	481	537
N-NH_4 nitrogen (1000 ppm N)	610	863	768	757
$(NH_2)_2CO$ nitrogen " " "	650	678	611	646
NH_4NO_3 nitrogen " " "	1056	924	863	948
Average=	718	760	681	
LSD for X % level of probability	A (up-down)		B (left-right)	A x B
X = 5.0	134		116	233
X = 1.0	183		158	317
X = 0.1	246		213	436

TABLE IX. PDFF, % (PHOSPHORUS DERIVED FROM FOLIAR FERTILIZERS) IN SUNFLOWER (CVR. ROMSUN 59) PLANT ORGANS, EVALUATED FROM THE SPECIFIC ACTIVITY RATIOS AFTER SIX APPLICATIONS OF DILUTED CFF SOLUTIONS WITH 1000 PPM P ON LEAVES (POT EXPERIMENT ON FUNDULEA-CĂLĂRAŞI, HAPLUDAL SOIL)

Sunflower plant organs	pH of 1% CFFS when N was present solely as NH_4^+ ion			LSD for a probability of 5%
	4.5	6.5	7.5	
Opposite[1] leaves	0.12[2]	0.21[2]	0.20[3]	0.04
Plant tops (inflorescence)	0.24[2]	0.43[2]	0.49[3]	0.16
Plant stems below the CFF treated leaves	0.08[3]	0.34[2]	0.05[3]	0.30

[1] to those on which ^{32}P labeled solution of CFF has been applied.

[2] significant at a level of at least 5% probability.

[3] the difference between two neighbouring averages, not significant.

4. CONCLUSIONS

Plant experimental and laboratory chemical research using ^{32}P dilution methodology have confirmed the possibility of enhancing PR-P bioavailability to ryegrass plants through a) the application of water-soluble P sources along with PR in an Agrudalf soil and b) the foliar application of an amino-acid ureide complex that possibly influences the PR-P absorption and accumulation in ryegrass.

Experiments with ^{32}P labeled foliar fertilizers on sunflower plants have shown the important role of N chemical forms in the composition of complex foliar fertilizers and the pH of diluted solutions in P absorption and translocation from CFFS applied on plants.

These findings need to be studied further in view of their practical importance to increase PR-P bioavailability to plants.

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REFERENCES

[1] CHIEN, S.H., MENON, R.G., BILLINGHAM, K. S., Estimation of phosphorus availability from phosphate rock as enhanced by water soluble phosphorus, Soil. Sci. Soc. Amer. J. **60** (1996) 1973-1177.

[2] IRETSKAYA, S.N., CHIEN, S.H., MENON, R.G., Effect of acidulation of high cadmium containing phosphate rooks on cadmium uptake by upland rice, Plant and Soil **201** (1998) 183-188.

[3] BORLAN, Z., SOARE, M., GAVRILUȚĂ, I., Use of the isotope dilution technique to monitor P absorption and translocation in sunflower (*Helianthus annuus* L) from leaf applied fertilizer solutions, Proc. Symp. "Nuclear Techniques in soil-plant studies for Sustainable Agriculture and Environment Preservation", IAEA, Vienna, 234/20P. (1995) 701-704.

[4] CALDWELL, A.C., The influence of various nitrogen carriers on the availability of fertilizers to plants, Trans. 7th Intern. Congr. Soil Sci. **3** (1960) 517-521.

[5] GRUNES, D.L., Effect of nitrogen on the availability of soil and fertilizer phosphorus to plants, Adv. Agron. **11** (1959) 369-396.

[6] LORENZ, O.A., JOHNSON, C.M., Nitrogen fertilization as related to the availability of phosphorus in certain California soils, Soil Sci. **75** (1953) 119-129.

[7] ROBERTSON, W.K., SMITH, P.N., OHLROGGE, A.J., KINCH, D.M., Phosphorus utilization by corn as affected by placement and nitrogen and potassium fertilization, Soil Sci. **77** (1954) 219-226.

CONDITIONS PROMOTING AND RESTRAINING AGRONOMIC EFFECTIVENESS OF WATER-INSOLUBLE PHOSPHATE SOURCES, IN PARTICULAR PHOSPHATE ROCK (PR): IV. CHARACTERIZATION OF MOBILE P STATUS OF SOILS TREATED WITH PR USING CONVENTIONAL METHODS

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Abstract. Determining plant-available P through chemical extraction procedures is a real challenge in soil chemistry because "mimicking" the plant abilities to take up phosphorus from soil and other natural and manufactured P sources is complex. Indeed, the idea of "mimicking" complex physiological processes like P absorption and translocation in plants by a chemical dissolution process seems unrealistic. Nevertheless data on mobile soil P are needed to assess the soil P status and thus provide adequate P fertilizer recommendations to ensure normal plant growth and good yields. In this paper the appraisal of several mobile P extracting methods was made through statistical correlation with P accumulated in plants over a limited period of time. Based on plant, PR and soil correlation studies conducted from 1994 through 1997 the ammonium heptamolybdate 0.3 and 0.6% in calcium chloride 0.01 M at pH 4.3 methods have both performed better the other tested extraction methods.

1. INTRODUCTION

Merits of mobile P extraction methods are evaluated by correlating P absorption and accumulation in plants over a certain time period with P extracted from soil upon completion of the pot and field experiments with plants. Though the P accumulation in plants and soil mobile P correlation will remain a main criterion for assessment of reagents proposed as extracting agents for mobile soil P, some other criteria are helpful. Among these are regression curves of P accumulation in plants versus mobile soil P extracted with tested conventional procedures. It is desirable for the plot to pass through the origin of x and y axes meaning that whenever mobile P diminishes to zero, P accumulated in the plant also approaches zero. Regression of P in plants versus mobile soil P extracted with conventionally chosen reagents is related to rules of classical agronomy such as the Maze-Mitscherlich rule of physiological relationships described by means of inverse exponential equations of the Mitscherlich-Baule type. This criterion will further ease the use of mobile P data for inclusion in complex indices along with other chemical soil testing data like PRUOIS (with adequate coefficients). Another criterion worth considering is assessing the merits of conventional reagents for extracting mobile P from all soils and especially from soils, which were subject to dressings with PR and other water-insoluble P fertilizers. Selecting a conventional equilibrium extraction method is always complex. The criteria used for this selection are in a mutual correlation and agreement. This is because PR interaction with the soil is a process with a peculiar dynamic, which ought to be reflected by the conventional method chosen to extract the mobile P.

Another important criterion for assessing conventional extraction methods is the universality of the method. A method should be applicable to a variety of soils differing in their genesis, texture, and chemical properties. Whenever satisfied, this criterion gives rise to a plant P versus mobile soil P relationship that is a single regression equation for contrasting soils. Reagent applicability for mobile P extraction to a wide range of soils is one of the most important criteria to be pursued in studies comparing conventional methods for mobile P.

2. CONVENTIONAL METHODS OF EXTRACTING MOBILE P FROM SOILS WITH PR RESIDUES

The following conventional methods were selected from widely used conventional reagents in European countries:

- ammonium lactate 0.1 M and acetic acid 0.4 N at pH 3.7 proposed initially by Riehm [1] and further developed by Egner [2];
- sodium bicarbonate 0.5 M at a pH 8.5 [3];
- ammonium fluoride 0.03 N in hydrochloric acid 0.1 N [4];
- ammonium heptamolybdate 0.3 and 0.6% in calcium chloride 0.01 M at pH 4.3 [5, 6].

All these methods were applied precisely according to author's original descriptions.

Chemical properties of soils used in comparative studies of conventional extraction methods have been presented in tables incorporated in previous 3 papers of this series (Table I in paper I; Table I and Table II in second paper). Analytical data refer to the pot experiments.

3. RESULTS

Dependent plant P variables established by ^{32}P dilution and by old difference methods were regressed against mobile soil P extracted by three conventional methods. Results of such a comparison are recorded in Table I.

The relationships were established from over 60 pairs of experimental data points. There was a very poor correlation of dependent plant variable established by ^{32}P dilution methodology (PdfPR as % from total P in plants and PdfPR/PdfCSP) as compared with P uptake determined by the old difference method.

The difference in correlation intensity in favor of plant P uptake is so great that accidental mistakes are out of the question. One possible explanation may be that the PdfPR pool is not identical with the pool from which P absorption has taken place in the experiments with ryegrass presented in Table I. Plant P uptake and mobile soil P correlation data have also shown that mobile P extracted from soils with MoCa solution at the termination of pot experiments were correlated better than with AL and sodium bicarbonate method. Due also to the great number of correlated pairs (in this case over 80%); the differences between MoCa and other compared methods (AL and $NaHCO_3$) were statistically significant.

3.1. Applicability of MoCa solution (ammonium heptamolybdate 0.3 and 0.6% in calcium chloride 0.01 M solution) as mobile P extracting agents from different contrasting soils

The data presented in Fig. 1 shows the possibility of using a single regression curve of P in plants versus P-MoCa in three contrasting soils (Ilişeşti, Suceava and Iţcani) which were subject to dressings with several PRs (Kola fluorapatite and Morocco, El Hasa Jordan, and Kneifiss-Siria PR). Indeed the experimental data obtained with 5 PR on 3 soils are accommodated on the same regression curve, which may be depicted by a single regression equation. Such findings have been obtained in numerous other pot and field experiments in which comparison of MoCa 0.3 and 0.6 extracting solutions with other conventional reagent was posed. Though in all situations a considerable statistical variation could be observed which is the case for most P correlation studies. The regression equation in Fig. 1 is an inverse exponential type with a clear-cut tendency to go through the xy origin.

3.2. Using conventional extraction of mobile P methods and plant pot experiments with PR to predict the opportunity of PR efficient use on low P base unsaturated soils

An experiment was carried out with ryegrass in small cubic form pots with perforated bottoms containing Hapludol and Hapludalf soils, whose chemical properties were recorded earlier in Table I from the first and second paper. Correlation ratios of P in grass and of grass dry matter with mobile P in the soil at experiment termination are recorded in Table II while the correlation pairs are exhibited in Figs. 1-6, each for one of the compared conventional mobile P extracting solution.

Again, this attempt was faced with considerable variations to such an extent that not all correlations were statistically significant. As in the other studies, MoCa 0.3 and 0.6 % performed better.

TABLE I. CORRELATION[1] OF PdfPR DATA AND OF P UPTAKE IN RYEGRASS PLANTS AT FIRST AND SECOND CUTS WITH MOBILE SOIL P AT POT EXPERIMENT TERMINA-TION (SUMMER 1994)

	Dependent variables (Y)			
Independent variables (X)	Y_1=PdfPR as % of total P	Y_2=PdfPR/Pdf CSP % / %	Plant P uptake mg P/pot	
			Y_5(first cut)	Y_6(2nd cut)
	n=60	n=60	n=84	n=84
$X_1 = P_{AL}$	0.2661	0.1447	0.8140	0.8592
Significance of YX correlation	n.s.	n.s.	xxx	Xxx
Significance of difference Y_5X_1/X_2			n.s.	
Significance of difference Y_6X_1/X_2				n.s.
X_2 = P – $NaHCO_3$	0.1779	0.0740	0.8823	0.8260
Significance of YX correlation	n.s.	n.s.	xxx	Xxx
Significance of $Y_{5.6}/X_1$ correlation difference to $Y_{5.6}/X_2$			n.s.	n.s.
X_3 = P – MoCa	0.3183	0.1715	0.9185	0.9679
Significance of YX correlation	x	n.s.	xxx	Xxx
Significance of $Y_{5.6}/X_1$ correlation. difference to $Y_{5.6}/X_3$			oo	Oo

[1] correlation ratios (ETA values); n.s. = not significant; x and o = significant; xx and oo = distinctly significant; xxx and ooo = very significant. positively and negatively, respectively. Samples from ploughed layer of different Hapludalf and Hapludol great soil groups presented in tables.

In an attempt to group the experimental findings around the same regression curve, the plant dependent variables were taken as $\frac{\sum_1^3 CP_{PR}}{\sum_1^3 CP_{CSP}}$ ratios of P taken up in plants (CP_{PR} = consumption of P) with 3 harvests in PR treatments versus P taken up in 3 harvests plants treated with concentrated superphosphate (CSP). Finally, the P consumption ratios were recorded versus mobile P_{PR}/mobile P_{CSP} ratios as shown in Figs. 2-6. In the field of variation delimited by the y axis (CP_{PR}/CP_{CSP}) and x axis (mobile P_{PR}/mobile P_{CSP}), the data corresponding to reactive PR (Gafsa, North Carolina and to some extend Arad-Israel) are located in right upper corner of the variation field irrespective of the conventional extraction methods. Data corresponding to reactive rock phosphates may be delimited from less reactive PR by a straight line going up and down and left to right, starting in each case from the y axis and going down and right to intercept the x axis. Efficiency of PR is estimated in terms of the efficiency of CSP or TSP applied at some rate of P. Though correlation studies have shown significant differences between conventional methods of extracting mobile P from soils in which PR were applied, all 5 of these compared conventional methods have permitted the distinction between reactive PR (Gafsa and North Carolina) and those less reactive (Kola FA and Morocco PR).

TABLE II. RESULTS OF TESTING EQUILIBRIUM MOBILE P EXTRACTION METHODS IN AN ATTEMPT TO DEVELOP A PROPER CHEMICAL SOIL TEST FOR PR TREATED BASE UNSATURATED SOILS (= CORRELATION COEFFICIENTS, R^2)[1] OF P IN RYEGRASS (=Y_1) AND OF RYEGRASS DRY MASS (=Y_2)

Y_1	Y_2	X
0.222	0.263	$x_1 = P_{AL}$
0.400	0.173	$x_2 = PNaHCO_3$
0.767	0.515	x_3 = PMoCa 0.3%
0.773	0.503	x_4 = PMoCa 0.6%
0.319	0.408	$x_5 = P(HCl + NH_4F)(B_2)$

[1] Number of correlated pairs was 42 (7*6). Differences between y1, 2 x3 and y1, 2 x4 and y1, 2 x1, x2 and x5 are statistically significant.

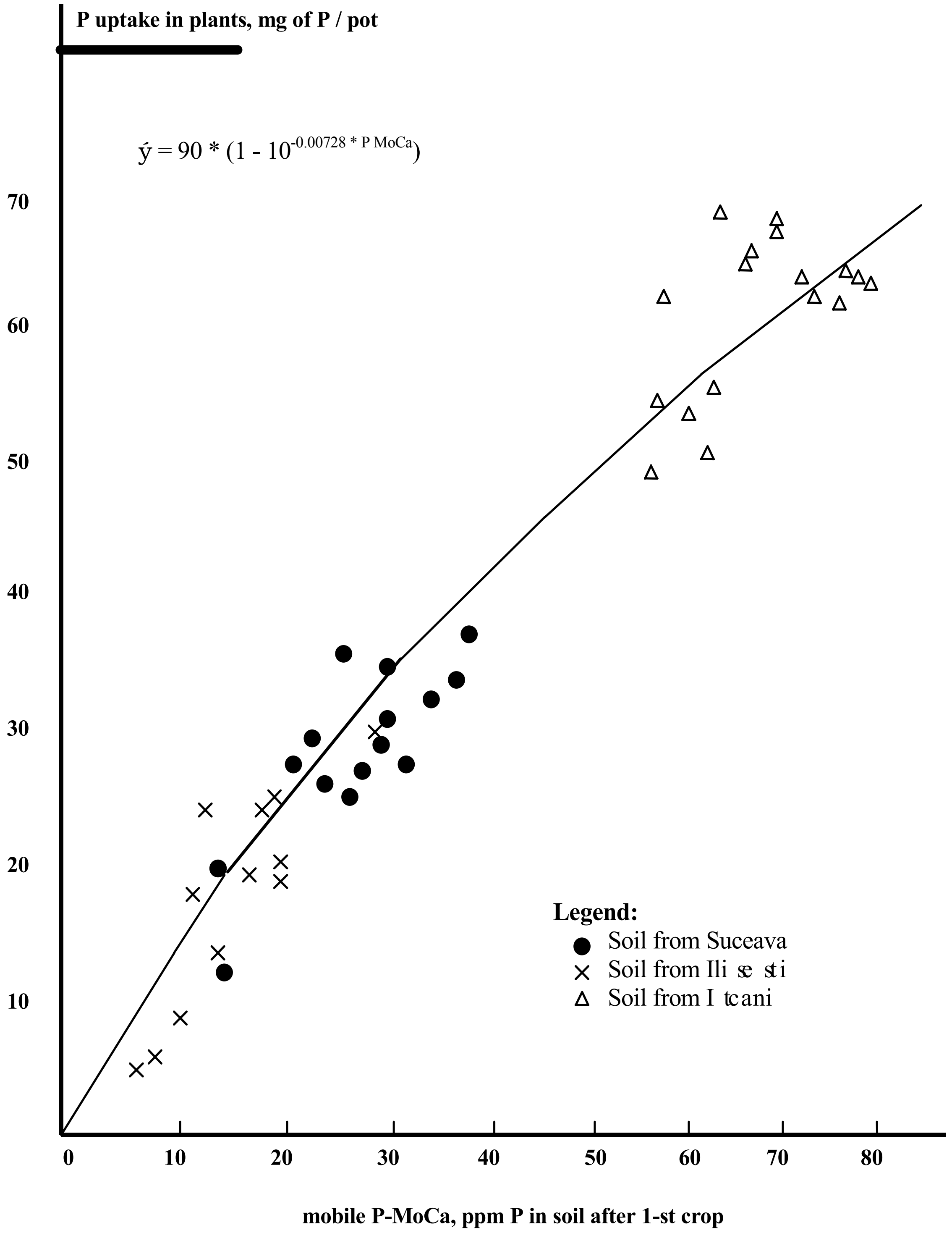

Fig. 1. P uptake in aerial parts of maize (DKH 120) for green fodder (2-nd year; 1-st crop) grown in Mitscherlich type 7 kg dry soil pots on Ilişeşti, Suceava and Iţcani soils (PRSIDU = 13.2, 24.3 and 0.2) versus diluted MoCa extracted mobile P in the soil at the end of experiment.

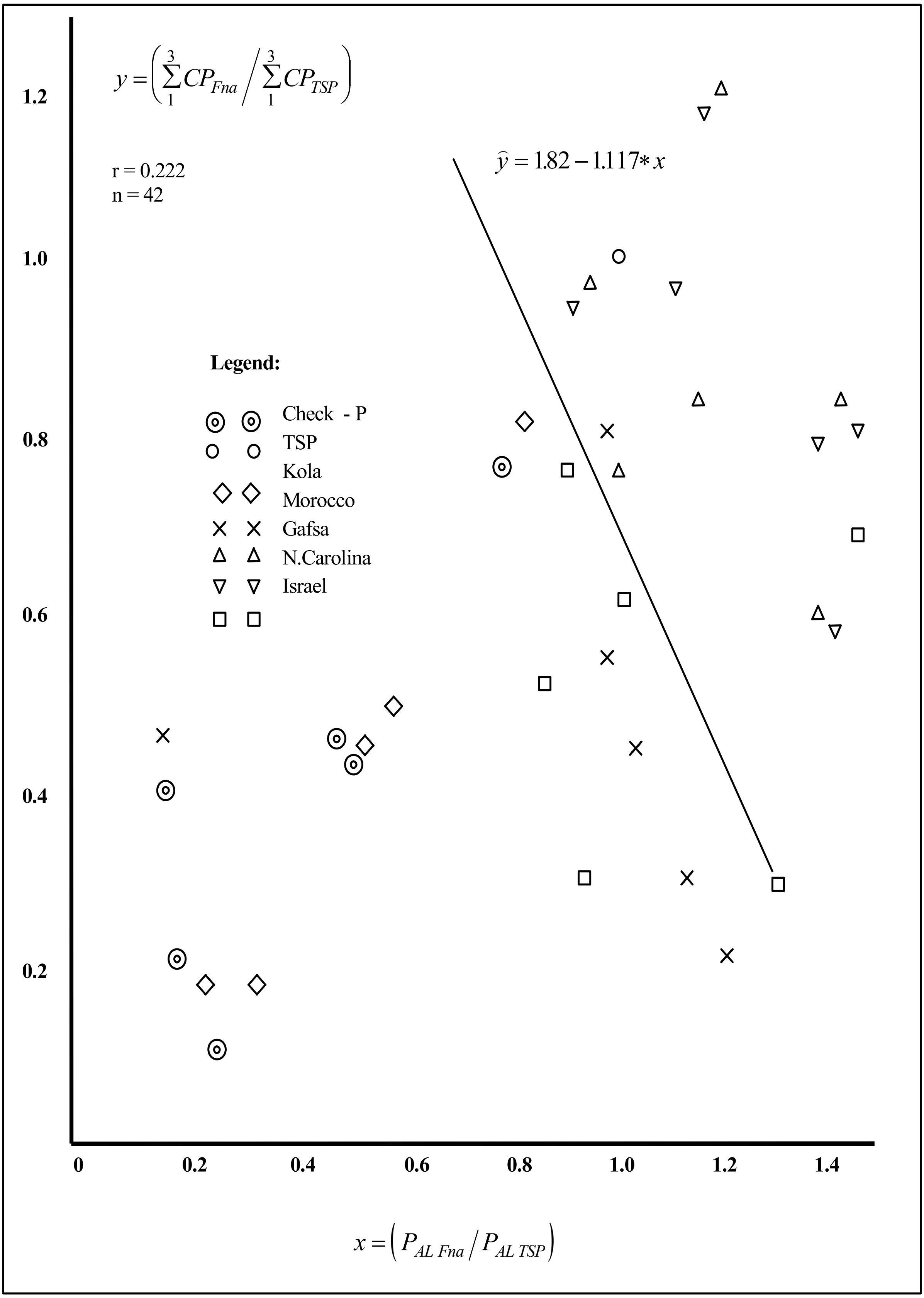

Fig. 2. Variation of $\sum_{1}^{3} CP_{Fna} \Big/ \sum_{1}^{3} CP_{TSP}$ *ratios versus* P_{ALFna} / P_{ALTSP} *at the end of ryegrass small pot experiment with PR in 1996.*

