SEMINAR ON PHOSPHATE ROCK FOR DIRECT APPLICATION

IFDC INTERNATIONAL FERTILIZER DEVELOPMENT CENTER

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ERRATA

Although W. E. Fenster, F. E. Khasawneh, L. A. Leon, and O. W. Livingston are listed as conference participants, they did not attend the meetings in Haifa, Israel, March 20-23, 1978.

Preface

The origin of direct application of phosphate rock to the soil for fertilization is not precisely known. However, A. N. Gray in his book "Phosphates and Superphosphates" (1930) refers to the practice as "a relatively modern development" and states that the shortage of sulfuric acid during the war (1914-18) gave an impetus to the sale and use of ground phosphate rock.

Since the beginning of the 20th century, the subject of direct application of phosphate rock to the soil has been studied extensively; the study has generated hundreds of papers leading to diverse conclusions and controversy. One reason for lack of agreement is that the subject involves two substances, "phosphate rock" and "soil," which vary widely in their characteristics. The variable nature of phosphate rocks was not recognized by early scientists. Today much more information is available about the diverse character of both phosphate rocks and soils as well as other variables that influence their interaction.

The purpose of this symposium is to bring together the results of modern research on the use of phosphate rock for direct application for the information and guidance of agriculturists and scientists who are concerned with the most economical means for supplying the essential element, phosphorus, for increasing the world's agricultural production and thereby supplying adequate food for the growing population.

This symposium is particularly timely for the guidance of developing countries and those who are concerned with their problems. In many of these countries, the low level of phosphorus in the soil is the most limiting factor in crop production, and the problem of supplying this element economically is difficult. The combinations of soils, crops, and climate encountered in tropical countries may present an environment in which the usefulness of phosphate rock may differ significantly from that of temperate zones where most of the previous studies have been

done. However, the information in this symposium will help scientists to decide what direction future studies should take.

Thanks are due to the Israel Fertilizer Research Center for organizing this symposium and to the scientists from several countries who participated.

THE IFDC PHOSPHATE PROGRAM

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Introduction

The International Fertilizer Development Center (IFDC) is a nonprofit, international organization dedicated to the goal of increasing agricultural productivity in developing countries through the use of improved fertilizers and fertilizer know-how. Program objectives include the development of new fertilizers, as well as expanding the use of current or modified fertilizer materials. Special emphasis is placed on food crops grown under tropical and subtropical conditions using, where economically feasible, indigenous raw materials and production capacities. Organized in October 1974, IFDC had by early 1978 a staff of more than 140--half of which are scientists, engineers, and technicians from 19 countries. The efforts of these personnel are being channeled into several areas, including work on nitrogen, phosphorus, sulfur, fertilizer policy, identification of factors influencing fertilizer use, technical assistance, technology transfer, and manpower development. Additional efforts are planned in the near future for potassium, magnesium, and calcium. The purpose of this paper is to describe the basic components of the IFDC Phosphate Program highlighting the key areas of work and questions to be answered.

Substantial thought has gone into the IFDC Phosphate Program. Two United States (U.S.) organizations in particular, the Tennessee Valley Authority (TVA) and the National Academy of Sciences (NAS), have had an impact on shaping IFDC's efforts. The influence of TVA has come predominantly from its long-standing efforts in research and development on phosphates, particularly for domestic needs. The contribution from NAS came through a very timely World Food and Nutrition Study done in 1976 by the National Research Council of NAS which highlighted the research needed over the next 25 years on fertilizer if this key input is to be used effectively in ensuring maximum food production in the developing world. Other organizations--universities,

national and international research centers, and the United Nations groups such as the Food and Agriculture Organization (FAO), the United Nations Industrial Development Organization (UNIDO), and the World Bank--have had an influence in shaping this program.

The IFDC Phosphate Program has three general objectives. These are:

1. Develop technology that will permit efficient beneficiation of phosphate ores common to developing countries.

2. Develop and/or identify technologies which permit conversion of phosphate rocks into fertilizers which are effective in tropical and subtropical agriculture.

3. Identify fertilizers which are effective sources of phosphorus, acceptable to the fertilizer industry and appropriate for use by farmers, particularly small farmers of the tropics and subtropics.

Development of Technology That Will Permit Efficient Beneficiation of Phosphate Ores Common to Developing Countries

Phosphate rock is widely distributed throughout the world (table 1; figure 1). Reserves are extremely large and are being discovered at a rate faster than they are being consumed (Emigh 1972, 1975). Estimates of world phosphate ore reserves range from 81 billion tons to 1,300 billion tons (Notholt, 1975; Emigh, 1975). The difference in these estimates is due mainly to the absence of an agreed-upon definition of what should be classed as a "reserve" and a "resource." Some estimates include total phosphorus in known deposits; others include only that recoverable under present technological and economic conditions.

While total reserves appear to be ample to meet global needs in the foreseeable future (Stangel, 1977), only 15%-20% of the world's known reserves can be used with present mining and beneficiation technology (McClellan, 1977). The remaining 80%-85% is considered unavailable under present economic conditions. Beyond that, the technology used to mine and beneficiate phosphate ores is extremely wasteful. It is not uncommon,

for example, to discard during processing up to 60% of the total P_2O_5 present in the ore.

Currently major commercial mining activities are restricted to a few dozen deposits. These are usually easily mined deposits found mainly in the United States (Florida and North Carolina), North Africa (Morocco and Tunisia), and the U.S.S.R. (Kola). Barring major new discoveries of reserves and the development of new technology for beneficiation or changes in environmental policy, current mining operations in Florida will soon have to shift to lower grade rock (NAS, 1977). Similar shifts to lower grade rock have already occurred in the Kola deposits of the U.S.S.R. and may be a major reason why Russia contracted for up to 17 million tons of phosphate rock annually from Morocco (British Sulphur, 1978). It does appear that easily mineable phosphate deposits could be exhausted by the end of this century.

The depletion of easily mineable reserves and the difficulties of beneficiating remaining phosphate ores have raised concern as to their potential effects on food production. If ways are not found to increase the recovery of phosphate from existing mines and new technology is not found to effectively mine and beneficiate the untapped phosphate reserves, the cost of finished phosphate can be expected to rise at an alarming rate in the next 25 years.

IFDC researchers feel the first step toward solving the problem is to make an accurate assessment of the real supply of phosphates of various quality. This is needed to guide research on the utilization of indigenous ores and to determine future investments in phosphate mines. At present, no comprehensive, up-to-date data base exists on world tonnage, ore quality, and the technical and economical potential of many deposits. This situation is partly due to incomplete or inaccurate geological data on world deposits. No standardized system of phosphate classification, including a clear distinction between total resources and economic reserves, exists. Work needs to be done to classify, characterize, and evaluate deposits in accordance with mutually agreed upon universal standards. To accomplish this, IFDC has begun a program of phosphate rock characterization according to various types and locations of deposits. This information is recorded and stored in a raw materials data file.

Creation of a Raw Materials Data File

The Technology Division has taken the leadership in the establishment of a fertilizer raw materials data file. While this file will eventually encompass basic data over a wide range of fertilizer raw materials, phosphate rock has received initial and major emphasis. Key components of the file will initially include a description of size and quality of various reserves, alternative uses of these deposits, and costs of mining and other investments required for development. If necessary and practical, this data file will be computerized and placed into IFDC's data retrieval system.

A critical review of the literature and evaluation of related data systems--including Computerized Resource Information Bank (United States Geological Service (CRIB [USGS]), Materials Assistance System (Bureau of Mines (MAS [BOM]), Institute of Geological Sciences (London), British Sulphur Corporation (London), Bureau de Recherches Geologique et Miniere (BRGM-Paris), Canadian Centre for Geoscience Data (Ottawa), and Japan's National Technical Information System (Tokyo)--have been completed and synthesized into file format. The full value of this file will be realized in 5-6 years. When completed, it will provide a picture of known world phosphate rock reserves, including capital investment estimates related to bringing a deposit into production and provide preliminary appraisals of the technical problems confronting commercial utilization.

IFDC has brought together a group of experts from France, Australia, the United Kingdom, and the United States to help guide the development of the data file and to provide judgments regarding work needed to fill certain gaps on what is known about raw materials. This work is continuing.

New and/or Improved Methods for Beneficiation of Phosphate Ores

In response to a large number of inquiries from developing countries for technical evaluation of indigenous phosphate deposits, IFDC is developing a major research program to improve current methods of beneficiating phosphate ores. Particular focus is being centered on the economic utilization of difficult or

low-quality ores. These include phosphate ores with the following properties: (1) high silica, (2) high organic matter, (3) high iron/aluminum content, (4) high content of aluminum/iron phosphates, and (5) high content of carbonates and chlorides (Hignett et al., 1976). Research priorities in improved beneficiation will be determined to a high degree by the information obtained from the raw materials data file.

Recovery of Phosphate Slimes--As stated earlier, up to 60% of the P_2O_5 in the original ore can be discarded in the mining and beneficiation process. The majority of this loss occurs in the slimes portion of the wet beneficiation process. This has led to huge stock piles of phosphate wastes. Recently IFDC researchers, using a laboratory-scale pilot plant, have successfully recovered over 95% of the P_2O_5 of a sample of slimes taken from the Taiba mine in Senegal. The implications of this work are significant since nearly 20 million tons of slimes is now on hand and additional quantities are being produced annually at the rate of 2 million tons. While information generated thus far is preliminary, IFDC will pursue this project further; the actual extent is dependent upon outside funding.

Upgrading of Phosphate Ores by Wet- or Dry-Beneficiation Methods--IFDC's program in beneficiation of phosphate ores is aimed at supplying the appropriate technology and expertise required for the most effective utilization of a country's indigenous phosphate deposits. This is done through research at IFDC as well as supplying technical assistance at the request of developing countries. In the future, it is possible that some of these research activities may be carried out directly in specific countries depending, of course, on the particular task and availability of trained manpower and other resources.

Laboratory beneficiation capabilities at IFDC include electrostatic and electrodynamic separation, magnetic and gravity separation, wet and dry screening, and air classification. Also, pressure filtering has been added, and the flotation capabilities have been increased. The recent addition of an electron microscope and a binocular microscope with photographic capabilities makes assessment of the mineralogy and textural characteristics of the rock samples much easier. An X-ray fluorescence

spectrometer has been installed for rapid chemical analyses. In addition, IFDC receives excellent technical support from TVA in characterization of phosphate ores. The TVA facility includes an electron microscope as well as various types of beneficiation capabilities. IFDC is now in the process of further expanding its laboratory equipment capability which can be used to support phosphate research.

A wet-beneficiation pilot plant capable of handling 100 kg/hour of phosphate rock and companion crushing pilot plant will be ready for operation by June 1978 (figures 2 and 3). A wide variety of operations can be performed in this plant. These include grinding, sizing, scrubbing, and desliming the feed before flotation, thickening, and flocculation. It also has the capability to simulate a simple washing plant or as a complex double flotation operation such as those used in the Florida phosphate industry and the potential to adapt to new technology as developed from laboratory studies. It will provide critical information concerning equipment specifications and design for scale-up to a production size operation as well as provide an opportunity for technology transfer and training and provide a basis for making economic estimates of alternative beneficiation schemes.

Current Activities and Plans--While the bulk of time spent thus far has been in the design, procurement, and installation of equipment, laboratories, and pilot plants, IFDC has been carrying out limited work in beneficiation over the past 2 years. For example, samples of phosphate rocks were prepared and tests carried out on ore deposits from Sardinata and Pesca, Colombia; the Tilemsi in Mali; Baja California, Mexico; Sechura, Peru; and Kodjari and D'Arly deposits from Upper Volta. Samples have also been received, and initial test work has begun on materials from the Philippines, India, Syria, and Greece. Potential pilot-plant tests are indicated for ores from Colombia and Upper Volta, and further laboratory investigations are indicated for the rocks from Senegal and the Philippines.

Present work is focusing mainly on high silica ores. Work is also planned in the immediate future on high-carbonate ores since this type constitutes by far the greatest body of phosphate rock in world reserves.

The long-term direction and magnitude of this work will be determined to a very high degree by the findings of current work now underway.

Development and/or Identification of Technologies Which Will Permit Conversion of Phosphate Rock into Effective Fertilizers in Tropical and Subtropical Agriculture

Perhaps the greatest challenge to the IFDC Phosphate Program is to develop and transfer technology that will ensure efficient conversion of phosphate ores into fertilizers that are effective in tropical and subtropical agriculture. IFDC is placing a major emphasis on the development of phosphate materials that are more compatible with transportation and storage systems likely to serve the farmers of the developing world. This includes development of materials that will be suitable for use in the humid and arid tropics and subtropics, bulk handling and bagging systems of varying sophistication, and storage situations ranging from large humidity-controlled warehouses to small damp places (areas frequently found under farmers' homes).

IFDC has installed a special environmental room and has plans for a physical properties laboratory whereby many of the environmental conditions fertilizer will encounter in the tropics and subtropics can be duplicated at IFDC Headquarters and the cause and effect studied. An intermediate-scale (150 kg/hour) granulation pilot plant is now in operation, and a large multipurpose granulation/bulk-blending pilot plant (1,500 kg/hour) (figure 4) is scheduled to begin operation by July 1978. The latter will have capabilities to: (1) allow preparation of special fertilizer mixes and/or compounds for test and demonstration in overseas locations; (2) serve as a model for fertilizer production training; (3) permit troubleshooting on production processes and provide technical assistance to fertilizer producers (including phosphate producers); and (4) tailor fertilizers best suited to the needs and constraints of a given region within the tropics and subtropics.

While current high-analysis, highly water-soluble and citrate-soluble phosphates are effective on large cropping areas in the tropics and subtropics, such materials may have three basic disadvantages. Conven-

tional phosphate fertilizer production facilities are capital and energy intensive--both potentially serious constraints for developing countries (table 2, figure 5). Additionally, some of the concentrated phosphates--diammonium phosphate (DAP), monoammonium phosphate (MAP), and triple superphosphate (TSP)--are ineffective on soils having a high phosphate retention capacity. These limitations have led IFDC to conclude that no single phosphate material is likely to be universally accepted and effective throughout the tropics and subtropics. Instead, a variety of phosphate fertilizers and associated technology need to be developed, each suitable to the conditions of a particular area. The long-term objective of IFDC is to identify the fertilizer needs of specific crops and locations and develop technology that can properly meet these needs. IFDC is in the early stages of developing this philosophy. The following represents only the first phase toward achieving this goal.

Phosphate Rock for Direct Application

It has been known for many years that certain highly reactive phosphate rocks, if finely ground, are effective sources of phosphorus, particularly on acid soils. Reportedly, one of the main objections to using even highly reactive phosphate rock directly is its dusty nature when processed to the finely divided state (<200-mesh [Tyler]); this process is considered essential to ensuring phosphorus availability to the crop. IFDC has been working toward developing a commercial method for producing an easy-to-handle, agronomically suitable phosphate product for direct application.

Granulation Of Phosphate Rock--Most researchers have shown that granulation of phosphate rock generally decreases its effectiveness as a phosphate source to the crop (Terman, 1967; Doll, 1975). This is due to the decrease in surface area and localized placement when using conventional minus 6- plus 16-mesh granule sizes.

IFDC researchers and engineers have demonstrated that granulation of highly reactive, finely divided phosphate (<200-mesh) with soluble salts (muriate of potash or urea) into minigranules (minus 50- plus 200-mesh) through the use of an intensive granulator has proven to be an effective way to improve the handling prop-

erties of phosphate rock without impairing agronomic effectiveness as a phosphate source to the crop (Livingston, 1978; Hammond, 1978).

Preliminary tests have also been made using acids such as phosphoric, sulfuric, nitric, and hydrochloric as a binder to promote granulation and, at the same time, produce some portion of phosphate product in an available form. While more work is needed, this approach may prove helpful in increasing the agronomic suitability of less reactive phosphate rocks found in many developing countries. Even more important, the use of an acid binder potentially allows minigranulation to be carried out without the need for a drying step. This could be very significant in fuel-short countries, especially if a byproduct acid is available.

Dust Suppressants and Suspensions of Phosphate Rock--Another means of minimizing the dust problem and still maintaining the reactivity of ground phosphate rock is to treat the finely divided rock with a dust suppressant or with suspending agents. The former is likely to prove only partially successful and perhaps does not solve the real problems of losses in transport or actual application.

IFDC/TVA researchers have a method of placing finely divided phosphate rock in suspensions resulting in less than a 5% increase in volume, but the material remains in suspension for at least 48 hours. Such characteristics overcome most objections to the use of liquids or suspensions in the tropics, provided the rock is locally ground and applied to the soil in situations where whole areas are treated at one time. This approach is not likely to be successful if the rock is shipped great distances and/or handled individually by the farmer.

While this assumption may be correct, IFDC has not field tested the merits of minigranulation versus suspensions versus straight, finely divided phosphate rock as to agronomic effectiveness, farmer acceptance, and total compatability in various distribution systems. Such testing is planned for Upper Volta, Malaysia, Indonesia, Colombia, or Brazil, depending on the availability of funds and the willingness of the host country to try this concept.

Specialty Phosphates

Specialty phosphates can be prepared from a variety of raw materials to meet the phosphate needs of developing countries and represent a level of technology between direct application of phosphate rock and conventional chemical fertilizer technology. Additional factors that may encourage the development of these types of materials involve the chemical and physical properties of available indigenous raw materials (low reactivity, low grade, composition, etc.) and problems related to transportation costs. Many of these materials have been prepared by thermal alteration of the phosphate rock, but current IFDC research is directed toward studying methods of partial acidulation through the use of inorganic and organic acids.

Thermal Phosphates--A variety of phosphatic fertilizers can be prepared from nonpremium grade rock by thermally promoted reactions in the range of 1000°-1450°C that destroy structures of the apatite and allow recombination of $(PO_4)^{-3}$ into more reactive compounds of higher solubility.

Although they have a long history of testing and use in agriculture, most of these fertilizers have become largely displaced in recent years by high-analysis, water-soluble, chemical fertilizers such as TSP, DAP, and MAP. Typical examples of thermal phosphate products are: defluorinated phosphate rock, Rhenania phosphate, basic slag, Thomas slag, silicocarnotite-nagelschmitite, fused rock, and other so-called "calcined phosphates." Most thermal phosphates are prepared from apatitic rocks alone or admixed with various inorganic reagents. Most of the reactions evolve fluorine as an attendant step in decomposing apatites.

Because these thermal phosphate products contain a primary water-insoluble phosphate phase, diluted by residual inert mineral matter in the rock, they are inferior in P_2O_5 grade and quality to present-day high-analysis chemical fertilizers (Doll, 1975). On the other hand, they contain more reactive phosphate compositions of much higher citrate solubility than the precursor apatites. On certain tropical and subtropical soils, these types of products may be better than water-soluble phosphorus forms; the identification of soils and potential demand for these materials require further research.

Thermal phosphates potentially fill a gap between highly reactive raw phosphate rock fertilizers for direct application and high-analysis chemical fertilizers. Although their energy-intensive processing and inferior quality in comparison to chemical fertilizers have restricted their importance to a relatively minor fraction of the total phosphate production, such cost factors must now be weighed against the advantages of using unbeneficiated low-quality phosphate rocks, as well as cheaper reagents than required in wet-beneficiation chemical processes. Also, their slow-release characteristics and retained contents of secondary and micronutrient elements may enhance their usefulness in some tropical agricultural practices.

IFDC Activities and Plans--The laboratories and greenhouse at IFDC are sufficient to produce and carry out preliminary tests on a wide range of thermal phosphates. Tests to date (primarily to check out equipment) include the synthesis of Rhenania phosphate and chlorospodiosite. Future direction in this area will depend upon agronomic testing now underway. Potential new projects are the production and testing (greenhouse and field) of Rhenania phosphate made from ores in Sri Lanka and Upper Volta. Proposals are being advanced to potential donors and the Governments of Upper Volta and Sri Lanka to test the feasibility of this approach. An additional research possibility is the production of calcined rock from sources in Christmas Island, Australia, and Thailand for use in East and South Asia.

Clinker Process for Direct Acidulation--As an alternative to the thermal processes described above for use on nonbeneficiated ores, IFDC is preparing to do some exploratory work on modification of the so-called "clinker" process described in the literature. In this process the ore is acidulated to a superphosphate-like composition and extracted to produce a 40+% phosphoric acid, thereby eliminating the need for beneficiation and the associated problem of slime disposal. This process has not been successful to date because phosphate extraction efficiency and clinker stability are inversely related. However, with a siliceous ore (like Pesca) the process problems encountered previously may be overcome. Preliminary results of tests conducted in IFDC laboratories have been promising. IFDC plans to look into this opportunity further.

Partial Acidulation of Phosphate Ores--There are numerous instances where local phosphate ores are not sufficiently reactive without modification to serve as an effective source of phosphate to the crop. Additionally, a small domestic market demand and lack of foreign exchange or both may be major constraints to the construction of a conventional-scale phosphoric acid complex (600-1,000 tpd P_2O_5). Partial acidulation of phosphates to upgrade the availability may be accomplished through either partial acidulation with inorganic acids such as sulfuric and phosphoric or through the use of organic acids obtained primarily through fermentation.

Recent research in Colombia (Centro Internacional de Agricultura Tropical [CIAT], 1975) and work previously reported by McClean (1964), coupled with recent breakthroughs in minigranulation (Livingston, 1978), prompted IFDC researchers to take a new look at the feasibility of partial acidulation of low-reactivity phosphate rocks with either sulfuric acid, phosphoric acid, or elemental sulfur. Greenhouse experiments were started in January 1978 at IFDC Headquarters, and field trials are planned for mid-1978 at CIAT in Colombia. Results of this work, plus a further evaluation of the minigranulation process, will be a major factor in determining how much emphasis will be placed on this in the future.

An alternative to either thermal treatment or partial acidulation with inorganic acids is the modification of P_2O_5 availability using residues from such agricultural products as cassava, rice, wheat, sugarcane, and cocoa. These agricultural wastes are fermented to produce organic acids (citric, lactic, acetic, etc.) which can be mixed with rock to yield a product with increased P availability. This technology is designed for implementation by the individual farmer or local cooperative and has the advantage of increasing the availability of indigenous rocks without importing expensive reagents. Work thus far has been done in the laboratory through a research contract with a U.S. university. A limited amount of effort is planned in this area for the next year; research is aimed primarily at establishing the quantity and strengths of acids that might be produced from various agricultural wastes. Their effectiveness in increasing the availability of various phosphate rocks remains to be proven.

Conventional Phosphate Research

Substantial funds have been committed to expanding the range of phosphate rocks which can be used to produce conventional high-analysis phosphate fertilizers. Major focus is initially to be on the wet-process phosphoric acid production using indigenous rocks. Future work will be aimed at development of nitric acid and hydrochloric methods of making acid.

Wet-Process Phosphoric Acid Research--Production of wet-process phosphoric acid is the ultimate goal in upgrading most phosphate rocks. The ease with which this is achieved is directly dependent upon the grade of ore, level of impurities, and general matrix of the phosphate ore. Therefore, a series of detailed tests on the actual ore must be run in the laboratory and pilot plant before a decision can be reached regarding the actual feasibility of producing phosphoric acid on a commercial scale.

IFDC, which will have two small phosphoric acid research plants operating by mid-1978, is well equipped to carry out research in this area. A bench-scale unit was installed and made operational in December 1977. Initial shakedown runs were made using Florida rock. Tests for direct acidulation of Pesca ore (high silica) have also been made. Trials to date with the bench-scale unit reveal that results comparable to those from large plants are possible from this small unit. The capacity of the laboratory unit is rated at 400 g/hour of rock feed. In normal operation, without acid concentration, an acid containing about 30% P_2O_5 (filter grade) can be made. With concentration, a grade of 54% P_2O_5 or more is possible. The unit includes a feed section, attack and agitation section, filtration, process controls, fume hood, and wet scrubber with a mist eliminator. The unit can be operated in varying modes from dihydrate to hemihydrate production, and also, with some modification, nitric phosphate processes can be studied. This unit will serve as an excellent model for research and training. It will be valuable in carrying out comparative tests of problem ores to distinguish the effect of variables.

A second phosphoric acid unit (small pilot-plant scale, 10 kg/hour of rock) is under construction and

will be operational in June 1978 (figure 6). This unit will be used to further substantiate findings obtained by the smaller unit. It has the same capabilities as the smaller unit and can be used as a valuable link between the benefication and the granulation pilot plants. It also has valuable attributes for training purposes.

Evaluation of Key Processes, Plant Investment Needs, and Production Costs of Phosphate Fertilizers

No real progress can be made in finding new or better ways of producing phosphate fertilizers until detailed technical and economic comparisons are made with conventional or existing processes to produce these materials. Such comparisons include the establishment of process input coefficients, raw material standards and requirements, investment requirements, production costs, and financial alternatives. IFDC has recognized this and has set up a unit having the responsibility of carrying out the key evaluations in the above-mentioned areas. The engineering service unit of the Outreach Division has identified the basic parameters of the important phosphate processes. Data have been collected from a wide range of sources including: The World Bank, UNIDO, TVA, various design companies, and, in some instances, private and public companies having recently built phosphate complexes. This information has been computerized and placed into the plant investment analysis component of the IFDC computer program. A diagram on how that subsystem functions is shown in figure 7.

IFDC will periodically bring together representatives from key organizations for purposes of evaluating data in the system. This group will be asked to suggest changes in battery-limits components, input coefficients, and investment costs and provide opinions as to confidence limits that can be ascribed to the data. The first meeting of this group is scheduled for April 4-5, 1978, at IFDC Headquarters.

The plant investment analysis subsystem has already been used by the IFDC staff. It has also been used by fertilizer groups from developing countries. IFDC has an open policy of sharing this information with other national and international organizations.

Programs to Identify the Effectiveness of Various Phosphate Fertilizers, Develop Recommendations, and Encourage Farmers, Particularly Small Farmers, to Use Phosphates Profitably

The basic mission of IFDC is to ensure that lack of fertilizer know-how is not a limiting factor in the farmer's effort to grow food and fiber in the developing world. Phosphate is a key input in meeting this objective and, in most instances, is one of two nutrients likely to be limiting on most soils in the tropics and subtropics. IFDC is attempting to (1) identify profitable methods to remove fertilizer constraints (phosphorus nutrition) that are preventing potentially arable land from being brought into production, and (2) identify and remove constraints that prevent fertilizers from being used at optimum economic levels on lands already under cultivation but producing far below their potential.

Research to Remove Fertilizer Constraints to Bringing New Land Into Production

Background--The world is currently cultivating approximately 35% or 1.4 billion of a total 4.5 billion ha of potential agricultural land in the world (Buringh et al., 1975).

The largest proportion (about 40%) lies in the vast tropical forest and savannah areas that have acid, highly weathered soils classed as Oxisols and Ultisols (Kellogg and Orvedal, 1969). These regions comprise approximately 1,660 million ha, of which 822 million ha is potentially arable (table 3). The largest contiguous areas are in interior regions of South America and Africa, with smaller but important areas in Central America, Indonesia, and Malaysia. Countries having high population densities have developed programs to disperse populations into Ultisol and Oxisol regions but with little chance of success because they lacked a sound agronomic-soil fertility program. Where population densities are low, national governments have not felt an immediate need to develop their "unused" lands, but the need to put them into production is approaching.

The bulk of these Oxisols and Ultisols are in their natural state or are devoted to shifting cultivation and extensive cattle grazing. The climate in the tropical

areas is ideal for year-round crop production since there are virtually no temperature limitations; about 70% of these areas have high annual rainfall with no prolonged dry season, while the remaining 30% have a 3-6 month dry season.

Many of these soils have excellent physical properties with gentle topography suitable for intensive crop production. However, the lack of well-developed physical, social, and economic infrastructures and low levels of native soil fertility have restricted the potential of these areas for agriculture. The luxuriant vegetation of Oxisols and Ultisols in tropical forests and savannahs is deceptive, since there is a tight nutrient cycle between vegetation and soil. When these areas are cleared, fertility declines rapidly and weed control becomes difficult (Nye and Greenland, 1960). Farmers without access to fertilizers or manures normally shift to other areas.

The terms "low soil fertility" and "low-base status soils" encompass a general deficiency of several macronutrients and micronutrients, low cation-exchange capacity of the clay fraction, high soil acidity, aluminum or manganese toxicity, and, in many loamy or clayey textured topsoils, high phosphorus-retention capacity.

Phosphorus is almost universally deficient in these areas, but adding conventional, high-analysis, water-soluble phosphorus fertilizers may not be economically feasible because of the large applications needed for satisfactory response levels. Overcoming this problem under present capital and energy constraints involves certain strategies (Sanchez and Uehara, 1977; IFDC, 1975) to: (1) improve the efficiency of phosphorus fertilization through better placement methods and use of cheaper, low-soluble phosphates including phosphate rock; (2) decrease the soil's capacity to temporarily immobilize phosphorus through means such as liming and/or silicate applications; and (3) develop varieties tolerant of phosphorus stress and maximize the utilization of mycorrhiza or microbial populations which increase phosphorus absorption by plant roots.

IFDC Activities--IFDC management is aware of the broader issues which need to be addressed if these areas are to be brought into crop production. It places great importance on developing a phosphate program

that is sound and in harmony with the broader issues. To accomplish this, seven areas of activity have been identified. These are (1) identification of chemical reactions of phosphates in pure systems and in soils, (2) evaluation of the agronomic and economic efficiency of various phosphate fertilizers, (3) identification of key plant/soil phosphorus interactions, (4) development of ways to minimize the phosphate-retention capacity of soils, (5) establishment of optimum levels of phosphate use under various cropping systems and input:output rates, (6) identification of constraints and determination of the demand for various phosphate products, and (7) identification of public policy alternatives for phosphate fertilizer that will maximize food production in accordance with national goals and still be profitable to the farmer and the fertilizer industry.

Reactions of Phosphate Fertilizers in Pure Systems and in Soils

Key to the development of more efficient fertilizers is the understanding of the basic phosphate reactions and the factors which control these in pure systems and in soils. Work in this area is underway in both the Technology and Agro-Economic Divisions of IFDC and on contract with the Soils and Fertilizer Branch of TVA and the Soils and Fertilizer Laboratory of Technion, Haifa, Israel. Following is a brief description of activities in this area.

Factors Affecting Phosphorus Release from Various Sources of Phosphate Rock--This project involves laboratory evaluations consisting of: (1) comparison of relative phosphorus levels in soil solution from various phosphate rocks, (2) determination of factors affecting phosphorus release, such as type of material, soil moisture conditions, soil pH, particle size, etc., and (3) identification of phosphate materials that potentially may be effective for tropical and subtropical soils.

Chemical Methods for Evaluating the Potential of Granulated Phosphate Rock for Direct Application--Granulation of finely ground phosphate rock generally leads to a reduction in short-term phosphorus availability. Greenhouse tests (Hammond, 1978) have confirmed this for two highly reactive phosphate rocks, North Carolina and Sechura, using maize as a test crop. The solubility as measured by the conventional AOAC citrate-solubility

method over varying granule sizes shows little relationship to measuring crop response. IFDC scientists are attempting to develop a simple laboratory method using resins to measure phosphorus availability to the crop as influenced by granulation. This is extremely important to quality control procedures in production of granulated phosphate rock.

Phosphate Concentration in Soil Solution in Relation to Plant Growth in Soils Treated With Phosphate Rocks--The main objectives of this greenhouse and laboratory study are to (1) measure the level of phosphate that can be sustained in soil solutions of soils treated with phosphate rocks varying in citrate solubility, (2) determine the rate of plant growth which can be attained in such amended soils, and (3) determine the relationship between rate of plant growth and phosphorus in soil solution. Work in the above-mentioned areas is critical to determining under what conditions PR may be suitable for direct application. Preliminary results indicate rocks vary in their phosphorus availability to the crop; however, the importance of this depends upon the crop grown, the level of management (cropping intensity), and the soil environment.

Additional Evaluation of Phosphate Rock for Direct Application

For the past 2 years the Agro-Economic Division of IFDC has contracted phosphorus research at the Soils and Fertilizer Laboratory of the Israel Institute of Technology, Haifa, Israel. This work has centered on greenhouse, incubation, and laboratory studies and focused mainly on the evaluation of phosphate rock for direct application. The key series of experiments are listed as follows:

1. Comparison of phosphate rock sources,
2. Comparison of effectiveness of various granulated phosphate rocks,
3. Influence of grinding on the availability of Arad phosphate rock,
4. Methods of placing Maktesh phosphate rock,
5. Effect of liming on the availability of phosphate rock,
6. Stability of phosphate rock granules,

7. Incubation studies with phosphate rock granules, and

8. Effects of phosphate rock treatments on available phosphorus in soils.

It should be pointed out that most of this work was started before IFDC facilities were completed and staff hired and proved helpful in setting research guidelines in IFDC's Phosphorus Program.

Field Evaluations of the Efficiency of Various Phosphate Materials Under Different Management Systems

The real measure of various phosphorus sources is to test them under farm-level field conditions. IFDC is making a major effort to initiate such testings. Cooperative projects are already underway with CIAT to conduct laboratory, greenhouse, and field tests in Colombia, Peru, Ecuador, and possibly Brazil. This project is being partially funded by the International Development Research Center of Canada (IDRC). Similar efforts are contemplated in the very near future for Africa and South Asia. A brief description of the projects for Latin America and Africa follows. The South Asia project is still in the early stages of development.

Efficient Utilization of Phosphate Fertilizers in Acid Soils of Latin America--The IDRC of Canada is funding this project which is being executed cooperatively by CIAT and IFDC. IFDC stationed a soil chemist at CIAT in July 1977 and a soil fertilizer specialist there in November 1977. The eventual target areas of this project are the acid soils (Oxisols, Ultisols, and Inceptisols) of tropical Latin America. These soils are generally of medium to fine texture, have a pH of 4.0-5.5, and contain 200-600 ppm total phosphorus. Available phosphorus is usually very low ranging from 1 to 5 ppm (using the Bray P_1 test). The soils have a high P-retention capacity which in many cases renders conventional high-analysis phosphates costly and ineffective. IFDC and CIAT have developed a project to help solve this problem. The objectives are to (1) evaluate the effectiveness of sources and methods of application of phosphate fertilizers on soils of tropical and subtropical Latin America, (2) determine the forms and the availability of the reaction products of these fertilizers in soils as related to their initial and

residual effectiveness, and (3) establish criteria for applying the first two objectives to different soils and crops at various locations by conducting field experiments on selected soils throughout the target area in Latin America.

Efficient Utilization of Phosphate Fertilizers in Acid Soils of the Tropics of West Africa--The Oxisol and Ultisol soils of tropical Africa, like those of Latin America, are unusually low in phosphorus and show high phosphorus-retention capabilities (Boyer, 1971). Fertilizer use in west Africa is low, mainly restricted to export crops, due in part to the unfavorable cost:price relationships of the fertilizer use on crops (Zalla et al., 1977). Studies involving the utilization of west African phosphate rock deposits have been limited in scope. Most of the agronomic evaluations consisted of yield comparisons with little emphasis on soil parameters (Juo and Kang, 1977). Additional research is needed to evaluate the feasibility of utilizing such alternative sources and application methods. A collaborative project is now being developed with the International Institute for Tropical Agriculture (IITA) and will be implemented first in Nigeria with extensions to the Cameroon and possibly Zaire or the Sahel. The direction of this project depends upon the availability of funds, personnel, and the interest of the host country in this type of activity.

Economics of Phosphate Use

There is an immediate need for sound economic analysis of the potential of phosphate rock for direct application, thermal phosphates, and partially acidulated phosphates for use on key crops grown in the tropics and subtropics.

IFDC is starting work in this area, commencing with a study of the economics of direct application of phosphate rock. A suggested methodology on how to do this will be presented later in the program. While this is a start, such efforts must be accelerated and broadened to include production and distribution economics. Additional efforts need to be focused on the profitability and policy implications of using phosphates on forages as well as food crops.

Conclusions

IFDC hopes to collaborate with a wide range of institutions in an effort to develop an effective phosphate program. It has already established linkages with the agronomic field-testing networks of international research centers such as the International Rice Research Institute (IRRI)--rice--and CIAT--pastures, beans, and cassava. Similar linkages will soon be established with International Crops Research Institute for the Semi-Arid Tropics (ICRISAT) and IITA to cover work in Africa and other parts of Asia. A strong linkage is being developed with appropriate national institutions in developing as well as developed nations. This base is particularly important since it provides access to some of the top phosphate expertise throughout the world. It also provides an opportunity to focus this expertise on specific and relevant problems. A good relationship already exists with key geologic institutions interested in the prospecting and mining of phosphates. IFDC also recognizes the contributions that can be made by European, North American, and Japanese institutions. Efforts will be made to involve their expertise as we carry out this program. The potential role of the various UN groups is also recognized. The opportunity exists for interaction with such groups as the Fertilizer Unit of the World Bank, Investment and Technical Assistance Groups of UNIDO, the Fertilizer and Plant Nutrition Service of FAO, Fertilizer Commission of FAO, Tropical Agricultural Research Institute (IRAT) of France, the World Phosphate Rock Institute, the North American Potash and Phosphate Institute, the International Superphosphate Manufacturers' Association (ISMA), and others to join in this effort. IFDC either already has or soon will extend its hand to each of these groups and try to utilize their resources and avoid duplication of effort where possible.

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Table 1. 1975 Known Phosphate Rock Reserves (Notholt 1975)

Location	Quantity (million tons)	Percent P_2O_5	Production Units, 600 tpd P_2O_5	
			Potential Demand[a]	Potential Supply[b]
North America	7,413	23-32	45	297
Europe (including U.S.S.R.)	4,700	6-26	125	122
Africa	45,883	12-32	15	2,041
Latin America	14,000	31	38	603
Asia[c]	9,632	15-38	100	228
TOTAL	81,628	6-38	323	3,291

a. Number of 600-(P_2O_5) tpd H_3PO_4 units needed to supply projected demand for 20 years. UNIDO (1977)
b. Number of 600-(P_2O_5) tpd H_3PO_4 units that known deposits can support for 20 years. Stangel (1976)
c. Includes Japan and Oceania.

Table 2. Summary of Plants Required and Total Capital Costs, 1980-2000
(costs in billion US $)

	Developing Countries				Developed Countries			
	1980-85	1985-90	1990-2000	1980-2000	1980-85	1985-90	1990-2000	1980-2000
No. of 600-tpd phosphate complexes[a]	21	28	92	141	14	47	121	182
Capital requirements	3.0	4.0	12.5	19.5	1.3	4.8	12.0	18.1

a. This analysis assumed that new phosphate fertilizer production will be 20% TSP and 80% DAP/MAP.

Source: UNIDO World-Wide Study of the Fertilizer Industry: 1975-2000, 1977, International Centre for Industrial Studies.

Table 3. Approximate Extension of Ultisols and Oxisols in the Tropics (million hectares)[a]

Soil Order	Dry Season (months)	America	Tropical Africa	Tropical Asia	Total Area	Potentially Arable
Oxisols	<3	390	380	0	770	460
	3-6	170	170	0	340	190
Ultisols	<3	165	75	190	430	122
	3-6	35	25	60	120	50
TOTAL		760	650	250	1,660	822

a. National Research Council NAS Study, 1977.

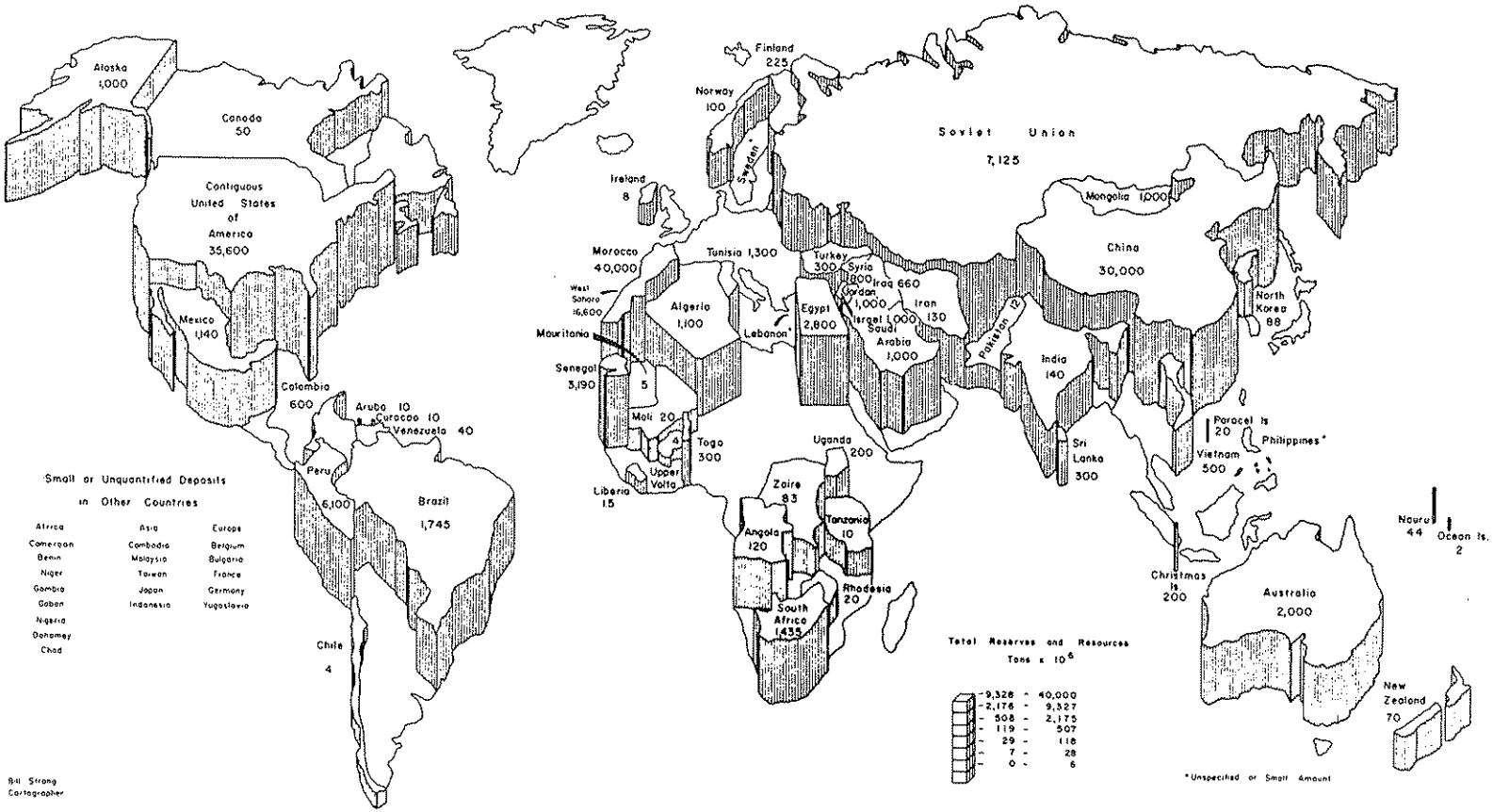

Figure 1. World Phosphate Reserves and Resources.

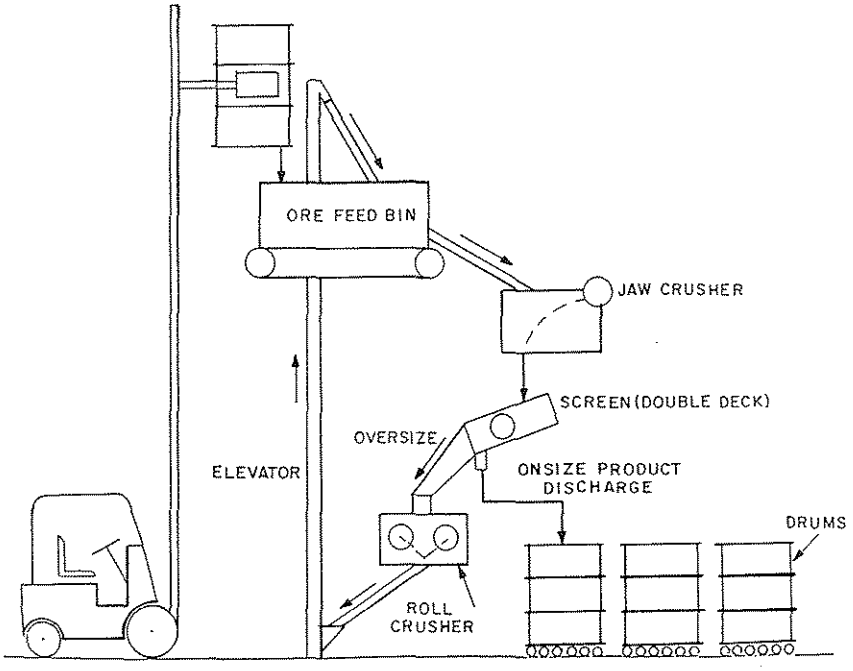

Figure 2. IFDC Crushing Pilot Plant.

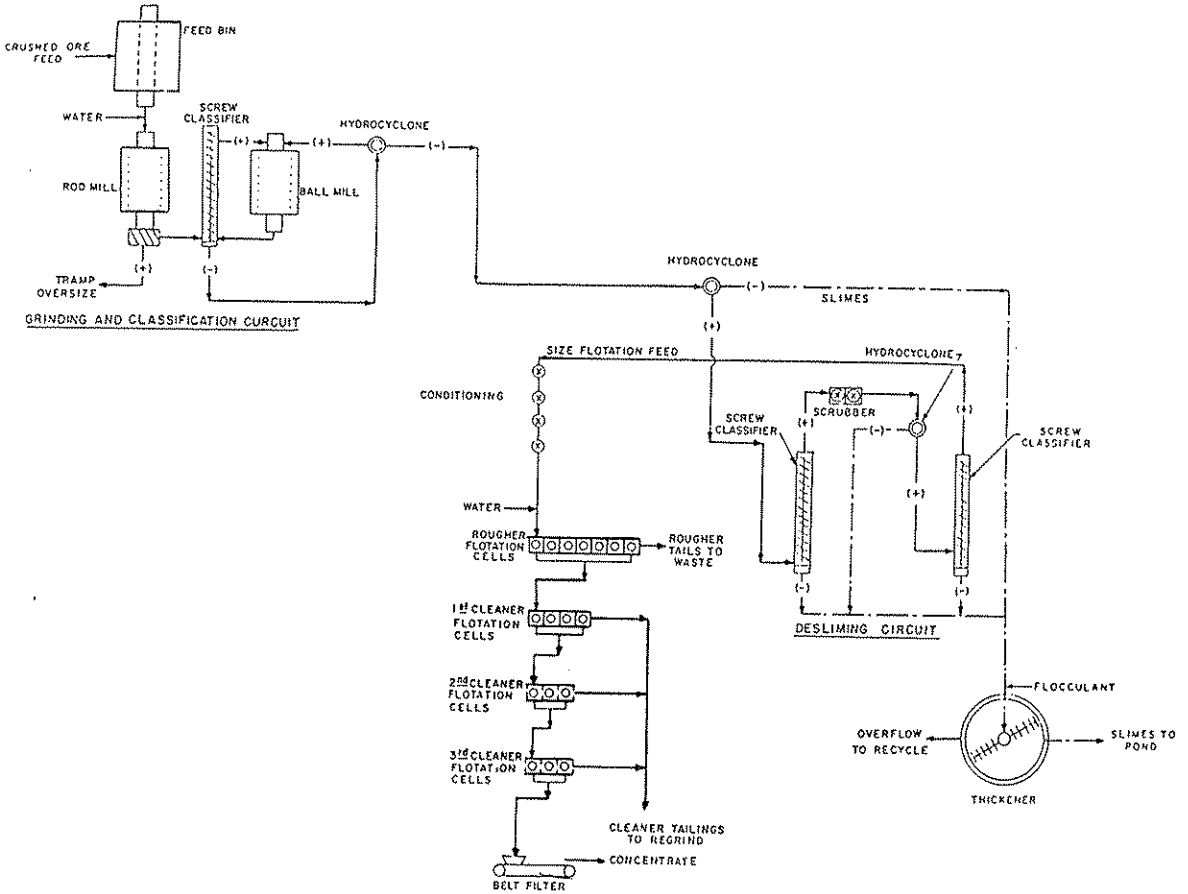

Figure 3. IFDC Wet-Beneficiation Pilot Plant.

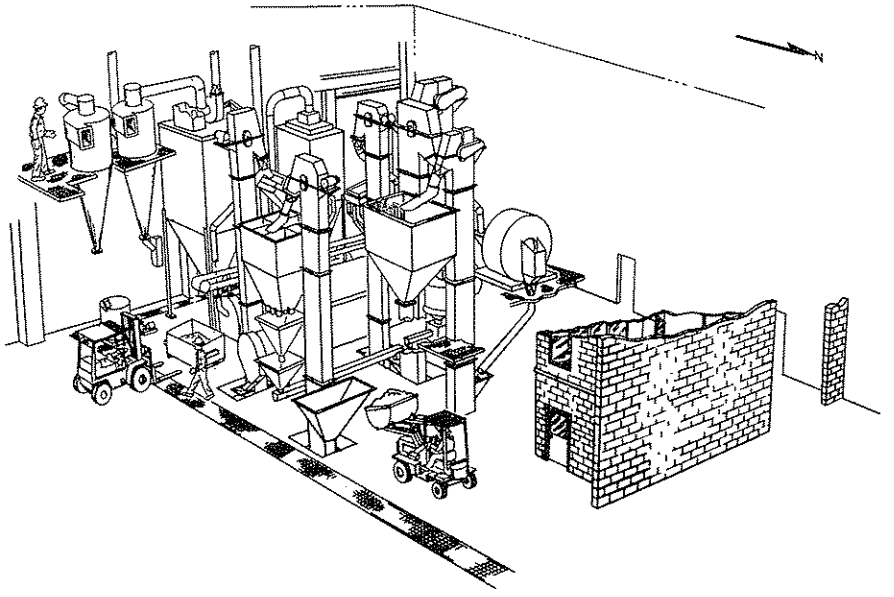

Figure 4. IFDC Bulk-Blending/Granulation Pilot Plant.

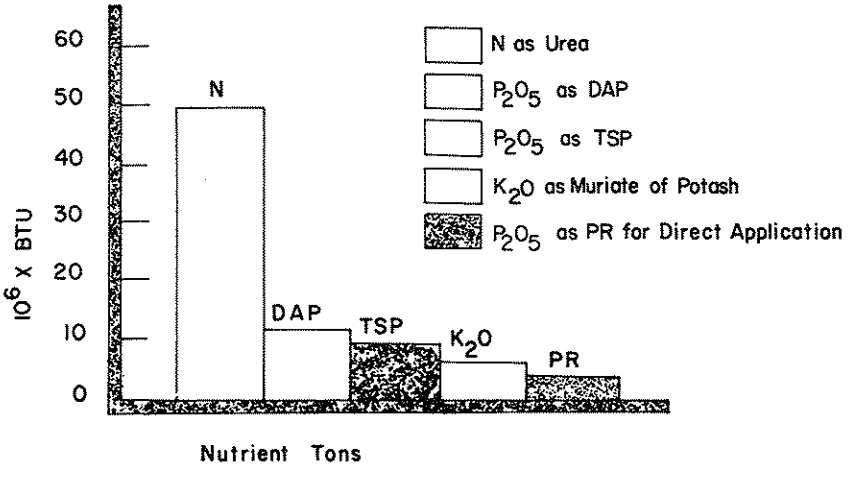

Figure 5. Energy Requirements (Per Ton) of Major Fertilizers.

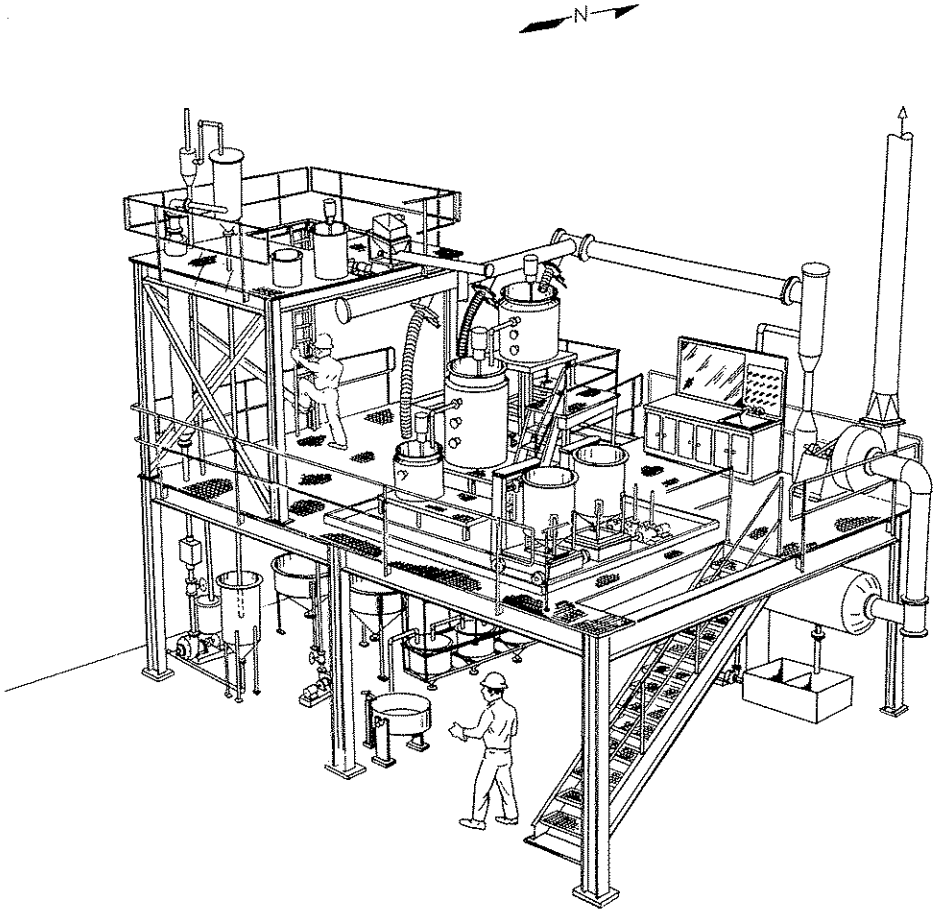

Figure 6. IFDC Wet-Process Phosphoric Acid Pilot Plant.

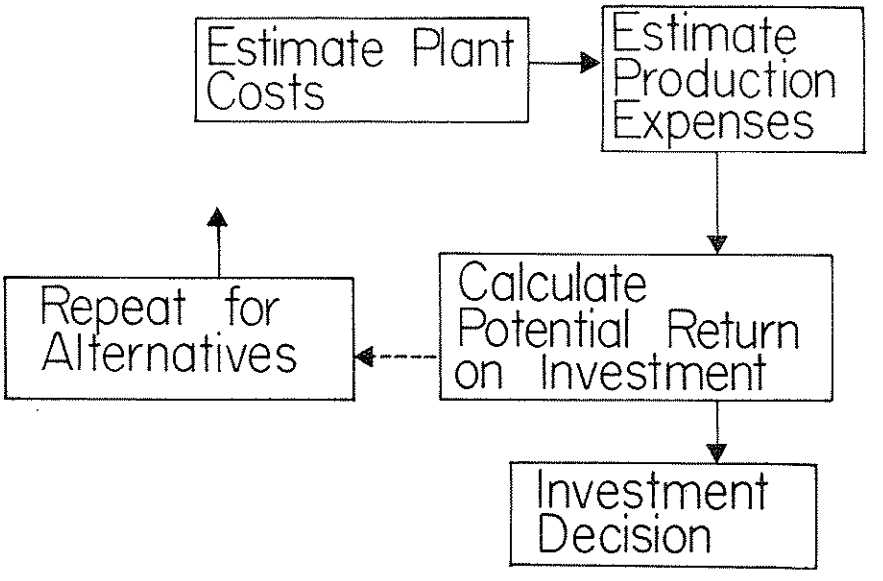

Figure 7. Major Components of IFDC Process Evaluation and Plant Investment System.

EVALUATION OF SOIL PHOSPHATE RESIDUES BY PLANT UPTAKE AND EXTRACTABLE PHOSPHORUS

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Introduction

When phosphate fertilization of soil exceeds plant P removal, the P residues gradually increase, and P concentration in the soil solution usually increases. If P concentration increases above saturation levels for precipitation of crystalline solid-phase phosphates, these new phases will form and subsequently control the P concentration in solution at levels characteristic of the solid-phase phosphates and soil pH. When this condition appears in soils, we need to evaluate the plant P availability of the soil P residues and determine the performance of soil tests to estimate the amount of P that crops can remove before the available P decreases to a level where crops will respond to added P fertilizer. A method of predicting the amount of residual P available to crops is important economically to a farmer and useful for advisory service in planning fertilizer practices.

In this paper we describe the results of experiments designed to measure plant P uptake and its relationship to various parameters of soil P availability. We evaluated soil properties, such as pH, $CaCO_3$ and clay content, as they affected the relationship between P uptake and soil parameters of P availability. These parameters were: soluble P in solution, $NaHCO_3$-soluble P, resin-extractable P, and labile P by isotopic dilution with ^{32}P. This study included 23 alkaline, calcareous soils.

Methods

Greenhouse Experiments

We collected 23 soils from irrigated fields in eastern Colorado. These soils were selected from fields showing high levels of available P. The $NaHCO_3$-soluble P ranged from 37 to 162 ppm of P (Watanabe and Olsen, 1965). None of these soils would be expected to respond to added P fertilizer in the field or greenhouse. We assumed these soils might contain octocalcium phosphate (OCP) in varying amounts and that essentially all the OCP would dissolve with time of cropping. Therefore, we continued cropping until the available soil P decreased to levels where we expected a response to added P (i.e. $NaHCO_3$-P levels < 15 ppm). The number of crops harvested varied from 5 to 8. Total P uptake was summed for 5 to 8 crops. Total P in the roots was also measured because the roots had to be removed in order to continue cropping, and the designed level of available soil P would be reached sooner by the procedure.

Two-kg samples of the soils were placed in 2-liter containers. Nitrogen as $(NH_4)_2SO_4$ was added at 100 ppm initially and 100 ppm 3 weeks later as KNO_3. Iron was added to all soils at 10 ppm as chelate-138. This general procedure was followed for subsequent crops. Sudan grass (Sorghum sudanenses Stapt.) was the first crop of which three cuttings were taken. The roots were separated and harvested for dry weight and total P content after the third cut. Sorghum (Sorghum bicolor L. Moench.) was the fourth crop and barley (Hordeum vulgare, var. Moravian) the fifth and sixth crop. Roots were separated and dry weight and P content determined for sorghum and barley and for each succeeding crop. After the fifth crop, $NaHCO_3$-soluble P was < 12 ppm in soil numbers 3, 7, 10, 11, 12, and 17; thus, cropping was discontinued. The last two crops were sorghum. After the sixth crop, $NaHCO_3$-soluble P levels were < 12 ppm in soil numbers 1, 4, 6, 8, 14, 16, 20, 21, and 22. After the seventh crop, $NaHCO_3$-soluble P levels were < 12 ppm in all samples except numbers 9, 19, and 23. Another crop of sorghum was grown on these three soils.

Following these 5 to 8 crops, two of the four replicates of each soil sample were fertilized with 50 ppm of P as concentrated superphosphate. Another crop of barley was grown, and then dry-matter yield and P content was measured.

Laboratory Experiments

Water-Soluble P--This fraction of soil P was measured in .01 M $CaCl_2$ extracts with a 1-hour shaking period. Soil-to-solution ratios were 20:50 and 10:50. The difference in P concentration between these two extractions was added to the higher P concentration (20:50) (Aslyng, 1954). Soil pH and (Ca + Mg) concentration were measured in each extract solution. The monocalcium phosphate potential (.5 p Ca + pH_2PO_4) and lime potential (pH - .5 p Ca) were calculated from these data using the Debye-Huckel equation to obtain activity coefficients, pH and pK_2 (7.20), to obtain the ratio of H_2PO_4 to HPO_4, and the method of Larsen (1965) to correct for the $CaHPO_4^\circ$ complex ion formation.

Solubility diagrams were constructed for hydroxyapatite (HA, pK_{sp} Y = 113.7), octocalcium phosphate (OCP, pK_{sp} =46.91), and dicalcium phosphate dihydrate (DCPD, pK_{sp} = 6.56) (Adams, 1971; Lindsay and Moreno, 1960).

$NaHCO_3$-Soluble P--The method of Watanabe and Olsen (1965) was used with a 1:20 soil-to-solution ratio and a 30-minute shaking period. With four successive extracts, the same soil sample was extracted four times by the standard procedure, and the amounts extracted were summed.

Resin-Extractable P--The amount of P extracted from the soil was measured using 2 g of Dowex-2 resin to 1 g of soil in 100 ml of water and a shaking time of 24 hours (Amer et al., 1955).

Labile P by ^{32}P Exchange--The amount of P in the soil that undergoes isotopic dilution with ^{32}P was measured using 5 g of soil per 100 ml of water and a 24-hour reaction period (Olsen and Watanabe, 1963).

Results

Some physical and chemical properties of the soils are listed in table 1. All the soils were calcareous

(0.05%-7.96% $CaCO_3$) with a pH > 7 in .01 M $CaCl_2$. Four soils, however, contained < 0.12% $CaCO_3$, and these same four soils showed the lowest pH. Soil texture ranged from a fine sandy loam to a clay loam with clay contents between 19.0% and 44.0%. Organic matter ranged from 1.02% to 2.83%, and it generally increased as clay content increased. The electrical conductivity values (EC) fell within the range considered as normal for good growth with respect to salt levels. Sulfate-S appeared adequate for crop growth. Extractable Fe and Zn levels (DTPA) were 7 to 39 ppm and 1.3 to 52 ppm, respectively. These levels are adequate for crop growth.

Monocalcium Phosphate Potential

Figure 1 shows these values and the lime potential for the 23 soils in relation to the solubility isotherms for Ha, OCP, and DCPD. These data suggest that OCP is present in most of these samples, but solubility is the only criterion indicating its possible presence as a solid-phase calcium phosphate. Soil numbers are shown by each point to identify the sample with data in table 1. Ten soils appeared to be somewhat supersaturated with respect to OCP, 12 soils showed solubility points very near the OCP line, and one soil appeared to be undersaturated with respect to OCP. The latter soil contained the lowest amount of $NaHCO_3$-soluble P. The spread of data points along the OCP isotherm is related to pH variation among the soils.

The fertilizer history for these soils is known in some cases. For example, soil No. 8 has received farmyard manure only for 30 years prior to sampling. Soil numbers 1, 2, 3, 4, 5, 6, 13, 19, and 23 have received P mainly as farmyard manure. In general, the farmers have applied 13-17 ppm per year as concentrated superphosphate or farmyard manure for 20-30 years.

Crop Removal of P

Table 2 shows the P removal by cropping from the soils in the tops, roots, and tops plus roots. Phosphorus removal ranged from 58 to 275 ppm. These amounts indicate the available soil P from present levels to lower levels where a yield response was observed from added fertilizer P. This variation in P uptake seems likely due to different amounts of OCP (and other available residual P forms) that have accumulated in the

soils. Eight crops were grown on three soils and five crops on all soils before P deficiency occurred.

Extractable and Soluble P

Table 2 shows the amounts of extractable P by anion resin and in four successive extractions by the $NaHCO_3$ method. Labile P by isotopic dilution with ^{32}P and soluble P in .01 M $CaCl_2$ extract are also shown in table 2. Resin-extractable P ranged from 64 to 226 ppm. With the resin method, 1, 2, and 3 g resin per gram of soil were compared, and the mean amounts extracted were 124, 128, and 130 ppm P, respectively. Four extractions with $NaHCO_3$ gave values between 61 and 230 ppm. The fourth extract showed values between 5 and 17 ppm with 16 soils showing < 10 ppm. Thus, in the fourth extract, P levels were similar to those of unfertilized soils. Mean values for the first, second, third, and fourth extracts were 74.6, 26.1, 12.1, and 8.8 ppm P, respectively. The labile P (by isotopic dilution with ^{32}P) ranged from 67 to 232 ppm with a mean value of 133 ppm. Similar amounts of P were measured by these three methods in the 23 soils. The average value of these three methods was 13% less than that removed by the crops.

Soluble P in .01 M $CaCl_2$ solution ranged from 12.7 to 107.8 μM. Variations in pH seem to be the major cause of differences in soluble P since OCP mainly controlled the solution P concentration in these soils.

Correlation of P Uptake With Soluble P

Table 3 shows the correlation coefficients and multiple regression coefficients for the relationship between P uptake by crops and soluble P. Multiple regression included soil pH and clay content. Phosphorus uptake correlated significantly with initial P concentration, but it accounted for only 47.6% of the variation in uptake. The correlation increased when uptake was related with the calcium phosphate potential, 0.5 p Ca + pH_2PO_4, or with log soluble P. However, these increases are due partly to the conversion to a log parameter, and the increase in the coefficient, r, was not significant.

Uptake of P also correlated significantly with soil pH, probably because P concentration increased as soil pH decreased. When pH was included with soluble P in a multiple regression, the effect of pH was not

significant. When the percent of clay was included with soluble P in a multiple regression, the correlation with P uptake increased significantly. Inclusion of pH in this latter multiple regression did not increase the correlation significantly.

Figure 2 shows P uptake in relation to P concentration ($r = .690$ and $y = 1.473X + 88.9$). The soil numbers are shown by each data point. To obtain a better understanding of the point spread from the regression line, various soil pairs were selected based on their position above or below the regression line. Soil pairs were selected for approximately equal P concentrations and for pairs where the soil below the regression line had a higher P concentration but a lower P uptake than a mate above the line. Table 4 lists these soil pairs with respect to P uptake, P concentration, extractable resin-P, and various soil parameters. The higher P uptake (points above the regression line) is shown first for each pair.

The higher P uptake of each soil pair in table 4 is correlated best with clay content and resin-P. Table 3 shows, from multiple regression analysis, that the percent of clay increased the correlation between P uptake and soluble P. This increase in correlation seems to occur because P uptake is larger in soils with higher clay contents in comparisons (soil pairs) where soluble P is approximately equal or even greater for the soil with less clay. Additional information concerning the effect of clay content on P uptake is shown in figure 3. The soils were separated into two groups. One group (11 soils) contained over 30% clay, as shown by the upper regression line, $y = 2.82X + 71.4$ with $r = .739$. The second group (12 soils) contained less than 30% clay, as shown by the lower regression line, $7 = 1.74X + 54.9$ with $r = .868$. Both correlation coefficients are significant ($P = .01$).

Two soils (3 and 9) showed a poor fit with the regression lines in figure 3. Soil 3 contains the largest $CaCO_3$ content (7.96%); it has a high pH (7.68) and is probably well buffered against pH changes during crop growth. Soil 9 has a trace of $CaCO_3$ (0.05%) and a low pH (7.07), and it is probably poorly buffered against pH changes during crop growth. These factors could account for the poor fit of these two soils.

The effect on P uptake of small or large amounts of $CaCO_3$ in the soils was examined by dividing the

23 soils into two groups, one with < 1.0% $CaCO_3$ and another with > 1.0% $CaCO_3$. This approach indicated 5 of 8 soils in group one and 5 of 15 soils in group two plotted above the regression line in figure 2. This result indicates a moderate tendency for the plants to extract more P from residual forms with similar initial soluble P levels in soils containing less $CaCO_3$.

Correlation of P Uptake With Quantity Parameters

Table 3 shows the percentage of P uptake variation accounted for and the correlation coefficients of P uptake with resin-P, $NaHCO_3$-P (1 and 4 extracts, and with addition of organic P extracted by the $NaHCO_3$ method), and labile P (by ^{32}P isotopic dilution). The correlation coefficients are higher for all these quantity parameters compared with soluble P in .01 M $CaCl_2$ (intensity parameter). A multiple regression analysis including the percent of clay with resin-P or $NaHCO_3$-P (4) did not increase the correlation coefficients, in contrast with an increase when the percent of clay was included with soluble P in .01 M $CaCl_2$.

Figure 4 shows the relationship between P uptake and resin-P. The individual soils are indicated to assist in identifying soil properties with deviations above and below the regression line. None of the soil properties in table 1 showed a consistent relationship with these deviations. Soils 2, 13, and 23 account for most of the deviation above the regression line. Two of these soils (2 and 23) had soluble P values above the mean of soluble P, and this factor could account partly for their position above the regression line. The resin-P accounted for 87.2% of the variation in P uptake, and the mean value of the resin-P was 14% less than the mean uptake.

Figure 5 shows the relationship between P uptake and $NaHCO_3$-P (4 extracts). The individual soils are shown to aid in identifying soil properties with deviations above and below the regression line. Eight soils contained < 1.0% $CaCO_3$. Five of these plotted above the regression line and none below it. This result suggests a tendency for the plants to absorb relatively more P from the soils with < 1.0% $CaCO_3$ than the P extracted in the $NaHCO_3$ solution. However, four of these five soils plotting above the regression line also

had soluble P values (in .01 M $CaCl_2$) above the mean soluble P. Thus, the soil properties do not clearly indicate a relationship with deviations of points above or below the regression line, but a low $CaCO_3$ content may favor an increased P uptake with respect to the $NaHCO_3$-soluble P. The $NaHCO_3P(4)$ accounted for 87% of the variation in P uptake, and the mean value for $NaHCO_3$-P(4) was 17% less than the mean for P uptake.

Figure 6 shows the relationship between P uptake and $NaHCO_3$-P (1 extract). Correlations of this relationship with soil properties showed similar results with those described for figure 5. The $NaHCO_3$-P(1) accounted for 78.7% of the variation in P uptake, and the mean value for $NaHCO_3$-P(1) was 51% less than the mean for P uptake.

Labile P (by ^{32}P isotopic dilution) showed a correlation with P uptake similar to the relationship with resin-P as shown in figure 5.

Calcium Phosphate Potential Changes With Cropping

Values of this potential after cropping were plotted in figure 7 and identified by soil number. These results are directly comparable with data in figure 1 showing the initial potentials. Phosphorus removal by cropping caused all potentials to move below the OCP isotherm, which suggests that all the OCP dissolved and became available to plants in these soils. Values for three soils (9, 16, 23) are missing from figure 7, but the low $NaHCO_3$-P for these soils after the eighth crop indicates that the potentials would plot near the other soils below the OCP isotherm.

Discussion

Evidence of OCP in Soils

When a soil sample tests higher than 22 ppm $NaHCO_3$-soluble P, we consider this field as high in available P and nonresponsive to fertilizer P additions. Twenty-three soils in this study ranged from 37 to 162 ppm $NaHCO_3$-soluble P. Solubility criteria indicated that 22 soils probably contained OCP and that the P in solution was mainly controlled presently by this solid-phase calcium phosphate. However, the amount of OCP was variable as suggested by the range

in $NaHCO_3$-soluble P and by P uptake variations of 58 to 275 ppm with 5 to 8 crops. A common, yearly fertilizer P addition is about 13 to 17 ppm; therefore, the available P in residues constitutes an important reserve.

We found that all the OCP dissolved during cropping. This material seems to have a very high availability coefficient for plants. Accumulation of fertilizer P residues in this form would appear to be beneficial, since this P is all potentially available to crops. Therefore, methods for estimating the amount of OCP in soils should be useful.

Long-term applications of manure or superphosphate produced OCP in Hoosfield and Broadbalk plots at Rothamsted (Aslyng, 1954; Warren and Johnston, 1967). In the Hoosfield plots both treatments caused formation of a solid-phase phosphate in equilibrium with OCP. In the Broadbalk plots the manure treatment yielded OCP, but the superphosphate treatment produced a less soluble phosphate. At the Barnfield plots, manure plus superphosphate brought about OCP, but a less soluble phosphate formed with the separate treatments (Warren and Johnston, 1962). All these soils were calcareous.

Olsen and Flowerday (1971) reviewed the evidence for OCP in soils. OCP has been observed under three contrasting conditions: (a) by hydrolysis of DCPD in neutral and alkaline soils, (b) by liming acid soils that have a high available-P status initially, and (c) as a result of long-term applications of manure to calcareous soils. These conditions seem to be related to the stability of OCP in alkaline soils. Initially, DCPD forms when monocalcium phosphate (MCP) dissolves and when the fertilizer solution reacts with the soil. Hydrolysis of DCPD produces OCP. Alkaline conditions and a high level of soluble P (also produced from manure applications) apparently favor persistence of OCP. A high rate of adsorption of P on hydrous oxides and clay minerals could limit or prevent OCP formation with low rates of MCP or DCPD application. In general, as P fertilization continues in soils with pH > 6.5 and phosphate reaction products accumulate, the conditions to form OCP become more favorable.

Correlation of P Uptake With Soluble P

In soils containing OCP, soluble-P levels indicate an ample P supply for plants, but we could not ade-

quately predict how much P plants could remove, apparently because soluble P in solution represents only 1%-3% of the plant P uptake or resin-P. By including the percent of clay with soluble P in multiple regression, the combined variables accounted for 62.9% of the variation in P uptake, an increase from 47.6% with soluble P. In other short-term experiments, we have shown that P uptake by roots was greater, as the percent of clay increased, from soil solutions with equal P concentrations (Olsen and Watanabe, 1970). This effect was attributed to diffusion and buffer capacity since both factors increased with clay content. The regression lines in figure 3 indicate that plants absorbed more P, at equal concentrations of soluble P (initial levels), from soils containing higher clay contents.

Although P uptake was highly correlated with resin-P, the mean resin-P was 131 ppm for one group (clay > 30%) and 124 ppm for the other group (clay < 30%) in figure 3. This result implied that the amount of OCP in the soils was not correlated with clay content. Therefore, we assume that clay content improves the correlation between soluble P and P uptake because of its effect on diffusion and buffer capacity.