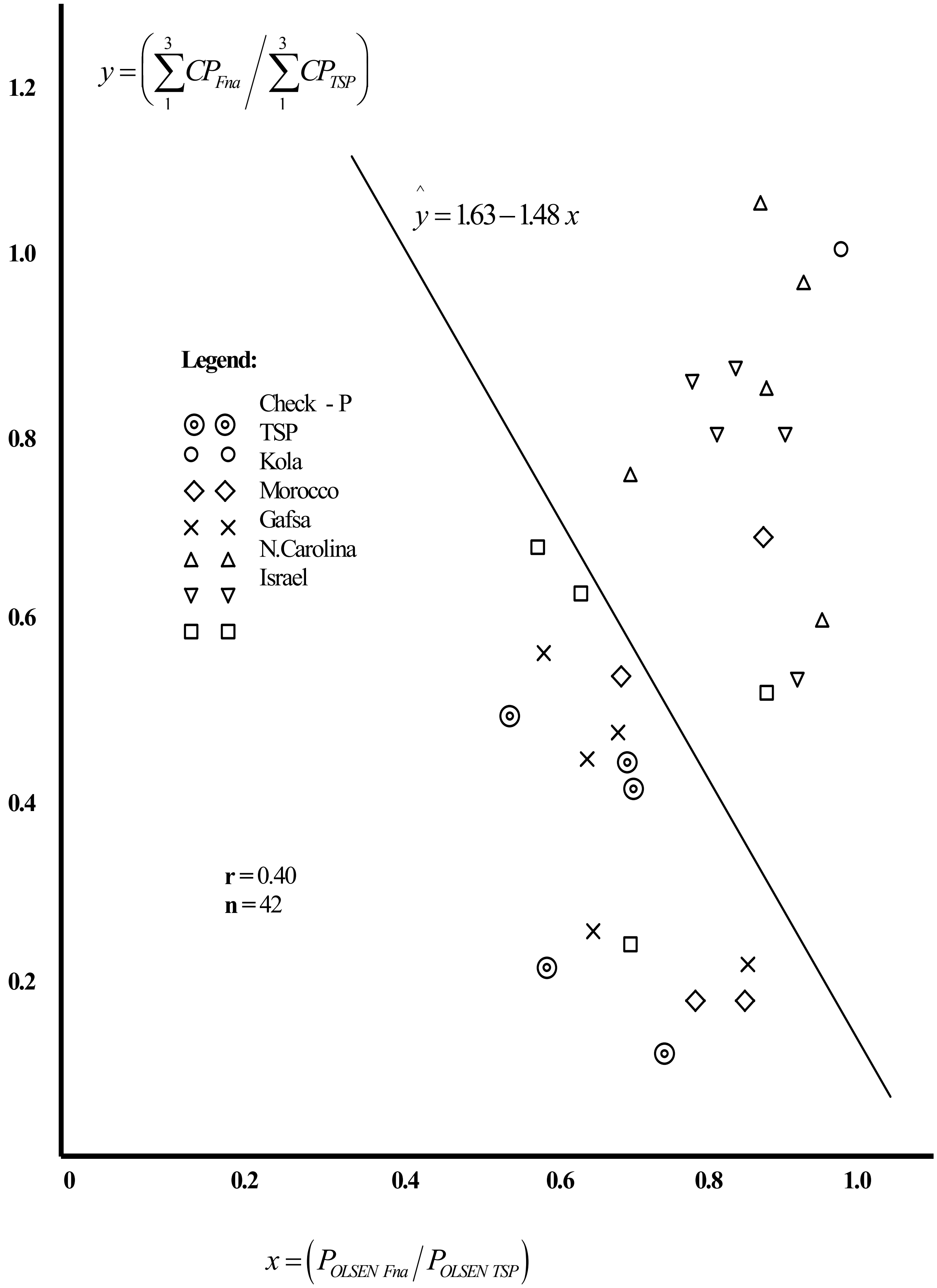

Fig. 3. Variation of CP_{PR}/CP_{CSP} *ratios versus* $P^{PR}_{NaHCO_3}/P^{CSP}_{NaHCO_3}$ *at the end of ryegrass pot experiment with PR in 1996.*

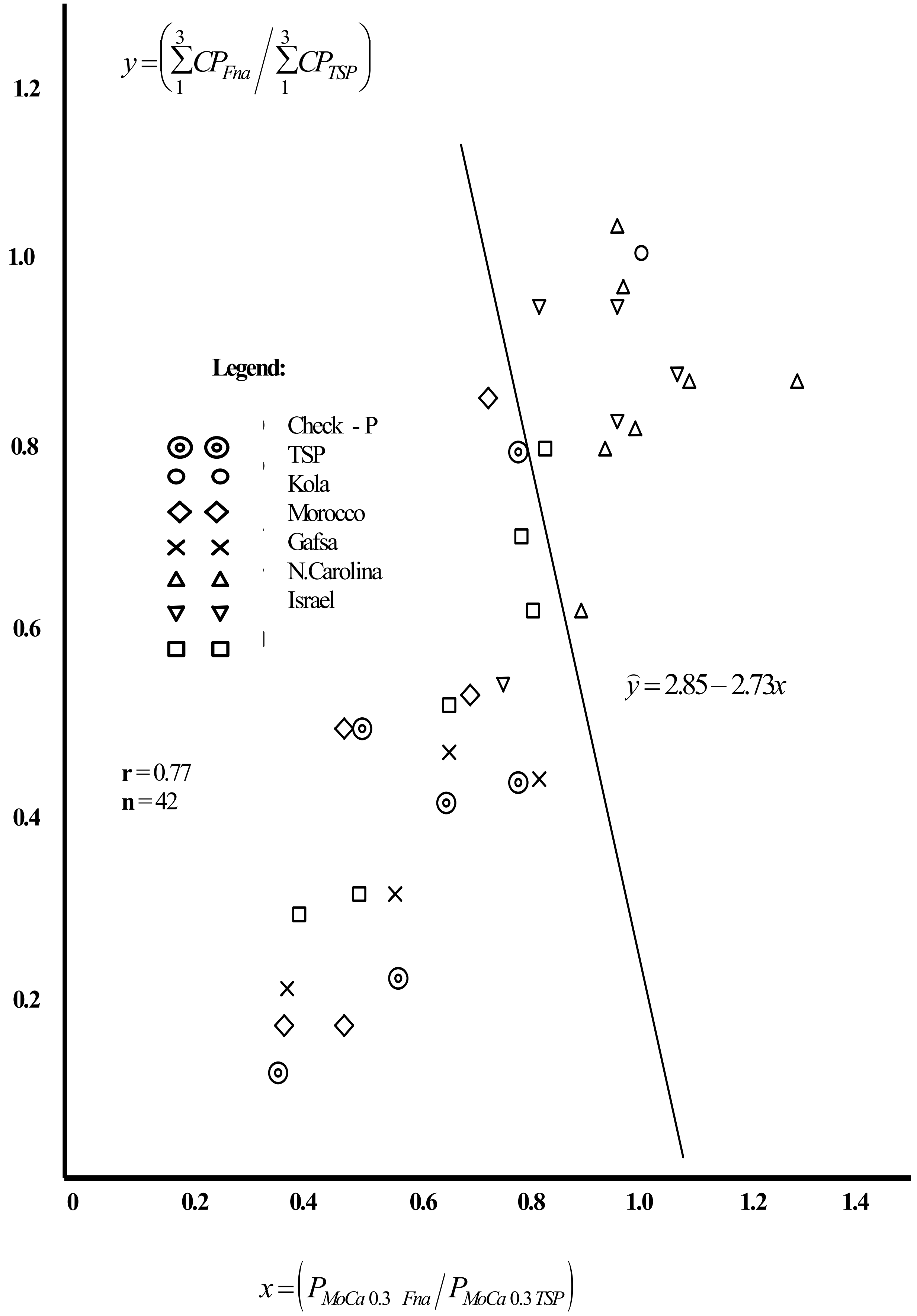

Fig. 4. Variation of $\sum_1^3 CP_{Fna} \Big/ \sum_1^3 CP_{TSP}$ *versus* $P_{MoCa0.3Fna}/P_{MoCa0.3TSP}$ *in the soil at the end of ryegrass pot experiment with PR in 1996. Y=2.85 – 2.73 x*

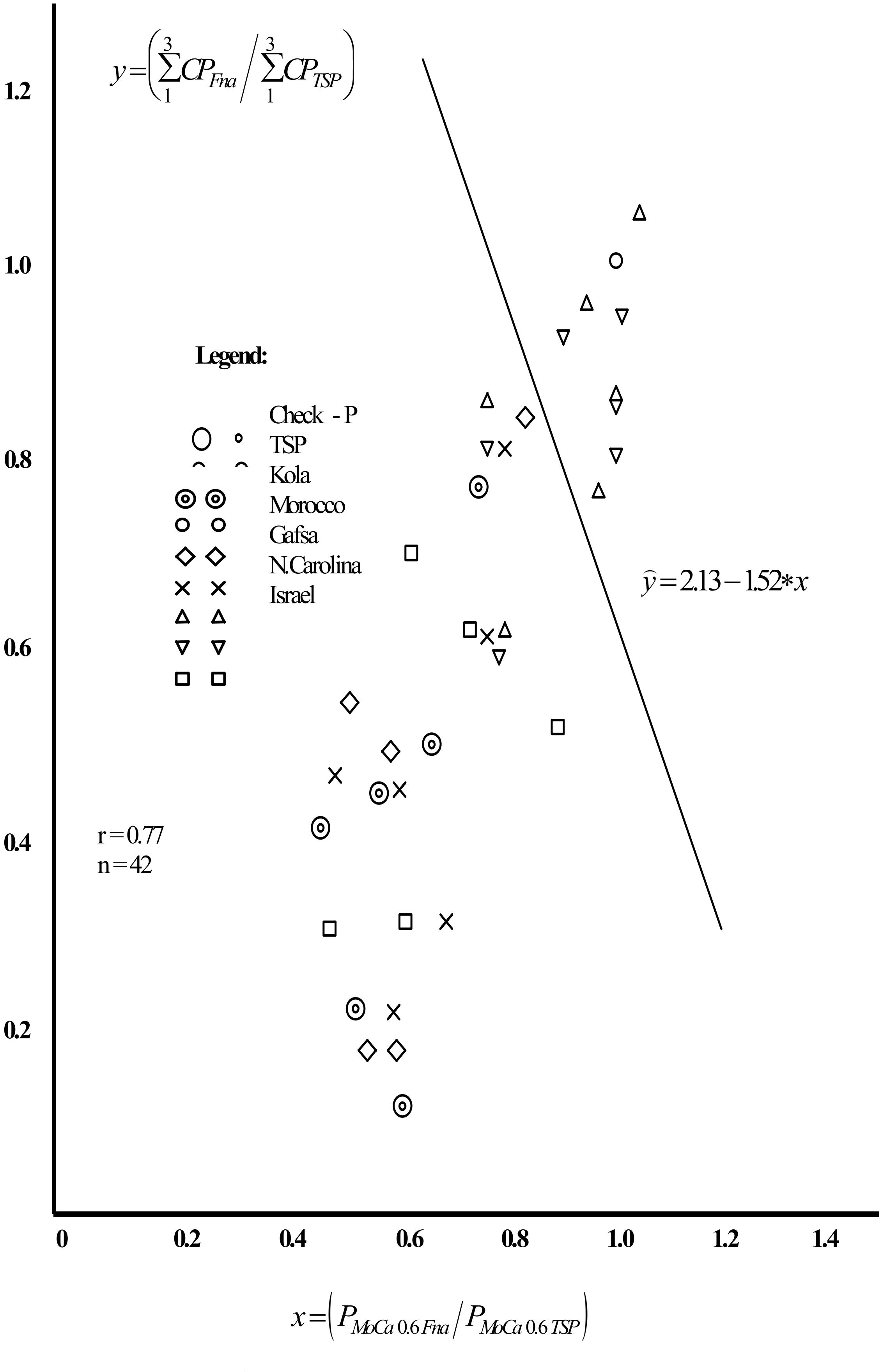

Fig. 5. Variation of $\sum_{1}^{3} CP_{Fna} \Big/ \sum_{1}^{3} CP_{TSP}$ *versus* $P_{MoCa0.6Fna} / P_{MoCa0.6TSP}$ *at the end of ryegrass pot experiment with PR in 1996. Y=2.13-1.52x.*

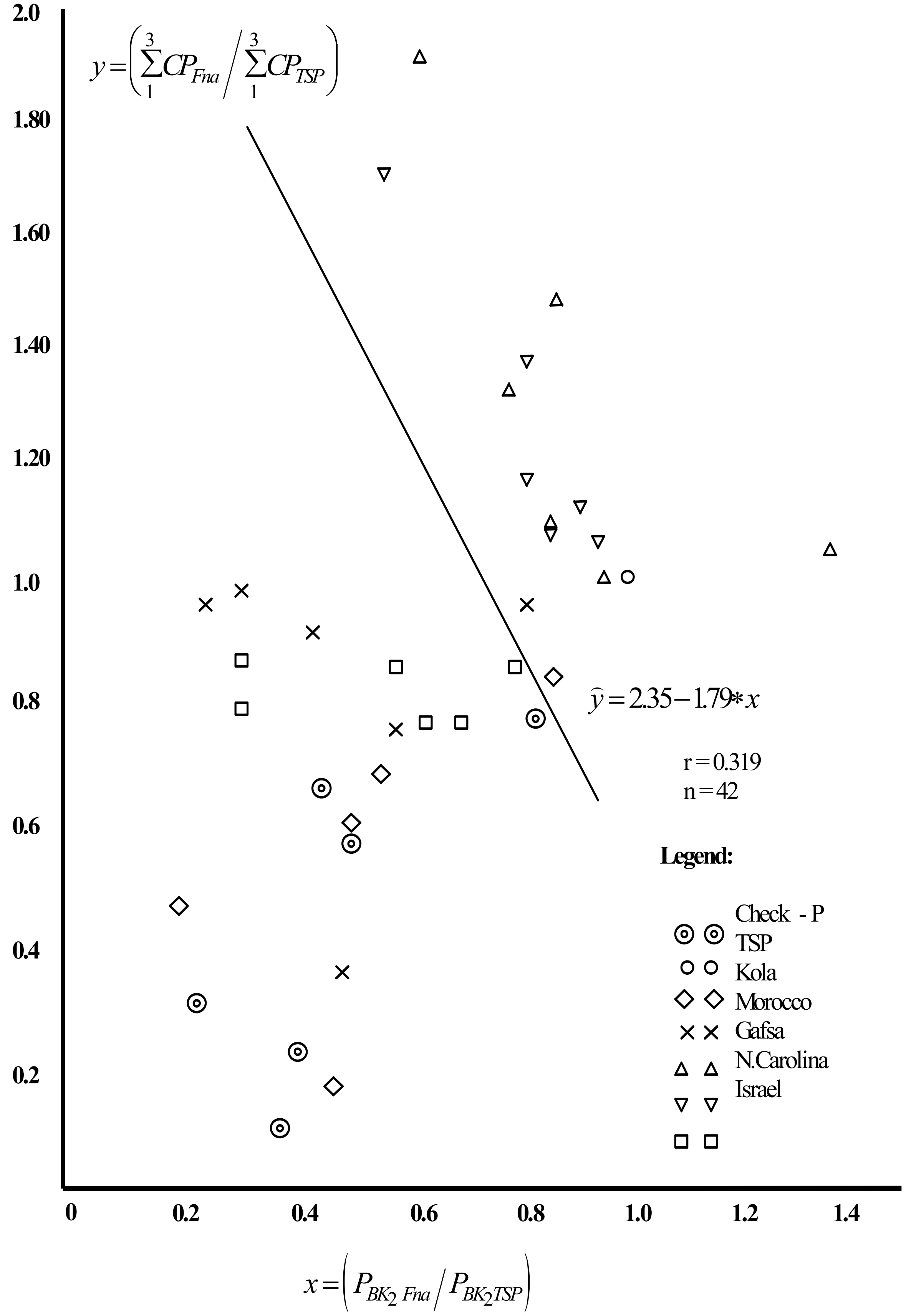

Fig. 6. Variation of $\sum_{1}^{3} CP_{Fna} \Big/ \sum_{1}^{3} CP_{TSP}$ *versus* $P_{BK_2Fna} / P_{BK_2TSP}$ *in the soil at the end of ryegrass pot experiment in 1996.*

4. CONCLUSIONS

Suitability of conventional extraction methods for monitoring easily soluble P (mobile P) in PR-amended soils was evaluated by correlating dependent plant variables (plant response to applied P; plant uptake of P and others) determined by ^{32}P isotope dilution methodology and the difference method, versus mobile soil P determined by conventional methods. The correlations of ^{32}P isotope-dilution dependent plant variables and of plant variables established by non-isotope difference method, were also compared. Regressions were made between plant determined parameters and mobile soil P. It is desirable that regression lines of plant dependent variables on soil mobile P pass through the origin of the xy rectangular co-ordinates so that the relationship can be expressed by means of a Mitscherlich-Baule equation.

Correlation studies of plant dependent variables with soil mobile P (P_{AL}; P_{NaOCO3} and $P_{MoCa0.6}$) showed that plant variables [PdfPR and (PdfPR/PdfTSP)] established by means of ^{32}P isotope dilution were not significantly related to soil mobile P extracted by conventional methods. It seems that mobile soil P as an independent soil variable is not enough to account for a significant proportion of dependent plant P variance, as determined by ^{32}P isotope methodology. Not withstanding this, the MoCa extraction method for mobile soil P performed better than P_{NaHCO3} and P_{AL} methods.

Based on plant, PR and soil correlation studies conducted from 1994 through 1997, it is possible to conclude that the MoCa 0.3 and 0.6% extraction methods of mobile soil P have both performed significantly better than other tested conventional extraction methods (P_{AL}, P_{NaHCO3} and $P_{NH4F-HClB2}$). The success for determining the PR relative efficiency based on mobile P determination arises from the extraction predicting the PR-P mobilization as a result of its prolonged interaction with moistened soil.

5. APPENDIX: DETERMINATION OF MOBILE SOIL PHOSPHATE REMOVED FROM SOIL BY EQUILIBRIUM EXTRACTION WITH 0.3 OR 0.6 % AMMONIUM HEPTAMOLYBDATE IN 0.01M CALCIUM CHLORIDE (BORLAN, HERA ET AL. 1982)

5.1. Extraction of mobile P from soil samples

2.5 g of air-dry soil crushed to pass completely through 0.2 mm sieve is taken with a precision of ±0.02 g and transferred in a plastic (polyethylene) flask of 250 cc. Then, with manifold dispenser 100 cc of MoCa 0.3 extracting solution (reagent 3.1 $(NH_4)_6Mo_7O_{24}.4H_2O$) is added. Provide vigorous shaking for 1h using a rotating shaker making 14-15 overhead rotations per minute in a temperature-controlled 20±1° C cabinet. Transfer the suspension on a thin-pore (less than 1μm) filter paper and let it go through completely.

5.2. Colorimetric determination of P in MoCa solution extracts by Osmond-Denigés molybdenum-blue method in a variant proposed by Chalmers (1953)

Transfer 50 cc aliquot of MoCa extract solution to a 150-200 cc round bottom flask. To it add successively: 2.0 cc of ammonium citrate 0.0375 N neutral solution (reagent nr.3.2); 3.0 cc of acid ammonium molybdate reagent (nr.3.3) and 2.0 cc of acid Mohr salt solution (nr.3.7), mixing the flask content after addition of these reagents. Wait for 1h at laboratory temperature (~ 20°C) and measure color absorbance in 750 nm red light. Calibrate spectrophotometric (SP) readings with samples containing 0, 10, 20, 30, 40, 60, 80, 100, 140 and 180 μg of P in 50 cc MoCa 0.3 solution plus the necessary color development and stabilization reagents. The readings will correspond to 0, 10, 20, 30, 40, 60, 80, 100, 140 and 180 ppm $P_{MoCa\ 0.3}$ in soil. Construct calibration graphs by plotting SP readings versus ppm P in soil. From the graph, read the contents of $P_{MoCa\ 0.3}$ as ppm P in soil.

According to existing measurements and observations made in Romania, the status of soil phosphorus supply is defined by the following $P_{MoCa\ 0.3}$ contents:

$P_{MoCa0.3}$ content (ppm P)	Soil P supply status
less than 5	very low
From 5 to 10	low
From 10 to 20	medium
From 20 to 40	good
more than 40	very good

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REFERENCES

[1] RIEHM, H., Die Ammonium laktatessigsure - Methode zur Bestimmung der leichtlslichen Phosphorsäure in Karbonathaltigen Böden, Agrochimica, **3** (1958) 49 - 65.

[2] EGNÉR, H.et.al., Untersuchumgen ber die chemische Bodenanalyse als Grundlage für die Beurteilung des Nahrstoffzustandes der Boden - II Chemische Extractions Methoden zur Phosphor und Kaliumbestimung, Kungl. Lanbruckhgs (1960)

[3] OLSEN, S.R., COLE, C.V., WATANABE, F.S., DEAN, L.A., Estimation of available phosphorus in soils by extraction with bicarbonate, U.S.Dept.Agric.Circ. **939** (1954).

[4] BRAY, R.H., KURTZ, L.T., Determination of total organic and available forms of phosphorus in soil, Soil. Sci. **59** (1945) 39:45.

[5] BORLAN, Z., HERA, CR. et al., Opredelenie potvijnîh fosfatov, ekshaghireie mîh molibdaton ammonia i hlovistîm kaltiem - MoCa în: Agrochimiceskie metodî issledovania fosfatuogo rejima pociv, Sbonik metodov, Acad. SH Nauk GDR Insit. Potania Rast. Jena. (1982) 45-48

[6] BORLAN, Z., HERA, CR., BUNESCU, OV., Agrochimia fosforului. Aspecte actuale de interes practic şi ştiinţific, Ed.Ceres. Bucureşti (1990).

COMPARISON OF SEVERAL NON-BIOLOGICAL METHODS FOR EVALUATING SOIL AND FERTILIZER PHOSPHORUS AVAILABILITY FROM ROCK PHOSPHATE

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Abstract. In this paper the results of a one-year laboratory experiment on the availability of fertilizer-derived phosphorus are presented. Samples of 20 representative soils were incubated for 100 days with superphosphate and two "soft" phosphate rocks. The soils were analyzed for available phosphorus content by 4 different non-isotopic methods and by the isotopic exchange method. Rock phosphates were very poor sources of available phosphorus while recovery coefficient of P from triple superphosphate was almost 50%. The most suitable method for estimating fertilizer-derived phosphorus availability was the Egner–Riehm DL extraction E value calculated from isotopic exchange kinetics. This method corresponded closely to the amount determined from paper strip extracted phosphorus (P_i) and phosphorus exchanged on anion membranes. The paper-strip P and anion membrane P were both good methods for measuring the C_p value (P concentration in soil solution).

1. INTRODUCTION

During the last 7 years the consumption of phosphorus has dramatically decreased in Poland. The doses of phosphorus in mineral fertilizers were more than halved and the consumption of manure showed also a downward trend. As a result, a negative phosphorus balance is occurring and the process of soil P depletion has started [1]. These results have influenced the policy of phosphorus fertilization, which shifted from the build-up and maintenance concept towards a sufficiency approach. This also calls for reliable determination of soil P status for providing more accurate P fertilizer recommendations. Moreover, considering the need for maintaining adequate crop production and protecting the environment the soil scientist is challenged with the task to develop new methods of soil testing for mobile phosphorus content. The most comprehensive method seems to be ^{32}P isotopic exchange kinetics but this method is unsuitable for routine analysis and is not utilised in any Polish soil testing laboratory. Hence, new chemical and physical methods are being developed and validated by comparison with the isotopic exchange method.

The aim of this investigation was to evaluate the suitability of several non–isotopic methods for estimating the availability of phosphorus derived from superphosphate and two "soft" rock phosphates and to validate these method by comparison with ^{32}P isotopic exchange method.

2. MATERIALS AND METHODS

In the autumn 1997, samples from 20 representative Poland soils were collected from the plough layer, dried at room temperature and sieved through a 1 mm sieve. Soils were Orthic Luvisols, Podzoluvisols and Leptic Podzols according to the FAO classification. These soil types are prevalent in lowland Poland. Some characteristics of the soils are shown in Table I. The soils were mainly sandy-loams and loamy-sands with few loams and one clay soil. Most soils were very acid to acid (pH in KCl below 5.5) and only 5 soils were slightly acid (pH above 5.5). The soil available phosphorus according to the Egner–Riehm method (the official method in Poland) was low (< 44 mg P kg^{-1}) to medium (45 to 66 mg kg^{-1}).

For the incubation experiment, soil sub-samples, 1 kg each, were mixed with phosphorus fertilizers in portions of 200 mg P kg^{-1} dry soil, brought to 60% of water holding capacity and incubated for 100 days at room temperature in plastic pots under plastic cover. Control (no P) samples were included. Treatments had three replications. The characteristics of the phosphorus fertilizers used are given in Table II. After the incubation period, soil samples were dried and analyzed for the content of available

TABLE I. BASIC CHARACTERISTICS OF THE SOILS

Soil	*Particle size composition*			*Soil reaction*		*Phosphorus content (mg/kg)*	
No	%< 20 um	%< 2 um	Soil type	pH	Reaction	Available[1]	Total
1	5	2	Sand	3.8	Very acid	30	195
2	7	2	Sandy-loam	4.1	Very acid	48	295
3	14	3	Loamy-sand	4.4	Very acid	26	275
4	4	2	Sand	4.1	Very acid	22	250
5	11	1	Loamy-sand	5.9	Slightly acid	55	783
6	7	2	Sandy-loam	5.0	Acid	76	410
7	10	3	Sandy-loam	4.8	Acid	84	607
8	5	1	Sand	5.3	Acid	60	515
9	13	2	Loamy-sand	6.1	Slightly acid	68	475
10	13	4	Loamy-sand	6.1	Slightly acid	49	360
11	13	4	Loamy-sand	5.7	Slightly acid	49	450
12	8	3	Sandy-loam	4.1	Very acid	43	370
13	18	4	Loam	4.2	Very acid	18	410
14	22	3	Loam	6.1	Slightly acid	66	530
15	13	3	Loamy-sand	4.9	Acid	13	380
16	19	4	Loam	4.5	Very acid	8	365
17	62	24	Clay	4.4	Very acid	15	876
18	10	2	Sandy-loam	4.6	Acid	62	575
19	19	7	Loam	4.6	Acid	1	250
20	12	3	Sandy – loam	5.3	Acid	59	675

[1] Determined by the Egner-Riehm method.

phosphorus by methods classified into three groups: chemical extraction (Table III), adsorption on paper strips (P_i) or anion exchange, and ^{32}P isotopic exchange kinetics. All non-isotopic analyses were performed in three incubation replications and two analytical replications. The isotopic analyses were conducted in composite samples after mixing together 3 incubation replications and conducting two analytical replications. Chemical extraction and adsorption–exchange analyses were conducted in the Central Chemical Laboratory of the Institute of Soil Science and Plant Cultivation in Puławy by the authors of this paper. Isotopic exchange kinetic analyses were performed and calculated in the FAO/IAEA Agriculture and Biotechnology Laboratory at Seibersdorf by J.C. Fardeau from INRA, France with the participation of the second author of this paper.

The procedure for adsorption of P on paper strips (P_i) was slightly modified from the method outlined by Menon at al. [2]. Paper strips were saturated with $FeCl_2$ and NH_3.

TABLE II. BASIC PROPERTIES OF PHOSPHORUS FERTILIZERS
USED IN THE INCUBATION EXPERIMENT

			P Contents (%)	
Raw material or fertilizer	Grade	Origin	Total	Soluble[1]
Triple superphosphate	Apatite made	Gdańsk factory	24.9	24.9
Rock phosphate	3	North Carolina	12.9	4.2
Rock phosphate	3	Tunisia	13.1	4.3

[1] in citric acid.

TABLE III. CHARACTERISTIC OF CHEMICAL EXTRACTION METHODS FOR AVAILABLE P

Method	Extractant	Soil/solution ratio	Extraction time	Remarks
Egner-Riehm DL	0.4 M. calcium lactate, 0.02 M. HCl, pH 3.6	1:50	1.5 hours	Official method in Poland
Houba	0.01 M $CaCl_2$	1:10	2 hours	Method tested in Poland

The strips were immersed in a mixture of soil and 0.01 M $CaCl_2$ solution (1 g of soil + 40 ml solution), shaken, left for 24 hours, shaken again, removed and soaked with distilled water. Adsorbed phosphorus was exchanged in 40 ml of 0.2 M H_2SO_4 for 2 hours and measured on a flow colorimetry line (SKALAR) using molybdenum blue method for color development. The anion-exchange procedure was based on Fernandez and Coutinho [3] and was slightly adapted in respect to exchange medium. Soil samples of 2 g were added to 40 ml 0.01 M $CaCl_2$ and 3x4 cm sheets of anion exchange membrane (CEM BDH 55165) saturated with Cl^- and HCO_3^- anions. The mixture was shaken and left to stand for 24 hours. The membrane was removed, soaked with distilled water and exchanged in 40 ml 0.5 M HCl on horizontal shaker for 1 hour. The desorbed phosphorus was measured on flow colorimetry line (SKALAR) using molybdenum blue method for color development. Isotopic exchange kinetics followed the method outlined by Fardeau [4]. In this method the intensity factor C_p (concentration of P in soil solution) and quantity factor E_1 (the amount of P isotopically exchangeable during the first minute of isotopic exchange) were calculated. All results are expressed in mg P per kg of dry soil or mg P per dm^3 solution (C_p value) and were processed statistically using analysis of variance and regression analyses by means of STATGRAPH software.

3. RESULTS AND DISCUSSION

The P concentrations in soil samples after incubation are presented in Table IV. The values calculated from isotopic analysis (C_p, E and n value) were used for validation of non-isotopic methods as opposed to defining independent characteristics of soil phosphorus availability. The reason for such an approach is that isotopic methods would never be used for routine soil analysis of available phosphorus and in Poland there is no radiosotope laboratory for these purposes.

The P content in fertilized soils was dependent on the initial soil P content and the rate of transformation of applied fertilizer in the available form, as measured by the specific method. Therefore, more interesting than the content itself is the rate of increase of the soil P concentration as influenced by the fertilizer additions (Table V and in Figs. 1-4).

TABLE IV. INDICES OF SOIL PHOSPHORUS AVAILABILITY

		Chemical extraction, mg P/kg soil				Isotopic exchange		
Treatment	Statistics	Egner	P_i	$CaCl_2$	$P_{exch.}$	$C_{p.}$ mg/l	E mg/kg	n^*
Control	Average	38.8	8.4	1.94	0.61	0.54	7.20	0.243
	Sd	20.9	5.4	1.97	0.56	0.49	5.41	0.149
	Minimum	2.6	1.0	0.01	0.01	0.01	0.32	0.089
	Maximum	69.5	19.4	6.02	2.04	1.40	16.12	0.570
Superphosphate	Average	133.8	51.5	21.5	3.75	3.60	40.81	0.120
	Sd	40.7	24.5	13.9	2.97	2.14	22.13	0.105
	Minimum	51.6	4.7	1.15	0.16	0.21	3.59	0.034
	Maximum	203.2	88.8	45.8	10.82	6.82	73.61	0.380
North Carolina	Average	64.4	13.2	3.02	0.81	0.78	9.64	0.190
	Sd	24.9	8.7	2.42	0.60	0.53	5.57	0.137
	Minimum	13.1	1.2	0.01	0.08	0.02	0.59	0.069
	Maximum	113.6	39.1	9.16	2.3	1.81	19.59	0.490
Tunisia	Average	57.6	12.7	2.8	0.75	0.71	8.82	0.191
	Sd	20.2	7.9	2.2	0.57	0.50	5.20	0.138
	Minimum	17.5	1.6	0.01	0.04	0.02	0.64	0.056
	Maximum	91.8	28.9	8.02	2.52	1.65	18.65	0.490

TABLE V. THE INCREASE RATE OF AVAILABLE PHOSPHORUS UNDER INFLUENCE OF FERTILIZERS

	P under influence of fertilizer (mg kg^{-1})	
Non-isotopic method	Superphosphate	Rock phosphates[1]
Egner-Riehm DL	95.0 a	22.40 a
Paper strips P_i	42.8 b	4.70 b
0.01 M $CaCl_2$	19.3 c	0.95 c
Exchange membrane P_{exch}	3.1 d	0.16 c
Least significance diff. LSD	6.0	2.01

[1] means for North Carolina and Tunisia rock phosphates.

The rate of increase of available P in fertilized soils expressed in percentage of applied P amount is called the recovery coefficient. From the 200 mg P per kg soil applied as superphosphate, on the average 47.5% was recovered by the Egner-Riehm DL method, 21.3% by the P_i method, 9.7% by the $CaCl_2$ method and only 1.5% by the resin exchange method. Figs. 1-3 for the first 3 methods corresponded very closely to those found in a previous experiment [5]. From the same P rate applied as North Carolina and Tunisia rock phosphates, the recovery coefficients were much lower and amounted to 11.2 %, 2.3 %, 0.4 % and 0.04 % for the methods used, respectively. These data were lower than those found in a previous experiment. There were no significant differences in recovery coefficients for the rock phosphates and therefore, their results are presented as an average.

The rate of P increase differed substantially among the soils studied (Figs. 1-4). Preliminary examinations of the data for several soils fertilized with superphosphate revealed that the rate of increase was positively correlated with the soil pH and with the content of “native” soil phosphorus (data not shown). This observation was particularly noticed for the Egner–Riehm method. There was no clear relationship between soil properties and the rate of phosphorus increase in soils treated with rock phosphates.

TABLE VI. CORRELATION COEFFICIENTS BETWEEN SEVERAL METHODS

Meted	Egner-Riehm	Paper strips P_i	P_{CaCl2}	P_{exch}	C_p	E	N
Egner – Riehm	1.00						
Paper strips P_i	0.82	1.00					
0.01 M $CaCl_2$	0.84	0.88	1.00				
Exchange membrane	0.83	0.82	0.94	1.00			
$C_{p.}$ Factor	0.83	0.89	0.98	0.94	1.00		
E factor	0.88	0.89	0.97	0.93	1.00	1.00	
N factor	-0.56	-0.54	-0.53	-0.52	-0.60	-0.58	1.00

The amounts of phosphorus determined by both non–isotopic and isotopic methods were highly correlated (Table VI). The intensity factor (C_p) showed the strongest correlation with all quantity factors but such relations have no practical consequences for evaluating the soil phosphorus status and fertilizer recommendations. In this respect, the intensity and quantity factors should be used simultaneously for better explanation of short term (intensity) and long term (quantity) ability of soils to supply crops with the proper amount of phosphorus at the proper time. The chemical methods used in this investigation for the intensity factor are 0.01 M $CaCl_2$ (P_{CaCl2}) and anion exchange membrane (P_{exch}). The regression equations for these pair of methods were as follow:

$$C_p = 0.2899 + 0.1524\, P_{CaCl2}\ , r = 0.98$$
$$C_p = 0.2389 + 0.7883\, P_{exch}\ , r = 0.94$$

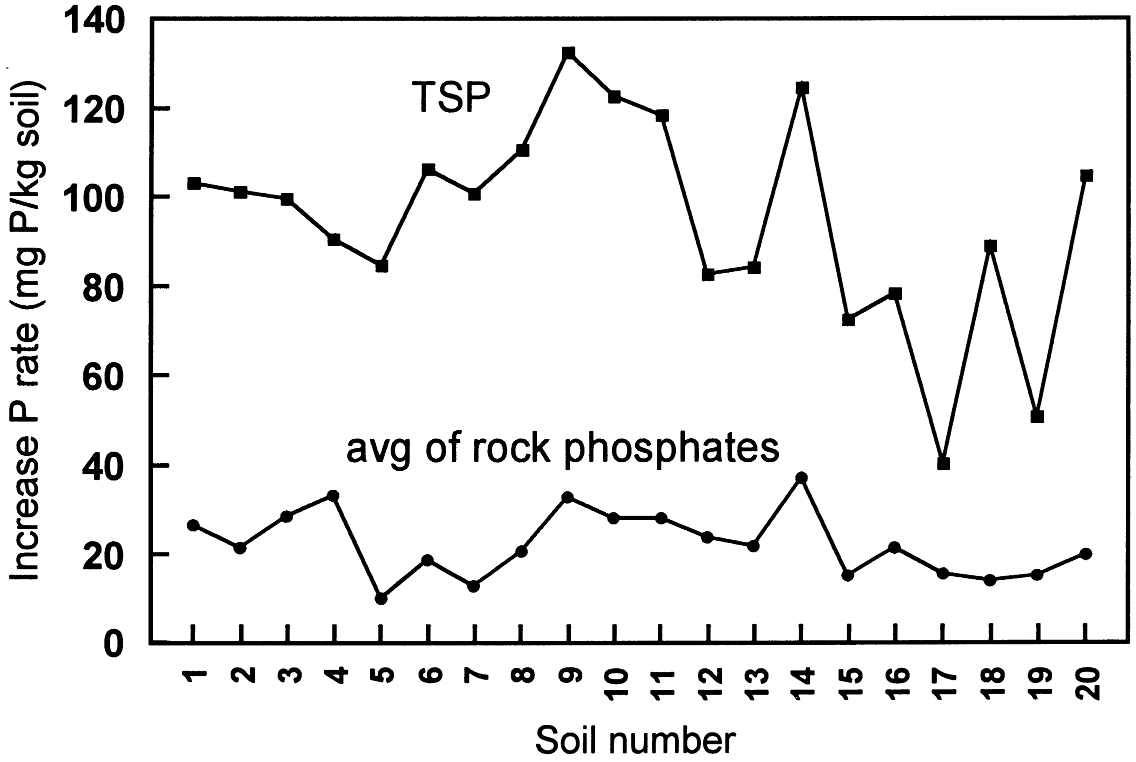

Fig. 1. Increase P rate for the Egner-Riehm method for 20 soils tested.

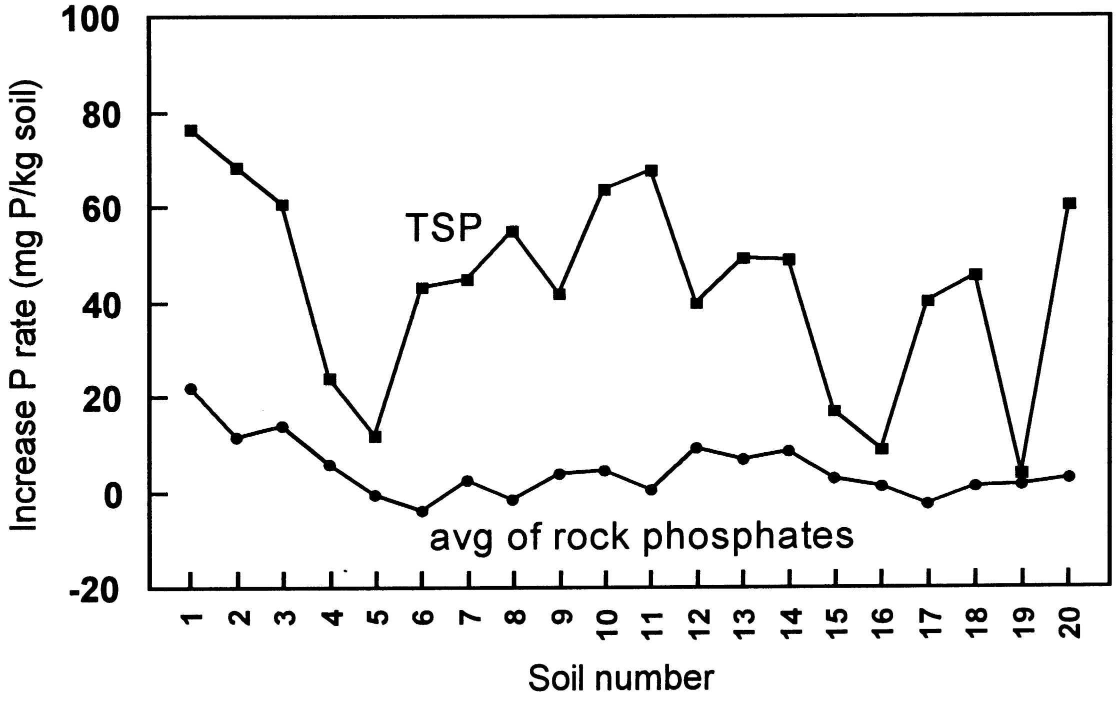

Fig. 2. Increase P rate for the paper strip P_i method for 20 soils tested.

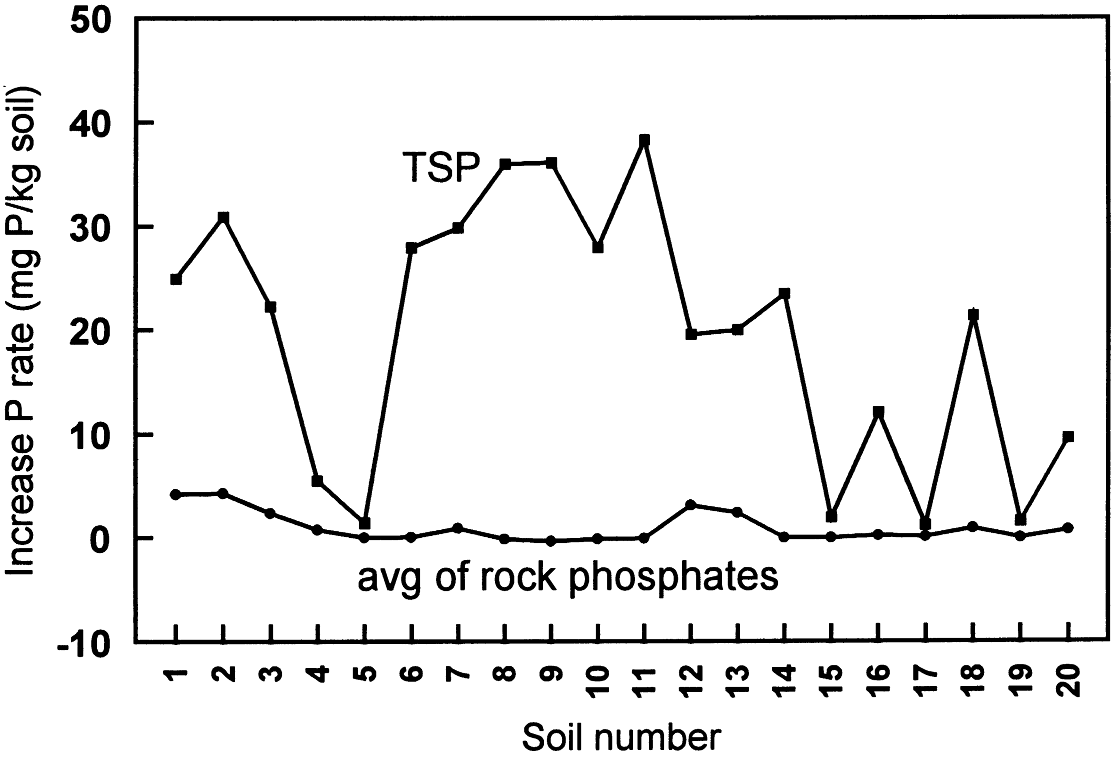

Fig. 3. Increase P rate for the 0.01 M $CaCl_2$ method for 20 soils tested.

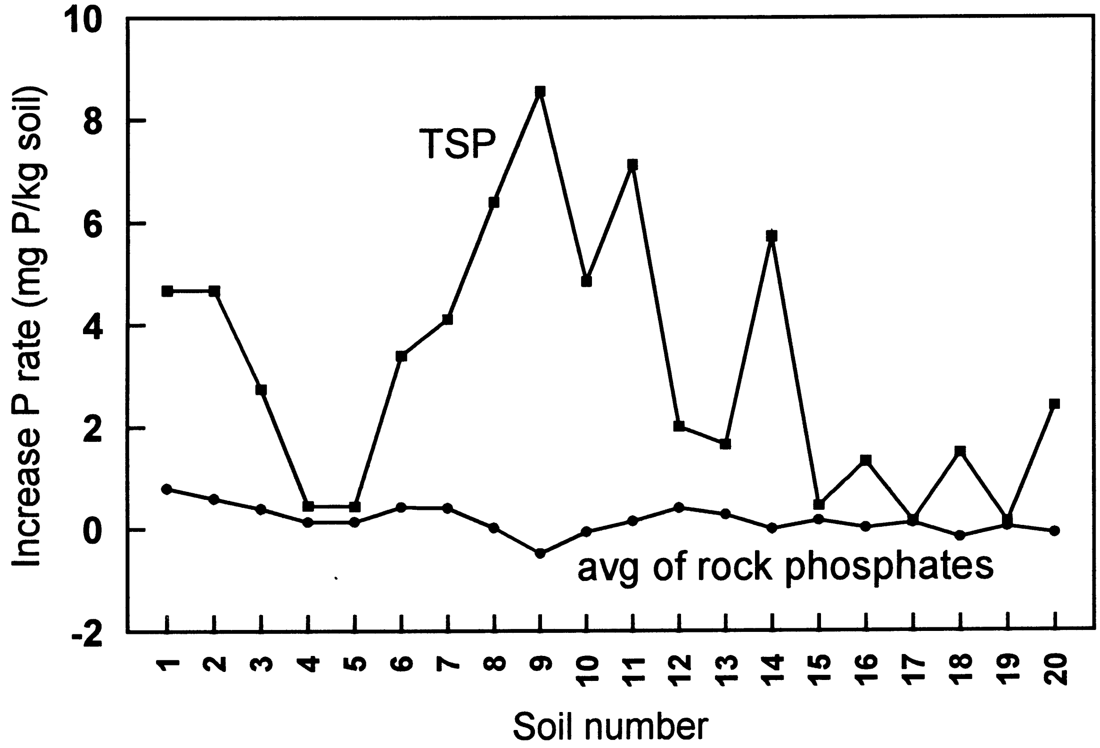

Fig. 4. Increase P rate for the exchange membrane method for 20 soils tested.

The slopes of these equations were significant but not the intercepts. Thus, it was possible to run the regression line through the origin. In such modified regression equations, the rounded values of the slopes were 0.2 and 0.8 for P_{CaCl2} and P_{exch}, respectively. Hence, the intensity factor, C_p, equals the concentration of phosphorus in 0.01 M. $CaCl_2$ multiplied by 0.2 or equals the amount of phosphorus extracted by anion membrane multiplied by 0.8. The slope for P_{CaCl2} differs substantially from the one found in previous investigations [3]. In this paper the relationship was based on 20 different soils whereas the other study was concerned with only one type of organo-mineral soil.

The quantity factor (E value), as determined by phosphorus exchange kinetics, seemed to be closely related to the amount of phosphorus adsorbed on paper strips P_i. The corresponding regression equation was as follows:

$$\text{E value} = 0.7237 + 0.7265\ P_i\ ,\ r = 0.89$$

Taking into consideration that only the slope term of this equation was highly significant, one can conclude that the amount of phosphorus adsorbed on paper strips give a very good approximation of the quantity factor of soil available P measured by the^{32}P isotopic exchange method.

To describe the phosphorus status based on intensity, quantity and buffer capacity, it is important to have simple indirect methods for estimating these parameters because the ^{32}P exchange kinetics cannot be used for routine analysis.

4. CONCLUSIONS

The recovery coefficient of phosphorus from finely ground, “soft” rock phosphate is several times lower than the coefficient of recovery from triple superphosphate. Therefore rock phosphates could not be recommended for direct use for annual crops in Polish agriculture.

For routine soil analysis, the officially used Egner–Riehm DL method for determining available nutrients was found the most suitable in Polish soils for analyzing soil fertilized with rock phosphate.

For more complete characterization of the soil P status based on intensity, quantity, and buffer capacity, the paper strip method (P_i) can substitute the E value (^{32}P isotope exchange) and the 0.01 M $CaCl_2$ (Houba method) and anion membrane (P_{exch}) methods can be used for measuring the intensity (C_p).

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REFERENCES

[1] FOTYMA, M., GOSEK, S. Long-term phosphorus balance in Poland. Bibliotheca Fragmenta Agronomica. **3** (1998) 317-326.

[2] MENON, R.G., CHIEN, S.H., HAMMOND, L.L., The P_i soil phosphorus test. International Fertilizer Development Center (1997).

[3] FERNANDEZ, M.L, COUTINHO, J., Anion and cation exchange resin membranes to assess the phosphorus status of some Portuguese soils. Commun. Soil Sci. Plant Anal. **28**: 6-8 (1997) 483-495.

[4] FARDEAU, J.C.et al., Dynamics of phopsahte in soils.An isotopic outlook. Fert. Res. **45** (1996) 91-100.

[5] FOTYMA, M., GOSEK, S., BORECZEK, B., Evaluation of fertilizer-derived soil phosphorus, particularly from rock phosphate, by biological and chemical methods (this IAEA TECDOC).