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Table 1. Physical and Chemical Properties of Soils

Soil Type	Soil No.	pH	Organic Matter %	$CaCO_3$ %	Clay %	EC mmhos/cm	NO_3-N ppm	SO_4-S ppm	$NaHCO_3$-P ppm
Weld cl 1	1	7.54	2.33	2.34	34.5	1.46	38	24	77
Weld cl 1	2	7.55	2.43	2.59	38.3	1.58	59	22	91
Weld cl 1	3	7.68	1.93	7.96	38.0	1.62	26	31	45
Nunn cl 1	4	7.44	2.83	0.53	44.0	1.89	36	16	66
Cass cl 1	5	7.43	2.04	0.48	31.0	2.40	53	46	96
Greeley sa cl 1	6	7.75	1.89	4.24	26.5	4.57	52	95	73
Greeley 1	7	7.69	1.20	1.05	26.5	2.57	24	43	61
Gilcrest sa cl 1	8	7.64	2.02	3.52	28.6	1.95	26	36	83
Gilcrest sa cl 1	9	7.07	1.71	0.05	24.8	3.73	43	27	86
Terry si cl 1	10	7.46	2.36	3.79	35.8	1.10	41	5	37
Weld 1	11	7.78	1.35	5.91	27.0	2.98	49	19	38
Weld 1	12	7.71	1.02	3.76	26.8	1.78	24	19	39
Fort Collins cl 1	13	7.58	2.57	4.37	36.1	0.75	27	8	81
Fort Collins cl 1	14	7.67	1.95	5.22	32.5	0.96	19	13	58
Greeley 1	15	7.53	1.83	0.44	24.4	1.82	38	27	82
Cass 1	16	7.20	2.13	0.40	21.9	2.55	46	21	93
Weld 1	17	7.65	1.35	4.55	27.4	1.50	27	28	49
Gilcrest sa cl 1	18	7.32	2.06	0.11	34.7	1.41	26	19	61
Nunn sa cl 1	19	7.10	2.39	0.05	31.7	2.43	49	38	107
Weld sa cl 1	20	7.48	1.86	1.17	32.2	1.78	36	19	65
Greeley f sa 1	21	7.48	1.76	2.70	26.0	2.01	38	27	91
Greeley f sa 1	22	7.04	1.43	0.07	19.0	0.85	23	8	72
Greeley f sa 1	23	7.48	1.79	6.20	24.7	1.61	50	21	162

Table 2. Phosphorus Removal by Crops, Soluble and Extractable P

Soil Number	P Uptake		Tops and Roots	Extractable P		Labile P	Soluble P
	Tops	Roots		Resin	$NaHCO_3$(4)	^{32}P	.01 M $CaCl_2$
	mg/kg						μM
1	82	49	131	120	135	120	25.0
2	120	83	203	159	153	166	52.0
3	54	48	102	85	89	94	30.0
4	88	52	140	115	110	142	19.4
5	128	74	202	207	160	181	39.5
6	66	39	105	112	112	108	27.3
7	50	37	87	94	94	83	17.2
8	78	56	134	118	128	110	40.2
9	141	82	223	211	150	169	51.9
10	52	35	87	64	61	80	12.7
11	36	22	58	68	69	68	13.8
12	42	31	73	69	67	67	13.6
13	115	71	186	128	137	144	20.7
14	83	45	128	101	99	115	19.3
15	89	75	164	143	127	134	59.2
16	94	68	162	139	139	162	84.7
17	51	37	88	80	84	84	21.8
18	99	54	153	133	106	152	25.1
19	148	94	243	226	192	232	48.0
20	82	46	128	109	108	128	34.2
21	90	57	147	134	132	170	64.1
22	91	74	165	128	108	136	84.2
23	155	120	275	195	239	214	107.8
Mean	88.4	58.6	147.1	127.7	121.7	133.0	39.6

Table 3. Correlation Coefficients and Percentage of Variation in P Uptake Accounted for by Soil Parameters

Factors Correlated	Coefficients		Variation Accounted For, %	
	r	R	r^2	R^2
Uptake vs. soluble P	.690**	-	47.6	-
Uptake vs. (0.5 p Ca + p H_2PO_4)	-.793**	-	62.9	-
Uptake vs. pH	-.624**	-	38.9	-
Uptake vs. log soluble P	-.724**	-	52.4	-
Uptake vs. soluble P plus pH	-	.750	-	56.3
Uptake vs. soluble P plus % clay	-	.792	-	62.7
Uptake vs. soluble P + % clay + pH	-	.830	-	68.9
Uptake vs. resin - P	.934**	-	87.2	-
Uptake vs. resin - P + pH	-	.934	-	87.3
Uptake vs. resin - P + % clay	-	.936	-	87.6
Uptake vs. $NaHCO_3$ - P(4)	.933**	-	87.0	-
Uptake vs. $NaHCO_3$ - P(4) + % clay	-	.934	-	87.2
Uptake vs. $NaHCO_3$ - P(1)	.887**	-	78.7	-
Uptake vs. $NaHCO_3$ - P(1) + organic P	.919**	-	84.5	-
Uptake vs. $NaHCO_3$ - P(4) + organic P	.962**	-	92.5	-
Uptake vs. labile - P (^{32}P)	.943**	-	88.9	-

**(P = .01)

Table 4. Comparisons of Soil Pairs, Selected from Above and Below Regression Line in Figure 1, in Relation to Various Soil Parameters

Soil Pair and Number	P Uptake mg/kg	P Concentration µM	pH	$CaCO_3$ %	Clay %	Resin-P mg/kg
2	203	52.0	7.55	2.59	38.3	159
22	165	84.2	7.04	0.07	19.0	128
4	140	19.4	7.44	0.53	44.0	115
17	88	21.8	7.65	4.55	27.4	80
5	202	39.5	7.43	0.48	31.0	207
8	134	40.2	7.64	3.52	28.6	118
5	202	39.5	7.43	0.48	31.0	207
21	147	64.1	7.48	2.70	26.0	134
5	202	39.5	7.43	0.48	31.0	207
15	164	59.2	7.53	0.44	24.4	143
9	223	51.9	7.07	0.05	24.8	211
16	162	84.7	7.20	0.40	21.9	139
13	186	20.7	7.58	4.37	36.1	128
6	105	27.3	7.75	4.24	26.5	112
13	186	20.7	7.58	4.37	36.1	128
8	134	40.2	7.64	3.52	28.6	118
14	128	19.3	7.67	5.22	32.5	101
11	58	13.8	7.78	5.91	27.0	68
19	243	48.0	7.10	0.05	31.7	226
22	165	84.2	7.04	0.07	19.0	128
18	153	25.1	7.32	0.11	34.7	133
3	102	30.0	7.68	7.96	38.0	85

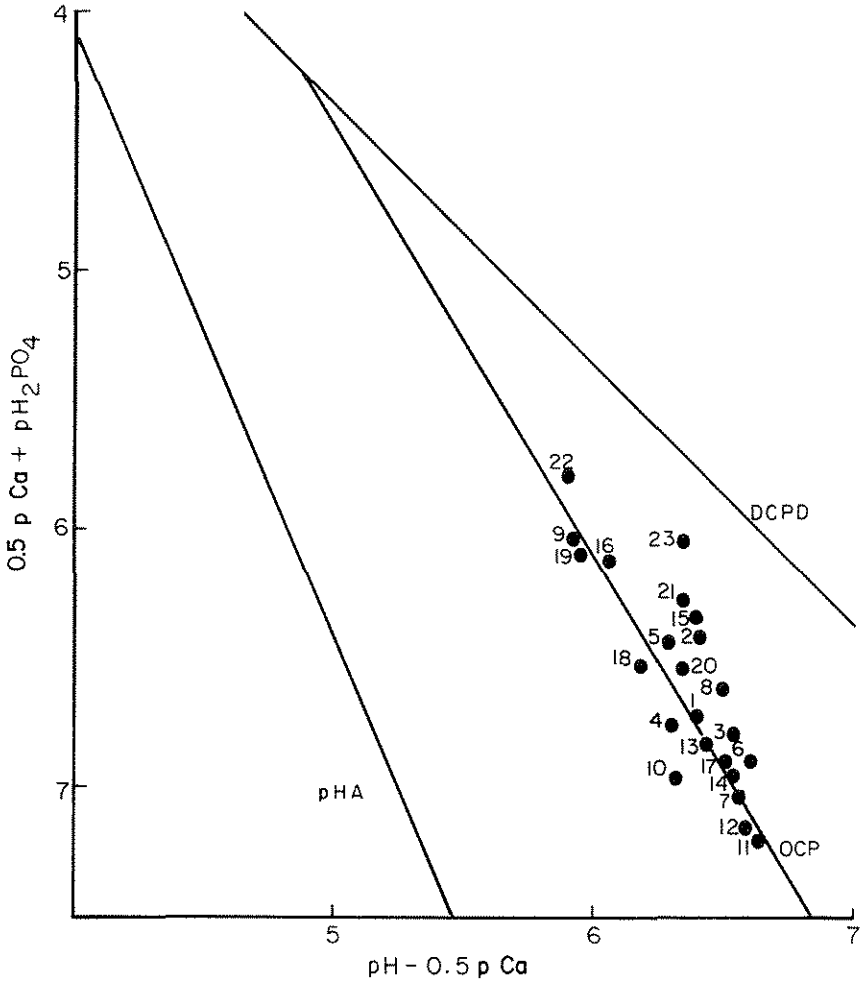

Figure 1. Monocalcium Phosphate Potentials of 23 Soils in Relation to Solubility Isotherms of HA, OCP, and DCPD.

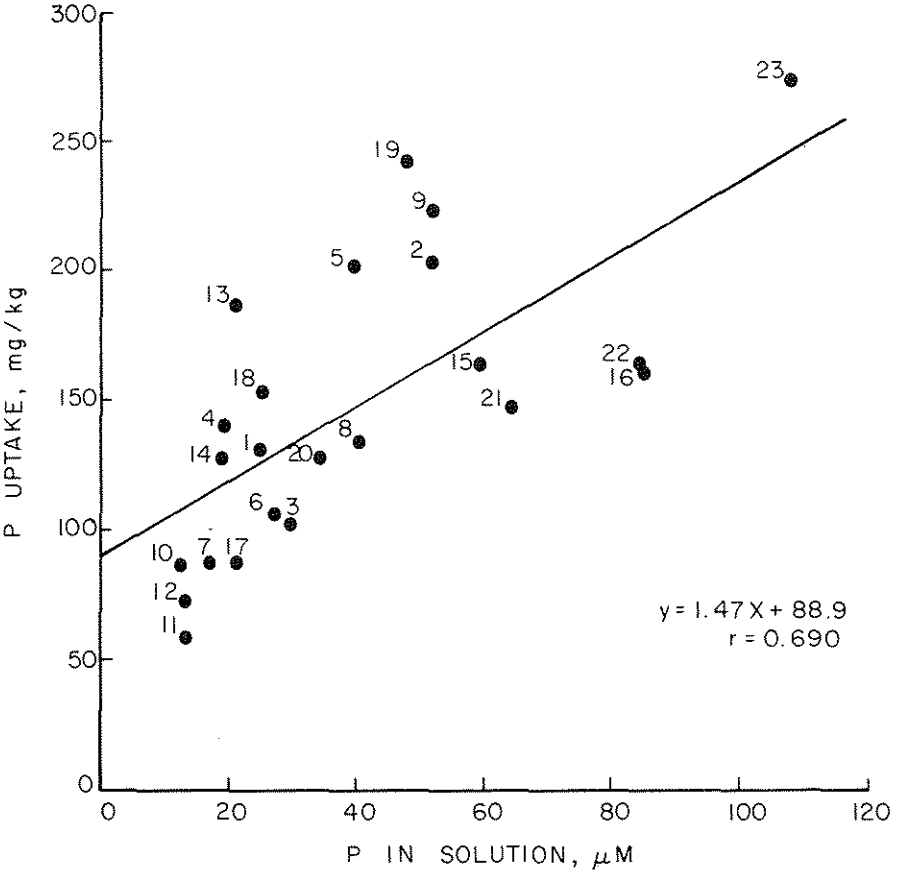

Figure 2. Phosphorus Uptake by Crops in Relation to Soluble P in .01 M $CaCl_2$ Extracts.

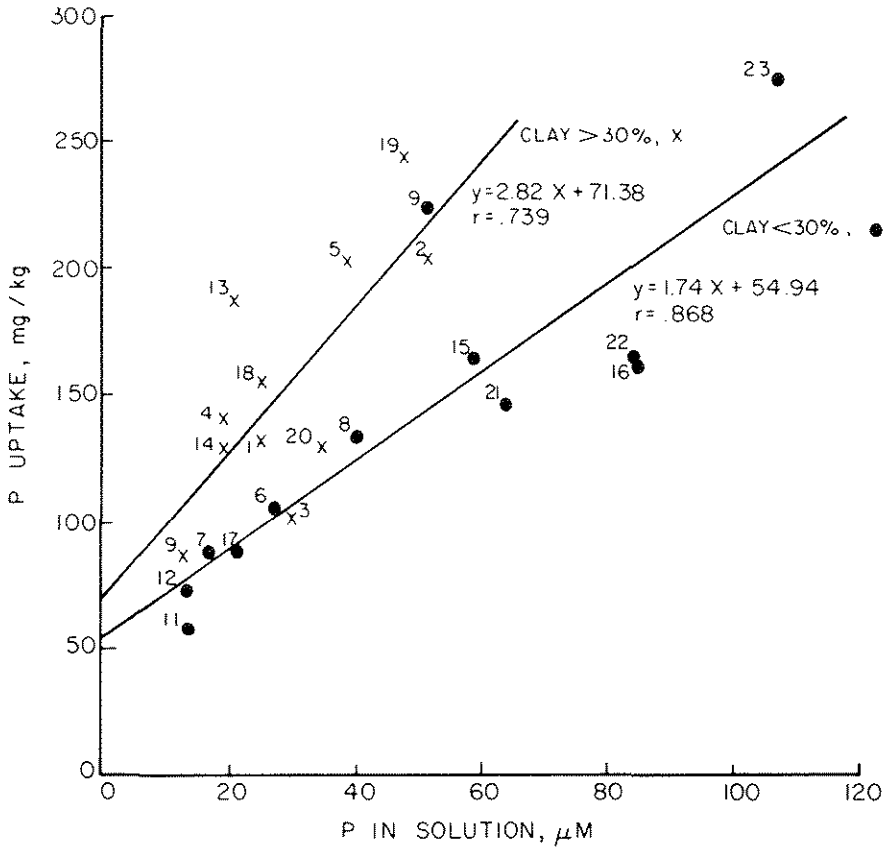

Figure 3. Effect of Clay Content on the Relation Between P Uptake and Soluble P in Solution.

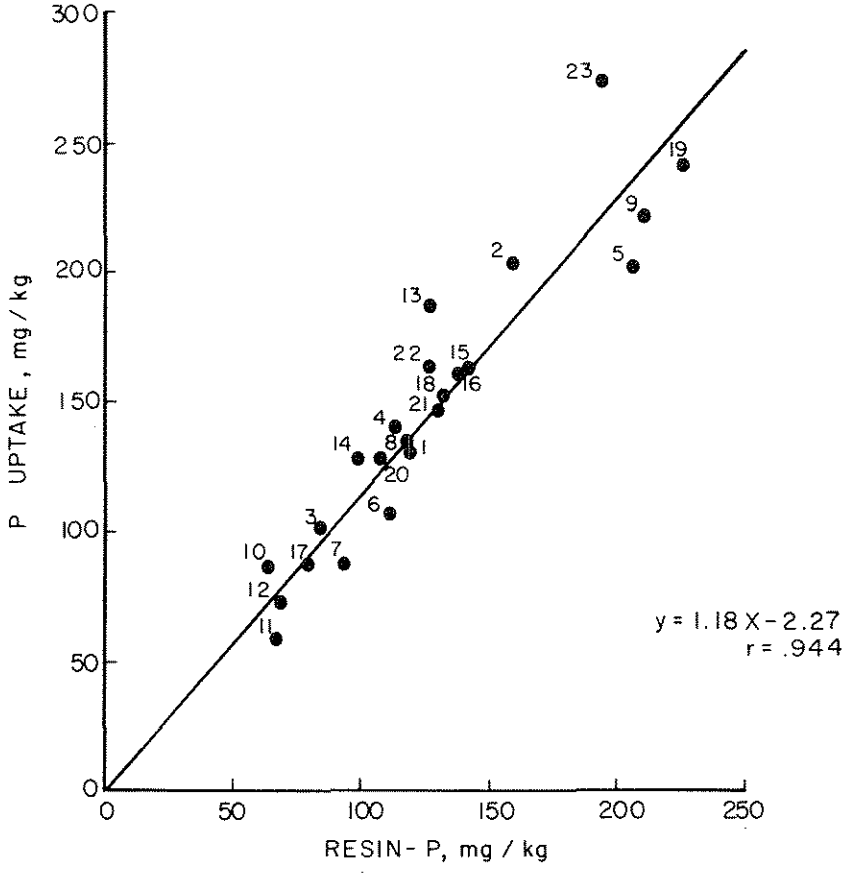

Figure 4. Phosphorus Uptake by Crops in Relation to Resin-Extractable P.

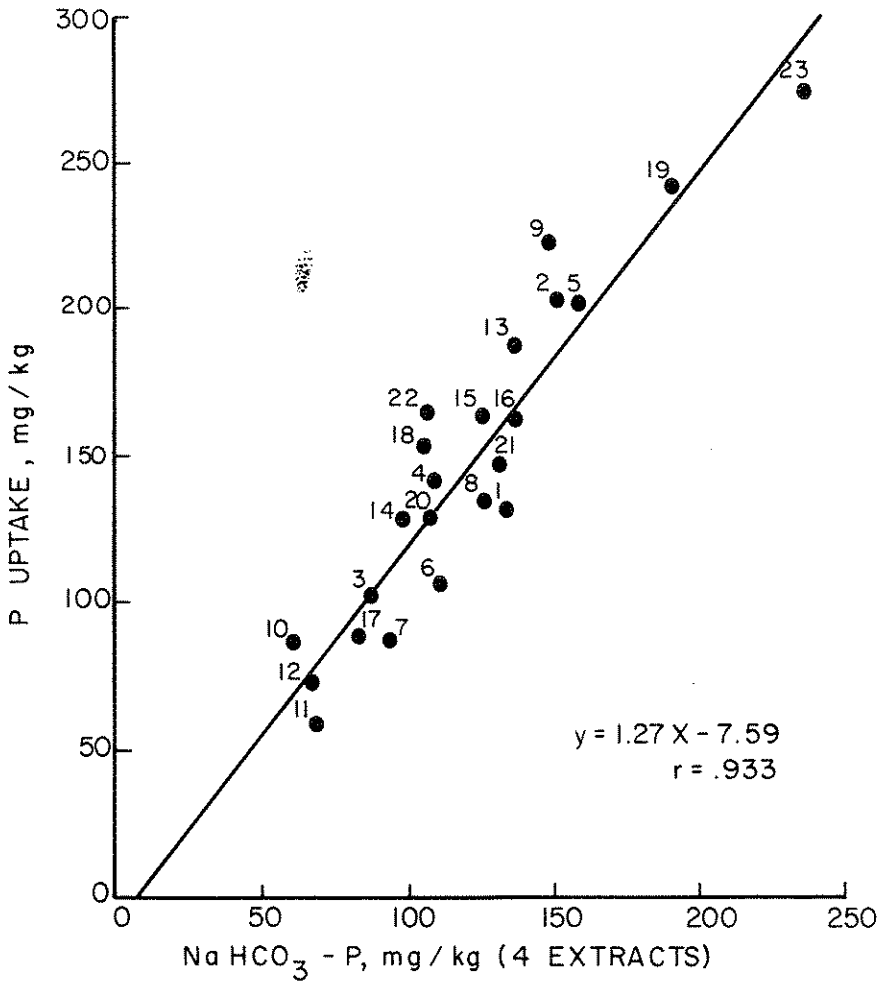

Figure 5. Phosphorus Uptake by Crops in Relation to $NaHCO_3$-Soluble P (4 extracts).

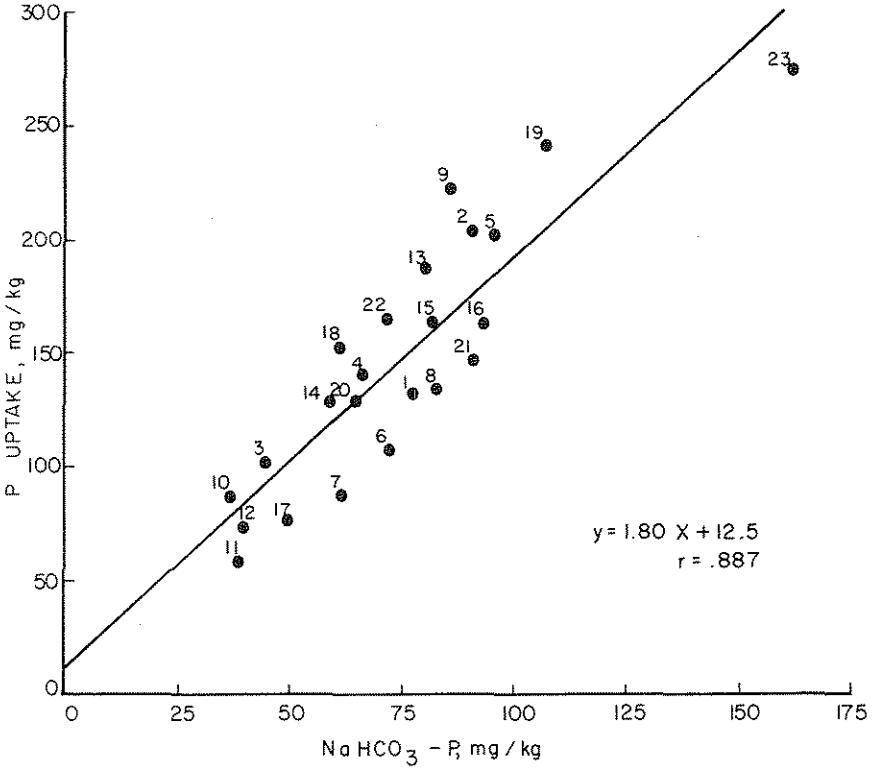

Figure 6. Phosphorus Uptake by Crops in Relation to $NaHCO_3$-Soluble P (1 extract).

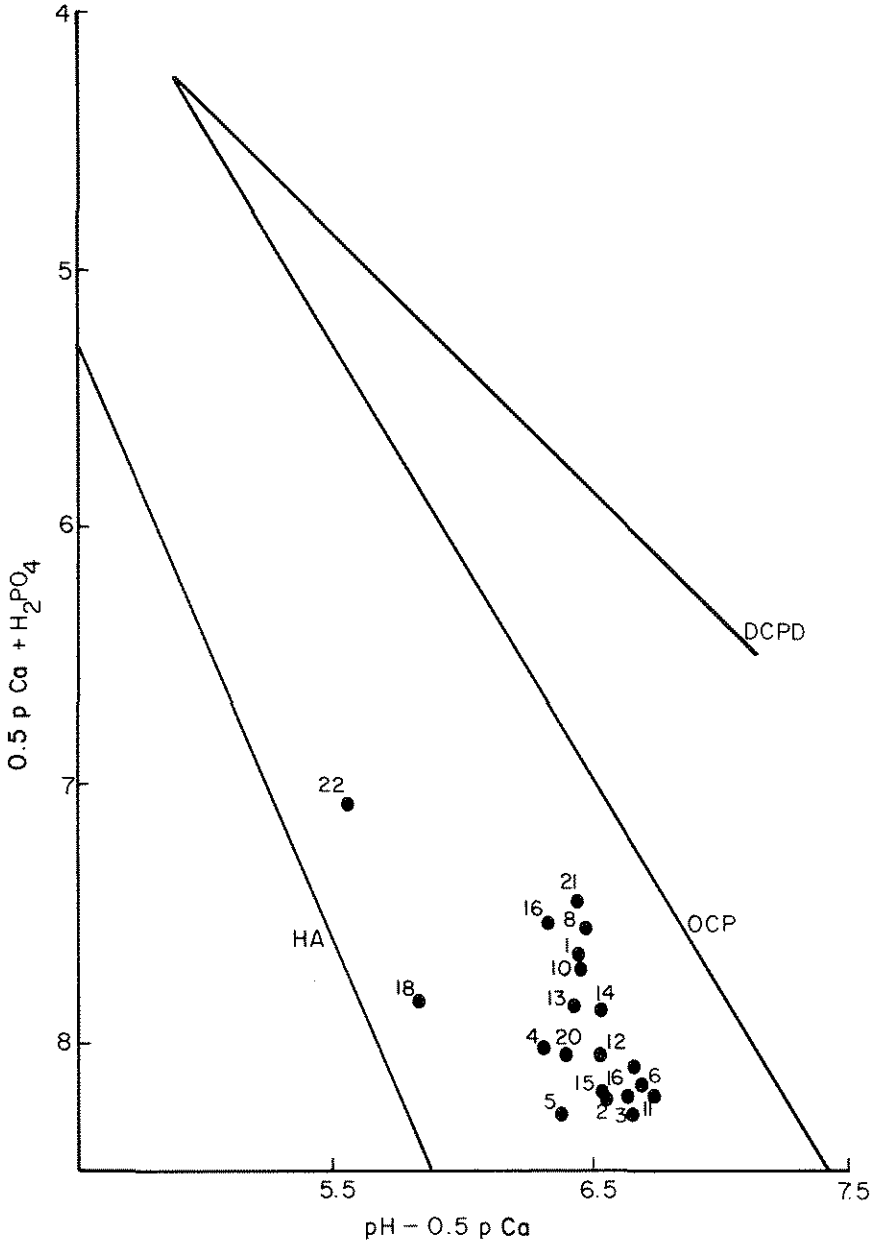

Figure 7. Monocalcium Phosphate Potentials of 23 Soils After Cropping in Relation to Solubility Isotherms of HA, OCP, and DCPD.

MINERALOGY AND REACTIVITY OF PHOSPHATE ROCK

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The phosphatic raw materials of interest to agronomists and the fertilizer industry are a complex assemblage of minerals grouped together under the generic heading of phosphate rock or phosphorite. Phosphate rock is essentially a trade name covering a wide variety of rock types having diverse modes of mineral compositions and textures which make phosphate raw material evaluation a complicated and fascinating field of mineralogical research. According to the American Geological Institute Glossary of Geology (M. Gary, R. McAfee, Jr., and C. L. Wolf, Editors, 1972, p. 535), a phosphate rock is a sedimentary rock composed principally of phosphate minerals; most commonly it is a bedded rock of marine origin composed of microcrystalline carbonate fluorapatite in the form of laminae, pellets, oolites, nodules, and skeletal and shell fragments. Aluminum and iron phosphates are usually products of weathering. Guano-derived phosphorite forms by replacement and characteristically has a complex phosphate mineral composition. The term phosphorite also has been applied to a sedimentary rock composed only of apatite and to an igneous rock containing appreciable apatite.

Most commercial deposits are composed of sedimentary marine phosphate rock, but a significant output also is obtained from alkaline igneous complexes and residual deposits produced by weathering of sedimentary phosphatic limestones and igneous carbonatite complexes. Deposits also occur on elevated stalls of coral limestone which are a combination of replacement deposits and marine origin (Notholt, 1974).

These diverse commercial occurrences have one common characteristic--nearly all of them contain one or more of the apatite group minerals. The differences in chemical composition of this mineral

species (McClellan and Lehr, 1969) are mainly responsible for the equally varied properties of the phosphate concentrates produced. In sedimentary marine phosphate rock, the phosphate rock is usually a carbonate fluorapatite; in igneous deposits the compositions of the phosphates approach fluorapatite. In the residual and replacement deposits, calcium-iron-aluminum and iron-aluminum phosphates are commonly associated with the apatites. In spite of these differences, the grade of commercial phosphate rock continues to be expressed in terms of tricalcium phosphate, $Ca_3(PO_4)_2$, known in the trade as "bone phosphate of lime" or BPL. This term originated at a time when tricalcium phosphate was thought to be the chief constituent of bone and phosphate rock. Later study confirmed that neither bone nor phosphate rock are tricalcium phosphate but have apatite compositions. Because of the wide use of these terms and the present trend toward elemental notation, the conversion factors are included:

$$P_2O_5 = 0.4576 \times BPL$$
$$BPL = 2.1852 \times P_2O_5$$
$$P = 0.1997 \times BPL$$

Commercial phosphate rock generally varies in grade from about 83% BPL to about 60% BPL (38% to 28% P_2O_5). About 85% of the world's annual phosphate rock supply is converted into phosphorus and phosphoric acid intermediates which are consumed as a wide variety of fertilizers.

Mineralogy

Phosphate rocks fall into three broad classifications based on the mineral assemblages found in deposits; these are iron-aluminum phosphates, the calcium-iron-aluminum phosphates, and the calcium phosphates. These three classifications can occur as a natural weathering sequence with the stable iron-aluminum phosphates representing the extreme case of weathering. Weathering also can produce transitional cases where the minerals from the broad classes occur as natural mixtures. The order of increasing economic importance for these classes is iron-aluminum phosphates, calcium-iron-aluminum phosphates, and calcium phosphates.

Iron-Aluminum Phosphates

The most common minerals in this group are wavellite $\{Al_3(PO_4)_2(OH)_3 \cdot 5H_2O\}$, variscite ($AlPO_4 \cdot 2H_2O$), and strengite ($FePO_4 \cdot 2H_2O$). There are a large number of less common iron-aluminum phosphates described in the literature (Moore, 1973).

Large deposits of the common iron-aluminum phosphates occur in several places, notably in Senegal, Liberia, Brazil, and Utah. Although these phosphates are not tractable in normal wet-process phosphoric acid processes, they can be processed to fertilizers in nitric acid processes (Knudsen, 1972) and thermally modified to produce direct application fertilizers (Phosphorus and Potassium, January-February 1975).

Calcium-Iron-Aluminum Phosphates

These phosphates comprise an intermediate class of ores of widely varying composition. The principal minerals are crandallite $\{CaAl_3(PO_4)_2(OH)_5 \cdot H_2O\}$ and millisite $\{(Na,K)CaAl_6(PO_4)_4(OH)_9 \cdot 3H_2O\}$, either mixed together or with either of the other classes of phosphate minerals. Two good examples of this class of phosphates are the Florida leached zone ore (Altschuler et al., 1956) and the Christmas Island zone C ore (Trueman, 1965). Materials in this class are not well suited for sulfuric and phosphoric acid treatments because they yield poor quality products. These ores can be used in nitric acid processes (Knudsen, Ibid.) or thermally treated to produce citrate-soluble direct application fertilizers (Doak et al., 1965).

Calcium Phosphates

Commercial mineral phosphates, known collectively as phosphate rock, have but one property in common; the structural arrangement of their ions identifies them as belonging to the broad category of apatitic minerals. Apatite is the tenth most abundant mineral in the earth's crust and occasionally occurs in massive concentrations of economic importance. Despite their crystal-structure similarity, the compositions of these apatites usually show significant departures from that of fluorapatite, $Ca_{10}(PO_4)_6F_2$, which is a commonly assumed

composition of phosphate rock. These differences in chemical composition are mainly responsible for the variable properties of commercial concentrates.

The principal reason for the various compositional types of apatites readily can be traced to their geochemical origins. Apatitic phosphates occur under all geological settings--igneous, metamorphic, and sedimentary environments. The apatite recovered from igneous and metamorphic rocks, including byproducts from iron ore deposits, has commercial importance but supply only a small fraction of the world market and that mainly for captive production (Kola, U.S.S.R.; Phalaborwa, South Africa; Araxa and Jacupiranga, Brazil).

Sedimentary apatites have been, and no doubt will continue for some time to be, the major source of commercial phosphate. Because of their widely differing modes of occurrence in geological periods ranging in age from Miocene to Precambrian, sedimentary apatites display a wide range of chemical compositions. In their structures, significant amounts of magnesium and sodium usually have been substituted for calcium; up to 25% of their phosphorus may be replaced by carbonate plus fluorine, placing these apatites in a distinct mineral class (McClellan and Lehr, 1969). Examples of the important sedimentary deposits occur in north Africa (Senegal, Togo, Morocco, Algeria, and Tunisia), the Near East (Jordan, Israel, and Egypt), Australia (Queensland), and the United States (Florida, North Carolina, and Idaho).

Characterization Methods

Apatites are the most important source of phosphate in commercial ores; therefore, the characterization methods described in this report will concentrate on these ore types. It is likely that a similar detailed study of the other classes of phosphate minerals would reveal systematic relationships in their compositions and properties.

This presentation summarizes the results of examinations of apatite concentrates from samples of about 600 phosphate rocks that represent almost all of the commercial phosphate deposits in the world. The examinations were made by chemical analysis, X-ray

powder diffraction, petrographic microscopy, infrared spectroscopy, and electron microscopy (see Lehr et al., 1967; McClellan and Lehr, 1969 for details on methods). Although a complete characterization of an apatite might require the results of all of these techniques, a rapid, preliminary characterization suitable for broad classification of samples can be made using a combination of X-ray and petrographic techniques.

The relationships that were established during these examinations are helpful in selecting suitable methods of processing a phosphate ore from a particular deposit. The results show also that samples of ore from each major geographical deposit differ enough among themselves to require mineralogical characterization as well as chemical analysis for selection of the optimum processing conditions for a particular sample.

Chemical Characterization

Of the more than 25 elements that have been reported to occur in fluorapatites usually from igneous or metamorphic sources (table 1), most are present in insignificant amounts. Previous work (McClellan and Lehr, 1969; Lehr et al., 1967) has shown that the compositions of apatites in sedimentary phosphate rocks can be closely approximated by their contents of CaO, Na_2O, MgO, P_2O_5, F, and CO_2.

The compositions of some representative apatites in terms of these six major constituents are shown in table 2. More extensive reports of analytical data collected on the apatites in phosphate rocks have been reported in the earlier related publications.

The electrostatic unbalance resulting from the substitution of planar CO_3^{-2} for tetrahedral PO_4^{-3} is only partially corrected by substitution of F^{-1} in vacant oxygen sites so that a coupled monovalent cation substitution for calcium is necessary to maintain electrostatic neutrality. In sedimentary apatites that formed in marine environments, the cations most likely to replace calcium are sodium Na^{+1}, magnesium Mg^{+2}, and potassium K^{+1}.

Gulbrandsen (1966) found a statistical correlation between the sodium content and degree of CO_3^{-2}

substitution in apatites from Wyoming and a similar coupled substitution in an apatite from Ontario, Canada. Ames (1959) synthesized carbonate apatites under simulated marine conditions, except without fluorine, and found a coupled substitution in which sodium replaced about 10% of the calcium at the highest level of carbonate substitution. Simpson (1964) reexamined Ames' precipitation system with consideration of both potassium and sodium and confirmed the coupled substitution of alkalies for calcium as CO_3^{-2} replaced PO_4^{-3}. He reported sodium contents of 2%-3% Na_2O at the highest level of carbonate substitution (5.6% CO_2), but potassium showed little tendency to replace calcium (the ionic radius of K^{+1} is more than 30% larger than that of Ca^{+2}, whereas Na^{+1} is less than 5% smaller than Ca^{+2}) and even suppressed the substitution of CO_3^{-2} for PO_4^{-3}. Simpson reported also that the degree of substitution of CO_3^{-2} and Na^{+1} increased with rising pH of the precipitation medium. Neither Ames nor Simpson, however, considered the effects of magnesium and fluorine on the composition of carbonate apatites. LeGeros and Trautz (1965, 1967) reported evidence of magnesium and sodium in their synthetic carbonate apatites and also showed the effects of F^{-1}, Mg^{+2}, and CO_3^{-2} on the crystallinity of the apatites.

The studies of apatites in phosphate rocks showed that the replacement of calcium by sodium and magnesium is systematic (figure 1). These findings were determined by analyzing many apatite concentrates for Na_2O, MgO, K_2O, CaO, P_2O_5, and CO_2. To minimize interferences from clays, feldspars, and other accessory minerals, each apatite was dissolved rapidly in warm dilute (3 N) HCl, and the filtrates were analyzed to obtain the composition of the apatite.

Analyses of similar data in previous work by McClellan and Lehr (see bibliography) have shown that the compositions of sedimentary apatites can be expressed by the generalized formula:

$$(Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{0.4x}F_2$$

in which a ranges to about 0.35, b to 0.14, and x to 1.26 moles/formula weight. Apatites with these compositions are normally called carbonate apatites or francolites (McConnell, 1938). This will be discussed in more detail in a later section.

X-Ray Characterization

The X-ray patterns of the francolites (carbonate apatites) that occur in commercial phosphate rocks are typically apatitic with slight shifts in peak positions and intensities that indicate changes in the cell parameters. Changes in the unit-cell a-axis with changes in carbonate content were reported by Maslennikov and Kavitskaya in 1956, but no relationship was established between variations in the unit-cell dimensions of the apatites and their carbonate content. Later work by Smith and Lehr (1966) and others (Lehr et al., 1967; McClellan and Lehr, 1969; McClellan and Gremillion, 1976) clearly established that a relationship does exist (figure 2) and defined it in terms of variations in crystal chemical compositions.

The method for determining unit-cell parameters of apatites has been described in detail and will be summarized here. Basically, the procedure is to take a sample of the minus 200-mesh concentrate, free of rhombic carbonates, and to record a high resolution powder diffraction pattern over the range of 25° to 54° 2θ for copper radiation. An internal standard of spinel ($MgAl_2O_4$) is used to correct for any goniometer misalignment. The cell parameters are calculated using an iterative least-squares computer program that solves a truncated Taylor series by the Newton-Raphson method for two unknowns. The apatite reflections used have the following Miller indices: 002, 300, 302, 310, 222, 312, 213, 321, 410, 402, and 004. The standard errors of the cell constants are usually 0.003 Å. The greater range of observed variations in a indicates that substitutions have a greater effect along this direction. Work by Kreidler (1967) has confirmed that the a direction in apatites shows the greatest change when substitutions are made for PO_4.

Apatites with a-values between 9.376 and 9.421 Å are not francolites but belong to a series of fluorhydroxyapatites. Apatites from island deposits (Christmas, Nauru, Ocean) and carbonatites fall in this series, which is complex and quite different from the francolite-type apatites found in the more common deposits. True hydroxyapatites are rare minerals. One occurrence is at Holly Springs, Georgia, and the others are usually modern organically derived materials (bones, teeth). Such materials usually have a-values

of 9.421 or greater, depending on composition and can have very complex crystal chemical structures.

Petrographic Characterization

The carbonate apatite in most sedimentary phosphate rocks often is submicrocrystalline (0.02 μ to 0.2 μ) and occurs in a number of varieties of complex aggregates. Among the common textural forms are oolitic and ovulitic pellets of marine precipitates; angular to subrounded polished grains of clastic phosphorite; replacement forms of phosphatized shell, coral, and fecal pellets; and fossil vertebrate bones and teeth. The major accessory minerals (quartz, carbonates, feldspars, and heavy minerals) usually are present as discrete free mineral grains. Apatite particles frequently are stained by occlusions of finely divided iron oxides and carbonaceous matter; in addition, colorless occlusions of clays, opaline silica, and diatom frustules are occasionally present. Although petrographic examination provides much useful information on the accessory minerals and the distribution of other impurities, the submicroscopic sizes of the carbonate apatite crystals preclude detailed optical study (only a mean index is measured); and the occluded colloidal impurities can be a source of error in measurements of refractive indices. Fortunately, the refractive index of an apatite concentrate is remarkably uniform, even though the aggregates may be present in several textural forms.

Because of the homogeneity of the apatite in most sedimentary ores, a carefully measured mean refractive index of a carbonate apatite can be used as the basis for an estimate of the degree of carbonate substitution. This refractive index relationship for 36 apatite samples of variable crystal chemical composition is shown in figure 3. Microscopic examination provides a reliable measure of most apatite compositions in 5-10 minutes but is less precise than the more complicated X-ray procedure.

Textural descriptions, which include the size, shape, and arrangement of the mineral constituents as well as the method of consolidation, are important parts of a complete evaluation of any phosphate rock and represent data which can be obtained only by petrographic analysis.

Statistical Evaluation

The chemical compositions and unit-cell a parameters of nearly 600 francolites have served as a data base for developing the statistical correlations of the crystal chemical compositions with the physical and chemical properties of these francolites. The best statistical models developed have established the relationships that exist between the francolite composition (as indicated in the general empirical formula) and the a-axis dimension of the unit cell, the most sensitive indicator of variations in crystal chemical composition.

Sedimentary apatites have been shown to have compositions that can be represented quite adequately by the series with end-member empirical formulas of:

$Ca_{10}(PO_4)_6F_2$ $Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{0.4x}F_2$
(fluorapatite) (francolite types)

These correspond to the chemical compositions shown in table 3.

These apatite compositions can be derived by the statistical models shown below, which have been found to be quite satisfactory for routine analytical appraisals of concentrates.

Statistical models:

$$\underline{a}_{obs}\ (\text{X-ray}) = 9.374 - 0.024\ \{x/(6-x)\}$$
$$(Na)_a = 1.327\ \{x/(6-x)\}$$
$$(Mg)_b = 0.515\ \{x/(6-x)\}$$

In the above equation, the $\underline{a}_{obs}$ term is the crystallographic a-axis dimension determined by the X-ray diffraction procedure, and $x/(6-x)$ is the CO_3:PO_4 mole ratio.

Compositions of typical phosphate rock samples from several well-known deposits are shown in table 4. These examples show a range of apatite compositions but do not cover the entire range of possible compositions indicated in table 3.

The most significant features revealed by this comparison are the relative increases in amounts of F, Mg, Na, and CO_2; the decrease in P_2O_5 content; and the nearly constant CaO content, as the degree of carbonate substitution in the apatite increases. Note also that all these compositions contrast sharply with the fluorapatite composition that is commonly assumed for phosphate raw materials.

Factors other than mineralogy which significantly affect the utilization of phosphate rocks are texture, accessory minerals, and weathering. The sedimentary rocks that dominate commercial production have a wide range of textures (consolidated and unconsolidated) but generally have simple mineralogies. Texture is of prime importance in evaluating the potential of a phosphate rock for beneficiation, because liberation of the ore from the gangue is significantly affected by this property. The type and amount of accessory minerals present in a rock also are important. Of particular importance are the carbonate minerals (calcite and dolomite), silica, silicates, iron-aluminum oxides and hydroxides, and evaporites. The acid-soluble accessories can degrade the chemical and physical properties of the products as well as increase the consumption of process reagents. The acid-insoluble components can erode the processing equipment making their use expensive. Chloride-containing evaporites present significant corrosion problems that can damage equipment and will require expensive specialized processing units.

Weathering can significantly change the texture of any rock type (igneous, sedimentary, and metamorphic). The results can be either beneficial or nonbeneficial. For example, weathering can improve the texture by liberating the phosphate from the matrix, as in the case of the removal of carbonates. On the other hand, weathering can result in changes in the phosphate mineralogy in which the apatite is converted to the less desirable iron and aluminum phosphates. It can change the mineral assemblage in such a way that the accessories become more soluble in the processing technology and introduce problems with the product. In any case, weathering can cause very significant changes in the physical and chemical properties of a phosphate rock to such an extent that the rock may be rendered economical or uneconomical, depending on the type and extent of alteration.

Utilization of Characterization Data

The characterization data on phosphate rocks describe the minerals present, their relative proportions, and the manner in which they are combined. In this section, the application of the results from the detailed study of a phosphate rock will be demonstrated in a few practical examples. This discussion will demonstrate how such characterization data can be incorporated into plans to put a phosphate rock into its best use from an economic, technical, and environmental point of view.

Beneficiation

The basic beneficiation technology of phosphate rock processing consists of two steps, liberation and separation, the second step being impracticable if the first has not been successfully accomplished. Liberation is usually accomplished by size reduction or by particle detachment. The object of liberation is to form free particles of the desired minerals so that separation can be accomplished. Frequently, locked particles of two or more mineral phases are formed, and liberation is measured in terms of degree, the percentage of free particles of a mineral occurring in relation to the total of that mineral occurring in free and locked particles.

In some phosphate rocks, the grade of the ore is high enough that size reduction is all that is needed to prepare the ore for commercial use. More often this reduction is followed by a sizing operation (screening or classification) to remove the over- and undersize materials. In some cases, this sizing is sufficient to remove enough free gangue minerals to produce commercial concentrates. In others, a concentration step (washing, flotation, calcination, magnetic separation, electrostatic separation) is required. Phosphate rocks are normally concentrated by some combination of washing, flotation, and calcination.

A knowledge of the texture and mineralogy of an ore is indispensable in making recommendations for beneficiation. This information can indicate the type and amount of grinding, if any, a particular ore requires; knowledge of the distribution of the free and occluded gangue minerals can be used to predict what the properties of the finished concentrate will be

and when the beneficiation treatment has reached a productive end.

Some examples of the application of characterization data are the possible direct chemical extraction of phosphate from lightly ground, silica-cemented ores or their use directly in an electric furnace; the nitric acid extraction of phosphate from ores very high in occluded iron oxides to take advantage of the low nitric acid solubility of the undesirable iron minerals; the direct acidulation of ores containing up to 10% free carbonates where extra acid consumption is cheaper than a complex removal scheme for the carbonates; and the use of low energy attrition washing to remove clay hulls from the surface of phosphate particles.

The application of different beneficiation technologies with varying results is clearly demonstrated in table 5, where concentrates of equal grade are shown to contain variable amounts of apatite and gangue minerals. Being able to anticipate the properties of the final product can be extremely useful in selecting a technology for processing a concentrate.

The variables in phosphate ores necessitate that fertilizer processes cannot be conveniently interchanged simply because the ores have the same grade. The beneficiation of a phosphate rock should be a custom-designed process. Significant problems develop when a beneficiation technology developed on one ore is borrowed and applied to a different ore with no consideration for their mineralogical and textural differences.

The compositions of several phosphate rocks selected to represent both well-known sources and some more recently developed deposits are compared in table 4. For simplicity, only the major constituents have been included. All of these samples were selected for demonstration purposes only and may or may not represent current production from these locations but do illustrate the variations that exist in commercial concentrates.

Direct Application

One of the simplest uses of phosphate rock is as a direct application fertilizer. Rocks for this use are

usually finely ground and applied as dry powders, slurries, or easily water-degradable granules. Variations in the composition of the apatites in phosphate rocks can significantly affect their agronomic performance.

The effectiveness of a phosphate rock used as a direct application fertilizer has been demonstrated by greenhouse and field tests and has been shown to be directly related to the degree of substitution of carbonate for phosphate in the apatite structure. The degree of carbonate substitution influences the solubility of the apatite in the rock and controls the amount of P_2O_5 which is released under soil conditions. Because rock solubility can be related to agronomic effectiveness, the potential value of a phosphate rock to be used as a direct application fertilizer can be determined by subjecting the rock to laboratory dissolution tests. These laboratory tests can be made very quickly and can be used as a guide in the selection of rocks to be used in greenhouse or field tests.

The use of phosphate rocks as direct application fertilizers has not always enjoyed the popularity that it does today. One reason for the slow growth in popularity was the confusing way in which earlier workers expressed rock reactivity. The practice of using the ratio of solvent soluble P_2O_5 to rock grade as a guide to agronomic effectiveness was misleading and caused many experimenters to make erroneous judgments when buying phosphate rocks to be used as direct application fertilizers. The poor choice of rocks led to poor agronomic results which, of course, discouraged further use of rocks for this purpose. Phosphate rock solubility is dependent primarily upon the type of apatite which is in the rock, and the bulk of the phosphatic materials from a given deposit consists of one type of apatite whose chemical and physical characteristics are relatively uniform for that deposit. However, field studies show that the amount of apatite in an ore deposit varies considerably from one spot to another, and the rock grade of concentrates produced also will vary. Thus, it is clear that reactivity of a rock from a given deposit should not be related to a changeable factor such as rock grade, as is often done.

Recognizing this problem, it was proposed (Lehr and McClellan, 1972) that rock solubility be expressed

in terms of the grade of the apatite, which is relatively consistent for a given deposit, instead of rock grade, which is not consistent. Thus, when using neutral ammonium citrate as an extractant (AOAC) method, it was proposed that the absolute citrate solubility (ACS) of a rock be expressed as follows:

$$ACS = \frac{\text{AOAC Citrate-Soluble } P_2O_5(\%)}{\text{Theoretical } P_2O_5\ (\%) \text{ of Apatite}}$$

One disadvantage of relying upon the absolute citrate solubility (ACS) as a guide to rock selection is that the method is dependent upon the use of sophisticated X-ray analyses and computer programs which may not be available to many laboratories that are attempting to evaluate phosphate rocks as direct application fertilizers.

Recent investigations (McClellan et al., 1976) have shown that unadjusted solubility data obtained on rocks with a minimum P_2O_5 grade of a least 20% can be used as effectively as ACS values as a guide to rock selection. By using unadjusted data, the need for X-ray and computer analyses can be eliminated.

The three solvents which are most commonly used throughout the world in making solubility tests are neutral ammonium citrate, 2% citric acid, and 2% formic acid, but because of the diverse chemical nature of these solvents, the amount of P_2O_5 which can be extracted from any given rock may differ by more than 200% when tested in different solvents. Differences of this magnitude may be the source of confusion and misinterpretation when making comparative evaluations of phosphate rocks which are being considered for use as direct application fertilizers. As a partial solution to this problem, statistical models were devised correlating the soluble P_2O_5 (%) of 36 phosphate rocks in neutral ammonium citrate, 2% citric acid, and 2% formic acid with variations in unit-cell $\underline{a}$ dimensions (figure 4). These models (table 6) can now be used to convert the solubility data of an apatite in one solution to its statistically equivalent solubility in either of the other two solutions. In addition, the statistical models can be used to predict the potential effectiveness of a phosphate rock as a direct application fertilizer by comparing it to the crystallographic or solubility data of a rock of known agronomic value.

When the data were carefully analyzed, it was noted that rocks from certain geographic areas had solubilities in 2% citric and 2% formic acid solutions that did not vary randomly from the line-of-best-fit. They had solubilities significantly lower than what would be predicted on the basis of their apatite compositions. It was assumed that the rocks were deficient in some component, which influenced the solubilities in the test solvents. It was found that addition of small amounts of soluble aluminum increased the solubility of phosphate rocks in 2% citric acid and decreased solubilities in neutral ammonium citrate and 2% formic acid (compare figures 4 and 5). The reason for these changes is not fully understood, but it is thought to be related to the ability of aluminum to complex fluorine which is evolved during dissolution.

The presence of soluble aluminum in 2% citric acid and 2% formic acid solutions improved the correlation coefficients and the standard errors of the estimate of the solubility data to such an extent that they predicted solubility results with about the same degree of reliability as a neutral ammonium citrate solution (table 7). The solubility data obtained from these acid solutions containing soluble aluminum show a wide range of values as well as improved statistical correlation.

The main conclusions to be drawn from measurements of reactivity are that laboratory measurements of reactivity only indicate the agronomic potential of a rock and should be used as an approximate guide in ranking rocks for further testing. Also, the presence of soluble impurities in phosphate rocks that interfere with apatite reactivity measurements should be recognized. A method for removing most of these impurities is to extract a quantity of the rock with the desired solvent to solubilize the impurities. This liquor is recovered and discarded. The extracted solids are then used as the phosphate rock sample for evaluation. Laboratory tests of this method have shown it to be effective in minimizing soluble interferences such as calcium, magnesium, iron, and aluminum.

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Table 1. Substitutions in the Apatite Structure

Fluorapatite
$Ca_{10}(PO_4)_6F_2$

Constituent Ion	Substituting Ion
Ca^{+2}	Na^{+1}, Sr^{+2}, Mn^{+2}, K^{+1}, U^{+4}, Mg^{+2}, RE^{+2}, $^{+3}$ (lanthonons and yttrium)
P^{+5}	C^{+4}, S^{+6}, Si^{+4}, As^{+5}, V^{+5}, Cr^{+6}, Al^{+3}
F^{-1}	OH^{-1}, Cl^{-1}
O^{-2}	F^{-1}, OH^{-1}

Francolite
$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{0.4x}(F,OH)_2$

Table 2. Some Typical Compositions of Apatite in Phosphate Rocks

Source	CaO	MgO	Na_2O	P_2O_5	CO_2	F
Western U.S.	55.6	0.13	0.26	40.1	1.59	4.1
Tennessee, U.S.	55.5	0.24	0.47	38.7	2.71	4.3
Florida, U.S.	55.5	0.36	0.72	37.1	3.95	4.6
Morocco	55.4	0.43	0.85	36.3	4.5	4.7
North Carolina, U.S.	55.3	0.52	1.04	35.3	5.4	4.8
Tunisia	55.2	0.60	1.20	34.7	5.7	4.9

Table 3. Variation in Apatite Mineral Composition

Constituent (%)	Fluorapatite: (x = 0)	Francolites: $x/6 - x \cong 0.30$[a]
CaO	55.6	55.1
P_2O_5	42.2	34.0
CO_2	0	6.3
F	3.77	5.04
Na_2O	0	1.4
MgO	0	0.7

a. Maximum degree of substitution found and predicted for francolite-type apatites.

Table 4. Chemical Composition of Selected Phosphate Rocks

Deposit Source	BPL Grade	Constituent, % CaO	P_2O_5	F	CO_2	R_2O_3	Na_2O	MgO	SiO_2
Central Florida	72	48.9	33.4	3.9	3.0	2.12	0.53	0.29	4.5
North Carolina	66	48.5	30.2	3.7	5.5	1.14	0.83	0.54	2.1
Morocco	70	51.6	32.1	4.1	5.3	0.55	0.79	0.43	1.4
Gafsa, Tunisia	63	48.3	28.8	3.4	6.3	1.22	1.30	0.59	1.8
Taiba, Senegal	82	51.2	37.4	4.0	1.7	2.06	0.20	0.06	2.9
Togo	80	52.3	36.6	4.0	1.8	1.78	0.27	0.11	1.8
Spanish Sahara	78	51.9	35.8	3.8	2.3	1.17	0.40	0.14	3.4
Angola	81	51.3	37.2	4.0	2.1	1.47	0.62	0.10	1.5
India (Udaipur)	88	54.2	40.1	3.6	0.7	0.7	0.11	0.04	1.2
Jordan	74	53.0	33.8	4.0	4.9	0.34	0.51	0.18	5.6
Israel (Oron)	68	52.7	31.3	3.6	7.5	0.45	0.75	0.24	0.2
Sechura, Peru	66	46.5	30.2	2.9	4.4	1.65	1.85	0.50	3.2
Algeria	63	49.3	29.0	3.6	7.4	0.70	2.00	0.81	1.0

Table 5. Modal Analysis of Minerals in Selected Phosphate Rocks[a]

Source	Weight, % Apatite[b]	Gangue Minerals
Western U.S.	79.8	20.2
Tennessee, U.S.	82.7	17.3
Florida, U.S.	86.3	13.7
Morocco	88.2	11.8
North Carolina, U.S.	90.7	9.3
Tunisia	92.2	7.8

a. Calculated assuming all samples contain 32% P_2O_5.
b. Weight, % apatite = actual P_2O_5/theoretical P_2O_5 (100% apatite).

Table 6. Conversion Factors for Phosphate Rock Solubility Data

	Neutral Ammonium Citrate, Soluble P_2O_5, %	2% Citric Acid, Soluble P_2O_5, %	2% Formic Acid, Soluble P_2O_5, %
Neutral Ammonium Citrate, Soluble P_2O_5, %	1	1.159N + 3.0	2.546N - 0.866
2% Citric Acid, Soluble P_2O_5, %	0.863C - 2.6	1	2.196C - 7.5
2% Formic Acid, Soluble P_2O_5, %	0.393F + 0.34	0.455F + 3.4	1

Where: N = P_2O_5 soluble in neutral ammonium citrate, %
C = P_2O_5 soluble in 2% citric acid, %
F = P_2O_5 soluble in 2% formic acid, %

Source: McClellan et al., 1977

Table 7. Solubility Versus Unit-Cell a

Solubilizing Solution	Correlation Coefficient, r	Standard Error of Estimate, s	Equation for y
Without Aluminum			
NAC	0.915	2.162	340.58 (9.376-X)
2% C.A.	0.854	3.748	428.81 (9.393-X)
2% F.A.	0.733	10.976	822.99 (9.376-X)
With Al-Acetate			
NAC	0.913	2.116	330.32 (9.377-X)
2% C.A.	0.945	2.346	473.46 (9.393-X)
2% F.A.	0.902	3.641	527.53 (9.382-X)

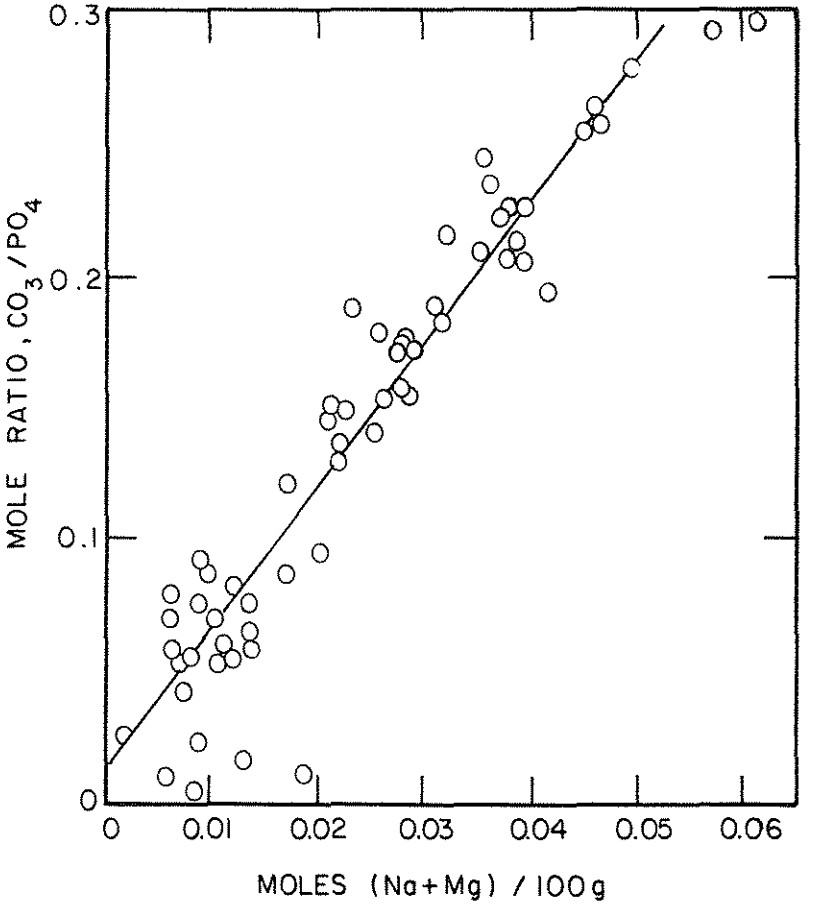

Figure 1. Relationship Between Sum of Magnesium and Sodium Contents of Apatite and Degree of Carbonate Substitution.

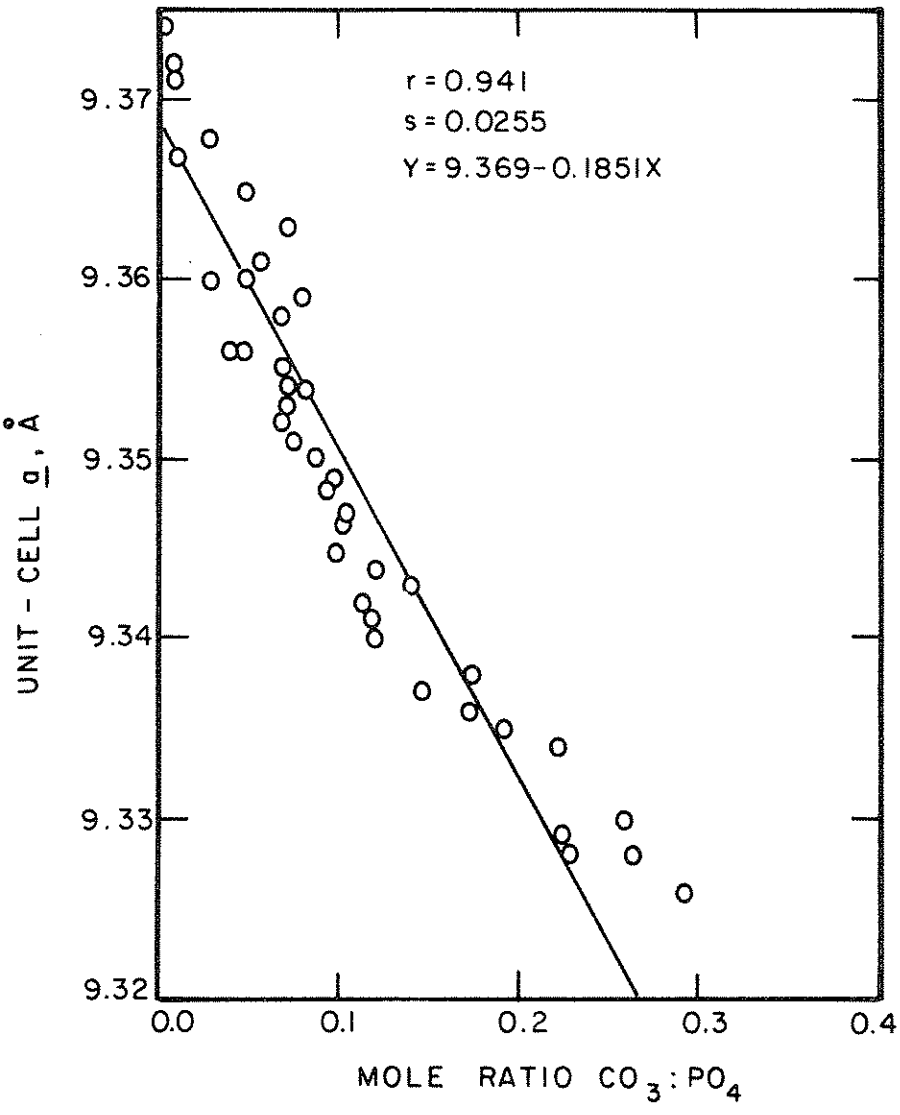

Figure 2. Relationship Between Unit-Cell a Dimension and Mole Ratio of CO_3:PO_4 in Apatite.

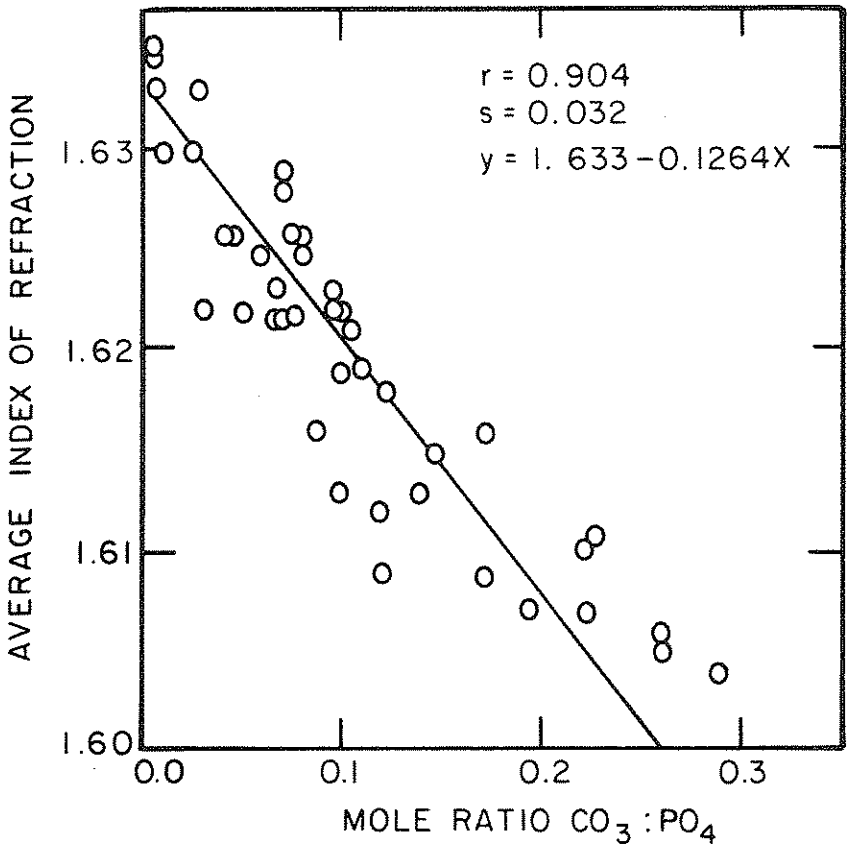

Figure 3. Relationship Between Index of Refraction and Mole Ratio of CO_3:PO_4 in Apatite.

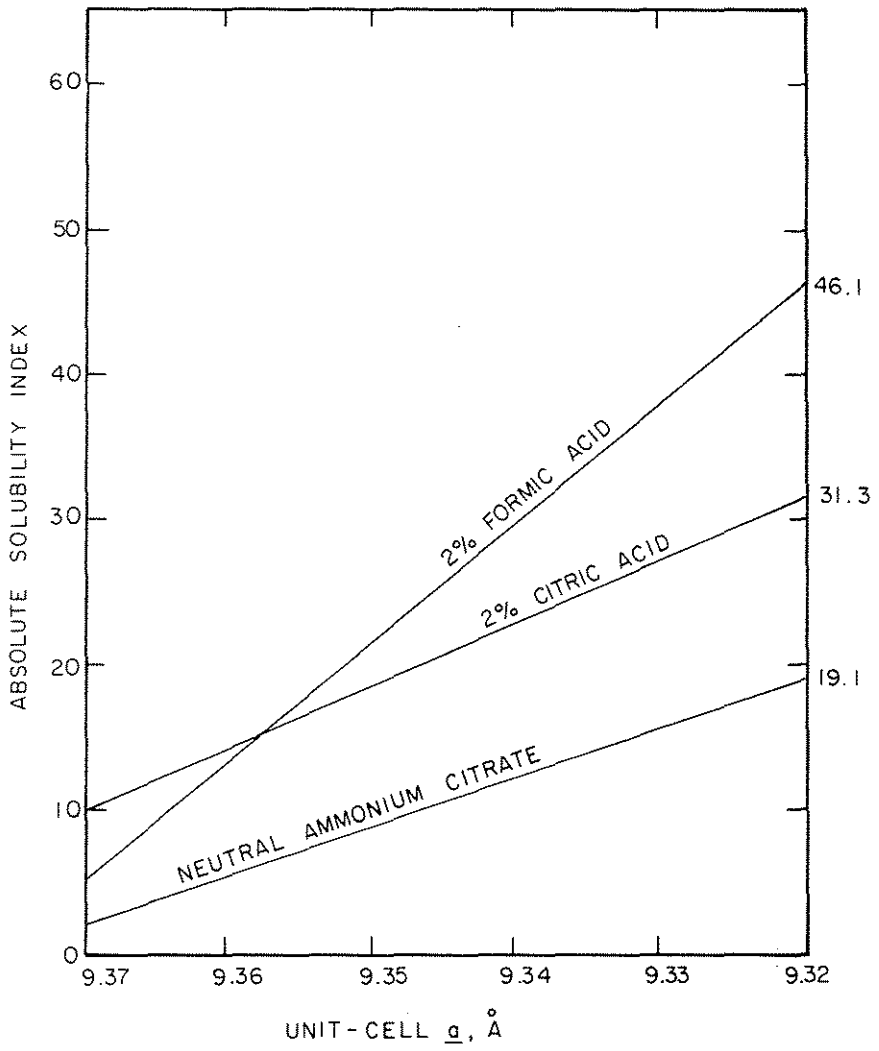

Figure 4. Relationship Between Absolute Solubility Index and Unit-Cell a, Å (No soluble aluminum added).

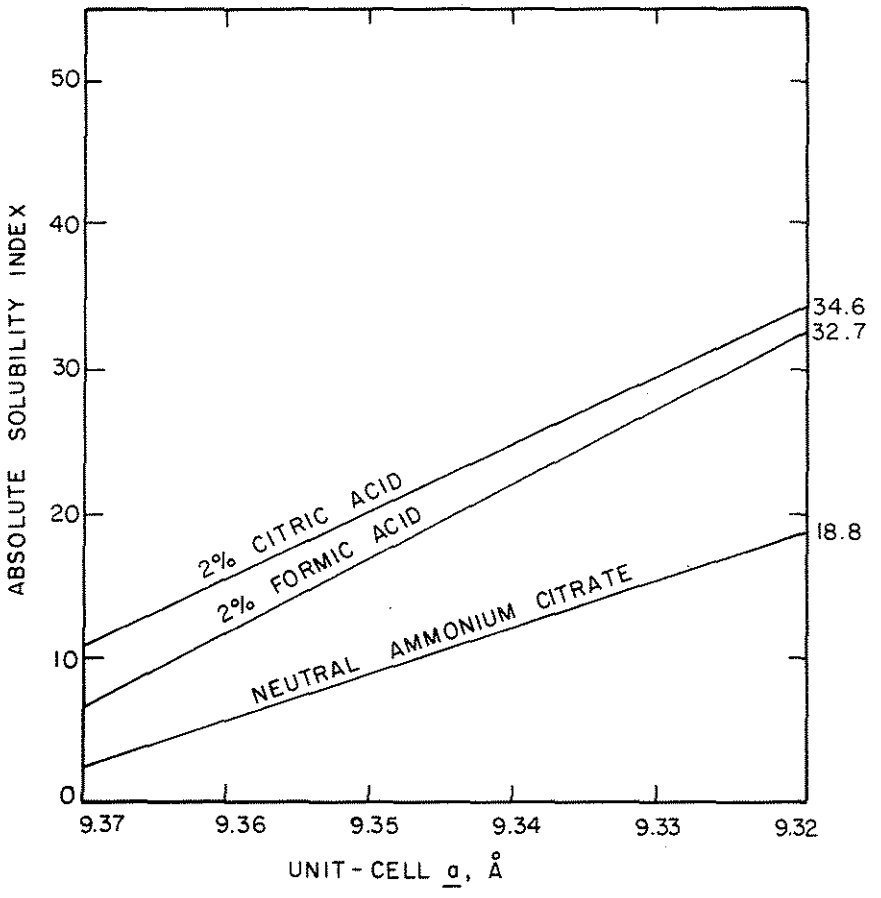

Figure 5. Relationship Between Absolute Solubility Index and Unit-Cell a, Å (Soluble aluminum acetate added to extracting solution).

PHOSPHATE FOR DIRECT APPLICATION--PHOSPHORITE CHARACTERIZATION AND FIELD SURVEY OF FIELDS IN THE NEGEV, ISRAEL

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Abstract

A field survey and phosphorite characterization of several phosphate fields of the northern Negev, Israel, were carried out to evaluate the suitability of these phosphate reserves for direct application. The survey was made of the following fields: Hor Hahar, Ein Yorke'am, Ein Akrabim, and Arad.

The survey and characterization included: determination of total P_2O_5, P_2O_5 soluble in 2% formic and citric acids, separation of apatite, partial chemical analysis of apatites, X-ray diffraction, and microscopic and scanning electron microscopic examinations.

The relatively high solubility of the bottom layer of the Arad phosphate field in 2% formic acid (F.A.), around 60% and above, and the moderate to high degree of carbonate substitution for PO_4 in the apatite lattice place this ore in the category of very reactive phosphorites which are useful for direct application. It was proved that this phosphate bed is highly homogeneous permitting a continuous mine to be established.

Introduction

The Mediterranean phosphorite deposits form a belt extending from Morocco in the west to Iraq and Turkey in the northeast, which passes through the southern part of Israel, the Negev, where about 30 phosphate fields have been discovered. Only one-half of these fields have been geologically explored. Four fields in the northern part of the Negev are being exploited with full facilities of mining, beneficiation, and transportation.

Because of the growing interest in rock phosphate as a fertilizer, an intensive survey of some phosphate

fields located in the northern Negev was carried out. The main purpose of the survey was to determine the best location of a continuous and homogeneous mine as a source of phosphate for direct application.

Experimental

Sampling

Samples were collected from drilling sites and open trenches, based on previous geological surveys carried out by the Israel Geological Survey and the Negev Phosphates Company geologists. For a general layout of the phosphate fields of the area surveyed, see figure 1.

Most of the samples were collected along a line approximately parallel to the synclinal axis. Locations of sample sites in the Arad phosphate field are given in figure 2. The sampling sites cover the whole length of the Arad field.

Each sample used in the survey represents a composite sample of a phosphate bed at a given location. Altogether about 250 composite samples were collected and analyzed.

Methods

1. Solubility determinations:
   - 1.1 2% formic acid solubility - according to the Common Market standard method:
     A mixture of 1-g sample, ground to pass 200-mesh, in 100 ml of 2% formic acid (F.A), agitated in a Wagner apparatus for 30 minutes at room temperature. The suspension was immediately filtered, and soluble P_2O_5 was determined.
   - 1.2 2% citric acid solubility - identical to the above, except for the nature of the solvent.
2. Apatite isolation:
   Apatite samples were extracted according to Silverman's method (1952).
3. Unit cell dimensions of the apatites were determined by X-ray diffraction powder method.
4. Phosphate fractions in the size range of minus 35-plus 200-mesh from the top and bottom layers of

Arad phosphate were extracted with Silverman's solution in order to isolate the apatite particles. The isolated apatite materials were checked with a scanning electron microscope (JEOL type). Phosphate samples were inspected and correlated under a polarizing microsope (Universal Zeiss).

5. Natural calcite from a pure limestone outcrop in the Arad area was ground together with a high-grade phosphate sample taken from the bottom layer of Arad phosphorite. The total P_2O_5 was lowered gradually by adding varying amounts of calcite. The solubilities of the phosphate samples thus prepared were determined.

Results

In samples taken from the Hor Hahar, Ein Yorke'am, and Ein Akrabim fields, the solubilities in 2% formic acid of the first and third layers are in general below 55% of total P_2O_5, whereas the solubilities of the second layer are in the range of 13.7%-19.4% P_2O_5 or 50%-63% of total P_2O_5 (see tables 1, 2, and 3).

The solubilities of samples from the Arad phosphate field are as follows (see table 4):

Top layer: 2.2%-5% P_2O_5 or 12%-20% of total P_2O_5 in 2% citric acid. 9.4%-11.4% P_2O_5 or 41%-50% of total P_2O_5 in 2% formic acid.

Bottom layer: 8.3%-13.8% P_2O_5 or 30%-41% of total P_2O_5 in 2% citric acid. 15.8%-20.4% P_2O_5 or 56%-63% of total P_2O_5 in 2% formic acid.

Apatite samples from the top and bottom layers of Arad phosphate are similar in chemical composition, carbonate substitution, and solubilities in 2% formic and citric acids (see table 5). The P_2O_5 content of the apatites is in the range of 34.2%-35.4%, and the average is 34.75%. About 4% CO_2 replaces P_2O_5 in the apatite lattice. As shown by SEM microphotographs, most of the apatite particles from both layers are porous and of biogenic origin (see figures 3 through 8).

Apatite samples from the third layer of the Hor Hahar and Ein Yorke'am fields have a lower carbonate replacement and lower solubilities than apatite samples from the second layer, as can be seen from table 6.

The addition of calcite to a high-grade phosphate sample (containing 93%-95% apatite), taken from the bottom layer, decreases the apparent solubility in 2% formic acid (see table 7).

Scanning electron microscope examinations show that the porous apatite pellets from the Arad phosphate field are of biogenic origin (see figures 3 through 8).

Discussion

From the results obtained and tests carried out in the past, it may be concluded that the first and third layers of the Hor Hahar, Ein Yorke'am, and Ein Akrabim fields do not fulfill the requirement of solubility of 55% of total P_2O_5 in 2% formic acid; their solubilities are lower than the accepted values in the Common Market. The solubility of the second layer is generally in the vicinity of 55% of total P_2O_5 and higher, and this layer can be considered as a large potential reserve for phosphate for direct application.

From the apatite parameters of Hor Hahar and Ein Yorke'am (see table 6), it appears that differences in apatite composition contribute to the differences in the apatite solubilities.

Since the variations in apatite parameters of samples taken from the second layer of Hor Hahar and Ein Yorke'am are small, it can be concluded that the variations in formic acid solubilities of rock samples of this layer are mainly due to variation in rock composition, especially in calcite content.

As shown in the results, the apparent solubility of a high-grade sample of the bottom layer is depressed by adding varying amounts of calcite, which, however, does not change the properties of the phosphorus component, the apatite. Similar results have been observed in our previous investigations, using samples from other phosphate fields (Axelrod and Greidinger, 1979). The presence of carbonate minerals, especially calcite, depresses the apparent solubility in all of the accepted test methods: 2% formic acid, 2% citric acid, and neutral ammonium citrate.

Large differences in solubilities between the top and bottom layers of the Arad field have been reported

above. As shown above, the apatites in these two layers are practically identical with respect to general composition and properties. Carbonate ion is substituted in the apatite lattice to the same degree, and the principal chemical constituents are very similar. The apatites of both layers are of biogenic origin. The apatite component is therefore not responsible for the differences in laboratory solubility tests. The mineralogical compositions of the two layers differ from each other by the calcite content: a much higher amount of calcite is found in the top layer. As stated above, the presence of carbonate mineral, and especially calcite, decreases considerably the apparent solubilities in chemical laboratory tests. By leaching out the calcite from top layer samples, solubilities as high as those from the bottom layer are obtained (see table 5). On the other hand, by adding sufficient amounts of calcite to a high-grade sample taken from the bottom layer, solubilities characteristic of the top layer can be achieved.

The solubility of the bottom layer of the Arad field conforms to the Common Market accepted standard, i.e., 56%-63% of total P_2O_5 in 2% formic acid. These solubility values have been found over the total length of the field, about 4.5 km, with almost no variations. In order to prove the homogeneity of the ore, the apatite from the samples from various locations was extracted, and its properties were investigated. The chemical composition of the isolated apatites is very similar, and the carbonate ion substitution is almost uniform, with unit cell dimension $\underline{a}$ varying in the range of 9.330-9.340 Å. SEM examination showed that the porous apatite particles are of biogenic origin. The data collected permit the conclusion that the bottom layer phosphate is highly homogeneous over the entire length of the field and that the mined ore will be uniform, reactive material suitable for direct application.

Despite the depression of the apparent solubilities in laboratory measurements, we do not know how the presence of carbonate affects the solubility of apatite in acidic soils and its availability to field crops under conditions of constant acidity. Repeated cycles of leaching, as they may occur in the soil, can be expected to leach out the carbonate minerals and leave calcite-free reactive apatite to supply the phosphorus to the nutrition cycle.

Conclusions

On the basis of the data collected, the bottom layer of the Arad phosphate field is proposed as the best potential site in the northern Negev for operating a homogeneous and continuous mine to supply phosphate for direct application. The biogenic origin, the relatively high solubility, and the moderate to high degree of carbonate substitution for PO_4 in the apatite lattice place this ore in the category of very reactive phosphates which are useful for direct application.

The second phosphate layers of the Hor Hahar, Ein Yorke'am, and Ein Akrabim fields can be considered as another large reserve which needs some more investigation and characterization.

Acknowledgment

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Table 1. Hor Hahar Phosphate Field--Solubility of Phosphates (Common Market Standard Method)

Drill No.	Layer	Total P_2O_5, %	Soluble P_2O_5 in 2% F.A. mg P_2O_5	Soluble P_2O_5 in 2% F.A. % of Total P_2O_5	Soluble P_2O_5 in 2% C.A. mg P_2O_5	Soluble P_2O_5 in 2% C.A. % of Total P_2O_5
K-154	1st	25.6	121/125	47.3/48.8	63	24.6
K-157	1st	23.4	108/112	46.1/47.8	60	25.6
K-163	1st	27.4	152	55.5	77	28.1
K-172	1st	24.3	120/121	49.4/49.7	55	22.6
K-179	1st	28.5	164/165	57.5/57.9	84	29.5
K-183	1st	27.4	147/150	53.6/54.7	73	26.6
K-187	1st	25.6	129/132	50.4/51.5	60	23.4
K-150	2d	21.9	131/134	59.8/61.2	n.d.	n.d.
K-154	2d	26.0	137/141	52.7/54.2	68	26.1
K-157	2d	28.1	140/141	49.8/50.9	71	24.4
K-163	2d	27.2	161/166	59.2/61.0	58	21.3
K-171	2d	25.5	157/161	61.5/63.1	61	23.9
K-172	2d	28.4	168/171	59.1/60.2	92	32.4
K-176	2d	25.7	153/155	59.5/60.3	53	20.6
K-179	2d	30.0	175/175	58.3/58.3	90	30.0
K-183	2d	25.6	148/150	57.8/58.6	74	28.9
K-187	2d	29.5	170	57.6	97	32.9
K-157	3d	26.9	89/90	33.1/33.4	n.d.	n.d.
K-187	3d	n.d.	110		63	

Table 2. Ein Yorke'am Phosphate Field--Solubility of Phosphates (Common Market Standard Method)

Drill No.	Layer	Total P_2O_5, %	Soluble P_2O_5 in 2% F.A. mg P_2O_5	Soluble P_2O_5 in 2% F.A. % of Total P_2O_5	Soluble P_2O_5 in 2% C.A. mg P_2O_5	Soluble P_2O_5 in 2% C.A. % of Total P_2O_5
E.Y.N.2	Main	29.2	126/127	43.1/43.5	n.d.	n.d.
K-203	Main	27.9	122/126	43.7/45.2	n.d.	n.d.
E.Y.N.2	1st	32.9	106/109	32.2/33.1	44	13.4
K-206	1st	25.5	128/131	50.2/51.4	58	22.7
E.Y.N.2	2d	32.4	190/194	58.6/59.8	114	35.2
E.Y.N.8	2d	32.6	190	58.3	116	35.6
K-201	2d	29.0	175	60.3	n.d.	n.d.
K-203	2d	28.7	160/162	55.7/56.4	86	29.9
K-205	2d	29.3	172/175	58.7/59.7	95	32.4
K-206	2d	26.0	156/157	60.0/60.4	84	32.3
E.Y.N.2	3d	32.5	140	43.1	73	22.5
K-201	3d	29.2	122	41.7	59	20.2

Table 3. Akrabim Phosphate Field--Solubility of Phosphates (Common Market Standard Method

Drill No.	Layer	Total P_2O_5, %	Soluble P_2O_5 in 2% F.A. mg P_2O_5	Soluble P_2O_5 in 2% F.A. % of Total P_2O_5	Soluble P_2O_5 in 2% C.A. mg P_2O_5	Soluble P_2O_5 in 2% C.A. % of Total P_2O_5
A'in-4	Main	29.0	120/123	41.4/42.4	n.d.	n.d.
A'in-4	1st	26.0	129/130	49.6/50.0	63	24.2
A'in-4	2d	32.7	177/180	54.1/55.0	105	32.1
A'in-6	2d	31.1	158/159	50.8/51.1	n.d.	n.d.
A'in-7	2d	32.0	165/168	51.5/52.5	n.d.	n.d.
A'in-9	2d	32.5	174/177	53.5/54.4	105	32.3
A'in-4	3d	33.8	145/148	42.9/43.8	79	23.4
A'in-9	3d	33.1	161/162	48.6/48.9	96	29.0

Table 4. Arad Phosphate Field--Solubility of Phosphates (Common Market Standard Method)

Sample No.	Coordination on Israeli Map	Taken From	Layer	Total P_2O_5, %	CO_2, %	Soluble P_2O_5 in 2% F.A.		Soluble P_2O_5 in 2% C.A.	
						mg P_2O_5	% of Total P_2O_5	mg P_2O_5	% of Total P_2O_5
K-6	168100/055500	drill	bottom	31.4	n.d.	189	60.2	122	38.8
K-9	168050/055300	drill	bottom	30.7	n.d.	185	60.2	120	39.1
K-12	168100/055150	drill	bottom	31.5	n.d.	184	58.4	120	38.1
K-0508	168650/057700	drill	bottom	33.7	n.d.	203	60.2	138	40.9
K-0701	168700/058300	drill	bottom	30.8/31.0	5.2	181	58.6	130	40.7
K-0707	168800/058700	drill	bottom	33.8/33.8	4.7	196	58.0	133	39.3
K-0709	169000/058900	drill	bottom	33.2/33.1	4.6	192	57.8	129	38.9
K-0712	168900/059150	drill	bottom	32.0/32.1	n.d.	190	59.4	124	38.5
K-1401	168100/056850	drill	bottom	31.1/31.3	6.0	177	56.7	110	35.2
K-1402	168100/057050	drill	bottom	30.4	n.d.	188	61.8	124	40.8
K-1403	168300/057150	drill	bottom	31.0/31.0	5.0	194	62.8	118	38.1
K-2101	168250/055200	drill	bottom	33.3/33.3	5.9	193	58.0	124	37.2
K-2302	167900/055950	drill	bottom	32.2/32.4	5.6	191	59.1	119	36.8
K-2304	167850/156150	drill	bottom	30.7/30.9	7.3	173	56.2	n.d.	n.d.
K-3101	168200/055300	drill	bottom	32.1/32.1	5.9	188	58.6	123	38.3
Bit-4	16650/ 05335	drill	bottom	27.6	10.3	158	57.2	83	30.0
Bit-6	1672/ 0539	drill	bottom	26.9	9.4	160	59.5	87	32.2
F-28	1692475/0597951	drill	bottom	30.7	5.9	185	60.3	111	36.1
F-29	1695152/0602827	drill	bottom	29.8	8.1	174	58.4	93	31.2
F-30	1691433/0593748	drill	bottom	32.0	n.d.	192	60.0	114	35.6
F-45	1699699/0610117	drill	bottom	33.0	6.0	194	58.8	113	34.2
F-65	1689634/0604960	drill	bottom	30.7	6.9	176	57.3	102	33.2
F-66	1677693/0596833	drill	bottom	27.3	n.d.	159	58.2	87	31.9
F-73	1688644/0607398	drill	bottom	30.8	6.7	177	57.5	98	31.8
A-1	1677163/0600310	trench	bottom	32.8	5.6	188	57.3	118	36.0
A-10	1683961/0573846	trench	bottom	32.3	5.8	201	62.2	111	34.4

(Continued)

Table 4. Arad Phosphate Field--Solubility of Phosphates (Common Market Standard Method) (Continued)

Sample No.	Coordination on Israeli Map	Taken From	Layer	Total P_2O_5, %	CO_2, %	Soluble P_2O_5 in 2% F.A.		Soluble P_2O_5 in 2% C.A.	
						mg P_2O_5	% of Total P_2O_5	mg P_2O_5	% of Total P_2O_5
A-12	16858/05576	Trench	Bottom	32.0	4.4	201	62.8	127	39.7
A-13	168300/055350	Trench	Bottom	33.4	4.8	204	61.1	127	38.0
A-14	1688024/0558882	Trench	Bottom	32.8	4.9	204	62.2	132	40.2
Arad standard	Field No. 3	Trench	Bottom	33.2	4.6	204	61.4	129	38.8
Average				31.45		186.7	59.4	116.1	36.7
K-0701	168700/058300	Drill	Top	25.7/25.8	13.7	114	44.2	50	19.4
K-0709	169000/058900	Drill	Top	22.9/23.0	16.4	94	41.0	30	13.1
K-1403	168300/057150	Drill	Top	23.1/23.2	n.d.	100	43.1	33	14.2
K-2302	167900/055950	Drill	Top	21.6/21.6	14.1	100	46.0	27	12.4
K-3101	168200/055300	Drill	Top	22.5/22.6	14.2	113	50.0	38	16.8
Average				23.2		104.2	44.8	35.6	16.2

Table 5. Some Apatite Parameters--Arad Phosphorite (apatite samples extracted according to Silverman's method)

Sample No.	Layer	Chemical Analysis P_2O_5 %	CaO %	CO_2 %	F %	Na %	Weight Ratio CaO/P_2O_5	Weight Ratio F/P_2O_5	Unit Cell a, A°	Unit Cell C, A°	2% F.A. Solubility mg P_2O_5	2% F.A. Solubility % of Total P_2O_5	2% C.A. Solubility mg P_2O_5	2% C.A. Solubility % of Total P_2O_5
K-0508	Bottom	35.2	53.5	4.0	4.1	0.60	1.520	0.116	9.336	6.884	206	58.5	131	37.2
K-0701	Top	34.7	n.d.	3.9	4.0	0.60	n.d.	0.115	n.d.	n.d.	195	56.2	124	35.7
K-0709	Bottom	35.2	53.4	3.9	4.0	0.60	1.517	0.114	9.330	6.884	214	60.8	132	37.5
K-0709	Top	34.6	52.5	3.9	4.0	0.55	1.517	0.115	9.330	6.885	196	56.6	122	35.2
K-1401	Bottom	34.8	52.8	3.9	4.0	0.60	1.526	0.115	9.327	6.882	207	59.5	132	37.9
K-1403	Bottom	35.4	53.8	3.8	4.1	n.d.	1.519	0.116	9.336	6.892	211	59.6	133	37.6
K-2101	Bottom	34.2	51.8	4.2	3.9	0.60	1.515	0.114	9.340	6.896	211	61.7	133	38.9
K-2302	Bottom	34.8	52.6	4.1	4.1	0.70	1.512	0.118	9.339	6.891	213	61.2	132	37.9
K-2302	Top	34.4	52.4	4.2	4.0	0.70	1.523	0.116	n.d.	n.d.	210	61.0	128	37.2
K-2304	Bottom	34.8	53.0	4.0	4.05	0.60	1.523	0.116	n.d.	n.d.	211	60.6	131	37.0
K-3101	Top	34.3	52.1	n.d.	4.0	0.60	1.519	0.117	9.337	6.894	214	62.4	132	38.5
K-3101	Bottom	34.6	52.4	4.0	4.0	0.65	1.514	0.116	9.329	6.884	215	62.1	134	38.7

Table 6. Some Apatite Parameters--Hor Hahar and Ein Yorke'am Phosphorites (apatite samples extracted according to Silverman's method)

Field	Sample No.	Layer	Chemical Analysis					Weight Ratio		Solubility 2% F.A.		Solubility 2% C.A.		Type of Apatite
			P_2O_5	CaO	CO_2	F	Na	CaO/P_2O_5	F/P_2O_5	P_2O_5 %	% of Total P_2O_5	P_2O_5 %	% of Total P_2O_5	
Hor Hahar	K-176	2d	33.9	50.1	4.0	3.83	0.53	1.478	0.113	18.9	55.7	11.9	35.1	biogenic
Hor Hahar	K-179	2d	34.2	51.6	4.3	4.00	0.50	1.508	0.117	19.2	56.1	12.3	35.9	biogenic
Hor Hahar	K-183	2d	33.7	50.4	4.0	3.98	0.52	1.495	0.118	18.9	56.1	12.2	36.2	biogenic
Ein Yorke'am	EYN-2	2d	34.6	51.4	4.1	4.10	0.50	1.485	0.118	18.3	52.9	11.5	33.2	biogenic
Hor Hahar	Tech. trench	3d	36.7	51.9	3.0	4.16	0.34	1.414	0.113	16.8	45.8	10.8	29.4	pelletal
Hor Hahar	K-157	3d	36.2	51.8	2.7	4.10	0.30	1.431	0.113	15.6	43.1	10.1	27.9	pelletal
Ein Yorke'am	EYN-2	3d	36.7	53.1	3.0	4.10	0.30	1.447	0.112	16.1	43.9	9.9	27.0	pelletal

Table 7. Influence of Calcite ($CaCO_3$) on Solubility of Arad Phosphate in 2% Formic Acid (F.A.)

Total P_2O_5 in Sample %	Calcite Added %	Soluble in 2% F.A. P_2O_5 %	Soluble in 2% F.A. % of Total P_2O_5
32.6	0	20.8	63.8
32.0	2	20.0	62.5
31.0	5	18.9	61.0
30.0	8	17.8	59.3
29.0	11	16.7	57.6
28.0	14	15.9	56.8
27.0	17	14.8	54.8

Sample: Arad bottom layer, standard sample.
Fraction 20/100-mesh. Ground to pass 200-mesh.
Calcite ($CaCO_3$): Natural limestone taken from Arad area, ground to pass 200-mesh.
Procedure of solubility test: According to European Common Market Standard Procedure.

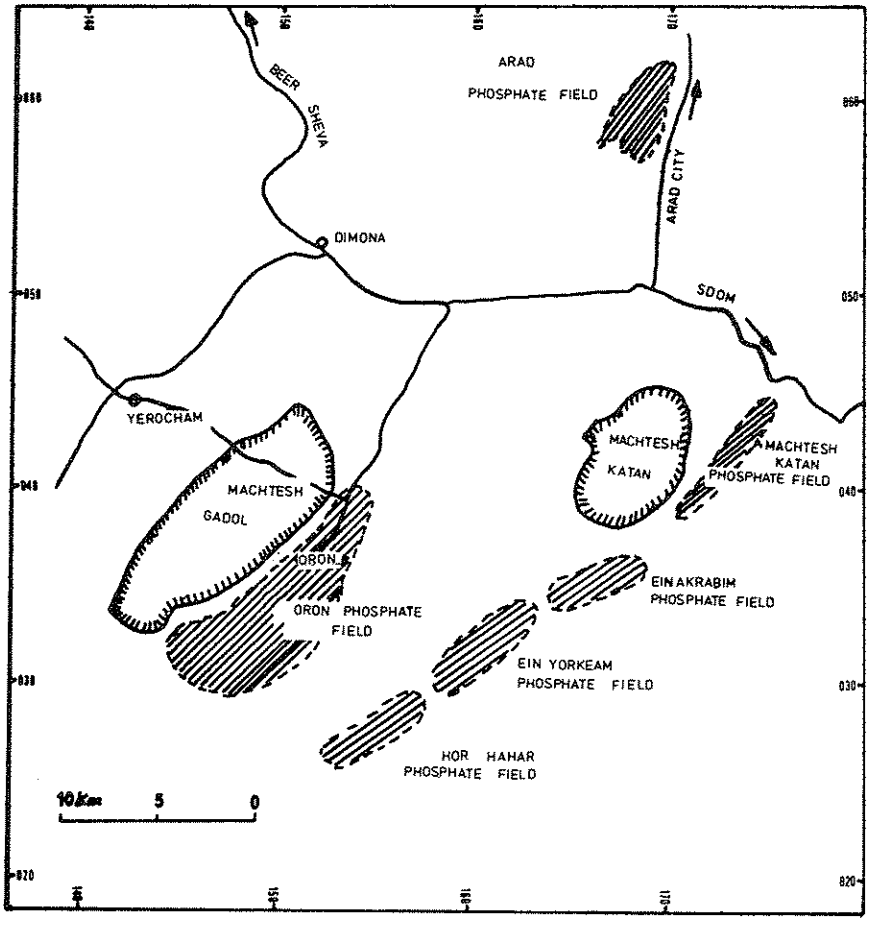

Figure 1. General Location of Some Phosphate Fields of the Northern Negev.

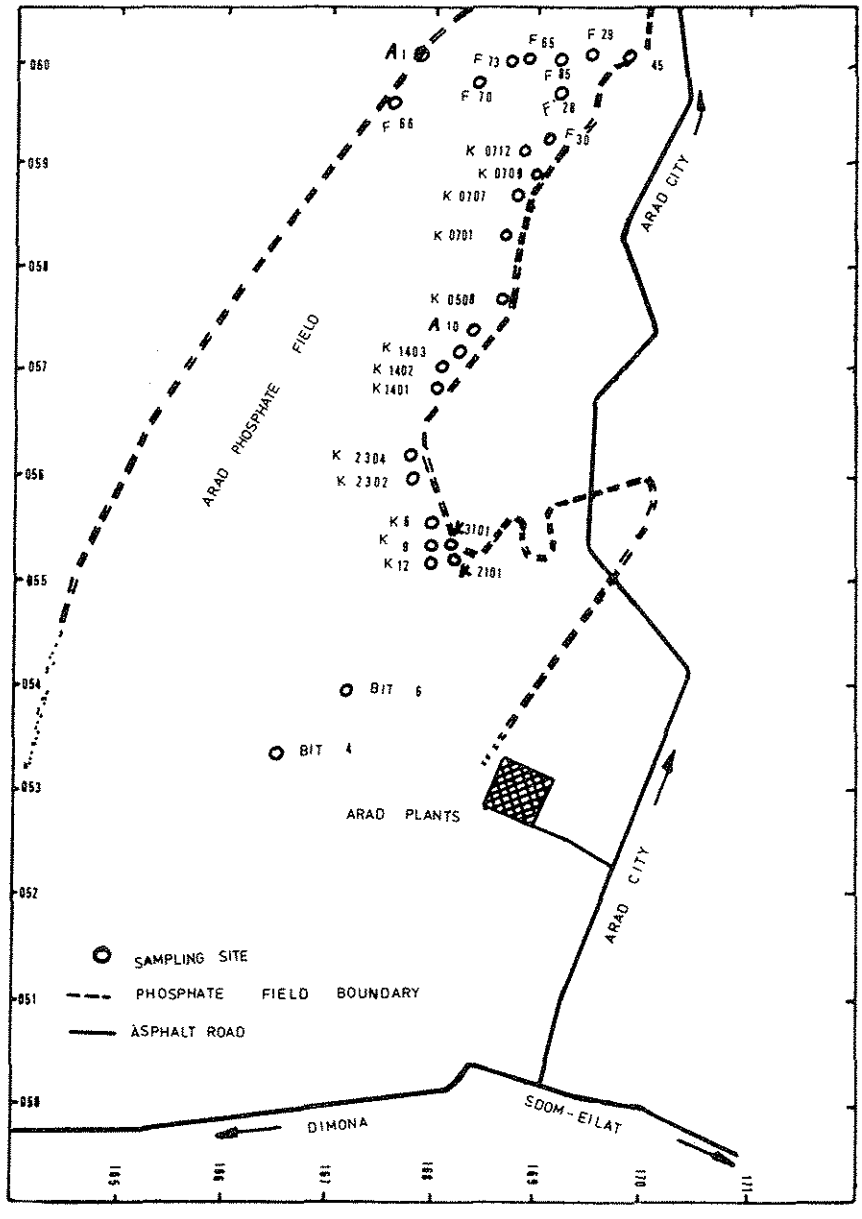

Figure 2. Arad Phosphate Field—General Layout of Sampling Sites.

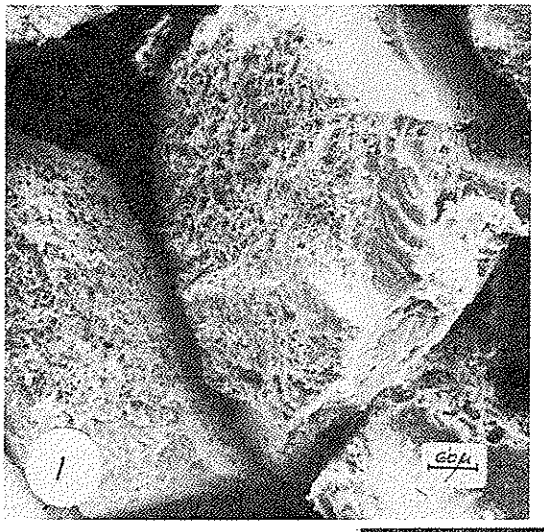

Figure 3. Arad Phosphorite. Sampling Site No. 3101, Bottom Layer. Porous Organogenic Apatite Fragments.

SEM. x 150.

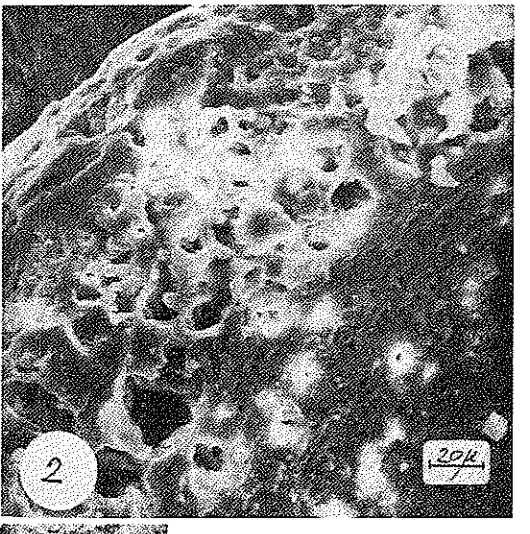

Figure 4. Arad Phosphorite. Sampling Site No. 0709, Bottom Layer. Porous Organogenic Apatite Fragments.

SEM. x 500.

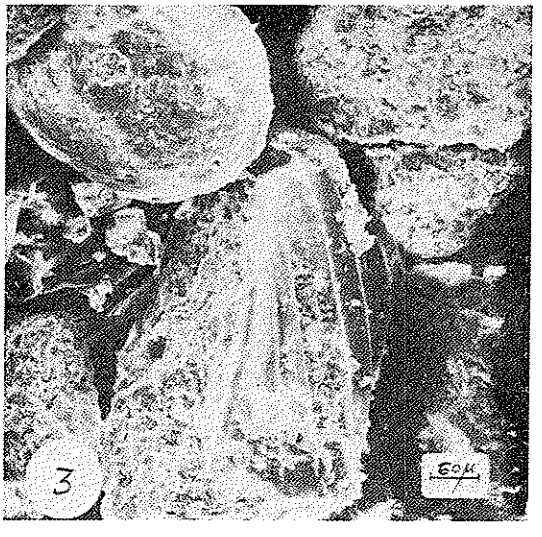

Figure 5. Arad Phosphorite. Sampling Site No. 1403, Bottom Layer. Organogenic Apatite Fragments.

SEM. x 150.

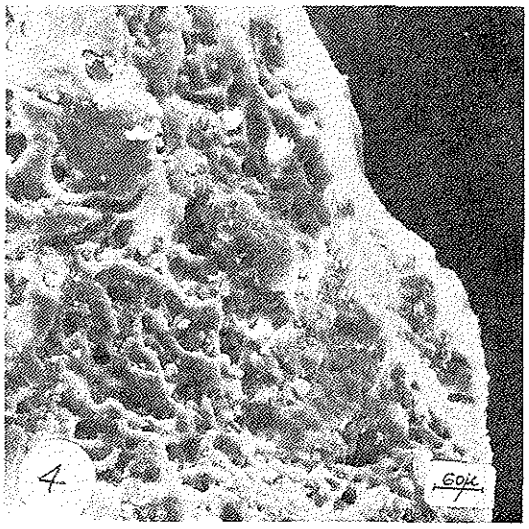

Figure 6. Arad Phosphorite. Sampling Site No. 2101, Bottom Layer. Organogenic Apatite.

SEM. x 150.

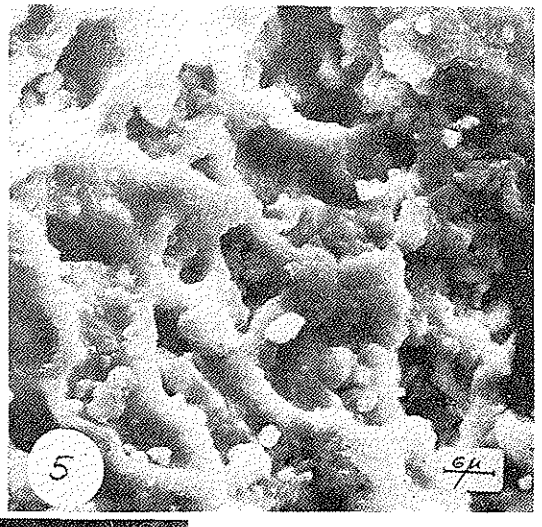

Figure 7. Enlargement of the Same Area as in No. 6.

SEM. x 1500.

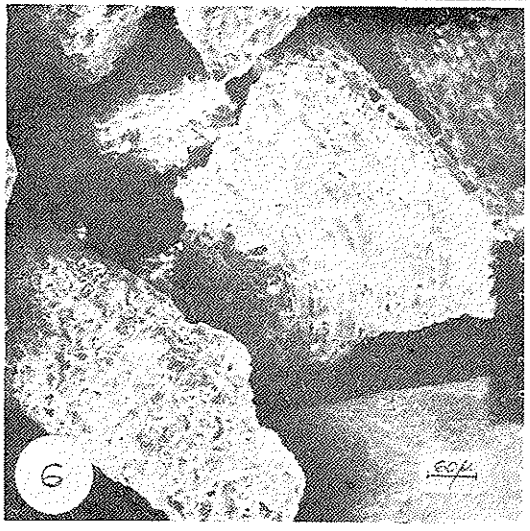

Figure 8. Arad Phosphorite. Sampling Site No. 2302, Top Layer. Porous, Organogenic Apatite Fragments.

SEM. x 150.

DISSOLUTION OF PHOSPHATE ROCKS IN SOLUTIONS AND SOILS

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Abstract

Factors such as time, temperature, agitation, calcium ion, concentration of solution, and particle size were found strongly affecting the dissolution rates of various phosphate rocks in 1 N ammonium citrate solution at pH 4.8. The results suggest that a meaningful comparison of the dissolution rates of various phosphate rocks in solutions needs to specify a given set of conditions for measurement.

Chemical methods can be used to evaluate the agronomic potential of phosphate rock for direct application. Good correlations were found between the solubility of phosphate rocks as measured by the chemical solvents and the actual crop response. Among the methods tested, neutral ammonium citrate (second extraction), 2% formic acid, and ammonium citrate at pH 3 are about equally accurate, and they are the best three methods tested in the present study. A new proposed nonshaking H-resin method can be used to predict the potential of the granulated phosphate rock for direct application according to the size of the granules.

Phosphorus concentrations in the soil solution or soil extracts (water and 0.01 M $CaCl_2$) were found to relate closely to the degree of carbonate substitution for phosphate in the apatite structure of various phosphate rocks. The phosphorus concentrations in the solutions follow the order: soil solution > water extract > 0.01 M $CaCl_2$ extract.

Introduction

Although phosphate rocks have long been used for direct application, most of the attention has been given to comparing the effectiveness of a particular phosphate rock with soluble phosphate on several soils, and little attention has been given to the

source of the rock or its mineralogical and chemical characteristics. The phosphate mineral in phosphate rock was previously assumed to be in the form of either tricalcium phosphate or fluorapatite so that the differences in effectiveness were attributed to the physical properties of the phosphate rock (particle size, surface area, porosity, etc.) and the soil factors such as pH, texture, cation-exchange capacity, clay minerals, and organic matter. Results of recent research show that the phosphate minerals in phosphate rocks, particularly the sedimentary types used widely in commerce, have compositions markedly different from those of tricalcium phosphate and fluorapatite (McClellan and Lehr, 1969; Lehr and McClellan, 1972). Thus, there is a need to investigate the dissolution behavior of phosphate rocks in solutions and soils as related to their mineralogical and chemical characteristics.

The objectives of this paper are to present and discuss the results recently obtained from experiments in the following research areas: (1) some factors affecting the dissolution of phosphate rocks in solution; (2) chemical methods for evaluating the reactivity of phosphate rocks for direct application; and (3) dissolution of phosphate rocks in acid soils.

It is hoped that the results from these studies will provide additional information for understanding the selection of various phosphate rocks as a directly applied fertilizer and the interactions of phosphate rocks with soils.

Some Factors Affecting the Dissolution of Phosphate Rocks in Ammonium Acetate Solution

The phosphate rocks used in this study were: Huila and Pesca rocks, Colombia; Sechura rock, Peru; Tapira rock, Brazil; Gafsa rock, Tunisia; and North Carolina and Central Florida rocks, United States. The objective of this study was to investigate some of the factors that affect the dissolution of ground phosphate rocks (80% through 100-mesh) in a buffered solution (ammonium acetate, NH_4OAc) under gently agitated conditions. The strongly buffered solution of 1 N NH_4OAc at pH 4.8 was used for all the experiments except the one for the effect of concentration.

The buffered solution was used to maintain a constant pH and ionic strength of the solvent during the course of the dissolution of phosphate rocks although the concentration was much higher than that of the soil solution generally encountered. The pH of 4.8 was used to represent the average soil pH of most acid soils in developing countries (Engelstad et al., 1972) to which phosphate rock may be economically applied for crop production.

Time of Reaction

In general, three types of dissolution curves are obtained, depending on the sources of phosphate rock (figure 1): (1) fast dissolution as it reaches the maximum solubility in 1-3 hours and then declines as time increases; this type includes North Carolina and Gafsa rocks; (2) fast dissolution as it reaches the maximum solubility in 10-60 minutes or 1 day and remains saturated thereafter; this type includes Central Florida, Huila, Tapira, and Pesca rocks; (3) slow dissolution in the beginning and reaching the maximum solubility in about 14 days; this type includes Sechura rock.

It was rather surprising to see the solubilities of two reactive rocks (North Carolina and Gafsa) start declining after reaching the maximum in about 3 hours. Precipitation of less soluble P compounds may cause this decrease of P concentration in the equilibrated solution. The curve obtained with Sechura rock suggests that the dissolution of this rock in the solution is a strongly diffusion-controlled process.

The results obtained in this experiment suggest that a comparison of the dissolution rates of various phosphate rocks in solutions needs to specify a given time of reaction because different shapes of dissolution curves may exist.

Temperature

Temperature has a marked effect on the reactive rocks (North Carolina and Gafsa), whereas this effect is relatively small or nonexistent on less reactive

rocks (figure 2). Since the dissolution of apatite mineral in acid solution is an exothermic reaction (Chien, 1977a; Chien and Black, 1976) and the mechanism is a diffusion-controlled process (Brown and Wallace, 1965; Chien, 1977b), temperature may have a varying effect on the solubility of phosphate rock. Increasing temperature would depress the exothermic reaction while it would enhance the diffusion-controlled process. Hence, the net effect depends on the magnitude of these two opposite effects. The relatively fast dissolution of North Carolina and Gafsa rocks (figure 1) suggests that the temperature effect may depress the exothermic reaction rather than enhance the diffusion-controlled process for these two rocks. Sechura rock is the only one which shows an increase of the solubility as temperature increases. This suggests that the dissolution of Sechura rock is strongly oriented toward the diffusion-controlled process as can be seen from its dissolution curve in figure 1 and the agitation effect which will be shown later.

Another possible explanation for the decrease of the solubility of North Carolina and Gafsa rocks as temperature increases might be the formation of less soluble phosphorus compounds in the solution at high temperature. Figure 1 shows that such precipitation might occur after 3-hour equilibration at room temperature. Precipitation might occur after 1-hour equilibration at higher temperature.

Agitation

Stirring greatly increased the dissolution rate of all phosphate rocks (figure 3). Further increase of agitation speed, however, did not increase the dissolution rates of North Carolina, Tapira, and Pesca rocks. A slight increase was observed for Central Florida rock from speed 1 to 2 and no further increase from 2 to 4. On the other hand, Sechura rock showed that the dissolution rate was strongly dependent on agitation as can be seen from figure 3, increasing from almost zero without agitation to 3.5 mg P/10 minutes as the relative stirring speed was increased to 4. The dependence on this variable clearly showed that the reaction was diffusion-controlled (Moelwyn-Hughes, 1933; Barton and Wilde, 1971).

Calcium Ion

It can be seen that the addition of $CaCO_3$ significantly depresses the solubility of phosphate rocks, especially the reactive North Carolina rock (figure 4). Because the pH of the solution remained the same after the reaction, it is the calcium common-ion-effect that depresses the solubility of phosphate rock. Other data showing this effect are presented in figure 5. Here calcium in the form of $CaCl_2$ also depresses the solubility of North Carolina and Central Florida rocks.

The results from this study suggest that the phosphorus concentration in the soil solution would increase only when the calcium concentration decreases as the phosphate rock is applied to the soil. In other words, there has to be a calcium sink in the soil in order to utilize phosphate rock effectively. Another implication from this study is that, if the presence of calcite has no significant effect on the dissolution of apatite in the soil solution, any alkaline-earth carbonates in phosphate rock have to be removed before measuring the reactivity of the rock by chemical methods. This will be discussed further later.

Concentration of Solution

The solubility of phosphate rock increases as the concentration of NH_4OAc increases as shown in figure 6, despite the fact that solution pH was maintained at the same level (pH 4.8) before and after the reaction. These results thus suggest that the dissolution of phosphate rock may depend on the concentration of the soil solution. Application of soluble, nonphosphate fertilizers may increase the dissolution of phosphate rock in the soil solution by increasing the concentration of the solution, provided the P sorption capacity of the soil remains unchanged.

Particle Size

The results of the particle-size effect are shown in figure 7. It should be noted that the solubility values of each fraction as shown in figure 7 were plotted against the upper limit of the particle size of

that fraction. For example, the solubility values of the fractions of minus 24- plus 65-mesh and minus 325-mesh were plotted against 24-mesh and 325-mesh on the x-axis, respectively.

The results of this investigation show that both particle size and reaction time significantly influence the solubility values. In general, solubility values increased as the reaction time increased for a given fraction of each rock. Likewise, solubility values increased as the particle size of the fractions decreased for a given time of reaction, and the effect is most pronounced for the finest fraction (minus 325-mesh). However, the particle-size effect is gradually diminished as the reaction time increases. As a matter of fact, after 1-week equilibration, there was essentially no particle-size effect on the solubilities of Pesca and Sechura rocks. A significant decrease of the solubility values for the finest fraction (minus 325-mesh) of North Carolina rock was observed from 1-hour to 1-week equilibrations. This suggests that precipitation of less-soluble P compounds might occur for this rock during the prolonged equilibration as was shown in figure 1.

It may be concluded from this study that particle size may affect the rate of dissolution of phosphate rock, rather than the maximum solubility at equilibrium, although the data did not indicate whether the equilibrium was attained as shown in figure 7. This may explain why the effectiveness of phosphate rock increases as the particle size decreases if the rate of dissolution of phosphate rock in the soil solution is the limiting factor to the P uptake by the plant. On the other hand, particle-size effect may not be significant if the maximum P concentration that a phosphate rock can maintain in the soil solution is the limiting factor. Thus, it is not surprising to see wide variations of the particle-size effect on the effectiveness of phosphate rocks among various researchers' reports.

Chemical Methods for Evaluating the Reactivity of Phosphate Rock for Direct Application

Laboratory evaluations of the chemical reactivity of phosphate rock can be used to select the

potentially reactive rock sources for direct application so that needless testing of unresponsive phosphate rocks can be avoided. Such evaluations, however, merely predict the ability of the phosphate rock to supply available P. They cannot predict how efficiently the supply of available P will be utilized by crops under actual field conditions. Soil factors such as pH, texture, exchangeable Al, soil P level, and organic matter cannot be ignored.

The common laboratory chemical methods currently being used to measure ground phosphate rock reactivity in the world are: neutral ammonium citrate (e.g., U.S.); 2% citric acid (e.g., Brazil); and 2% formic acid (e.g., Europe). Lehr and McClellan (1972) proposed a new concept of absolute citrate solubility (ACS). Unpublished work at the International Fertilizer Development Center (IFDC) and Tennessee Valley Authority (TVA) also shows that ammonium citrate (pH 3) was another potential solvent for measuring the chemical reactivity of phosphate rocks for direct application.

There is some interest in granulating finely ground phosphate rock as one method of improving its handling and application characteristics. However, many agronomic research reports have indicated that the effectiveness of phosphate rock for direct application would be reduced when the rock was granulated. This is a consequence not only of reduced surface area for dissolution but also of reduced physical distribution of the granulated rock in the soil (locality effect). Conventional extraction methods cannot be suitable for evaluating the potential of granulated phosphate rock for direct application because the granulated rock would disintegrate during extraction. Therefore, there is a need to develop a simple, reliable, and reproducible chemical method for evaluating the potential of granulated phosphate rock for direct application.

This section of the report discusses: (1) a comparison of the various laboratory methods for evaluating the potential of ground phosphate rocks for direct application and (2) a preliminary test on a proposed resin method for evaluating granulated rocks.

Chemical Solvents and X-Ray Methods for Ground Phosphate Rock

Table 1 shows the reactivity scales of seven ground phosphate rocks (80% through 100-mesh) as measured by the chemical extractions (neutral ammonium citrate, 2% citric acid, 2% formic acid, and ammonium citrate pH 3) and X-ray diffraction (absolute citrate solubility). The neutral ammonium citrate solubility remained relatively constant in the first and second extractions for each rock except Huila. The citrate-soluble P_2O_5 of this rock increased from 0.8% in the first extraction to 3.4% in the second. The explanation is that the associated free carbonates in this rock (approximately 6% as CO_2) depressed the solubility of the apatite in the first extraction, since free carbonates are more soluble than apatite in neutral ammonium citrate solution (Silverman et al., 1952). Thus, the citrate solubility increased in the second extraction because the associated free carbonates were removed during the first extraction.

Tables 2 and 3 show the simple linear correlation obtained with the crop yield[1] at each application rate and the reactivity scale of the phosphate rocks as measured by the five methods. Surprisingly, the correlation coefficient obtained by a given method varied with the application rate of phosphorus, and the variation changed with the experiments. In general, the correlation coefficients were highest at the high application rate in the Guinea grass experiment and at low application rate in the beans experiment, respectively. These results make it rather difficult to select a best method for recommendation. Nevertheless, it appears that neutral ammonium citrate (second extraction), 2% formic acid, and ammonium citrate (pH 3) are about equally accurate, and they are the best three methods tested in this study.

1. L. L. Hammond. 1977. Effectiveness of Phosphate Rocks in Colombia Soils as Measured by Crop Response and Soil Phosphorus Levels, Ph.D. Thesis, Michigan State University.

The relatively low correlation coefficients obtained with neutral ammonium citrate in the first extraction in the beans experiment were due to the associated free carbonates in the Huila rock. The citrate solubility of Huila rock was significantly depressed by the associated free carbonates in the first extraction as compared with that in the second extraction (table 1). Apparently, the associated free carbonates had no significant effect on the dissolution of the apatite in the soil solution. Thus, the citrate solubility of Huila rock as obtained in the second extraction should be more comparable to the solubility in the soil solution.

It was rather surprising to see that the correlations were relatively low with 2% citric acid as compared with 2% formic acid and ammonium citrate (pH 3) in the beans experiment (table 3). The solubility data in table 1 indicate that the associated free carbonates in Huila rock may also depress the solubility of this rock in 2% citric acid as compared with 2% formic acid and ammonium citrate (pH 3). The relative solubilities of Huila rock with respect to Pesca rock in 2% citric acid, 2% formic acid, and ammonium citrate (pH 3) were 74%, 117%, and 124%, respectively. In other words, the effect of the free carbonates on the solubility of Huila rock decreased as the solvents used increased in strength. When the solubility of Huila rock in 2% citric acid was removed from the correlation, the coefficients significantly increased in the beans experiment. For example, the coefficient increased from 0.649 to 0.883 at the rate of 200 kg/ha P_2O_5. However, correlations increased only slightly in the Guinea grass experiment. Nevertheless, the results suggest that the solubility of a phosphate rock containing a significant amount of free carbonates, as measured by the conventional neutral ammonium citrate solution as well as 2% citric acid, may underestimate the potential of that type of rock for direct application.

H-Resin Method for Granulated Phosphate Rock

The proposed method was carried out as follows: a 50-g sample of acid-washed sand was mixed with 2.5 g of H-resin (Dowex 50W-X8) and 1 g of rock sample of the desired granule size in a small beaker. Fifty milliliters of distilled water was gradually added

to the beaker without disturbing the mixture. After 2 hours the mixture was filtered, and the P concentration of the filtrate was then determined.

Figure 8 shows the effect of granule size on the dissolution of the granulated North Carolina rock (granulated from minus 200-mesh material) as measured by the proposed H-resin method. The range of granule size used was from minus 4- plus 6-mesh (average diameter of the granules = 4.00 mm) to minus 200- plus 300-mesh (average diameter of the granules = 0.05 mm). It can be seen clearly in figure 8 that the dissolution of the granulated rock decreased drastically in the range of granule size from 0.05 mm to 1.00 mm. The most common commercial products of the granulated rocks are generally in the size, minus 6- plus 16-mesh (average diameter of the granules = 2.18 mm).

Very recently, Dr. L. L. Hammond, Soil Scientist of the Agro-Economic Division, IFDC, obtained first crop response data of granulated phosphate rocks in a greenhouse study. This agronomic information is now used to test the applicability of the proposed H-resin method as a tool for evaluating the potential of granulated rock for direct application.

Table 4 shows the solubility data of granulated North Carolina and Sechura rocks (granulated from minus 200-mesh material) with various granule sizes as measured by the conventional citrate extraction method and the proposed H-resin method. It can be seen clearly that the conventional citrate extraction method cannot be used to measure the solubility of the granulated rocks because the granules disintegrated upon being shaken, and this resulted in essentially the same solubility being recorded for all samples regardless of the granule size. On the other hand, the proposed non-shaking, H-resin method was able to measure the solubility of the granulated rocks as influenced by the granule size.

Figure 9 shows the relationship between the dry matter yield of corn and the solubility of the granulated rocks as measured by the proposed H-resin method. The corn was grown for 6 weeks on Mountview soil (limed from pH 4.8 to 5.2) from

Tennessee at four application rates of P with four granule sizes. A highly significant (at 1% level) linear relationship between the dry matter yield of corn and the solubility of the granulated rock suggests that the proposed H-resin method can be used to predict the potential of the granulated phosphate rock for direct application according to the size of the granules. However, more data are needed to test this relationship.

Dissolution of Phosphate Rocks in Acid Soils

Many reports have indicated that growth rate of plants and, hence, the final yield, are functions of the P concentration in the soil solution. The objectives of this study were: (1) to investigate the dissolution of various phosphate rocks in acid soils under flooded and unsaturated conditions as related to their apatite composition and (2) to compare P concentration in the soil solution equilibrated with phosphate rock under unsaturated conditions as measured by various extraction methods.

Dissolution of Phosphate Rocks in Acid Soil Under Flooded Conditions

In this experiment, seven phosphate rocks were used: Huila, Sechura, Gafsa, North Carolina, Central Florida, Tennessee, and Kodjari (Upper Volta). The soil used was Mountview silt loam (pH 4.8) from Tennessee. Ten-gram samples of soil were thoroughly mixed with various amounts of phosphate rocks to give 400 ppm P in the soil. These samples were then equilibrated with 35 ml of distilled water under undisturbed conditions at 25°C for various time intervals.

The concentration of P in the soil solution during the incubation period varied considerably for phosphate rocks, ranging from 0.03 to 0.35 ppm in 1 week and 0.04 to 0.11 ppm in 10 weeks after the soil was flooded (figure 10). The P concentration in the soil solution with no added phosphate remained relatively low throughout the incubation period. The differences in the solubility of various phosphate rocks decreased as incubation time increased. This suggests that, after prolonged incubation, factors

other than apatite composition were also affecting the dissolution of phosphate rocks in the soil solution.

A plot of the average P concentration in the soil solution during incubation as a function of the mole ratio of CO_3:PO_4 in the apatite structure is shown in figure 11. A significant (at 5% level) linear correlation coefficient ($r = 0.869$) was obtained with the rocks. The trend as shown in figure 11 indicates that the P concentration in the soil solution equilibrated with phosphate rocks under flooded conditions increases as the isomorphic substitution of carbonate for phosphate in the apatite structure increases. This suggests that there may be a linear relationship between the P uptake by flooded rice and the mole ratio of CO_3:PO_4 in the apatite structure. Data from Lehr and McClellan (1972) and Engelstad et al. (1974) with other sources of phosphate rocks indeed support this supposition (Chien, 1977c).

Dissolution of Phosphate Rocks in Acid Soil Under Unsaturated Conditions

In this experiment, four phosphate rocks were used: North Carolina, Sechura, Central Florida, and Kodjari. The soil was Weston sandy loam (pH 4.5) from Florida. Twenty-gram samples of soil thoroughly mixed with various amounts of phosphate rocks to give 400 ppm P in the soil were incubated at 25% moisture content for various time intervals at 25°C. Soil samples were than extracted with water (soil:water as 1:1.5) for 30 minutes.

The concentration of P in the soil water extract during incubation varied widely among various phosphate rocks (figure 12). The levels of water-soluble P maintained in the soil by all the rocks, except Sechura, declined drastically in 1 week of incubation. With Sechura rock, on the other hand, the water-soluble P increased drastically after 1 week of incubation as compared with that found at time zero, because of the relatively slow P-release characteristic of this rock shown in figure 1.

Figure 13 shows the relationship between the average P concentration in the soil water extract during incubation and the mole ratio of CO_3:PO_4 in the apatite structure. Again, there is a significant

(at 5% level) correlation coefficient (r = 0.957) indicating the effect of the apatite composition on the dissolution of phosphate rocks in the soil.

The results obtained from this experiment (figure 12) and the previous experiment (figure 10) suggest that the P concentration in the soil solution is mainly controlled by the P release from the phosphate rock during the early stage of incubation, but after prolonged incubation some of the P originally released from the rock reacts with the soil to decrease the P remaining in the soil solution. This implies that the differences in the initial agronomic effectiveness among various sources of phosphate rock would be less pronounced in residual effect because of the involvement of soil factors. Indeed, several researchers have reported that this is the case (Sahu et al., 1974; Bengtson et al., 1974; Engelstad et al., 1974; and Chien and Hammond, 1978).

Phosphorus Concentration in the Soil Solution Equilibrated with Phosphate Rock Under Unsaturated Conditions

Because of the numerous difficulties encountered when attempts are made to separate the true soil solution from its harboring solid phase, it is only natural that attempts be made to define soil solution composition in terms of water extract composition. However, the addition of water affects the equilibrium concentrations of the soil solution ions differently because dilution results in ion exchange, precipitation, and dissolution reactions (Adams, 1974). The objectives of this study were to: (1) measure the P concentration in the true soil solution equilibrated with phosphate rock and (2) compare the P concentrations in the soil solution with those in soil extracts removed by water and 0.01 M $CaCl_2$ solution which have long been used to approximate the soil solution. The soil solution was displaced by CCl_4 through high-speed centrifugation (Mubarak and Olsen, 1976). The soil extracts were obtained by shaking the soil with water or 0.01 M $CaCl_2$ (1:1) for 1 hour. Concentrated superphosphate (CSP) was also included for comparison.

Figure 14 shows the P concentrations in the soil solution from the Mountview soil (pH 4.8) treated with various rates of North Carolina rock and CSP after

2-week incubation at 25% moisture content in the soil. Phosphorus concentrations in the soil solution increased as the rate of P added to the soil increased for both North Carolina rock and CSP. However, P concentrations in the soil solution equilibrated with North Carolina rock reached saturation at a rate of approximately 1,200 ppm P added to the soil; presumably it was fixed by the solubility product of apatite (Chien and Black, 1976). On the other hand, P concentrations in the soil solution from the soil treated with CSP continued to increase as rate of application increased up to 1,600 ppm P added to the soil. The results as shown in figure 14 may explain why the crop response to phosphate rock is generally lower than that to CSP, regardless of how high the application rate of phosphate rock goes; the P concentration in the soil solution equilibrated with phosphate rock is fixed at saturation.

Figure 15 shows the relationship between the P concentrations in the soil solution and the soil extracts. Note the x and y scales for CSP are in logarithms. There are two salient features as shown in figure 15:

1. The P concentrations in 0.01 M $CaCl_2$ extract were lower than those in water extract for both North Carolina rock and CSP. This may be due to the fact that the calcium common-ion-effect from the $CaCl_2$ solution depressed the dissolution of apatite during extraction (also see figure 5), and/or the P-sorption capacity of the soil was greater in the presence of 0.01 M $CaCl_2$ solution than that in water (Ryden and Syers, 1975; Singh and Tabatabai, 1976).

2. The P concentrations in water extract were lower than those in the soil solution at rates of application below 800 ppm P for North Carolina rock and at rates above 400 ppm P for CSP. Above 800 ppm P for North Carolina rock and below 400 ppm P for CSP, the P concentrations in the soil solution and water extract were essentially the same (figure 15). Since the normal rates of application of phosphate rock are much less than 800 ppm P, this raises a question whether the P concentration in a water extract can be used to approximate the P concentration in the true soil solution. More research is needed to investigate this relationship.

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Table 1. Reactivity Scales of the Phosphate Rocks as Measured by Five Methods

Rock Sample	Soluble P_2O_5, % of Rock: Neutral Ammonium Citrate 1st	Neutral Ammonium Citrate 2nd	2% Citric Acid	2% Formic Acid	pH 3 Ammonium Citrate	Absolute Citrate Solubility[a] (%)
Huila	0.8	3.4	5.2	6.2	10.5	12.2
Pesca	1.9	1.9	7.0	5.3	8.5	9.7
Sechura	5.3	5.4	15.2	21.8	24.1	14.9
Gafsa	4.9	5.6	14.1	22.4	21.1	18.5
North Carolina	7.2	6.7	15.9	25.7	24.8	19.8
Central Florida	3.0	3.2	8.4	8.2	14.0	10.1
Tennessee	2.6	2.7	8.8	6.9	9.8	5.1

a. Calculated by the method of Lehr and McClellan (1972).

Table 2. Correlation of Various Reactivity Scales of Seven Phosphate Rocks and Dry-Matter Yield of Guinea Grass (Greenhouse Experiment)

Method of Evaluation	Correlation Coefficient, r: P added, ppm 50	100	200	400
Neutral ammonium citrate (first extraction)	0.651^{ns}	0.776*	0.887**	0.883**
Neutral ammonium citrate (second extraction)	0.679^{ns}	0.879*	0.931**	0.955***
2% citric acid	0.784*	0.863*	0.930**	0.916**
2% formic acid	0.761*	0.890**	0.946**	0.957***
Ammonium citrate (pH 3)	0.776*	0.942**	0.990***	0.993***
Absolute citrate solubility[a]	0.580^{ns}	0.754*	0.801*	0.858*

^{ns}Not significant.
*Significant at the 5% level.
**Significant at the 1% level.
***Significant at the 0.1% level.
a. Calculated by the method of Lehr and McClellan (1972).

Table 3. Correlation of Various Reactivities of Seven Phosphate Rocks with Yield of Beans (Field Experiment)

Method of Evaluation	Correlation Coefficient, r			
	P_2O_5 added, kg/ha			
	50	100	200	400
Neutral ammonium citrate (first extraction)	0.754*	0.653^{ns}	0.590^{ns}	0.641^{ns}
Neutral ammonium citrate (second extraction)	0.893**	0.866*	0.855*	0.880**
2% citric acid	0.792*	0.714^{ns}	0.649^{ns}	0.740^{ns}
2% formic acid	0.888**	0.811*	0.759*	0.849*
Ammonium citrate (pH 3)	0.894**	0.858*	0.779*	0.836*
Absolute citrate solubility[a]	0.927**	0.809*	0.737^{ns}	0.845*

^{ns}Not significant.
*Significant at the 5% level.
**Significant at the 1% level.
a. Calculated by the method of Lehr and McClellan (1972).

Table 4. Solubilities of Two Granulated Phosphate Rocks as Measured by the Conventional Citrate Extraction Method and the Proposed H-Resin Method

(Mesh)	Soluble P_2O_5, % of Rock			
	Conventional Citrate Extraction Method[a]		Proposed H-Resin Method[b]	
	North Carolina	Sechura	North Carolina	Sechura
-6 + 14	6.8 ± 0.3	6.7 ± 0.2	1.4 ± 0.3	1.8 ± 0.1
-14 + 28	7.0 ± 0.5	6.2 ± 0.7	3.4 ± 0.2	4.7 ± 0.3
-48 + 100	8.6 ± 0.1	7.2 ± 0.6	7.0 ± 0.1	7.5 ± 0.3
-100 + 200	6.4 ± 0.4	6.3 ± 0.5	8.0 ± 0.1	8.6 ± 0.2

a. Means of duplicates and their standard errors.
b. Means of triplicates and their standard errors.

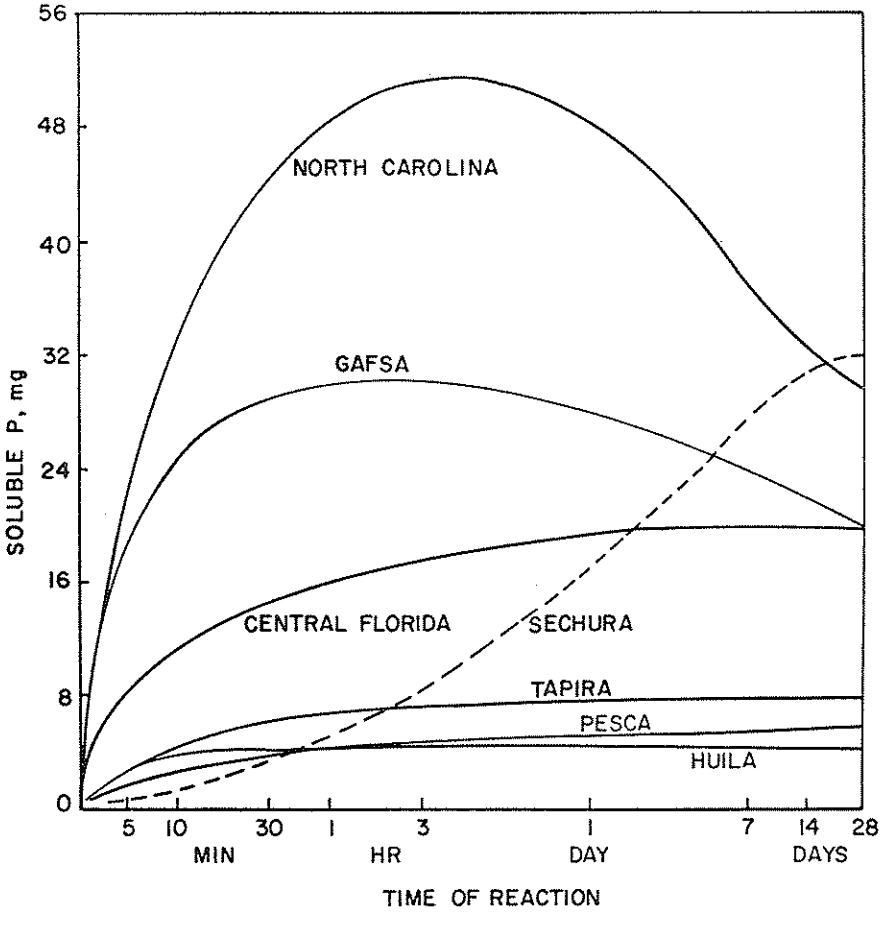

Figure 1. Dissolution of Phosphate Rocks in 1 N NH_4OAc Solution (pH 4.8) at 25°C with Solid/Solution of 5 g/500 ml.

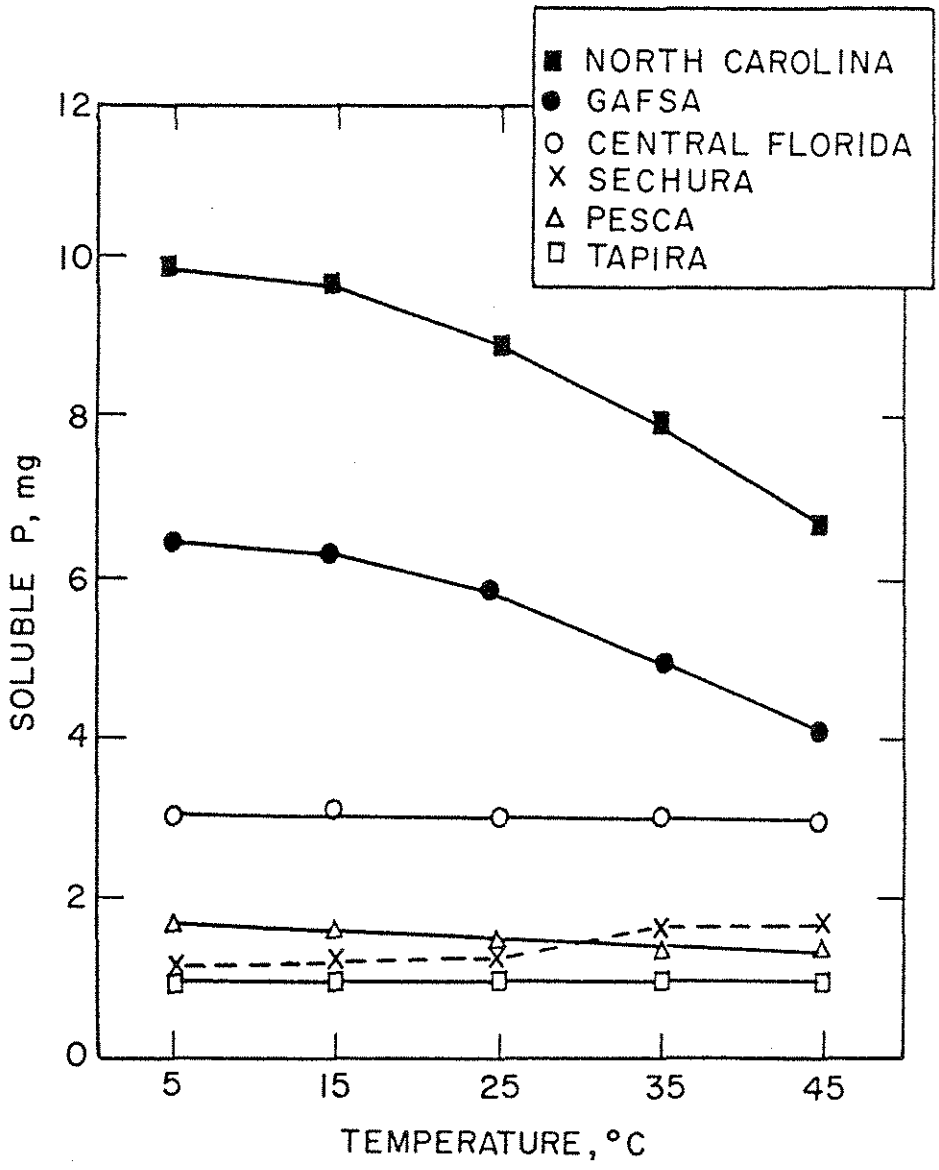

Figure 2. Effect of Temperature on the Dissolution of Phosphate Rocks in 1 N NH_4OAc Solution (pH 4.8) for 1 Hour with Solid/Solution of 1 g/100 ml.

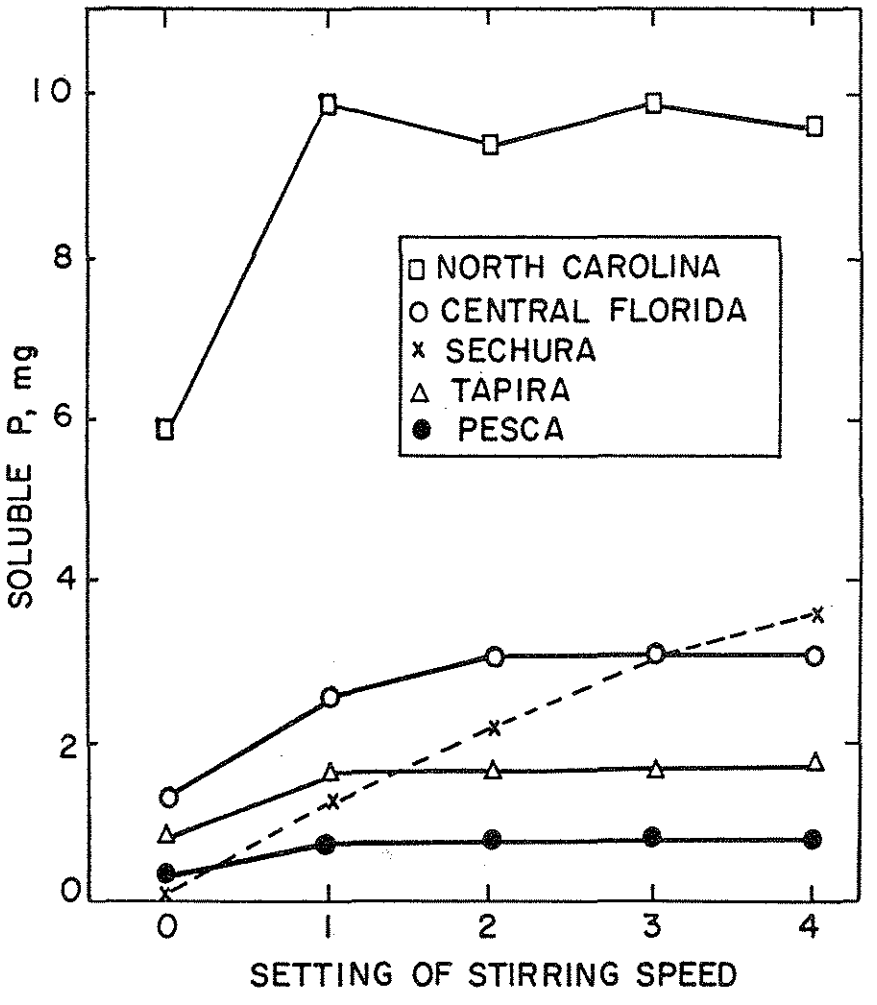

Figure 3. Effect of Agitation on the Dissolution of Phosphate Rocks in 1 N NH_4OAc Solution (pH 4.8) at 25°C for 10 Minutes with Solid/Solution of 1 g/100 ml.

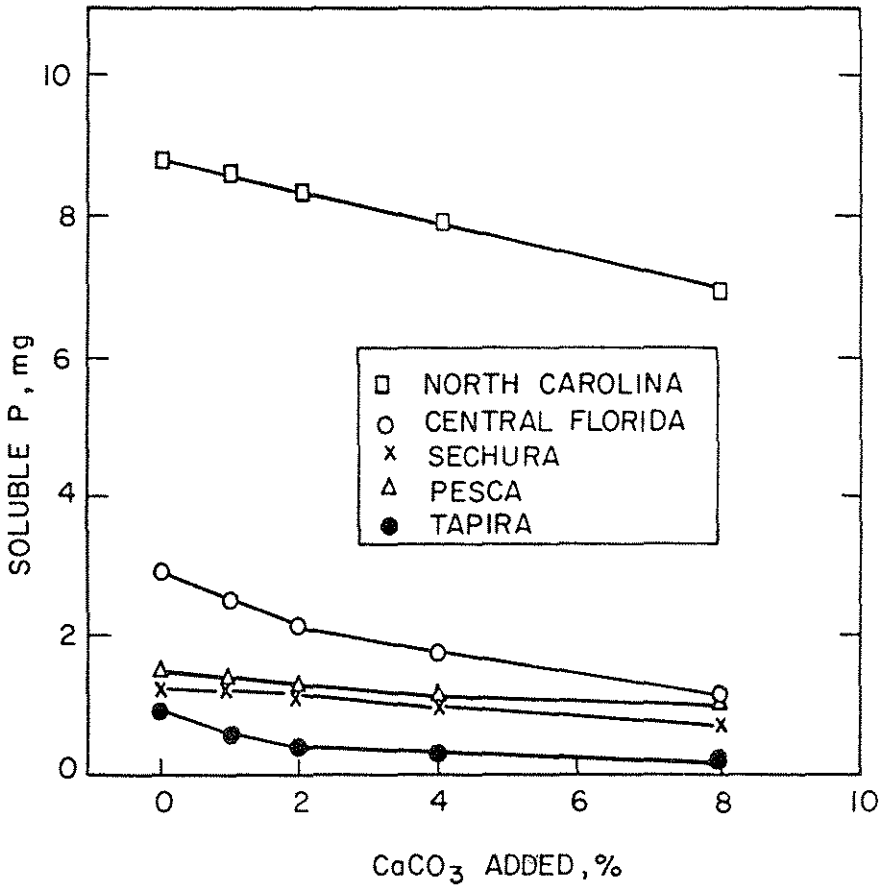

Figure 4. Effect of $CaCO_3$ on the Dissolution of Phosphate Rocks in 1 N NH_4OAc Solution (pH 4.8) at 25°C for 1 Hour with Solid/Solution of 1 g/100 ml.

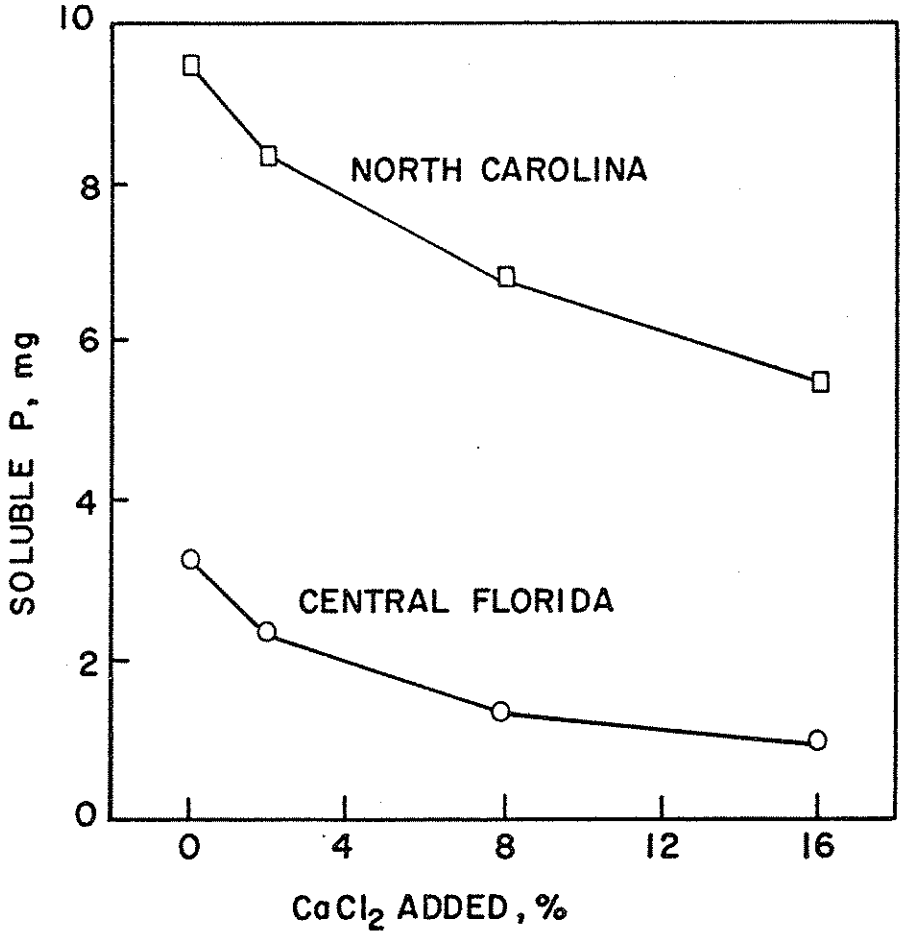

Figure 5. Effect of $CaCl_2$ on the Dissolution of Phosphate Rocks in 1 N NH_4OAc Solution (pH 4.8) at 25°C for 1 Hour with Solid/Solution of 1 g/100 ml.

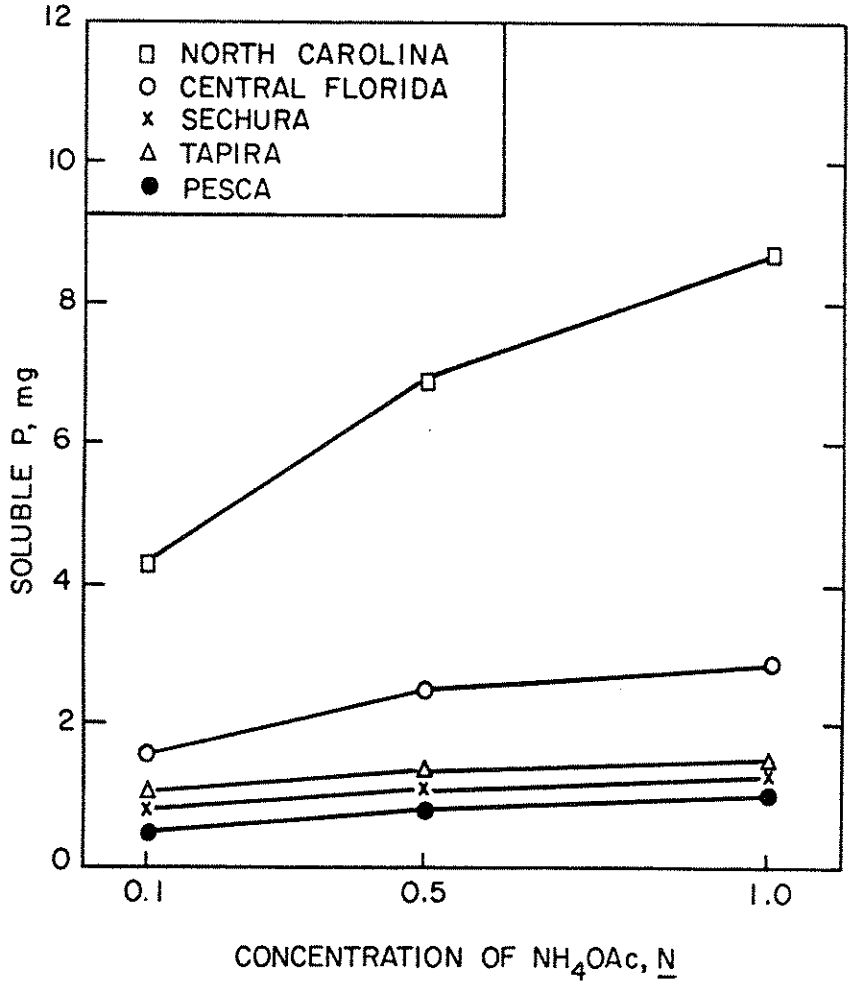

Figure 6. Effect of Concentration on the Dissolution of Phosphate Rocks in NH_4OAc Solution (pH 4.8) at 25°C for 1 Hour with Solid/Solution of 1 g/100 ml.