EVALUATION OF SOIL AND FERTILIZER-DERIVED PHOSPHORUS AVAILABILITY, PARTICULARLY FROM ROCK PHOSPHATE, BY BIOLOGICAL AND CHEMICAL METHODS

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Abstract. In this paper, the availability of soil and fertilizer-derived phosphorus were determined in laboratory and vegetation experiments. In the laboratory experiment, soil was incubated with triple superphosphate (TSP) and several rock phosphates RPS) for 100 days and afterwards analyzed for available phosphorus content by various methods including the ^{32}P isotopic exchange kinetic method. The vegetation experiment was carried out in a growth chamber with 3 test crops (oats, lupine and buckwheat). Kola apatite and Togo rock phosphate were found entirely unavailable to the crops. The chemical method that extracted more P from soil was the Egner Riehm extract. The least amount of P was extracted with 0.01 M $CaCl_2$ solution. The E value corresponded closely to the amount of phosphorus extracted with paper strips (P_i method).

1. INTRODUCTION

In Poland, in spite that over 70 % of the soils is acid and hence, theoretically suitable for direct application of rock phosphates (RP), they never have been commonly used as phosphorus fertilizers. In the period of peak fertilizer consumption from 1975 to 1998, the share of finely ground phosphate rock from Morocco and Tunisia did not exceed 1% of the total amount of phosphorus used in agriculture. In vegetation experiments, the efficiency of finely ground “soft” rock phosphates was 80-90 % of that from single or triple superphosphate [1,2].

The official method of soil testing for available phosphorus in Poland is the Egner- Riehm DL extractant (calcium lactate buffered to pH 3.6 with HCl). This test is well-calibrated [3] and commonly used in fertilizer recommendation systems. In the last few years the universal soil test of 0.01 M $CaCl_2$ has been intensively checked for its suitability under Polish conditions to determine available potassium, magnesium and phosphorus [4]. The most comprehensive method for characterization of soil phosphorus status is the ^{32}P isotopic exchange kinetics but it has never been performed in Poland, even in research laboratories.

The aim of this investigation was to compare the availability of phosphorus from different rock phosphates and triple superphopshate, and to evaluate the suitability of several methods, including isotopic exchange kinetics, for measuring available soil phosphorus.

2. MATERIALS AND METHODS

The incubation and vegetation experiments were carried out in 1997 utilising an organo-mineral soil classified as marsh. The soil was very acid with a pH_{KCl} of 4.0 and pH_{CaCl2} of 4.1 with high exchangeable acidity (22.0 $cmol_c kg^{-1}$ soil) and low base saturation (34%). The content of available potassium (370 mg K kg^{-1} soil) and magnesium (277 mg Mg kg^{-1} soil) was very high according to Polish calibration figures. Therefore, no deficiencies of these elements were expected. The content of available phosphorus was low, 38.8 mg P kg^{-1} (Egner - Riehm DL), hence a good response of crops grown on this soil should be expected.

Samples (0.5 kg) of air-dry soil were mixed with the phosphorus fertilizers at a rate of 400 mg P kg^{-1} dry soil, brought to 60 % of water holding capacity (0.35 g g^{-1}) and incubated for 100 days at room temperature in plastic pots (four replications) under plastic covers. The characteristic of phosphorus fertilizers used is given in Table I.

TABLE I. BASIC PROPERTIES OF PHOSPHORUS FERTILIZERS USED IN THE EXPERIMENTS

Raw material or fertilizer	Grade	Origin	P content (%) Total	P content (%) Soluble in citric acid
Triple superphosphate[1]	-	Gdansk factory	24.9	24.9
Apatite	super	Kola Pennisula	17.3	1.4
Rock phosphate	extra	Togo	16.3	2.9
Rock phosphate	2	Morocco	13.9	4.6
Rock phosphate	3	North Carolina	12.9	4.2
Rock phosphate	3	Tunisia	13.1	4.3

[1] made from apatite.

Rock phosphates utilised, except North Carolina, represent the most common raw materials used by fertilizer plants in Poland. North Carolina rock phosphate was included due to the previous, positive, experience with this “soft” phosphate [1].

After the incubation period, soil samples were analyzed for their content of available phosphorus by several methods classified into three groups: chemical extraction (Table II), isotopic exchange kinetic and adsorption on paper strips P_i.

Isotopic exchange kinetics has been performed and calculated in the CEA-Department of Plant Physiology and Ecosystems, Centre de Cadarache, France [5]. Paper strips for P_i method were prepared according to Menon et al. [6]. This method is quite new in Poland and therefore, it has been slightly modified. Paper strips saturated with $FeCl_2$ and NH_3 were prepared according to the original method [6]. The strips were immersed in a mixture of soil and 0.01 M $CaCl_2$ solution (1 g of soil + 40 ml solution) shaken and left to stand for 24 hours, shaken again, removed and soaked with distilled water. Adsorbed phosphorus was exchanged in 40 ml 0.2 M H_2SO_4 for 2 hours and measured on flow colorimetry line (Skalar) using molybdenum blue method for color development.

A vegetation experiment was carried out in small pots with the capacity of 0.5 kg of dry soil in three series with oats, lupine and buckwheat as test plants. The one factorial experiments (6 phosphorus sources and control treatment) with each test plant were arranged separately in complete randomization with three replications. Supplementary fertilization with nitrogen (300 mg N per kg soil) and micronutrients (Zn, Cu, Fe, Mo) was applied to the pots directly before seeding. The experiment was carried out in a growth chamber for 21 days (from plant emergence) at a constant temperature of 20^o C with soil moisture held at 60 % water holding capacity (0.35g water g^{-1} soil). The plants were harvested after 21 days, dried and analyzed for the total content of phosphorus and other elements.

Statistical analysis of the laboratory and vegetation date was performed by means of Stagraphic plus package for a PC computer.

TABLE II. CHARACTERISTIC OF METHODS BASED ON CHEMICAL EXTRACTION

Method	Extractant	Soil/solution ratio	Extraction time	Remarks
Bray-Kurtz	0.03 M. NH_4F, 0.025 M. HCl, pH 2.9	1:7	1 minute	
Egner-Riehm DL	0.4 M. calcium lactate, 0.02 M. HCl, pH 3.6	1:50	1.5 hours	Official method in Poland
Olsen	0.5 M $NaHCO_3$, pH 8.5	1:20	0.5 hour	
Houba	0.01 M $CaCl_2$	1:10	2 hours	Tested in Poland

3. RESULTS AND DISCUSSION

Upon completion of the incubation (after 100 days), all indices of phosphorus availability by means of chemical extraction, isotopic exchange and paper strips P_i were measured in the soil samples. Results expressed in mg P per kg soil or mg P per dm^3 solution are presented in Table III.

The control soil was incubated without the phosphorus sources and was below threshold values for available P as tested by Bray-Kurtz, Egner-Riehm and E value methods (Table III). The threshold values according to the literature are: 125 mg P kg^{-1} soil for Bray-Kurtz, 71 mg P kg^{-1} soil for Egner-Riehm, 23 mg P kg^{-1} soil for Olsen [3], 0.02 mg P dm^{-3} for C_p and 10 mg P kg^{-1} soil for E [5]. The high value for C_p and low values for the other tests in the control treatment leads to the conclusion that this soil is characterized by low quantity and capacity factors of phosphorus availability while the intensity factor is high.

The indices of soil phosphorus availability were significantly increased by addition of all P sources, except Kola apatite and Togo rock phosphate. The rate of increase of these indices for the various P sources was in the order: triple superphosphate>North Carolina>Tunisia>Morocco (rock phosphates). Any addition of Kola apatite and Togo rock phosphate was undetectable by any of the methods of estimating soil phosphorus availability.

The methods with the highest extraction power for phosphorus, both from native soil and soil enriched with fertilizers, were Bray-Kurtz and Egner-Riehm methods. The extractant with the lowest extraction power for P was the Houba method. The relative amount of phosphorus in fertilizers extracted by the various methods is presented in Table IV. Acid solutions employed in Bray-Kurtz and Egner-Riehm methods extracted higher proportion of phosphorus from rock phosphate than neutral or alkaline Olsen or Houba solutions.

The relative amounts of native phosphorus extracted from the soil in the control were 14.3%, 7.7%, 7.8%, 0.5%, 1.5% and 1.2% for the methods ranked in Table IV respectively. The availability of native phosphorus is therefore much lower than the availability of fertilizer-derived phosphorus, even originating from soft rock phosphates.

The amounts of phosphorus extracted by several methods were highly correlated (Table V). The intensity factor, C_p was highly and significantly correlated with all quantity factors but such relationships have no practical consequences for evaluating the soil phosphorus status and making fertilizer recommendations. The intensity and quantity factors should be used simultaneously for better explanation of the short term (intensity) and long term (quantity) ability of soils to provide crops with the proper amount of phosphorus at the proper time. The only chemical method used in the investigations, which corresponded to the intensity factor was 0.01 M $CaCl_2$ solution (Houba method). Therefore, the values of the intensity factor C_p were regressed against the concentration of phosphorus in 0.01 M $CaCl_2$ solution. The regression equation was as follows :

$$C_p = 0.1519 + 1.3933\ P_{CaCl2}\ ,\ r = 0.99$$

The linear model was well matched to the experimental data and the correlation coefficient was close to 1. The intercept in this equation proved to be insignificant, while the slope was significant at 0.01 confidence level. Therefore the regression was rerun forcing the intercept through the origin. The equation was simplified to the form:

$$C_p = 1.42\ P_{CaCl2}$$

Hence, the intensity factor equals the concentration of phosphorus in 0.01 M $CaCl_2$ (Houba) extract multiplied by 1.4. Therefore, the concentration of phosphorus in the universal extract of 0.01 M $CaCl_2$ seemed to be the best indirect measure of the phosphorus intensity calculated from exchange kinetics.

TABLE III. INDICES OF SOIL PHOSPHORUS AVAILABILITY

	Chemical extraction mg P. kg^{-1} soil					Isotopic exchange		
Treatment	Bray-Kurtz	Egner-Riehm	Olsen	Houba	Paper strips P_i	C_p mg P dm^{-3}	E mg kg^{-1} soil	P. total mg kg^{-1}
Control	71.9	38.8	39.2	2.51	7.42	0.42	6.1	502
Superphosphate	227	230	144	43.5	89.3	5.72	74.9	969
Apatite Kola	71.1	41.0	36.6	2.41	8.57	0.39	5.6	890
Togo RP	69.8	43.6	35.8	2.74	9.40	0.47	7.5	947
Morocco RP	119	117	53.2	11.3	36.9	2.33	34.6	837
N. Carol. RP	149	161	85.4	19.1	35.3	3.10	43.0	884
Tunisia RP	178	148	57.6	16.3	32.5	2.13	29.5	836
LSD	12.5	8.9	7.8	0.80	2.9	n.a[1]	n.a.	n.a.

[1] Data not available, analysis performed in one replication only.

TABLE IV. EXTRACTION POWER OF SEVERAL SOLUTIONS FOR FERTILIZER-DERIVED PHOSPHORUS

	Percentage of phosphorus extracted from P sources					
Extraction method	Super-phosphate	Apatite Kola	Togo Rock ph.	Morocco Rock ph.	N. Carolina Rock ph.	Tunisia Rock ph.
Bray-Kurtz	38.8	none	none	12.0	19.4	23.7
Egner-Riehm DL	47.9	none	none	19.5	30.6	27.3
Olsen	26.1	none	none	3.4	11.5	4.5
Houba	10.3	none	none	2.2	4.2	3.5
Paper strips P_i	19.9	none	none	5.0	6.7	6.9
E value	17.2	none	none	7.1	9.2	7.1

The quantity factor, E value, is another parameter of phosphorus exchange kinetics and is directly related to the amount of phosphorus adsorbed on paper strips (P_i method). The corresponding regression equation was as follows:

$$\text{E value} = 0.3612 + 1.0368\ P_i\ ,\ r = 0.94$$

The intercept was barely significant, while the slope was highly significant which means that the regression line practically passes through the origin and the amount of phosphorus adsorbed on paper strips gives a very good approximation of the E value. Both discussed relations are very important for determining C_p and E indirectly because phosphorus isotope analysis is not performed in Poland.

Direct measures of the value of fertilizer-derived phosphorus in the soil are plant indices. The total yield of dry matter, phosphorus content and phosphorus uptake by oats, lupine and buckwheat grown for 21 days were taken into consideration. The data from the vegetation experiments are presented in Table VI.

The response of phosphorus fertilization in respect to the yield of dry matter was low for all test plants, particularly for yellow lupine. This result can be explained by presumably high concentration of phosphate in soil solution, which can be concluded from the high value of the intensity factor, C_p. The quantity of phosphorus was low, but this parameter of phosphorus availability did not influence significantly the plant yield due to a very short vegetation period (21 days). If the plants were grown to full maturity, the efficiency of phosphorus would have been much higher because the phosphorus

TABLE V. CORRELATION COEFFICIENTS BETWEEN SEVERAL METHODS

Method	Bray-Kurtz	Egner-Riehm	Olsen	Houba	Paper strips P_i	E value	C_p
Bray-Kurtz	1.00						
Egner-Riehm	0.94	1.00					
Olsen	0.82	0.83	1.00				
Houba	0.92	0.94	0.91	1.00			
Paper strips P_i	0.92	0.92	0.93	0.97	1.00		
E value	0.95	0.96	0.89	0.97	0.94	1.00	
C_p	0.95	0.96	0.92	0.99	0.97	0.99	1.00

TABLE VI. THE DATA FROM THE VEGETATION EXPERIMENTS

Phosphorus Source	Oats			Buckwheat			Lupine		
	Dry matter g	Total P %	P uptake g	Dry matter g	Total P %	P uptake g	Dry matter g	Total P %	P uptake g
Control	4.19	0.44	0.019	2.15	0.58	0.013	2.82	0.45	0.011
Superphosphate	4.51	1.27	0.057	2.62	0.88	0.023	3.07	1.03	0.030
Kola apatite	4.06	0.49	0.020	2.44	0.58	0.014	2.84	0.44	0.014
Togo RP	4.26	0.50	0.021	2.20	0.59	0.013	2.93	0.43	0.013
Morocco RP	4.30	0.77	0.033	2.61	0.85	0.022	3.19	0.59	0.017
N.Carolina RP	4.53	1.13	0.051	2.30	0.97	0.022	3.05	0.72	0.022
Tunisia RP	4.60	1.04	0.048	2.36	0.91	0.021	3.06	0.70	0.020
LSD	0.21	0.08	0.015	0.30	0.11	0.006	0.15	0.14	0.005

fertilizers, except Kola apatite and Togo rock phosphate, significantly increased the concentration of this element in plant dry matter. Kola apatite and Togo rock phosphate incubated with the soil for 100 days were found to be entirely unavailable for the plants. This was reflected by both plant dry matter production and total P concentration. The best source of phosphorus was triple superphosphate, but “soft” rock phosphate from Tunisia, North Carolina and Morocco did not have significantly different effects on plant dry matter and total P concentration in plants.

4. CONCLUSIONS

In the incubation experiment, the soil tests and plant indices showed that Phosphorus from Kola apatite and Togo rock phosphate did not supply available phosphorus.

The P availability from finely ground “soft” rock phosphate, North Carolina, Tunisia and Morocco for plants grown on this acid soil under optimal moisture and temperature conditions is comparable to that of triple superphosphate.

The most suitable method for evaluating the availability of fertilizer-derived phosphorus in the soil is Egner-Riehm DL.

^{32}P isotopic exchange kinetic gives the most comprehensive description of soil phosphorus availability. Alternatively, as this method is not suitable for routine analysis, the amount of P extracted with 0.01 M $CaCl_2$ is a good measure of C_p (intensity parameter) extracted and the amount of phosphorus adsorbed on P_i paper strips gives a ggo estimate of the E value (quantity parameter).

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REFERENCES

[1] FOTYMA, M., HAMMOND, L., KĘSIK, K., Suitability of North Carolina natural phosphate to Polish agriculture, In C. Rodriguez-Barrueco (ed.). Fertilizers and Environment, (1996) 151-154.

[2] KĘSIK, K., FOTYMA, M., Assessment of fertilizer value of superphosphate- ground phosphate rock mixtures (in Polish). Pamiętnik Puławski **84** (1988) 85-203.

[3] ADAMUS, M., FOTYMA, M., GOSEK, S., KĘSIK, K., Threshold values of the tests for assessing the available phosphorus form in the soil. (in Polish). Pamiętnik Puławski **76** (1981) 79 -95.

[4] FOTYMA, M., GOSEK, S., BORECZEK, B., Modification of 0.01 M $CaCl_2$ soil test in respect to phosphorus. Commun. Soil Sci. Plant Anal. **30** (1999) 15-16.

[5] FARDEAU, J.C., et al., Dynamics of phosphate in soils. An isotopic outlook. Fert. Res. **45** (1996) 91-100

[6] MENON, R.G., CHIEN, S.H., HAMMOND, L.L., The P_i soil phosphorus test. International Fertilizer Development Center (1997).

LIMING EFFECT ON P AVAILABILITY FROM MAARDU PHOSPHATE ROCK

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Abstract

Thirty years ago phosphate rock from the Maardu deposit was intensively used for soil fertilization in Lithuania. However, the application of finely ground product caused an undesirable dusty operation. Afterwards, a superphosphate production plant was built in Kedainiai and the use of phosphate rock was completely abandoned.

Field experiments with fodder beets and barley were carried out to evaluate the P availability of granulated superphosphate and Maardu phosphate rock. The comparison was made at three acidity levels: a) unlimed acid soil with a high content of Al (pH_{kcl} 4.3-4.4, hydrolytic acidity was 41-44 meq/kg soil), b) soil limed with 0.5n rate $CaCO_3$ powder limestone based on hydrolytic acidity, and c) soil limed with 1.0n rate $CaCO_3$.

Two field experiments were carried out with fodder beets. In 1997 the yield increased significantly due to liming. However, no significant yield increases were found due to the application of phosphorus fertilizers. Differences between the effect of superphosphate and phosphate rock were also not observed. This might have been caused by a severe drought during the vegetative growth of plants. In the following year, 1998, a soil with similar acidity was chosen, however it contained even lower amounts of available phosphorus in the arable soil (about 50 mg/kg soil A-L method). In the unlimed soil the yield was low, the effect of superphosphate was better than that of phosphate rock. A good fodder beet yield of 32 to 35 t/ha was obtained and the effect of phosphate rock was better than that of superphosphate at 0.5n $CaCO_3$ rate. When liming with at the high rate (1.0n $CaCO_3$ rate according to hydrolytic acidity) the action of phosphate rock declined, and a better yield was obtained with superphosphate.

Barley was grown after fodder beets in the 1997 experimental field and the residual effect of superphosphate and phosphate rock was investigated. Weather conditions were favorable for barley growth. Therefore a normal yield (4.1 to 4.8 t/ha) was obtained on limed soil. Although yield differences due to different phosphorus fertilizers were small, a significant yield increase through phosphate rock application was obtained in the soil limed with a 0.5n $CaCO_3$ rate, as compared with superphosphate. The P fertilizer studied did not have any effect on fodder beet and barley yield quality changes. The changes in the yield of the by-product of the investigated plants (barley straw and fodder beet tops) were analogous to those of the primary yield.

1. INTRODUCTION

Lithuania climate is determined by its geographical location in the Northwest of the Eurasian continent and by its closeness to the Baltic Sea. Lithuania has a more severe climate than Western Europe because it is located in the transition zone from the Atlantic marine climate to the continental one. The average annual temperature is approximately 6°C. The average temperature in January is -4.8°C, and that of July is 17.2°C. The annual precipitation ranges from 700 mm in the very west to 559 mm in the east and the average precipitation rate is 626 mm. Most of the rain falls in summer, which often hampers farming operations, such as haymaking and harvesting of field crops. The eastern half experiences colder winter temperatures and the western coastal areas experience higher precipitation levels. Lithuania is crossed by an average of 120-140 cyclones annually, which cause frequent meteorological changes. Due to the influence of cyclones, the summer temperatures are slightly lower, but winter temperatures higher than the average at middle latitudes. Lithuania is a relatively low-lying country, the highest point being 290 meters above sea level.

Land resources of Lithuania cover 65.2 million ha and are distributed as follows: 54% farming land (3.5 million ha), 70.5% arable land (2.5 million ha), 27.5% grassland, 2.0% shrubs, sands and slopes, 27.6% forest (61.0% coniferous and 39.0% deciduous), 18.4% cities, towns, villages, lakes, rivers, roads, etc.

The territory of Lithuania is divided into three zones; namely, the West, the Middle and the East. They reflect some common features of climate peculiarities, organic matter accumulation and mineralization rate. Moreover, the territory of Lithuania is divided into 15 soil-agronomic regions. These regions are defined according to both soil and agronomic characteristics in order to include consideration of the productive capacity of the soils. In Lithuania, 6 principal genetic types of soils can be distinguished: podzol, podzol-bog, sod-calcareous, sod-gley, bog and alluvial soils. Soddy-podzolic soils prevail (45.3%). Soil properties depend not only on the texture of topsoil, but also on subsoil. Seven groups of soil texture are distinguished: sand, loamy-sand, sandy-loam and loam, clay-loam and clay, muck sod, shallow peat and peat. Loamy-sand and different loams make up almost 60% of all soils.

Crops sold in internal or foreign markets are 53.4% of total crops with 46.6% of these crops being fodder crops. Crops for sale in agricultural companies are 49.8% and 55% in other farms. Agricultural companies cultivate 40% of the national grain crop, 45% of sugar beet but only 1.5% of potatoes, 11% of fruit and berries, and 3.1% of vegetables. Average Lithuania yields are well below those achieved in other Baltic/Scandinavian countries with similar climates. The best level of cereal production quoted for Lithuania is 3,1 t/ha during the former Soviet Union.

Political, social and economic changes as well as decreasing fertilizer application rates might have caused the decrease of the yield. Fertilizer application rates have decreased dramatically since 1992. Nitrogen fertilizers are mainly used as the most effective fertilizer in Lithuania. The amount of phosphorus and potassium fertilizer application has even decreased more severely than nitrogen. According to the experimental data of 1985-1993, one fifth of Lithuanian soils had a very low content of available phosphorus. About 42% of the soils were low in phosphorus, 22% medium in available phosphorus and only 16% of soils were relatively high in available phosphorus.

However, during the recent years the decline in the use of mineral fertilizers is likely to result in an increase of the soil area with low status of available phosphorus and potassium. Therefore, it is very important to find cost-effective sources of fertilizers. Rock phosphate could be a potential source in acid soils. In order to maintain the current soil acidity level it would be necessary to lime 174 thousand hectares of soil annually. However, this is hardly possible to achieve. Therefore the acid soil area will inevitably increase.

Thirty years ago, phosphate rock accounted for 40% in the total range of phosphoric fertilizers. This was determined by its simpler and cheaper production. Later, due to its application only on acid soils and the dust operation in its application, the use of phosphate rock was gradually abandoned. At present, superphosphate has completely replaced phosphate rock.

Experiments were carried out with large rates of phosphate rock to choose the best type and to determine its efficiency conditions. Posphate rock from the Maardu deposit showed a better action in soils with low acidity without mobile aluminum. In soils with a higher acidity and a small content of mobile aluminum, Jegorovsk phosphate rock was more effective. Other researchers [6, 12] also noted a high efficiency of Jegorovsk phosphate rock.