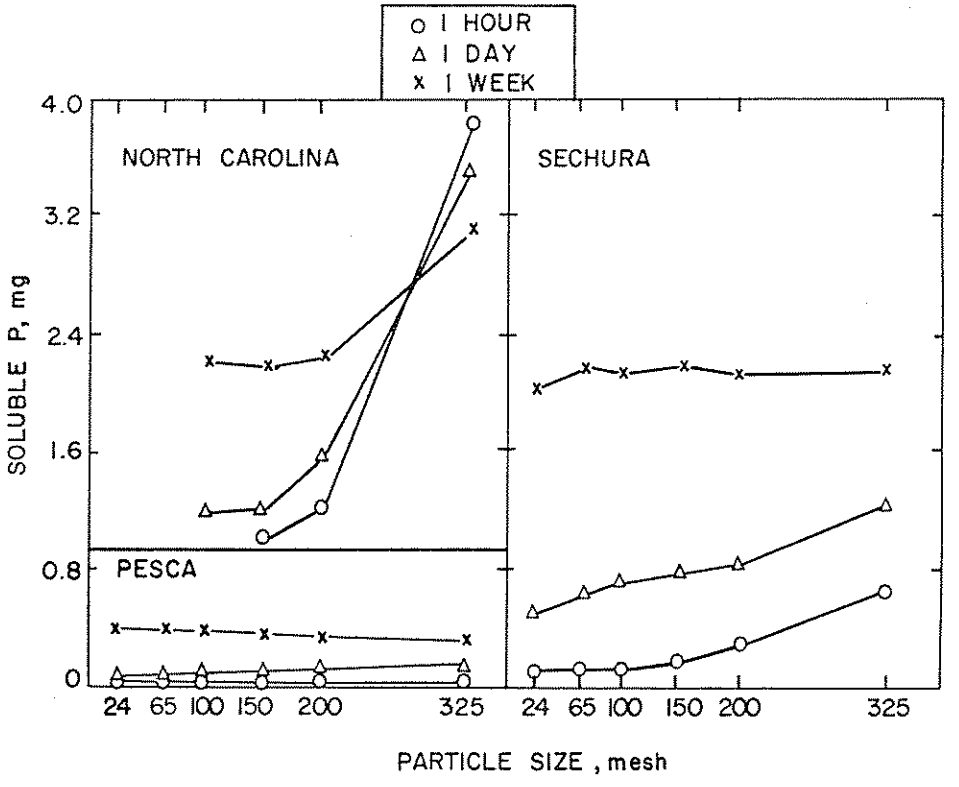

Figure 7. Effect of Particle Size on the Dissolution of Phosphate Rocks in 1 N NH_4OAc Solution (pH 4.8) at 25°C with Solid/Solution of 0.5 g/50 ml.

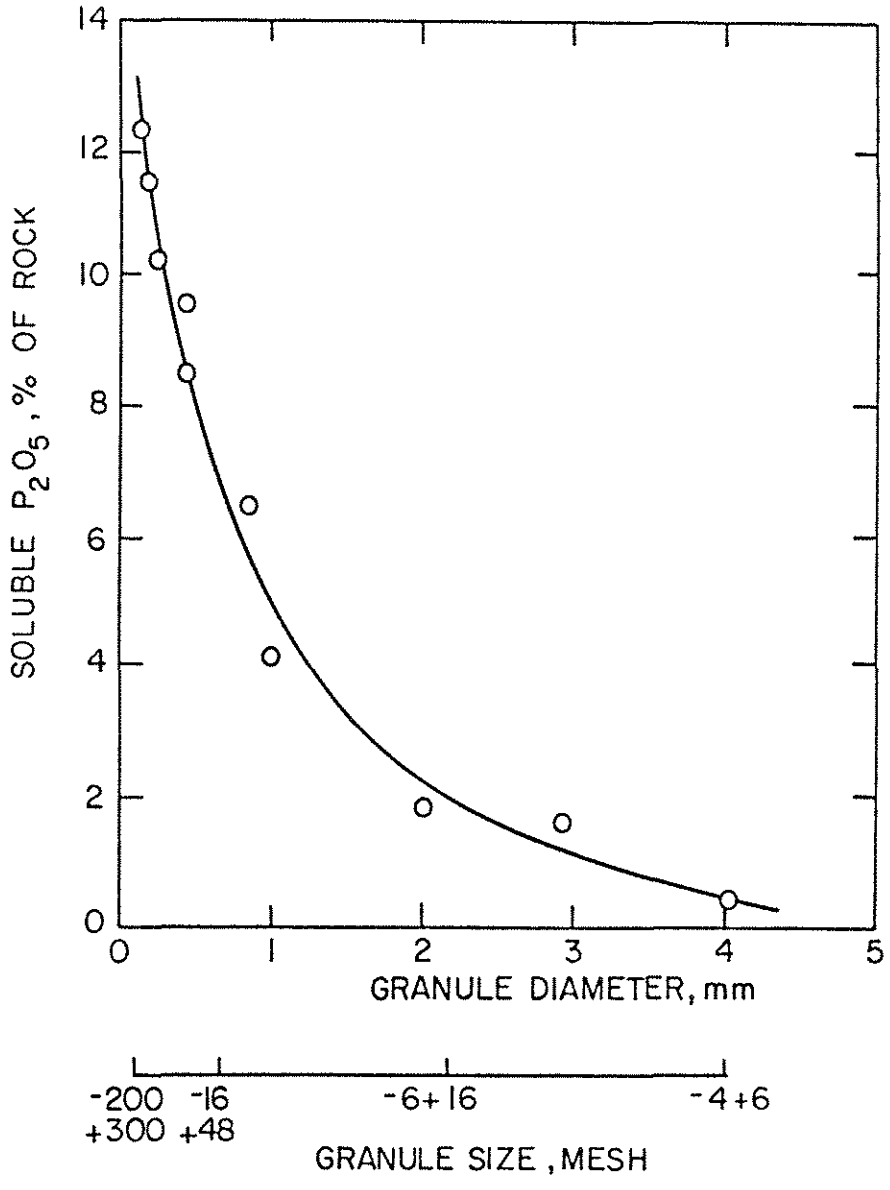

Figure 8. Effect of Granule Size on the Dissolution of the Granulated North Carolina Rock as Measured by the H-Resin Method.

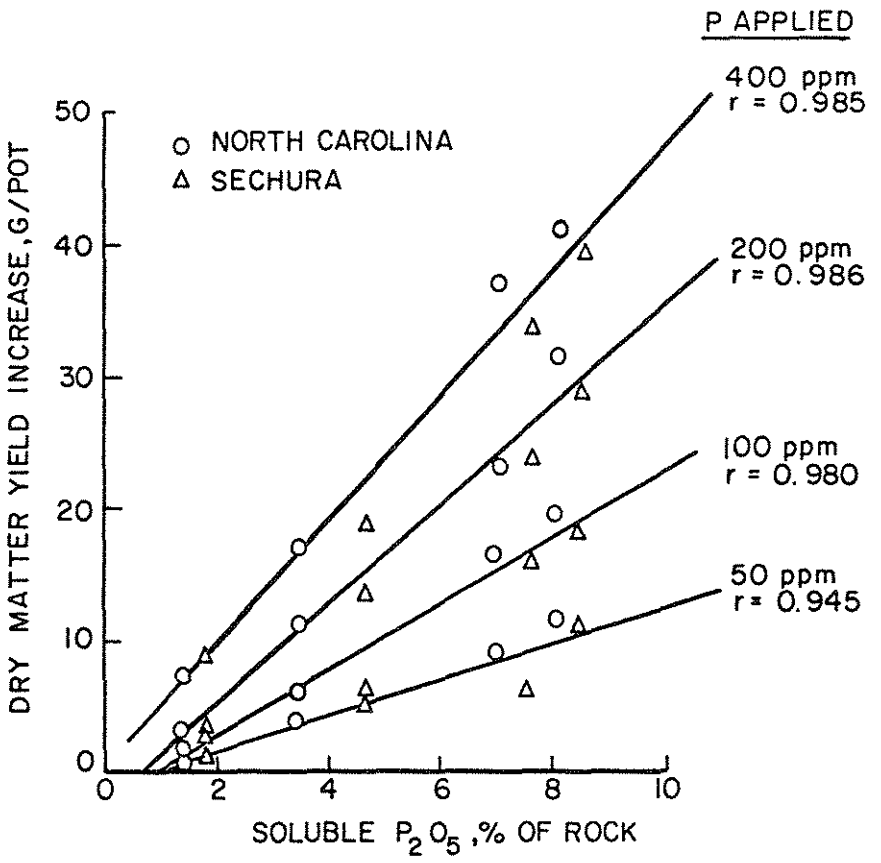

Figure 9. Correlation Between the Dry-Matter Yield Increase of Corn and the Solubility of Granulated Rocks as Measured by the Proposed H-Resin Method.

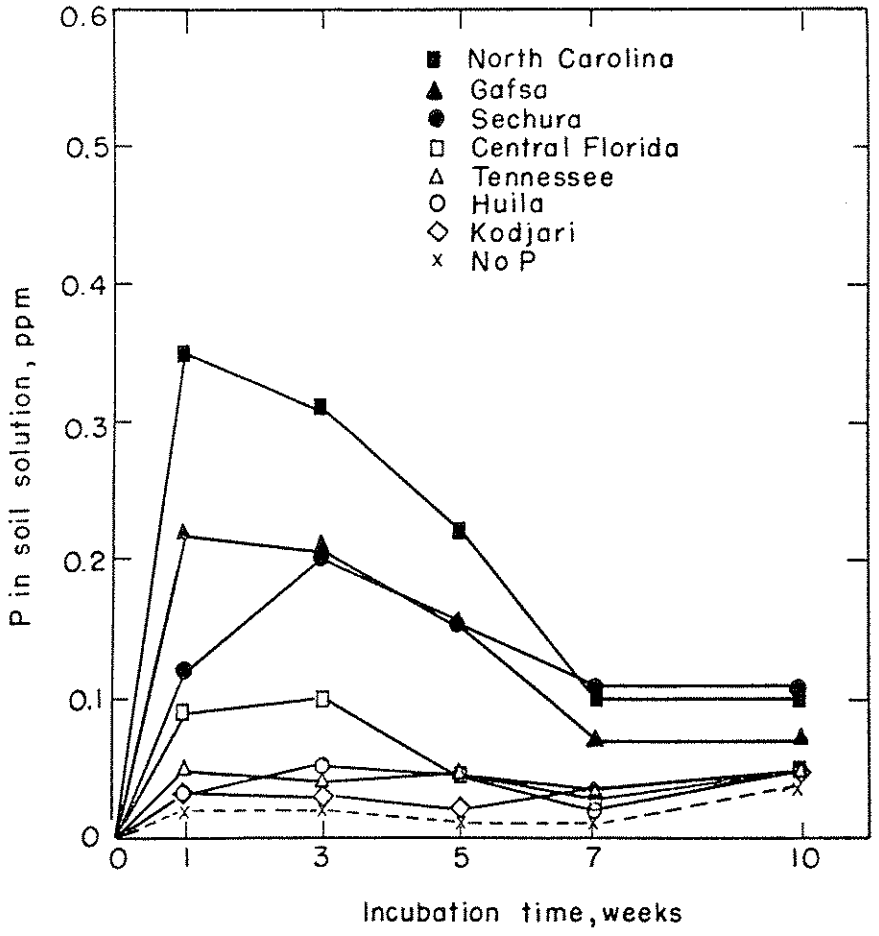

Figure 10. Dissolution of Various Phosphate Rocks in a Flooded Acid Soil (Mountview silt loam, pH 4.8) at Rate of 400 ppm P During Incubation at 25°C.

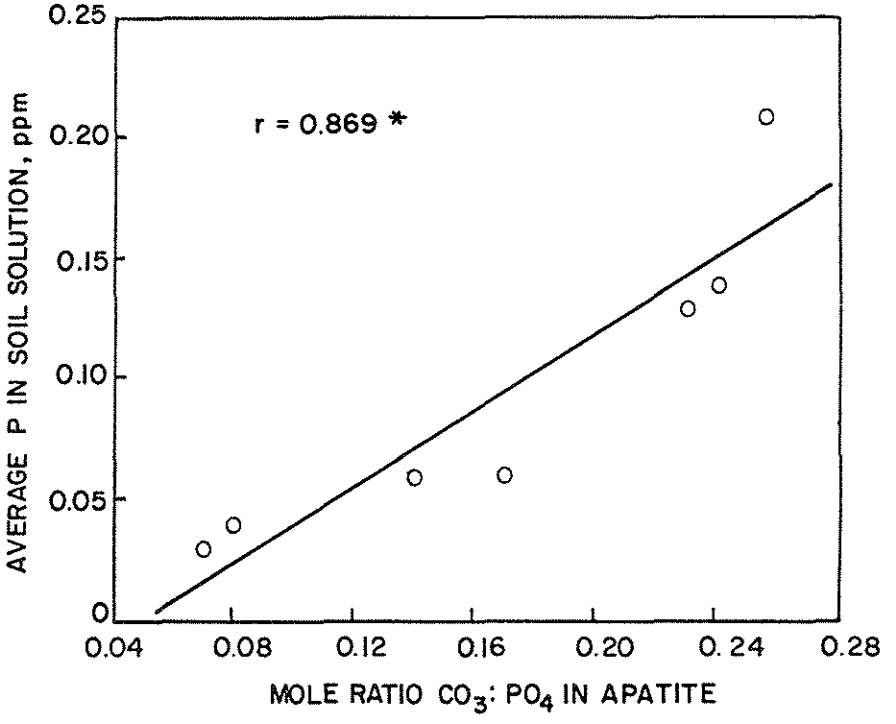

Figure 11. Relationship Between the Average P Concentration in Soil Solution During Incubation Under Flooded Conditions and the Mole Ratio of CO_3:PO_4 in the Apatite Structure.

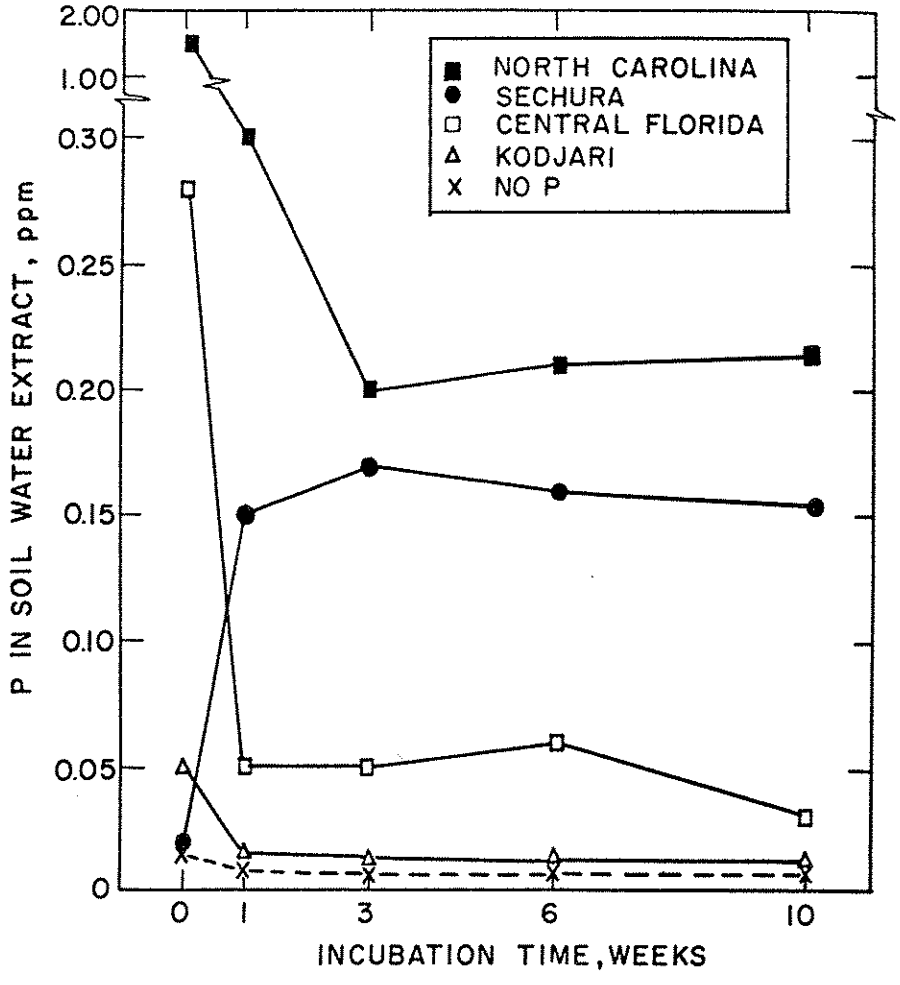

Figure 12. Dissolution of Various Phosphate Rocks in an Acid Soil (Weston sandy loam, pH 4.5) at Rate of 400 ppm Under Unsaturated Conditions During Incubation at 25°C.

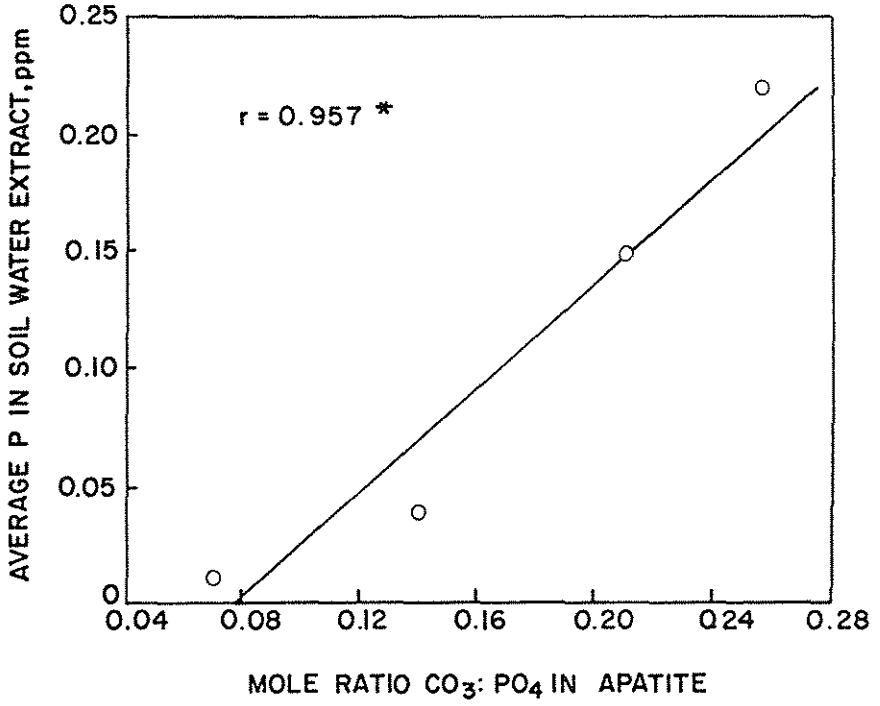

Figure 13. Relationship Between the Average P Concentration in Soil Water Extract During Incubation Under Unsaturated Conditions and the Mole Ratio of CO_3:PO_4 in the Apatite Structure.

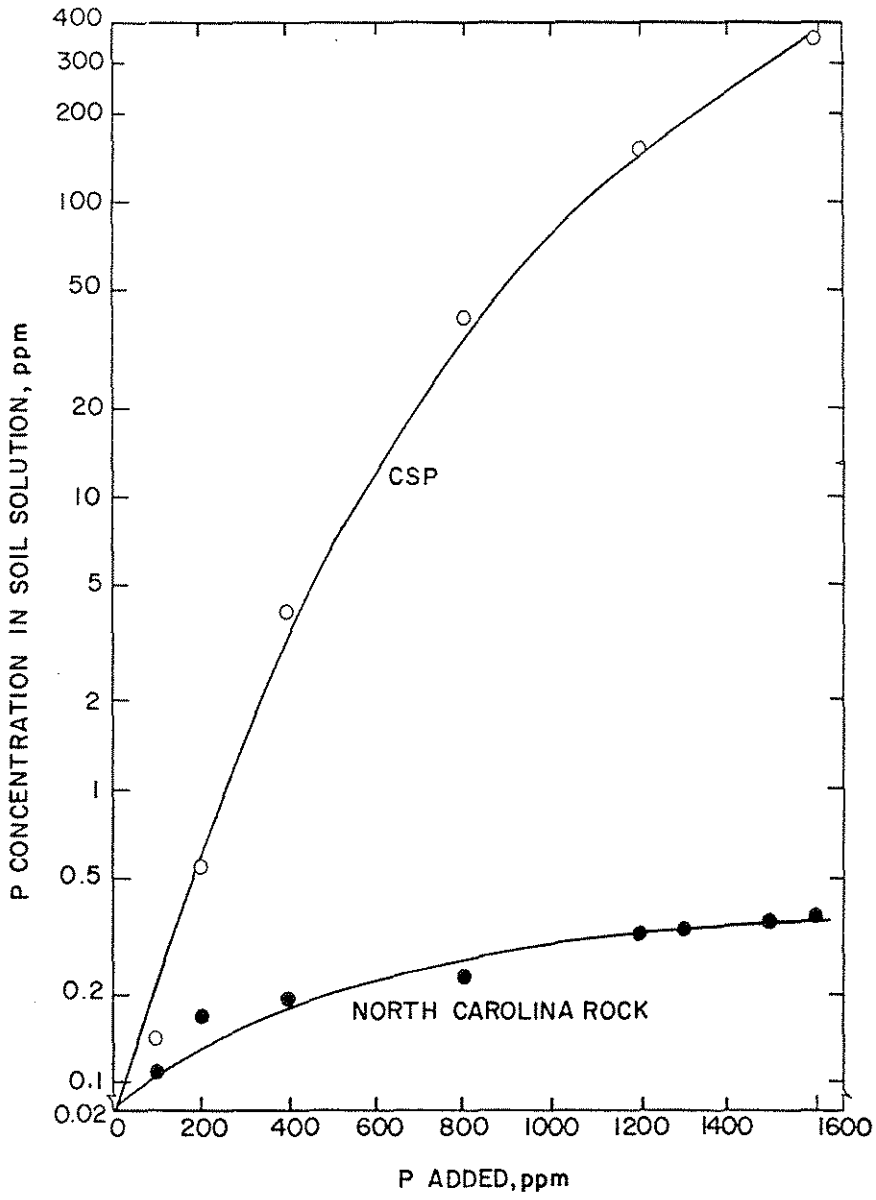

Figure 14. Phosphorus Concentrations in the Soil Solution from the Mountview Soil (pH 4.8) Treated with Various Rates of North Carolina Rock and CSP After 2-Week Incubation at 25% Moisture Content in the Soil.

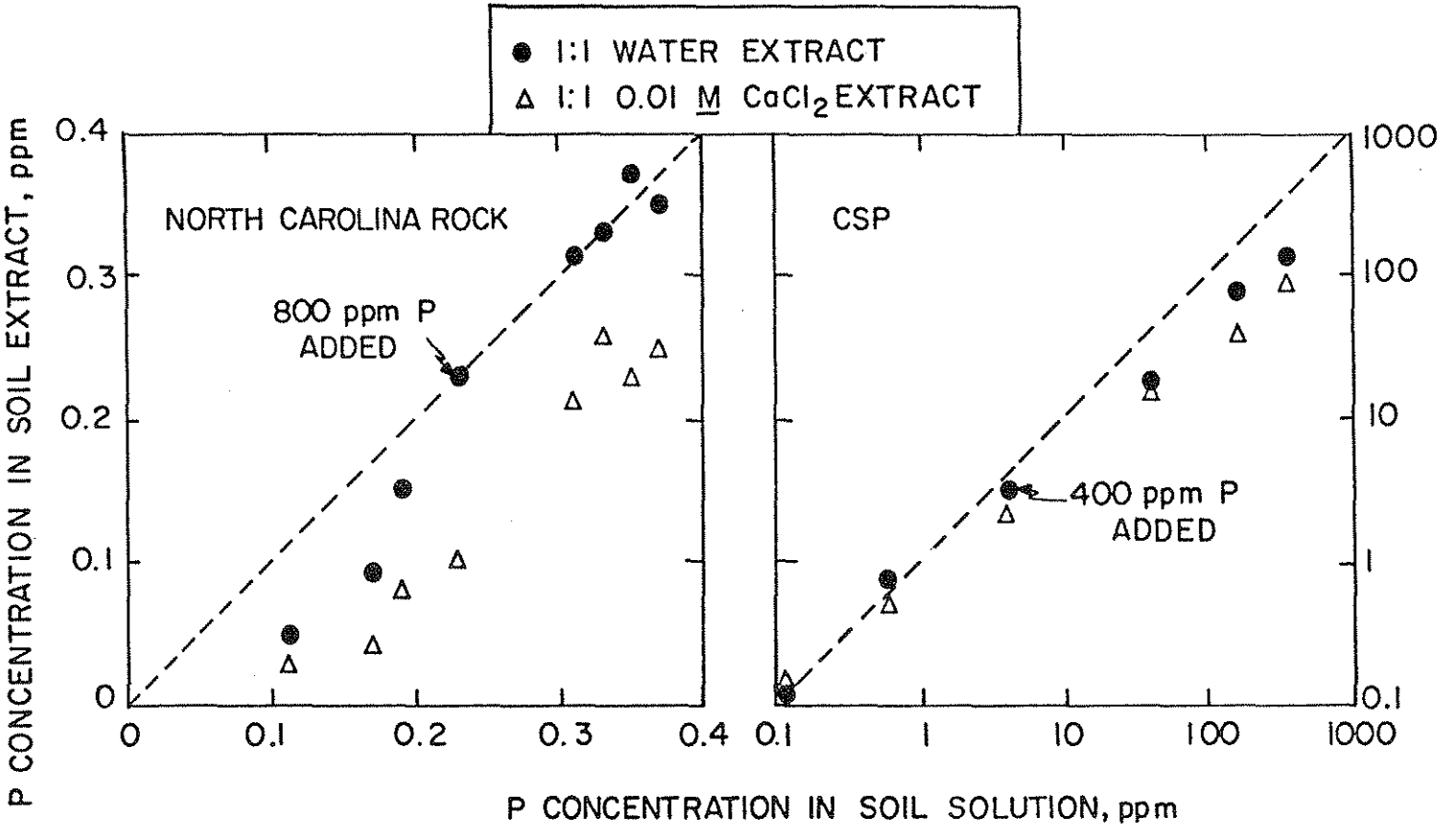

Figure 15. Relationship Between the P Concentrations in the Soil Solution and Soil Extracts from the Mountview Soil (pH 4.8) Treated with Various Rates of North Carolina Rock and CSP After 2-Week Incubation at 25% Moisture Content in the Soil.

PHOSPHORUS CONCENTRATION IN SOIL SOLUTION AS A FACTOR AFFECTING PHOSPHATE ROCK EFFECTIVENESS

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Introduction

Phosphate rocks (PR) from many geographical regions have been evaluated as direct application P fertilizers in numerous greenhouse and field studies. It is a common observation that the yield maximum attained by increasing rates of PR varies among rock sources. It is also commonly observed that these maxima are invariably less than the maximum yield attained with increasing rates of water-soluble P sources, such as superphosphates (Ensminger et al., 1967; Engelstad et al., 1974).

Numerous reports in the literature indicate that crop yield and uptake of P are related to the concentration of P in the soil solution or in water extracts of soils (Khasawneh and Copeland, 1973). Plots of yield or uptake against P concentration in soil solution appear to be hyperbolic and can be used to define a P concentration below which a plant will not reach its yield potential and above which the marginal yield increases are progressively small. The concentration defined in this manner has ranged from 20 to 100 ppb of P. The finding of a range of concentrations rather than a finite level is due to variation in soil characteristics and variations in nutritional requirements of different plant species.

Khasawneh and Copeland (1973) found that the relative growth rate of cotton (Gossypium hirsutum) was directly related to the rate of P uptake by roots; when rate of uptake was high, the ensuing growth rate was also high, and when uptake was low, the growth rate was low. Since the rate of P uptake is highly dependent on P concentration in soil solution, then this concentration effectively determines the growth rate of the plant and thus the general nutritional requirements of the plant.

The relationships among P concentration in soil solution, rate of P uptake, and rate of growth seemed pertinent to the study of PR as a material for direct application to soils and its ability to supply P to plants. A series of experiments was designed based on two premises:

1. That the P concentration in soil treated with PR is dependent on the amounts and reactivities of the PRs when measured within specific time intervals; and
2. That the relative growth rate of a crop is related to the P concentration in soil treated with PR up to some "critical" range of P concentrations.

The objectives of the research project were:

1. To measure the level of P that can be sustained in soil solution in soils treated with PRs of varying reactivities (as indicated by citrate solubilities);
2. To determine the rate of plant growth which can be attained in such amended soils; and
3. Based on the above two measurements, to determine the relationship between the rate of plant growth and P concentration in the soil solution.

These studies were a portion of a joint Tennessee Valley Authority/ International Fertilizer Development Center cooperative project.

Procedure

In 1976 four sources of PR were selected: North Carolina, central Florida, Jordan (El Hasa mines), and Tennessee. These PRs were chosen to give a wide range in reactivities, as discussed by McClellan in these Proceedings. Mountview silt loam, an extremely P-deficient Typic Paleudult, was limed to pH 5.2 with a 4:1 mixture of Ca and Mg carbonates at the rate of 0.5 g/kg of soil. After three cycles of wetting-drying-mixing over a 3-week period, the limed soil was weighed into pots at 6 kg/pot on an oven-dry basis. Treatments included rates of 50, 200, and 800 mg of P/pot for each PR source and for dicalcium phosphate anhydrate (DCPA) and a no-P control treatment, all in triplicate. The following

materials were added to each pot: 600 mg of K as KNO_3; 180 mg of Mg as $MgSO_4 \cdot 7H_2O$; 785 mg of N as NH_4NO_3 treated with 2% N-Serve; and 500 mg of a complete micronutrient mixture. Two series of pots were prepared. The first, cropped to maize (Zea mays L.), included sufficient pots for plants to be sequentially harvested at selected time intervals. The second uncropped series was incubated at 18% moisture at 24° C. Maize (Funk's 4455 hybrid) was planted on February 24, 1976, and emergence was complete by March 1. Harvests were made 3, 4, 5, and 6 weeks after emergence, at which times soil samples were removed for analysis. The uncropped soils were sampled at selected intervals. Soil samples that could not be extracted within 8 hours were frozen until extracted.

Extraction of soil samples was as follows: a 1:1 soil:water suspension was shaken for 30 minutes and then centrifuged for 10 minutes at 600 G to remove the bulk of the solids. The supernatant solutions were then recentrifuged at a constant temperature for 20 minutes at 12,000 G and filtered through 0.26-μm Millipore® filters to yield a clear extract. Electrical conductivity and pH of the extracts were determined immediately, and the solutions were refrigerated until analyses for P and Ca could be performed.

In 1977 Hiwassee clay loam (Typic Rhodudult, clayey kaolinitic, oxic) was used in two greenhouse experiments using essentially the same general outline as in 1976. In the first experiment, PRs from North Carolina, central Florida, and Upper Volta, and DCPA were applied at rates of 150, 300, 600, and 1,200 mg of P/pot. Maize was grown and sequentially harvested 3, 4, 5, and 6 weeks after emergence. In the second experiment, PRs from Gafsa, Mali, and Upper Volta and DCPA were applied at the same rates for Crowder cowpeas (Vigna unguiculata L. Walp). Soil was sampled from harvested pots, and the soil was extracted with water as outlined above. In both experiments, blanket additions of N, K, Mg, and micronutrients were as outlined for the 1976 experiment. No uncropped series of pots was prepared in 1977.

Results

Crop Growth Data

Responses of maize in 1976 and of maize and cowpeas in 1977 to P rates are shown in figures 1, 2, and 3, respectively, for the 6-week harvest. The reactivities of the various PR sources, as reflected by citrate solubility, are shown in parentheses for each plot. Response was greater as reactivity increased in all three experiments, as would be expected. Uptake of P in relation to P rates and PR reactivities behaved similarly (not shown).

For the two maize experiments, only those treatments receiving North Carolina PR approached the standard response curve achieved with DCPA. With cowpeas, only those treatments receiving Gafsa PR approached the DCPA response curve.

Dry-matter yields for the sequential harvest of maize in 1977 at all rates of North Carolina PR are shown in figure 4, in which yields for the various P rates are plotted against the age of the plant at harvest. Similar plots (not shown) were constructed for all P rates and P sources in all three experiments. At low rates of applied P or with less reactive PRs, growth proceeded at a slow rate, and dry-matter accumulation was substantially below an apparent maximum. To estimate the relative growth rates with various application rates and sources of P, dry-matter yield data such as those in figure 4 were fitted to either a concurrent exponential growth model (equation 1) or a mixed exponential/ logistic model (equation 2):

$$Y = \Sigma\, Y_0 \cdot \exp\,(k_i t_i) \qquad (1)$$

or

$$Y = \Sigma\, Y_0 \cdot \exp\,(k_i t_i) + \Sigma\, A_j / \left[1 + \frac{A_j Y_0}{Y_0} \cdot \exp\,(k_j t_j)\right] \qquad (2)$$

In these equations Y is the dry-matter yield of tops for a given source, A can be interpreted as a limiting dry-matter yield as P rate and time (t) increase, k is

the relative growth rate, and Y_0 is the dry-matter content of the seedling at time zero (emergence date). The subscripts (i and j) refer to the P rates used in the experiment (for example, using the data from figure 4, i = 1 for 150 mg P, 2 for 300 mg P, etc.). The mixed model (equation 2) was used for these data in figure 4: for the two lowest rates of P in figure 4, the exponential growth equation was used, and at the three highest rates, the logistic model was used. The 1976 data for all PRs except North Carolina were described using equation 1.

The relative growth rates of maize tops and their standard errors for all rates and sources of P in the 1977 experiment are shown in table 1. The relative growth rates of maize grown in soil treated with DCPA and with North Carolina PR are similar at a given amount of applied P. With central Florida and Upper Volta PRs, 1,200 mg of P/pot is required to give growth rates attained with only 300 mg of P/pot as DCPA or North Carolina PR. Relative growth rates achieved in the other two experiments are shown in a succeeding section.

Soil Extraction Data

Analyses of water extracts of samples of Mountview silt loam cropped to maize and Hiwassee clay loam cropped to maize or cowpeas are shown in tables 2, 3, and 4, respectively, in which the concentrations of P in soil solution supported by the various rates and sources of P are listed. For a given P source, P concentrations increased as the rate of application increased. The increases were largest with DCPA and the most reactive PR sources (North Carolina and Gafsa) and least with the nonreactive Tennessee and Upper Volta PRs. Additions of PRs from central Florida, Mali, and El Hasa had intermediate increases, reflecting their medium reactivities. Within a given P rate, P concentrations generally increased with time, and the magnitude of the increases was again related to reactivities of the PRs.

Relationship Between P Concentration and Crop Growth

The data on the relative growth rates of corn and cowpeas at various levels of P additions, examples

of which are shown in table 1, were combined with data on P concentrations in soil solution at the same levels of P additions (tables 2, 3, and 4) to describe the relationship between growth rate and P concentration in solution. Plots of relative growth rates of maize in 1976 and of maize and cowpeas in 1977 at various P concentrations in soil extracts (averaged across time) are shown in figures 5, 6, and 7, respectively. In each experiment, data from all P sources and all P rates fall on the same curvilinear line.

Comparison of the maize data on the two soils (figures 5 and 6) shows that P concentrations of 60 ppb or higher are needed for maximum growth potential (maximum relative growth rate). The exact concentration required for maximum growth is difficult to pinpoint because the lines in these plots are still ascending at the highest P concentrations attained. The important point of these plots, however, is the location of the cluster of data points associated with each P source. In figure 5, for instance, the three data points for Tennessee PR represent additions of 50, 200, and 800 mg of P. The P concentrations sustained by Tennessee PR range from 18 to 21 ppb, which support relative growth rates of only 0.04-0.07 g/g·day, rates which are considerably lower than the apparent maximum. Likewise, the El Hasa and central Florida PRs cluster considerably below the P concentrations and relative growth rates sustained by the highest application of DCPA and North Carolina PR. Similar results are shown in figure 6, where P concentrations and resulting relative growth rates are considerably less with Upper Volta and central Florida PRs than with North Carolina PR.

Data for cowpeas (figure 7) show that relative growth rate tends to level off at P concentrations above 30-40 ppb, although there is a continued gradual increase as concentrations increase to very high levels. Again, the important point is that additions of Upper Volta PR at the highest levels studied were not sufficient to sustain P concentrations required for maximum growth potential of cowpeas. The Mali PR at the highest level of P addition sustained growth rates for cowpeas comparable to those with the reactive Gafsa PR but somewhat lower than that with the highest DCPA addition.

The maize data (figures 5 and 6) reveal that about the same P concentration is needed for maximum growth

rate on two different soils. Comparison of the maize and cowpea data on the same soil (figures 6 and 7) indicates that cowpeas may require a concentration of P for maximum growth potential that is only two-thirds that required for maize. Thus, it appears that variation in P requirements is more influenced by crop species than by properties of these soils. Additional data on such comparisons are needed.

Summary and Conclusions

Maize and cowpeas grown in greenhouse pots responded to additions of various PRs, and the magnitude of the responses increased with increase in reactivities of the PRs. Concentrations of P in soil solution were usually increased by additions of PR, and again the magnitude of this effect was more pronounced with the more reactive PRs. Concentrations of P in soil solution sufficiently high to promote maximum plant growth were obtained only with high rates of the most reactive PRs. Less reactive PRs supported relative growth rates greater than the no-P controls but less than that required for maximum growth.

These results provide adequate explanations of numerous field studies in which maximum yields varied among PR sources and were always less than those attained with soluble-P sources. The concentrations of P in soil solutions supported by dissolution of PRs simply were not sufficiently high to ensure maximum growth rates.

The usefulness of these studies with respect to use of PR for direct application depends largely on the level of productivity existing under a given system of agriculture. In developed areas where soluble fertilizers are commonly used and where crop yields approach their maximum potential, use of even the most reactive PR for direct application would be uneconomical. The concentrations of P in soil solution in many soils in these areas already exceed the level which can be sustained by PR. Dissolution of PR would not be appreciable at such high soil-P concentrations. There are vast regions of the world, however, in which soluble fertilizers are not readily obtainable and where crop production is nowhere near maximum potential yields. In these regions, the goal

is to increase crop production, but not necessarily to achieve the maximum yield. Under these conditions, use of PRs of moderate to high reactivity can achieve this short-term goal of increasing crop production. As crop yields are pushed to the limits dictated by a given PR, decisions must be made to move to more soluble P sources; but until then, PRs can fill a need in areas of widespread P deficiency.

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Table 1. Relative Growth Rate of Maize Tops (Hiwassee Clay Loam, 1977)

Source	Rate mg P/pot	Relative Growth Rate, k, g/g·day k x 10^2	S.E. x 10^2
North Carolina	150	7.62	0.37
	300	9.41	0.31
	600	13.48	0.13
	900	15.07	0.15
	1,200	15.65	0.16
Central Florida	150	6.45	0.77
	300	7.74	0.62
	600	9.40	0.53
	1,200	9.89	0.50
Upper Volta	150	3.02	1.22
	300	4.49	0.81
	600	5.69	0.62
	1,200	7.81	0.46
DCPA	150	7.24	0.57
	300	8.64	0.48
	600	10.09	0.44
	1,200	15.93	0.24
No P	0	4.3	0.90

Table 2. Concentration of P (ppb) in Water Extracts of Mountview Silt Loam, Uncropped or Cropped to Maize

Source	Rate mg P/pot	P Concentration in 1:1 Soil Water Extracts		
		Cropped[b]	Uncropped[a] 70 days	Uncropped[a] 315 days
No P	0	16	9	10
DCPA	50	17	15	10
	200	22	22	17
	800	73	186	83
North Carolina	50	19	19	16
	200	23	20	18
	800	41	42	82
El Hasa	50	18	11	10
	200	20	15	16
	800	23	22	31
Central Florida	50	17	12	13
	200	18	15	13
	800	22	18	33
Tennessee	50	17	11	11
	200	18	11	12
	800	21	12	17

a. Means of samples taken from replicated pots 70 and 315 days after treatment.
b. Means of triplicate samples taken after harvest dates 4, 5, and 6 weeks from emergence.

Table 3. Concentration of P (ppb) in Water Extracts of Hiwassee Clay Loam Sampled After Sequential Harvesting of Maize

P Source	P Rate mg P/pot	Weeks After Emergence 3	4	5	6	Mean
No P	0	10	11	12	13	11.5
North Carolina	150	15	13	19	26	18.0
	300	21	29	34	33	29.0
	600	41	35	44	47	42.0
	900	52	47	56	63	54.5
	1,200	56	64	61	71	63.0
Central Florida	150	13	13	13	21	15.0
	300	13	13	18	24	17.0
	600	17	26	23	36	25.5
	1,200	25	41	31	44	35.0
Upper Volta	150	12	12	12	12	12.0
	300	13	11	13	13	12.5
	600	12	9	15	17	13.3
	1,200	16	13	19	27	19.0

Table 4. Concentration of P (ppb) in Water Extracts of Hiwassee Clay Loam Sampled After Sequential Harvesting of Cowpeas

P Source	P Rate mg P/pot	Weeks After Emergence 3	4	5	6	Mean
No P	0	15	16	12	11	14
DCPA	150	21	19	19	19	20
	300	25	24	31	32	28
	600	69	52	67	72	65
	1,200	183	148	180	159	168
Gafsa	150	18	16	18	27	20
	300	19	19	26	30	24
	600	29	32	37	42	35
	900	44	44	50	53	48
	1,200	42	55	60	72	57
Mali	150	17	14	20	20	18
	300	18	16	26	24	21
	600	19	23	33	40	29
	1,200	26	35	46	55	41
Upper Volta	150	14	12	13	14	13
	300	15	15	15	15	15
	600	15	16	16	15	16
	1,200	16	15	17	19	17

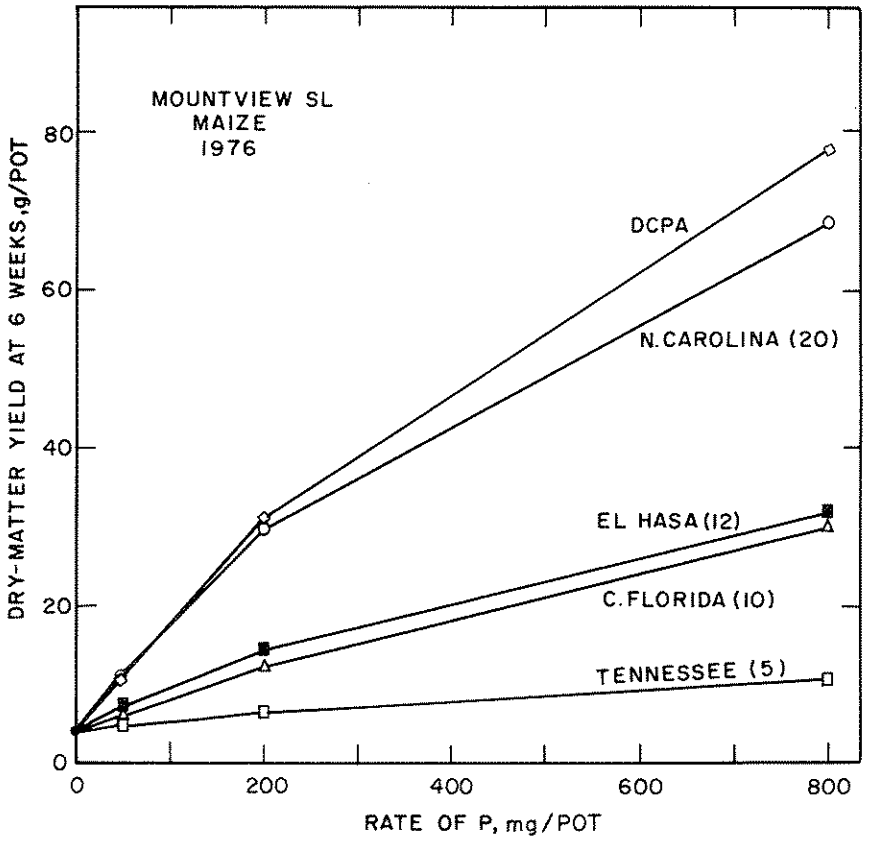

Figure 1. Dry-Matter Yields of Maize at the 6-Week Harvest as Affected by Rates and Sources of P (Mountview silt loam, 1976).

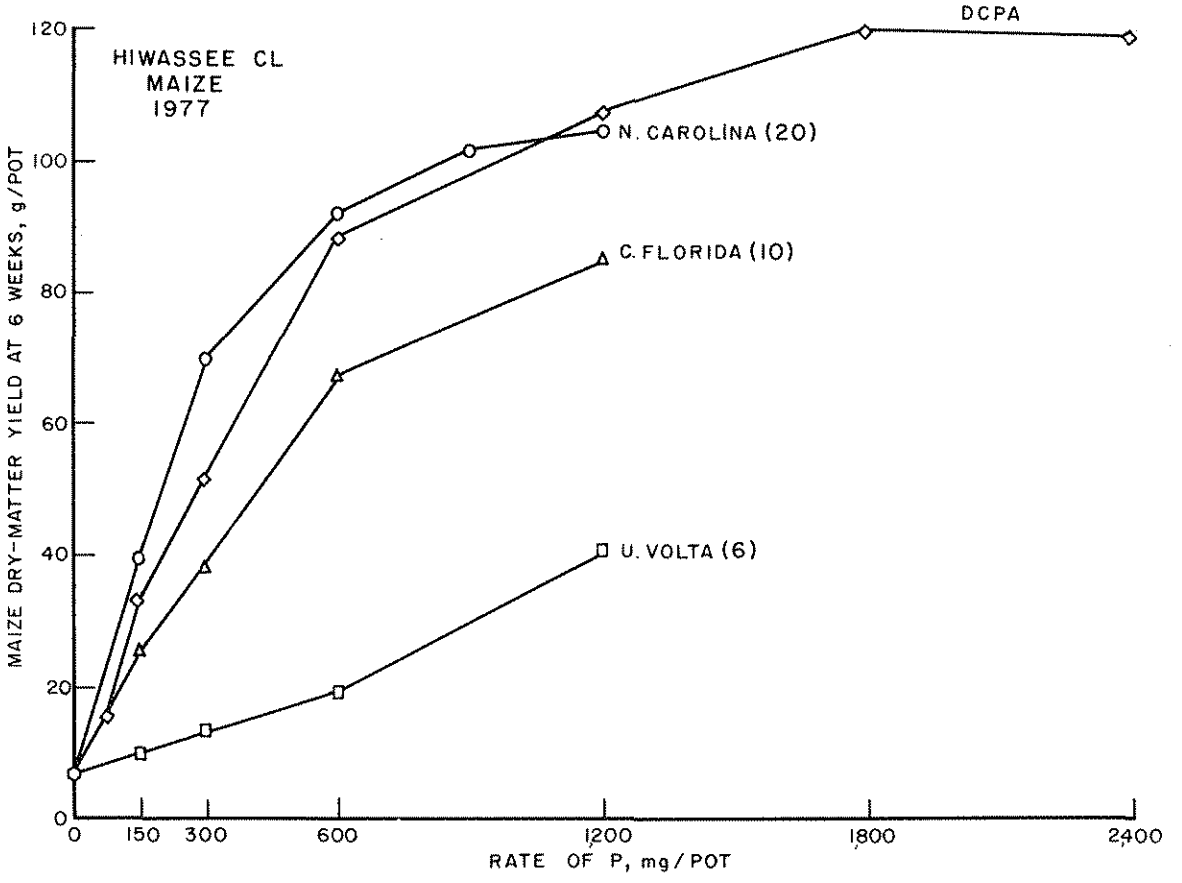

Figure 2. Dry-Matter Yields of Maize at the 6-Week Harvest as Affected by Rates and Sources of P (Hiwassee clay loam, 1977).

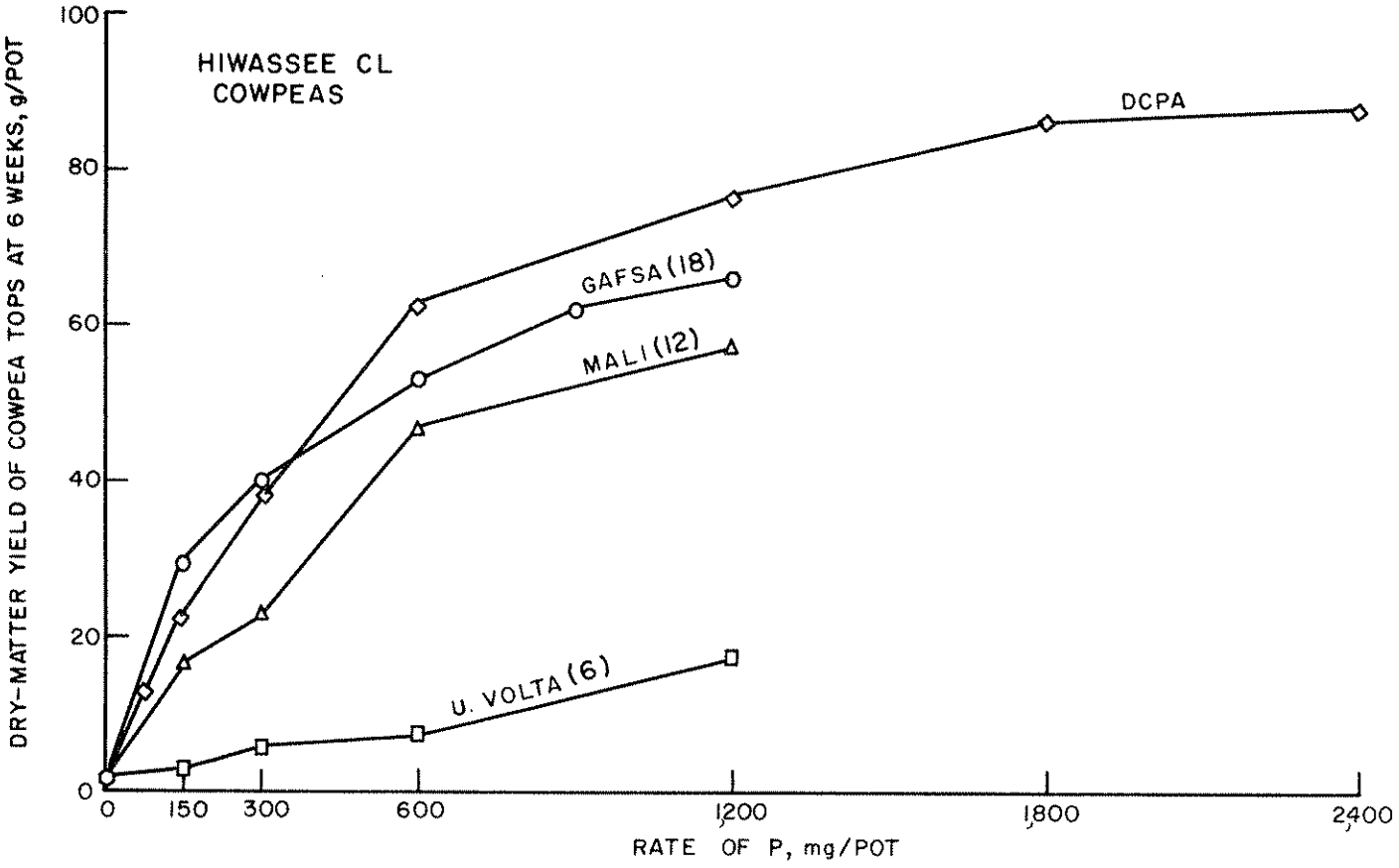

Figure 3. Dry-Matter Yields of Cowpeas at the 6-Week Harvest as Affected by Rates and Sources of P (Hiwassee clay loam, 1977).

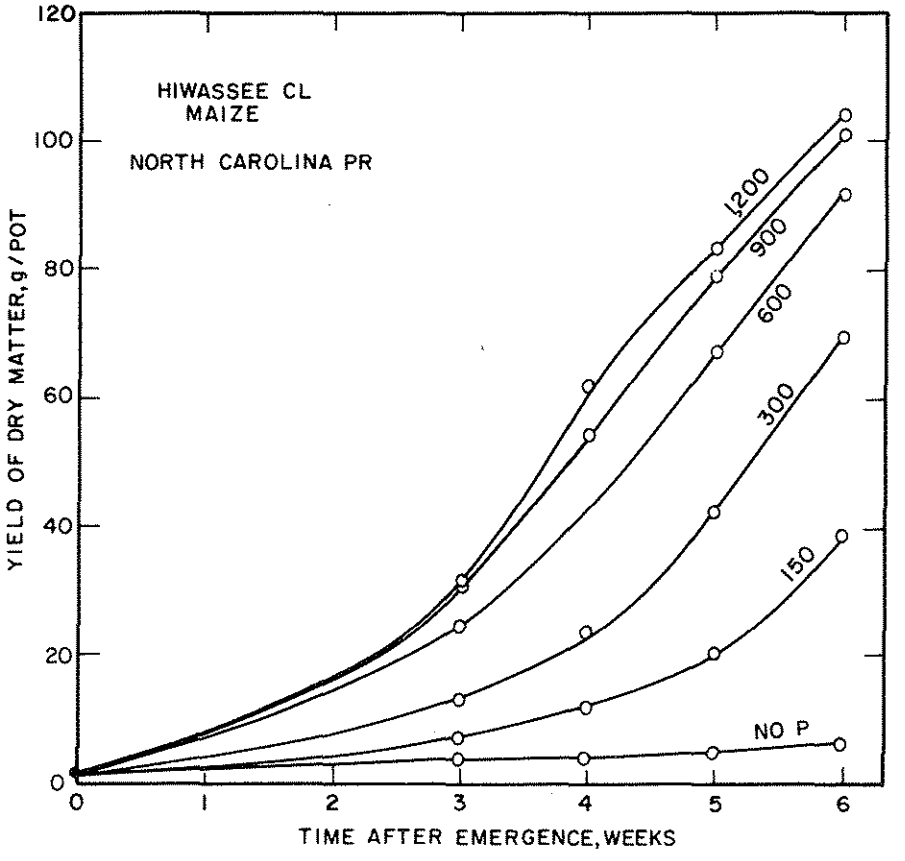

Figure 4. Dry-Matter Yields of Maize at Varying Harvest Periods as Affected by 0 to 1,200 mg of P/pot Applied as North Carolina PR (Hiwassee clay loam, 1977).

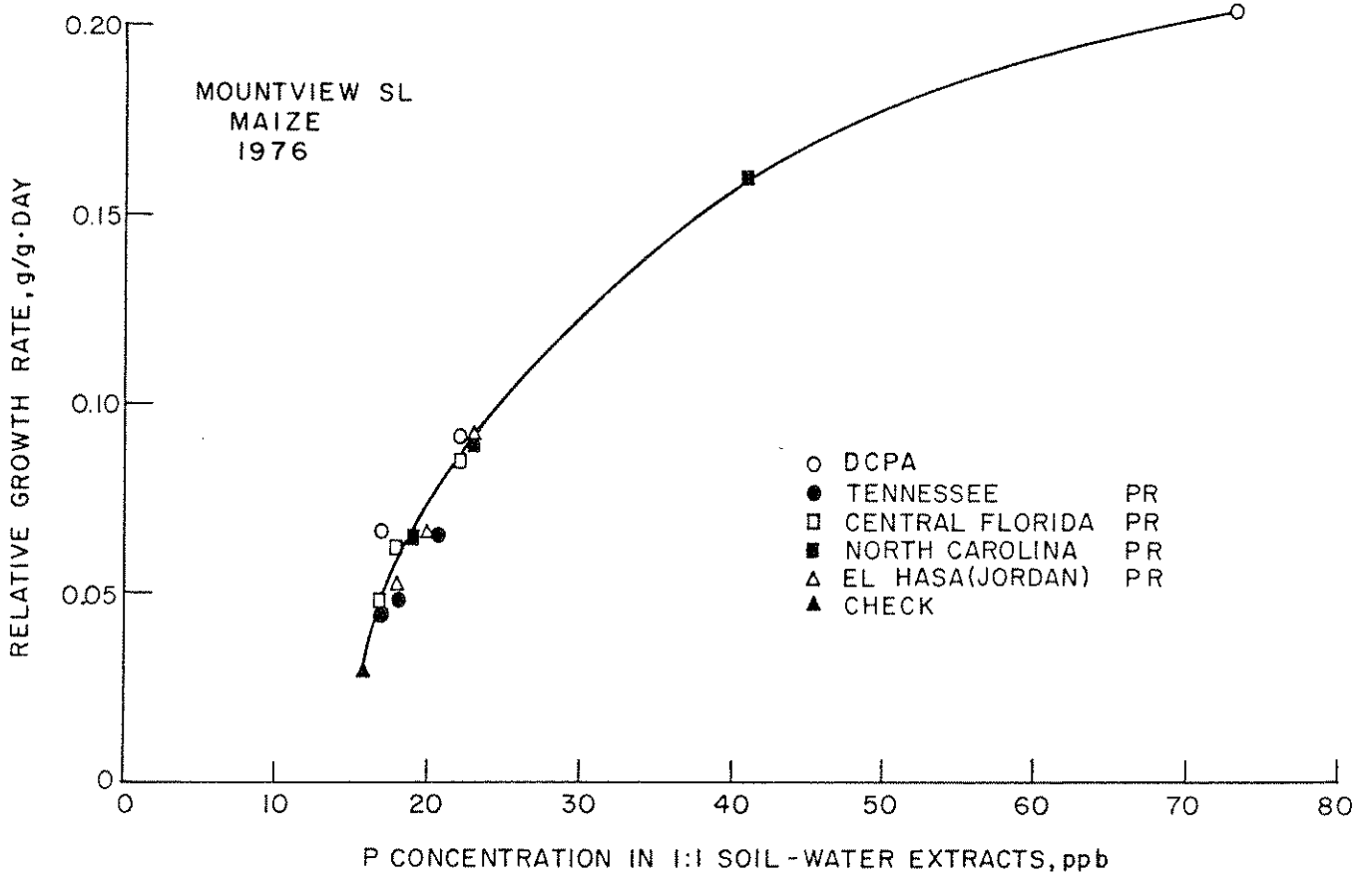

Figure 5. Relative Growth Rates of Maize Grown on Mountview Silt Loam (1976) as Influenced by Concentration of P in 1:1 Soil-Water Extracts.

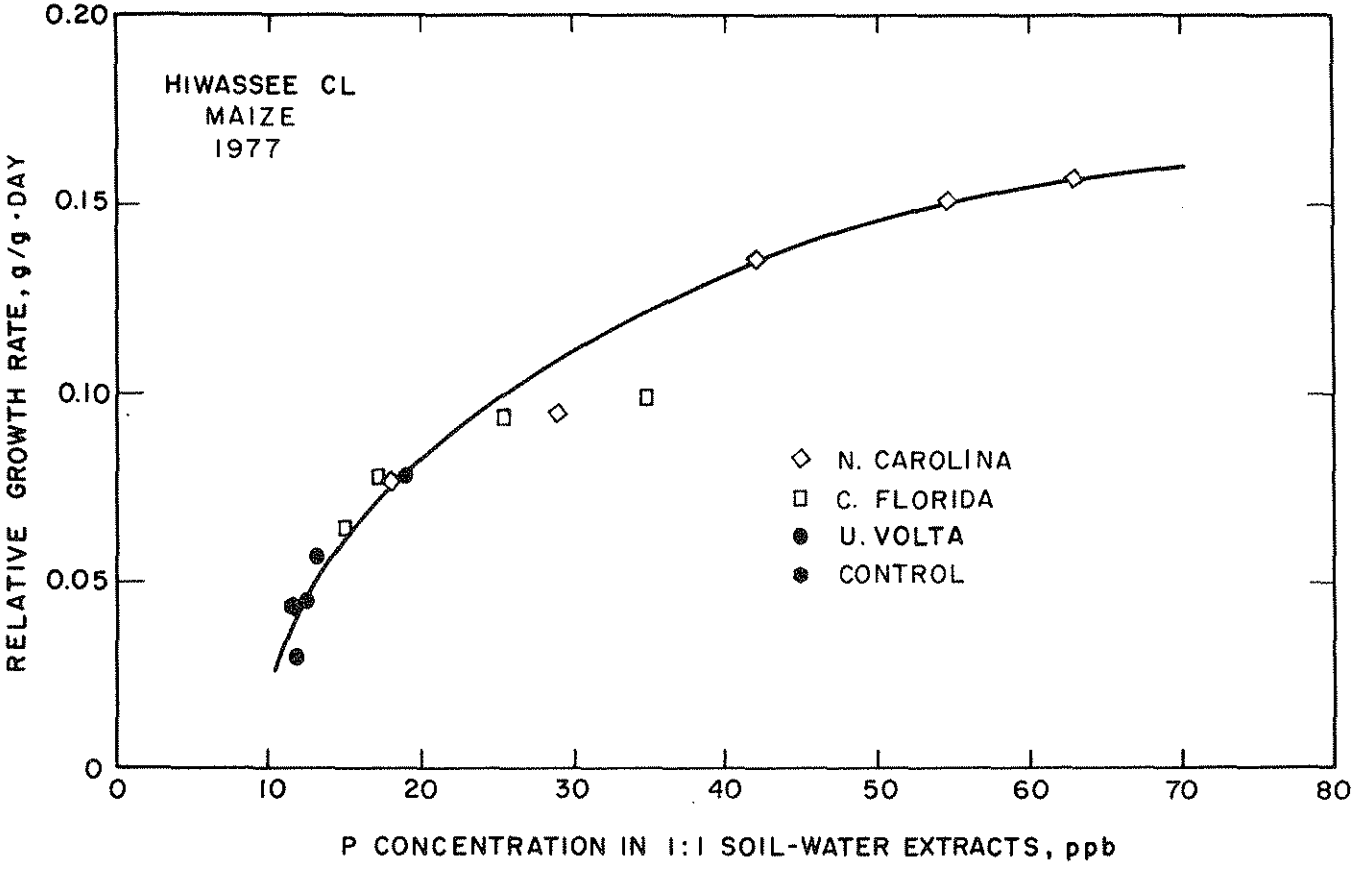

Figure 6. Relative Growth Rates of Maize Grown on Hiwassee Clay Loam (1977) as Influenced by Concentration of P in 1:1 Soil-Water Extracts.

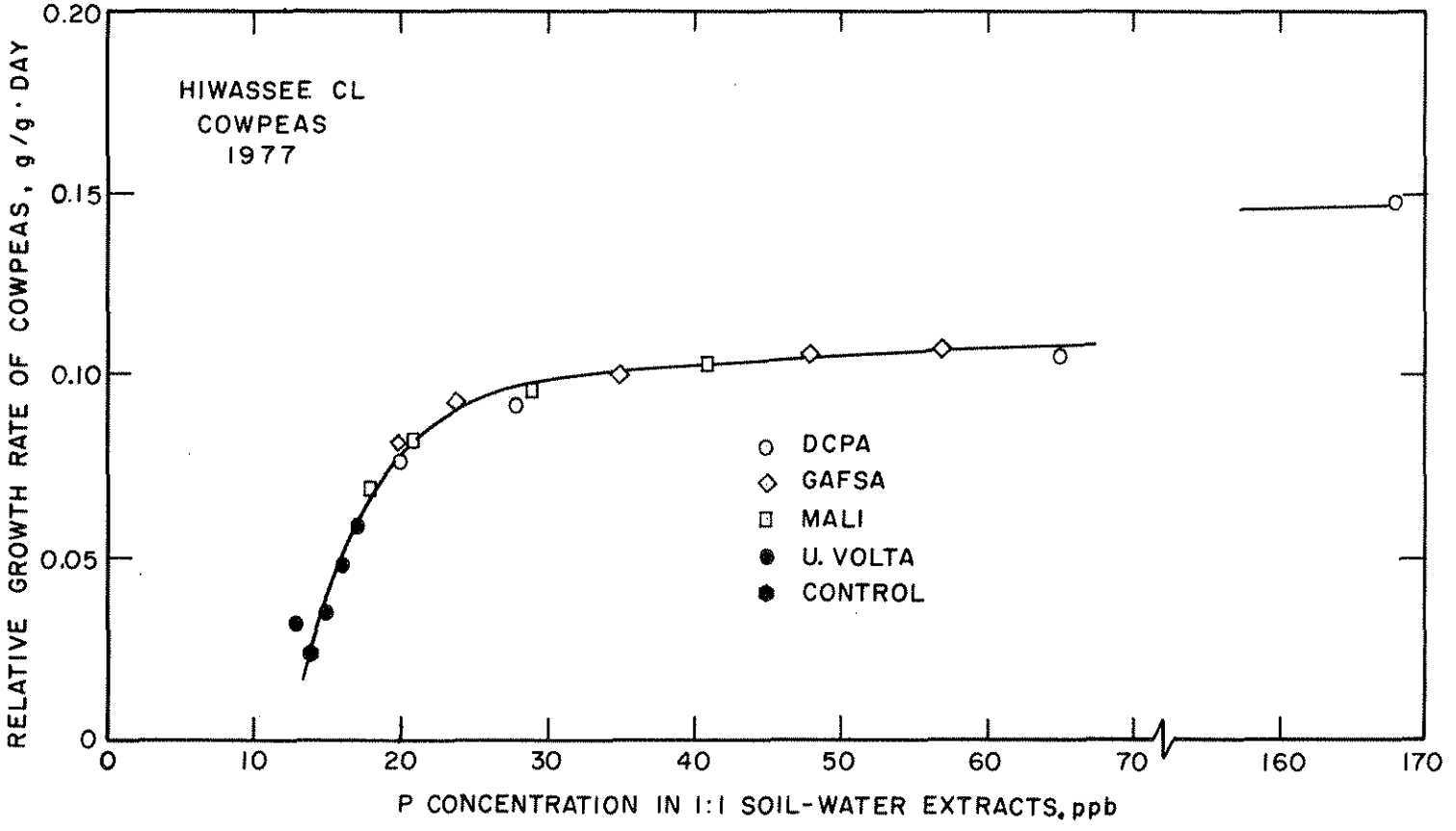

Figure 7. Relative Growth Rates of Cowpeas Grown on Hiwassee Clay Loam (1977) as Influenced by Concentration of P in 1:1 Soil-Water Extracts.

AGRONOMIC MEASUREMENTS OF PHOSPHATE ROCK EFFECTIVENESS

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Introduction

The direct application of phosphate rock to the soil as a possible alternative to utilization of the more expensive soluble phosphate fertilizers in tropical cropping systems has received considerable attention in recent years. Contributing to the interest being shown are the combined factors of (1) extensive areas in developing countries characterized by acid soils high in phosphorus-fixation capacity which are extremely deficient in phosphorus and, therefore, present favorable soil conditions for dissolution of relatively insoluble apatites and (2) the desire of developing countries with local deposits of phosphate rock to utilize their rock, if possible, through direct application which requires far less capital investment than does a conventional soluble P manufacturing plant.

Many variables have an effect upon whether or not direct application of phosphate rock is feasible. These factors will be briefly discussed in light of recent investigations on this subject. The factors related to the agronomic effectiveness of phosphate rock for direct application discussed in this paper include:

1. Phosphorus availability from phosphate rocks,
2. Liming effect of phosphate rocks,
3. Initial effectiveness as related to source and crop,
4. Residual effect of P from phosphate sources, and
5. Effect of grinding and granulation of phosphate rock.

The experiments discussed include two which were conducted in a greenhouse and three conducted under field conditions. All experiments were designed to

compare the direct application of phosphate rock with a soluble phosphorus fertilizer source throughout a range of application rates, both in terms of initial and residual phosphorus availability. Seven sources of phosphate rock were utilized (table 1) which ranged from 1.9% to 6.7% citrate-soluble phosphorus (AOAC method), expressed as percent of the rock. The reactivity of the phosphate rock is defined in this paper as high when the citrate solubility is > 5.4%, medium when in the range of 3.2%-4.5%, and low when < 2.7%.

The first greenhouse experiment was conducted on an unlimed Oxisol (Carimagua) from the eastern plains of Colombia with guinea grass (Panicum maximum) as the indicator crop while the second was conducted on a phosphorus-deficient Ultisol from the United States (Mountview) limed to pH 5.2, with maize (Funks G4762) as the test crop. In both greenhouse experiments, phosphorus treatments were applied at rates of 0, 50, 100, 200, and 400 ppm phosphorus, and all treatments were replicated three times.

Two of the field experiments were conducted on the Colombian Oxisol which was utilized in the first greenhouse experiment, while the third field trial was grown on an Andosol from Popayan in Colombia. Table 2 identifies the initial properties of the Colombian soils. Brachiaria decumbens and cassava (Manihot esculenta crantz) were the indicator crops grown on the Oxisol while the test crop on the Andosol was beans (Phaseolus Vulgaris L.) variety Huasano P588. The levels of phosphorus applications in these experiments ranged from 0 to 400 kg/ha P_2O_5 and were also replicated three times. All experiments received constant applications of support nutrients at levels recommended to provide adequate nutrition from all nutrients except phosphorus.

Results from Colombia are more fully described in Hammond (1977), Ph.D. Thesis, Michigan State University.

Phosphorus Availability from Phosphate Rocks

The reactivity of the phosphate rock is often the single most important factor influencing the agronomic results associated with the direct application of phos-

phate rock when applied to an acid soil. Russell (1973) stated that "rock phosphates differ considerably in their fertilizer value, ranging from samples that are completely ineffective on all soils and on all crops to others that can be as good as triple superphosphate (TSP) for some crops with a pH below 6." It has been shown that the chemical reactivity can be adequately evaluated by measurement of the citrate-soluble phosphorus in the phosphate rock (Caro and Hill, 1956; Armiger and Fried, 1957; Terman et al., 1971; and Engelstad et al., 1972, 1974).[1] This measure, however, cannot be directly compared to the citrate-soluble phosphorus in a soluble phosphorus fertilizer. The citrate solubility in soluble phosphate fertilizers is a measure of the total amount of plant-available phosphorus in the fertilizer while, in a phosphate rock, it gives only a measure of the dissolution characteristics of the phosphate rock.

The effect of phosphate rock reactivity on the level of water-soluble P which could be maintained following application was measured in the Oxisol utilized in the greenhouse experiment (figure 1). It can be seen that relatively insoluble phosphate rock is initially much lower than the soluble TSP and that all sources rapidly decreased during the early stages of incubation. It was only after approximately 100 days that the highly reactive rocks equaled the level of water-soluble phosphorus maintained by TSP. The low reactivity rocks failed to approach TSP during the 190-day incubation period.

The level of water-soluble phosphorus at the time of planting the guinea grass on the Oxisol in the

1. Data by Chien and Hammond ("A Comparison of Various Laboratory Methods for Evaluating Agronomic Potential of Phosphate Rocks for Direct Application," (1978) Soil Science Society of America Journal, 42:935-939) show that phosphate rocks with a high percentage of free calcite require a double extraction with neutral ammonium citrate for removal of associated carbonates which can depress the solubility and give a low measurement of reactivity. Modification of the AOAC method is desirable when comparing phosphate rocks containing calcite or gypsum or with rocks of low grade.

greenhouse was highly correlated with citrate-soluble phosphorus in the phosphate rocks at both the 200 and 400 ppm P rate of application (figure 2). However, at the low rates of application, water-soluble phosphorus levels were extremely low and were not significantly correlated with citrate solubility. Figure 3 indicates, however, that these water-soluble phosphorus levels were well correlated with phosphorus uptake by the guinea grass ($r = 0.918$). In the field experiment with cassava which was also conducted on an Oxisol from eastern Colombia, the water-soluble phosphorus in the soil, measured 51 days following treatment application, was not as well related to yield as the measurements obtained in the greenhouse but did show the same general trends (figure 4). In all cases, the concentration of water-soluble phosphorus was extremely low, ranging from 0.004 to 0.028 ppm phosphorus.

Available phosphorus as measured by Bray P_1 extracting solution was well related to citrate solubility at all rates of application using the same soil described above (figure 5). It was also noted that the extractable phosphorus was well related to crop yield (figure 6). However, the response curve was distinctly different from the crop response to phosphorus supplied by soluble sources. The observation that yields related to a given level of phosphorus from phosphate rock were higher than yields from the same level of extractable phosphorus from soil treated with TSP is in agreement with the observations of Barnes and Kamprath (1975). One of their explanations was that there could be some "acidulation products" from phosphate rock that the plant can utilize but the extractant cannot dissolve. Chien (1978) presented evidence for the explanation that the distinct response curves may be due to the fact that the Bray P_1 extracting solution was able to extract significant amounts of phosphorus from the unreacted phosphate rock as well as the reaction products from soils treated with phosphate rock, while extraction was limited to phosphorus reaction products in the case of TSP.

Chien (1978) also noted that the contribution of phosphorus from the unreacted phosphate rock to the total Bray 1 extractable phosphorus decreased as the reaction time increased. If plants are able to utilize phosphorus from both sources, this would tend to

indicate that Bray P_1 extractions may not be adequate to describe the expected plant response from soil treated with phosphate rock when the time following application is substantial. This was in fact observed in the experiment with beans where Bray P_1 measurements obtained 30 days after application were well correlated with the yield of beans at the time of the first harvest (figure 7), but Bray P_1 extractable phosphorus measured at the time of planting of the second crop was not well related to the yield of the second crop.

Liming Effect of Phosphate Rock

In the experiment conducted on the Andosol, 4.7 t/ha of lime was applied prior to cropping and, therefore, no liming effect was observed. In the greenhouse, however, no lime was applied, and only 0.5 t/ha of lime was applied to the same Oxisol in the field. In these cases, the pH, extractable aluminum, and exchangeable calcium following the first cropping period all were well correlated to the citrate solubility of the phosphate rock.

In the greenhouse, pH was significantly increased by all sources of phosphate rock except Tennessee and Pesca. The pH ranged from 0.22 to 0.44 units higher than the control treatment for the other sources at the 200 and 400 ppm P rates and from 0.02 to 0.23 units higher at the 50 and 100 ppm P rates (table 3). In the field experiment with cassava on the same soil, the pH was raised 0.25 to 0.34 units with 400 kg/ha of P_2O_5 using North Carolina, Gafsa, and Huila phosphate rocks, but no differences were observed with the other sources or at lower rates.

As the soil pH increased in each case, a corresponding decrease in the aluminum saturation of the effective CEC was observed (figure 8). This reduction was shown to be related not only to a decrease in the extractable aluminum (figure 9) but also to increases in the level of exchangeable calcium (figure 10). At the time of the field harvest of cassava, 360 days after application, aluminum saturation had been reduced from the level of the control treatment by 44% and 39% with the North Carolina and Gafsa phosphate rocks, respectively, at the 400 kg/ha of P_2O_5 rate of application. The least observed decrease in aluminum saturation at

that rate of application was 15% with the Pesca phosphate rock. There was no significant reduction at either the 50 or 100 kg P_2O_5/ha rates.

The implications of these observations may be significant in those soils receiving direct applications of phosphate rock where lime is not available or traditionally has not been applied. Although these results indicate that significant increases in pH would not be expected in the field at the usual low rates of application, the liming effect may function to counteract the soil acidification associated with nitrogen fertilization and, therefore, prevent rapid reductions in soil pH during cropping.

Initial Agronomic Effectiveness and Crop Effect

The initial effectiveness of directly applied phosphate rock has been reported over the years to be relatively low when compared to that of TSP. However, until the 1950s, the differences in the agronomic potential of phosphate rock from different deposits had not been recognized. As a result, the sources largely utilized for direct application were not usually those best adapted for that use (Terman, 1976). Additionally, it has been shown that the efficiency of utilization of phosphorus from phosphate rock varies considerably with different crops. Russell (1973) reports a striking contrast in the effectiveness of Gafsa phosphate rock when utilized for the production of swedes and potatoes. The Gafsa rock was nearly as effective as TSP when applied to acid soils while it was only about one-third as effective with potatoes in the same pH range.

The effect of citrate solubility and crop type on the initial relative agronomic effectiveness (RAE) in the experiments on Colombian soils is illustrated in figures 11-14. It can be observed that the factor with primary influence is the reactivity of the phosphate rock. In each of the four experiments, phosphate rocks with high citrate solubility are nearly as effective as the basic slag or TSP standards. This is especially true in the case of bean production. The relative differences between the high, medium, and low solubility were very similar in the bean experiment and the experiment with guinea grass grown under greenhouse conditions. Both of these crops were grown over a period of approximately 3 months, and the mean RAE ranged from 79% to 94%

for high, 41%-65% for medium, and 27%-40% for low reactivity rocks. The cassava and brachiaria production, which spanned a 1-year growing season, showed much less difference between the sources with even the lowest mean response with cassava equaling 66% of that obtained with soluble phosphate fertilizers. In the case of the brachiaria production, yield increases were significant even with low rates of phosphate rock application. The accumulative dry-matter yield after four cuttings shows yield increases of 1.5 to 2.3 times the yield obtained without phosphorus with only 25 kg P_2O_5/ha. With respect to sources with low or medium citrate solubility, this is in agreement with the findings of Brown and Jacob (1945) who concluded from greenhouse and field tests that raw phosphates could be used to a better advantage for long-season and perennial crops than for short-season crops.

Residual Effect of Phosphorus from Phosphate Rock

It can be seen from figures 11-14 that, in the initial cropping period, the highly reactive phosphate rocks can approach the effectiveness of soluble phosphate fertilizers, while those with lower citrate solubility may increase yields but only to levels which would be disappointing to a farmer in comparison to TSP. The overall value of phosphate fertilizers, however, must include an evaluation of the residual benefits provided.

The concentration of phosphorus in the soil following application of TSP is initially high, leading to a rapid and relatively complete reaction with an acid soil in the formation of iron and aluminum phosphate compounds. The phosphorus availability is then controlled by the desorption characteristics of the soil. The phosphorus from phosphate rock, on the other hand, is much slower to enter the labile pool of phosphorus in the soil. The availability of phosphorus to the plants may be controlled by the concentration of phosphorus which can be maintained in the soil solution resulting from the dissolution of the phosphate rock over a long period of time. Mattingly (1963) found that up to 80% of the phosphate rock in the sand fraction of a soil had not reacted 3 years following application.

Table 4 illustrates the increased agronomic effectiveness of residual phosphorus from phosphate rock sources as compared to TSP in the experiment with beans. This represents a relatively short period of time for an evaluation of residual effectiveness since two crops were grown each year, limiting the time period to only 1½ years. Despite this, it can be seen that by the third harvest all sources were approaching or had already surpassed the residual effectiveness of TSP at all rates of application.

Focusing attention on production obtained at 200 kg/ha of P_2O_5, which represented 87% of maximum yield obtained with TSP during the initial cropping period, it can be seen from figure 15 that the highly reactive phosphate rocks were more effective than TSP in both the second and third crops. Improvement in efficiency was also shown with rocks of medium and low citrate solubility. The most unreactive rocks, in fact, increased in RAE from 29% in the first crop to 85% in the third crop. Due to this improvement with time, it can be seen that an effectiveness rating based on one cropping period is not sufficient. Total bean production over a 1½-year period with highly reactive rocks was 5% more effective than TSP rather than the 90% effectiveness indicated by one cropping. For rocks with medium and low citrate solubility, the RAE increased from 71% to 77% and from 29% to 51%, respectively, when total production was considered. Residual evaluations are being continued with this experiment as well as with the cassava and brachiaria experiments.

Effect of Grinding and Granulation of Phosphate Rock

It has been shown that the mechanism which most commonly limits the uptake of P by plants is the diffusion of phosphorus to the thin absorption zone surrounding the plant root (Barber et al., 1963). Because the concentration of phosphorus made available during the dissolution of phosphate rock is low, the diffusion of phosphorus from the apatite is small. As a result, distribution of phosphate rock in the soil as affected by physical form, method of application, and rate of application, all influence agronomic effectiveness.

The agronomic response to fine grinding of phosphate rock has been evaluated with a variety of sources

(Salter and Barnes, 1935; Joos and Black, 1950; Armiger and Fried, 1957; Howeler and Woodruff, 1968; Fassbender, 1967; and Barnes and Kamprath, 1975). In reviews of experiments with finely ground phosphate rock in the United States (Rogers et al., 1953) and in the United Kingdom (Cooke, 1956), it was concluded that increases in phosphorus availability were obtained by increasing fineness of grinding, but the degree of benefit rarely justified grinding finer than for 80% of the material to be less than 100-mesh.

Since the handling and application characteristics of finely ground rock are undesirable due to excessive dust, an investigation has recently been conducted to determine the relative effectiveness of phosphate rock ground and granulated to a wide range of sizes. Corn response to applications of these materials confirms that North Carolina phosphate rock is most effective when ground to less than 200-mesh and that significant reductions in yield are encountered as the size of the ground phosphate rock is increased (figure 16). It is interesting to note, however, that phosphate rock, when granulated to a size range of minus 100- plus 200-mesh, can provide desirable handling characteristics with only a slight reduction in initial phosphorus availability. At a rate of application of 200 ppm P, the RAE of the mini-granulated phosphate rock was 84% when compared to the finely ground phosphate rock prior to granulation (figure 17). This is in contrast to 62%, 29%, and 7% for granules of increasing size as identified. The objection, in the past, to granulating phosphate rock has been based upon experience only in the range of large-size granules. Evidence has also been obtained that the residual effectiveness of granulated phosphate rock is superior to that of the initial cropping period and, therefore, investigations are continuing in this area.

Acknowledgments

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Table 1. Sources and Citrate Solubility of P in the Phosphate Rocks

Source	Country	Citrate-Soluble Phosphorus				Absolute Citrate Solubility
		First Extraction		Second Extraction		
		% Rock	% Total P_2O_5	% Rock	% Total P_2O_5	
North Carolina	United States	7.2	24.1	6.7	22.4	19.8
Sechura	Peru	5.3	17.7	5.4	18.0	14.9
Gafsa	Tunisia	4.9	16.3	5.6	18.7	18.5
Central Florida	United States	3.0	9.2	3.2	9.8	10.1
Tennessee	United States	2.6	8.6	2.7	9.0	5.1
Pesca	Colombia	1.9	9.6	1.9	9.6	9.7
Huila	Colombia	0.8	3.8	3.4	16.3	12.2

Table 2. Initial Soil Properties

U.S. Classification	Greenhouse Panicum Maximum Typic Haplustox	Field Experiment 1 Manihot Esculenta C. Typic Haplustox	Field Experiment 2 Phaseolus Vulgaris L. Typic Unbrandept	
			Before Liming	At Planting
Organic matter (%)	4.3	1.9	12.4	
pH (1:1 soil:water)	4.7	5.0	4.9	5.5
Bray P_1 (ppm P)	1.9	1.2	2.6	2.6
Exch. Ca (meq/100 gm)	0.12	0.15	2.16	12.30
Exch. Mg (meq/100 gm)	0.08	0.02	0.76	1.31
Exch. K (meq/100 gm)	0.04	0.04	0.51	0.60
Exch. Al (meq/100 gm)	2.70	1.50	2.55	0.39
Effective CEC (meq/100 g)	2.94	1.71	5.98	14.60
Al saturation (% Effective CEC)	92	88	43	3

Table 3. The pH in 1:1 Soil-Water Mixture in Uncropped Greenhouse Soil 70 Days After Application

Source	Rate of Application (ppm P) 50	100	200	400	Average*
			pH		
Triple superphosphate	4.77	4.63	4.65	4.67	4.68 d
Basic slag	4.78	5.00	5.18	5.80	5.19 a
Sechura PR	4.75	4.83	4.87	4.97	4.85 bc
North Carolina PR	4.80	4.88	4.97	5.05	4.93 b
Gafsa PR	4.77	4.67	4.92	4.92	4.82 c
Central Florida PR	4.78	4.73	4.88	4.98	4.85 bc
Huila PR	4.67	4.82	4.90	5.07	4.86 bc
Tennessee PR	4.70	4.62	4.70	4.70	4.68 d
Pesca PR	4.78	4.63	4.75	4.70	4.72 d
Control					4.65

* Means with the same letter are not significantly different with Duncan's Multiple Range Test (p = .05).

Table 4. Relative Agronomic Effectiveness of Phosphate Sources with Beans on the Andosol as Affected by Time

Phosphate Source	Rate of Application (kg P_2O_5/ha)											
	Crop 1				Crop 2				Crop 3			
	50	100	200	400	50	100	200	400	50	100	200	400
Triple superphosphate	100	100	100	100	100	100	100	100	100	100	100	100
North Carolina PR	84	92	90	92	58	111	105	107	100	112	115	133
Gafsa PR	99	109	105	113	95	113	104	92	101	99	117	114
Sechura PR	80	103	90	102	52	113	107	83	77	192	132	127
C. Florida PR	61	77	62	64	63	76	74	73	100	175	92	96
Huila PR	52	75	80	83	46	65	56	61	86	146	98	103
Tennessee PR	26	43	49	58	45	69	52	56	114	173	90	96
Pesca PR	36	29	8	49	34	37	27	49	105	80	79	93

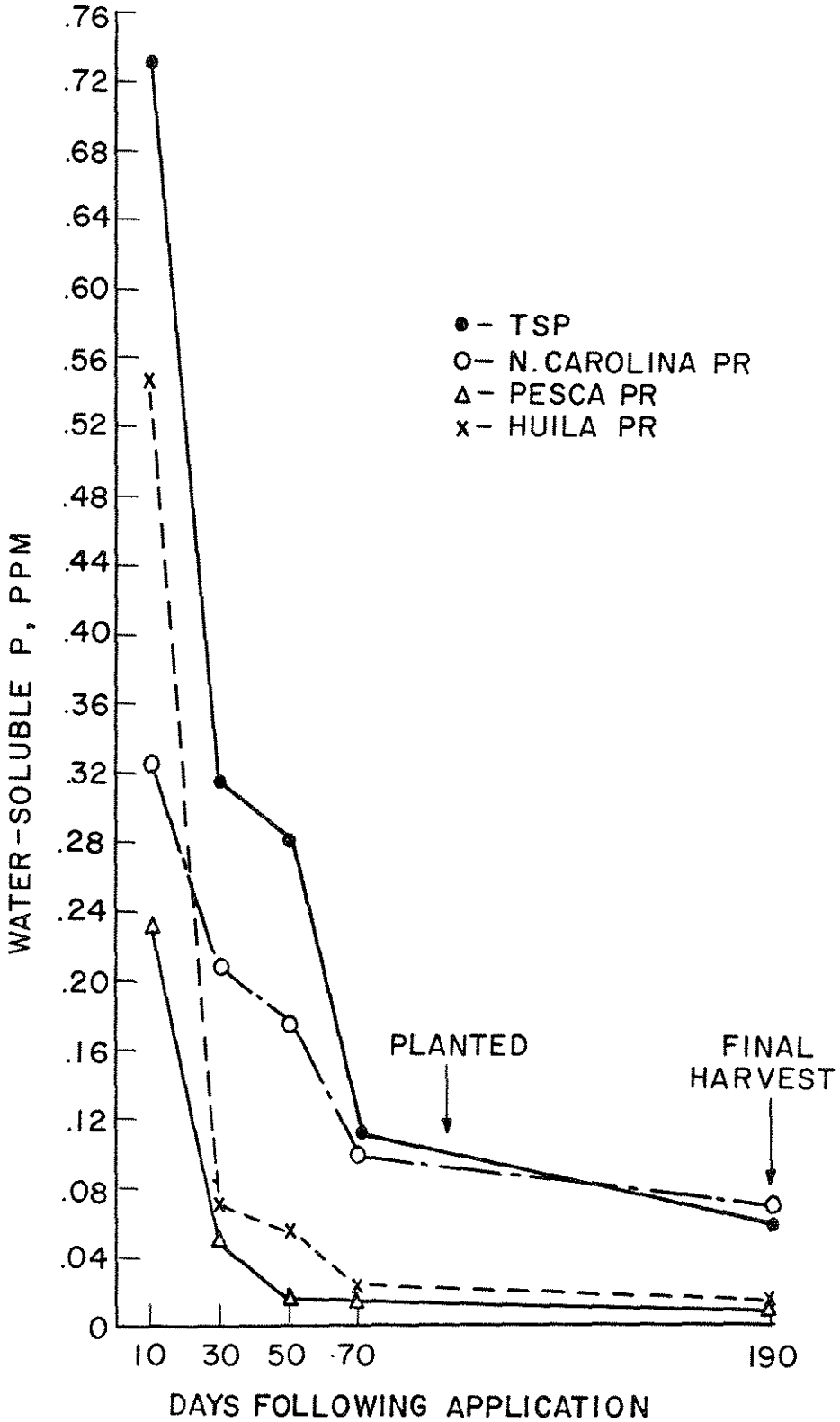


Figure 1. Relationship Between Concentration of Water-Soluble P in Greenhouse Soil Receiving 400 ppm P and Time Following Application.

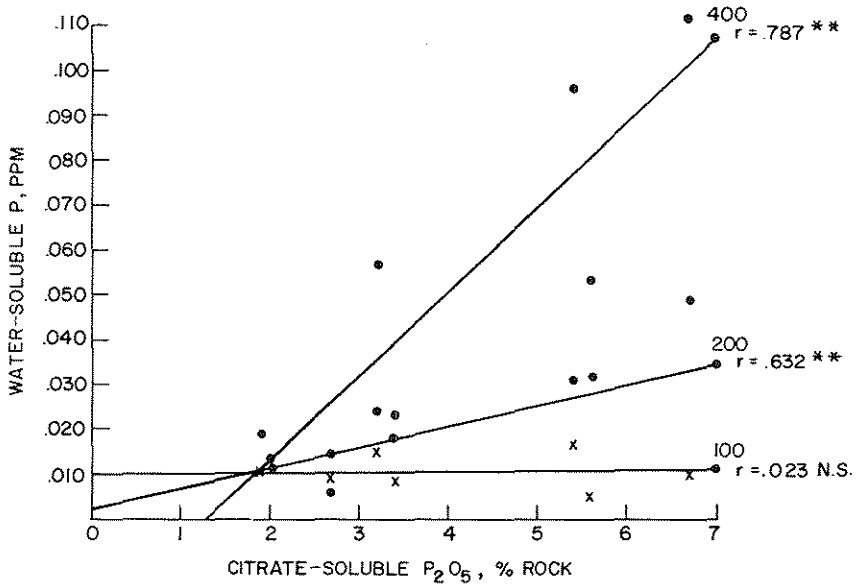


Figure 2. Relationship Between Water-Soluble P in Greenhouse Soil 70 days Following Application and Citrate-Soluble P in Phosphate Rocks.

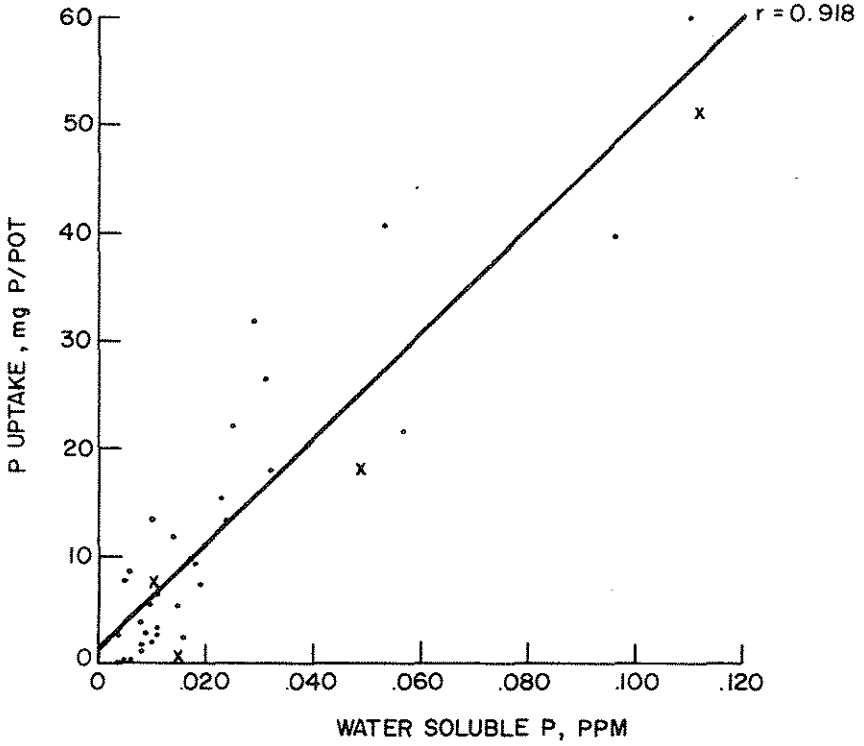


Figure 3. Relationship Between Uptake of P by Three Cuttings of Guinea Grass and Water-Soluble P in Greenhouse Soil.

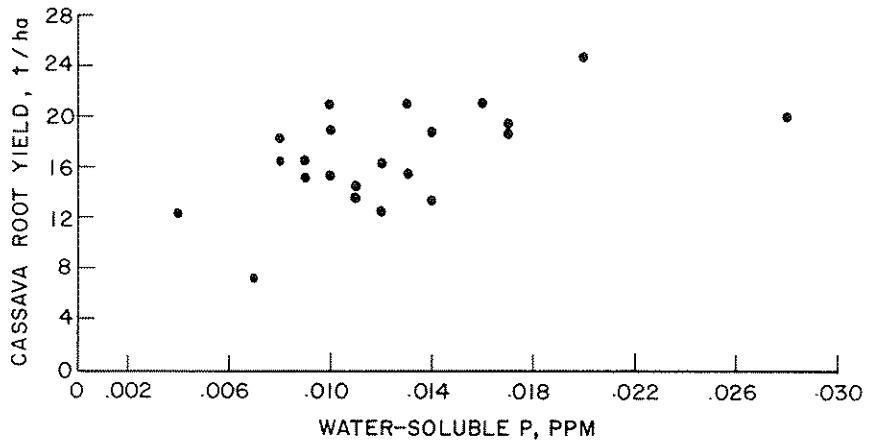


Figure 4. Relationship Between Yield of Cassava and Water-Soluble P in the Carimagua Soil.

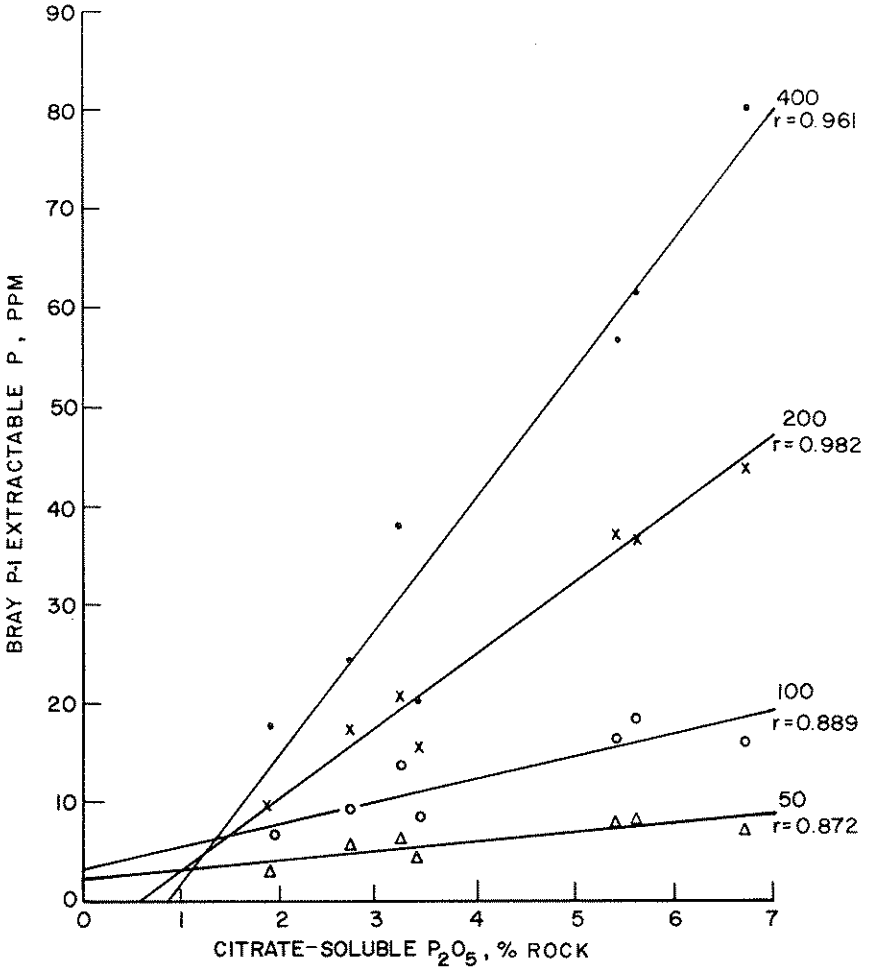


Figure 5. Relationship Between Bray P-1 Extractable P in Greenhouse Soil and Citrate-Soluble P in Phosphate Rocks.

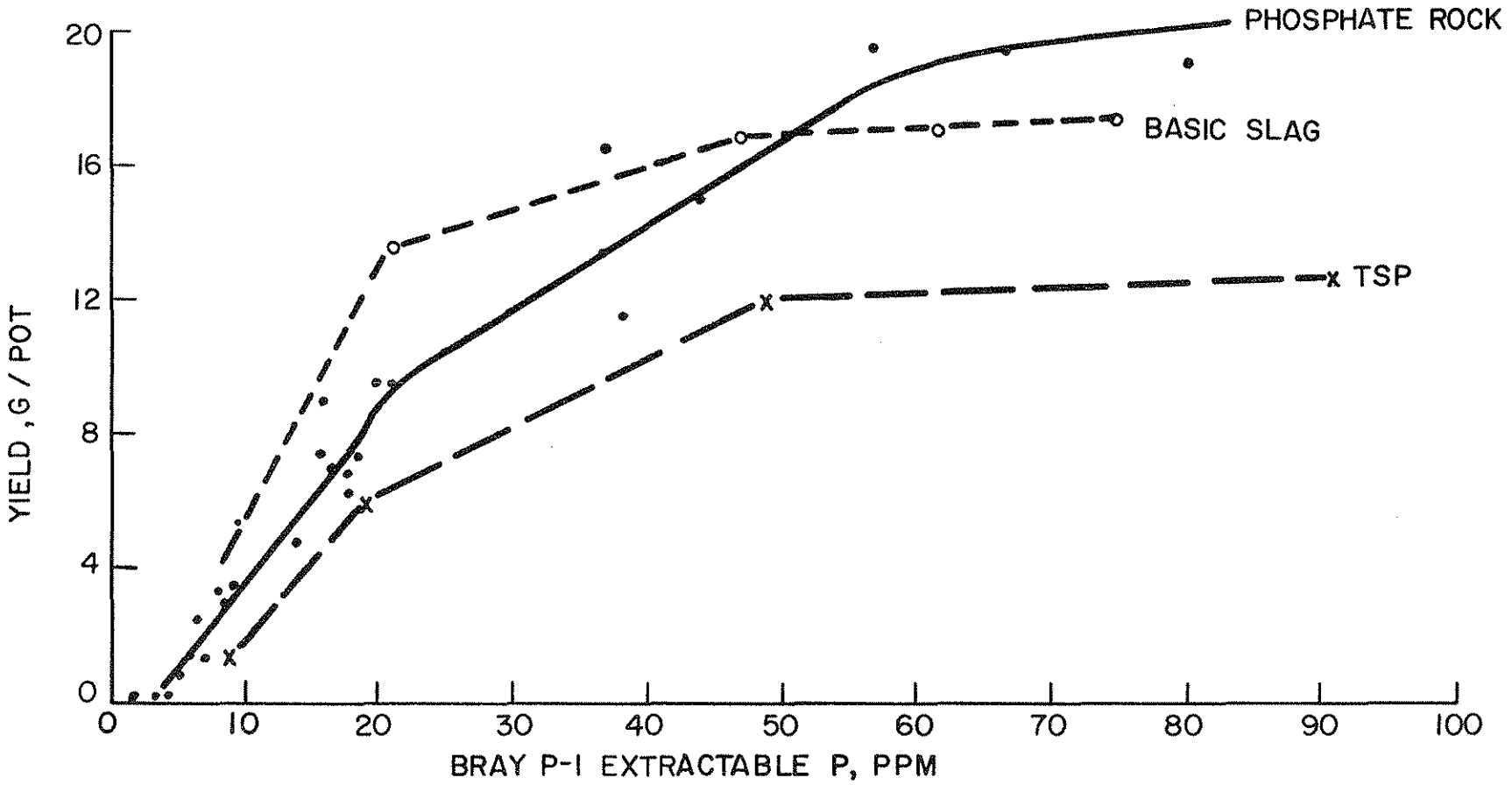


Figure 6. Relationship Between Yield of Three Cuttings of Guinea Grass and Bray P-1 Extractable P Measured 90 Days After Application.

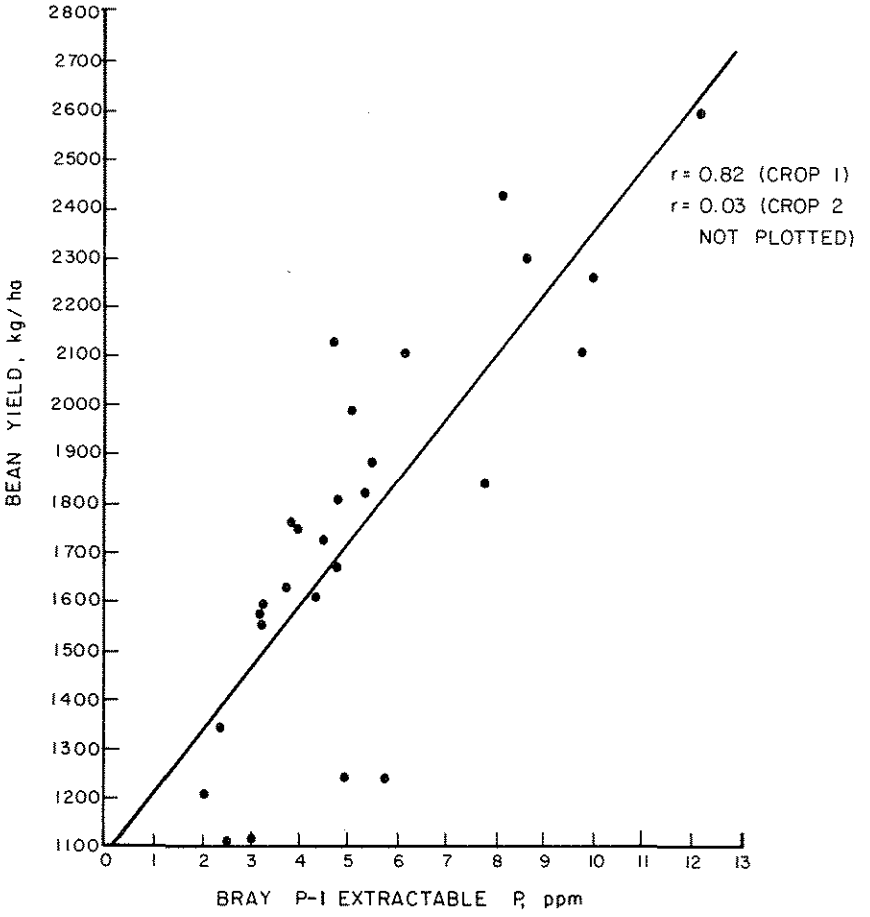


Figure 7. Relationship Between Bray P-1 Extractable P and Bean Yield in Field Experiment on Colombian Andosol.

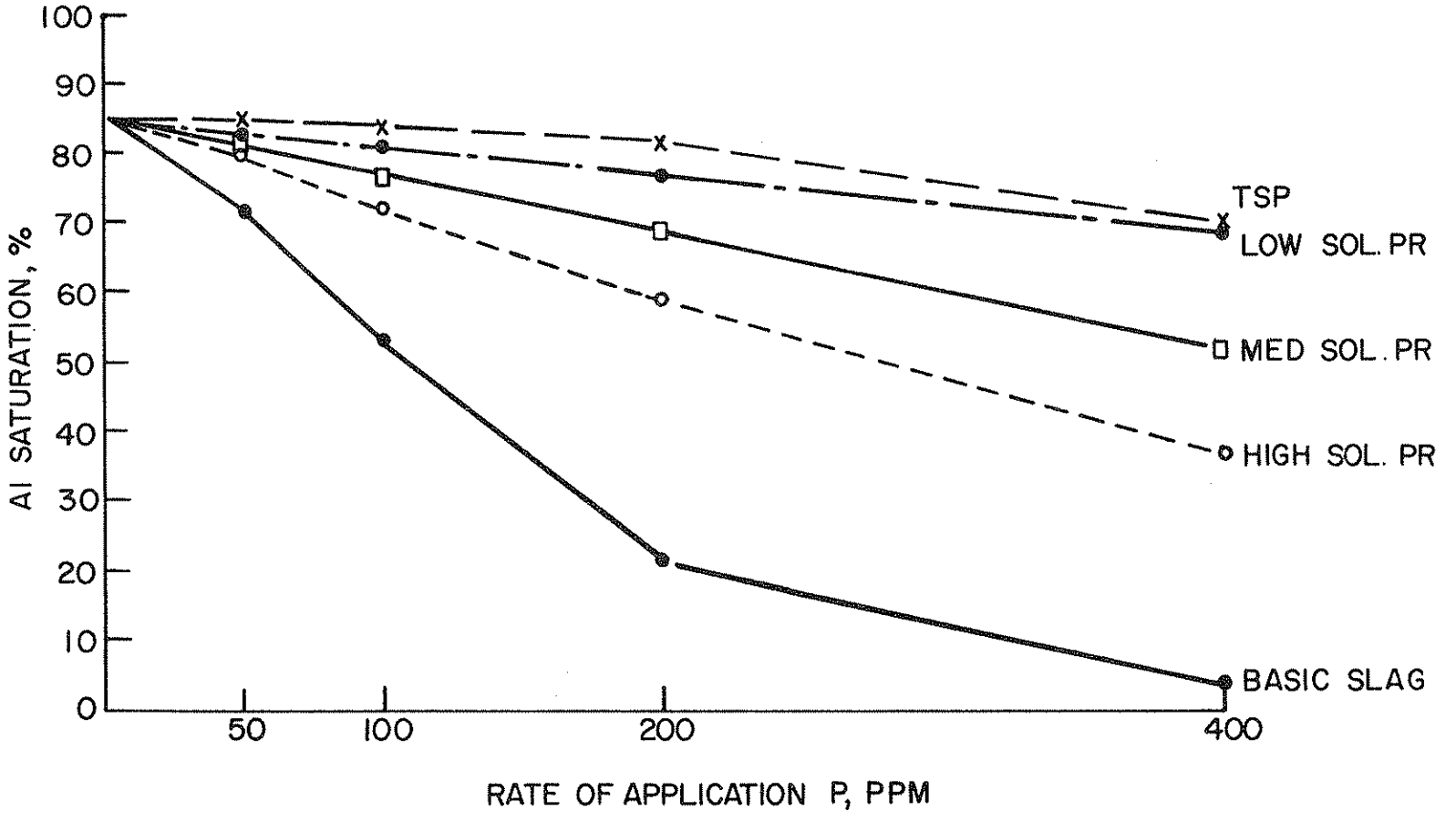


Figure 8. Aluminum Saturation in the Carimagua Soil as Affected by Rate of P Application.

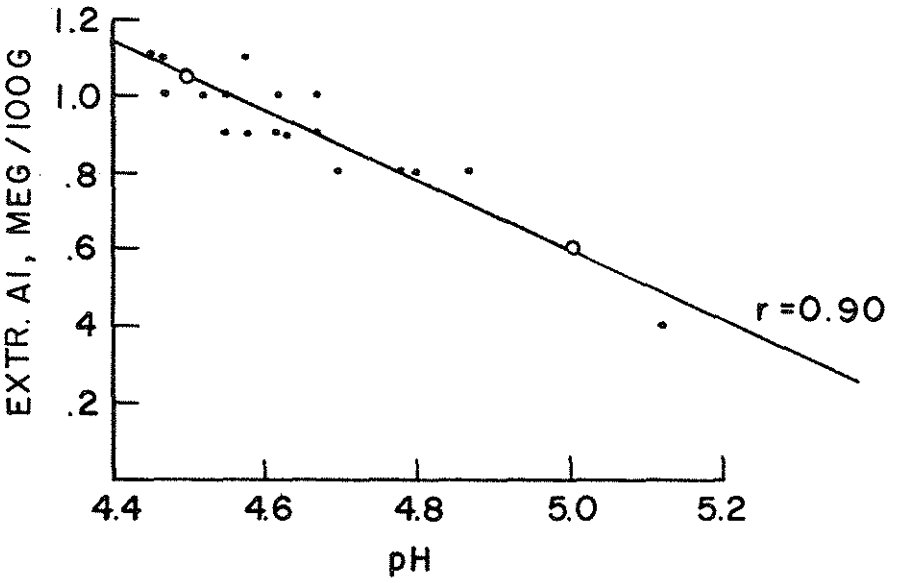


Figure 9. Relationship Between Extractable Al in the Carimagua Soil and Soil pH.

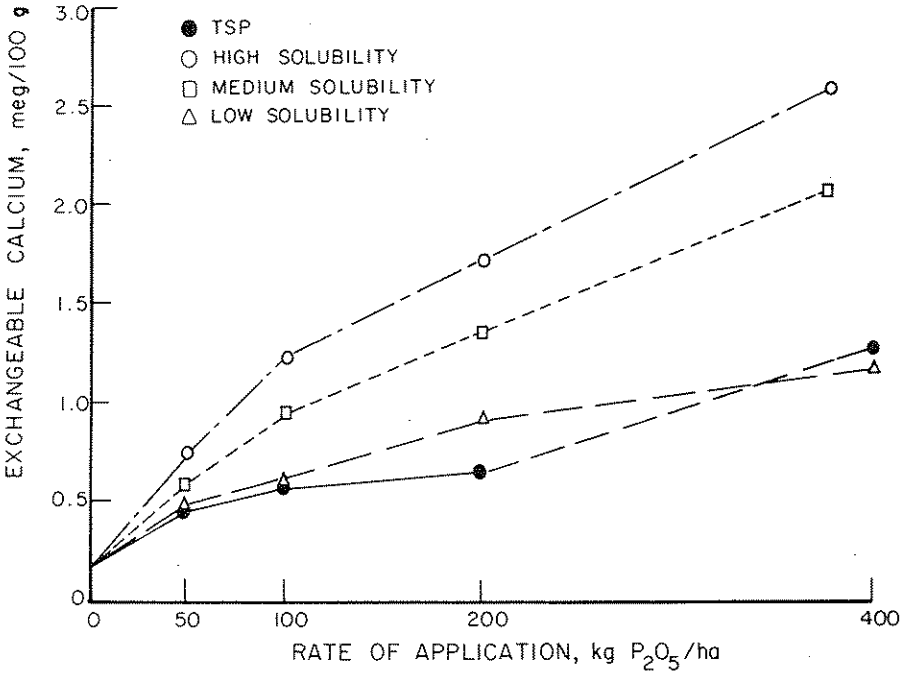
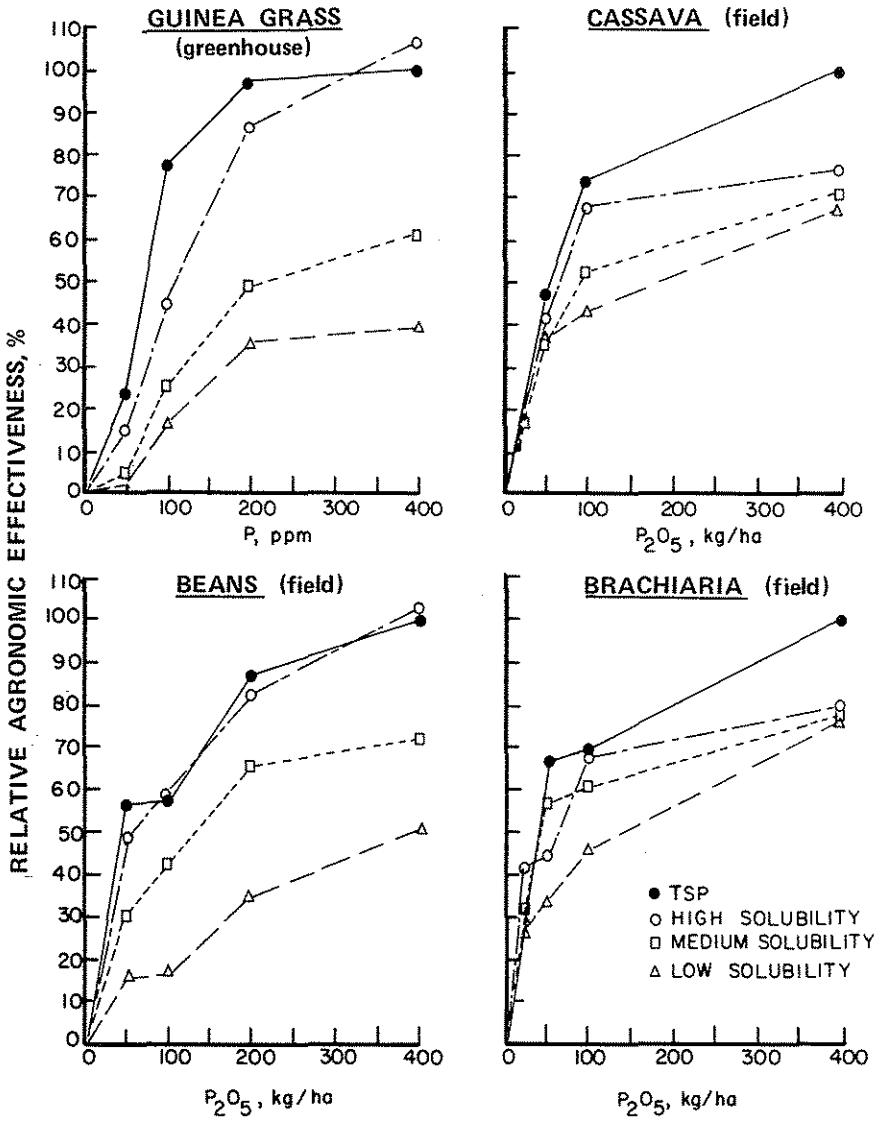


Figure 10. Exchangeable Soil Calcium in the Carimagua Soil as Affected by Rate of Application of Phosphorus Sources.



Figures 11–14. Relative Agronomic Effectiveness of Different Phosphate Sources.

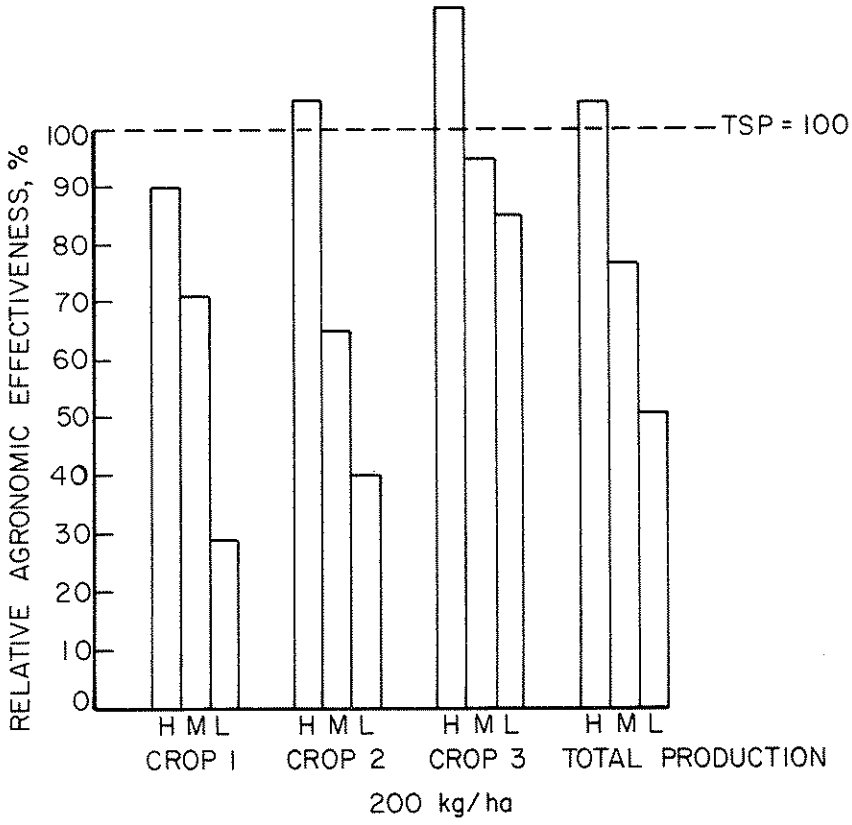


Figure 15. Relative Agronomic Effectiveness of Phosphate Sources With Beans on an Andosol at 200 kg P_2O_5/ha as Affected by Time.

H = High Citrate Solubility PR
M = Medium Citrate Solubility PR
L = Low Citrate Solubility PR

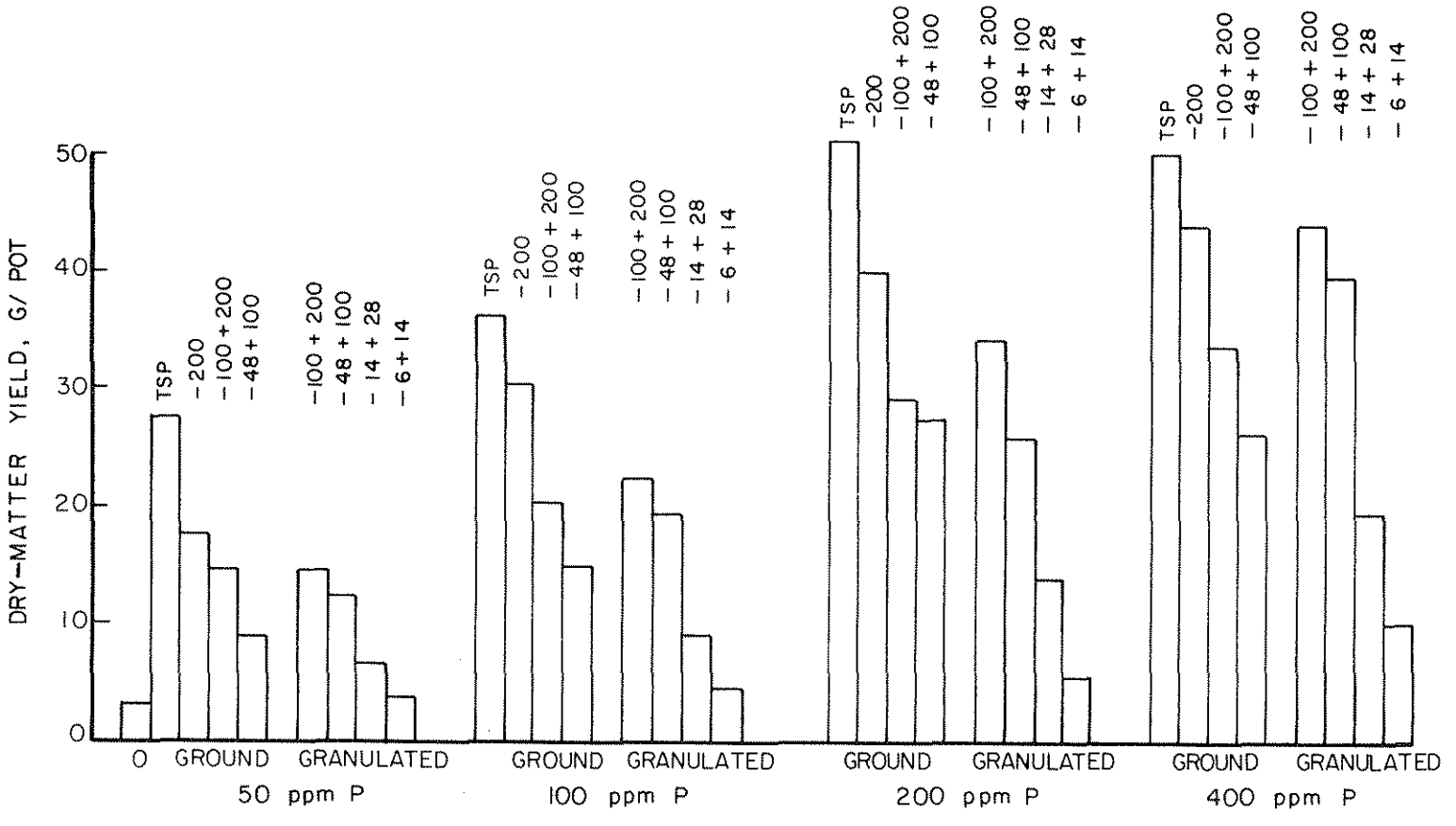


Figure 16. North Carolina Phosphate Rock Comparison of Ground and Granulated Material in Varying Size Ranges (Tyler mesh).

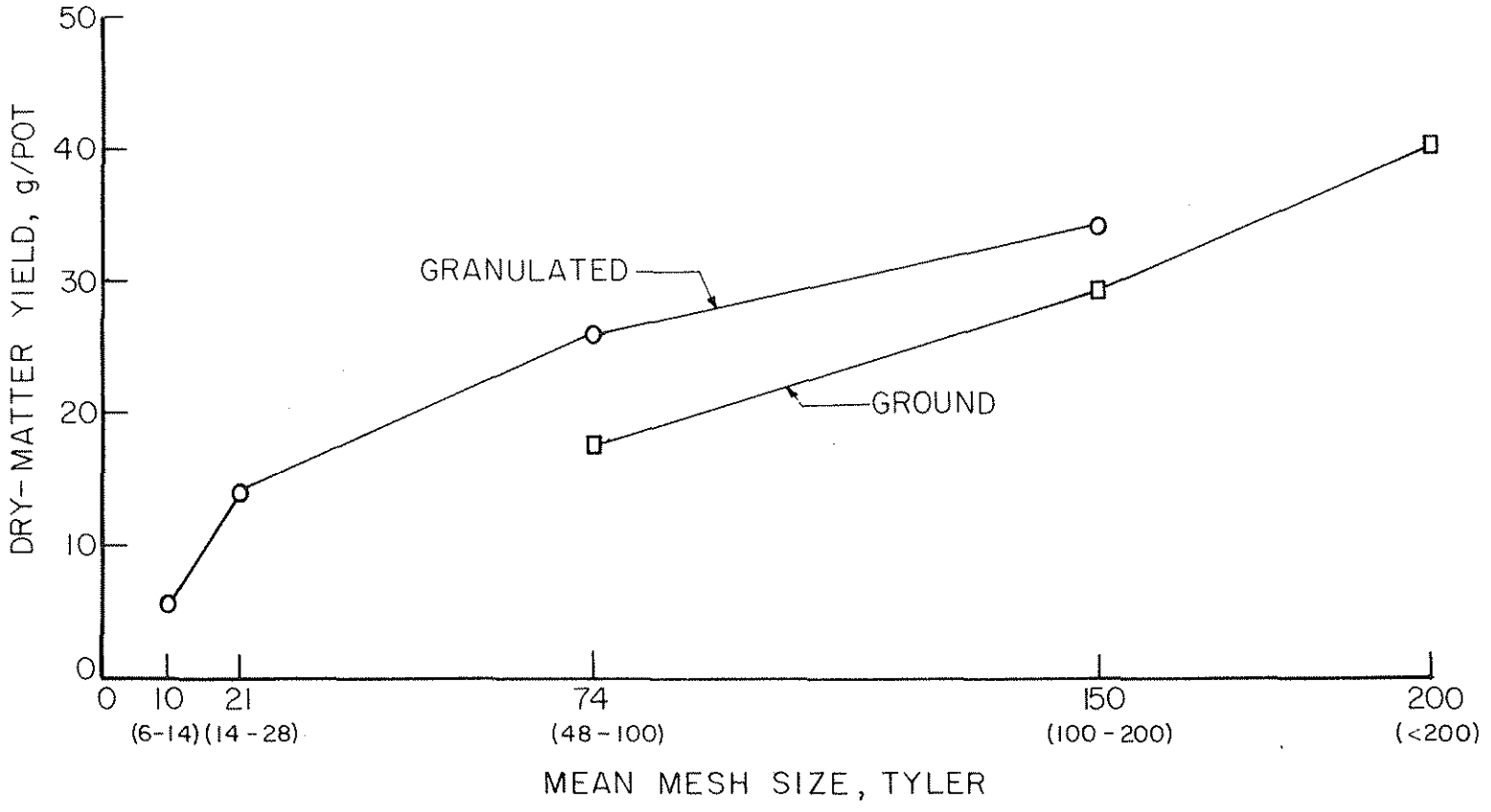


Figure 17. Effect of Grinding and Granulation of North Carolina Phosphate Rock on Yield of Corn at 200 ppm P in the Greenhouse.

UTILIZATION OF PHOSPHATE ROCK IN TROPICAL SOILS OF LATIN AMERICA

(A RESEARCH PROPOSAL)

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Introduction

The direct use of phosphate rock (PR) as a phosphorus (P) fertilizer is not a new concept in either the temperate or tropical areas of the world. The great majority of PR experiments, however, have been conducted in temperate climates on soils with a reaction of 5.5 or above. The voluminous amount of literature would indicate in general that a direct relationship exists between fineness of particle size and yield response. Most of these experiments were usually conducted from a soil fertility standpoint whereby a particular PR was applied to a particular soil, and yield responses were noted. It has been pointed out that this empirical approach had various limitations not only because of the tremendous variability among soils but also the large variabilities among PRs. As a consequence, the experimental results varied markedly from experiment to experiment, thus making the predictability of PR effectiveness as a P fertilizer almost impossible to ascertain. In addition, the residual value of PR was not in most instances determined because most of the experiments were designed for only 1-2 years.

In recent years, however, laboratory studies have been made with the objective of characterizing PRs from a P availability standpoint (Centro Internacional de Agricultura Tropical [CIAT], 1977; Hammond, 1977; Lehr and McClellan, 1972). Also long-term experiments have been set up in tropical Latin America to determine the residual value of the rocks. This, combined with a thorough and meaningful soil analysis, should help to clarify the PR effectiveness from a generalized fertilizer recommendation standpoint.

The objectives of this paper will be to review the soils and phosphorus fertilizer problems in the acid Oxisols, Ultisols, and Inceptisols (target area) of trop-

ical Latin America (approximately 20°N and 20°S latitude); selectively review the literature; state the research objectives; and attempt to lay out a research program to meet those objectives.

Soils and Phosphorus Problems in Tropical Latin America

The soils in the target area of tropical Latin America are primarily Oxisols and Ultisols (figure 1). These soils are generally medium to fine textured, present an acid reaction of from 4.0 to 5.5, and contain only about 200-600 ppm total P. Available P is also very low in these soils, ranging only from about 1 to 5 ppm. It is quite obvious that without additions of P neither arable nor forage crops can be grown effectively. Due to the extremely acid conditions, these soils are also high in free iron and aluminum oxides and hydroxides which tend to rapidly fix large amounts of P when it is applied in soluble forms such as simple (SSP) or triple superphosphate (TSP). Although P is generally the most limiting element, other nutrient deficiencies of nitrogen, potassium, sulfur, calcium, and magnesium are common (CIAT, 1977) (figure 2). In addition to these nutrient management problems, there is also the problem of aluminum and manganese toxicity.

From a physical standpoint, the soils which have potential for arable and forage crop production, in general, possess excellent structure and good infiltration capacities and are well drained. According to Sanchez (1976), "the excellent structure of these soils is caused by primary particles being aggregated in very stable sand-sized granules. Their high stability is associated with high clay content and cementing or coating of amorphous iron and aluminum oxides." He further states that the organic-matter content is also directly associated with the aggregated stability. It is clear that the soil physical properties of these tropical Latin American soils will not present major problems in most crop production schemes.

One of the most limiting factors in increasing crop production in tropical Latin America would appear to be the high cost of fertilizers, especially those containing high amounts of available P. This is primarily due to the high cost of manufacturing which results from the

high input costs of sulfuric and/or phosphoric acid used in the acidulation process. Transportation costs are also extremely high. Given the fact that high rates of these P fertilizers are required to be effective, it is easy to see why immediately available forms of P fertilizers are not used on most arable or forage crops, except those of high monetary value such as potatoes and other vegetable crops.

The direct use of PR or some of its low-input, altered products would seem to present an interesting and logical approach to take in overcoming the monetary and soil chemical constraints in crop production which have been mentioned previously. Over the years, hundreds of PR trials have been conducted to increase crop production. These experiments lend credibility to the idea that PR or its low-cost, altered products could be used to increase crop production both from short- and long-term viewpoints. Given the amounts of exchangeable and nonexchangeable acidity in these tropical soils, it would seem natural that PR could and should be used in some form to make increased arable and forage crop production an economically feasible reality.

Review of Literature

The authors recognize and have reviewed much of the scientific literature pertaining to the use of PR as a source of P for crops in the temperate areas of the world. Most of the literature cited here, however, will be from research conducted in tropical Latin America as our proposed research will be focused in this area.

General Phosphorus and Soils Review

In a review chapter on P, Kamprath (1977) states, "the highly weathered soils, Oxisols and Ultisols of the tropics along with Andosols, are generally very deficient in phosphorus. Many of the soils fix large quantities of added phosphorus. Therefore, without the application of phosphorus, sustained crop production at high yields is not possible." After a rather exhaustive review of crop responses to phosphate fertilization in the tropics, Kamprath (1977) further indicates that, "Rates of phosphorus on deficient soils generally giving optimum yields were 100-150 kg P_2O_5/ha for corn, soybeans, sugarcane, and forages; 120-240 kg P_2O_5/ha for

wheat; 120-180 kg P_2O_5/ha for potatoes; and 60 kg P_2O_5/ha for rice."

Fassbender et al. (1968) in a greenhouse study with tomatoes as the test crop on 110 different soils of Central America showed that most of the soils studied were extremely deficient in P (66%) and only 15% contained an adequate supply. In another greenhouse study with tomatoes, Fassbender (1969) showed that 96% of the applied monocalcium phosphate (MCP) was transformed into iron and aluminum forms after 8 weeks with a P-deficient Latosol, Colorado series (pH KCl 4.6).

In characterizing some of the main Oxisols and Ultisols in Colombia at the Santander and Carimagua experiment stations and in Brazil at the Cerrado Center station, Leon and Sanchez (CIAT, 1977) found soil pH values from 4.2 to 4.9 and percent aluminum saturation ranging from 64 to 82 (table 1). The available P ($Bray_2$) levels were extremely low, showing values from only trace amounts to 1.8 ppm in both surface and subsamples. Also, using a Santander soil in a greenhouse missing element trial with Centrosema plumieri, Leon, Sanchez, and Ayarza (CIAT, 1977) found this soil to be severely deficient in P as well as sulfur, boron, and to some extent calcium (figure 2). In further studies, these investigators indicated that a soil test of about 3 ppm P ($Bray_2$) was a critical level for achieving 80% of maximum yield with both Panicum maximum and a Centrosema hybrid (figure 3). It was also suggested that a rate of about 240 kg P_2O_5/ha would be needed to satisfy this requirement.

In order to characterize the P fixation capacity of the Brasilia, Santander, and Carimagua experiment station soils, Leon and Sanchez (CIAT, 1977) ran P-fixation isotherms (figure 4). Using a 0.2 ppm P in solution as a critical level, it took 620-750 ppm P for Santander and Brasilia and about 350 ppm for Carimagua to achieve this, thus indicating the extremely high fixation capacity of these soils.

Direct Application of Phosphate Rock to Soils

The direct application of PR to temperate soil conditions is well documented in the literature. It is also well recognized that much of the research, resulting in contributions to the understanding and use of PR as a

P source for plants, was conducted in Europe, the United States, and other parts of the world.

In tropical Latin America, the information on direct application of PR is more limited; nevertheless, important and applicable studies have been and are being conducted in several of the countries. This section will be devoted primarily to these investigations.

Characterizing Phosphate Rocks--Over the years it has been well understood that fineness of particle size of the PR and soil reactivity were extremely important in predicting the value of PRs. Since it was generally and erroneously assumed that most were fluorapatite, variable agronomic responses in field and greenhouse studies were usually attributed to particle size of the rock and/or different soil characteristics. Lehr and McClellan (1972) state, "new insight into the composition of phosphate rocks was obtained recently from characterization studies which showed that the compositions of their apatitic phosphate minerals varied markedly. With few exceptions, the apatites were not fluorapatite, but belonged to the series of carbonate apatites in which PO_4 is replaced by CO_3 and F, and Ca is replaced by Na and Mg in the fluorapatite structure. Chemical reactivity of the apatite increased as the degree of substitution increased." Based on this the citrate solubility was redefined on an absolute basis. This "absolute citrate solubility" (ACS) index for any given rock was defined as the ratio of its citrate-soluble P_2O_5 to the theoretical P_2O_5 content of its particular apatite composition (Lehr and McClellan, 1972). Working with 50 representative PRs, Lehr and McClellan showed that the ACS index "correctly associated P_2O_5 solubility with the kind of apatite supplying the P_2O_5 grade of the phosphate rock." They further showed a high degree of correlation between the ACS indices of the rocks and agronomic response to their P in greenhouse studies. More recently, Hammond and Leon (CIAT, 1977) have shown that the relative availability of P from PR sources correlated well with the citrate-soluble P content of the material when expressed as "percent of the rock" rather than "percent of total P_2O_5 in the rock." In a greenhouse study with Panicum maximum, the researchers also concluded that the degree of correlation was higher when higher rates of the various PRs were applied (figure 5).

The characterization of the PRs has really elucidated many of the heretofore erratically appearing

research results with the many different rocks. Even more importantly, the relative agronomic effectiveness (RAE) can be predicted for the various PRs. For example Gafsa (Morocco), Sechura (Peru), and North Carolina (United States) rocks are considered highly reactive; Huila (Colombia) and Florida (United States) of medium reactivity; and Pesca (Colombia) and Tennessee (United States) are of low reactivity. Hammond and Leon (CIAT, 1976-77) have confirmed this predictability with citrate-soluble P in the total rock with both greenhouse and field studies (table 2).

Greenhouse and Field Investigations with Phosphate Rock--A number of experiments have been conducted in tropical Latin America using the direct application of PR. Although many of the results have been quite variable, recent works in Brazil and Peru by North Carolina State University (40) and in Colombia by the International Fertilizer Development Center (IFDC) and CIAT (Hammond, 1977) have shown very encouraging results.

Alvarez et al. (1965) in several experiments with sugarcane on acid soils in Sao Paulo, Brazil, using various sources and rates of P, showed that four naturally occurring PRs gave 10%-28% yield increases while other more available phosphate fertilizers gave 35%-49% yield increases. In another series of experiments in Sao Paulo with corn, Miranda et al. (1970) showed that three PRs from Brazil gave yield increases from 37% to 71% of that attained with ordinary superphosphate over a 2-year period.

In 1969 significant experiments with PR were also initiated by Leon et al. (1976) in several geographic areas of Colombia on Oxisol, Ultisol, and Andept soils. Varying rates of PR, basic slag, SSP, and TSP were compared using oats for forage, several forage grasses, peanut, corn, rice, and onions as the test crops. On selected treatments of 200 kg P_2O_5/ha for TSP, Turmeque (Pesca-like) rock, and Florida rock with three cuttings of Kikuyo grass, the researchers found that all forms of P gave significant yield increases over the check and that TSP was slightly inferior to both forms of PR. Similar broadcast treatments at two other locations with different grasses showed no significant yield increases after five to seven cuttings, regardless of the source of P. At other locations with orchoro grass,

only slight yield increases with TSP were noted. When oats (2 crops) was the test crop, 200 kg P_2O_5/ha gave significant yield increases with TSP and Turmeque rock. In this same experiment no increases were realized with Florida rock. With onions, applications of 100-200 kg P_2O_5/ha, either broadcast or row applied, gave significant yield increases regardless of the P source.

In the Llanos Orientales region of Colombia, with corn the response to P was slightly significant (figure 6). Although the results varied the first year, in the second and third years Turmeque and Florida PRs were equal to and in some cases superior to TSP. Leon et al. concluded that in the highly acidic P-deficient soils of Colombia, almost all crops showed some degree of response to applications of PR.

In the Cerrado of Brazil, North Carolina State University and Cornell (1973-75) initiated a long-term experiment with various phosphate carriers on pastures to determine the effect of using cheaper sources of P. Initially, the two highly soluble PRs, Gafsa (Morocco) and North Carolina, performed about as well as SSP. The low reactive Araxa PR from Brazil was ineffective at first; however, after 2 years the availability was increased significantly, and yields were comparable to other P carriers, indicating it may be economically competitive with time (figure 7). Rates of P_2O_5 used were 86, 345, and 1,380 kg/ha. In the Amazon Jungle of Peru, North Carolina State University (1973-75) and Sanchez (1977) in another series of pasture experiments also showed that Gafsa, Florida, North Carolina, and Fosbayovar (Peru) PRs were comparable to SSP in forage production with Panicum maximum. These experiments in Brazil and Peru will be continued to assess the residual values of the P carriers.

In the highlands of Peru, Davelouis and Cano (1976) conducted a series of P experiments with potatoes and wheat over a 2-year period. In comparing Sechura rock, Gafsa rock, SSP, and combinations of rock plus super, these researchers reported that marginal money returns were better for the PRs than SSP. The best economic returns were noted with potatoes when 160 kg P_2O_5/ha of Sechura PR and 80 of SSP were applied (figure 8). Although the results with wheat were not very encouraging using PR, the residual effect the following year with potatoes showed promise.

In Colombia, Howeler (CIAT, 1974) on an acid low-P soil reported that 200 kg P_2O_5/ha as TSP increased bean yields from 0.7 to 1.8 tons/ha while only slight responses were noted with Huila and Turmeque PRs (figure 9). In another bean experiment (IFDC cooperating) on an acid low-P Andept, Howeler, Hammond, and Leon (CIAT, 1976) state, "a positive response to application rates as high as 400 kg P_2O_5/ha was obtained. Although TSP produced the best response, relatively soluble rock phosphates from Gafsa (Morocco), North Carolina (United States), Sechura (Peru), and Huila (Colombia) also gave good responses. Yields with more insoluble rock phosphates from Tennessee and Florida (United States) were lower but still significantly better than the control. The agronomic effectiveness of the sources followed closely their solubility in N ammonium citrate, a commonly used measure of available phosphate" (figure 9). These same researchers found similar results using the same P carriers in a Carimagua Oxisol with cassava. Yields range from 18 to 25 tons/ha with 400 kg P_2O_5/ha down to 8 tons/ha on the check. Rates of 100 kg P_2O_5/ha also appeared very encouraging, especially with the more soluble sources of PR.

Hammond (1977) in a greenhouse experiment with Panicum maximum grown on a Carimagua Oxisol reported that the high-reactivity PRs, Sechura and North Carolina, were superior to application rates of TSP ranging from 50 to 400 ppm P (figure 10). Huila and Pesca PRs were less effective than TSP but significantly better than the checks. Using an RAE scale with basic slag equal to 100, Sechura, North Carolina, TSP, Huila, and Pesca were scaled at 94, 82, 62, 41, and 27, respectively (figure 10). In a long-term field experiment at Carimagua using Brachiaria decumbens and comparing six PR sources with TSP at P_2O_5 rates varying from 0 to 400 kg/ha, Hammond and Leon (CIAT, 1977) concluded that, "triple superphosphate was only superior to rock phosphates during the first cut; afterwards all rock phosphate sources increased their effectiveness with time or surpassing the yields of superphosphate during the third and fourth cuts (figure 11). The overall results during the first 16 months show the high reactivity rocks, Gafsa and Sechura, were 105% and 99% as effective as superphosphate; the medium reactivity Huila rock was 91% as effective; and the low reactivity rocks, Tennessee and Pesca, were 87% and 88% as effective as triple superphosphate." This experiment will be continued to further

evaluate the residual effects of the PRs, but already there appears to be opportunity for the use of the low-cost, low-reactivity rocks on the acid soils for pasture production.

Greenhouse and Field Investigations with Partially Acidulated Phosphate Rock--The use of partially acidulated PR may present an attractive alternative to the use of either PR or superphosphate alone or in combination in the acid P-deficient soils of tropical Latin America.

McLean and Wheeler (1964) conducted a growth chamber study with German millet and alfalfa in which finely ground Florida PR was acidulated with phosphoric acid to the following degrees: 0%, 10%, 20%, 50%, and 100%. Two Ohio soils were limed to pH levels of about 6.0 and 6.5, and P was added at a rate of 90 pp2m.

The P was applied both in bands and broadcast. These researchers concluded that, "in general, German millet and alfalfa yielded about as much and contained as much P in the tissue from 10% acidulated phosphate as from 100% acidulated." The comparative favorable plant response to the partially acidulated material and the economy of its production make partial acidulation appear to have very promising practical applications."

Terman and Allen (1967) acidulated Florida PR with phosphoric acid to levels of 0%, 10%, 25%, 50%, 75%, and 100% and then granulated the resulting materials to minus 6- plus 9- and minus 35-mesh. Two experiments were conducted with corn on soils with pH values of 6.5 and 5.6, and P was applied at rates of 40, 80, and 160 lb/acre. The authors concluded that dry-matter yields were directly related to the amount of P applied and the content of water-soluble P. They further noted that the conclusions from these studies differ markedly from the works of McLean et al. (1964) and suggest that the reason may be that these researchers used ungranulated materials applied at only one rate.

In Colombia, McCormick and Galiano (1968) acidulated Turmeque PR with sulfuric acid to levels of 0%, 25%, 50%, 75%, and 100%. Four pot experiments were conducted with soils from the savanna of Bogota and the eastern plains of Colombia with barley as the test crop. The rate of phosphorus applied was 200 kg

P_2O_5/ha. In another experiment a 5:1 mixture of Huila PR:sulfur gave cassava yields which were equal to those of TSP at rates of up to 400 kg P_2O_5/ha (figure 12).

In other experiments in Colombia, however, when elemental sulfur or ammonium sulfate was added to PR and applied to the soil, no yield responses were noted and in some cases yield depressions occurred (CIAT, 1975; Galiano, 1969; IIT Technologia, 1969).

Greenhouse and Field Investigations with Thermally Altered Phosphate Rock--One of the products is made by heating PR, sodium carbonate, and silica to temperatures of 1200°-1400°C. The P in the resulting material is almost completely citrate and water soluble (Doll, 1976).

After reviewing the pertinent literature from Europe and the United States on the Rhenania phosphates, Doll (1976) indicated that under a wide range of soil conditions they appear to be nearly equal to superphosphate as a source of P for long-season crops when the material is finely ground, broadcast, and thoroughly mixed with the soil. He further indicated that they are not suitable as a P source when banded in the soil. In general, however, the reviewing author did indicate that the Rhenania phosphates would appear to be quite effective on the more acid soils.

Leon (CIAT, 1977) conducted a greenhouse experiment on a Carimagua Oxisol, in Colombia, with Stylosanthes guyanensis (2 cuttings) and showed that the Rhenania phosphate was superior to TSP but inferior when magnesium oxide and calcium silicate were incorporated with the TSP (figure 13). This would indicate that there was a magnesium deficiency in the soil in addition to P.

Fused magnesium phosphates (FMP) are made by fusing PR, serpentine or olivine, and silica at about 1250°C. This phosphate, depending upon the composition and ratio of materials used, will usually contain about 29%-33% CaO, 17%-19% MgO, 19%-21% P_2O_5, 22%-26% SiO_2, plus small percentages of Fe and Al oxides, all of which are almost completely soluble in 2% citric acid (Ando, 1959).

Early investigations by Walthall and Bridger (1943) in a pot experiment with two soils, pH 4.9 and 5.3,

using sudan grass (2 cuttings) as the test crop found that the FMP was equally as effective as a P source as both TSP and SSP. The application rate of P_2O_5 for all P carriers was 40 pp2m.

In Brazil, where a Japanese-manufactured FMP is commonly used for certain crops, research results have been most favorable. Alvarez et al. (1965) conducted five experiments with sugarcane on three different soil types with varying rates of phosphate in the state of Sao Paulo. They showed that thermophosphate was substantially better than any other carrier used. The average of the five experiments, with three rates of P_2O_5 (50, 100, and 150 kg/ha) included, gave percentage yield increases of 49 for the FMP and only 35 for SSP. In another series of experiments with corn in the state of Sao Paulo, Miranda et al. (1970) showed similar results using the FMP. In three experiments with P_2O_5 rates of 60 and 120 kg/ha, these researchers found that the thermophosphate fertilizer outperformed SSP on a relative scale by 127 to 100.

In Colombia, Leon (CIAT, 1977) conducted a greenhouse experiment on an acid Carimagua Oxisol with Stylosanthes guyanensis and showed that the Japanese FMP was superior to TSP at all levels of application (figure 13). When MgO and SiO_2 were incorporated with the TSP, the FMP and TSP gave similar results. In another experiment on a Colombia Andept, Howeler (CIAT, 1975) concluded that FMP was not significantly different from TSP as a P source on yields of beans.

Research Proposal

Objectives of the Research Proposal

The objectives are to:

1. Evaluate the effectiveness of sources and methods of application of phosphate fertilizers on soils of tropical Latin America,
2. Determine the forms and availability of the reaction products of these fertilizers in soils as related to their initial and residual effectiveness, and
3. Establish criteria for applying the results of the first two objectives to different soils and

crops at various locations by conducting field experiments on selected soils throughout tropical Latin America.

Currently it is planned that research will be conducted in Colombia, Brazil, Peru, Ecuador, and other countries as may be appropriate.

It is hoped that these objectives can be accomplished through interrelated and pertinent laboratory, incubation, greenhouse, and field experiments. In the following discussion, the authors will attempt to be succinct but thorough in their reasoning and justification for the proposed research.

Situation Statement

Given the facts that the acid Oxisols, Ultisols, and Inceptisols in tropical Latin America are not only low in both available and total P but also fix large quantities of P, it becomes obvious that proper soil management of P fertilizers is extremely important. It is also apparent that the traditional sources of phosphate fertilizers such as SSP or TSP may not be acceptable sources for most crops because of their relatively high costs and because high rates are necessary even when they are banded (CIAT, 1977). The direct application of ground PR alone is probably not a suitable alternative either due to its initial rate of release of P or cost of transportation. The authors realize that certain crops, such as cassava and some legume and grass forages, are capable of foraging for P quite effectively from even the medium or low reactivity rocks, but nevertheless this situation is not true for most crops. It is also understood that some of the PRs are high in reactivity, but due to geographic distribution and infrastructural problems, the direct application of these rocks is probably limited to certain areas.

Although the use of combinations of broadcast PR with banded TSP or SSP has shown promise as overall sources of immediate and residual forms of P, once again the previously discussed restrictions still apply. Furthermore, a normal practice of banding TSP or SSP is not feasible in either a pasture or forage production scheme which is so important in tropical Latin America.

The use of other altered PR products, however, may have some advantages over the previously mentioned

P carriers. In the few trials which have been conducted, for example, with partially acidulated PR and FMP, the responses have been generally equal to or superior to TSP (figures 12 and 13). There would also appear to be some economic advantages in using these forms. In addition, it is feasible to granulate these products, thus overcoming the handling problems normally associated with PR. The potential merits of these altered products will be discussed in more detail later.

Phosphate Materials to Be Tested

Currently there are three long-term field experiments being conducted in Colombia on rates and sources of several PRs, TSP, and basic slag. The residual value of the phosphate carriers is being ascertained with test crops of cassava, beans, and Brachiaria decumbens. These experiments, which were set up by a previous investigator (L. L. Hammond, Soil Scientist, IFDC) will be continued. Also, several other PR experiments which have been reported on were conducted in Colombia by IFDC. In addition, another experiment was set up by Dr. Sanchez and Dr. Leon this past year in which three PRs (Pesca, Huila, and Gafsa) are being compared with TSP at six different rates of P. Various combinations of the PRs and TSP are also included. The test crops are Panicum maximum and Andropogon gayanus, each interseeded with Centrosema 1733. Forage production and uptake and removal of P will be determined in this long-term residual study. Based on the studies that have been and are currently being conducted with PR and TSP, it is the opinion of the authors that emphasis should now be directed towards the use of partially acidulated PR and thermophosphates. Phosphate rock and TSP will be used for comparative purposes.

Partially Acidulated Phosphate Rocks--Since the soils in the target area fix large quantities of P (CIAT, 1977) (figure 4), it would seem reasonable that applying a P material that contains a large percentage of its P in a relatively unfixable form would have some advantages. Once this partially acidulated material is applied to the soil, the monocalcium phosphate is converted to dicalcium phosphate and phosphoric acid. It is hoped that the PR and the acidulated materials would remain in intimate enough contact in the soil so that at least a portion of the phosphoric acid would then react with the PR, thus making it available for plant uptake. In addition, the

acidic nature of the soils themselves should also help to solubilize the remaining PR. Since the P is probably becoming available over a period of time, thus providing a continuous supply to the plants, perhaps the adverse common ion effect of the iron and aluminum can be somewhat overcome.

McLean and Wheeler (1964) state that, "the smaller quantity of soluble P in the partially acidulated material compared to the triple superphosphate (100% acidulated) might then cause less H_3PO_4 to form; and, if part of that formed were dissipated on the rock phosphate, then less Al and Fe would be activated to revert the P to unavailable forms." They further indicate, "the soluble P in the partially acidulated material might stimulate the plant initially, so that they (the plants) can make more efficient use of the unreacted rock phosphate when the soluble P accessible to the roots has been exhausted."