The most comprehensive studies on phosphate rock in Lithuania were carried out by K. Plesevicius [2, 4, 5]. It was determined that phosphate rock acts in the soil when hydrolytic acidity is above 25 meq/kg soil. Combination of phosphate rock with farmyard manure, granular superphosphate and its use for grassland fertilization was also investigated. Experiments were conducted where lime and phosphate rock application was combined and lime and phosphate rock were placed as separate layers. Other researchers confirmed these findings [17]. Studies were conducted on composting materials (with peat and manure) and their incorporation in the soil, and fertilization with increased phosphate rock rates for several years (3-6 years) [16]. This practice resulted from the better effect of phopshjate rock in the second or third year after incorporation in the soil [9, 18].

Finely ground phosphate rock is a very dusty material and to improve its application conditions it is recommended to granulate it or to make mixtures with other hygroscopic fertilizers such as potassium chloride [8]. The efficiency of broadcast application of phosphate rock is also increased by combining it with 50 kg/ha superphosphate applied in rows [10].

Due to economic difficulties, liming rates have been markedly reduced which, in turn, has resulted in increased soil acidification. Therefore, a new interest in phosphate rock is emerging. Moreover, its production requires less energy costs. Production of 1 t of superphosphate requires 38-40 GJoules, while that of phosphate rock requires only 7-8 GJoules [15]. Besides, there are more than 160,000 ha of karstic soils in Northern Lithuania. According to environmental regulations, it is forbidden to apply chemical and commercial fertilizers. Therefore, phosphate rock is an extremely important source of phosphoric fertilizers in this particular region.

Field experiments with fodder beets and barley were carried out to evaluate the P availability of granulated superphosphate and Maardu phosphate rock. The comparison was made at three acidity levels: a) unlimed acid soil with a high content of Al (pH_{kcl} 4.3-4.4, hydrolytic acidity was 41-44 meq/kg soil), b) soil limed with 0.5 rate $CaCO_3$ powder limestone based on hydrolytic acidity, and c) soil limed with 1.0 rate $CaCO_3$.

2. MATERIALS AND METHODS

In 1998, experiments were carried out at the LIA's Vezaiciai Branch on soddy-podzolic, medium podzolized loam. The soil was acid with the following properties: pH_{Kcl} of 4.3-4.4, hydrolytic acidity of 42-44 meq/kg, exchange acidity of 5.0-5.1 meq/kg, total absorbed bases of 33-35 meq/kg soil, available aluminum of 45-48 mg/kg soil [7].

In the experiments, standard granular superphosphate and phosphate rock from Maardu deposit in Estonia were used. Phosphate rock was of sedimentary origin enriched by the flotation method up to 20-2% of phosphorus active ingredient.

The experiment design included the following treatments:

1. Control
2. NK
3. NK+P_{Sp}
4. NK+P_{PR}
5. NK+0.5n $CaCO_3$
6. NK+0.5n$CaCO_3$ +P_{Sp}
7. NK+0.5n $CaCO_3$+P_{PR}
8. NK+1.0n $CaCO_3$
9. NK+1.0n $CaCO_3$ +P_{Sp}
10. NK+1.0n $CaCO_3$+P_{PR}

where N refers to nitrogen application, K refers to potassium application, P_{sp} refers to the application of P as superphosphate, P_{pr} refers to the application of P as phosphate rock. 1.0n is the recommended rate of $CaCO_3$ necessary for neutralization of soil acidity to the optimum level for crops or crop rotation. The 0.5n $CaCO_3$ rate is half the recommended rate [3].

A crop rotation of fodder beets (cv. Ekendorfo geltonieji) and spring barley (cv.Ula) was sown at the end of April or beginning of May depending on the climatic conditions. Spring barley was harvested in August and fodder beet in early October. The plot area was 68 m^2. The harvested area was 45 m^2. Plots were replicated four times.

Fertilizer rates for spring barley were 45 kg/ha N, 30 kg/ha P, and 45 kg/ha K. For fodder beet the rates were 90 kg/ha N, 60 kg/ha P, and 90 kg/ha K. Before fertilizer and lime application, soil samples from the arable layer (25cm) was taken for the determination of total nitrogen, humus, exchangeable phosphorus, potassium, aluminum, hydrolytic and exchangeable acidity, cation exchange capacity and pH.

Total nitrogen was determined using the Kjeldahl procedure. Available phosphorus and potassium was determined by the Egner-Riem-Domingo (A-L) method. Humic materials were determined by the Turin procedure. Hydrolytic acidity was determined by the Kappen method. Exchangeable acidity and exchangeable aluminium was extracted by potassium chloride by the Sokolov method. Cation exchange capacity was determined by the Hilkovic method and pH in extract of potassium chloride was determined with a pH glass electrode [7, 14].

At harvesting spring barley in autumn, soil samples were taken to assess the changes in soil pH level, hydrolytic and exchangeable acidity, cation exchange capacity, exchangeable phosphorus, potassium and aluminium.

Plant samples were collected for the determination of total nitrogen, phosphorus and potassium. Ashes and plant biometrics analyses were collected as well. Total nitrogen was determined using the Kjeldahl procedure. Phosphorus was determined after ashing using a molybdovanadate colorimetric method. Potassium was determined after ashing using flame photometry. Raw ash content was determined by weighing the sample before and after ashing at 525°C [13].

2.1. Weather conditions

Meteorological conditions of the 1998 experimental period were favorable for the growth and development of spring barley and fodder beets. In May, rather warm weather prevailed. There was a sufficient amount of moisture in the soil arable layer. The crust, which had formed on the soil surface after heavy rain, made it difficult for the seeds to emerge. Conditions for spring barley establishment and growth were favorable during the whole month.

In the first half of June, the weather was very warm. While in the second half the weather was cool. At the end of month the weather became warmer again. During the second ten-day period, moisture reserve was replenished and was close to average. Spring barley and fodder beets grew well and beet leaves covered the inter rows.

In July, cool and rainy weather was prevalent which was not favorable for the formation of high-quality spring barley grain. Conditions for grain maturation improved only during the third ten-day period, when the weather became warmer. During the whole month the reserve of productive moisture was markedly higher than many year’s average. Conditions for beet growing were good as well.

In August, the conditions for spring barley ripening were normal as warm and relatively dry weather was prevailing. Cool and rainy weather in the second five-day period slowed down grain ripening process. In many fields, spring barley was in wax ripeness. The reserve of productive moisture during the whole month exceeded average levels. Although the conditions during the larger part of the month were favorable for beet growth, the weather conditions became worse during the last ten-day period.

In September, relatively warm and dry weather prevailed. Conditions for fodder beet growth were most often good, especially during the second to third five-day period. Reserve of productive moisture in fodder beet fields was close to average.

3. RESULTS AND DISCUSSION

3.1. Effect of phosphate rock and superphosphate on fodder beet yield

The comparison of superphosphate and phosphate rock effectiveness was made at three soil acidity levels: background 1 — not limed, acid soil, with a high content of aluminum (pH_{kcl} 4.3-4.4, hydrolytic acidity: 41-44 meq/kg soil, mobile aluminum: 44-49 mg/kg soil); background 2 — the soil was limed with 0.5 rate $CaCO_3$ powder limestone, the content of mobile aluminum was reduced and pH_{Kcl} was 5.7-5.8; background 3 — the soil was limed with 1.0 rate of $CaCO_3$ and the soil acidity was reduced even more with pH_{Kcl} 6.0-6.1 (Table I). There was a sufficient amount of mobile potassium in the soil for plant growth, whereas phosphorus was very low. Thus a good plant growth response from the application of superphosphate and phosphate rock was expected.

Fodder beets showed a very poor performance in the control (unlimed and unfertilized soil) because of its sensitivity to soil acidity (Table II). With NK fertilization, the action of superphosphate was significantly higher than that of phosphate rock. This result may have been due to high mobile aluminum content in soil causing small and gradual release of mobile forms of P from phosphate rock to bind into aluminophosphates that are not readily taken up by plants. The mobile forms of P from superphosphate are released rapidly and taken up by the plants.

Soil acidity declined with liming at the 0.5n $CaCO_3$ rate. The harmful effect of aluminum on plant growth was eliminated and the yield of fodder beets increased. Both phosphatic fertilizers gave a significant yield increase, as the soil acidity was sufficient for P dissolution from phosphate rock into mobile forms.

When liming with the 1.0n rate $CaCO_3$, fodder beet yield in the soil treated with phosphate rock was lower and its efficiency lagged behind superphosphate. The P availability from phosphate rock was reduced by lower soil acidity present at the 1.0n $CaCO_3$ rate.

3.2. Effect of phosphate rock and superphosphate on the chemical indicators of fodder beet

Chemical indicators of fodder beet roots and leaves did not change significantly under the effect of liming and fertilizing with superphosphate and phosphate rock (Table III). Liming and mineral fertilizers had a tendency to increase nitrogen, phosphorus and potassium content in the roots of fodder beets. Ash content varied little. Ash content in leaves increased slightly. Nitrogen content in leaves also increased. Content of phosphorus varied little, and the content of potassium had a tendency to decline.

3.3. Soil chemical indices in spring barley experiment

In the same place where the efficiency of superphosphate and phosphate rock on fodder beets was evaluated in 1997 with fodder beet, the residual effect of these P fertilizers was measured in 1998 with spring barley. The soil was analyzed in spring before planting and it had three acidity levels (Table IV). The first level included unlimed acid soil with pH of 4.4-4.5, hydrolytic acidity of 37.2-41.2 meq/kg soil, mobile aluminum of 32.5-40.2 mg/kg, P_2O_5 of 89.8-121.5, K_2O of 214-256 mg/kg soil. In the second acidity level, the soil was limed with 0.5 rate of $CaCO_3$, which resulted in pH of 5.0-5.1, hydrolytic acidity of 17.9-18.4 meq/kg soil, and very little mobile aluminum from 0.8-2.2 mg/kg soil. The P_2O_5 and K_2O contents were analogous to that of the unlimed soil. For the third acidity level the soil was limed with 1.0 rate of $CaCO_3$ resulting in pH of 5.6-5.7, hydrolytic acidity of 15.9-19.1 meq/kg soil. Mobile aluminum, P_2O_5 and K_2O content were analogous to the second acidity level.

3.4. Effect of phosphate rock and superphosphate on barley yield

In the soil where 0.5n rate of $CaCO_3$ was applied to fodder beets a year ago, a significant barley grain yield increase was obtained in the plots treated with phosphate rock compared to superphosphate (Table V). At the high liming (1.0 $CaCO_3$) rate, the soil acidity declined even more and the grain yield of spring barley fertilized with phosphate rock was 0.21 t/ha lower than the barley yield fertilized with superphosphate.

3.5. Effect of phosphate rock and superphosphate on the chemical indicators of spring barley grain yield

Liming and mineral fertilization increased ash content in barley grain (Table VI). The highest ash content was found in the treatment limed with one lime rate. No significant differences in the ash content in barley grain were found between the treatment fertilized with superphosphate and phosphate rock.

A more distinct tendency of nitrogen, phosphorus and potassium content in barley grain was not identified. In addition, no regularities were observed when analyzing variations of ash, nitrogen and phosphorus content in barley straw. The content of potassium in barley straw had a tendency to increase in the treatments that had received lime and mineral fertilizers.

TABLE I. THE EFFECT OF SUPERPHOSPHATE AND PHOSPHATE ROCK ON THE SOIL CHEMICAL PROPERTIES IN FODDER THE BEET TRIAL

Treatment	pH_{KCl}	Total N	Hydrolytic acidity	Exchange acidity	Total absorbed bases	Available		
						Al	P_2O_5	K_2O
		%	---------------- meq/soil kg ---------------			------------ mg/soil kg ----------		
1. Control	4.38	0.13	43.17	5.18	34.6	49.5	58.3	221.0
2. NK	4.31	0.14	42.08	4.98	36.2	44.8	62.5	208.9
3. NK+P_{Sp}	4.40	0.13	44.01	5.11	37.6	46.6	71.4	198.6
4. NK+P_{PR}	4.39	0.13	41.83	5.17	33.9	45.6	61.5	210.6
5. NK+0.5n $CaCO_3$	5.76	0.14	21.18	1.27	51.8	1.2	66.5	230.8
6. NK+0.5n $CaCO_3$ +P_{Sp}	5.80	0.14	18.61	1.14	53.6	0.8	74.5	217.5
7.NK+0.5n $CaCO_3$+P_{PR}	5.71	0.14	17.18	1.11	55.0	1.5	68.2	209.8
8. NK+1.0n $CaCO_3$	6.10	0.13	11.63	0.47	86.7	0.6	64.8	211.7
9. NK+1.0n $CaCO_3$ +P_{Sp}	5.95	0.14	10.18	0.51	91.2	1.0	61.7	209.9
10. NK+1.0n $CaCO_3$+P_{PR}	6.05	0.14	9.83	0.49	88.5	0.7	62.4	213.4
$LSD_{0.05}$	0.59	0.02	8.03	1.89	8.16	14.31	18.30	46.71

TABLE II. THE INFLUENCE OF SUPERPHOSPHATE AND PHOSPHATE ROCK ON FODDER BEET YIELD

Treatment	Yield, t/ha			
	Natural moisture		Dry matter	
		Tops	Roots	Tops
1. Control [Without NPK and liming]	1.01	0.89	0.13	0.12
2. NK	3.04	3.39	0.43	0.44
3. NK+P_{Sp}	6.19	6.90	0.87	0.83
4. NK+P_{PR}	4.88	5.48	0.63	0.66
5. NK+0.5n $CaCO_3$	32.08	12.56	4.49	1.38
6. NK+0.5n $CaCO_3$ +P_{Sp}	34.70	15.71	4.86	1.73
7.NK+0.5n $CaCO_3$+P_{PR}	35.95	16.19	5.75	1.78
8. NK+1.0n $CaCO_3$	33.45	13.81	5.35	1.80
9. NK+1.0n $CaCO_3$ +P_{Sp}	36.55	15.65	5.48	1.88
10. NK+1.0n $CaCO_3$+P_{PR}	34.52	13.87	5.52	1.80
$LSD_{0.05}$	1.30	1.23	0.19	0.14

TABLE III. THE EFFECT OF SUPERPHOSPHATE AND PHOSPHATE ROCK ON FODDER BEET YIELD QUALITY

	Roots				Tops			
Treatment	Ash	N	P	K	Ash	N	P	K
		%				%		
1. Control	7.94	1.38	0.19	2.44	26.1	1.62	0.31	6.80
2. NK	7.81	1.47	0.21	2.52	26.2	2.32	0.28	6.42
3. NK+P_{Sp}	7.62	1.52	0.22	2.65	26.4	1.80	0.27	5.95
4. NK+P_{PR}	7.43	1.44	0.23	2.03	26.2	1.83	0.29	5.41
5. NK+0.5n $CaCO_3$	7.89	1.58	0.18	2.86	25.8	1.84	0.24	6.28
6. NK+0.5n $CaCO_3$ +P_{Sp}	7.65	1.48	0.20	2.47	26.3	1.70	0.29	6.43
7.NK+0.5n $CaCO_3$+P_{PR}	7.48	1.52	0.19	2.61	26.4	1.82	0.27	6.78
8. NK+1.0n $CaCO_3$	7.52	1.47	0.20	2.87	25.4	1.74	0.30	6.58
9. NK+1.0n $CaCO_3$ +P_{Sp}	7.65	1.46	0.21	3.05	26.3	1.92	0.27	6.16
10. NK+1.0n $CaCO_3$+P_{PR}	7.44	1.50	0.22	2.82	26.2	1.94	0.28	5.97
$LSD_{0.05}$	1.04	0.11	0.07	0.62	3.47	0.10	0.07	0.18

TABLE IV. THE EFFECT OF SUPERPHOSPHATE AND PHOSPHATE ROCK ON THE SOIL CHEMICAL PROPERTIES IN THE FIELD TRIAL WITH BARLEY

Treatment	pH_{KCl}	Total N%	Hydrolytic Acidity	Exchange Acidity	Total absorbed bases	Available		
						Al	P_2O_5	K_2O
			---------------- meq/soil kg ---------------			------------ mg/soil kg ----------		
1. Control	4.42	0.12	41.16	4.26	38.2	32.5	89.8	214.2
2. NK	4.46	0.12	38.12	4.72	36.1	33.0	94.5	243.5
3. NK+P_{Sp}	4.43	0.13	37.26	5.01	40.1	40.2	118.4	256.1
4. NK+P_{PR}	4.48	0.13	38.01	4.89	38.2	37.3	121.5	235.4
5. NK+0.5n $CaCO_3$	5.10	0.13	18.53	0.63	62.8	1.2	109.5	261.2
6. NK+0.5n $CaCO_3$ +P_{Sp}	5.08	0.13	19.42	0.78	60.7	2.2	110.6	231.5
7.NK+0.5n $CaCO_3$+P_{PR}	5.01	0.13	17.94	0.67	59.8	0.8	114.7	235.0
8. NK+1.0n $CaCO_3$	5.71	0.14	19.13	0.32	84.5	1.4	103.7	239.5
9. NK+1.0n $CaCO_3$ +P_{Sp}	5.65	0.14	16.17	0.31	86.8	0.9	120.5	241.2
10. NK+1.0n $CaCO_3$+P_{PR}	5.68	0.13	15.94	0.27	92.5	1.0	119.5	238.8
$LSD_{0.05}$	0.39	0.02	8.13	1.32	13.04	12.1	31.6	53.4

TABLE V. THE EFFECT OF SUPERPHOSPHATE AND PHOSPHATE ROCK ON BARLEY YIELD

Treatment	Yield, t/ha Grain	Yield, t/ha Straw	1000 kernel weight, g
1. Control	1.67	2.45	37
2. NK	1.95	2.54	37
3. NK+P_{Sp}	2.15	2.41	39
4. NK+P_{PR}	2.30	2.39	39
5. NK+0.5n $CaCO_3$	3.99	4.25	39
6. NK+0.5n $CaCO_3$ +P_{Sp}	4.23	4.43	38
7.NK+0.5n $CaCO_3$+P_{PR}	4.51	4.60	39
8. NK+1.0n $CaCO_3$	4.36	4.72	40
9. NK+1.0n $CaCO_3$ +P_{Sp}	4.82	4.71	40
10. NK+1.0n $CaCO_3$+P_{PR}	4.61	4.46	40
$LSD_{0.05}$	0.16	0.42	1.9

TABLE VI. THE EFFECT OF SUPERPHOSPHATE AND PHOSPHATE ROCK ON BARLEY YIELD QUALITY.

	Grain				Straw			
Treatment	Ash	N	P	K	Ash	N	P	K
		%				%		
1. Control	1.98	1.36	0.24	0.53	6.38	0.94	0.18	1.69
2. NK	2.21	1.32	0.38	0.73	6.83	0.89	0.16	2.12
3. NK+P_{Sp}	2.39	1.60	0.36	0.60	6.71	0.90	0.20	1.97
4. NK+P_{PR}	2.25	1.50	0.39	0.57	6.92	0.93	0.17	2.05
5. NK+0.5n $CaCO_3$	2.14	1.23	0.30	0.56	6.23	0.90	0.21	1.96
6. NK+0.5n $CaCO_3$ +P_{Sp}	2.24	1.34	0.34	0.58	6.18	0.98	0.18	2.07
7.NK+0.5n $CaCO_3$+P_{PR}	2.27	1.47	0.36	0.57	6.43	0.96	0.17	1.98
8. NK+1.0n $CaCO_3$	2.31	1.40	0.32	0.53	6.22	0.89	0.20	2.14
9. NK+1.0n $CaCO_3$ +P_{Sp}	2.40	1.38	0.34	0.58	6.72	0.94	0.17	2.07
10. NK+1.0n $CaCO_3$+P_{PR}	2.39	1.47	0.36	0.57	6.63	0.96	0.19	1.99
LSD_{05}	0.09	0.22	0.08	0.18	0.53	0.21	0.09	0.47

4. CONCLUSIONS

In conclusion, our study showed:

1. Phosphate rock showed better effects and it was identical to the efficiency of granulated superphosphate in the slightly acid soil (soil limed at 0.5n $CaCO_{3)}$.
2. When the soil acidity decreased more (soil limed at 1.0n $CaCO_3$) the efficiency of phosphate rock was also reduced.
3. In the very acid soil (unlimed), the efficiency of phosphate rock was low.
4. No significant effects on the chemical indicators of fodder beets and spring barley were found between plants fertilized with phosphate rock and superphosphate.

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REFERENCES

[1] ADOMAVICIUTE, J., Comparison of the efficiency of rock phosphate from various deposits in different soils of Lithuanian SSR. Research works of the Lithuanian Agricultural Research institute **2** (1967) .209-248.

[2] Agrochemistry. Compiled by K. Plesevicius. Vilnius (1970) 70-74.

[3] KNASYS, V., Soil liming. Vilnius (1985) 264 p.

[4] PLESEVICIUS, K., Efficiency of rock phosphate in a crop rotation on a heavy loam soil. Research works of the Lithuanian Agricultural Research institute **23** (1978) 66-88.

[5] PLESEVICIUS, K., Rock phosphate — cheap and efficient fertilizer. Vilnius (1962) 57 p.

[6] ZALYS, A., Varanaviciute J. Enhancement of rock phosphate fertilization effect by peat. Research works of the Lithuanian Agricultural Research institute **6** (1961) 259-270.

[7] Agrochemical soil research methods, Moscow (1975) 656 p.

[8] BABENKO, N.V., Klassen L.D. Efficiency of rock phosphate and complex granulated fertilizers produced on the basis of rock phosphate and potassium chloride. Agrochemistry **9** (1978) 22-29.

[9] BAZEGULSKIJ, E.L., Belkov A.P. Qualitative evaluation of the effect of phosphoric fertilizer solubility on their efficiency. Agrochemistry **5** (1978) 29-34.

[10] BEZUGLAJA, J.M., Bolsakova L.A., Riabizina T.E. Comparative efficiency of phosphoric fertilizer forms on a Soddy podzolic soil. Agrochemistry **2** (1976) 33-39.

[11] BEZUGLAJA, J.M., Bulancev J.B., Riabizina T.E. Comparative efficiency of rock phosphate from different deposits. Agrochemistry **1** (1990) 19-25.

[12] EFIMOV, V.N., BULAKOV, D., KOPYLOVA, P.A., Agrochemical assessment of various forms of phosphoric fertilizers in the Northwest economic region of the USSR. Proceedings of conference Prospects for the expansion of the range of phosphorus containing fertilizers, Moscow (1987) 45-48.

[13] Methods of biochemical plant analyses. Leningrad. VO Agroprom Publishing house. (1987) 432 p.

[14] Determination of mobile forms of phosphorus and potassium by method of Egner-Riem-Domingo (A-L method). State standard USSR, GOST 26208-91, Moscow. (1991) 25-30.

[15] POSTNIKOV, A.V., CHUMACHENKO, I.N., SUSCENICA V.A., The current state and prospects of phosphoric fertilizer application in the agriculture of the USSR. Proceedings of the conference.” Prospects of the expansion of the range of phosphorus containing fertilizers”, Moscow (1987) 36-38.

[16] SDOBNIKOVA, O.V., SULTANOVA, R.A., LITVINOVA, E.S., The current state and prospects of rock phosphate application, Agrochemistry **10** (1978) 23-28.

[17] KIRPICHNIKOV, N.A., POHLEBINA, L.P., SERGEJEVA, Z.G., Effect of high lime rates on the efficiency of rock phosphate, Agrochemistry **6** (1990) 18-24.

[18] KORICKAJA, T.D., Use of radioactive phosphorus isotope for the determination of assimilation of various phosphates by plants, Izvesti AN USSR **2** (1964) 36-41.