Another potential advantage to the partially acidulated PR is that of granulation. Past attempts at granulating PR have not been successful because of decreasing the effective surface area of the PR in contact with the soil. It may now be possible through the "minigranulation" process (new granulation concept developed by IFDC--Tyler minus 50- plus 200-mesh) with the partially acidulated PR to have a P fertilizer that is both effective as a P source and easy to handle from a physical standpoint.

There are also indications that surface applications of soluble forms of phosphate may be effective in stimulating vegetative growth on existing savannas (North Carolina State University, 1973-75). In some areas of Brazil, aerial applications of SSP are fairly commonplace in native forage production (personal communications with Clinton Shock, IRI, Brazil.) The "minigranulated" partially acidulated PR might also lend itself to this type of application.

The economics of producing the partially acidulated PR should be quite favorable because of the smaller amounts of the sulfuric or phosphoric acids being used. This is especially true in tropical Latin America where the costs of these acids are very high.

Greenhouse and field experiments are being planned and initiated in 1978 using varying levels of partially

acidulated PR. These materials will be made using sulfuric acid and rocks of low, medium, and high reactivity. Whenever possible, local sources of PR will be used. The experiments will also include rate studies, methods of application, and granulated versus ungranulated materials. Efficiency of the test materials will be compared to that of TSP and ground PR. Several different test crops will be studied for uptake and removal of P. The cropping philosophy will be discussed in more detail later.

Thermophosphates--Thermophosphates especially FMP also appear to have good potential as phosphate fertilizers in tropical Latin America. It has been shown previously (Alvarez et al., 1965; McCormick and Galiano, 1968; Miranda et al., 1970) that this material is generally superior when compared with TSP (figures 13 and 14). The implications of this are not clear; however, Leon in preliminary studies indicates that both soil and plant calcium and magnesium contents are somewhat higher when FMP is used versus TSP. In addition, the P content also appears to be marginally higher. There is also the possibility that the available soil silicates may be involved either directly or indirectly, but the experiments were not designed to sort this out. Fox et al. (1967), for example, increased sugar yields by 12 tons/ha through the use of a calcium silicate slag.

There is also a marked difference in solubilities of P in TSP and FMP. The TSP is mostly all water soluble whereas the FMP is citrate soluble but not water soluble. Although both forms of P are generally considered available to plants, perhaps the P in the FMP is not as vulnerable to fixation by Al and Fe in the soil.

At this time it is difficult to know if the FMPs would have an economic advantage over other P sources such as TSP or SSP because of the high energy inputs in fusing the materials. In future years, however, FMPs may become very competitive economically when the hydroelectric potentials of the Latin American countries are realized. Since large known reserves of PR (Leon, 1977) (figure 15) and serpentine/olivine (Cathcart, 1975; Emigh, 1972; Fassbender, 1967; Japan Consulting Institute, 1974) are also present in these countries, the essential raw materials are there for making FMP.

It is interesting to note that FMP may become a manufactured product in Colombia in the near future. In 1974 the Colombian government commissioned a Japanese consulting firm to make a feasibility study on PR uses and specifications for an FMP plant (Japan Consulting Institute, 1974). The results of the study were quite favorable for its production.

Greenhouse experiments will be designed to try to determine why plants in general respond better to FMP than to TSP. Treatments of FMP will also be an integral part of the greenhouse and field studies proposed under the previous section on partially acidulated PR.

Other Materials--Although the partially acidulated PRs and FMPs have been highlighted in this paper, other combinations of PR and sulfur and PR and silica, for example, will be experimented with in greenhouse trials. If any of these appear promising, field experiments at representative sites will also be conducted.

Other Laboratory, Incubation, and Greenhouse Studies

Another aspect of the proposal is chemical and mineralogical characterization of the acid Oxisols, Ultisols, and Inceptisols in the target area. It is extremely important to be able to predict the behavior of different P carriers under the varying soil conditions. It was noted earlier (CIAT, 1977), for example, that P fixation capacities of 350-750 ppm are quite common in these soils (figure 4). These sorts of ranges would significantly alter both the P carrier used and amounts of phosphate to apply. In order to further quantify the spectrum of soils in tropical Latin America, representative soils will be collected for analysis and study from several areas in Colombia.

Phosphorus fractionation of these soils will be included in the initial laboratory analyses. Subsequently, the proposed P carriers will be incubated with the soils, and time studies on available, fixed, and labile forms of P will be determined. Greenhouse trials with several crops will also be conducted in conjunction with these studies to correlate plant P uptake and removal values with the results obtained in the laboratory and incubation studies.

These sorts of investigations will be important in giving a better understanding and direction when establishing other greenhouse and field experiments in this overall project.

Cropping and Management Strategy

The phosphorus project has responsibility for testing a number of potential P fertilizers on a variety of different crops. In general, these crops will include: cassava, beans, rice, and both grass and leguminous forages. Other test crops could include corn, soybeans, peanuts, sesame, sugarcane, and cowpeas. Although this seems like a confusing number of crops, it must be remembered that experiments will be conducted on several different soils under varying climes. Furthermore, the authors feel that using test crops which are normally grown in a given area is very important.

Because of the importance of the beef industry in tropical Latin America, a considerable effort will be devoted to improving forage production through P fertilization. Although P fertility trials will be conducted on direct pasture fertilization and forage production, the concept of crop rotation appears to have added merit.

Since the cost of P fertilizers is relatively high, it is not reasonable in many instances for a farmer or rancher to plow up existing savanna, incorporate fertilizer, and immediately replant a forage. In order for the farmer to realize an immediate monetary return from the fertilizer investment, it is suggested that high-value arable crops be planted for one or more seasons before going into forage production. This allows for defraying some of the immediate input costs and increasing forage production in the long run.

From a research standpoint this cropping scheme offers the opportunity to gain results from the immediately available P as well as residual effects of the P fertilizers. It also lends itself to working with a variety of crops to the extent that their P requirements from the various fertilizers can be ascertained.

If the requirements of the different crops are known, it seems feasible that a tailored P fertilizer and management program could be packaged to include the

arable and forage crop sequence scheme. In order to make P fertilizer recommendations crop specific, the behavior of the P carriers, the plant requirements, and the soil chemical characteristics must be well understood.

Length of Project

The very nature and scope of the proposed phosphorus fertility research program dictate a minimum period of 4-5 years to accomplish the objectives of this IFDC project proposal.

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Table 1. Characteristics of the Main Soils at Santander, Carimagua, and Cerrado Center Stations

Horizon (cm)	Clay %	Sand %	pH (H_2O)	Org. C %	Exchangeable Cations (meq/100g) Al	Ca	Mg	K	CEC	Al satn. %	Avail. P[a] (ppm)	Avail. H_2O (%, vol.)
CIAT - Santander: Ultisol (Orthoxic Palehumult, clayey, kaolinitic, isohyperthermic).												
0- 20	71	4	4.1	4.1	2.7	.65	.49	.36	4.2	64	1.8	16
20- 35	77	5	4.0	2.3	2.7	.31	.04	.13	3.2	83	1.1	13
35- 62	84	2	4.3	1.1	3.2	.24	.02	.09	3.6	88	0.9	16
62- 91	88	1	4.4	0.4	1.1	.15	.02	.06	1.4	77	0.9	9
91-150	90	1	4.4	0.3	2.0	.22	.01	.04	2.3	85	1.2	14
CARIMAGUA: Oxisol (Tropeptic Haplustox, fine-clayey, mixed, isohyperthermic).												
0- 20	37	6	4.9	3.1	2.8	.2	.2	.10	3.4	82	0.9	9
20- 51	39	5	5.0	1.5	2.0	.1	.1	.10	2.3	85	0.4	7
51- 82	40	5	4.8	0.8	1.9	.1	.1	.10	2.2	84	0.9	5
82-117	40	5	5.4	0.6	1.1	.1	.1	.10	1.6	69	0.4	5
117-132	48	5	5.8	0.4	-	.2	.2	.30	0.8	-	0.4	6
132-152	52	4	5.9	0.3	-	.2	.2	.30	0.7	-	0.4	7
CERRADO CENTER: Oxisol (Typic Haplustox, fine, kaolinitic, isohyperthermic - LVE).												
0- 10	45	36	4.9	1.8	1.9	0.4		.10	2.4	79	tr	11
10- 35	48	33	4.8	1.2	2.0	0.2		.05	2.2	89	tr	11
35- 70	47	35	4.9	0.9	1.6	0.2		.03	1.8	88	tr	9
70-150	47	35	5.0	0.7	1.5	0.2		.01	1.7	88	tr	9
150-260	42	39	4.6	0.3	0.7	0.2		.02	0.9	76	tr	9

a. Bray II extraction method.

Table 2. Percentage Relative Agronomic Effectiveness of Various Phosphorus Carriers as Compared to Basic Slag and/or Triple Superphosphate

Source	Panicum Maximum	RAE (%) Cassava	Beans 1	Beans 2
TSP	62	100	100	72[a]
Basic Slag	100	100	-	-
Sechura	94	-	82	65
North Carolina	82	82	79	72
Gafsa	80	84	93	72
Central Florida	53	73	57	52
Huila	41	70	65	42
Tennessee	35	66	40	40
Pesca	27	67	28	28

a. Residual

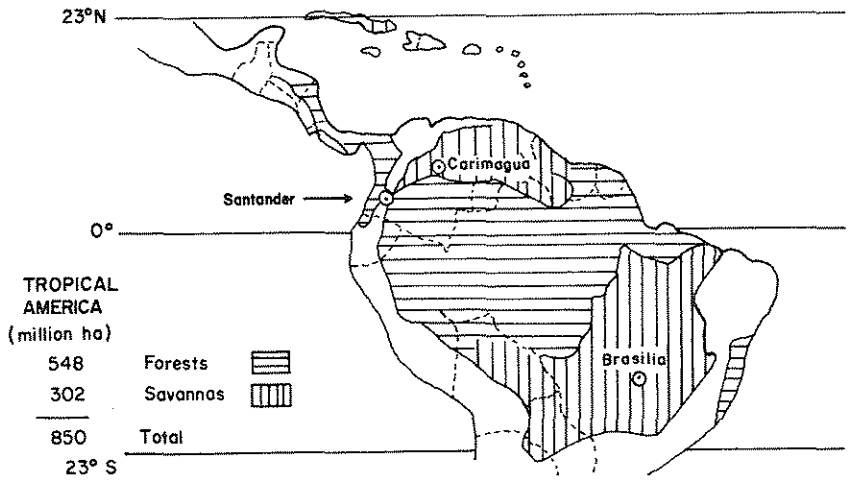

Figure 1. Geographical Distribution of Oxisols and Ultisols in Tropical Latin America.

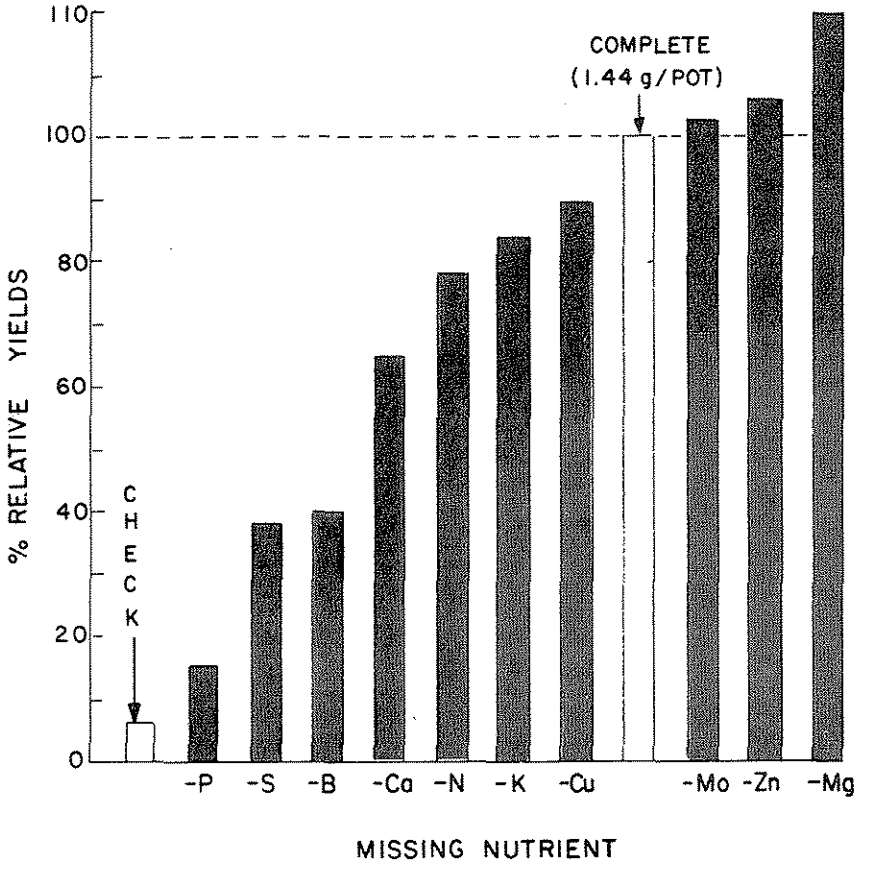

Figure 2. Response of Centrosema plumieri to Missing Nutrient Elements in the Santander Ultisol. (Dry-matter production, first cut; mean of four replications.)

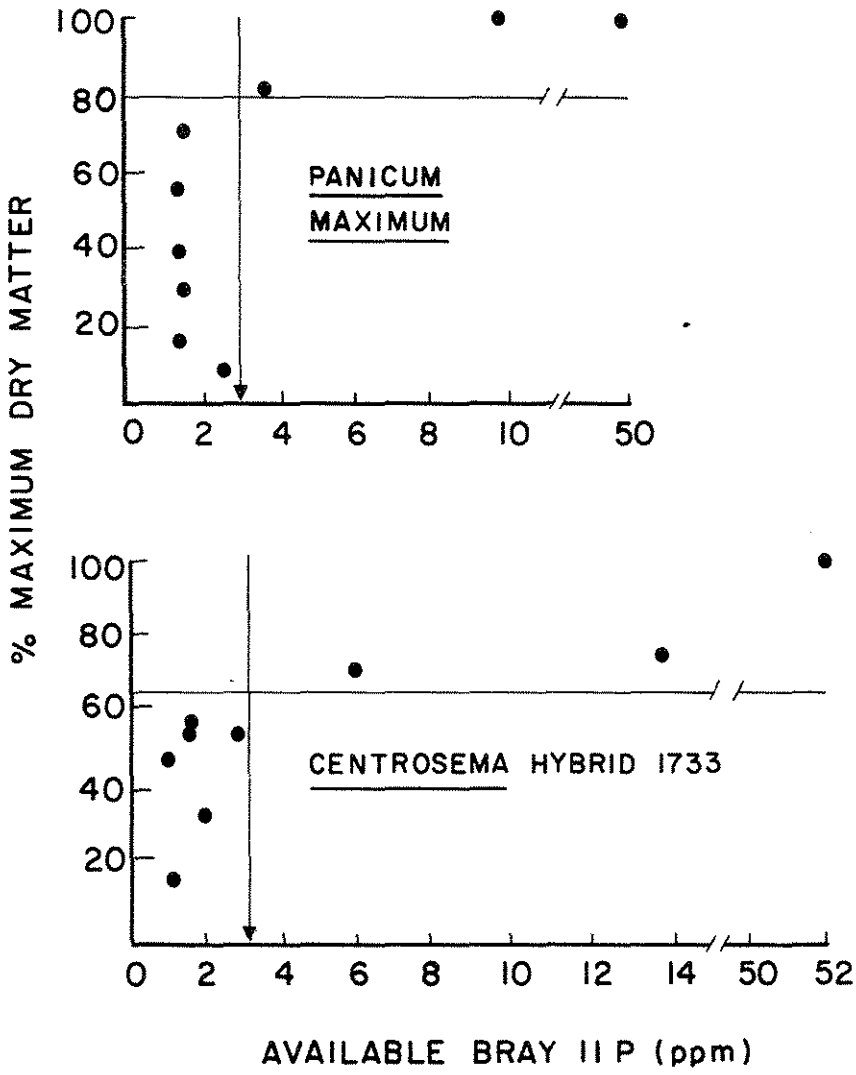

Figure 3. Estimation of the Critical Phosphorus Levels in the Santander Ultisol Under Greenhouse Conditions. (Sum of two cuts and mean of four replications.)

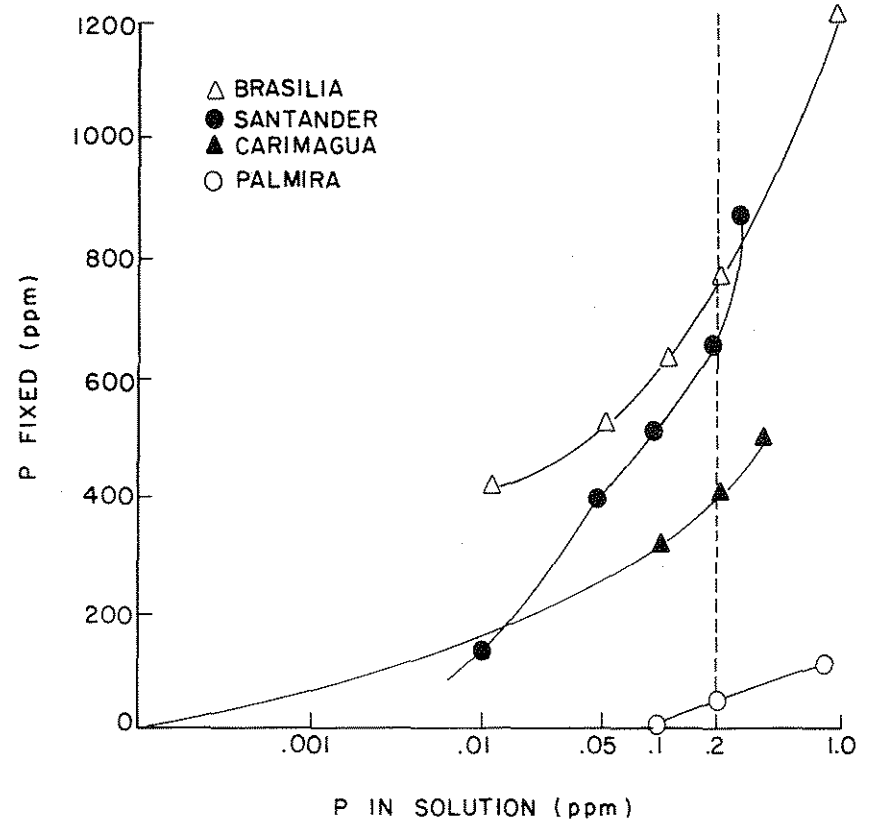

Figure 4. Phosphorus Fixation Isotherms of CPAC (Brasilia), CIAT-Santander, CNIA - Carimagua, and CIAT-Palmira.

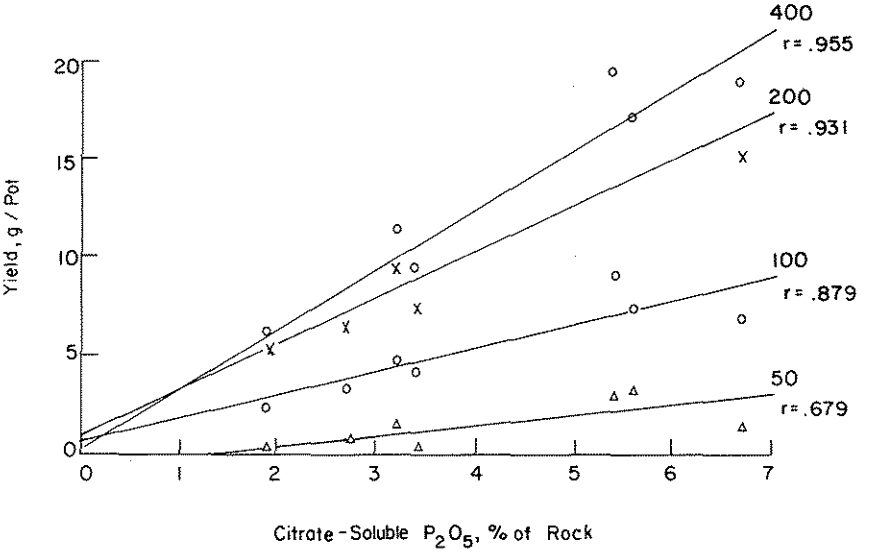

Figure 5. Relationship Between Yield of Three Cuttings of Guinea Grass and Citrate-Soluble Phosphorus in Phosphate Rocks.

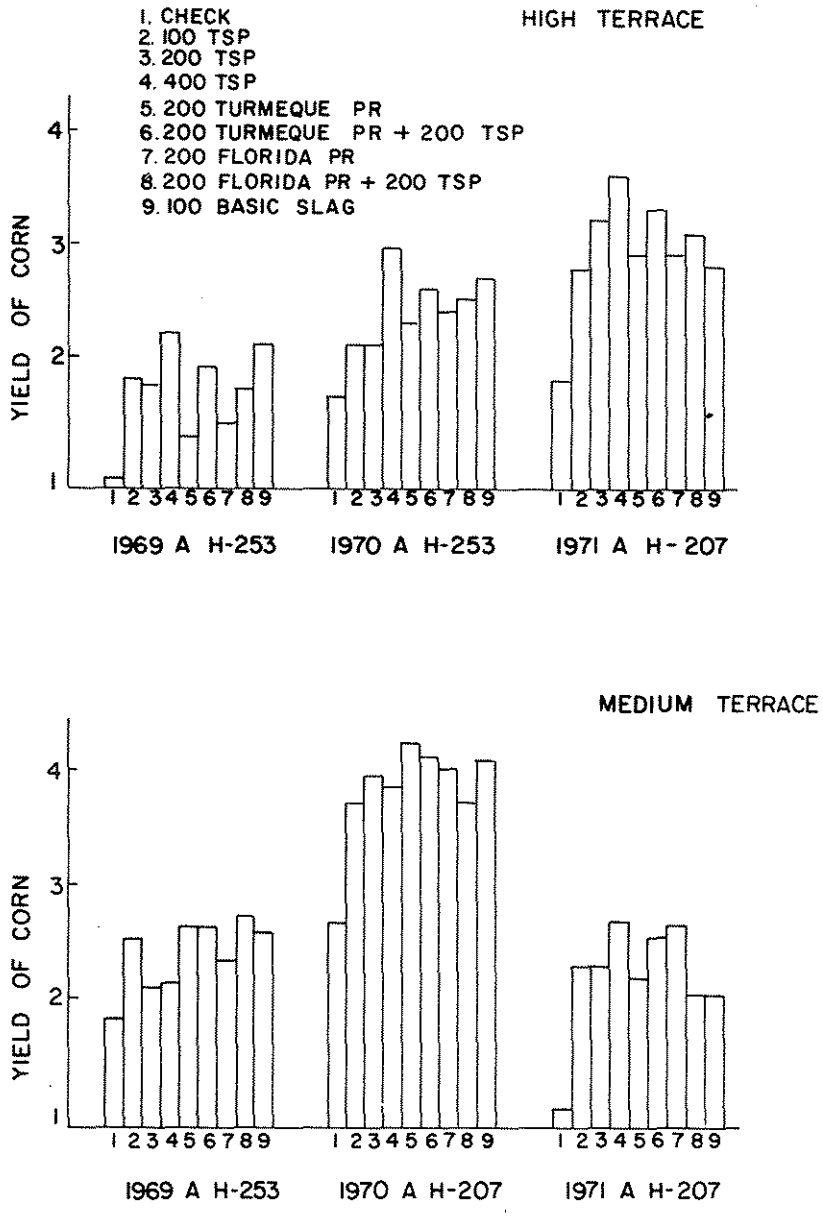

Figure 6. Effect of Broadcast Application of Different Forms and Rates of Phosphorus to Corn Grown on the High and Medium Terraces of the Eastern Plains of Colombia (La Libertad Experiment Station).

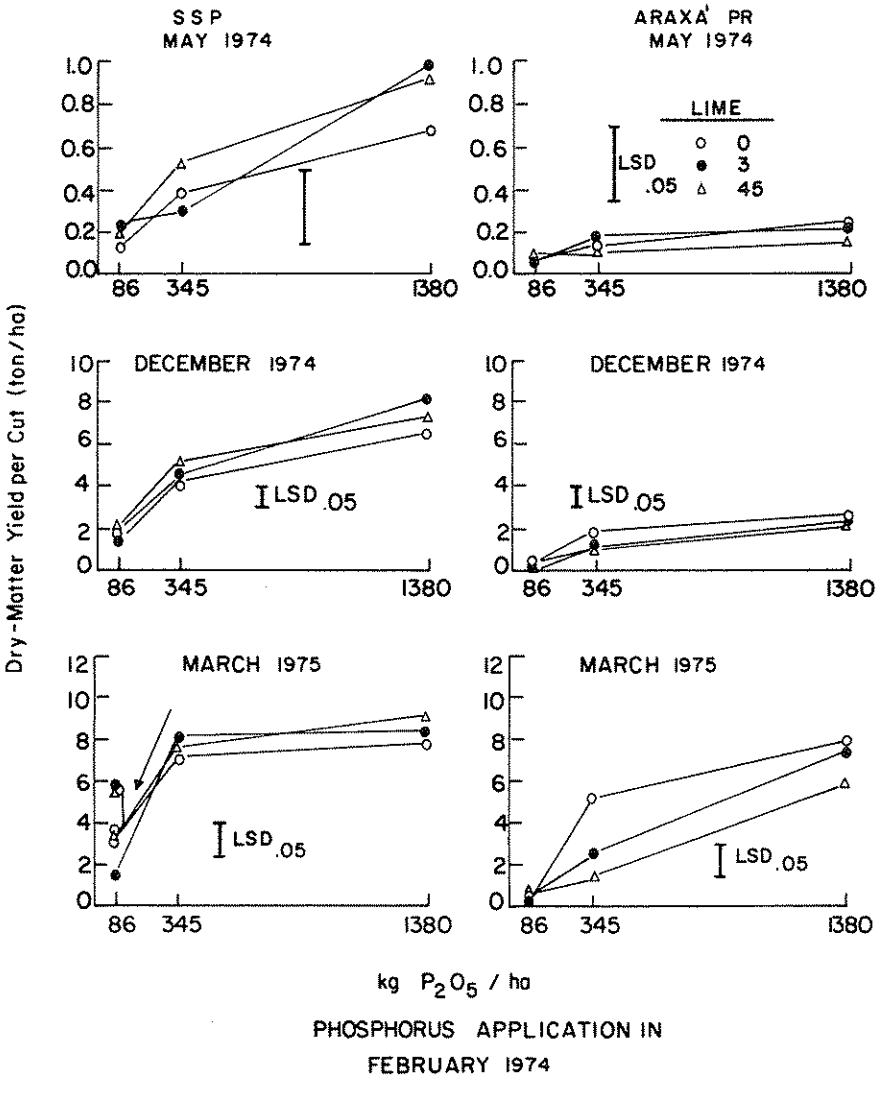

Figure 7. Availability of Araxá PR With Time Using Brachiaria decumbens.

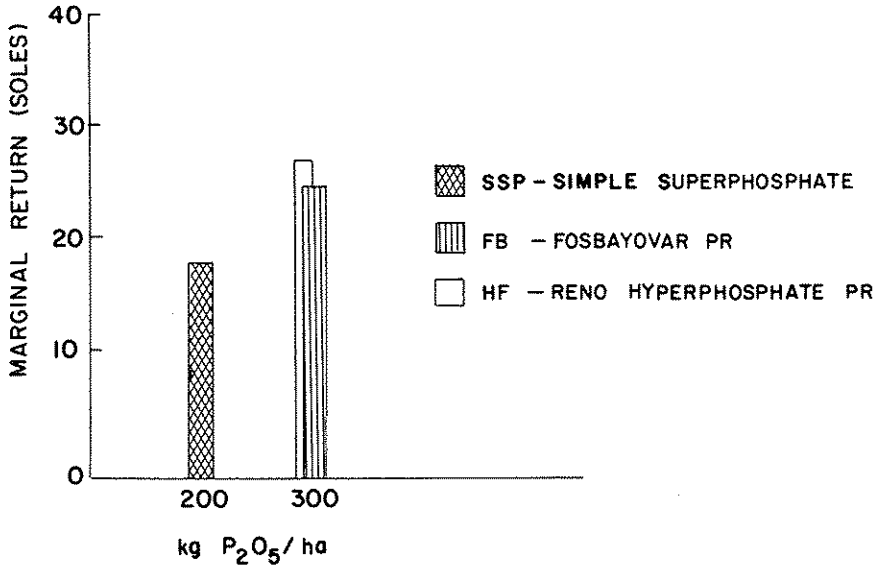

Figure 8. Comparison of Marginal Monetary Returns With Simple Superphosphate and Two Phosphate Rocks With Potatoes in the Highlands of Peru.

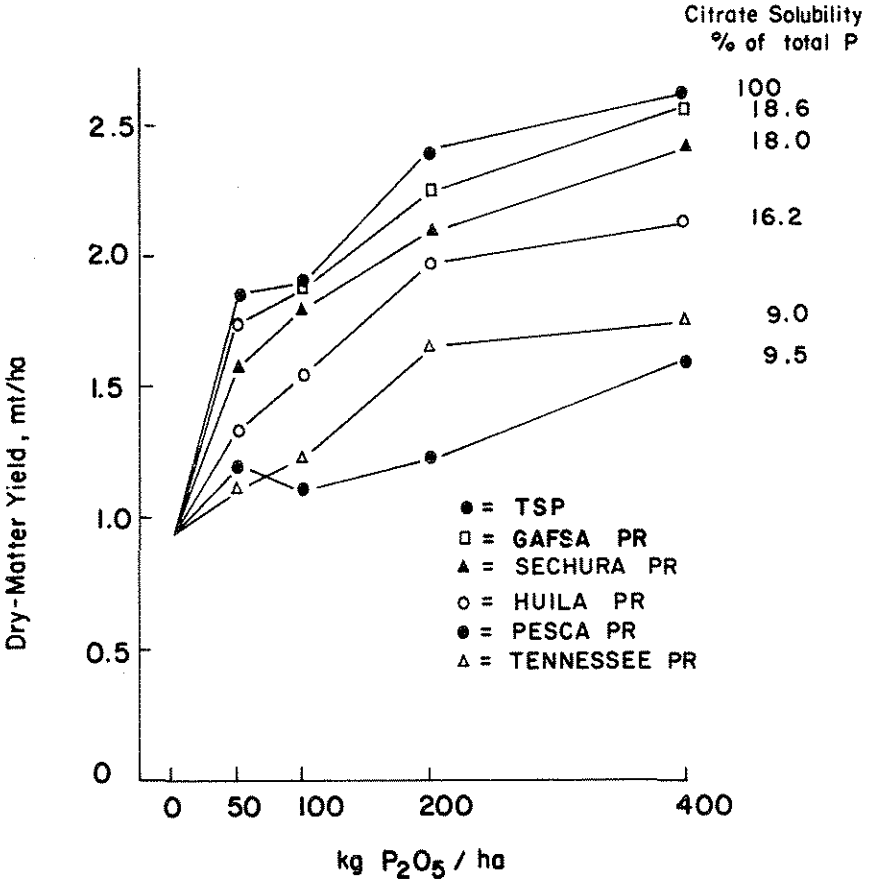

Figure 9. Response of Huasanó Beans to Forms and Rates of Phosphorus on an Andosol from Popayán, Colombia.

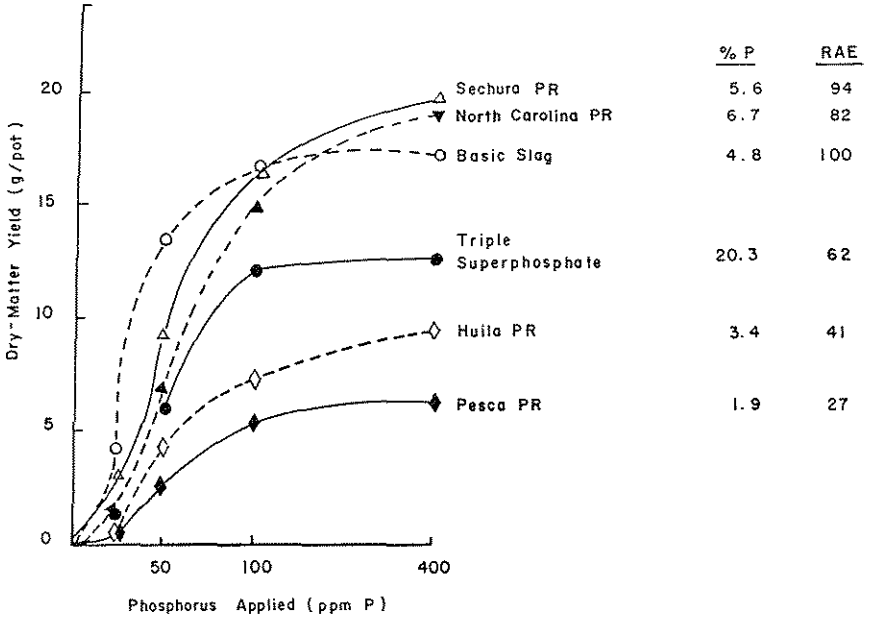

Figure 10. Effect of Sources of Phosphorus on Panicum Maximum Dry-Matter Production (sum of 3 cuts) Grown in the Carimagua Oxisol Without Liming in the Greenhouse. (% P=citrate-soluble P of entire material; RAE=relative agronomic effectiveness).

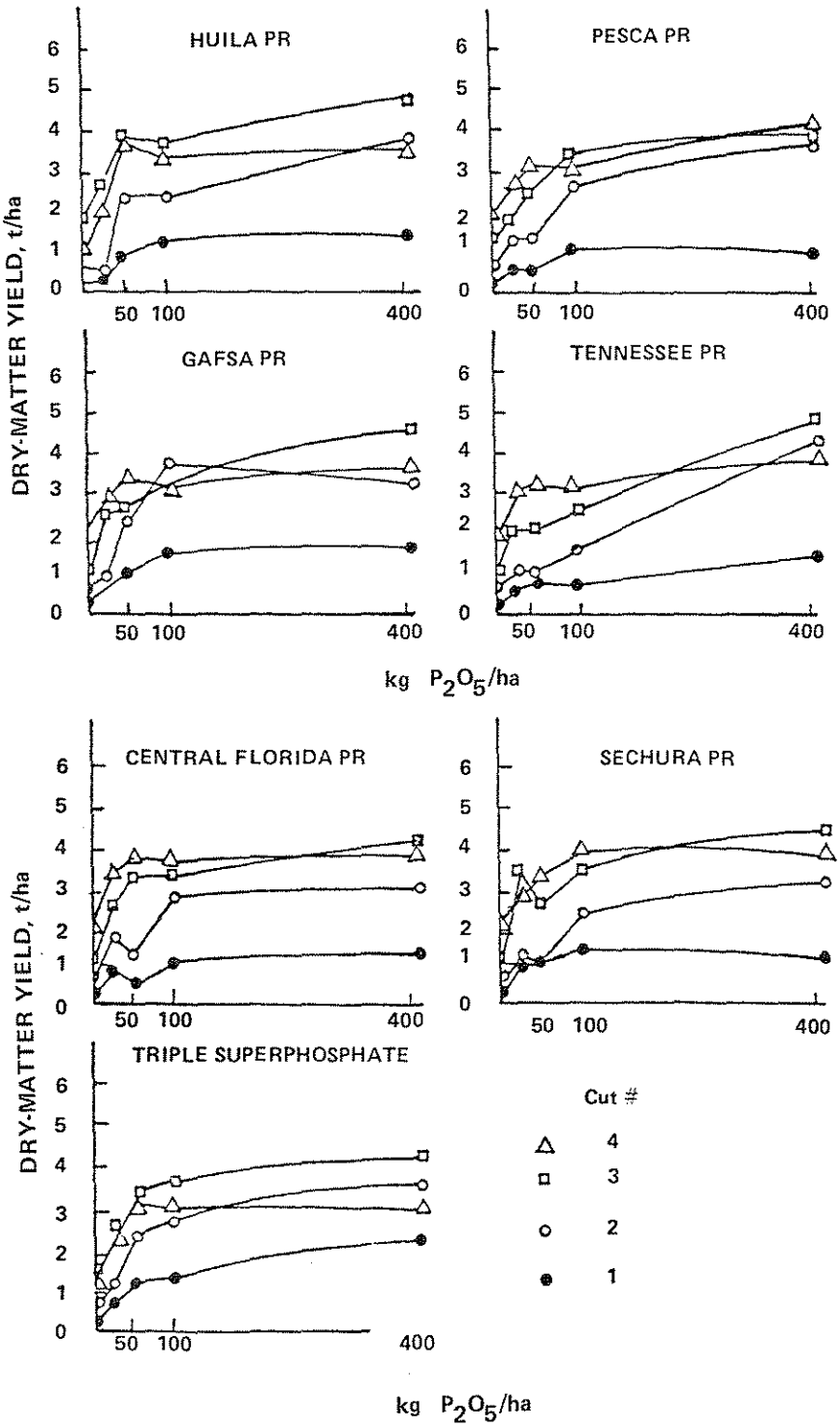

Figure 11. Dry-Matter Yield of Four Cuttings of Brachiaria decumbens in the Field Experiment as Affected by Rate and Source of Phosphorus.

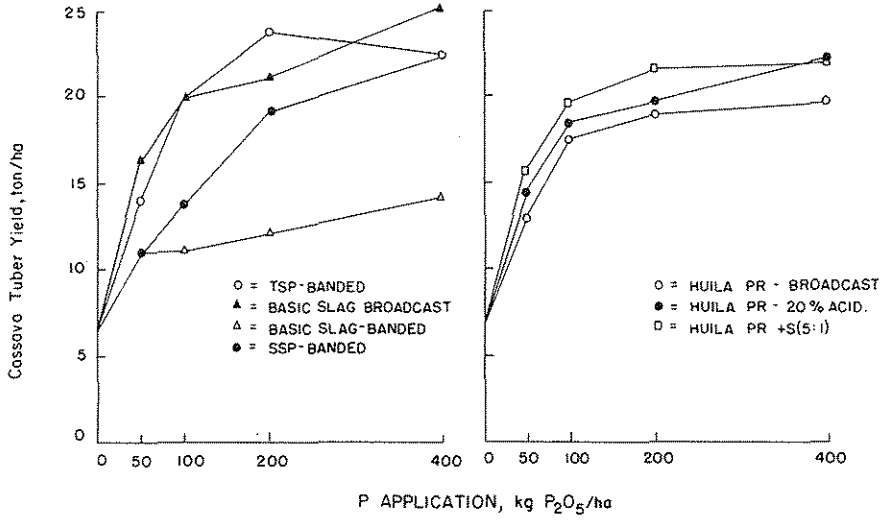

Figure 12. Response of Cassava to Forms and Rates of P on an Oxisol from Carimagua.

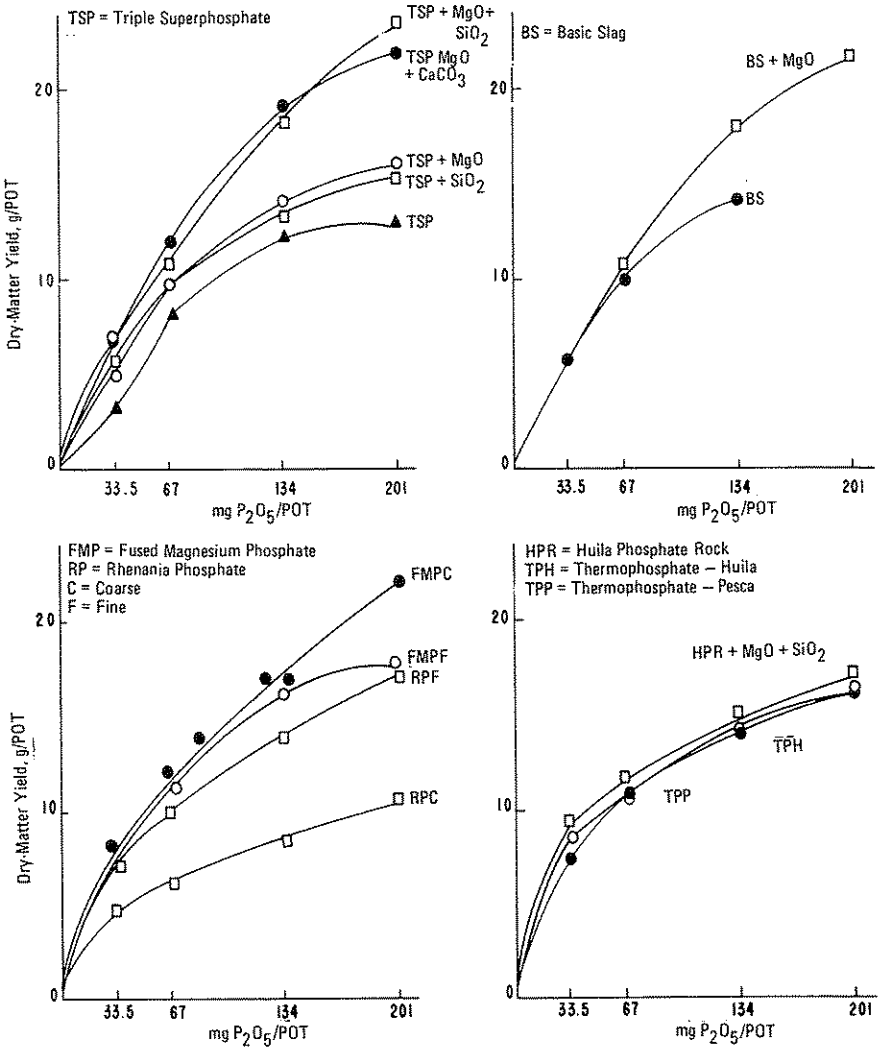

Figure 13. Dry-Matter Yield of Two Cuttings of Stylosanthes guyanensis 136 in a Greenhouse Experiment as Affected by Ratio of Phosphorus With MgO, $CaCO_3$, and SiO_2 and by Different Thermophosphates on Carimagua Soil.

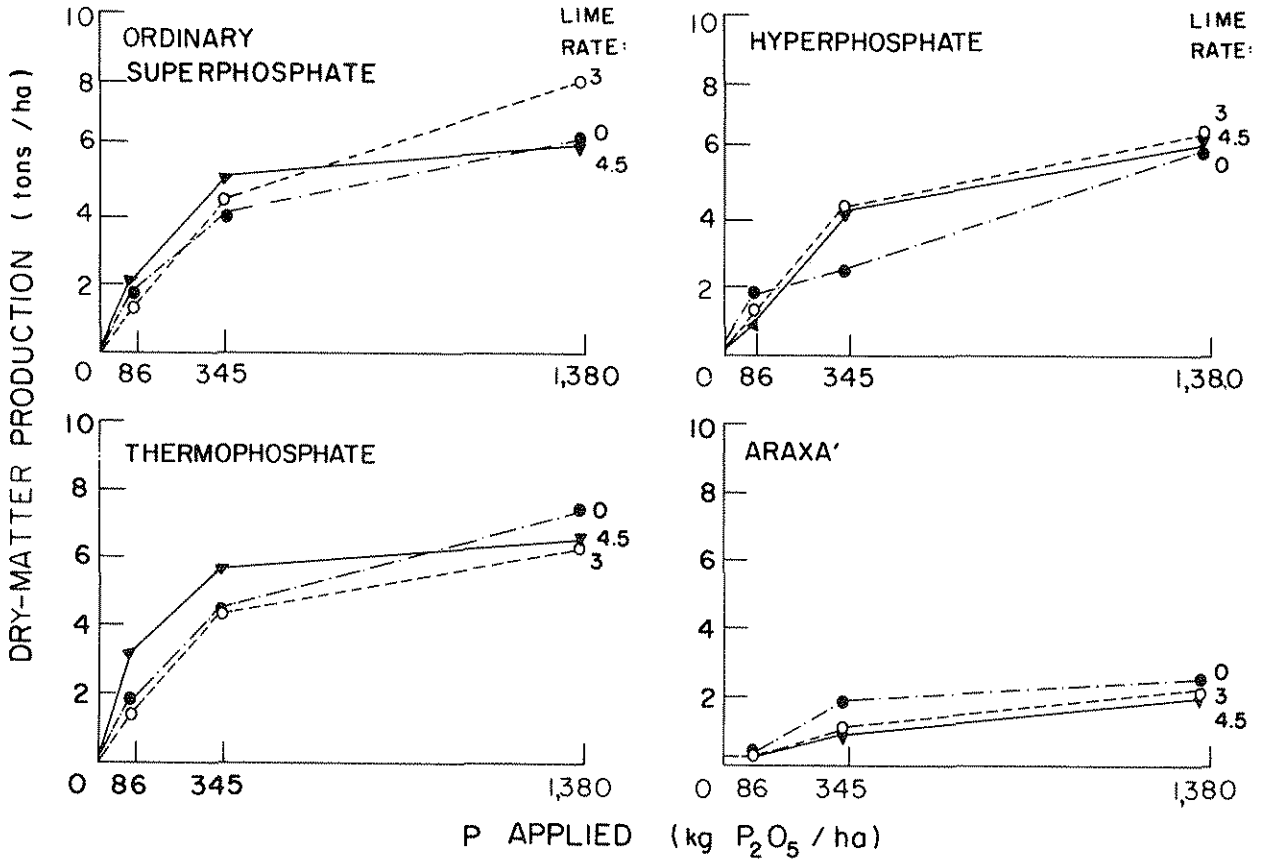

Figure 14. Growth of Brachiaria decumbens as Affected by Phosphorus Sources, Rates, and Liming. (Second cut, December, 1974; Brachiaria on North Carolina rock plots at 345 kg P_2O_5/ha yielded 2.97, 4.28, and 4.79 tons/ha at 0, 3.5, and 4.5 tons lime/ha).

Figure 15. Rock Phosphate Deposits in Tropical South America, 1977.

REACTIONS OF A PHOSPHATE ROCK WITH SOIL

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Abstract

An acid (pH 4.6) clay loam was mixed with ground (<200-mesh) phosphate rock (PR), containing 14.4% P of which 62.7% was soluble in formic acid, to give a concentration of 2,000 ppm added P in the soil. The mixture was either kept dry or incubated in wetting and drying cycles for 4-12 weeks. In a water extract the nonincubated mixture gave a concentration of 1.00 µg P/ml, whereas incubation decreased the concentration to 0.46 and 0.38 µg P/ml. No P was detected in the PR extract. Bray P_1 solution extracted 209 µg P/g from the nonincubated soil and 90 and 103 µg P/g from the incubated samples. From the PR alone 1,819 µg P/g was extracted.

Continuous extraction in the presence of a cation exchange resin (CER) or an anion exchange resin (AER) showed that less P was extracted from an incubated soil-PR mixture than from a nonincubated one. The time-dependent curves obtained in the presence of CER indicate a complete dissolution of all the phosphate in finite time, whereas those in presence of AER show a back precipitation in the soil-PR mixtures after some time and a complete dissolution of the PR sample. Extractions of incubated soil-PR-CER and PR-CER mixtures show clearly a secondary reaction between soil and P released from PR.

It was concluded that for predicting the agronomic value of a PR, the soil-PR system has to be characterized in addition to the characterization of the PR itself.

Introduction

The use of phosphate rock for direct application gained renewed interest during recent years as a result of rising costs of manufactured, more soluble

products and of efforts to encourage usage of local resources where available. This is reflected in a project initiated by the International Fertilizer Development Center (IFDC) aimed at studying the properties and agronomic values of various phosphate rocks. Work done in our laboratory is a part of a cooperative effort in these studies. Some of the aspects and results are reported in this paper.

Attempts are often made to relate the availabilities to plants of various phosphate rocks to some index of their solubility, such as solubility in ammonium citrate, citric or formic acids; absolute citrate solubility (Engelstad et al., 1974; Lehr and McClellan, 1972); and solubility in the presence of EDTA (Olsen, 1975). Chien (1977b) reviewed the relationship between the solubilities of different phosphate rocks and their crystallographic properties and explained them by thermodynamic considerations. However, it may be assumed that the availability of phosphate rock is influenced by soil factors to which it is applied in addition to the rock properties themselves. The factors mentioned are rate of dissolution and rate of movement of ions from the solid phase of the soil (Olsen, 1975). The solid phase may include residual soil P, P in the phosphate rock, and P in the reaction products of soil components with P released from the phosphate rock.

In the study presented here an attempt was made to define the P status in a soil mixed with a relatively reactive phosphate rock.

Materials and Methods

The soil used in the experiments was a clay loam, having a pH of 4.6, with a cation exchange capacity of 33.1 meq/100 g, with moisture at "field capacity" of 29.4% and 2.0% organic C. The phosphate rock (PR) was sampled in Arad in the Negev area of Israel and was ground to pass a 200-mesh sieve. It contained 14.4% total P, of which 62.7% was soluble in 2% formic acid and 38.5% in 2% citric acid. It contained 4.4% CO_2 as carbonate.

The PR was mixed into batches of 1,500 g of air-dry soil to provide 2,000 ppm added P. The batch was separated into three portions, and they

were incubated for 0, 4, and 12 weeks with wet and dry cycles. The samples were kept wet at field capacity and room temperature for 5 days and then dried at about 30°C for 2 days and again wetted. At the end of the incubation period, the mixtures were air dried, moisture contents were determined, and the mixtures were stored for subsequent measurements. It is assumed that during air-dry storage no further processes occurred. Soil samples without PR additions received the same treatment.

Water Extract

Ten grams of soil, or a mixture of soil and PR after predetermined times of incubation, or an amount of PR equivalent to that in the mixture was shaken in 100 ml of water for 8 varying periods of time, ranging from 10 minutes up to 8 days. The materials were centrifuged and filtered, and P and pH were determined in the solution.

Bray P_1 Extract

Five-gram samples were shaken with 50 ml of a 0.03M NH_4F + 0.025 M HCl solution for 5 minutes and filtered; P was determined.

P Extraction in Presence of a Cation Exchange Resin (CER)

The resin was a strongly acidic, sulphonated polystyrene type-Na form, Amberlite C G 120 (100- to 20-mesh), analytical grade. One gram of the sample and 2 g of resin were shaken with 50 ml of water for different periods of time and centrifuged; P and pH were measured.

P Extraction in the Presence of an Anion Exchange Resin (AER)

The resin used was strongly basic with trimethyl benzyl ammonium groups in Cl form, with a particle size of 16- to 20-mesh. Prior to use, the resin was washed with an NaCl solution and water, stored wet, and air dried shortly before usage. The soil samples were ground to pass a 0.25-mm sieve. For various periods of time 0.5 g of the sample was shaken with

1 g AER in 100 ml of water. After shaking the resin was separated from the sample on an 0.25-mm sieve by washing with a jet of water. The resin retained on the sieve was transferred to a flask with 90 ml of water, 10 ml of HCl 1M was added, the mixture was shaken for 1 hour, and the supernatant liquid was analyzed for P.

In another experiment, 2-g samples of the nonincubated soil and PR batch were mixed with 2 g of CER, moistened to "field capacity," and incubated up to 20 days. PR alone was incubated by mixing 0.1 g of it with 2 g of resin. At the end of the predetermined incubation period, 50 mg of water was added; the samples were shaken for 24 hours and filtered; and P was determined.

P in solution was determined in all cases by the method described by Murphy and Riley (1962) and pH by glass-calomel electrodes.

Results and Discussion

The concentration of P and pH in water extracts of soil, soil-PR mixture, and PR was determined after various periods of shaking. The results did not show a dependence of concentration on time of shaking, although the results obtained were quite variable. Therefore, average values and standard deviation over all shaking times were calculated and presented in table 1. The results indicate an interaction of soil and PR. A short contact of soil and PR enhances P solubility over that of PR alone, whereas during a prolonged period of contact P solubility is somewhat lowered, probably due to a secondary reaction.

The Bray P_1 solution (table 1) extracted approximately 90% of P from PR alone but only 5%-10% from the soil-PR mixtures. This may be related to changes in the pH of the extracting solution. After interaction with the soil-PR mixtures, the pH rose from 2.9 to 3.9 while after contact with PR alone a pH of 3.0 was obtained.

There is a decrease of Bray P_1 values during the first 4 weeks of incubation of the soil-PR mixtures, followed by a slight increase during the following 8 weeks of incubation, indicating again a

fixation of P from PR while in contact with soil. These results are different from those obtained by Chien (1978) and Barnes and Kamprath (1975) who found increase in Bray P_1 values after incubation of PRs from different sources in acid soils.

The results of phosphate dissolution in water in the presence of a cation exchange resin (figure 1) show that during a period of 15 days about half of the PR was solubilized. Slightly less was solubilized when the PR was mixed with soil and incubated 4 weeks prior to extraction. On the other hand, more of the P is released when the PR is mixed with soil and immediately extracted.

The data presented in figure 1 were used for calculating rate constants of the dissolution process. Kinetics of phosphorus reactions were extensively studied (Amer et al., 1955; Evans and Jurinak, 1976; Larsen, 1971; Olsen, 1975; Munns and Fox, 1976). Calculations were done using a first order reaction equation following Amer et al. (1955). Plotting of the calculated data showed two distinct slopes for each treatment, indicating an initial fast reaction and a later slower one. The calculated constants are given in table 2. In the fast reaction stage, the rate of dissolution of nonincubated soil-PR mixture is faster than that of the incubated one. The fast stage came to an end at approximately the same time in all three samples. The amounts of P calculated to be released at the end of this stage were 640 µg/g from the nonincubated mixture and 350 µg/g from the incubated one. In the slow rate dissolution stage, although the rates are lower by nearly one order of magnitude, the ratio of the slopes of the nonincubated and incubated mixtures is similar--1.57 for the fast stage and 1.42 for the slower one. This indicates that first dissolution and then sorption reactions occurred when the PR was in contact with the soil. Similar effects for dissolution of phosphate rocks in acid solutions were found by Chien (1977a).

In another experiment, soil and PR mixtures were incubated for various periods with CER prior to P extraction by shaking in water. Results of these determinations are given in table 3. According to these results the solubility of P in PR mixtures with CER remains quite constant through the incubation

period, while that in the mixtures of soil, PR, and CER decreases appreciably with incubation time. This may again indicate that the decrease in solubility with time of contact is due to a fixation process induced by soil components and not to variability in the PR composition.

The pattern of P release in presence of an AER (figure 2) is different from that seen with the CER (figure 1). The rate of P release from the PR alone is higher in the presence of AER than that when CER is present. For the soil-PR mixtures and during the first 4-5 days of shaking, the release is similar in the presence of either one of the resins. However, after that time a desorption of P from the anion exchange resin occurs. Results in figure 2 indicate, as in figure 1, a P fixation during PR incubation in the soil. According to results in figure 2, this process is faster during the first 4 weeks of incubation than during the next 8 weeks.

Conclusions

The series of experiments performed on an acid soil and a relatively reactive phosphate rock indicate clearly that in this system an interaction exists between the phosphate rock and the soil. More P is brought into solution in a water extract and in presence of a cation or an anion exchange resin when the phosphate rock is mixed with soil than when only phosphate rock is extracted. However, after incubation the P recovered declines. It seems that upon solubilization a secondary precipitation or coating reaction occurs in the presence of soil resulting in a decrease of soluble P. Our results indicate that the soil exerts a solvent effect upon the PR added but that with prolonged contact a fixation process takes place.

These findings point to the fact that solubility tests of phosphate rocks can give only first indications as to their availability to plants. A more accurate prediction of their agronomic value should be gained by studying phosphate rock reactions with soils. Obviously, the values obtained by the methods reported should then be correlated to agronomic evaluation indices.

In addition, the results indicate that PR additions to the experimental soil improve considerably the P status of this soil. Even after incubation and fixation have taken place, the PR-treated soils supply much more P to the extractants (water, AER, and CER) than did the untreated soil.

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Table 1. P Concentration and pH in Water Extracts of Soil, Soil-PR Mixtures, and PR After Various Incubation Times and P Extracted by Bray P_1 Solution

Material	Incubation Period, Weeks	P (water extract) µg/ml (st. dev.)	pH	P in Bray P_1 Extract, µg/g
PR	None	0.00	7.7	1,819
Soil	None	0.09 (0.03)	5.5	24
Soil + PR	None	1.00 (0.48)	5.9	209
Soil + PR	4	0.46 (0.32)	6.0	90
Soil + PR	12	0.38 (0.30)	6.0	103

Table 2. Constants of First Order Reaction Equations[a] Describing Kinetics of Solubilization in Presence of CER of Soil and PR Mixtures

Material	Incubation Period, Weeks	Fast Reaction			Slow Reaction		
		k_1	a	r	k_1	a	r
PR	None	0.009	0.09	0.96	0.0012	0.28	0.99
Soil + PR	None	0.011	0.15	0.97	0.0017	0.35	0.97
Soil + PR	4	0.007	0.05	0.95	0.0012	0.17	0.99

a. $\ln \frac{P_o}{P_o - P} = k_1 t + a$

P_o = P added, µg/g
P = P released to solution, µg/g
k_1 = first order reaction constant ($hour^{-1}$)
a = intercept of regression line
t = time, hours
r = correlation coefficient

Table 3. P Solubilized from Incubation Mixtures of PR, Soil and CER, and pH in Solution

Sample	Incubation Period with CER (days)			
	0	7		20
	P µg/g			pH
PR+CER	420	442	430	9.4
Soil+PR+CER	571	160	47	7.7
Soil + CER	6	7	4	7.6

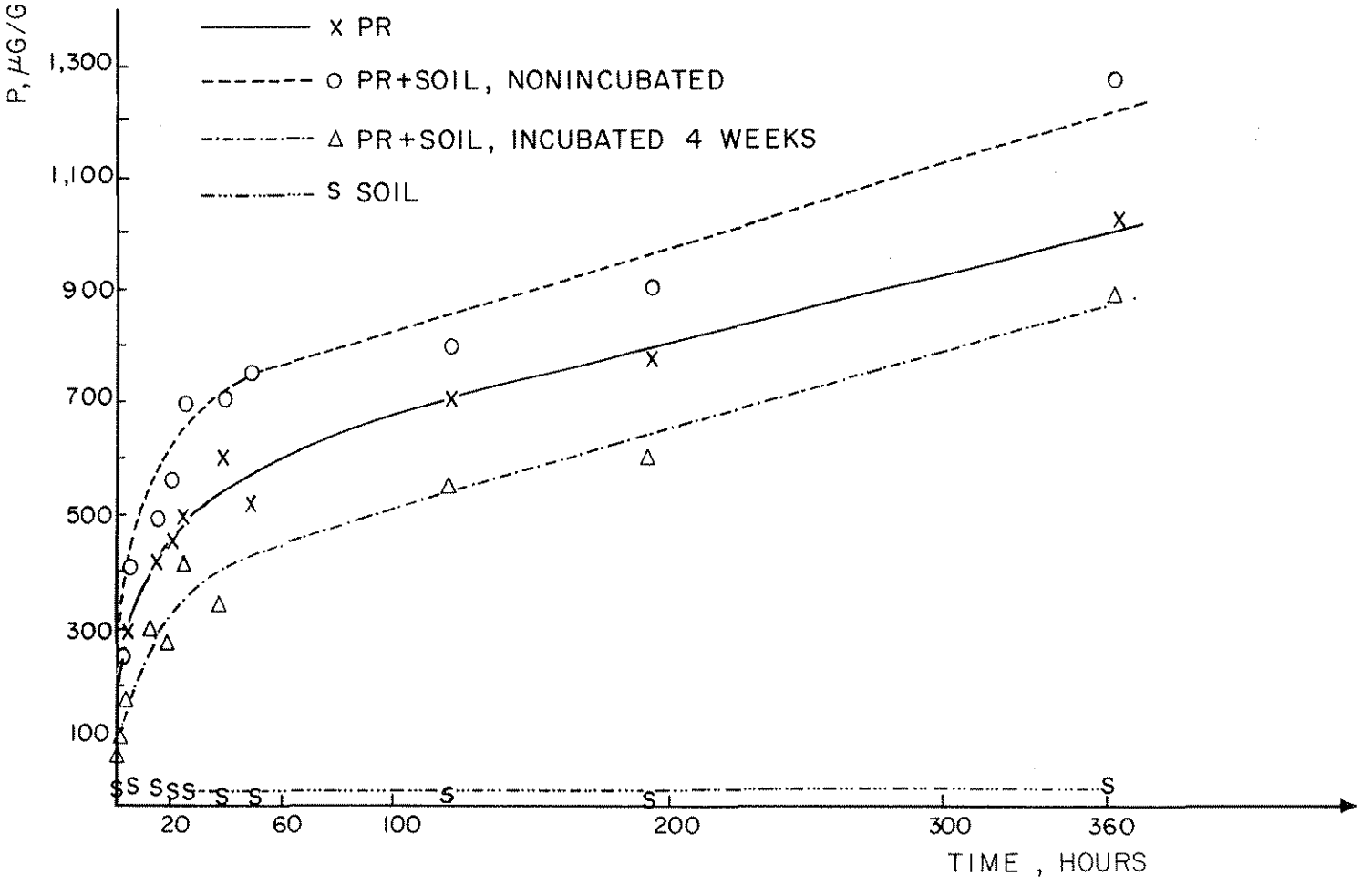

Figure 1. Amounts of P Solubilized in Presence of a CER From Soil, Soil + PR, and PR at Different Shaking Times.

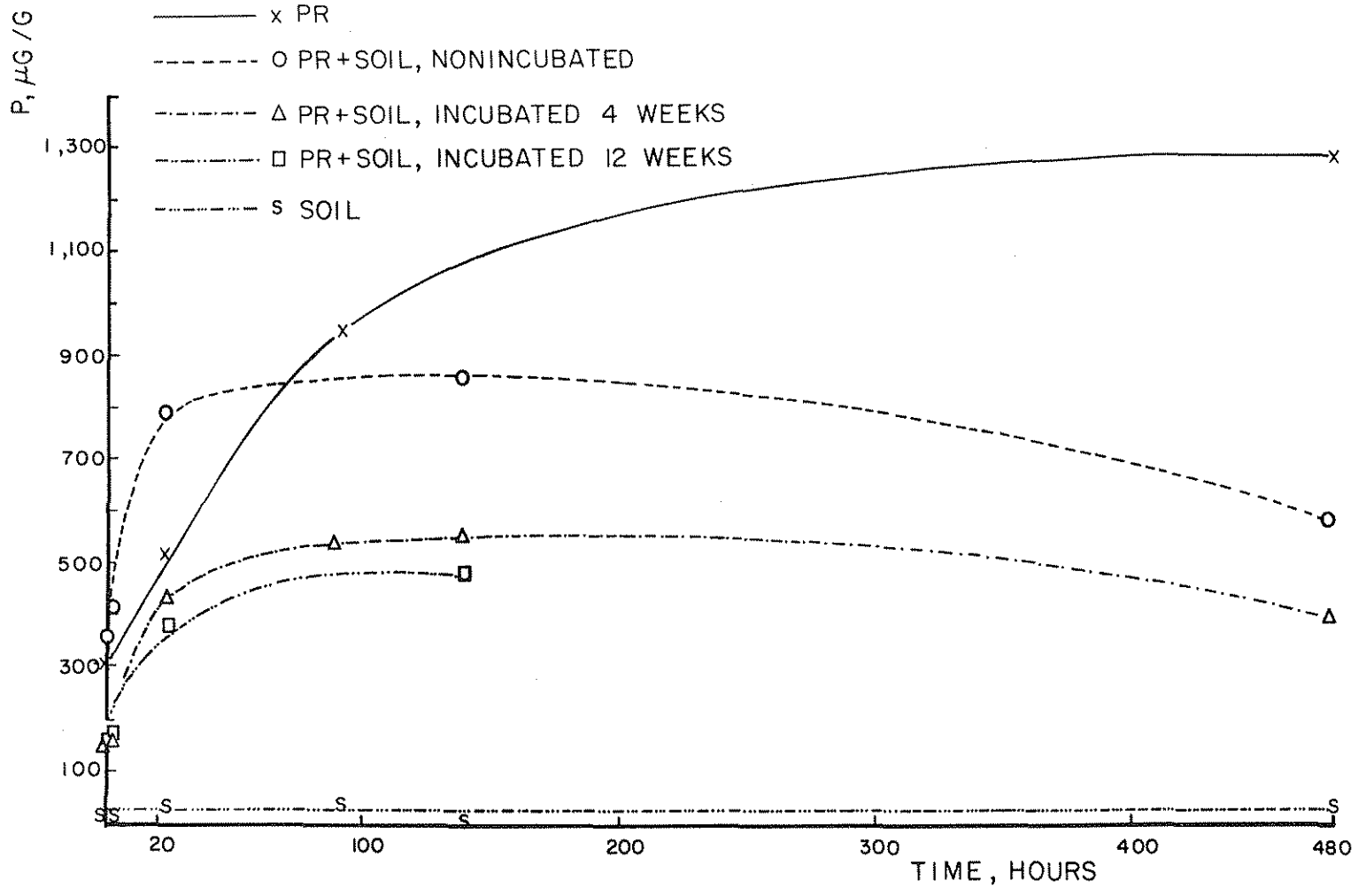

Figure 2. Amounts of P Solubilized in Presence of an AER From Soil, Soil + PR, and PR at Different Shaking Times.

METHOD FOR ESTIMATING GRANULATED PHOSPHATE ROCK AVAILABILITY FOR CROPS

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Summary

Dissolution rate of granulated phosphate rocks in a mixture of moist soil and cation exchange resin was measured by successive extractions with an anion exchange resin. Amounts of P extracted correlated well with the effectiveness of the granules measured in greenhouse experiments.

Introduction

Methods commonly used for estimating availability of ground phosphate rock as phosphate source to plants are not always applicable to granulated rock. Usually a sample of phosphate rock is shaken in solutions of citric or formic acids, and the amount of P solubilized is determined. Granulated phosphate rock will give a lower supply of P than predicted by the solubility of the ground form because of the reduced surface area that comes into contact with the soil and with the plant roots (Bouldin and Sample, 1959). Supply of P will be further influenced by the hardness of granules and by binders used for granulation. Availability of a granulated P fertilizer of low water solubility is dependent on the concentration of P in the soil solution it produces and on the probability of a root finding the P source (Moreno, 1959, and Van Burg, 1963); hence, the distribution of granules in soil influences their availability.

The proposed method is based on successive P extractions by an anion exchange resin (AER) and removal of Ca from phosphate rock granules embedded in a mixture of moist soil and a cation exchange resin (CER). The constant removal of Ca cations and phosphate anions should influence phosphate rock rate of dissolution (Johnson and Olsen, 1972; Olsen, 1975; Asher and Ozanne, 1961).

Materials and Methods

The anion exchange resin (AER) used in experiments was Dowex 11, 16/20 mesh, strongly basic charged with Cl, and the cation exchange resin (CER) was Amberlite CG - 120, 200-400 mesh (Na^+) or Dowes 50 WX8, 200-400 mesh H^+ charged. P sources were Maktesh and Arad phosphate rocks from the Negev area in Israel and North Carolina phosphate rock supplied by the International Fertilizer Development Center (IFDC). Some characteristics of the P sources are given in table 1.

Characteristics of soils used in experiments are given in table 2. All soils were crushed and sieved to pass 2 mm. The soil from Ireland was limed to pH 5.3 and inoculated with a manure extract. This soil was used in the greenhouse experiment. Other soils did not receive any treatment. The sand was sieved to a 40- to 100-mesh size and washed by acid.

Available P was measured by the Bray P_1 method (Black 1965). The fixing capacity was determined by shaking soil samples in a solution of 50 ppm KH_2PO_4 (soil:solution ratio was 1:10) for 24 hours, centrifugating and measuring P concentration in the supernatant liquid. Fixing capacity is expressed as the amount of P(µg) fixed by 1 g of soil during a 24-hour period.

$$F_C = \frac{P_o - P}{W}$$

W - Weight of soil
P - P concentration after 24 hours
P_o - Original P concentration

In laboratory experiments the samples were prepared in the following way: 1.2-g AER, saturated with water, was placed on a plastic cover of 5-cm diameter and covered with a circle of moist Wattman No. 1 filter paper of 5.5-cm diameter. Phosphate rock granules were placed on top of it (0.3 g) and covered with a 6-g mixture of soil + 10% CER, water saturated. A perspex ring of 3-cm interior diameter kept the soil in place. The experimental setup is shown in figure 1. Samples were closed in a desiccator with water to prevent drying. AER was changed at predetermined times, and P extracted by it was measured. AER of each sample was transferred to a 50-ml bottle, 40 ml of 0.1N HCl was added, and the

samples were shaken for 1 hour. P was determined in an aliquot by the spectrophotometric method (Murphy and Riley, 1962).

Results and Discussion

Preliminary experiments were conducted in order to establish the optimal soil:CER ratio and the optimal period of contact with the AER. Results presented in figure 2 show that the soil:CER ratio had a pronounced influence on the amount of P extracted by the AER and on the dissolution rate of the granules. According to the results obtained and taking into account that the Arad and Maktesh granules were less soluble than the North Carolina ones, the measurements were conducted with 10% CER relative to soil. It is interesting to notice that more P was released in the presence of sand than of soil with the same CER content.

In additional preliminary experiments AER was either exchanged daily (successive 24-hour contact periods) for 7 days (figure 3) or exchanged every 1, 2, 3, 4, 5, and 6 days (figure 4). As may be seen from the results plotted in figures 3 and 4, a daily renewal of the resin gives higher extraction values with a tendency to limiting values than a prolonged continuous contact. Therefore, it was decided to change the AER daily.

Further, results in figure 3 show that granule size had an influence on dissolution, the finest granules being more soluble than the coarser ones. The binders used also affected the solubility. The Maktesh rock, granulated with H_2SO_4, was much more soluble than the same rock granulated with $MgSO_4$ or KCl (same granule size), because of partial acidulation.

The KCl-bound granules were more quickly solubilized by the AER than those bound with $MgSO_4$, probably because granules containing KCl were softer and disintegrated rapidly in contact with water (see table 1).

The average amounts of P extracted daily by the AER from each of the P sources were calculated from the dissolution curves and correlated to the P uptake

in corresponding greenhouse experiments at the 1.0 g P/pot level. The resulting regression line is shown in figure 5. The correlation coefficient was r = 0.985 (Data were taken from greenhouse experiment reported by Gillon et al. in these proceedings and some from yet unpublished experiments).

In another experiment granules were incubated with a mixture of soil and CER and AER added later. Amounts of P extracted by AER after incubation are shown in figure 6. It seems that P solubilized during the first days of contact became subsequently fixed by the soil.

Dissolution rates of P sources were measured in the presence of different soils with 6% CER. Their characteristics are listed in table 2, and the results are plotted in figure 7. Different P release patterns were observed in the presence of different soils. Some relation between P release and soil-fixing capacity (table 2) may be seen.

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Table 1. Characteristics of Granulated Phosphate Rocks

Origin	Binder	Size Range (mm)	Stability to Water (No. of Water Drops)	Total P (%)
Maktesh	5% $MgSO_4$	2-4	39	12.5
	10% KCl	2-4	14	11.9
	14% H_2SO_4	2-4	>450	11.1
Arad	5% KCl	2-4	14	13.7
		0.8-0.4	-	13.6
	5% $MgSO_4$	2-4	50	13.5
		0.8-0.4	-	13.3
North Carolina	10% $MgCl_2$	1.2-3.3	41	11.8

Table 2. Soil Characteristics

Origin	Texture	pH	Bray P_1 Extraction, µg P/g Soil	P Fixing Capacity, µg P/g Soil
Germany	Loam	5.8	57.5	153.4
Georgia	Silt loam	4.8	56.0	334.0
Carimagua	Silt loam	4.8	5.8	452.0
Popayan	(Peat)	4.6	6.1	599.8
Ireland	Clay loam	4.6 (5.3)	20.0	340.0
	(Sand)	-	-	40.0

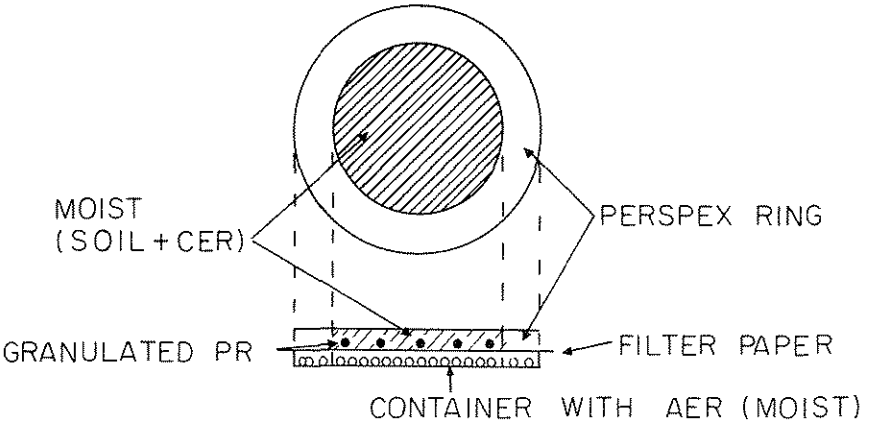

Figure 1. Experimental Setup.

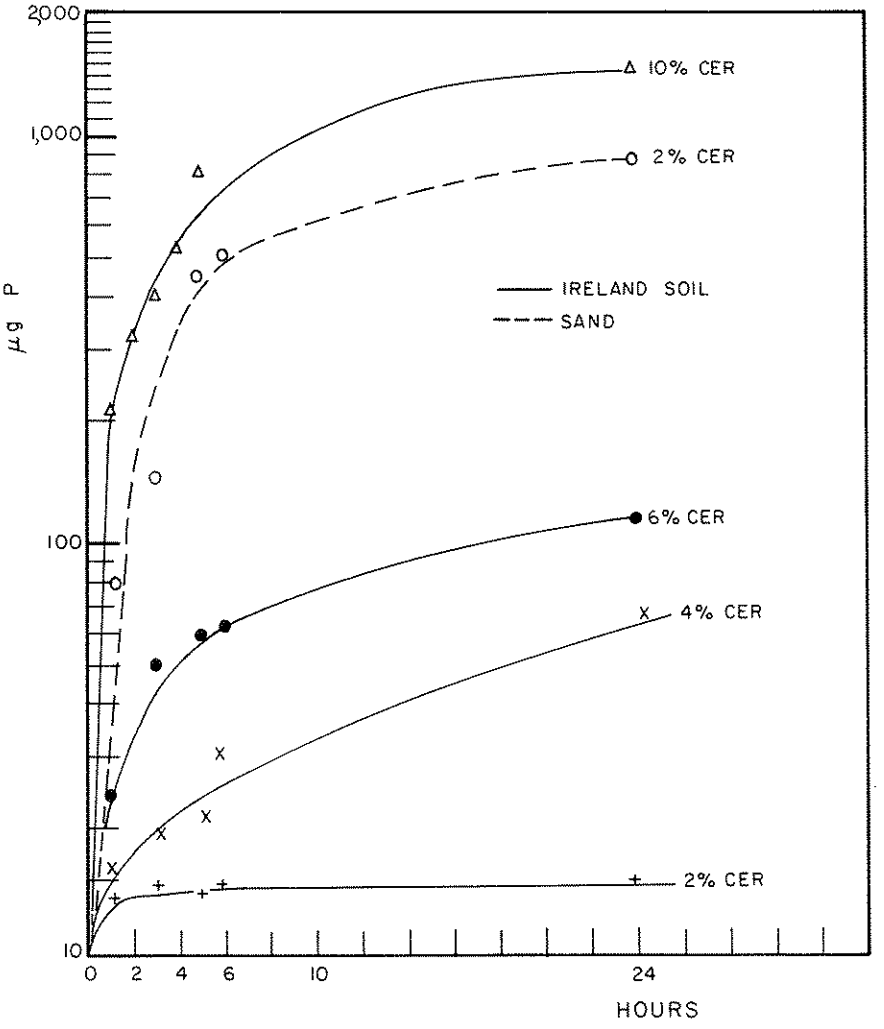

Figure 2. Influence of Soil: CER Ratio on Dissolution Rate of North Carolina Rock (6/16 mesh).

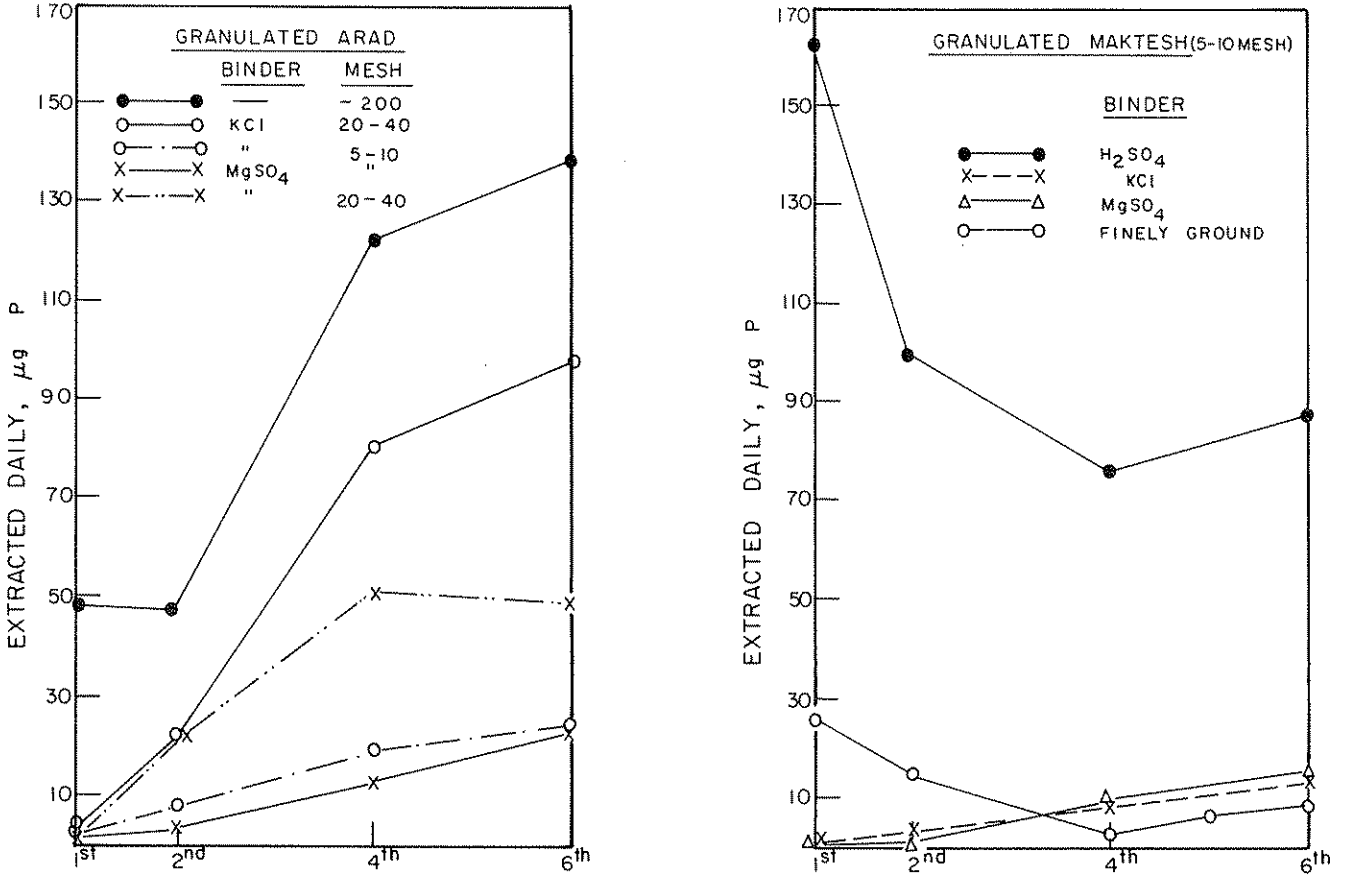

Figure 3. Solubilization of Granulated PR by AER (not cumulative).

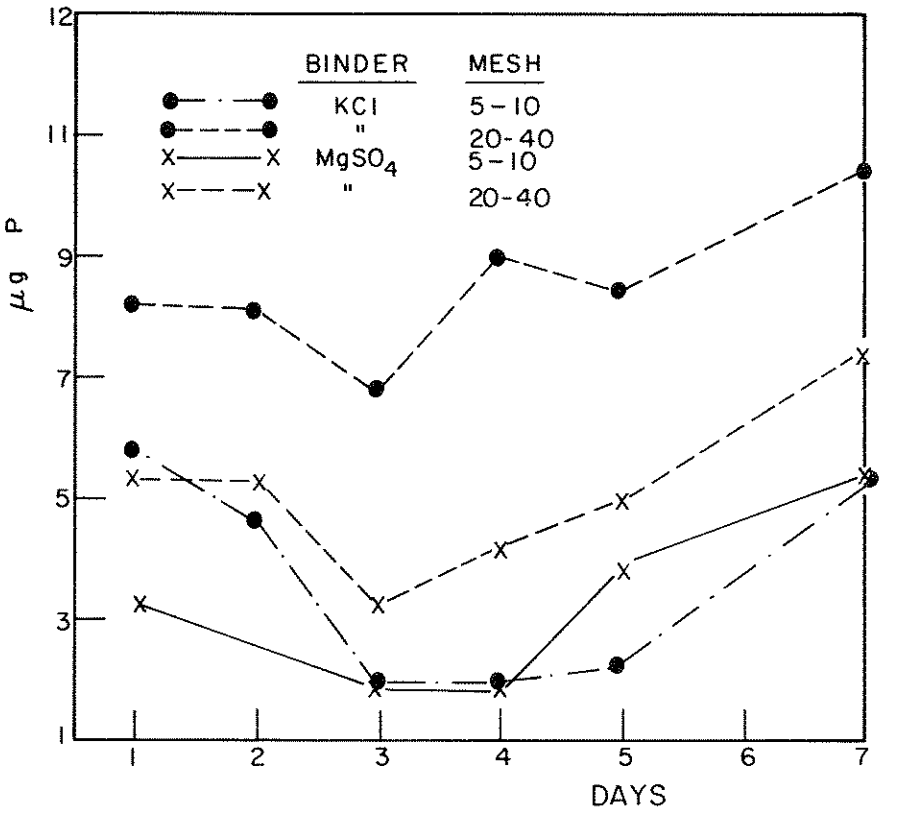

Figure 4. Dissolution of Granulated Arad Phosphate Rock (without renewing the AER).

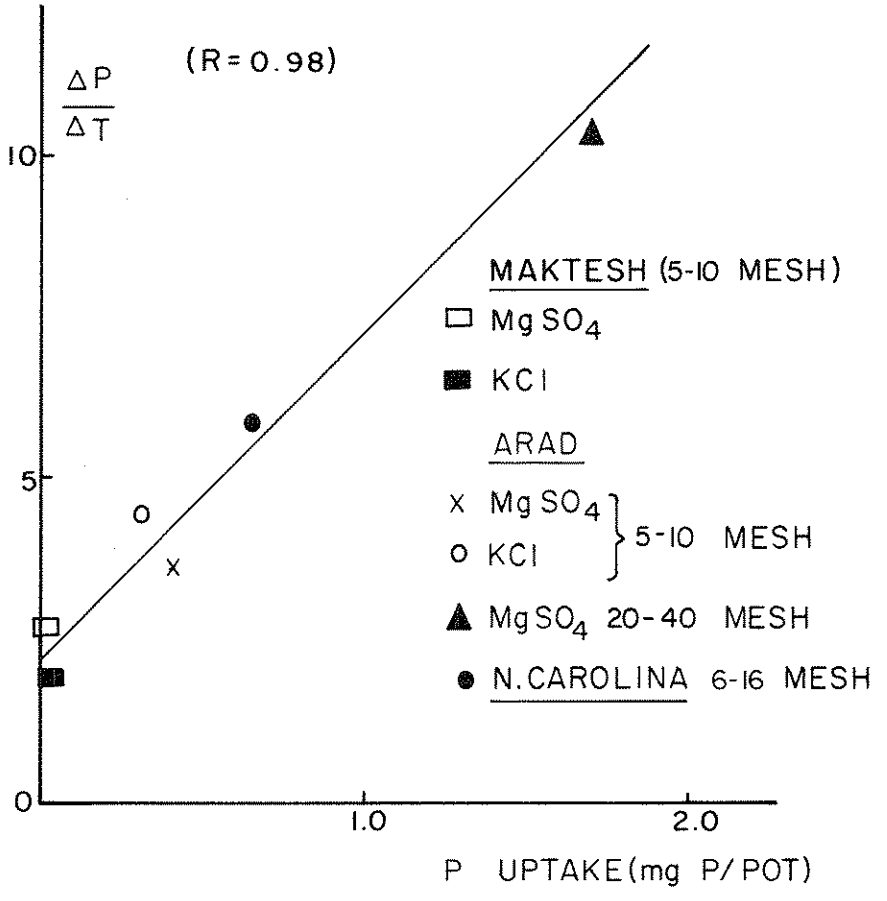

Figure 5. Dissolution Rate Versus P Uptake.

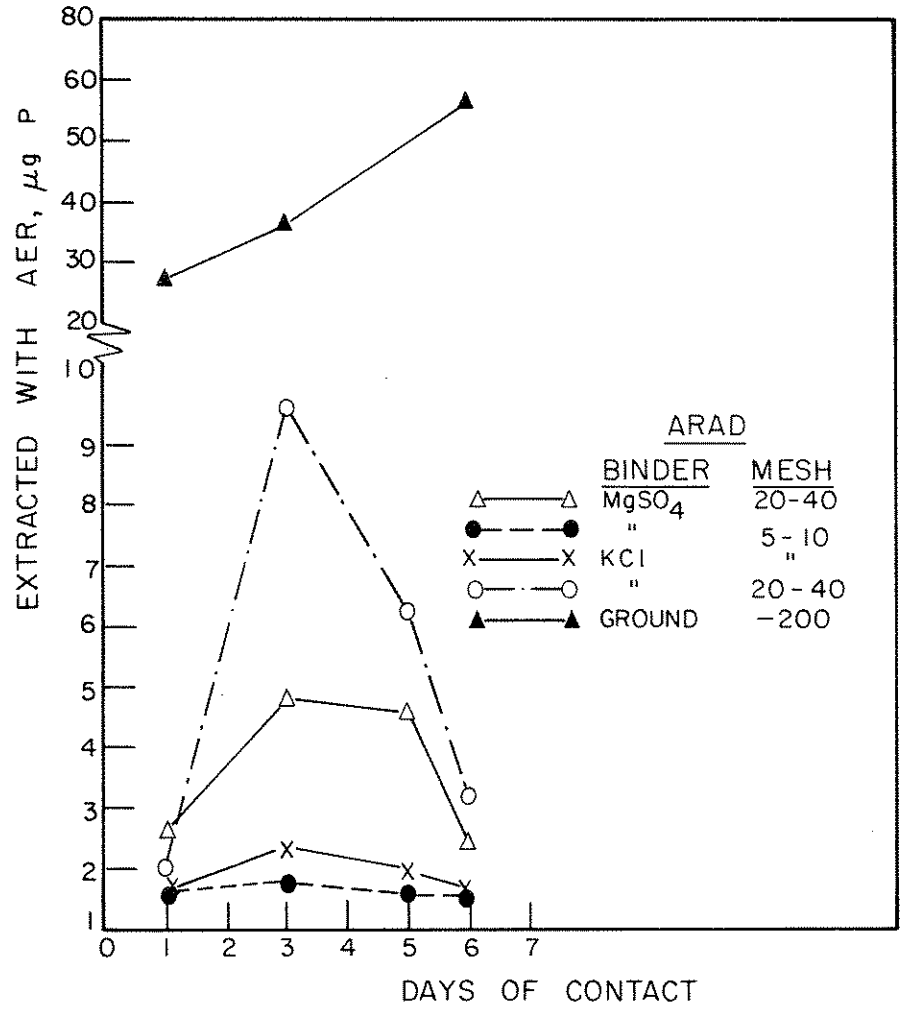

Figure 6. Relation Between Time of Soil-CER and Phosphate Rock Contact and P Extracted by AER.

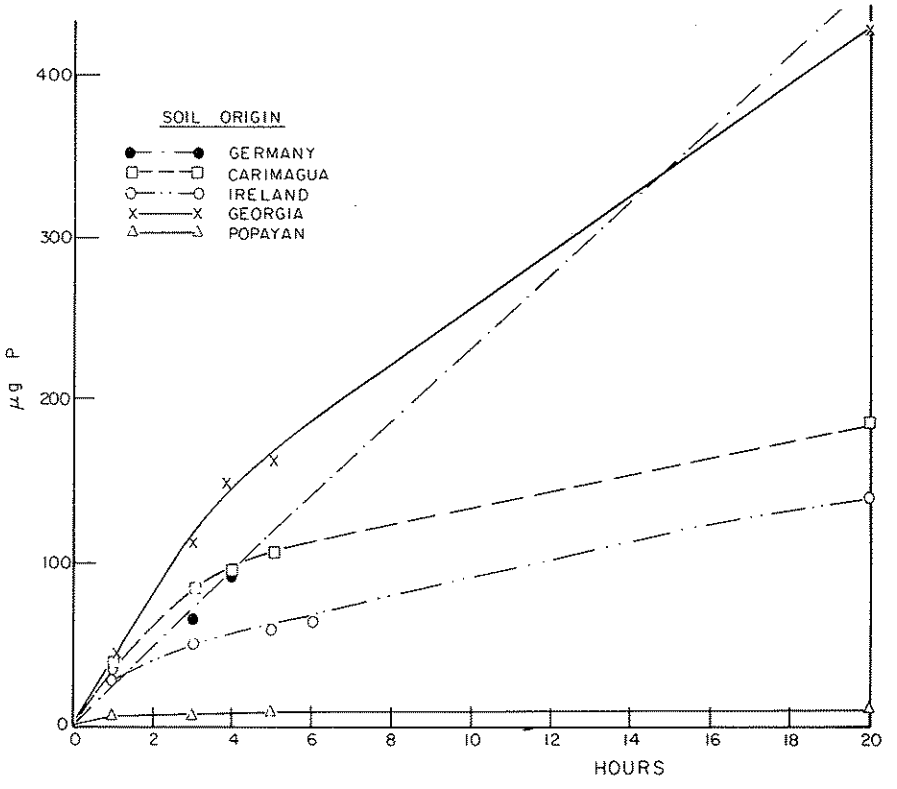

Figure 7. Dissolution of North Carolina Phosphate Rock (6/16 mesh) in Several Soil-CER Mixtures.

RELATION OF PHOSPHATE ROCK AVAILABILITY TO SOME SOIL PROPERTIES AND CULTIVATION TIME

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Summary

The effectiveness of a medium reactive phosphate rock (A) was compared to that of a highly reactive phosphate rock (B) and to concentrated superphosphate in greenhouse experiments on four acid soils.

The effectiveness of phosphates to the first crop on three of the soils was related to their solubility, while in one of the soils the phosphate rocks were as effective as concentrated superphosphate. This difference in behavior of phosphates was not related to soil pH, but it could be related to an index of P adsorption by soils.

During the cropping period, differences between effectiveness of P sources decreased or completely disappeared. Slope coefficients were calculated from an empiric equation relating cumulative changes in yield to cropping time. Highest slope coefficients were obtained for the medium reactive phosphate rock A, next for the highly reactive phosphate rock B, and lowest for superphosphate. It was concluded that the calculated slope coefficients may be used for comparing residual values of P sources.

Introduction

Suitability of a phosphate rock for direct application is primarily dependent on its solubility (Caro and Hill, 1956; Lehr and McClellan, 1972) and on the pH of the soil that it is applied to (Peaslee et al., 1962; Ellis et al., 1955). However, it seems that some additional factors should be considered.

According to McLean and Logan (1970) scarcely soluble P sources are more available than the soluble ones in soils with a high fixing capacity for phosphates. Whereas, van der Paauw (1965) found

that the availability of phosphate rocks decreased quantitatively more than that of soluble sources in such soils.

A number of workers (Cooke and Widdowson, 1959; Mattingly and Widdowson, 1963) found that the availability of phosphate rocks compared to that of a soluble source increased with time of cropping which accounts for phosphate rock residual value. A kinetic model, assuming that phosphate rock behaves like a slow-release P source, has been proposed by Larsen and Probert (1968). Chien (1977) found that dissolution of phosphate rocks occurred in two stages.

Materials and Methods

Some of the properties of phosphate materials are listed in table 1. The phosphate rocks were ground to pass a 200-mesh sieve. Total phosphate content of the materials was determined by the Association of Official Analytical Chemists (AOAC) method (Horowitz, 1975). Phosphate rock solubilities were determined in 2% citric and 2% formic acid solutions at a solid:solution ratio of 1:100 and after one-half hour shaking and filtration.

The experiments were performed on four acid soils. Some of their properties are listed in table 2.

Texture was determined by a sedimentation and decantation method (Black, 1965). In soil paste pH was measured at water saturation percentage by glass calomel electrodes (Jackson, 1958). Organic carbon was determined by a wet combustion method and potentiometric titration of dichromate residues (Raveh and Avnimelech, 1972). Available P was determined by the Bray and Kurtz method (Bray P_1) (Black, 1965) using a 1:10 soil to solution ratio. Phosphorus was determined after filtration by the molybdo-phosphoric blue color method (Murphy and Riley, 1962). The maximum buffer capacity (MBC) was determined by an adsorption experiment according to the definition of Holford and Mattingly (1976). A sample of 2.5 g soil was shaken for 24 hours in 25 ml of solution containing KH_2PO_4 at concentrations ranging from 0 to 50 ppm P (C_o) and centrifuged, and P concentration (C_t) was

measured. Phosphorus adsorbed (ΔP) was calculated according to: $\Delta P = (C_o - C_t) \cdot 10$. Holford and Mattingly (1976) derived the buffer capacity (BC) from Langmuir isotherm equation:

$$\frac{C}{\Delta P} = \frac{C}{S} + \frac{1}{KS}$$

where C = C_t = measured P concentration (µg/ml)
ΔP = amount of P adsorbed (µg/g)
S = adsorption maximum (µgP/g)
K = equilibrium constant for adsorption/desorption process related to bonding energy

and

$$\frac{d(\Delta P)}{dC} = \frac{KS}{(1 + K \cdot C)^2} = BC$$

Further, the MBC was given by:

$$\frac{d\Delta P}{dC}_{C \to 0} = K \cdot S = MBC$$

Greenhouse experiments were performed on soils which passed a 4-mesh sieve in 3-liter containers. Phosphate materials were mixed with the whole soil volume. Phosphorus levels were: 0.2, 0.5, 1.0, 4.0 g P/pot in three replicates. In some of the soils only one or two levels of P application were given. During the growth periods, water was added frequently to "field capacity." In soils from Germany, Turkey, and England, clover (Trifolium alexandrinum) was grown in autumn 1974 and cut once; alfalfa (Medicago sativa), which was cut three times, grew in winter 1974-75 and spring 1975. A third crop, alfalfa, was sown in part of the treatments in autumn 1975 and cut twice in winter 1975-76. In soil from Ireland, ryegrass (Lolium perenne) grew in winter 1976-77 and spring 1977 and was cut three times.

In addition to the phosphates, fertilizers were applied as follows: The first crop received a fertilizer solution containing KNO_3, NH_4NO_3, $MgSO_4 \cdot 7H_2O$ and minor elements to supply 0.6 g N, 0.5 g K, 0.3 g Mg, 1.3 mg B, 0.7 mg Zn, 0.2 mg Cu, 1.7 mg Fe, 2.5 mg

Mn, and 0.01 mg Mo per pot. The second crop received the same solution but in a quantity to supply half of the above amounts. A solution supplying 0.5 g of N and K each and micronutrients as above was added to the third crop.

Dry-matter yields were determined. The relative agronomic effectiveness (RAE) was calculated (Engelstad et al., 1974):

$$(1) \quad RAE = \frac{Y_F - Y_c}{Y_R - Y_c} \cdot 100$$

where Y_F and Y_R are the yields obtained in treatments that received 1 g P/pot as phosphate rock, or as concentrated superphosphate, respectively, and Y_c is the yield in the control treatment. At the end of the first year of cropping, soil samples were taken from some of the pots, and available P was measured by the Bray and Kurtz method. Extractability coefficient ratios were calculated according to the equation described by Barnes and Kamprath (1975), which is similar to equation 1, except for using extractable P instead of yield.

Results

Effectiveness of phosphate rocks as P sources to plants was evaluated on four acid soils in a greenhouse experiment. Yield results are presented in tables 3-6 and the calculated RAE for the first crop in table 7. Although the more soluble phosphate rock B is a more effective P source to the first crop than the less soluble phosphate rock A, the relation between their effectiveness varies from one soil to another (tables 3, 4, 5, and 7). With consecutive cropping, the differences in effectiveness between both phosphate rocks and concentrated superphosphate disappear in the soil from Germany (table 3) and show a similar tendency in the soil from Ireland. However, in the soil from Turkey the effectiveness of phosphate rock A, relative to phosphate rock B and that relative to superphosphate, increases with time of cropping.

Cumulative yield increases were related to cropping time. The following equation fitted the experimental results:

$$(2) \quad \log (Y - Y_o) = a + b \cdot t$$

where:
Y - cumulative yields in P fertilizer treatments
Y_o - cumulative yields in check treatments
t - time of cropping (days)
b - slope coefficient (days-1)
a - intercept

Parameters calculated according to equation (2) for cumulative yields of the first and second crop on three soils and of one crop on the fourth, the soil from Ireland (tables 3-6), are presented in table 8. Slope coefficients for phosphate rock treatments were almost in all cases larger than those for concentrated superphosphate treatments, and those for phosphate rock A were partly larger than those for phosphate rock B and in a few cases nearly equal. These data confirm that the less reactive phosphate rock A has a higher residual effectiveness than the more reactive phosphate rock B and that the phosphate rocks have a better residual value as P sources to plants in acid soils than superphosphate.

Phosphorus extractable by the Bray P_1 solution was determined in soil samples collected from some of the pots after the second crop or in soil from Ireland after the first one. The results are presented in table 9. Extractability ratio, relative to concentrated superphosphate for the 1-g P/pot rate of application, was calculated from data in table 8, and the results are given in table 10. Data on P solubility in the Bray P_1 extraction are in good accordance with the yield data and may explain the difference in response obtained in the experimental soils. The response pattern of the soil from Turkey varies from that of the other two soils. Soil characteristics presented in table 2 show a very high value for the MBC of the soil from Turkey (1294 ml/g) as compared to about 200 ml/g of the other soils. It seems that this soil parameter is better related to phosphate rock availability in soils than their pH values.

Discussion

Examination of interaction of phosphate rocks with soils indicated that the experimental soils could

be divided into two groups. In soils having a low P-adsorbing capacity, as indicated by the MBC values, of about 200 ml/g (from Germany, Ireland, and England), differences in solubility of phosphate rocks may explain variations in their availability to the first crops. While in the soil from Turkey, having a relatively high MBC, the effectiveness of all phosphate materials to the first crop was similar. Soil pH had no clear effect on the availability of different phosphate materials. This conclusion disagrees with the most accepted one stating that phosphate rock availability increases with soil acidity (Peaslee et al., 1962; van der Paauw, 1965). However, Bennett et al. (1957) received good response to phosphate rocks after liming the soil from pH 5.0 to 5.7. In some experimental locations Cooke and Widdowson (1959) received equal or better responses with Gafsa phosphate rock than with superphosphate, even on soils having pH values higher than 6.5. The effect of soil fixing capacity on the availability of phosphate materials with different solubilities was considered by McLean and Logan (1970). They found that in highly P-fixing soils the P content of plants decreased with increased water solubility of P sources. Whereas van der Paauw (1965) came to an opposite conclusion. This discussion indicates that several factors have to be taken into account for predicting the availability of a phosphate rock as a P source to plants in a certain soil. Definitions of phosphate rock solubilities and soil pH are not sufficient.

For evaluation of residual values of phosphates an empirical equation was proposed describing the change of cumulative yield increase due to P fertilizer with period of cropping (equation 2). During the cropping period, differences in availabilities of phosphate materials decreased, so that the residual value of phosphate rocks was equal in the soil from Germany or nearly equal in soils from Ireland to that of concentrated superphosphate. Similar results were obtained by Engelstad et al. (1974) and Hammond (in these Proceedings). In the soil from Turkey, the residual value of phosphate rocks was larger than that of concentrated superphosphate.

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Table 1. Some Properties of Phosphate Materials

Material	P, Total %	P, % of Total Soluble in Acids	
		Citric	Formic
Phosphate rock A	13.7	33.8	54.7
Phosphate rock B	12.9	43.7	71.2
Concentrated superphosphate	21.2		

Table 2. Some Properties of Experimental Soils

Location of Sampling	Texture	pH	Organic C, %	Bray P_1, P, ppm	Maximum Buffer Capacity, ml/g
Germany	Clay loam	6.1	0.98	30.5	200
Ireland	Clay loam	5.5	2.00	20.0	203
Turkey	Clay	5.4	0.79	1.1	1,294
England	Clay	5.3	2.25	7.6	150

Table 3. Dry-Matter Yields on Soil from Germany

Phosphate Materials	P Applied, g/pot	Dry-Matter Yields, g/pot					
		1st Crop	2d Crop--Alfalfa			3d Crop--Alfalfa	
		Clover	1st Cut	2d Cut	3d Cut	1st Cut	2d Cut
Concentrated superphosphate	0.05	1.11	1.19	1.09	2.19		
	0.1	1.65	1.56	1.65	3.14	1.28	2.35
	0.2	2.38	2.26	2.69	4.78		
	0.5	3.92	4.84	4.57	7.02	3.27	5.95
	1.0	4.95	7.19	5.78	7.47	3.29	7.76
Phosphate rock A	0.1	1.02	2.05	1.83	2.96	1.20	2.56
	0.2	1.22	2.93	3.21	5.49	2.11	4.13
	0.5	1.44	5.46	5.52	7.73	3.56	6.82
	1.0	1.91	4.34	4.94	7.36	3.96	7.08
	4.0	2.96	6.82	5.72	7.46	4.34	8.85
Phosphate rock B	0.1	1.15	2.16	1.65	3.23	1.35	2.79
	0.2	1.78	3.66	3.70	6.05	2.33	4.64
	0.5	2.63	6.24	5.05	7.02	3.32	6.88
	1.0	3.89	7.20	5.71	7.24	3.63	8.03
	4.0	4.04	7.63	5.96	7.45	4.29	8.34
Check	-	0.70	0.76	0.65	1.38	0.69	1.56
Standard deviation[a]	-	0.16	0.48	0.26	0.29	0.31	0.48

a. Differences due to treatments are statistically significant at a 0.01 level.

Table 4. Dry-Matter Yields of Ryegrass on Soil from Ireland

Phosphate Materials	P Applied, g/pot	Dry-Matter Yields, g/pot 1st Cut	2d Cut	3d Cut
Concentrated superphosphate	-	5.26	4.84	4.30
	0.2	8.07	6.55	5.01
	0.5	9.00	7.27	6.48
	1.0	8.68	7.88	6.78
	4.0	8.70	8.56	6.51
Phosphate rock A	0.2	6.01	5.73	4.96
	0.5	6.54	6.04	4.85
	1.0	6.84	6.55	5.54
	4.0	5.94	6.85	6.16
Phosphate rock B	0.2	6.87	5.75	5.23
	0.5	7.30	6.55	6.58
	1.0	7.43	7.22	7.18
	4.0	7.99	7.77	7.31
Standard deviation[a]		0.98	0.94	1.31

a. Differences due to treatments are statistically significant at a 0.01 level.

Table 5. Dry-Matter Yields on Soil from Turkey

Phosphate Materials	P Applied, g/pot	Dry-Matter Yields, g/pot 1st Crop Clover	2d Crop--Alfalfa 1st Cut	2d Cut	3d Cut	3d Crop--Alfalfa 1st Cut	2d Cut
Concentrated superphosphate	-	0.40	0.15	0.07	0.20	0.12	0.27
	0.2	0.84	0.64	0.37	0.62	-	-
	1.0	2.66	2.85	2.94	4.16	0.91	2.12
Phosphate rock A	0.2	0.59	0.35	0.09	0.37	0.13	0.27
	1.0	2.35	3.55	4.45	6.34	1.47	2.60
	4.0	4.00	6.95	6.63	7.23	4.15	6.14
Phosphate rock B	1.0	3.18	4.50	5.21	6.13	2.83	4.53
	4.0	4.35	6.44	6.66	7.03	2.68	5.20
Standard deviation[a]		0.18	0.36	0.28	0.30	0.41	0.58

a. Differences due to treatments are statistically significant at a 0.01 level.

Table 6. Dry-Matter Yields on Soil from England

Phosphate Materials	P Applied, g/pot	Dry-Matter Yields, g/pot 1st Crop Clover	2d Crop--Alfalfa 1st Cut	2d Cut	3d Cut
Concentrated superphosphate	-	0.76	0.17	0.08	0.48
	1	6.00	7.58	8.59	8.62
Phosphate rock A	4	3.03	5.33	7.10	8.05
Standard deviation[a]		0.24	0.35	0.33	0.34

a. Differences due to treatments are statistically significant at a 0.01 level.

Table 7. Relative Agronomic Effectiveness of Phosphate Rocks in Four Acid Soils, Calculated for the First Crop

Phosphate Rock	P Applied, g/pot	Relative Agronomic Effectiveness, Soil From		
		Germany	Ireland	Turkey
Phosphate rock A	1	28.5	46.2	86.3
Phosphate rock B	1	75.0	63.4	123.0

Table 8. Slope Coefficients (b in $days^{-1}$) Derived from Calculations of Cumulative Yields According to Equation (2)

Phosphate Materials	P Applied, g/pot	Soil From			
		Germany	Ireland	Turkey	England
Concentrated superphosphate	0.05	0.013			
	0.1	0.013			
	0.2	0.014	0.014	0.011	
	0.5	0.013	0.018		
	1.0	0.014	0.022	0.014	0.014
	4.0		0.023		
Phosphate rock A	0.1	0.023			
	0.2	0.025	0.026	0.009	
	0.5	0.028	0.020		
	1.0	0.022	0.024	0.017	
	4.0	0.019	0.044	0.016	0.019
Phosphate rock B	0.1	0.020			
	0.2	0.021	0.016		
	0.5	0.019	0.024		
	1.0	0.016	0.027	0.016	
	4.0	0.016	0.026	0.015	

Correlation coefficients (r) for all regressions were 0.98 - 0.99.

Table 9. P Extractable by Bray P_1 Solution from Greenhouse Soil Samples Taken at the End of First Year of Cropping

Phosphate Materials	P Applied, g/pot	P Extracted, ppm, Soil From		
		Germany	Ireland	Turkey
Concentrated superphosphate	0	31.4	16.6	1.2
	0.2	50.5	46.2	3.8
	0.5	82.6	93.5	-
	1.0	132.6	193.0	23.9
Phosphate rock A	0.2	35.1	18.8	3.9
	0.5	40.1	22.5	-
	1.0	45.3	24.7	10.3
	4.0	66.0	39.0	42.4
Phosphate rock B	0.2	40.0	22.3	-
	0.5	44.4	28.6	-
	1.0	50.8	36.8	17.8
	4.0	82.6	73.7	53.2

Table 10. Extractability Ratio Relative to Concentrated Superphosphate Treatment of Phosphate Rocks Calculated from Data in Table 9

Phosphate Materials	P Applied, g/pot	Extractability Ratio, Soil From		
		Germany	Ireland	Turkey
Phosphate rock A	1.0	13.7	4.6	40.0
Phosphate rock B	1.0	19.2	11.5	73.0

COMPARISON OF FINELY GROUND PHOSPHATE ROCKS AS P SOURCES TO PLANTS

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Summary

Effectiveness of phosphate rocks (ground to pass a 200-mesh sieve) as P sources to plants was compared on an acid soil (pH 5.2) in greenhouse experiments. Phosphate rocks used in the experiment were Maktesh, Zin, and Arad from Negev, Israel; phosphate rocks from North Carolina and central Florida; and Gafsa and Christmas Island phosphate rocks. According to yield results of three cuts of ryegrass, P uptake, and calculated relative agronomic effectiveness (RAE), North Carolina phosphate rock was rated as the most available source (comparable to concentrated superphosphate), and next was the Gafsa phosphate rock. The rating of Negev phosphates was as follows: Arad, the best, then Zin, and Maktesh, the lowest. Central Florida and Christmas Island phosphate rocks had a relatively low effectiveness, ranking between Zin and Maktesh phosphate rocks.

Standard solubility tests of phosphate rocks did not prove to be adequately sensitive for evaluation of their agronomic effectiveness. It is suggested that equilibrated soil-phosphate rock mixtures may be a better test for that purpose.

Introduction

The Negev area of Israel contains rather extensive phosphate deposits. Phosphate rock characteristics found in different locations are somewhat varied (see "Phosphate for Direct Application--Phosphorite Characterization and Field Survey of Fields in the Negev, Israel" by Axelrod in these Proceedings). It was of interest to evaluate the agronomic effectiveness of some of these phosphate rocks. First evaluation of phosphate rocks as P sources to plants is in most cases based on some index of their solubility, such as solubility in am-

monium citrate, citric or formic acids; absolute citrate solubility (Engelstad et al., 1974; Lehr and McClellan, 1972); and solubility in presence of EDTA (Olsen, 1975). Chien (1977) reviewed the relationship between the solubilities of different phosphate rocks and their crystallographic properties and explained them by thermodynamic considerations. However, it may be assumed that the availability of phosphate rock is influenced by soil factors to which it is applied in addition to the rock properties themselves. Barnes and Kamprath (1975) reviewed the factors affecting rock availability in the soil. Hammond (see "Agronomic Measurements of Phosphate Rock Effectiveness" in these Proceedings) discusses the factors influencing the feasibility of phosphate rock for direct application, and Chien (see "Dissolution of Phosphate Rocks in Solutions and Soils" in these Proceedings) discusses dissolution of phosphate rock in solutions and soils. McClellan concludes in his paper, "Mineralogy and Reactivity of Phosphate Rock," in these Proceedings that reactivity measurements may only indicate the agronomic potential of a rock and that further testing is needed.

Materials and Methods

A greenhouse experiment was performed on a soil received from Ireland. The soil was sterilized at 120°C for 2 hours. Later, it was limed to pH 5.5 and inoculated with an organic manure extract. Some of the soil characteristics are given in table 1.

Characteristics of phosphate rock samples used in the experiment are given in table 2. The samples were ground to pass a 200-mesh sieve. Total P was determined by the Association of Official Analytical Chemists (AOAC) method (Horowitz, 1975). Solubilities in 2% citric and 2% formic acid solutions were determined at a 1:100 solid:solution ratio and after one-half hour shaking and filtration.[1]

1. The methods follow: (1) Fertilizers-Methods of Analysis used in Organization of European Economic Cooperation (OEEC) countries, Paris 16e, 1952; and (2) The Fertilizers and Feeding Stuff Regulation 1973, Her Majesty Stationery Office, p. 53.

The Maktesh, Zin, and Arad phosphate rocks are from the Negev area of Israel. The Gafsa phosphate is a Tunisian rock obtained from Propane Fertilizer, Ltd., London. The North Carolina and central Florida samples were sent by the International Fertilizer Development Center (IFDC). Superphosphate was produced by Fertilizers and Chemicals, Ltd., Haifa.

Texture of soils was determined by a sedimentation and decantation method (Black, 1965). In soil paste pH was measured at water saturation percentage or in a 1:1 soil water suspension by glass calomel electrodes (Jackson, 1958). Electric conductivity was measured by a 1:1 soil to water extract (Black, 1965). Organic carbon was determined by a wet combustion method and potentiometric titration of dichromate residues (Raveh and Avnimelech, 1972). Moisture at field capacity was measured on vertical soil columns open at both ends. Enough water was added to wet the upper half of the column. After 24 hours, the moisture content of the layer at 5- to 10-cm depth was determined. Cation-exchange capacity was determined according to Mortland and Mellor (1954).

Bray P available was determined in 1:10 ratio of soil to a dilute acid fluoride solution (Olsen and Dean, 1965). Phosphorus soluble in water was determined after 1 hour of shaking (Olsen and Dean, 1965).

Phosphorus was extracted in the presence of a cation-exchange resin (CER), a strongly acidic sulfonated polystyrene-type Na form Amberlite CG-120 (100- to 200-mesh), analytical reagent grade. One gram of the soil sample and 2 g of resin were shaken with 50 ml of water for 2 days and centrifuged; P was measured in the supernatant solution (Vaidyanathan and Talibudeen, 1970). Phosphorus extraction by an anion exchange resin (AER) was performed using Dowex 11, a strongly basic AER with trimethyl benzyl ammonium groups in Cl form (particle size, 16- to 20-mesh). The sample was washed with a solution of NaCl and water, stored wet, and air dried shortly before usage. The soil samples were ground to pass a 0.25-mm sieve. Samples of 0.5 g of soil were shaken with 1 g resin in 100 ml water for 24 hours. After the samples were shaken, the resin was separated from the soil on a 0.25 screen by washing with a jet of water. The resin retained on the screen was transferred to a flask with

90 ml of water; 10 ml of HCl 1M was added, the mixture shaken for 1 hour, and the supernatant liquid analyzed for P (Amer et al., 1955).

During extraction by a combination of AER and CER, 0.5 g of soil was shaken with 1 g AER and 1 g CER in 100 ml water for 48 hours. The AER was separated and P determined as above.

Double acid P extraction was performed in a dilute hydrochloric sulfuric acid mixture (Olsen and Dean, 1965). Phosphorus concentration in solutions was determined by the method described by Murphy and Riley (1962). Phosphorus in plants was determined by dry ashing (Chapman and Pratt, 1961).

The greenhouse experiment was performed in pots of about 3 liters. Phosphate materials were mixed into the whole soil volume. Phosphorus levels were: 0.2, 0.5, 1.0, 4.0 g P/pot in three replicates. The 0 level and CSP treatments were replicated six times. Each pot received 0.5 g N and 0.5 g K in solutions of NH_4NO_3 and K_2SO_4 and a minor element solution to supply 0.3 mg Mg, 1.3 mg B, 0.7 mg Zn, 0.2 mg Cu, 1.7 mg Fe, 2.5 mg Mn, and 0.01 mg Mo/pot. Additional minor element solution was applied after the first and second cuts and 0.5 g N/pot as NH_4NO_3 solution after the second cut. The pots were frequently watered to fill their "field capacity" by weighing.

Ryegrass (Lolium perenne) was sown on December 17, 1976, and cut three times (February 20, March 25, and April 25, 1977). Dry-matter yield and P concentration in it were determined, and P uptake was calculated. Some of the yield results were plotted, and freehand yield curves were drawn.

Relative agronomic effectiveness of P sources compared in the greenhouse experiment was calculated (Engelstad et al., 1974) according to the following equation:

$$RAE = \frac{Y_F - Y_C}{Y_R \quad Y_C} \cdot 100 ,$$

where:

Y_F = yield due to one of the tested fertilizers
Y_R = yield due to reference fertilizer
Y_C = yield obtained in control treatment, i.e., with no additions of P.

In addition RAEs were calculated based on phosphorus uptake. Phosphorus analyses of soil samples were done on mixtures prepared parallel to the greenhouse experiment representing the P status at the start of the experiment. Another set of soil analyses were done on samples taken from the pots after the third cut. Samples (15-20 g) were taken to the whole depth of each pot. Samples from three replicates were mixed and composed into one. The soils were air dried and sieved to pass 2 mm. Results of analyses were calculated on an air-dry basis.

Results

Dry-matter yields obtained in the three cuts of ryegrass and P uptake are presented in table 3. Sums of dry-matter yield in three cuts and P uptake are presented in figures 1, 2, 3, and 4. These curves were used for estimating maximal yields (table 4). Relative agronomic effectiveness values calculated on the basis of the estimated maximal yields or based on average yield at four levels of P application with CSP treatments as reference are presented in table 4. In addition, relative agronomic effectiveness was calculated according to P uptake at the 4-g/pot level and, according to average P uptake at four levels of application, with North Carolina treatments as reference (table 4). All the data presented in table 4 were calculated from the sum of three cuts of ryegrass.

The RAE indices based on average yields or P uptake show a lower value for the Arad, central Florida, and Christmas Island phosphate rock than those based on maximal yields or P uptake at 4-g P/pot level. This is due to smaller yield or P uptake differences at the highest level of application than at the lower ones.

According to the indices at hand (namely yield curves, P uptake, and RAE ratings of the phosphates as P sources to ryegrass on the experimental soil show that North Carolina phosphate rock performs

similarly to CSP (figure 3), although the curve of P uptake is very different for these two P sources. This indicates a different pattern of P supply to plants by CSP from that by the phosphate rocks (figure 4). The effectiveness of Gafsa phosphate rock is lower than that of North Carolina. Among the Israeli phosphate rocks, Arad has the highest effectiveness, followed by Zin and then Maktesh.

Air-dry soil samples were mixed with phosphate sources in the same way and proportion as for the greenhouse experiment and extracted immediately after mixing. Thus, the results of extraction reflect the initial P status of the mixture and they are given in table 5. Table 5 shows also the initial pH values of the soil-phosphate mixture. The Maktesh and Zin phosphate rocks raise appreciably the pH at higher levels of application. Other phosphate rocks have a smaller effect on pH. A general review of table 5 indicates that the water extraction differentiates between superphosphate and rock phosphates, but within the rock phosphates the differentiation is not clear. The Bray P_1 method extracts quantities of the Negev phosphates from the mixtures in accordance with the yield results obtained. The Gafsa and North Carolina mixtures gave lower values than may be expected. The cation exchange and anion exchange resin methods gave results which are more or less in agreement with the yield results. The double acid method extracted large quantities of phosphates from most treatments.

Soil samples were taken from pots after the third cut of ryegrass, and soluble phosphate in various extracts was determined. Results are presented in table 6. Also, pH was measured in the same soil samples. All values were between 5.2 and 5.4, and they are not recorded. Analysis of variance of data in table 6 shows highly significant differences for P sources and level of application. The extraction results were considered as representative of the P status in soils after some equilibration between P sources and soil in the presence of plant roots. They were related, as will be described, to yield results although we are aware of the difference in timing of sampling and yield.

Following the greenhouse experiment, attempts were made to relate indices of agronomic effectiveness

of fertilizers to indices expressing phosphate rock properties and availability in soil. Coefficients of correlation for these relations are listed in table 7. Correlations were calculated for all parameters given in tables 5 and 6, but, because coefficients of correlation related to the water and double-acid extracts were statistically not significant, they are not presented in table 7. A good correlation was found between formic and citric acid solubilities of phosphate rocks and their relative agronomic effectiveness. However, a better correlation was obtained between the Bray P_1 extractable phosphorus from soils after the third cut of ryegrass and the relative agronomic effectiveness. P extractions of fresh soil-phosphate rock mixtures were poorly correlated with the relative agronomic effectiveness.

Further, P applied in the greenhouse experiment was correlated to P extracted from soil samples taken after the third cut (table 6). Correlation coefficients are presented in table 8, and it may be seen that all extraction methods used, except water extract, reflect well the P applied to soil at the beginning of the experiment. That is also true for the Bray P_1 method if CSP treatments are omitted from correlation calculations.

Conclusions

Phosphate rocks from three sites in the Negev area of Israel were evaluated as P sources to plants and compared to other phosphates on one acid soil. The rating of phosphate rocks according to their RAE was in fairly good agreement with the standard tests of their formic or citric acid solubilities. However, a closer inspection of the presented data and calculations of correlation coefficients between these tests and the RAE showed that these tests may not be adequately sensitive for predicting phosphate rock effectiveness. Correlations of measured phosphate rock characteristics with some index of crop response gave in the best case a coefficient of correlation, $r = 0.85$, which means that this relation may explain only 72% of variations and 28% are due to other factors. Because we are dealing with individual phosphate rocks, it seems that a mere statistical significance is not adequate. A more precise measure of its effectiveness is desirable. The results

show, under the described experimental conditions, Bray P_1 extraction of a presumably equilibrated soil-phosphate rock mixture gives a much better measure of the phosphate rock effectiveness. Correlation coefficients having the value of 0.99 and 0.98 were obtained for the relation between results of this extraction and RAE for averages of all levels of application. Accordingly, it seems that for a reliable evaluation of phosphate rock effectiveness, short of a full-scale field experiment, a greenhouse experiment combined with soil extractions is needed. Standard phosphate rock solubility tests may indicate only the agronomic potential of a certain rock, as already cited in the Introduction.

The experiments show that, among the Negev phosphate rocks tested, the one from the Arad site is best suited for direct application.

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Table 1. Some Characteristics of Soil From Ireland

Texture	clay loam
pH	4.6
Electrical conductivity, mmhos/cm	0.4
C, organic, %	2.0
P soluble in:	
Bray P_1 solution, µg P/g	20.0
Water, µg P/ml	0.05
Moisture at field capacity, %	29.4
Cation exchange capacity, m.e./100 g	33.1

Table 2. Some Characteristics of Phosphates Used in Greenhouse Experiment

Phosphate Source	Original Fraction	Total P	2% Formic Acid Soluble P Soluble / P Total	2% Citric Acid Soluble P Soluble / P Total	CO_2
		%			
Maktesh	cyclone	13.1	56.5	31.3	6.8
Zin	20/200 mesh	13.9	59.7	36.0	6.0
Arad	-20 mesh	14.5	62.1	37.9	4.4
Gafsa	-20 mesh	12.8	71.1	39.1	6.0
North Carolina	-10 mesh	13.1	72.5	39.7	5.6
Central Florida	-10 mesh	14.2	21.8	21.8	3.2
Christmas Island		15.7	29.3	28.0	2.1
Superphosphate		20.7			

Table 3. Yield of Ryegrass and P Uptake in Greenhouse Experiment

Phosphate Source	P Applied	Dry-Matter Yield			P Uptake		
		1st Cut	2nd Cut	3rd Cut	1st Cut	2nd Cut	3rd Cut
	g/pot	g/pot			mg P/pot		
Check	-	5.26	4.84	4.30	10.5	7.6	5.1
superphosphate	0.2	8.07	6.55	5.01	23.7	16.2	11.0
	0.5	9.00	7.27	6.48	35.5	31.5	21.5
	1.0	8.68	7.88	6.78	48.6	53.8	41.4
	4.0	8.70	8.56	6.51	74.0	107.9	75.9
Maktesh	0.2	6.01	5.73	4.96	13.0	9.2	7.5
	0.5	6.54	6.04	4.85	17.8	13.5	10.5
	1.0	6.84	6.55	5.54	19.1	17.8	12.4
	4.0	5.94	6.85	6.16	20.4	23.6	21.4
Zin	0.2	5.82	5.70	5.04	14.0	10.5	8.3
	0.5	7.00	5.95	5.56	19.0	14.3	12.0
	1.0	7.31	6.09	6.15	19.9	17.5	12.8
	4.0	6.92	7.45	6.86	23.8	31.6	23.9
Arad	0.2	5.93	5.42	4.28	14.0	10.6	7.7
	0.5	6.92	5.94	5.03	19.4	15.2	10.5
	1.0	7.40	6.67	5.93	23.7	21.1	16.1
	4.0	7.73	8.06	6.69	30.9	39.3	24.6
Gafsa	0.2	6.87	5.75	5.23	16.8	12.0	9.4
	0.5	7.30	6.55	6.58	21.6	20.2	14.7
	1.0	7.43	7.22	7.18	25.6	31.2	22.7
	4.0	7.99	7.77	7.31	32.3	44.1	26.3
North	0.2	7.56	5.75	5.92	19.6	15.2	12.3
Carolina	0.5	8.30	6.68	6.90	22.6	24.0	16.0
	1.0	8.70	7.98	7.21	30.6	33.2	24.2
	4.0	8.68	7.94	6.45	36.8	47.6	35.6
Central	0.2	5.91	5.14	4.06	11.3	8.4	6.2
Florida	0.5	6.59	5.51	4.59	13.2	9.7	8.3
	1.0	7.04	5.61	4.51	15.5	12.6	9.4
	4.0	7.51	6.56	6.37	23.1	29.1	19.4
Christmas	0.2	5.61	5.11	4.55	11.7	8.2	5.8
Island	0.5	6.04	5.20	5.03	12.1	10.4	8.0
	1.0	6.25	5.71	5.17	13.0	11.9	8.7
	4.0	7.44	7.10	6.86	20.2	29.0	19.2
Analysis of variance	F	33.5**	33.1**	14.9**			
	standard deviation	0.98	0.94	1.31			

**Significant at a 0.01 level.

Table 4. Relative Agronomic Effectiveness (RAE) of Phosphate Rocks Compared in Greenhouse Experiments

Phosphate Source	Estimated Maximal Yield (Fig. 1 & 2)	RAE Based on: Maximal Estimated Yield	P Uptake at 4 g P/Pot	Yield	P Uptake
	- - g/pot - -			- - average - - -	
CSP	23.4	100.0		100.0	
North Carolina	23.9	105.5	100.0	95.0	100.0
Gafsa	23.2	97.8	82.1	80.0	81.9
Arad	22.5	90.0	74.1	57.5	62.5
Zin	21.3	76.7	58.0	57.5	51.1
Maktesh	18.9	50.0	43.6	45.0	41.7
Central Florida	20.6	68.9	50.0	36.2	32.7
Christmas Island	21.3	76.7	46.7	38.7	29.1

Table 5. P Extracted and pH in Soil Samples From Pots at Start of Experiment--Comparison of P Sources (-200 Mesh)

P Source	P Applied g P/pot	pH	Water Extraction µg P/ml	Bray P_1	Double-Acid Extraction	AER Extraction	CER Extraction
				µg P/g			
Check	0	5.3	0.10	27.2	11.2	20.7	16.6
CSP	0.2	5.3	1.65	89.0	55.7	117.3	77.5
	0.5	5.1	7.10	133.5	148.7	109.3	174.8
	1.0	5.0	21.66	374.0	344.0	457.3	365.0
	4.0	4.6	54.16	1,391.0	1,273.3	1,466.7	1,675.0
Maktesh	0.2	5.4	0.12	29.0	70.0	82.7	73.8
	0.5	5.5	0.13	29.1	62.8	74.0	66.6
	1.0	5.8	0.12	49.3	405.3	242.0	305.0
	4.0	6.1	0.25	106.0	1,386.6	491.1	515.0
Zin	0.2	5.4	0.03	30.0	54.9	77.3	70.6
	0.5	5.5	0.03	35.0	191.3	178.7	174.2
	1.0	5.6	0.09	53.6	412.0	298.6	282.5
	4.0	6.0	0.20	126.0	1,270.0	696.7	688.3
Arad	0.2	5.4	0.08	31.0	56.9	79.2	65.0
	0.5	5.4	0.08	42.0	187.3	169.4	188.3
	1.0	5.5	0.14	64.3	374.0	324.3	345.0
	4.0	5.7	0.73	182.0	1,648.0	693.3	710.0
Gafsa	0.2	5.5	0.09	33.0	79.3	59.3	82.3
	0.5	5.5	0.11	44.0	182.0	162.6	163.3
	1.0	5.5	0.26	54.0	356.0	218.6	326.6
	4.0	5.6	0.43	105.0	1,173.3	706.6	586.6
North Carolina	0.2	5.4	0.07	32.3	56.8	97.5	84.3
	0.5	5.3	0.11	44.8	133.8	180.0	165.0
	1.0	5.4	0.14	58.0	346.6	314.6	320.0
	4.0	5.7	0.28	140.6	1,150.0	643.3	796.6

(Continued)

Table 5. P Extracted and pH in Soil Samples From Pots at Start of Experiment--Comparison of P Sources (-200 Mesh) (Continued)

P Source	P Applied	pH	Water Extraction	Bray P_1	Double-Acid Extraction	AER Extraction	CER Extraction
	g P/pot		µg P/ml	µg P/g			
Central Florida	0.2	5.3	0.09	24.5	59.2	70.6	38.0
	0.5	5.4	0.13	29.6	112.0	106.6	63.0
	1.0	5.4	0.08	30.6	304.0	154.4	97.5
	4.0	5.4	0.22	48.3	806.6	358.6	265.0
Christmas Island	0.2	5.3	0.07	27.0	45.1	50.0	40.5
	0.5	5.3	0.12	28.0	117.3	103.3	55.0
	1.0	5.4	0.16	30.0	262.6	154.6	110.0
	4.0	5.5	0.42	42.3	1,000.0	321.3	266.6
Analysis of variance	F		546.0	2,366.0	8.3	524.0	142.0
	standard deviation		0.45	4.92	52.7	12.8	27.5

Table 6. P Extracted From Soils Treated With P Sources (-200 mesh) at Beginning of Experiment, Samples From Pots After Three Cuts of Ryegrass

Phosphate Source	P Applied g/pot	Water µg P/ml	Bray P_1	Double Acid	Anion Resin	Cation Resin	Anion+Cation Resin
					µg P/g		
CSP	0	0.05	16.6	20.5	13.0	7.5	24.3
	0.2	0.04	46.2	47.2	49.7	38.0	85.0
	0.5	0.16	93.5	58.1	82.4	84.0	169.3
	1.0	0.43	193.0	182.5	163.7	180.0	328.7
	4.0	4.59	831.5	1,344.8	796.0	860.0	1,403.3
Maktesh	0.2	0.10	18.8	52.8	37.3	59.0	80.0
	0.5	0.13	22.5	136.0	41.0	136.0	181.0
	1.0	0.06	24.7	340.0	66.0	245.0	353.0
	4.0	0.12	39.0	1,610.0	228.0	560.0	1,293.0
Zin	0.2	0.13	18.5	49.8	65.3	59.3	112.0
	0.5	0.15	24.2	129.0	133.2	113.3	229.3
	1.0	0.19	29.8	274.6	230.6	223.1	376.0
	4.0	0.45	52.3	1,054.5	446.6	590.0	1,430.0
Arad	0.2	0.04	17.3	74.0	31.3	56.0	80.0
	0.5	0.26	21.8	136.0	56.6	121.0	200.0
	1.0	0.27	29.0	338.0	78.6	237.0	426.0
	4.0	0.47	50.0	1,532.0	349.3	595.0	1,453.0
Gafsa	0.2	0.13	22.3	53.8	61.3	77.5	96.0
	0.5	0.26	28.6	110.6	164.0	169.9	196.0
	1.0	0.29	36.8	282.1	186.6	204.4	338.6
	4.0	0.37	73.7	1,033.3	514.6	643.3	1,440.0
North Carolina	0.2	0.04	23.3	73.0	60.0	97.0	106.0
	0.5	0.04	30.5	126.0	96.0	109.0	198.0
	1.0	0.07	35.7	418.7	152.7	193.7	269.3
	4.0	0.10	102.0	1,905.0	404.0	880.0	2,100.0
Central Florida	0.2	0.03	20.2	88.0	29.3	24.3	121.3
	0.5	0.04	24.1	129.3	45.3	60.0	250.6
	1.0	0.04	18.0	198.7	80.7	102.9	254.6
	4.0	0.08	29.5	1,028.0	204.0	380.0	953.0
Christmas Island	0.2	0.06	15.4	39.8	49.5	32.3	72.4
	0.5	0.05	15.9	73.5	43.3	38.3	141.3
	1.0	0.08	23.6	261.3	76.4	91.0	381.3
	4.0	0.16	35.7	1,037.3	96.6	216.6	1,313.3
Standard deviation		0.05	2.2	60.3	9.7	11.8	51.2

Table 7. Coefficients of Correlation (r) for Relations Between Indices of Agronomic Effectiveness (Table 4) of Phosphate Rocks and Their Properties (Table 2) or Availability in Soil (Tables 5 and 6)

Indices of Phosphate Rock Properties or Availability in Soil	Relative Agronomic Yield		Effectiveness Based on P Uptake	
	Maximum	Average	At 4 g/Pot	Average
Relative P solubility of PR in				
Formic acid	0.76[a]	0.84[b]	0.74[a]	0.85[b]
Citric acid	0.68[c]	0.84[b]	0.78[a]	0.84[b]
P extracted from soil-PR mixtures at start of greenhouse experiment, by: Bray solution from: 4 g/pot treatment	0.64[c]		0.60[c]	
average of treatments		0.66[c]		0.72[a]
Anion resin: 4 g/pot treatment	0.57[c]		0.64[c]	
average of treatments		0.75[a]		0.77[a]
Cation resin: 4 g/pot treatment	0.15[c]		0.35[c]	
average of treatments		0.79[a]		0.81[a]
P extracted from samples taken after 3rd cut of ryegrass by: Bray solution from: 4 g/pot treatment	0.81[a]		0.94[b]	
average of treatments		0.99[b]		0.98[b]
Anion resin: 4 g/pot treatment	0.61[c]		0.71[a]	
average of treatments		0.75[a]		0.71[a]
Cation resin: 4 g/pot treatment	0.56[c]		0.82[a]	
average of treatments		0.83[b]		0.37[c]

a. Significant at 0.05 level.
b. Significant at 0.01 level.
c. Not significant.

Table 8. Coefficients of Correlation (r) for Relations Between P Applied in Greenhouse Experiment and P Extracted From Soil Samples Taken After Third Cut (Table 6)

Phosphate Source	P Extracted By					
	Water	Bray P_1 Soluble	Double Acid	AER Method	CER Method	AER + CER Method
All sources	0.39	0.39	0.95	0.80	0.90	0.96
All sources less CSP	0.40	0.77	0.95	0.83	0.90	0.95
CSP	0.99	1.00	0.96	1.00	1.00	1.00
North Carolina PR	0.87	0.99	0.96	0.98	0.99	0.98
Gafsa PR	0.71	0.99	0.99	0.98	0.99	1.00
Arad PR	0.47	0.99	0.99	0.99	0.99	0.96
Zin PR	0.92	0.99	1.00	0.96	0.99	0.99
Maktesh PR	0.17	0.98	1.00	0.99	0.98	0.99
Central Florida PR	0.90	0.81	0.99	0.98	0.99	0.99
Christmas Island PR	0.96	0.95	0.99	0.79	0.97	0.99

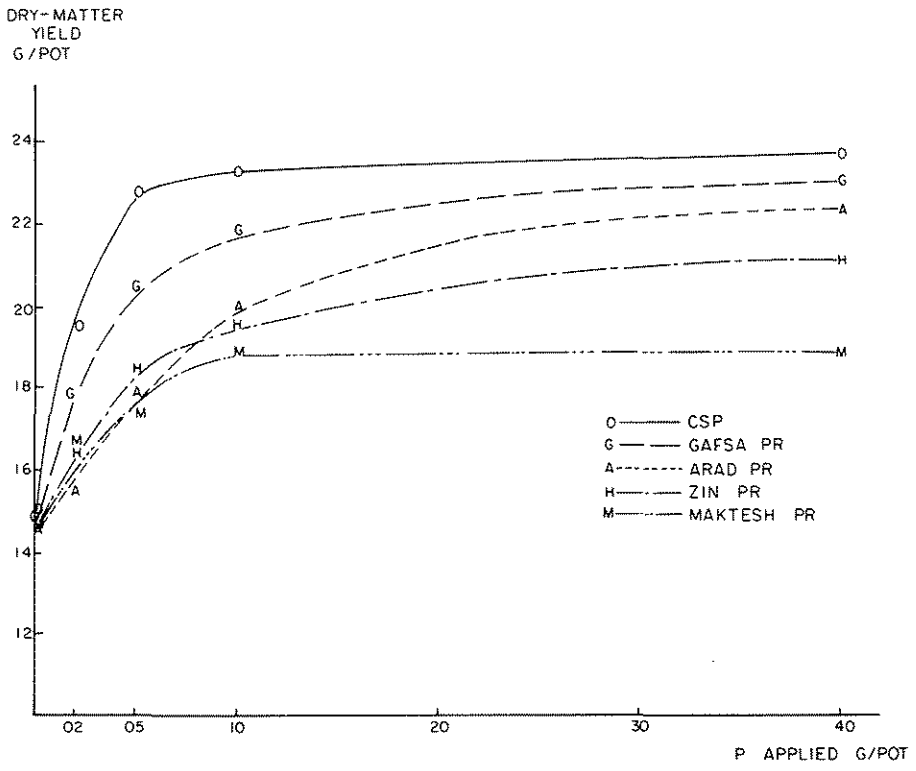

Figure 1. Comparison of P Sources (-200 mesh)—Total Dry-Matter Yields of Three Cuts of Ryegrass.

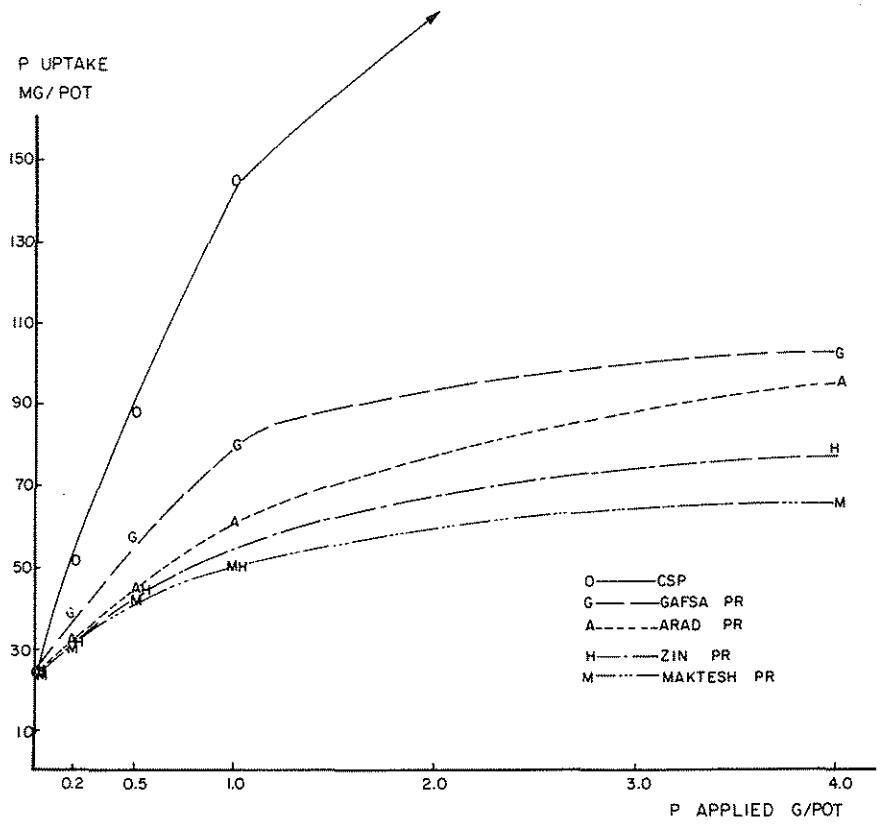

Figure 2. Comparison of P Sources (-200 mesh)—Total P Uptake by Three Cuts of Ryegrass.

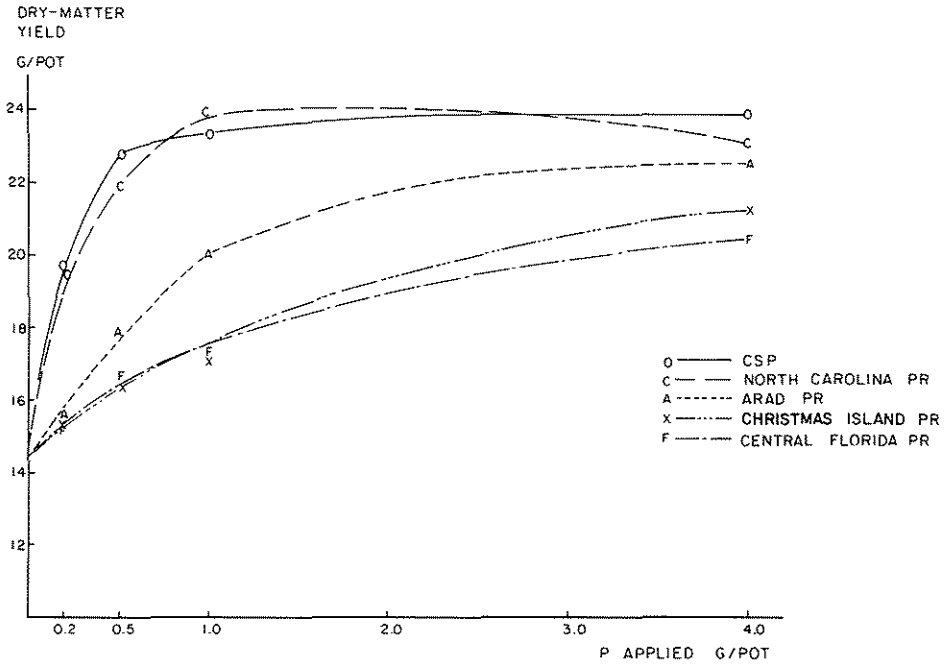

Figure 3. Comparison of P Sources (-200 mesh)—Total Dry-Matter Yields of Three Cuts of Ryegrass.

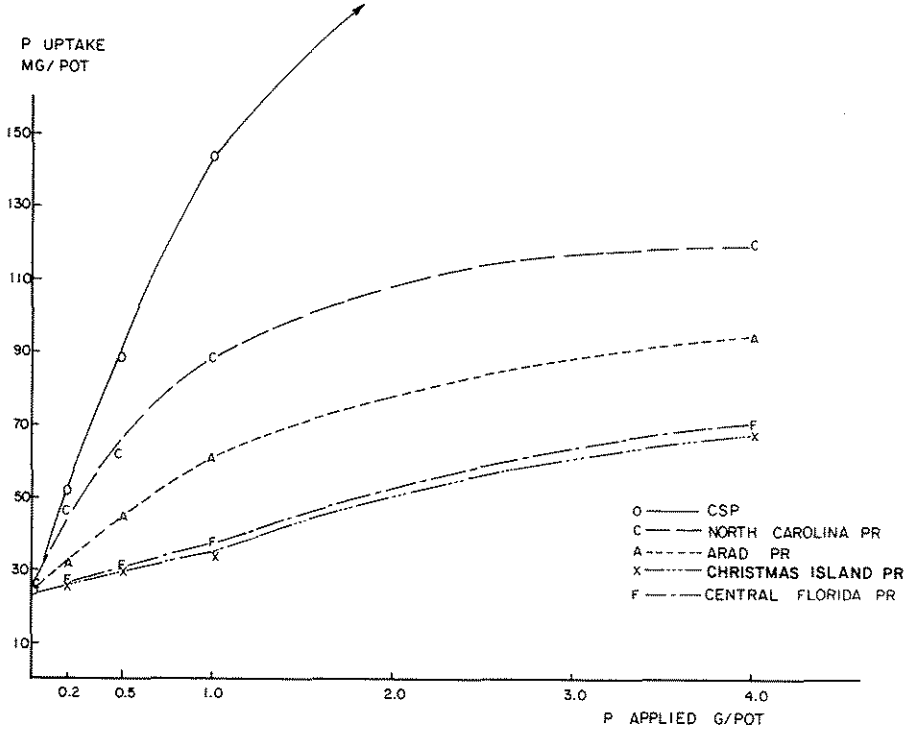

Figure 4. Comparison of P Sources (-200 mesh)—Total P Uptake by Three Cuts of Ryegrass.

A FRAMEWORK TO EVALUATE PHOSPHATE ROCK AS AN ALTERNATIVE IN PHOSPHATE FERTILIZATION

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The fertilizer shortage and high fertilizer prices of the early and mid-1970's cast some doubt as to whether the chemical fertilizer industry would continue to lead productivity growth in agriculture. Attention was being directed to seeking alternative sources of plant nutrition (Ruttan). In the case of phosphate, however, there appears to be no great potential for organic and biological sources of plant nutrition. At the same time, the situation with regard to the long-run availability of phosphate does not seem to warrant undue pessimism. The presently known phosphate reserves at the current annual rate of consumption are reported to be sufficient for 481 years and the ultimately recoverable phosphate resources for 1,601 years (Nordhaus). It is evident that the future growth in the use of phosphate as a source of plant nutrition will not be limited by sheer availability; rather any drag on its use will arise from increasing costs for extraction, processing, storage, and distribution. The last three categories of costs and thus the supply price of phosphate per unit of P_2O_5 depend upon the form in which phosphate is applied to the soil. A cheaper source of P_2O_5, however, may not necessarily be the economically more efficient source because of differences in technical efficiency. It is nevertheless important that the economically most efficient source be used to keep the real costs of phosphate to agriculture at the lowest possible level.

The unit cost of P_2O_5 obtained directly from phosphate rock (PR) is generally less than that of P_2O_5 obtained from manufactured sources, for example, triple superphosphate (TSP). However, a unit of P_2O_5 as PR involves approximately 50% more weight than in the case of TSP. Consequently, transport, storage, and distribution costs per unit of P_2O_5 are higher in the case of PR. The difference in

the marketing costs of a unit of P_2O_5 from the two sources increases with distance involved for movement of the material, time period required to keep the material unused in storage after production or importation, and inefficiency of the marketing system. This may offset the initial cost advantage that PR has over TSP. If shorter distances, shorter time requirement for storage, and larger efficiency of the marketing system are involved, PR would have advantage over TSP.

At some point the total unit cost of P_2O_5 from the two sources could be equal at the farm gate. The initial cost advantage in favor of PR, however, is substantial, and its marketing costs will have to be very high to seriously erode this advantage. It should also be pointed out that the effectiveness of directly applied phosphate rock could vary with the soil and crop conditions, the form in which rock is applied, and the method of application. There may be areas where soil and crop conditions may be such that a substantial portion of the phosphate needs can be met by the application of raw rock (Hignett, 1968). This would particularly be the case of countries having access to sufficiently reactive PR sources that are in relatively close proximity to intended markets. It is thus important to assess if, under some specific soil and crop conditions, direct application of phosphate rocks (without much processing) could be an economically feasible alternative source of phosphorus. The focus of this paper is, therefore, to develop a simple framework to compare the relative economic efficiency of different phosphate sources and to carry out a preliminary comparison of TSP and six different rocks used in an experiment conducted in Thailand.

The Economic Model

To start with, let the crop production function under given soil and environmental conditions be represented by:

$$(1) \quad Y = f(X,K)$$

where Y is the additional crop output from fertilizer per unit of land, and X and K are input rates of P_2O_5 and "all other inputs," respectively, also per

unit of land during a given period of production. Since we will be dealing only with experimental data where "all other inputs" are held constant, the crop production function (1) may be written as a function of X alone:

(2) $Y = f(X)$

The profit π, as a return to land and "all other inputs," is equal to total revenue minus total variable costs of phosphate:

(3) $\pi = P_y Y - PX$

where P_y is crop output price, and P is the price of P_2O_5.

The profit maximization condition for this case implies:

(4) $\frac{dY}{dX} = R$, where

R is the ratio of P_2O_5 price and crop output price.

In order to study relative economic efficiency, let us rewrite the production function (2) for two sources of P_2O_5 (1,2) as follows:

(5) $Y^1 = A^1 f(X^1)$; $Y^2 = A^2 f(X^2)$

where differences in the availabilities to crops of the two sources under given soil and climatic conditions create productivity differences in the technical efficiency parameters A^1 and A^2 of the two production functions.[1]

If the ratio of price of P_2O_5 to crop price differs for the two sources by a factor k, the marginal productivity condition (4) for the two production functions (1,2) can be rewritten as:

1. In the agronomy literature these differences are referred to as "differences in agronomic effectiveness." See for example: Engelstad et al., 1974; and Awasthi et al. It should be noted that here we are not concerned about differences due to soil factors.

$$(6)\quad \frac{dA^1f(X^1)}{dX^1} = R; \quad \frac{dA^2f(X^2)}{dX^2} = kR$$
$$k \geq 0.$$

The meaning of (6) is that the relative economic efficiency of the two sources can differ either because of the differences in their technical efficiency or because of differences in their prices or both. A more technically efficient source produces larger output from given input quantities of P_2O_5. Thus, if the price of P_2O_5 (at the farm gate) is equal for the two sources (that is, k is one), the source with higher technical efficiency is also more efficient economically. On the other hand, if the two sources have equal technical efficiency, the source with lower price of P_2O_5 (at the farm gate) is economically more efficient. It should be noted that the two sources can have equal economic efficiency with varying degrees of price and technical efficiency differences.

In farm-level comparisons of economic efficiency of different sources, it is important that analyses be based on appropriate price estimates. Output price should be the farm-gate price of average quality product. If only the market price is available, it should be adjusted for the marketing costs per unit of output. Such costs will include on-farm processing costs, selling costs, transport costs, etc. Adjustments should also be made for income from byproducts. Similarly, the P_2O_5 price should also be farm-gate price not factory-gate or import price. The total unit cost directly attributable to P_2O_5 at the farm level should include: (1) unit cost of production of P_2O_5 at the factory gate (or the unit import cost at the point of importation), (2) average unit cost of storage of P_2O_5 from the time it is produced (or imported) up to the time it is used, (3) transport cost per unit of P_2O_5 from the factory gate or place of importation to the farm gate, and (4) application cost per unit of P_2O_5 estimated for the method of application most likely to be used for each source.