LONG TERM FIELD EVALUATION OF PHOSPHATE ROCK AND SUPERPHOSPHATE IN ACID SOILS OF HUNGARY: INCUBATION AND POT EXPERIMENTS

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Abstract

A series of experiments was conducted to compare the agronomic effectiveness of phosphate rock (from Algeria) and of single superphosphate (from Russia, Kola) on a moderately acidic pseudogley brown forest soil (Szentgyörgyvölgy) and on a slightly acidic chernozem brown forest soil (Kompolt). Dynamics of water-soluble and ammonium lactate-soluble P-contents (AL-P) and soil pH-H_2O changes were studied in a half-year long incubation experiment. A follow-up pot experiment with the same soils was carried out with winter rape as test plants. Both experiments were set up with similar P fertilizer sources and P rates (100, 200, and 400 mg mineral acid soluble P_2O_5 per kg soil).

At the beginning of incubation experiment, the water-soluble P content of the pseudogley brown forest soil was influenced by both the sources of P and the experimental conditions. The water-soluble P content decreased with time. After the 15th to 20th day of incubation, when the fast binding process of the water-soluble P ended, the effects of the P forms decreased. In this stage, the effects of environmental conditions depended on the form of the P fertilizer. The water-soluble P content of the phosphate rock-treated samples was affected to a great extent by soil water content, while the incubation temperature had a greater effect in soils treated with superphosphate.

The AL-P content of soils was increased similarly by addition of equal rates of phosphate rock and superphosphate at the beginning of incubation. The AL-P content of phosphate rock-treated soils was higher throughout the incubation period than of the superphosphate-treated soils -treated. Temperature had a greater effect on the AL-P content of soils than soil water content. As the AL-extraction may dissolve a substantial amount of the undecomposed phosphate rock, this method is not applicable to soil testing of available P forms from phosphate rock-treated soils.

Initial soil pH decreased on average by 0.5 units in the superphosphate treatments. Phosphate rock slightly increased the pH of the slighly acidic chernozem brown forest soil. The increase in the moderately acidic pseudogley brown forest soil was greater, but no ”liming effect” could be observed.

In the pot experiment, the effects of P sources and P doses were compared both in incubated (for 202 days) and in non-incubated (fertilizers freshly mixed into the soil) experimental soils with winter rape as a test plant. In the moderately acidic pseudogley brown forest soil, the dry matter yield, P concentration, and P uptake of winter rape was affected similarly by the phosphate rock and superphosphate treatments. In the slightly acidic chernozem soil, superphosphate proved to be a more efficient P fertilizer, by significantly increasing the P concentration and P uptake of the plants. Incremental P doses in the chernozem brown forest soil increased P concentration, P uptake, and also dry matter yield of rape. In the case of the pseudogley brown forest soil, only the P concentration of the plants increased. These increases were dominant in the superphosphate treatments. Previous incubation of the soil with the P fertilizers significantly decreased all plant parameters in the pseudogley brown forest soil, but the incubated superphosphate treatments produced higher yields in the chernozem brown forest soil, as compared to the non-incubated P fertilizer treatments.

1. INTRODUCTION

Strongly acidic soils cover about 13 % of Hungary, and nearly 43 % of the soils are slightly acidic [1]. In the past decades, superphosphate was the main P fertilizer source on both calcareous and acidic soils. As soils are becoming more acidic and the costs of superphosphate application are rising, attention should be drawn to the direct use of reactive phosphate rock (PR) as P fertilizer.

Plant roots absorb only phosphate ions [2] as a source of phosphorus to satisfy their needs. Thus phosphate rocks, which are considered as insoluble P fertilizers, must first be dissolved in soils to yield phosphate ions. After PR dissolution, these ions will either be taken up by plant roots or react with soil components. Dissolution of a given phosphate rock depends mainly on soil characteristics, climate, plant and the properties of the phosphate rock (chemical reaction, size of particles). Some important soil characteristics that influence favourably the solubility of phosphate rock in soil are low available P, low exchangeable Ca, low pH (<pH 6), low base saturation, high cation exchange capacity, high humus content, and adequate soil water content [3-5].

Environmental factors have a major role in the transformation processes of phosphorus in the soil (soil water content, temperature) and on the dissolution of phosphate rock. The rate-limiting step in the dissolution of phosphate rock is the diffusion of soluble products (Ca and phosphate ions) from the surface of the particles [6, 7]. Increasing soil water contents increase the effective diffusion coefficients of ions [8]. Thus, precipitation and increasing soil water contents help the dissolution of phosphate rock [3, 4, 9-11]. In contrast, temperature has little effect on the dissolution of phosphate rock in the soil [12, 13].

A series of experiments was carried out with the aim to compare the agronomic effectiveness of single superphosphate (Kola, Russia) that is currently used in Hungary and a phosphate rock from Algeria in two main types of acidic soils of Hungary. In this paper, the effects of these two P fertilizers on available soil P in a half-year-long incubation experiment at different soil water contents and temperatures are discussed. Similarly the results on yield and P uptake of winter rape from a pot experiment are presented.

2. MATERIAL AND METHODS

2.1. Soils

The soils included in the incubation and pot experiments were a moderately acidic pseudogley brown forest soil (Szentgyörgyvölgy) and a slightly acidic chernozem brown forest soil (Kompolt). These soils originated from the control plots of comparative long-term field trials with Algerian phosphate rock [14]. The main characteristics of the soils are shown in Table I.A and I.B.

2.2. Single superphosphate and phosphate rock

Single superphosphate and phosphate rock were applied in powder form in both incubation and pot experiments. The total P contents of single superphosphate and phosphate rock were determined after extraction of the mineral acid-soluble phosphates (in HNO_3 + HCl mixture, according to method A described in ISO 7497-1984 E 1984. [25]). Phosphate concentrations in the filtrates of the extraction procedure were measured colorimetrically by the molybdovanado-phosphate method. The quantity of total P_2O_5 was 27.60% (w/w) in the Algerian phosphate rock, and 18.40% (w/w) in single superphosphate.

2.3. Incubation experiment

Four hundred g of air-dried soil passed through a 2-mm sieve was used per pot. Algerian phosphate rock and single superphosphate were applied to soils at three rates: 100, 200, 400 mg P_2O_5 kg^{-1} soil. The soil water contents were set at 30 and 50% of the maximum water-holding capacity and the incubation temperatures at 25 and 40°C.

Soils were mixed with the required amount of fertilizers to give 100, 200, and 400 mg P_2O_5 kg^{-1} based on the their total P contents. Samples were taken ten times. The first sampling was carried out on the first day followed by mixing in the P forms. The duration of the incubation was 202 days. Changes with time of the water-soluble P contents, AL-soluble P contents and pH-H_2O were measured.

TABLE IA. CHARACTERISTICS OF THE SOILS USED IN THE EXPERIMENTS

	Soils	
	Pseudogley brown forest soil (Szentgyörgyvölgy)	Chernozem brown forest soil (Kompolt)
pH_{H_2O}[a]	5.90	6.40
pH_{KCl}[b]	4.40	5.00
AL-P_2O_5[c], mg kg^{-1}	130	60
Water sol.-P[d], mg kg^{-1}	14.0	11.9
Total-P[e], mg kg^{-1}	1110	499
Cation exchange capacity, (CEC)[f] meq/100g	9.31	30.1
Base saturation, meq/100g	8.70	29.4
Exchangeable Ca, meq/100g	6.51	24.3
Exchangeable Mg, meq/100g	2.01	4.42
Oxalate-soluble Fe[g] mg kg^{-1}	6090	3660
Oxalate-soluble Al, mg kg^{-1}	422	568
Total salt content[h], %	<0.02	0.04
Saturation[i], % (SP)(plasticity)	52	50
Hydrolytic acidity[j], %, (y_1)	13.3	9.3
Organic matter[k], % (Humus)	1.86	3.49

[a] pH_{H2O} = 1: 2.5, soil:H_2O, [b] pH_{KCl} = 1: 2.5, soil: 1 M KCl, [c] AL-P_2O_5 =extracted by 0.1 mol L^{-1} ammonium lactate + 0.4 mol L^{-1} acetic acid (pH=3.75) [15], [d] Water soluble-P [16], [e] Total-P; determined by inductively coupled plasma emission spectrometry (ICP) after digestion of soil samples by cc. HNO_3 + H_2O_2, [f] Exchangeable Ca, Mg and CEC, neutral 1M NH_4-acetate method [17], [g] Oxalate-soluble Fe, Al [18], [h] Total salt content [19], [i] Saturation [20], [j] Hydrolytic acidity measured after first extraction by applying 0.5 mol/l Ca acetate at pH 8.2 [21], [k] Organic matter [22].

TABLE IB. INITIAL ISOTOPIC CHARACTERISATION OF THE SOILS

Soils	C_p, mg P L^{-1}	r_1/R	n	E_1/C_p	Total P mg kg^{-1}
Pseudogley brown forest soil (Szentgyörgyvölgy)	0.33	0.37	0.31	24	1050
Chernozem brown forest soil (Kompolt)	0.11	0.18	0.29	57	298
	P pools, mg P (kg soil)$^{-1}$				
Soils	E_1	A	B	C	D
Pseudogley brown forest soil (Szentgyörgyvölgy)	9.0	70	180	92	699
Chernozem brown forest soil (Kompolt)	6.3	37	71	29	154

Isotopic characterization of the soils [23]: c_p is the concentration of phosphate ions in the soil solution, *R* is the total quantity of radioactivity applied to the soil solution system as phosphate ions, r_1 is the quantity of radioactivity in the solution after one minute, r_1/R can reflect soil P-fixing capacity [24], *n* is the exponent of the power function describing the rate of exchange of the radioactivity in the solution with time *t, total-P* was determined by $HClO_4$- method, *pool* E_1 is the quantity of isotopically exchanged P within one minute, E_1/c_p is the P-buffering capacity of the soil, *pool A* corresponds to the ions exchangeable between 1 minute and 1 day, *pool B* corresponds to the ions exchangeable between 1 day and 3 months, *pool C* corresponds to the ions exchangeable between 3 months and 1 year, *pool D* corresponds to the ions exchangeable in more than 1 year.

2.4. Pot experiment

Soils of the incubation experiment (incubated, "I" treatments) and soils freshly mixed with P fertilizers (non-incubated, "NI" treatments) were used in the pot experiment. In the NI treatments, the P sources and rates described in the incubation experiment as well as 200 mg N and 200 mg K per kg soil as aqueous solutions of NH_4NO_3 and KCl, respectively, were freshly mixed into the soil at the beginning of the pot experiment. In the incubated treatments, equal amounts of soils previously incubated for 202 days with the same P fertilizer forms and P rates but at different soil water contents and temperatures were mixed to give the various "incubated" treatments in the pot experiment. Thus, the P forms and rates in the incubated treatments were 100, 200, and 400 mg P_2O_5 given either as phosphate rock or as single superphosphate (at the beginning of the incubation). These soil samples were also supplemented with N and K as done for the NI treatments.

A quantity of 0.8 kg air-dried soil was used per pot. Fertilizers were mixed into the soils on the day winter rape was sown. The randomized block experiment was conducted with 3 replications. Moisture levels were maintained at approximately 60% of field capacity at the beginning of the experiment and later according to the requirement of plants. Plants were harvested at 6 weeks of age. The air-dried plant samples were digested with a mixture of HNO_3 and H_2O_2, P contents were measured by the inductively-coupled plasma emission spectrophotometry method (ICP).

The incubation and pot experiments were carried out in triplicates, in a randomized block arrangement. Data were subjected to analysis of variance, using the FVA 7 and the SPSS ANOVA statistical programs. A 3-factorial (P rate, P form, soil water content) random block design was used to calculate the significant differences for the combinations of the treatments by the F-test and by calculation of the Least Significant Difference at the 0.05 probability level, $LSD_{5\%}$. The CV% values were calculated for a randomized block arrangement with 14 treatments to take into account the additional control treatments.

3. INCUBATION EXPERIMENT RESULTS

3.1. Effect of superphosphate and phosphate rock treatments on the available P content of experimental soils

3.1.1. Changes in the water-soluble P content

Due to the effect of the equal rates (100, 200, 400 mg P_2O_5 kg^{-1} active agent content) of the phosphate rock and superphosphate treatments, the water soluble P content of the pseudogley brown forest soil from Szentgyörgy increased at the beginning of the experiment in accordance with the solubility of the P fertilizers (Fig. 1A), P rates (Fig. 1B) and experimental conditions (temperature of incubation and soil water content — Figs. 2 and 3). The effects of the studied factors are shown as the average of other parameters.

The water-soluble P content of the soil samples treated with phosphate rock hardly changed in the first days of incubation, as a result of the biotic and abiotic dissolution and fixation processes. There was a 20-40% decrease in the values with time. Our findings are in accordance with Fardeau et al. [26], who also experienced a decrease in the water-soluble P content of soils treated with phosphate rock.

The water-soluble P content of soil was more greatly influenced by the soil water content than by temperature (Figs. 2A, 3A). In the experiment with phosphate rock from North Carolina, Chien et al. [12] also found that temperature had no significant effect on the water-soluble P levels in the soil. Irrespective of the application rate of phosphate rock, higher water-soluble P contents were measured throughout the incubation period at both temperatures in the case of higher soil water content.

At the beginning of incubation, the water-soluble P fertilizer, i.e. superphosphate increased the water-soluble P content of the initial samples to a greater extent than phosphate rock applied on the basis of equal active agent content (Fig. 1). The availability of applied P decreases when the time of contact between soil and water-soluble P fertilizers increases [27-29]. The changes in water-soluble P content of soils as a function of time differed in the samples treated with superphosphate and phosphate rock (Figs. 1 and 2). Water-soluble P content of superphosphate-treated soils decreased with time. This is similar to literature findings [29-32] and authors' previous kinetic studies [33-35]. In the first days of incubation (approx. up to 10-20 days), a rapid decrease could be observed, which was followed by a slow change.

The water-soluble P content of soils treated with superphosphate, in contrast to the phosphate rock-treated soils, was influenced to a greater extent by temperature than soil water content (Figs. 2B and 3B). Higher-water soluble P contents were measured at the lower temperature. On the basis of literature [28, 36] and authors' analytical results [37] this can be explained by the higher rate constants for the fixation of water-soluble P content of superphosphate in the soil at high temperatures. Such temperature effect can be mainly observed in the first half of the incubation period. In the case of similar temperature, higher-water soluble P contents were generally measured at higher soil water content.

The results of the experiment carried out with the moderately acidic pseudogley brown forest soil (Szentgyörgyvölgy) showed that at the beginning of incubation the water-soluble P content of samples was affected both by the P source and the experimental conditions, but the P source played the dominant role. After 15-20 days of incubation, when the fast binding process of soluble P fertilizer ended, the P form had a slighter influence on the water-soluble P content of soil. After 40 days, slightly higher or similar values were obtained for the phosphate rock-treated samples as compared to the superphosphate treated samples (Fig. 1B).

Due to filtration problems, we were unable to measure changes of water-soluble P contents as a function of time in the slightly acidic chernozem brown forest soil (Kompolt).

3.1.2. Change in the AL-soluble P content of the soils

In Hungary, AL-extractant has been used conventionally as the extractant to assess soil P availability. For this reason, changes in the AL-soluble P content of the experimental soils were also studied.

3.1.2.1. AL-soluble P content of the pseudogley brown forest soil (Szentgyörgyvölgy)

At the beginning of incubation, the low-medium initial AL-soluble P content of the soil increased to a similar extent due to the effect of equal rates of phosphate rock and superphosphate (Fig. 4).

Changes in the AL-soluble P content of phosphate rock-treated samples with time were similar to those of the control treatment. In the first days of incubation (up to about 30 days) the AL-soluble P contents of the phosphate rock-treated and control soils dropped to a similar extent, then there were practically no changes.

The AL-soluble P content of superphosphate-treated soils also decreased to a greater extent in the first days of incubation (up to 20-30 days). This decrease, however, was much greater than that of the control or phosphate rock-treated samples.

In the case of equal rates of P addition to soil, the AL-soluble P content of the phosphate rock-treated soils was higher than that of superphosphate treated soils. The probable explanation for this is that the AL-extractant with pH 3.75, dissolved part of the Ca-phosphate content of the phosphate rock not yet in soluble form.

Fig. 5 illustrates the effect of incubation temperature and water content of soil on the changes in AL-soluble P content during incubation. Temperature had a more expressed effect on soil AL-soluble P content than soil water content. Abd El-Galil et al. [38] reached similar results on calcareous sandy soil. The AL-soluble P content of soil was higher at lower temperature both in phosphate rock and superphosphate treatments. This effect was slighter at the beginning of incubation in control and phosphate rock-treated samples. On the contrary, temperature had an effect on the AL-P content of samples treated with superphosphate throughout the incubation period.

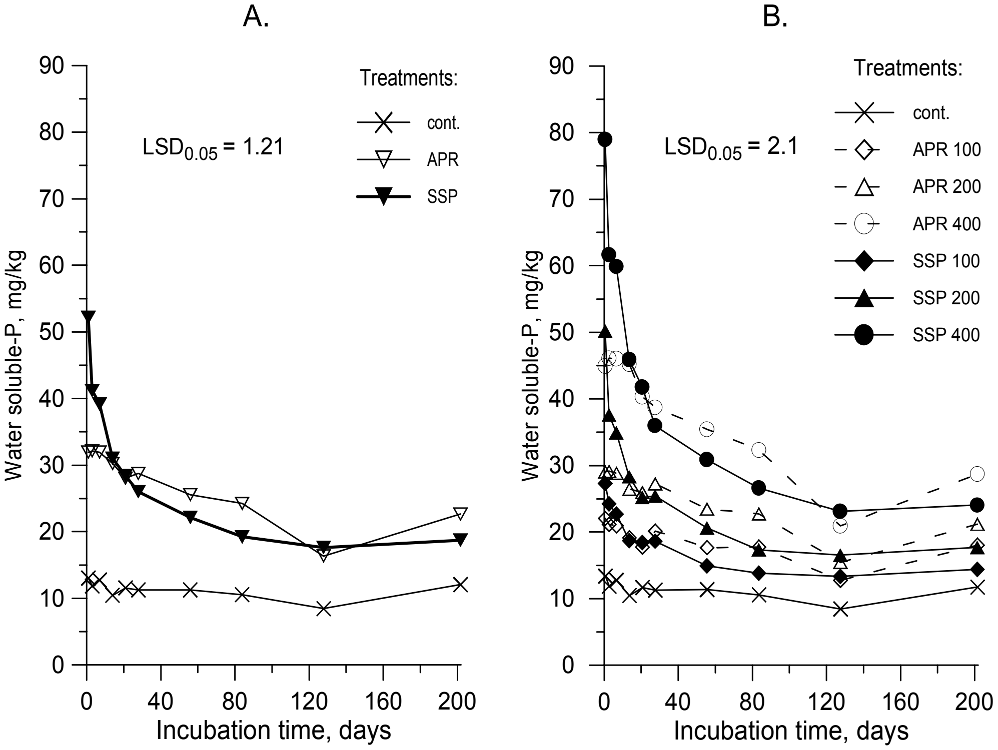

Fig. 1. Effect of Algerian phosphate rock (APR) and single superphosphate (SSP) on the water-soluble P content of the pseudogley brown forest soil (Szentgyörgyvölgy), as a function of incubation time. A. On the average of P doses. B. Separately. (Treatments: 100, 200, 400 = Active P ingredients, mg P_2O_5 kg^{-1} soil).

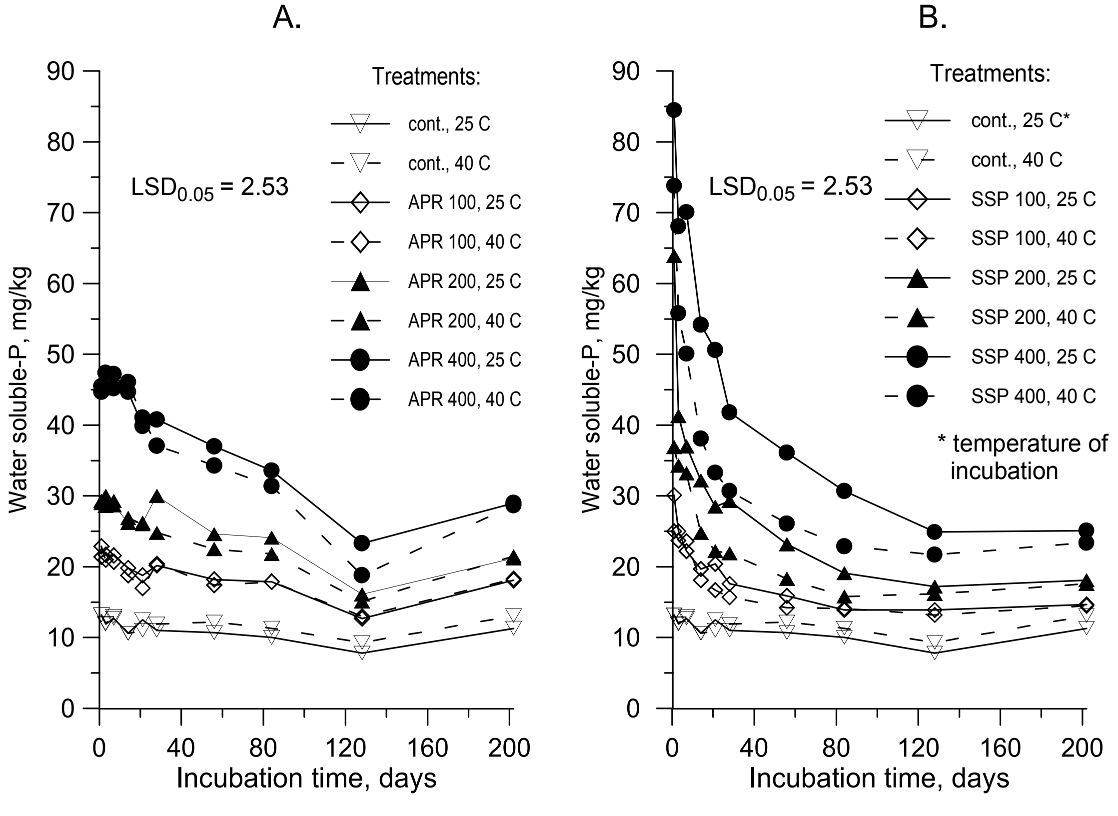

Fig. 2 Effect of temperature on the water-soluble P content of the pseudogley brown forest soil (Szentgyörgyvölgy) in the case of Algerian phosphate rock (APR) (A) and single superphosphate (SSP) (B) application (Treatments: 100, 200, 400 = Active P ingredients, mg P_2O_5 kg^{-1} soil).

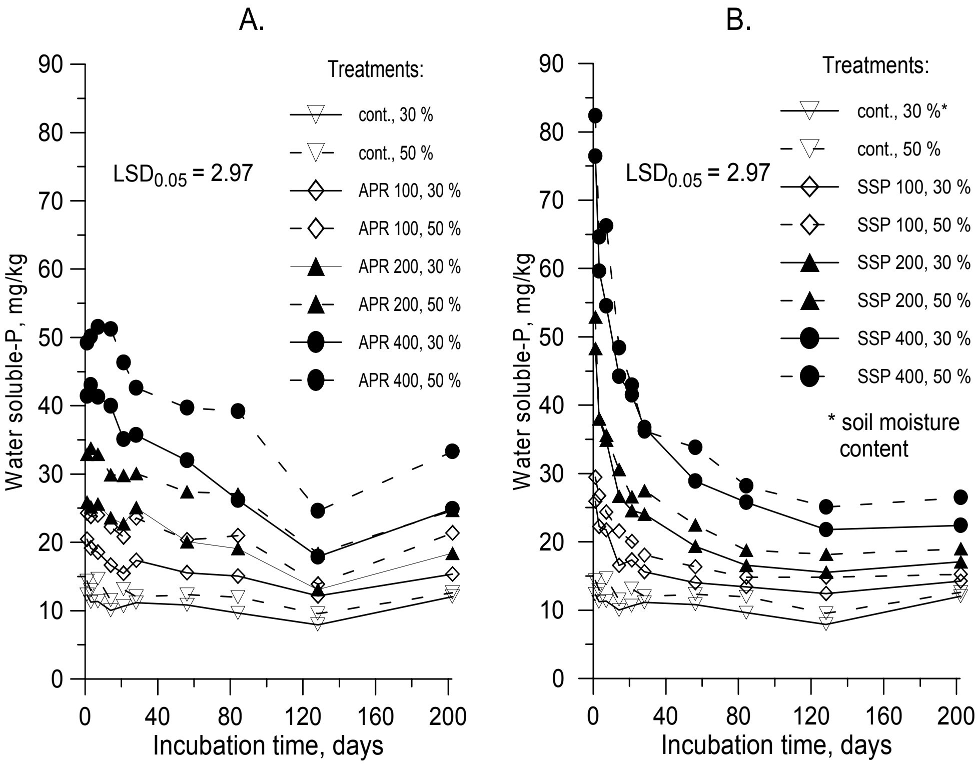

Fig. 3. Effect of soil moisture on water-soluble P content of the pseudogley brown forest soil (Szentgyörgyvölgy); A. Algerian phosphate rock (APR) application. B. Single superphosphate (SSP) application (Treatments: 100, 200, 400 = Active P ingredients, mg P_2O_5 kg^{-1} soil).

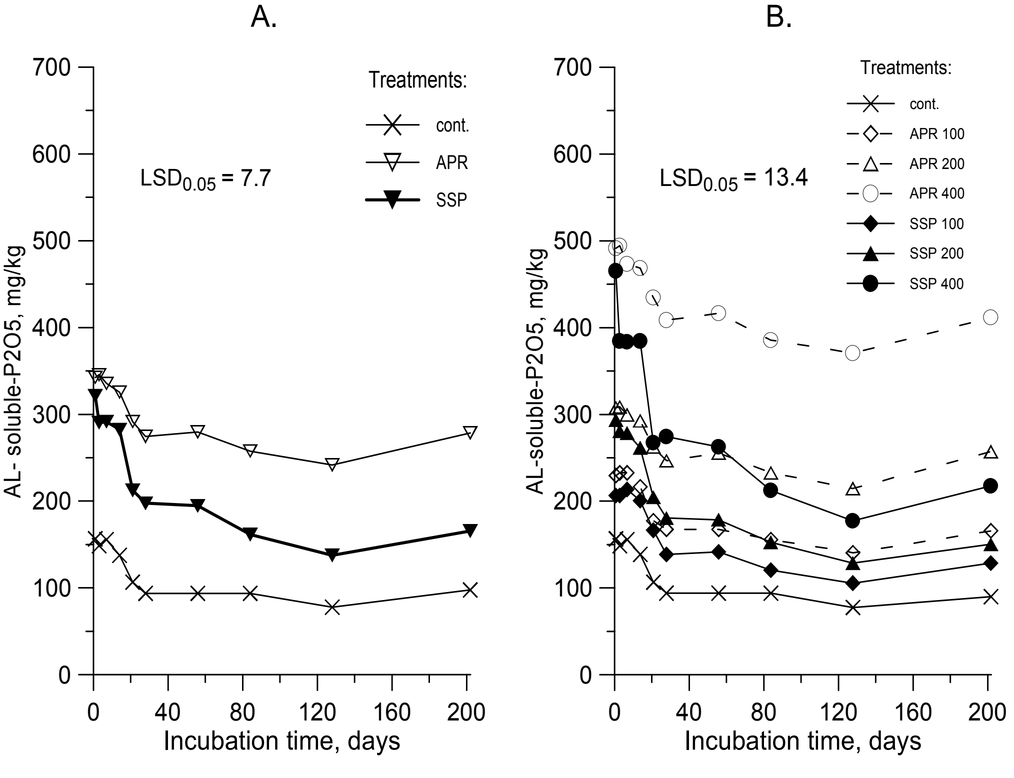

Fig. 4. Effect of Algerian phosphate rock (APR) and single superphosphate (SSP) on the AL-soluble P content of the pseudogley brown forest soil (Szentgyörgyvölgy) as a function of incubation time. A. On average of P doses. B. Separately. (Treatments:100, 200, 400 = Active P ingredients, mg P_2O_5 kg^{-1} soil).

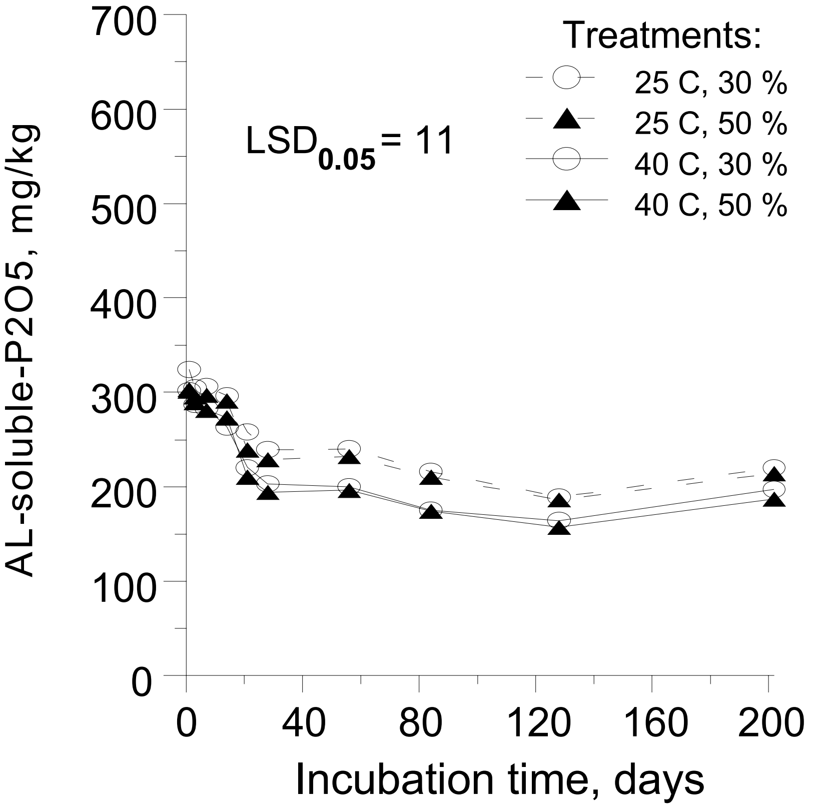

Fig. 5. The effect of incubation temperature and soil water content on the AL-soluble P content of the pseudogley brown forest soil (Szentgyörgyvölgy).

3.1.2.2. AL-soluble P content of the chernozem brown forest soil (Kompolt)

At the beginning of incubation the very low initial AL-soluble P content (60.0 mg kg^{-1}) of the chernozem brown forest soil from Kompolt increased to a similar extent due to the effect of the equal rates of phosphate rock and superphosphate (Fig. 6).

In case of equal rates of P, similar to the results gained for the pseudogley brown forest soil, the AL-soluble P content of the chernozem brown forest soil samples treated with phosphate rock were higher throughout the incubation period**.** After a few days the AL-soluble P content of phosphate rock-treated samples showed practically no changes during the incubation period (202 days) (Fig. 6). Neither temperature nor soil water content had an expressed effect.

The AL-soluble P content of superphosphate-treated samples decreased to a greater extent in the first days of incubation (Fig. 6). In the first days of incubation in the superphosphate treatments, both soil water content and incubation temperature affected the AL-soluble P content of samples. However, the effects could hardly be separated from each other. Throughout the experiment, the AL-soluble P contents of superphosphate-treated soils were higher at lower temperature. Figure 7 shows average values for the effect of incubation temperature and soil water content on the AL-soluble P content of the chernozem brown forest soil from Kompolt throughout the incubation experiment.

In Hungary, the AL-extractant is used conventionally as the extractant to measure soil available P. This method, however, was developed for fertilizer recommendation for water-soluble P-sources. The AL-extractant (pH = 3.75) may dissolve a substantial amount of the undecomposed phosphate rock during extraction and thus the available P from phosphate rock in the soils can be overestimated

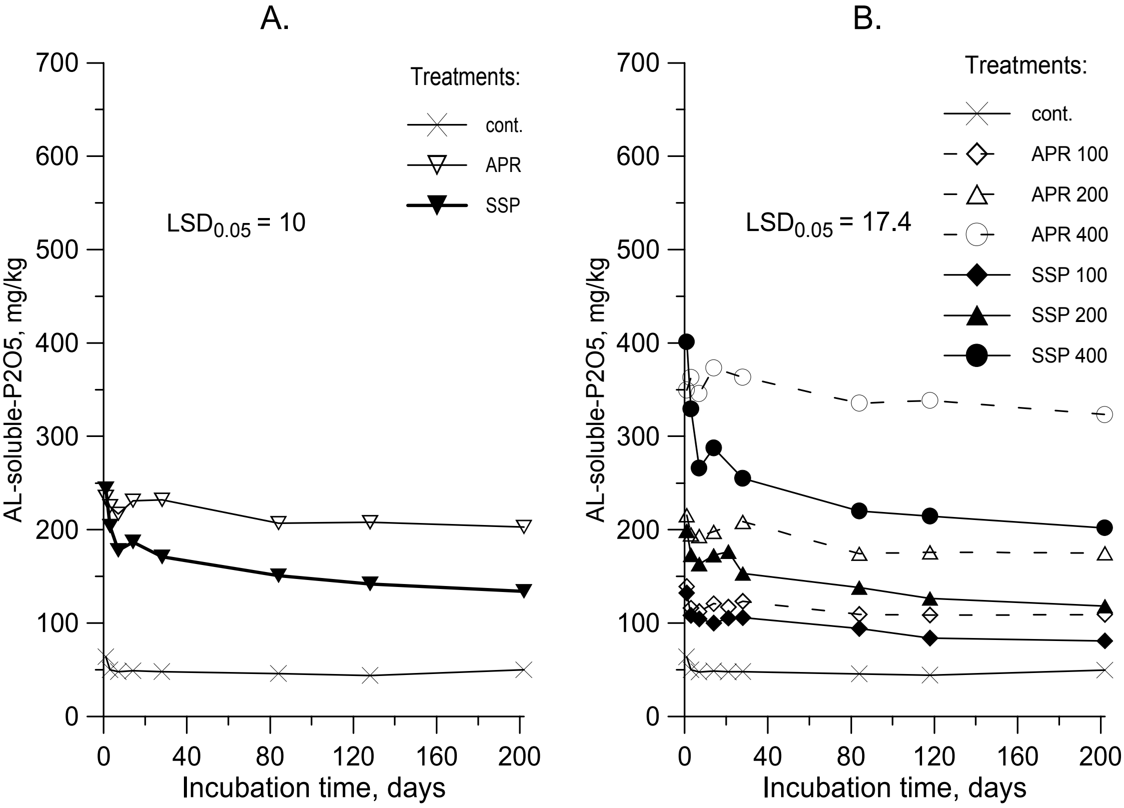

Fig. 6. Effect of Algerian phosphate rock (APR) and single superphosphate (SSP) on the AL-soluble P content of the chernozem brown forest soil (Kompolt) as a function of incubation time.
***A**. On the average of P doses. **B**. Separately. (Treatments: 100, 200, 400 = Active P ingredients, mg P_2O_5 kg^{-1} soil).*

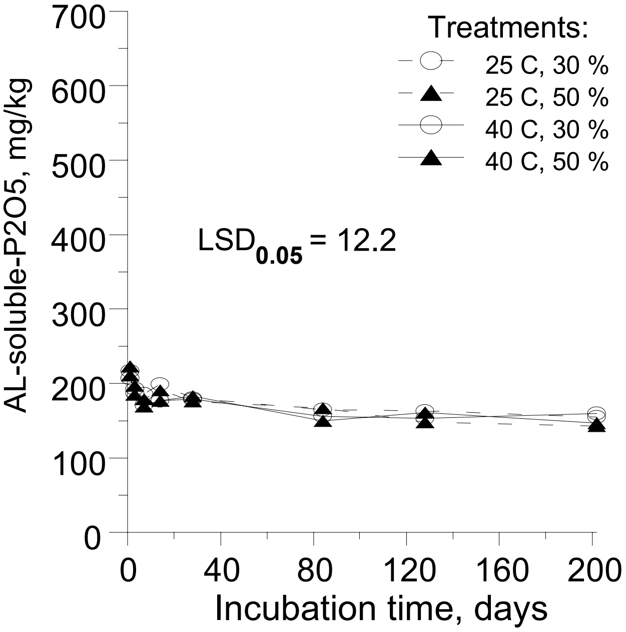

Fig. 7. The effect of incubation temperature and soil water content on the AL-soluble P content of the chernozem brown forest soil (Kompolt).

as compared to that from single superphosphate. Bray-II and double acid methods have been observed to solubilize phosphate rock in soil [4]. Our experimental results confirm the inapplicability of the AL-method for soil testing of available P from phosphate rock-treated soils.

3.2. Effect of superphosphate and phosphate rock treatments on the soil pH-H_2O

3.2.1. Pseudogley brown forest soil (Szentgyörgyvölgy)

At the beginning of the experiment, the initial soil pH (5.90) increased by 0.3 due to the effect of the 400 mg P_2O_5 kg $^{-1}$ P dose given in the form of phosphate rock - Thus no liming effect could be observed. Fardeau [39] and Xiong [40] obtained similar results in incubation experiments conducted with phosphate rock. The same P dose of superphosphate decreased the initial soil pH by 0.5 unit pH (Fig. 8). At the beginning of incubation, the rate of the P dose had a greater effect for both P forms. This effect, however, became less expressed with time. Studying the changes in pH on the average of incubation temperature and soil water content (Fig. 8). The decrease in pH was more expressed at the beginning of incubation while with time this decrease became slighter. The pH value of the control sample ranged between that of the two P forms throughout the incubation experiment.

Changes in the pH-H_2O value of the soils differed at 25 and 40 °C incubation temperature (Fig. 9). In the control and phosphate rock treatments in the first days of incubation (up to 20 days) pH decreased to a greater extent (to 5.1-5.2) at 40°C than at 25°C, and changed no further during incubation (Fig. 9A). At lower temperature, however, pH decreased continuously throughout the incubation period (to 4.6-4.9). In the second half of the incubation period, temperature had a greater effect on the pH of samples with higher soil water content. Similar effects were observed in the superphosphate treatments as in the phosphate rock treatments during incubation (Fig. 9B).

3.2.2. Chernozem brown forest soil (Kompolt)

Changes in the pH-H_2O value of the chernozem brown forest soil from Kompolt were evaluated on the average of incubation temperature and soil water content. As shown in Fig. 10, phosphate rock treatments resulted in a very slight increase (0.10), while superphosphate treatments decreased the initial soil pH-H_2O by 0.3 to 0.6 at the beginning of incubation.

In the first days of incubation, the decrease in pH was not as expressed as in the case of the pseudogley brown forest soil (Szentgyörgyvölgy). Incubation temperature and soil water content also had a slighter influence on the pH-H_2O value of the chernozem brown forest soil (Kompolt) than on that of the pseudogley brown forest soil (Szentgyörgyvölgy).

4. POT EXPERIMENT RESULTS

In the pot experiment, the effects of different P forms, P doses and incubation were studied on the dry matter yield, P concentration and P uptake of winter rape as a test plant. The experimental soils were a moderately acidic pseudogley brown forest soil (Szentgyörgyvölgy) and a slightly acidic chernozem brown forest soil (Kompolt).

4.1. The effect of superphosphate and phosphate rock treatments on the dry matter accumulation of winter rape grown in pot experiment

The effect of P treatments and incubation on the dry matter mass of rape is shown in Table II. P treatments on the pseudogley brown forest soil (Szentgyörgyvölgy) increased the quantity of dry matter both in the incubated and non-incubated soils as compared to the control. Based on the F-test, this increase however (Tables II and V) was not significant between superphosphate and phosphate rock treatments.

Incremental P doses had no effect on yields either in the incubated (I) or in the non-incubated (NI) pseudogley soils. The application of phosphate rock and superphosphate fertilizers resulted in similar dry matter yields (Incubated soil: R = 1.90 and S = 1.95 g pot^{-1} and Non-incubated soil: R = 2.31 and S = 2.45 g pot^{-1}).

In case of the pseudogley brown forest soil, the effect of incubation on dry matter yields was much more expressed than that of P forms or the amount of P applied. Higher rape yields were obtained on non-incubated soils than on incubated soils. On the basis of the F test, the difference in rape yield of incubated and non-incubated samples on the average of P form and dose (1.93 and 2.38 g pot^{-1}) was significant ($LSD_{5\%}$ 0.34) (Tables II and V). As it can be seen from Table V, the incubation treatment was the only factor that had a significant effect on the dry matter yield of winter rape grown on the pseudogley brown forest soil (Szentgyörgyvölgy).

TABLE II. THE EFFECT OF P TREATMENTS AND INCUBATION ON ON THE DRY MATTER MASS[1] OF RAPE (g POT^{-1})

	Soils					
	Moderately acidic pseudogley brown forest soil (Szentgyörgyvölgy)			Slightly acidic chernozem brown forest soil (Kompolt)		
Treatment	Incubated soil (I)	Non-incubated soil (NI)	Average of I and NI	Incubated soil (I)	Non-incubated soil (NI)	Average of I and NI
NK	1.64	1.70	1.67	1.95	2.07	2.01
NKP_{R100}	1.44	2.27	1.85	2.12	1.87	2.00
NKP_{R200}	2.46	2.51	2.48	1.88	2.08	1.98
NKP_{R400}	1.80	2.14	1.97	2.09	2.05	2.07
Average of R treatments	*1.90*	*2.31*	*2.10*	*2.03*	*2.00*	*2.02*
NKP_{S100}	1.89	2.70	2.30	2.37	1.89	2.13
NKP_{S200}	1.88	2.27	2.07	2.13	1.74	1.94
NKP_{S400}	2.09	2.39	2.24	2.84	2.13	2.49
Average of S treatments	*1.95*	*2.45*	*2.20*	*2.45*	*1.92*	*2.18*
Main average			2.083			2.086
CV%			24.25			16.56
$LSD_{5\%}$			0.845			0.578

[1] Average of three replications;
R = Phosphate rock, S = Single Superphosphate;
100, 200, 400 = Active P ingredients, mg P_2O_5 kg^{-1} soil;
N = 200 mg kg^{-1} soil; K = 200 mg kg^{-1} soil.

In spite of the lower total and available P content of the chernozem brown forest soil (Kompolt), the dry matter yield obtained in its control treatment was higher than that of the control samples of the pseudogley brown forest soil (Szentgyörgyvölgy). In contrast with the pseudogley brown forest soil (Szentgyörgyvölgy), there was no increase in yield as compared to the control in the phosphate rock and superphosphate treatments on non-incubated soils. In the incubated soil only superphosphate increased the yield in comparison to the control. This yield increase was significant for the highest superphosphate dose. On the average of P forms and P doses, incubation had a significant effect on rape yield in the chernozem soil. The yield of the incubated sample of the chernozem brown forest soil (Kompolt) was higher than that of the incubated pseudogley brown forest soil (Szentgyörgyvölgy) (2.24 and 1.96 g pot^{-1}, $LSD_{5\%}$ = 0.24).

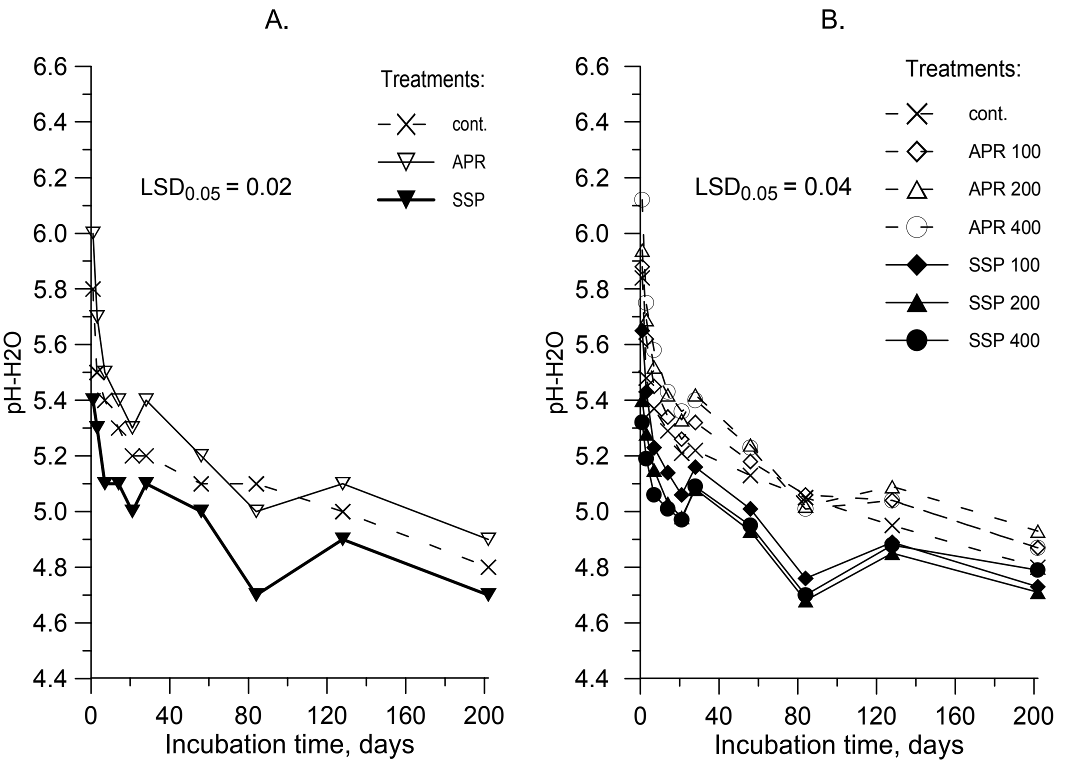

Fig. 8. The effect of Algerian phosphate rock (APR) and single superphosphate (SSP) on soil pH (H_2O) of the pseudogley brown forest soil (Szentgyörgyvölgy) as a function of incubation time.
***A.** On the average of P doses. B. Separately. (Treatments: 100, 200, 400 = Active P ingredients, mg P_2O_5 kg^{-1} soil).*

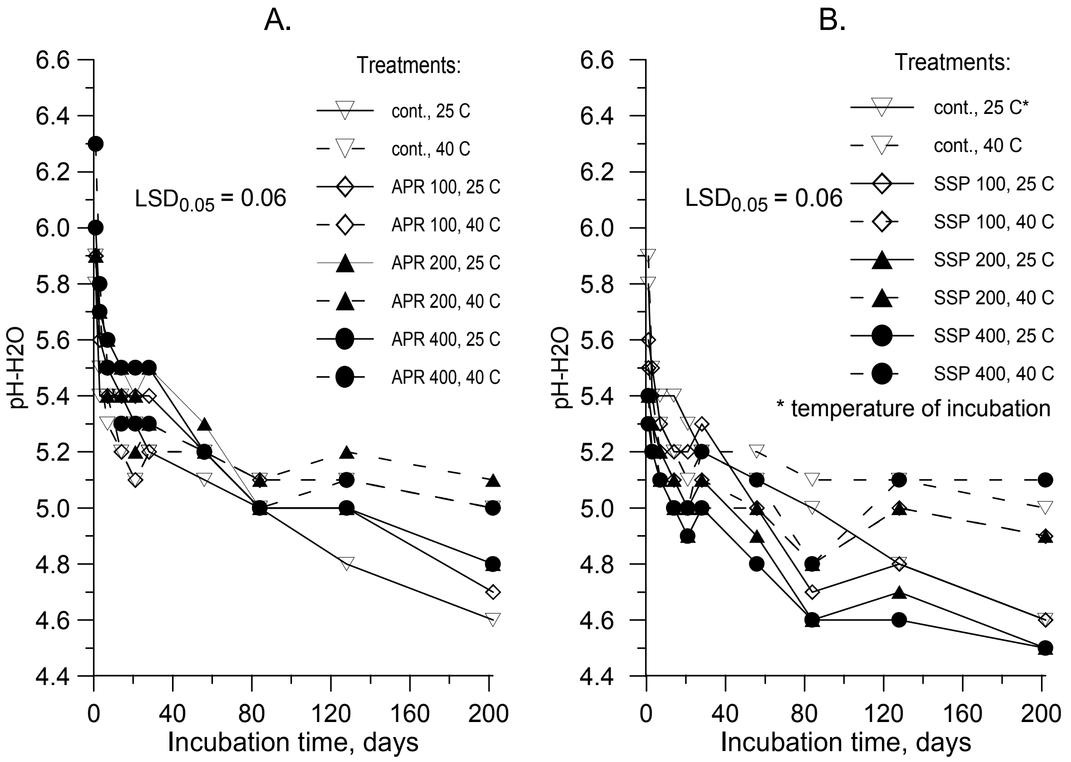

Fig. 9. The effect of Algerian phosphate rock (APR) (A) and single superphosphate (SSP) (B) on the pH-H_2O of the pseudogley brown forest soil (Szentgyörgyvölgy) (Treatments: 100, 200, 400 = Active P ingredients, mg P_2O_5 kg^{-1} soil).

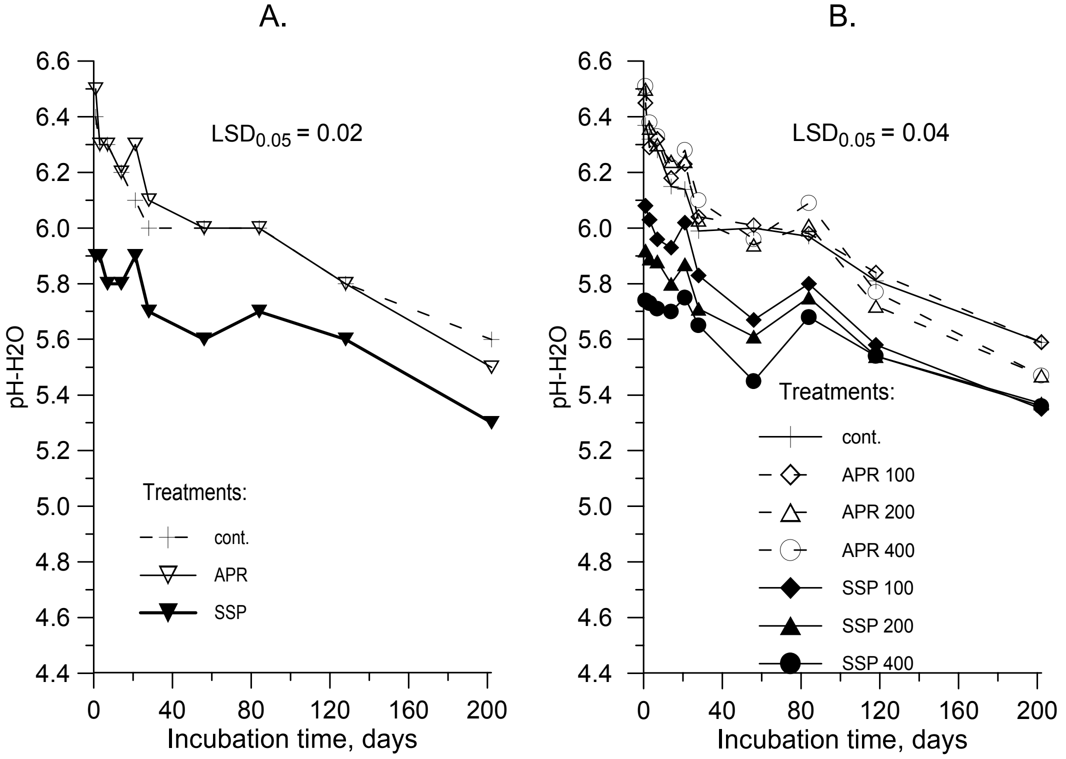

Fig. 10. The effect of Algerian phosphate rock (APR) and single superphosphate (SSP) on the soil pH-H_2O of the chernozem brown forest soil (Kompolt), as a function of incubation time.
A. On the average of P doses. B. Separately. (Treatments: 100, 200, 400 = Active P ingredients, mg P_2O_5 kg^{-1} soil).

4.2. Comparison of P concentration of plants grown in the pot experiment

The P concentration of winter rape grown in the pseudogley brown forest soil (Szentgyörgyvölgy) increased to a significant extent as a consequence of P treatments, as compared to the control samples (Table III). In the non-incubated soil this increase in P concentration, with the exception of one sample, was significant at all P doses. In the incubated soil, however, only the highest P rates of phosphate rock and superphosphate increased the P concentration significantly as compared to the control samples.

On the average of incubation and P forms, the highest P treatment increased the P concentration of winter rape significantly in comparison to the lowest P dose. On this soil, similarly to the dry matter quantity, the P concentration of rape was the highest in the non-incubated soils. Tables III and V show that, on the average of P dose and P form, incubation had a significant effect on the P concentration of winter rape (I = 5180 and NI = 5840 ppm, $LSD_{5\%}$ 490).

The P concentration of winter rape grown on the chernozem brown forest soil (Kompolt) also showed a marked increase due to the effect of P treatments in comparison to the control samples. This increase was significant in all P treatments in the non-incubated soil. In the incubated soil, however, the increase was significant only in case of the highest P doses.

On the average of incubation and P form, it was found that the higher P doses increased the P concentration of winter rape significantly as compared to the lower P doses. In case of the chernozem brown forest soil the incubation did not affect the P concentration of the test plant, while P form, on the average of P dose and incubation, had a significant influence (6070 ppm for phosphate rock, 6610 ppm for single superphosphate; $LSD_{5\%}$ 380). A significant interaction was found between P dose and incubation, as well as P dose and P form (Table V).

TABLE III. P CONCENTRATION (ppm) OF WINTER RAPE[1] GROWN IN A POT EXPERIMENT

Treatment	Soils					
	Moderately acidic pseudogley brown forest soil (Szentgyörgyvölgy)			Slightly acidic chernozem brown forest soil (Kompolt)		
	Incubated soil (I)	Non-incubated soil (NI)	Average of I and NI	Incubated soil (I)	Non-incubated soil (NI)	Average of I and NI
NK	4130	4000	4070	5090	4570	4830
NKP_{R100}	5090	5530	5310	5630	6340	5990
NKP_{R200}	4370	5620	5000	6190	6170	6180
NKP_{R400}	5450	6080	5770	6310	5770	6040
Average of R treatments	*4970*	*5740*	5360	*6040*	*6090*	*6070*
NKP_{S100}	5070	5050	5060	5250	6340	5840
NKP_{S200}	4920	6360	5640	6660	7110	6880
NKP_{S400}	6170	6390	6280	7090	7150	7120
Average of S treatments	*5390*	*5930*	*5660*	*6330*	*6870*	*6610*
Main average		5200			6130	
CV%		13.5			9.00	
$LSD_{5\%}$		1200			930	

[1] Average of three replications; for designations: See Table III.

A significant increase was found in the P uptake of winter rape grown in the incubated and non-incubated chernozem brown forest soil (Kompolt) only in case of the higher doses of superphosphate, as compared to the control. On the average of P forms and incubation, the highest dose increased the P uptake of rape in comparison to the lower doses. On the average of incubation and P dose, P form also had a significant effect (phosphate rock: 12.2; superphosphate: 14.4 mg pot^{-1}; $LSD_{5\%}$ 1.5).

On the basis of the pot experiment carried out with winter rape, the experimental factors studied (P dose, P form and incubation) had different effects on the dry matter yield, P concentration and P uptake of winter rape grown in the moderately acidic pseudogley brown forest soil (Szentgyörgyvölgy) and the slightly acidic chernozem brown forest soil (Kompolt). The P dose only influenced the P concentration of the test plant in the pseudogley brown forest soil (Szentgyörgyvölgy), while the effect of P dose could be proven for all three studied factors in the treatments carried out with the chernozem brown forest soil (Kompolt). The effect of incubation could be confirmed for all three factors in the case of the pseudogley brown forest soil (Szentgyörgyvölgy), but only for the dry matter yield for the chernozem brown forest soil (Kompolt). Fertilizer P forms resulted in significant changes in the P concentration and P uptake of winter rape only in the Kompolt soil. Significant interactions between the factors were found only for the chernozem brown forest soil (Kompolt). These correlations were valid for the 5% probability level of significance.

4.3. Effect of superphosphate and phosphate rock treatments on the P uptake of winter rape in the pot experiment

The P uptake of winter rape grown in the non-incubated pseudogley brown forest soil (Szentgyörgyvölgy) increased significantly in both phosphate rock and superphosphate treatments

TABLE IV. THE EFFECT OF P TREATMENTS AND INCUBATION ON THE P UPTAKE[1] OF WINTER RAPE (mg POT^{-1})

	Soils					
	Moderately acidic pseudogley brown forest soil (Szentgyörgyvölgy)			Slightly acidic chernozem brown forest soil (Kompolt)		
Treatment	Incubated soil (I)	Non-incubated soil (NI)	Average of I and NI	Incubated soil (I)	Non-incubated soil (NI)	Average of I and NI
NK	6.8	7.0	6.90	9.8	9.4	9.60
NKP$_{R100}$	7.3	12.6	10.00	11.9	11.9	11.90
NKP$_{R200}$	10.1	14.2	12.10	11.7	12.8	12.30
NKP$_{R400}$	9.9	13.2	11.50	13.1	11.8	12.50
Average of R treatments	*9.10*	*13.4*	11.20	*12.20*	*12.20*	*12.20*
NKP$_{S100}$	9.6	13.6	11.60	12.2	12.1	12.10
NKP$_{S200}$	8.4	14.3	11.40	14.2	12.4	13.30
NKP$_{S400}$	12.9	15.3	14.10	20.2	15.2	17.70
Average of S treatments	*10.30*	*14.40*	*12.30*	*15.50*	*13.20*	*14.40*
Main average		11.08			12.77	
CV%		23.93			17.7	
LSD$_{5\%}$		4.44			3.78	

[1] Average of three replications; for designations: See Table III.

TABLE V. SIGNIFICANT EFFECTS AND CORRELATIONS ON THE BASIS OF THE ‘F’ TEST

	Moderately acidic pseudogley brown forest soil (Szentgyörgyvölgy)			Slightly acidic chernozem brown forest soil (Kompolt)		
Designation	Dry matter g pot^{-1}	P content of plant ppm	P uptake mg pot^{-1}	Dry matter g pot^{-1}	P content of plant ppm	P uptake mg pot^{-1}
P-dose (A)		*		+	*	**
Incubation (I)	*	**	***	*		
P form (F)					**	**
A x I					*	
A x F					*	*
I x F				*		
A x I x F						
Between any 2 combinations		**	**	+	***	**

Significance levels: + 10%, * 5%, ** 1%, *** 0.1%.
Designations: A: P dose; 100, 200, 400 mg P_2O_5 kg^{-1} (mineral acid soluble);
I: Incubation; incubated for 202 days or fresh; F: P form; phosphate rock or superphosphate.

due to the effect of P doses as compared to the control, while only the effect of the highest superphosphate dose could be proven in the incubated soil (Table IV). Incubation had a significant effect on the quantity of P taken up (I = 9.7 and NI = 13.9 mg pot $^{-1}$; LSD$_{5\%}$ 1.8). This effect was significant at the 0.1% level of probability.

On the pseudogley brown forest soil (Szentgyörgyvölgy), phosphate rock had a similar effect to that of superphosphate on the dry matter yield, P concentration and P uptake of winter rape. This was confirmed by the statistical analysis. In the case of the slightly acidic brown forest soil (Kompolt), the P concentration and P uptake of winter rape in the superphosphate treatments proved to be higher statistically than those values obtained for the plants grown in the phosphate rock treatments. On this soil, superphosphate proved to be a more effective P fertilizer form for the winter rape test plant than phosphate rock.

We compared the effect of phosphate rock and superphosphate in a pot experiment set up previously with spring barley and red clover test plants with the same two acidic soils [41-43]. We obtained similar results for spring barley and red clover as for winter rape where superphosphate proved to be a more effective P fertilizer in case of the slightly acidic Kompolt soil. On the moderately acidic Szentgyörgyvölgy soil, the effect of phosphate rock was similar to that of superphosphate.

4. CONCLUSIONS

In the beginning of incubation, the water-soluble P content of the pseudogley brown forest soil was influenced both by the form of P and by the experimental conditions. The water-soluble P content decreased with time. After the 15th to 20th day of incubation, the effects of the P forms decreased. In this stage, the effects of environmental conditions depended on the form of the P fertilizer. The water-soluble P content of the phosphate rock-treated samples was affected to a great extent by soil water content, while the incubation temperature had a greater effect in soils treated with superphosphate.

The AL-P content of phosphate rock-treated soils was higher throughout the incubation period than that of the superphosphate-treated soils, at equal rates of P-active agent content. The AL-extraction may dissolve a substantial amount of the original phosphate rock and therefore, the available P in the soils from phosphate rock can be overestimated. Thus the AL-method is not applicable for soil testing of available P forms from phosphate rock-treated soils. Temperature had a greater effect on the AL-P content of soils than soil water content. Phosphate rock increased the pH of soils, but no liming effect could be observed.

In the pot experiment set up with the moderately acidic pseudogley brown forest soil, the dry matter yield, P concentration, and P uptake of winter rape was affected similarly by the phosphate rock and superphosphate treatments. In contrast to the slightly acidic chernozem soil, superphosphate proved to be a more efficient P fertilizer. Previous incubation of the soil with the P fertilizers significantly decreased all three-plant parameters in the pseudogley brown forest soil. The incubated superphosphate treatments produced higher yields in the chernozem brown forest soil, as compared to the non-incubated P fertilizer treatments.

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REFERENCES

[1] VÁRALLYAY, GY., Soil quality and land use. In: State of the Hungarian Environment. (Eds. Hinrichsen, D., Enyedi, Gy.) Hungarian Academy of Sciences — Ministry of Environment — CSO of Hungary, Budapest, (1990) 91-123.

[2] BARBER, S.A., Soil nutrient bioavailability. A mechanistic approach, Wiley Interscience Publication. John Wiley and Sons, New-York (1984).

[3] KHASAWNEH, F.E., DOLL, E.C., The use of phosphate rock for direct application, Adv. Agron. **30** (1978) 159-206.

[4] HAMMOND, L.L., CHIEN S.H., MOKWUNYE, A.U., Agronomic value of unacidulated and partially acidulated phosphate rocks indigenous to the tropics, Adv. Agron. **40** (1986) 89-140.

[5] CHIEN, S.H., MENON, R.G., Factors affecting the agronomic effectiveness of phosphate rock for direct application, Fert. Res. **41** (1995) 227-234.

[6] KIRK, G.J.D., NYE, P.H., A simple model for predicting the rates of dissolution of sparingly soluble calcium phosphates in soil. I. The basic model, J. Soil Sci. **37** (1986) 529-540.

[7] KIRK, G.J.D., NYE P.H., A simple model for predicting the rates of dissolution of sparingly soluble calcium phosphates in soil. II. Applications of the model, J. Soil Sci. **37** (1986) 541-553.

[8] NYE, P.H., Diffusion of ions and uncharged solutes in soils and soil clays, Adv. Agron. **31** (1979) 225-272.

[9] ANDERSON, G.C., SALE, P.W.G., Application of the Kirk and Nye phosphate rock dissolution model, Fert. Res. **35** (1993) 61-66.

[10] WATKINSON, J.H., Modeling the dissolution rate of reactive phosphate rock in New Zealand pastoral soils, Aust. J. Soil Res. **32** (1994) 739-753.

[11] SIKORA, F.J., GIORDANO P.M., Future directions for agricultural phosphorus research, Fert. Res. **41** (1995) 167-178.

[12] CHIEN, S.H., CLAYTON, W.R., MCCLELLAN G.H., Kinetics of dissolution of phosphate rocks in soils, Soil Sci. Soc. Am. J. **44** (1980) 260-264.

[13] RAJAN, S.S.S., WATKINSON, J.H., SINCLAIR, A.G., Phosphate rocks for direct application to soils. Adv. Agron. **57** (1996) 77-159.

[14] CSATHÓ, P., NÉMETH, T., The direct and residual effect of different P-sources in Hungarian field trials. In: Proc. 11th World Fertilizer Congress, (Eds.Cleemput von, O. et al.) Ghent, Belgium, (1997) 101-108.

[15] EGNER, H., RIEHM, H., DOMINGO, W.R., Untersuchungen über die chemische Bodenanalyse als Grundlage für die Beurteilung des Nahrstoffzustandes der Böden. II.Lantbr. Högsk. Ann. **26** (1960) 199-215.

[16] SARKADI, J., Opredelnie „vodorasztvorimogo" foszfora. In: Agrochemische Methoden für die Untersuchung des Phosphathaushaltes der Böden: Methodensammlung. Ak. der Landw. DDR. IPE Jena, (1982) 1-13.

[17] RICHARDS, L.A., (ed.) Diagnosis Improvement of saline and Alkali Soils. USDA Handbook No. 60 (1954) 100-101.

[18] ROSS, G.J., WANG, C., Extractable Al, Fe, Mn and Si. In: Carter, M.R. (Ed). Soil Sampling and Methods of Analysis, Canadian Society of Soil Science, Lewis Publishers, (1993) 239-246.

[19] RICHARDS, L.A., (ed.) Diagnosis Improvement of saline and Alkali Soils, USDA Handbook No. 60 (1954) 91.

[20] RICHARDS, L.A., (ed.) Diagnosis Improvement of saline and Alkali Soils, USDA Handbook No. 60 (1954) 84-107.

[21] BUZÁS, I., (Ed.) Methods for soil and agrochemical analyses. 2. (In Hungarian) Mezőgazdasági Kiadó, Budapest, (1988) 93-94.

[22] BUZÁS, I., (Ed.) Methods for soil and agrochemical analyses. 2. (In Hungarian) Mezőgazdasági Kiadó, Budapest, (1988) 152-155.

[23] FARDEAU, J.C., Dynamics of phosphate in soils. An isotopic outlook. Fert. Res. (1996) 91-100.

[24] FROSSARD, E.C., FELLER, H., TIESSEN, J.W.B., STEWART, J.C., FERDEAU, MOREL. C., Can an isotope method allow for determination of the phosphors-fixing capacity of soils. Commun. Soil Sci. Plant Anal. **24** (1993) 367-377

[25] International Standard Fertilizers - Extraction of phosphates soluble in mineral acids. Ref. No. The International Organization for Standardization (ISO) (1984) 7497-1984 (E.).

[26] FARDEAU, J.C., MOREL, C., JAHIEL, M., Does long contact with the soil improve the efficiency of rock phosphate? Results of isotopic studies, Fert. Res. **17** (1988) 3-19.

[27] LARSEN, S., Soil phosphorus, Adv. Agron. **19** (1967) 151-210.

[28] BARROW, N.J., The slow reactions between soil and anions. 1. Effect of time, temperature and water content of a soil on the decrease of effectiveness of phosphate for plant growth, Soil Sci. **118** (1974) 380-386.

[29] BARROW, N.J., A discussion of the methods for measuring the rate of reaction between soil and phosphate, Fert. Res. **40** (1983) 51-59.

[30] FOX, R.L., KAMPRATH, E.J., Phosphate sorption isotherms for evaluating the phosphate requirements of soils, Soil Sci. Soc. Am. Proc. **34** (1970) 902-907.

[31] ENFIELD, C,G., Rate of phosphate sorption by five Oklahoma soils, Soil Sci. Soc. Am. Proc. **38** (1974) 404-407.

[32] RYDEN, J.C., MCLAUGHLIN, J.R., SYERS J.K., Time-dependent sorption of phosphate by soils and hydrous ferric oxides, J. Soil Sci. **28** (1977) 585-595.

[33] OSZTOICS, E., The investigation of phosphorus sorption in the sandy soils (in Hungarian), Agrokémia és Talajtan **33** (1984) 228-232.

[34] OSZTOICS, E., VARRÓ, T., Kinetics of phosphorus isotope exchange in soils (in Hungarian), Agrokémia és Talajtan **35** (1986) 276-294.

[35] OSZTOICS, E., FÜLEKY, GY., VARRÓ, T., The investigation of the kinetics of phosphorus fixation in soils. (in Hungarian) In: XVIII. HUNGAROCHEM Fertilizers, Plant Protection Keszthely, (ed.: Blaske Zoltánné) (1988) 204-209. NEVIKI Veszprém

[36] BARROW, N.J., SHAW, T.C., The slow reactions between soil and anions. 2. Effect of time and temperature on the decrease in phosphate concentration in the soil solution. Soil Sci. **119** (1975) 167-177.

[37] OSZTOICS, E., KÓNYA, J., NAGY, N.M., VÁRALLYAY L., Effect of temperature on kinetics of phosphorus isotope sorption by soils Soil-Plant Relationships Proceedings of the XXlVth Annual ESNA/IUR Meeting Sept. 12-16, 1994. Varna, Bulgaria ed. M. H. Gerzabek/ Forschhungszentrum Seibersdorf, Austria, (1994) 283-292.

[38] ABD EL-GALIL, A., RADIMSZKY, L., BACZÓ GY., NÉMETH, T., Study of the AL -soluble phosphorus content in incubation experiments. Proc. Ist Conf. Egypt. Hung. Env. Egypt, (1993) 185-186.

[39] FARDEAU, J.C., Soil P fertility replenishment and 'liming' using phosphate rocks in soils with a low pH and developped under tropical climates. Abstracts. Third Res. Co-ordination Meeting of Rock Phosphates FAO-IAEA Res. Program. 17-21 March 1997, Vienna, Report D1-RC-542, 3, IAEA, (1997) Vienna.

[40] XIONG, L.M., ZHOU, Z.G., LU, R.K., Enhanced Plant Growth by Uniform Placement of superphosphate with Rock Phosphate in Acidic Soils, Commun. Soil Sci. Plant Anal. **27** (1996) 2837-2850.

[41] NÉMETH, T., OSZTOICS, E., BACZÓ, GY. Effect of different sources on spring barley in a pot experiment with six acid soils. In: (Eds. Welte, E., et al.) Soil Fertility and Fertilizer Management. Proc. 9th International symposium of CIEC, 25-30, September, 1995, Kusadasi, Turkey, (1995) 99-106.

[42] NÉMETH, T., OSZTOICS, E**.,** Effect of different phosphorus fertilizer sources on red clover in a pot experiment with six acidic soils. In.: 11th World Fertilizer Congress, (Eds:Cleemput von, O. et al.) Gent, Belgium, (1997) 419-427.

[43] OSZTOICS, E., CSATHÓ, P., NÉMETH, T., Studies on the effect of Algerian phosphate rock and superphosphate I. Comparative studies on the effect of phosphorus fertilizers on the yield and phosphorus content of spring barley in pot experiments using various soils, (In Hung.) Agrokémia és Talajtan **46** (1997) 289-310.

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1998	The Use of Nuclear Techniques in the Management of Nitrogen by Trees to Enhance Fertility of Fragile Tropical Soils (IAEA-TECDOC-1053)
1998	Crop Yield Response to Deficit Irrigation. Edited by C. Kirda, P. Moutonnet, C. Hera and D.R. Nielsen. Kluwer Academic Publishers; Developments in Plant and Soil Sciences, Number 84. ISBN 0 7923 5299 8
2000	Comparison of soil water measurement using the neutron scattering, time domain reflectometry and capacitance methods (IAEA-TECDOC-1137)
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