This procedure for comparing the relative economic efficiency of two sources of fertilization is valid only if there is no significant carryover effect (residual effect) in the case of either source. In the case of phosphates, however, the residual effects are well known in that a

substantial part of the benefits from phosphate fertilization accrues in succeeding years after application (Engelstad et al., 1972 and 1974; Awasthi et al., 1977; Arndt et al., 1963; and McLachlan, 1960). Furthermore, the availability of phosphate from processed fertilizers and phosphate rock differs and is influenced by soil, crop, and fertilizer material characteristics. The annual crop response to residual P_2O_5 from phosphate rock becomes equal or exceeds that from processed sources of P_2O_5 within a few years after application. These considerations necessitate modification of the procedure developed above.

Equations (4) and (6) are different versions of the usual single period condition for profit maximization. But, in the case of phosphates, account must also be taken of the value of additional output (i.e., extra output after subtracting the control plot yield) obtained during subsequent periods after the initial application of phosphate.[2] This, however, is quite a complicated matter. In contrast to the price of P_2O_5 which is known at the time of application, the estimation of output prices in the future involves uncertainty. The output itself pertains to future periods and may be uncertain. In addition to these elements of uncertainty, there is the usual consideration of time preference in the sense that returns forthcoming in the future are worth less at present. The simplest procedure to account for these elements of uncertainty and time preference is to discount future returns to present values by using a rate of discount acceptable to the decisionmaker.

2. This accounting of the carryover or residual effect can influence the policy for optimal phosphate application. Some important papers focusing on this problem have recently appeared (Russel; Kennedy et al.; Gunnarsson). These papers, however, are not directly involved in economic comparison of different phosphate sources. Gunnarsson derives the profit maximizing condition for Mitscherlich equation in terms of certain rate constants calculated from the experimental data and current period input and output prices. The yearly application rate thus depends upon the prices and the rate constants.

Because future output prices are unknown, their expected future values are assumed to remain constant at present levels. With this assumption only the additional yields of future crops, not monetary returns, need to be discounted to present values. This simplifies the estimation of response functions, which may be obtained as a relationship between the sum of discounted present values of future additional crop yields and application rates of P_2O_5. The profit maximizing condition also stays the same.

For this purpose the entire stream of the future values of additional yields should be summed up to a present value figure after applying an appropriate discount rate for yields in each period. We may simply write

$$(7) \quad Y' = \sum_{t=1}^{n} [1/(1+\gamma)^t] Y_t, \text{ where}$$

Y' = the sum of present values of additional yields of n crops after appropriate discounting

Y_t = additional yield of the t^{th} crop after subtracting the control plot yield

γ = the discount rate acceptable to the decisionmaker

n = the number of crops for which additional crop yield, Y_t, remains positive

It should be noted that the length of yield streams Y_t for different phosphate sources could be different. Also, the level of Y_t for the same crop but for different sources could be different. Thus, the sum of present values Y' for a given level of P_2O_5 applied from different sources could be different.

We can now replace Y by Y' in equation (2) and proceed to empirically compare the economic performance of different phosphate sources. It should be pointed out that under the assumption that the price of output P_y remains constant, equations (2), (3), and (4) remain unchanged except that Y is replaced with Y'.

An Empirical Implementation

The preceding economic model provides a framework for economic evaluation of different sources of phosphate. The Tennessee Valley Authority (TVA) has long been engaged in work on improving the efficiency of fertilizers used on rice. A set of their experiments testing several phosphate rocks and TSP in Thailand is reported by Engelstad et al., 1972, in Tailoring Fertilizers for Rice. The experiment under analysis was conducted on a flooded acid sulfate soil with a pH of 4.6.[3] Results reported in this paper are based on data from the above-mentioned experiment, reproduced in part in table 1. P_2O_5 at rates of 25, 50, 100, and 200 kg/ha was applied in the form of TSP and five different rocks.[4] The data, averaged for replications, are reported up to the fifth crop (it should be noted that the fourth crop was lost).

The data from table 1 are reported in table 2 after subtracting the control plot yields. The fourth crop yield is a linear interpolation, and sixth and seventh crop yields are linear extrapolations from first, second, third, and fifth crops. The sum of the discounted net yields from table 2 is presented in table 3 using 10% and 20% discount rates.[5] These are the relevant output figures for estimating response functions for comparing technical (agronomic) efficiency of different phosphate sources.

3. It should, however, be recognized that the soil used in this experiment is rather unique. In the B-horizon, it has pH values around 3.3 to 4.0. The true acidity of this soil thus may be far greater than indicated by the pH of the plow layer (Breemen and Wielemaker).
4. Missouri rock was the sixth rock included in the experiment. It gave very poor results and is not included in our analysis.
5. These discount rates are used arbitrarily. As pointed out earlier the actual discount rate to be used depends upon the subjective judgment of the decision-maker. One way may be to use the prevailing market rate of interest on long-term investment loans.

Response functions with the following form were estimated for the different sources.[6]

$$(8) \quad Y_j' = \beta_o X_j + \beta X_j^2 + e$$

where:

j = TSP, Central Florida rock, North Carolina rock, North Florida rock, and Tennessee rock,

Y_j' = discounted sum of net yields of seven crops after subtracting the control plot yields (kg/ha of rough rice) pertaining to j^{th} source,

X_j = four application rates of 25, 50, 100, and 200 kg/ha of P_2O_5 corresponding to j^{th} source of P_2O_5,

e = error term.

The estimated response functions for the five sources are presented in table 4.[7] The optimal

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6. The simple second order polynomial is preferred for convenience in subsequent analyses. It fitted the data quite well. Other functional forms were tried but rejected in favor of (8). If one has a larger number of observations, logarithmic form may be preferable in the sense that technical (agronomic) efficiency differences between two sources can be directly evaluated in percentage terms by comparing the efficiency parameter of the Cobb-Douglas production function maintaining that exponents are the same. The exact nature of differences in the response functions of the two sources, however, is an empirical matter and should be ascertained by comparing alternative forms and using appropriate statistical procedures. In the case of estimates of response functions presented in table 4, however, no statistical tests to compare different sources were carried out. The small number of observations at our disposal precludes such a possibility. Comparisons of these sources presented subsequently, thus, have no implications of statistical inference.

7. For comparing economic efficiency, Idaho rock is not considered further since its technical (agronomic) efficiency is quite low relative to other sources, and North Carolina rock is dropped because a sensible estimate of its response function could not be obtained.

values of X, that is, kilograms of P_2O_5 per hectare for each source corresponding to a range of P_2O_5 and rough rice price ratios, are obtained from the profit-maximizing equation (4) and are presented in tables 5 and 6 for 10% and 20% discount rates, respectively. Also presented in these tables are the corresponding optimal output figures and the profit figures.[8] The profit figures are also stated in kilograms of rough rice per hectare.

No information is presented in tables 5 and 6 about NCR. Whereas the optimal use levels of P_2O_5 from TSP, CFR, NFR, and TR for "reasonable" ratios of farm-gate prices of P_2O_5 and rough rice fall within the range of application rates of P_2O_5, this is not the case for NCR. The coefficient estimate of the quadratic term for NCR, presented in table 4, is not different from zero. This implies that 200 kg/ha of P_2O_5 is the most profitable rate of application for NCR. However, the unusually low response to NCR at 50 and 100 kg/ha of P_2O_5 as seen in tables 2 and 3 is unexplainable. Therefore, NCR is eliminated from further analysis, and estimated response functions for only four sources--TSP, CFR, NFR, and TR--are depicted in figure 1.

The type of information presented in tables 5 and 6 is necessary to compare economic efficiency of different phosphate sources with different farm-gate prices. Information in these two tables is constructed by using 10% and 20% discount rates, respectively. Each table allows a direct comparison of the relative profitability of a given source with any other source and for any combination of the ratios of P_2O_5 price and rough rice price. As an illustration, one may compare TSP with NFR when $R_{(TSP)} = 5$ and $R_{(NFR)} < 2$ at the 10% discount rate. It can be readily seen from table 5 that with these price ratios NFR is more profitable. But if $R_{(NFR)} \geq 3$, and $R_{(TSP)} = 5$, then TSP is more profitable than NFR. Actually, for a given R for one source, there exists a corresponding

8. Profit in this case simply is the value of output per hectare less the cost of corresponding (optimal) amount of P_2O_5. It is a return to a hectare of land and "all other inputs" used, which accrues as a result of use of phosphate.

R for the second source at which the second source is equally profitable, and if the second source can be delivered at the farm gate cheaper than this R, it is an economically more efficient source in the sense that its use yields larger net returns to the fixed resources at the farm. Thus, for given estimates of the two response functions, a condition in the form of an equation can be developed which gives combinations of R for equal profit from the two sources. Three such equations to compare TSP with NFR, TSP with CFR, and NFR with CFR are calculated using a 10% discount rate and are presented below.[9]

(9) $R_{(TSP)} = 2.196 + 0.957\ R_{(NFR)}$,

(10) $R_{(TSP)} = 9.006 + 0.941\ R_{(CFR)}$, and

(11) $R_{(NFR)} = 7.118 + 0.983\ R_{(CFR)}$, respectively.

Such equations can be used to compare any pair of resources for which response estimates have been obtained. They permit more exact comparisons (than tables 5 and 6) in the sense that any pair of price ratios can be considered, and comparisons are not limited to the price ratios used in the tables.

For example, if $R_{(TSP)}$ in (9) is greater than the right-hand side for a given $R_{(NFR)}$, NFR is a more profitable and, hence, economically a more efficient source than TSP at the farm level.[10], [11] The reverse is true if $R_{(TSP)}$ is smaller.

These equations also facilitate graphic comparisons. Figures 2, 3, and 4 are the graphs of equations (9), (10), and (11), respectively. In these figures the lines demarcate the areas where for any paired combination of the price ratios one or the other source is more profit-

9. For a detail of the procedures to develop these iso-profit equations, see Baanante.
10. Larger economic efficiency, as defined earlier, means larger net returns to the fixed resources of land and labor, etc., over fertilizer costs.
11. Here it should be pointed out again that prices of P_2O_5 are inclusive of application costs which could be different for the two sources. In general, application costs are higher for PR compared to those for TSP.

able. For example, in figure 2, if $R_{(TSP)} = 4$, then for $R_{(NFR)} > 1.885$, TSP is more profitable than NFR, and for $R_{(NFR)} < 1.885$, NFR is more profitable than TSP. Similarly, if $R_{(TSP)} = 6$, then for $R_{(NFR)} > 3.975$, TSP is more profitable than NFR, and for $R_{(NFR)} < 3.975$, NFR is more profitable than TSP. Thus, a comparison of relative economic efficiency of the two sources becomes possible for the combination of actually prevailing (or possible) price ratios.

Some further insight can be gained in terms of relative economic efficiency of NFR applied directly as an alternative source of phosphate, compared to TSP, with the help of table 7. The figures in columns (1) and (2) in this table represent combinations of $R_{(NFR)}$ and $R_{(TSP)}$ points at which the two sources are equally profitable. Column (3) represents the difference between $R_{(TSP)}$ and $R_{(NFR)}$ necessary to make them equally profitable. It should be noted that this difference becomes smaller at higher P_2O_5 prices. This implies that, at higher prices of P_2O_5, the competitive position of NFR relative to TSP becomes better than at lower P_2O_5 prices.

Analyses to compare alternative phosphate sources have so far been carried out in terms of comparing net returns per unit of fixed-farm resources from different sources. Such analyses provide gainful insights and have important implications for decisionmakers to choose among alternative sources or ways of phosphate fertilization. The limited amount of data analyzed here, using the criteria of net returns per unit of fixed-farm resources, lends some support in phosphate fertilization for direct application of NFR as an alternative to TSP within reasonable price differences.

Prior to choosing between long-run investment alternatives, however, a decisionmaker may be interested, in addition to the net returns per unit of fixed-farm resources, in comparing net returns per dollar of investment. One simple way to do this may be to compare net benefits of the two sources per dollar of P_2O_5 used. If farm-gate prices (costs) of P_2O_5 are assumed to include production and marketing costs of P_2O_5 with normal rate of return on invested capital, the benefit:cost ratios for different materials can simply be computed by dividing the profit

function (3) by the cost of P_2O_5. The two sources can then be compared in terms of P_2O_5 to rice price ratios by equating their net benefit:cost ratios. For TSP and NFR such an equation works out to be:

$$(12)\quad R_{(TSP)} = 0.972\ R_{(NFR)}$$

Equation (12) is shown graphically in figure 5.[12] It is obvious from this graph that, from the point of view of investment decision, NFR is almost as good as TSP. The net benefit cost criterion thus lends further support for direct application of NFR as an alternative to TSP.

At this point, it should be reiterated that the numerical estimates presented in this paper are only illustrative because of data limitations. Comparisons of different sources are only as good as estimates of the response functions. The small number of observations precludes the possibility of any strong statements. The main contribution of this paper is the conceptual framework for comparing economic efficiency of different nutrient sources which have long-run residual effects of a varying nature. Comparisons with better data are necessary for better quantitative judgments to compare different sources.

Summary

There has been a resurgence of interest in studying direct application of phosphate rock as an alternative source of phosphate, since the fertilizer shortage and high fertilizer prices of the early and mid-1970's. A framework to evaluate phosphate rock for this purpose has been developed. Comparative analyses for six different rocks and TSP have been completed for rice crop from an experiment conducted on acid sulfate soil with a pH of 4.6 in Thailand.

The results of this experiment indicate conditions where the direct application of NFR would be a

12. In case application costs are larger for NFR than for TSP, equation (12) would have a small positive intercept.

feasible alternative to TSP, given reasonable price differences for the two sources and after residual effects are properly captured. Using the criterion of net returns to fixed-farm resources, comparison is made graphically of the two sources at varying ratios of P_2O_5 and rough rice price at the farm gate. Such comparisons are possible for any two sources of phosphate for which response functions capturing residual effects could be estimated.

The relative position of NFR improves further if the criterion of net benefit:cost ratio rather than net returns to fixed-farm resources is used; for investment decisions, this may be the more relevant criterion.

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Table 1. Sources and Rates of P_2O_5 and the Yields of Rough Rice in Kilograms per Hectare, Klong Luang Rice Experiment Station, Thailand

Source	P_2O_5, kg/ha	Crop 1 1969 Wet	Crop 2 1970 Dry	Crop 3 1970 Wet	Crop 5 1971 Wet
TSP	25	5,556	2,430	3,252	2,179
	50	5,960	2,968	2,814	1,357
	100	6,223	4,621	3,630	1,660
	200	5,866	4,723	4,714	2,966
Idaho Rock	25	4,417	1,977	2,837	1,481
	50	5,158	2,181	2,111	1,521
	100	5,195	3,420	3,272	2,497
	200	5,855	3,791	3,815	3,123
Central Florida Rock	25	4,840	1,823	2,346	1,904
	50	5,148	2,475	3,253	2,176
	100	5,620	3,255	3,483	2,825
	200	5,644	4,243	3,522	2,997
North Carolina Rock	25	4,989	1,641	2,806	2,038
	50	5,254	1,478	1,730	2,234
	100	5,327	3,112	1,878	2,708
	200	5,672	4,498	3,844	4,099
North Florida Rock	25	5,036	2,549	2,860	2,347
	50	5,180	2,400	2,429	1,360
	100	5,881	3,548	3,901	2,955
	200	5,636	4,451	3,763	3,279
Tennessee Rock	25	3,795	2,745	2,760	2,098
	50	4,432	2,331	2,246	1,711
	100	4,720	3,181	2,876	2,305
	200	5,098	4,062	3,141	2,358
No P	0	2,672	1,204	1,681	1,505
Soil pH			4.6		

The yield of crop 4 was lost by an attack of mealy bugs.

Source: Tailoring of Fertilizers for Rice, Tennessee Valley Authority, 1972, table 26, p. 31.

Table 2. Yields of Rough Rice in Kilograms per Hectare for Different Sources and Application Rates of P_2O_5 after Subtracting the Control Plot Yields

Source	P_2O_5, kg/ha	C_1	C_2	C_3	C_4	C_5	C_6	C_7
TSP	25	2,884	1,226	1,571	1,008	674	82	0
	50	3,288	1,764	1,133	477	0	0	0
	100	3,551	3,417	1,949	1,132	155	0	0
	200	3,194	3,519	3,033	2,205	1,461	1,249	771
Idaho Rock	25	1,745	773	1,156	429	0	0	0
	50	2,486	977	430	270	16	0	0
	100	2,523	2,216	1,591	1,338	992	550	156
	200	3,183	2,587	2,134	1,905	1,618	1,143	762
Central Florida Rock	25	2,168	619	665	545	399	0	0
	50	2,476	1,271	1,572	1,013	671	239	0
	100	2,948	2,051	1,802	1,560	1,320	810	435
	200	2,972	3,039	1,841	1,811	1,429	973	554
North Carolina Rock	25	2,317	437	1,125	687	533	23	0
	50	2,582	274	49	470	729	0	0
	100	2,655	1,908	197	1,015	1,203	255	0
	200	3,000	3,294	2,163	2,569	2,594	2,261	2,107
North Florida Rock	25	2,364	1,345	1,179	1,010	842	334	0
	50	2,508	1,196	748	302	0	0	0
	100	3,209	2,344	2,220	1,799	1,450	987	581
	200	2,964	3,247	2,082	2,070	1,774	1,358	1,002
Tennessee Rock	25	1,123	1,541	1,079	865	593	513	343
	50	1,760	1,127	565	438	206	0	0
	100	2,048	1,977	1,195	1,082	800	404	65
	200	2,426	2,858	1,460	1,333	853	375	0

Notes: 1. C = crop.
2. C_4, C_6, and C_7 are linear extrapolations from C_1, C_2, C_3, and C_5.

Table 3. Sum of the Discounted Yield Streams from Table 2 (kg/ha)

Source	P_2O_5, kg/ha	Rate of Discount 10 %	20 %
TSP	25	6,651	6,038
	50	6,114	5,664
	100	9,239	8,456
	200	13,337	11,958
Idaho Rock	25	3,723	3,414
	50	3,866	3,608
	100	8,211	7,413
	200	11,490	10,294
Central Florida Rock	25	3,971	3,632
	50	6,424	5,823
	100	9,486	8,529
	200	10,992	9,873
North Carolina Rock	25	4,586	4,167
	50	3,716	3,411
	100	6,415	5,822
	200	15,105	13,369
North Florida Rock	25	6,247	5,661
	50	4,376	4,064
	100	10,901	9,788
	200	12,429	11,107
Tennessee Rock	25	5,220	4,673
	50	3,716	3,410
	100	6,660	6,022
	200	8,232	7,455

Table 4. Estimates of Response Functions of Rough Rice for Different Sources of P_2O_5, Thailand

A. Discount rate = 10%

1. $\hat{Y}'_{(TSP)} = \underset{(3.768)}{145.634X} - \underset{(1.864)}{0.402X^2}$ $R^2(adj) = 0.928$

2. $\hat{Y}'_{(CFR)} = \underset{(15.459)}{145.196X} - \underset{(8.655)}{0.454X^2}$ $R^2(adj) = 0.995$

3. $\hat{Y}'_{(NCR)} = \underset{(2.388)}{76.344X} - \underset{(0.057)}{0.0102X^2}$ $R^2(adj) = 0.944$

4. $\hat{Y}'_{(NFR)} = \underset{(3.972)}{149.895X} - \underset{(2.085)}{0.439X^2}$ $R^2(adj) = 0.928$

5. $\hat{Y}'_{(TR)} = \underset{(3.269)}{105.843X} - \underset{(1.813)}{0.328X^2}$ $R^2(adj) = 0.886$

B. Discount rate = 20%

1. $\hat{Y}'_{(TSP)} = \underset{(3.885)}{134.480X} - \underset{(1.967)}{0.380X^2}$ $R^2(adj) = 0.929$

2. $\hat{Y}'_{(CFR)} = \underset{(14.419)}{131.320X} - \underset{(8.110)}{0.412X^2}$ $R^2(adj) = 0.994$

3. $\hat{Y}'_{(NCR)} = \underset{(2.464)}{70.813X} - \underset{(0.158)}{0.0253X^2}$ $R^2(adj) = 0.943$

4. $\hat{Y}'_{(NFR)} = \underset{(4.067)}{136.226X} - \underset{(2.162)}{0.404X^2}$ $R^2(adj) = 0.930$

5. $\hat{Y}'_{(TR)} = \underset{(3.344)}{95.860X} - \underset{(1.855)}{0.297X^2}$ $R^2(adj) = 0.891$

Notes: 1. For comparative purposes estimates of only four sources, triple superphosphate (TSP), Central Florida rock (CFR), North Carolina rock (NCR), and North Florida rock (NFR) are presented. Idaho rock and Tennessee rock had considerably lower response and are thus ignored.
2. T values are in parentheses.
3. Y′ is the sum of present values of stream of net yields after subtracting control plot yields (table 3).

Table 5. Optimal Use Levels of P_2O_5, Output of Rough Rice and Profit per Hectare, with Residual Effects Captured up to the End of the Seventh Crop, Using 10% Discount Rate

Source	kg/ha of	P_2O_5 Price and Rough Rice Price Ratio						
		0.5	1	2	3	5	7	10
TSP	P_2O_5	181	180	179	177	175	172	169
	Y´	13,190	13,189	13,188	13,183	13,175	13,156	13,130
	π	13,099	13,009	12,830	12,652	12,300	11,952	11,440
CFR	P_2O_5	159	159	158	157	154	152	149
	Y´	11,608	11,608	11,607	11,605	11,593	11,580	11,555
	π	11,528	11,448	11,291	11,134	10,823	10,516	10,065
NFR	P_2O_5	170	169	168	167	165	163	159
	Y´	12,795	12,794	12,792	12,789	12,781	12,769	12,735
	π	12,710	12,625	12,454	12,288	11,956	11,628	11,145
TR	P_2O_5	160	160	158	157	154	151	146
	Y´	8,538	8,538	8,535	8,532	8,521	8,504	8,461
	π	8,458	8,378	8,219	8,061	7,751	7,447	7,001

Notes:
1. Output of rough rice is the sum of discounted values of rough rice over seven crops using 10% discount rate and after subtracting the control plot yields.
2. Profit is kilograms of rough rice per hectare. It takes into account residual effects of P_2O_5 up to the seventh crop. It is a return to a hectare of land and "all other inputs" used per hectare resulting from phosphate application.
3. In computing the unit price of P_2O_5 for each source, its delivery price at the farm gate and application costs should be included.
4. Price of rough rice is at the farm gate.

Table 6. Optimal Use Level of P_2O_5, Output of Rough Rice and Profit per Hectare, with Residual Effects Captured up to the End of the Seventh Crop, Using 20% Discount Rate

Source	kg/ha of	P_2O_5 Price and Rough Rice Price Ratio 0.5	1	2	3	5	7	10
TSP	P_2O_5	176	176	174	173	170	168	164
	Y′	11,900	11,900	11,897	11,895	11,882	11,870	11,837
	π	11,812	11,724	11,550	11,376	11,032	10,694	10,197
CFR	P_2O_5	159	158	157	156	153	151	147
	Y′	10,462	10,460	10,459	10,457	10,445	10,433	10,399
	π	10,382	10,302	10,145	9,989	9,680	9,376	8,929
NFR	P_2O_5	168	167	166	165	162	160	156
	Y′	11,486	11,485	11,483	11,481	11,468	11,456	11,422
	π	11,402	11,318	11,151	10,986	10,658	10,336	9,862
TR	P_2O_5	161	160	158	156	153	150	145
	Y′	7,735	7,734	7,732	7,723	7,714	7,697	7,655
	π	7,655	7,574	7,416	7,255	6,949	6,647	6,205

Notes:
1. Output of rough rice is the sum of discounted values of rough rice over seven crops using 20% discount rate and after subtracting the control plot yields.
2. Profit is kilograms of rough rice per hectare. It takes into account residual effects of P_2O_5 up to the seventh crop. It is a return to a hectare of land and "all other inputs" used per hectare resulting from phosphate application.
3. In computing unit price of P_2O_5 for each source, its delivery price at the farm gate and application costs should be included.
4. Price of rough rice is at the farm gate.

Table 7. Combinations of $R_{(NFR)}$ and $R_{(TSP)}$ Necessary for Equal Profitability of NFR and TSP[a]

$R_{(NFR)}$ (1)	$R_{(TSP)}$ (2)	$R_{(TSP)}-R_{(NFR)}$ (3)
0.5	2.68	2.18
1.0	3.15	2.15
2.0	4.11	2.11
3.0	5.07	2.07
5.0	6.98	1.98
7.0	8.89	1.89
10.0	11.78	1.78

a. Calculated from equation (9) in the text.

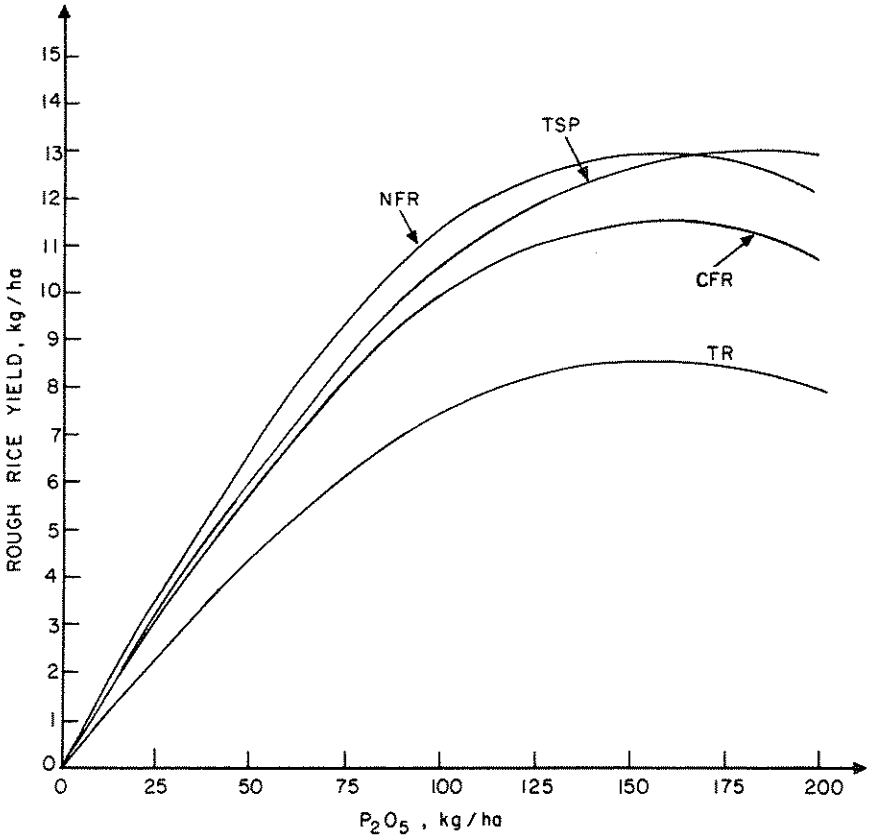

Figure 1. Response Functions for Rough Rice for Four Different Sources of Phosphate—TSP, NFR, CFR, and TR. (Output of rough rice is the sum of net yields of seven crops after subtracting control plot yields and applying a 10% discount rate.)

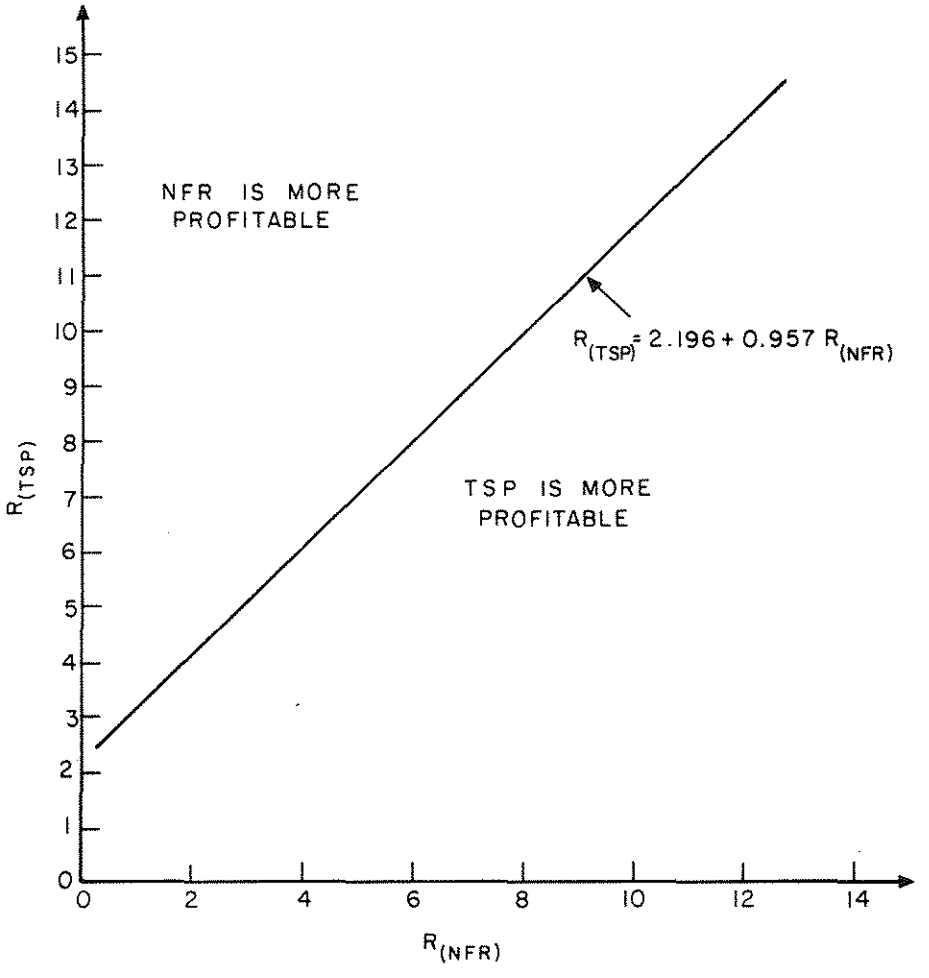

Figure 2. Profitability Comparison of TSP and NFR at Varying Ratios of P_2O_5 Price and Rough Rice Price at the Farm Level.

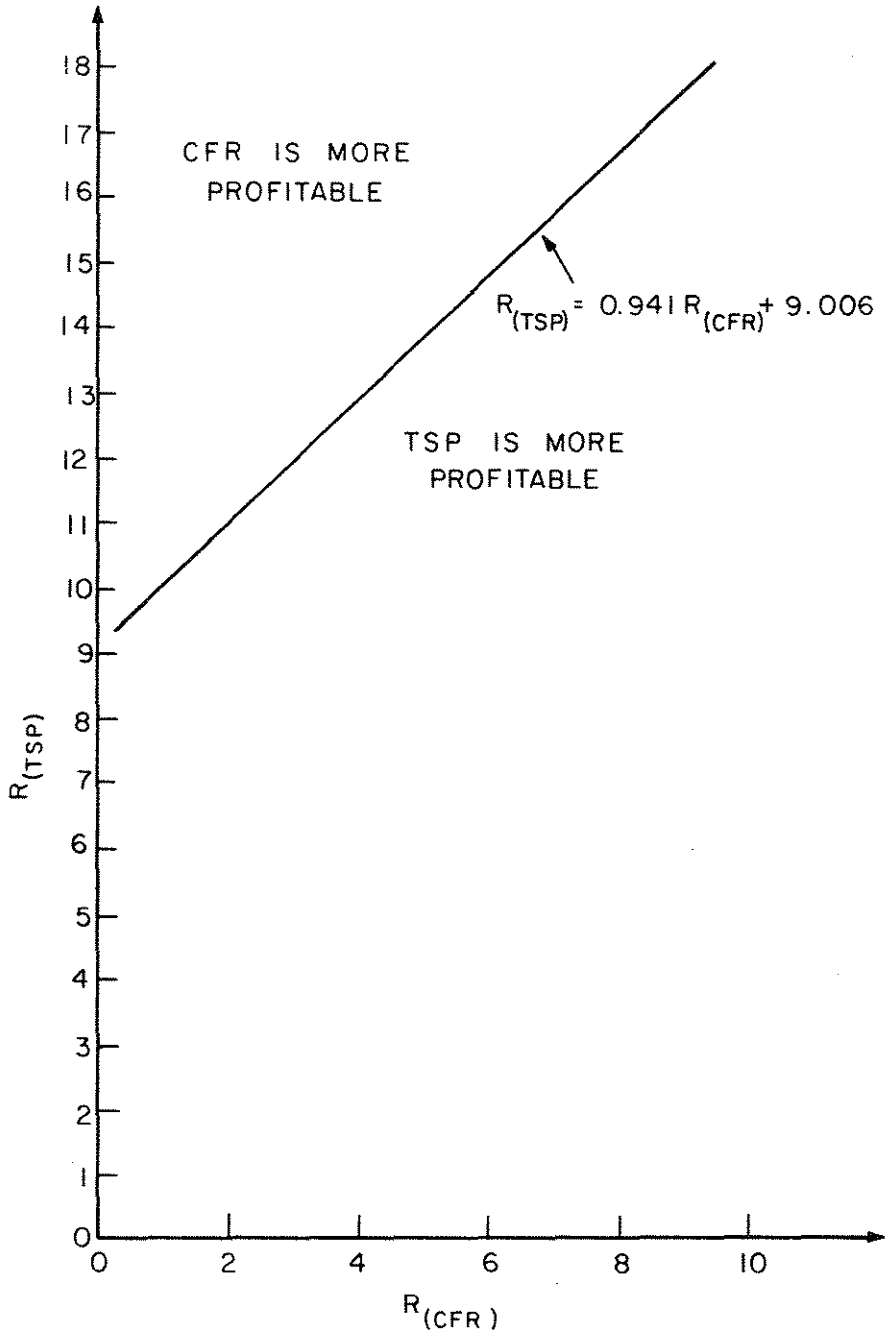

Figure 3. Profitability Comparison of TSP and CFR at Varying Ratios of P_2O_5 Price and Rough Rice Price at the Farm Level.

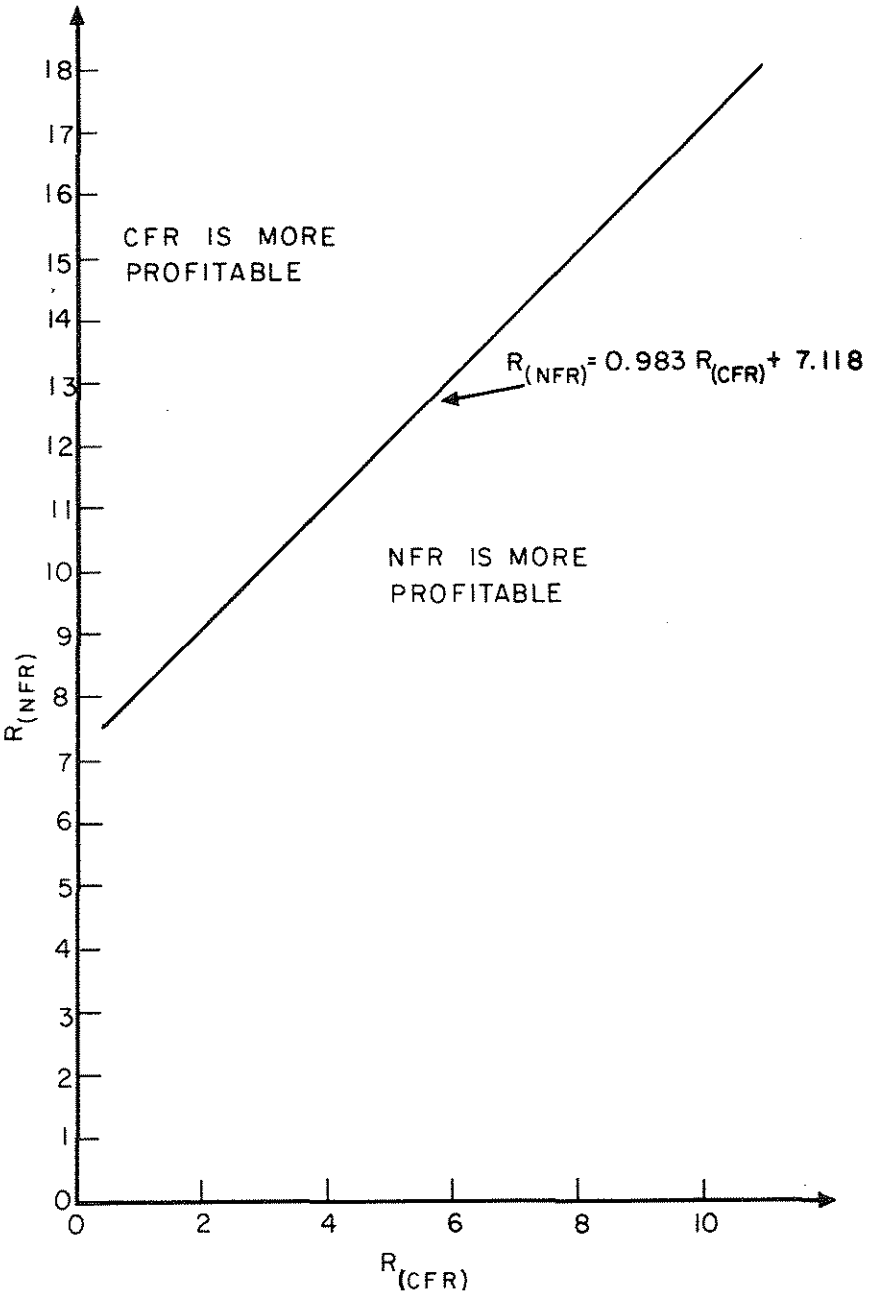

Figure 4. Profitability Comparison of NFR and CFR at Varying Ratios of P_2O_5 Price and Rough Rice Price at the Farm Level.

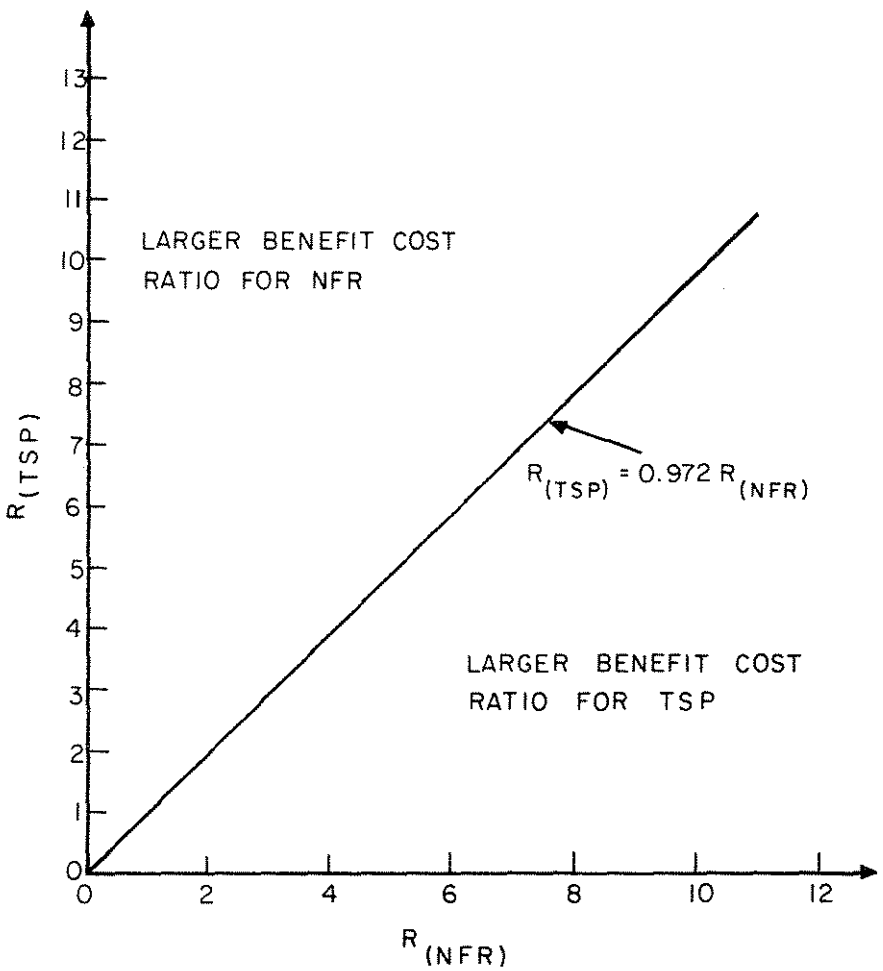

Figure 5. Comparison of Net Benefits and Cost Ratios of TSP and NFR for Varying Ratios of P_2O_5 Price and Rough Rice Price at the Farm Level.

RELATIVE AGRONOMIC AND ECONOMIC EFFECTIVENESS VALUES FOR PHOSPHATE ROCKS

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Introduction

The evaluation of a new fertilizer as a nutrient source for crop plants is basically an empirical procedure, requiring comparison with an accepted standard source.

The calculation of agronomic effectiveness values has been standardized by use of mathematics to reduce the element of personal bias and judgment to a minimum. However, difficulties arise when the data do not follow the underlying theory; at this point, personal judgment becomes an important element in the calculation. In some cases, an extension of the analysis to include economic comparisons may prove useful as a way of dealing with difficulties in the agronomic procedure. This is of special relevance for phosphate rocks.

The purposes of this paper are to discuss (1) special procedural problems in calculating relative agronomic effectiveness values for phosphate rocks and (2) the extension of the agronomic effectiveness procedure to include an economic evaluation of these sources.

Calculation of Relative Agronomic Effectiveness

The classical biological assay approach as described by Black and Scott (1956) applies where fertilizers being compared contain differing dilutions of the same compound. The medium being used to create the various dilutions (or concentrations) is inert and has no effect on the behavior of the

source. Black and Scott suggested ammonium nitrate-sand mixtures as exemplifying such dilutions. In such cases, different soils, crops, or climate would have no effect on the outcomes.

Since such dilutions are rarely of concern in fertilizer comparisons, classical biological assay has relatively little to offer to evaluation of fertilizers in the strict sense. In practice, one applies the approach to imperfect situations, i.e., where the outcome may be affected by the soil, crop, or climate. This is because the nutrient sources being compared usually vary in physical and chemical properties.

Black and Scott suggested a physiological test to determine whether one is justified in making comparisons between sources of the same nutrient. This essentially involves the plotting of crop yield versus the uptake of the nutrient in question. If all points fall on or near a common line, it can be assumed that the growth or yield effect for each unit of nutrient taken up is the same regardless of source. In such cases, relative agronomic effectiveness calculations are justified.

If, in fact, there are differences among sources, as evidenced by the above plot of yield versus uptake, this is interpreted to mean that there are other effects associated with these sources that result in unequal yield effects per unit of nutrient taken up. In such cases, calculation of relative effectiveness values is not justified.

To illustrate the case for phosphate rocks versus superphosphate, data on yield versus P uptake are plotted in figure 1 from a greenhouse experiment with flooded rice. There were no serious deviations from the general population in this case, indicating that calculation of relative effectiveness values is valid. The range in these mutually dependent parameters resulted in turn from the range in citrate-soluble P content among the phosphate rocks represented.

Another requisite for calculation of relative effectiveness values is that limiting (maximum) yields for all sources with increasing rate of applied P be equal (Terman and Engelstad, 1971). Here is where the main problems occur with respect to phosphate rocks. Because the phosphate rocks support a

generally low solution P concentration in acid soils (and even lower in calcareous soils), initial P uptake, growth, and subsequent yield response are limited accordingly. Figure 2 illustrates a set of dry matter yield response curves for triple superphosphate (TSP) and several phosphate rocks. In no case did the phosphate rocks attain the same limiting yield as for TSP within the range of rates used. This is a very common, and in fact the usual, result in comparisons of phosphate rocks with acidulated or soluble phosphates. It is possible that certain of these would ultimately have equaled TSP in limiting yield with higher rate of application; however, this is unlikely.

Using rice yield data obtained in Thailand (see figure 3) and reported by Engelstad, Aroon, and De Datta (1974), relative effectiveness values were calculated from yield increases for the lower rates of applied P (25, 50, and 100 kg of P_2O_5 per hectare). These values are shown in table 1. The choice of the lower rates avoided the "flat" portions of the curves; however, there is no real reason to believe that the same mechanism that resulted in lower limiting yield would not apply to all portions of the response curves. Therefore, there is serious question as to the validity of these relative effectiveness values since they underestimate differences in effectiveness.

There are other approaches to evaluation of P sources that could be used as alternatives. These involve an economic interpretation.

Economic Comparisons of P Sources

Using Net Returns at Optimum Rate

Economic calculations were also made of the Thailand rice data. The first step was to fit a polynomial of the form $y = a + b_1x^{\frac{1}{2}} + b_2x$ to each of the response curves shown in figure 3, with the exception of that from the Missouri rock. These functions were then used to calculate economically optimum rates, wherein the first derivative of the function was set equal to the ratio of the price per kilogram of P_2O_5 in the fertilizer to the price of rough rice. This is shown as follows:

$$\frac{dy}{dx} = \frac{P_x}{P_y}$$

where y = yield of rice and x = the rate of P_2O_5 per hectare. This is solved for x or the optimum rate of P_2O_5. Using this value, yield responses and net returns to applied P were calculated for each source. The optimum rates and corresponding net returns for each source are shown in table 2, along with the prices used in the calculations.

These net returns were in turn used to calculate relative effectiveness values as shown in table 3. The values for phosphate rocks range from 65% to 89% as effective as TSP at Klong Luang and from 57% to 90% as effective as TSP at Bangkhen. While certain sources approached TSP in net return, none were equal. These failures to equal TSP represent real economic losses. The magnitude of these losses can be seen by comparing net returns as shown in table 2. It could only be concluded that, at the price ratio of 2:1 for P_2O_5 in TSP and phosphate rocks, TSP would be preferable if the objective is to maximize net returns per hectare.

This example does not take into account the residual effectiveness of these sources. If such is considered, the gap in yield and profit between the phosphate rocks and TSP may narrow a bit. However, in the Klong Luang experiment, the residual effectiveness of TSP was superior to that of the phosphate rocks through the fourth successive crop.

Using Net Returns per Dollar Invested

If, on the other hand, funds are restricted and the objective is to maximize the return per dollar invested in P fertilizers, the situation looks quite different. Since lower rates would be used if funds were severely limited, net returns per dollar invested and corresponding relative effectiveness values were calculated at the lowest rate in each case (25 kg of P_2O_5 per hectare); these are shown in table 4 for the two locations. The values for phosphate rocks ranged from 95% to 165% as effective as TSP at Klong Luang and from 100% to 165% as effective as TSP at Bangkhen. The difference in cost of fertilizer P is a greater factor in this case than where net return per

hectare at the optimum rate was used as the basis for calculation. Incidentally, these and other data show a greater variability in yield response at lower rates of application of phosphate rocks. This is a factor that should be kept in mind in choosing a P source and rate.

It should be pointed out that only one set of prices was used in these economic analyses. However, it was felt that the prices chosen were representative and that it was unnecessary to show the effect of price changes in this example.

Discussion and Conclusions

The calculation of relative agronomic effectiveness values is suspect for the phosphate rock case because of the generally lower limiting yields compared with those obtained with acidulated phosphates. The economic losses represented by these differences in limiting yields can be quite significant and should be included in the analysis where maximum net return per hectare is desired.

The commercial farmer seeks to maximize net returns to all inputs on the hectare basis. This is particularly true where land is expensive or in short supply; he cannot afford to sacrifice crop yield or profit in an effort to save money on source or rate of phosphate fertilizers. Based on these considerations, soluble phosphate would be preferred by most commercial farmers.

The farmer who has little or no investment in land and is quite short of funds may seek to maximize the return per dollar invested in phosphate fertilizer if he uses fertilizer at all. He is concerned with risk aversion and survival of his family unit. In this sense he seeks self-sufficiency. In this case, limiting yields are not as important as are the differences in cost of fertilizer P. Using this goal, the more reactive phosphate rocks would be preferred over the acidulated phosphate, particularly at the lower rates of application.

In summary, the use of phosphate rock for direct application to agronomic crops is limited to the

low-income farmer who is concerned with risk aversion and self-sufficiency.

Comments by Other Participants

Dr. Cooke commented that he was most interested in the case where net return would be maximized on a per-hectare basis. He felt that this was the only stand that most commercial farmers could afford to take and, therefore, was the more relevant approach.

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Table 1. Relative Agronomic Effectiveness Values[a] for P Sources Compared for Flooded Rice in Thailand[b] (crop 1)

Source	Location	
	Klong Luang	Bangkhen
North Carolina	78	76
Florida (north)	83	64
Florida (central)	78	63
Idaho	69	40
Tennessee	51	23
Missouri	0	24
Triple superphosphate	100	100

a. Calculated after averaging the yield response of rough rice to 25, 50, and 100 kg P_2O_5/ha.
b. Engelstad, Aroon, and De Datta (1974).

Table 2. Calculated Optimum Rates of Fertilizer P, and Corresponding Net Returns for Two Locations in Thailand[a]

Source	Klong Luang		Bangkhen	
	Optimum Rates, kg P_2O_5/ha	Corresponding Net Return, $/ha	Optimum Rates, kg P_2O_5/ha	Corresponding Net Return, $/ha
North Carolina	143	264	145	175
Florida (north)	116	299	136	154
Florida (central)	130	283	199	173
Idaho	200 +	283	156	111
Tennessee	200 +	218	b	b
Triple superphosphate	91	336	112	194

a. Prices used: rough rice--$0.10/kg; TSP--$0.28/kg P_2O_5; phosphate rock--$0.14/kg P_2O_5.
b. Could not be calculated because of illogical signs in the function.

Table 3. Relative Economic Effectiveness Values for P Sources Compared for Flooded Rice in Thailand, Using Net Return at Optimum Rates

Source	Location	
	Klong Luang	Bangkhen
North Carolina	78	90
Florida (north)	89	79
Florida (central)	84	89
Idaho	84	57
Tennessee	65	a
Triple superphosphate	100	100

a. Could not be calculated because of illogical signs in the function.

Table 4. Net Return Per Dollar Invested at the Lowest Rate of Application (25 kg P_2O_5/ha) of the Various Phosphate Sources and Corresponding Relative Effectiveness Values[a]

Source	Klong Luang		Bangkhen	
	Net Return Per Dollar Invested, $	Relative Economic Effectiveness	Net Return Per Dollar Invested, $	Relative Economic Effectiveness
North Carolina	50	135	33	165
Florida (north)	61	165	30	150
Florida (central)	55	149	29	145
Idaho	45	122	20	100
Tennessee	35	95	b	b
Triple superphosphate	37	100	20	100

a. Prices are the same as used in table 2.
b. Could not be calculated because of illogical signs in the function.

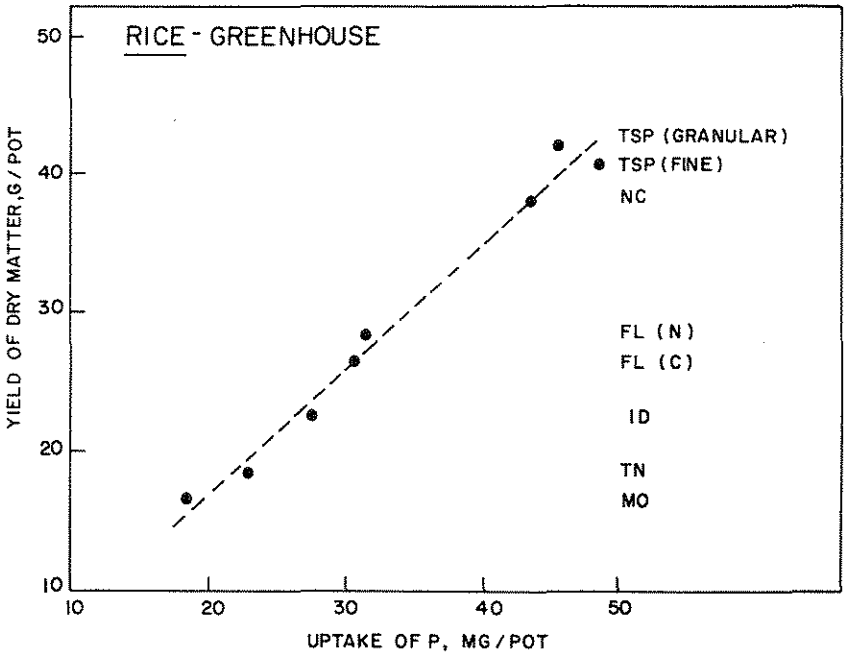

Figure 1. Plot of Rice Forage Yield on Uptake of P. (Data averaged over 50, 100, and 200 mg P/pot.)

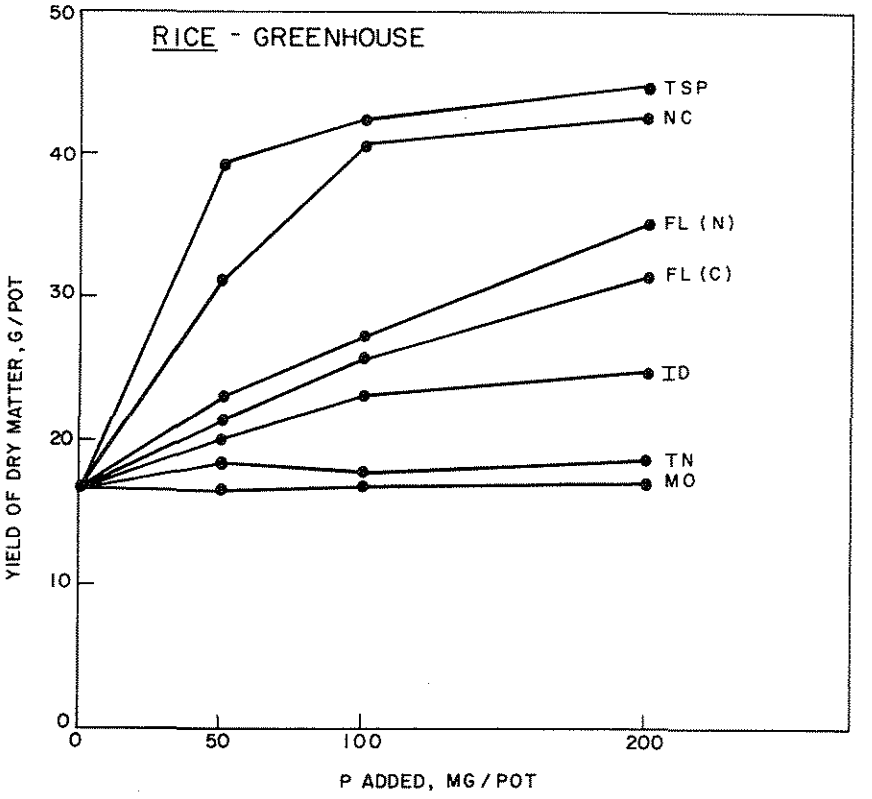

Figure 2. Effect of Various P Sources on the Forage Yield of Flooded Rice in a Greenhouse Experiment. From Engelstad, Aroon, and DeDatta (1974).

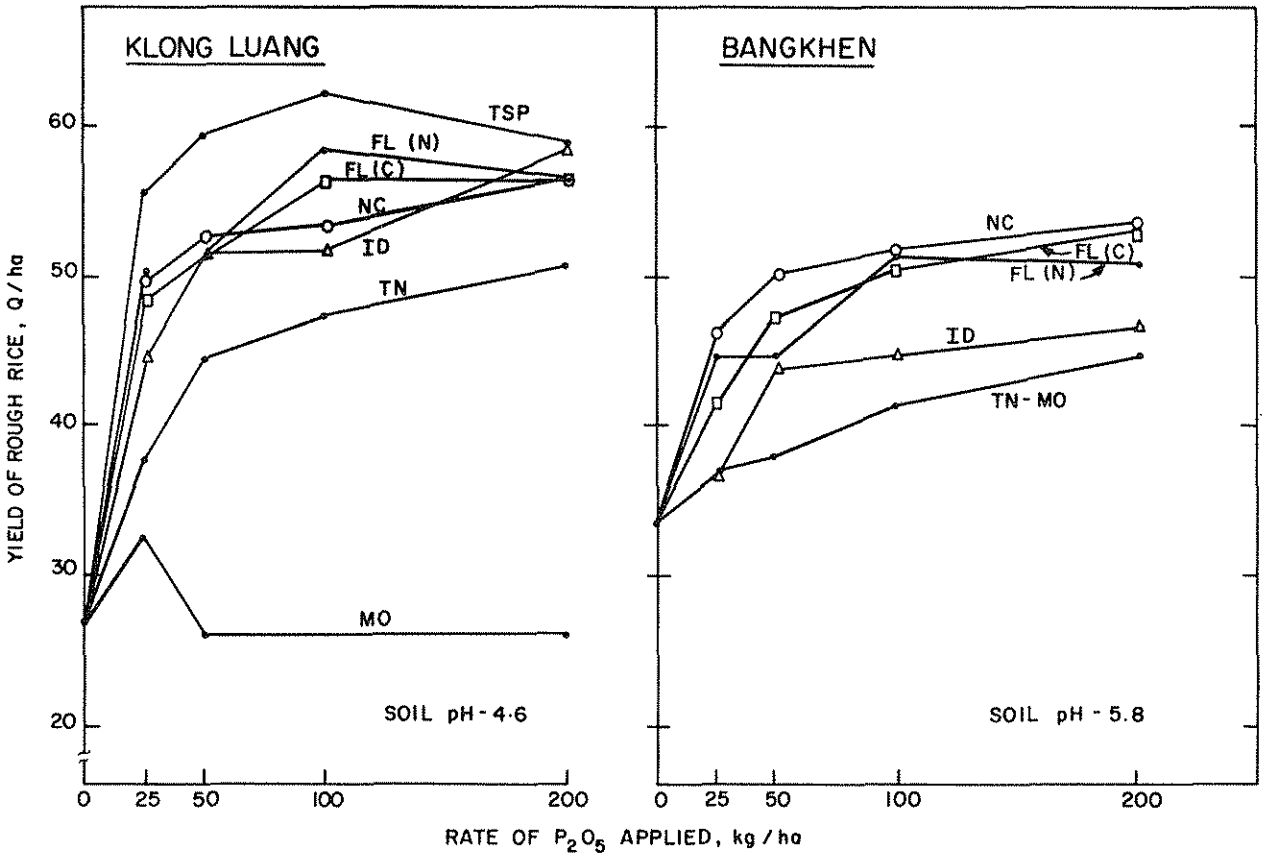

Figure 3. Yield of Rough Rice at Two Locations in Thailand, as Affected by Source and Rate of P. From Engelstad, Aroon, and DeDatta (1974).

EXPERIMENTAL WORK IN THE UNITED KINGDOM ON THE AGRICULTURAL VALUE OF ROCK PHOSPHATES

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Introduction

Large numbers of field experiments have been made in Britain to examine the practical value of rock phosphates for applying directly to land. The work began in the last century, and some is still being done. As a result, we have good indications of the value of different kinds of phosphates and of the soils and crops for which they are useful. Much less research has been done in laboratory and greenhouse experiments to explain the mode of action of rock phosphates or to investigate some of the anomalous results that have been obtained. The investigations fall into three periods: (1) up to 1939, (2) 1941-57, and (3) since 1957. This paper summarizes the results of the three groups. Interest in rock phosphates is maintained in the United Kingdom: (1) because they supply P at smaller unit prices than processed phosphates and (2) since little good quality basic slag, traditionally used to improve acid grassland, is now available, rock phosphates are considered as a substitute.

Early Experiments

The earliest test of rock phosphate in the United Kingdom was made by J. B. Lawes at Rothamsted. His results on turnips in 1843, 135 years ago, were:

	t/ha
No phosphate	5.5
Rock phosphate	7.7
Rock phosphate treated with acid	17.1

Later experiments showed that rock phosphates must be carefully selected and be finely ground. Many comparisons of ground coprolites and apatites with the same materials dissolved in sulfuric acid were made in Scotland since 1970. For example, Hendrick

reported the results of 66 experiments on turnips in 1911-14:

	t/ha
No phosphate	35
Superphosphate	52
Ground north African phosphate	49

In experiments in northern Ireland, Gafsa phosphate gave yields of turnips nearly equal to those from superphosphate but was much less effective for potatoes. Nauru phosphate was much less effective than Gafsa phosphate. Other experiments in Britain during the 1920s and 1930s tested north African phosphates on turnips and grassland. The results of these, and of most other earlier work, were summarized by Russell (1929) who reported that rock phosphate was sometimes almost as good as highly soluble basic slag but was sometimes much inferior. No simple generalizations could account for this varying effectiveness. Russell said that rock phosphate acted best on acid soils, under high rainfall and for perennial crops--conclusions which are still valid! In 1939 about 10% of all the phosphate used in the United Kingdom was rock phosphate.

Coordinated Experiments in 1941-56

Several large series of experiments were begun in 1941 to test phosphate fertilizers which economized in sulfuric acid (which was in short supply during the 1939-45 war) or which needed no acid in manufacture. The work, which had the secondary purpose of improving the efficiency of phosphate fertilizers, continued until 1946. The second phase of the investigation began in 1950 as a result of the worldwide shortage of sulfur. Field experiments began in 1951 and were continued until 1956. During this period the main series which tested rock phosphates were:

Crop	No. of Field Experiments
Swedes	112
Kale	7
Grass	49
Potatoes	38

Full reports on the work on all rock phosphates were published by Cooke (1956) and Cooke and Widdowson (1959). In addition, large numbers of greenhouse experiments were made to screen new products, to investigate the effects of soil pH on phosphate availability, to compare the effects of different phosphates on many kinds of crops, and to investigate the effects of particle size and properties.

The field experiments included newly developed silicophosphates and nitrophosphates, dicalcium phosphate, superphosphate treated with basic materials (ammonia, lime, serpentine), basic slags, and calcium metaphosphates. In the first series several kinds of ground rock phosphates were tested, as were mixtures of rock phosphate and superphosphate. In the later series, only Gafsa phosphate was tested. The work done on rock phosphates up to 1954 was summarized by Cooke (1956a); this paper included the important results of greenhouse experiments which (1) tested all the rocks for which large samples were available in England in the 1940s, (2) showed how soil pH governed availability, (3) compared coarse and fine materials, (4) compared crops, and (5) investigated rate of action of rock phosphates. The summary of the paper is repeated below.

Summary

In field experiments Gafsa, Curacao, and Morocco rock phosphates were more effective than Florida pebble phosphate. For swedes and turnips Gafsa phosphate was nearly equivalent to superphosphate on soils with pH values below 6.5; for potatoes and for grassland Gafsa phosphate was only one-third as effective as superphosphate, even on acid soils. In both pot and field experiments rock phosphates were almost useless on neutral and alkaline soils.

A number of different crops were grown in a pot experiment. Morocco phosphate was equivalent to superphosphate for radish; for swedes, rape, and buckwheat it was about half as effective. For mustard, clover, ryegrass, timothy, wheat, barley, rye, and lettuce Morocco phosphate was of little use.

Rock phosphates from a number of countries were tested in pot experiments on radish. Materials from Morocco, Algeria, Java, Egypt, and Curacao were a little less effective than that from Gafsa. Nauru Island phosphate was much less effective than Gafsa phosphate. Florida pebble phosphate, phosphatic chalk from Taplow (Berks.), and phosphates from Nigeria, Christmas Island, Kola (U.S.S.R.), Uganda, and Rhodesia were of very little use when applied to radishes grown in acid soils.

Field and pot experiments failed to provide any consistent evidence that rock phosphates should be ground more finely than is customary (80% to 90% passing the 100-mesh B.S. sieve).

Rock phosphates acted more slowly than superphosphate in pot experiments on radishes; their efficiencies tended to increase as the experiments were continued. The solubilities of rock phosphates were not appreciably increased by 'composting' under acid conditions with wheat chaff in laboratory and pot experiments.

The results from the field experiments are summarized by giving below the conclusions and summaries from the two papers published in 1956 and 1959.

From Cooke (1956b)

Discussion

(i) Rock phosphates

In swede experiments carried out in 1941-2 Gafsa phosphate was roughly three-quarters as efficient as super-phosphate on very acid soils but in a few later experiments it was rather less effective. Curacao phosphate and Gafsa phosphate behaved similarly for swedes and for reseeded grass in 1941-2. Florida rock phosphate was tested for both crops in 1941 and was of so little value that it was not used in later years. Very few swede experi-

ments tested both Gafsa and Morocco phosphates but in parallel experiments the two materials behaved similarly. Morocco phosphate was slightly inferior to Gafsa phosphate for establishing grass.

In recent field experiments carried out from 1951 to 1953 Gafsa phosphate was nearly as effective as superphosphate for swedes grown on soils having pH values below 6.5. Swedes are now mainly restricted to the north and west of the United Kingdom where most of the soils are acid and the rainfall is often high, in these areas swedes could receive Gafsa rock phosphate instead of superphosphate. Ground rock phosphate is generally much cheaper (per unit of P_2O_5) than superphosphate. Comparisons of rock phosphate and superphosphate for other fodder crops and for grass are needed to determine how far this cheap material can be used to replace more expensive fertilizers.

Ground rock phosphate was useless for potatoes grown on neutral soils; even on acid soils Gafsa phosphate produced yields equivalent to those given by only one-third as much phosphorus applied as superphosphate.

Mixtures of superphosphate with rock phosphate were tested from 1943-6 and gave disappointing results. The 'Semsol'-type mixture, made with cold superphosphate, was satisfactory for swedes grown on very acid soils; for potatoes it was only half as efficient as superphosphate and the mineral phosphate component of the mixture appeared to have little value. A mixture of rock phosphate with hot superphosphate was compared with Morocco phosphate (from which it was made) in a few swede experiments; the mixture was less effective than rock phosphate alone, suggesting that secondary reactions gave products which were less soluble than the untreated apatite. Cold mixtures of superphosphate and mineral phosphate have no special

advantage, for crops where they are useful, rock phosphate alone is almost as good, for other crops and on neutral soils the mineral phosphate cannot be regarded as more than a diluent. The hot ('Kotka' type) mixture is an example of an under-acidulated superphosphate; if sulphuric acid supplies are restricted it is more satisfactory to use the quantities available to make reduced amounts of normal superphosphate. The deficiency in supplies of superphosphate must be covered by reducing rates of dressing and by using rock phosphate directly on the soils and crops for which it is suitable.

For grassland sown in wet areas on acid soils rock phosphate may form the bulk of the phosphate manuring provided that a little readily soluble phosphate is applied to the seedbed (or drilled with the seed) to secure satisfactory establishment. Rock phosphates were somewhat inferior to high-soluble basic slag for permanent grass but, if necessary, they could form the bulk of the phosphate applied in areas where soils are acid so that more quickly acting phosphate fertilizers could be reserved for arable crops.

A few of the war-time experiments suggested that it may not be necessary to grind rock phosphates intended for direct application very finely. Coarser grinding would allow greater output from the mills and should cheapen the cost of the phosphate.

Summary

The results of over 400 field experiments testing different kinds of phosphate fertilizers are summarized and are discussed with special reference to the reactions of the soils used. The classifications were: 'very acid' soils--pH below 5.5, 'acid soils'--pH 5.6 to 6.5, neutral soils--pH over 6.5. All comparisons are made in terms of

fertilizers supplying the same amounts of total phosphorus.

In war-time experiments Gafsa and Morocco rock phosphates were about two-thirds as efficient as superphosphate for swedes and turnips grown on very acid soils. In 1951-3 experiments on very acid and acid soils Gafsa phosphate was practically equivalent to superphosphate for swedes, but for potatoes it was as effective as only one-third as much phosphorus supplied as superphosphate; on neutral soils Gafsa phosphate was useless. For establishing grassland on acid soils Gafsa and Morocco phosphate were equivalent to about one-third as much phosphorus supplied as high-soluble basic slag. Rock phosphates were somewhat more effective for promoting growth of established grassland but they remained inferior to high-soluble basic slag. Rock phosphates were somewhat more effective for promoting growth of established grassland but they remained inferior to high-soluble basic slags and to superphosphate. Curacao rock phosphate was roughly equivalent to Gafsa phosphate for swedes and grass. Florida pebble phosphate was much less effective and was judged unsuitable for direct application. Mixtures of rock phosphate with superphosphate were not more efficient than equivalent amounts of the separate components used correctly."

In the 1941-46 experiments "coarse" and "fine" grinding refer to materials of which 60% and 80%, respectively, passed a 100-mesh B.S. sieve.

From Cooke and Widdowson (1959)

Gafsa Rock Phosphate

In giving practical advice on the use of Gafsa phosphate the low unit price of rock phosphate relative to superphosphate should be taken into account. Both coarse and finely ground Gafsa phosphates gave yields of swedes and kale similar to those given by two-thirds as much phosphorus applied as superphosphate. Since the cost of phosphorus in Gafsa phosphate is not more

than half the cost of phosphorus in superphosphate, Gafsa may be used with advantage for swedes and kale grown on acid soils.

For grassland both grindings of Gafsa phosphate were of very little value in the year of application. Before it can be effective, rock phosphate must be washed by rain through the mat of herbage to the soil surface so that it may react with the soil. Average dates for applying the fertilizers and cutting the grass were the end of March and end of June, respectively, and it is not surprising that the rock phosphates were not as effective as superphosphate. The few experiments which were continued to measure residual effects showed that on acid soils Gafsa phosphate was as effective as superphosphate in the second year. Only four experiments on neutral soils were continued for a second year and in these Gafsa phosphate had very little immediate or residual value. Rock phosphates should not be condemned as grassland fertilizers from these experiments, since under the conditions of the work the Gafsa phosphate did not have sufficient time to react with the soil. In future investigations the fertilizers should be applied in autumn or early winter so that the dressings may be washed down to the soil surface well before growth starts in spring. Gafsa rock phosphate may prove to be quite a suitable fertilizer for grassland on acid soils in wet areas if it is assessed over a run of seasons following application.

The two grindings of Gafsa phosphate gave very similar yields on average of all experiments on each crop. On the basis of these experiments as a whole there is no justification for the extra cost of grinding rock phosphate intended for direct application more finely than is customary. In a few experiments, however, there were significant gains from fine grinding. Further comparisons of normally ground (100-mesh) rock phosphate with finer (300-mesh) material are needed to determine

whether there are conditions of soil, climate, and cropping where the finer phosphate is superior.

Armiger & Fried (1958) investigated the effect of particle size on the fertilizer value of a number of rock phosphates mined from North Africa and North America. In general, fine grinding was not as important as the nature and origin of the phosphates tested in determining their agricultural value. Rocks ground so that all passed a 325-mesh sieve were rather more effective than much coarser materials, but batches ground so that all passed the 100-mesh sieve were only a little less efficient than finer batches which passed the 325-mesh sieve. The slight superiority of fine rock phosphate in this American work is in agreement with the results of some of the experiments reported here.

Summary

The results of about ninety field experiments carried out over three years to test dicalcium phosphate, nitrophosphate, ammoniated fertilizer and Gafsa rock phosphate are summarized and discussed. Soils with pH values of 6.5 and below are listed as 'acid', those with higher pH values as 'neutral'. All comparisons were made in terms of fertilizers supplying the same total amounts of phosphorus.

Gafsa rock phosphate used on acid soils gave yields of swedes and kale similar to those given by two-thirds as much phosphorus applied as superphosphate. Rock phosphate had little effect on the yield of grass cut three months after the fertilizer was applied even on acid soils; superphosphate applied at the same time increased yields. A few grass experiments on acid soils were continued to measure residual effects; in the second year after application Gafsa phosphate was as effective as superphosphate. Gafsa was of very little immediate or residual value for grass

grown on neutral soils. Rock phosphates are cheap fertilizers and are suitable for certain crops grown on acid soils in wet areas, they may also be suitable for grassland in these areas if their effects are assessed over a run of seasons following the application. Gafsa phosphate ground to pass a 300-mesh sieve gave average yields of swedes, kale and grass similar to those given by coarser materials of which 50-80% passed the 100-mesh sieve. For the experiments as a whole there was no general justification for grinding rock phosphate more finely than is customary; in a few individual experiments however there were significant gains from fine grinding.

In each year the 'coarse' and 'fine' samples of Gafsa phosphate were prepared from a single batch of imported rock. In 1954 and 1955 the 'coarse' material was ground to the fineness customary for rock phosphate intended for superphosphate-making (about half passing the 100-mesh B.S. sieve); in 1956 nearly 90% of the material used passed this sieve). The 'fine' rock phosphate was prepared by further grinding and in each year practically all passed the 300-mesh B.S. sieve.

Experiments in Scotland

Related experiments made by the Macaulay Institute for Soil Research were described by Williams and Reith (1948). The conclusions drawn on the value of rock phosphates were similar to those recorded above.

Recent Experiments (1950-77)

Residual Effects in Long-Term Experiments

A weakness of most of the work described in Parts I and II was that residual effects were not measured accurately. Most of the experiments were only planned to last for 1 year. Small dressings were tested so that immediate comparisons could be made on

the sensitive part of the response curve; the residual effects of these amounts (125 kg P_2O_5/ha or less) were too small to be measured accurately in later years. For these reasons other experiments were designed to measure long-term effects which are particularly important where slow-acting insoluble fertilizers like rock phosphate must react with soil before crops can use them.

Experiments at Rothamsted

Crowther (1946) reported a rotation experiment which began on slightly calcareous soil at Rothamsted in 1930 and continued to measure direct and residual effects of superphosphate and Gafsa rock phosphate on potatoes, barley, ryegrass, and wheat. The rock phosphate had no value for any of the crops even after being in the soil for several years.

Mattingly (1968) described the results of two rotation experiments at Rothamsted testing the residual value of nitrophosphates, potassium metaphosphate, basic slag, and Gafsa rock phosphate against the immediate and residual effects of dressings of superphosphate. Initial soil pH on the two sites was 5.1 and 4.8 (in 0.01 M $CaCl_2$ solution). Large dressings (165 kg P/ha) of the phosphates were applied in 1959 and were thoroughly mixed with the soil; their residual effects were compared from 1960 to 1965 with the direct and cumulative effects of smaller dressings of P as superphosphate applied annually; potatoes, barley and swedes were grown. In 1960 and 1961 rock phosphate residues were inferior to other phosphates, particularly for potatoes; in later years residues of the water-insoluble fertilizers were only slightly less effective than residues of superphosphate. Average residual values calculated from yield responses, P uptake, and soil analyses were: superphosphate 100; nitrophosphates, 100-102; potassium metaphosphate, 95; basic slag, 94; Gafsa phosphate, 92.

Experiments by National Agricultural Advisory Service (NAAS) and by Agricultural Development and Advisory Service (ADAS)

Arable Crops--Six long-term rotation experiments were started by NAAS on Experimental Husbandry

Farms during 1951-53; reports on the results have been made by Patterson and Williams (1962); by Williams, Farrar and Boyd (1971); and by Boyd, Williams, and Forbes (1972). Soil pH ranged from 5.5 (Trawscoed, Wales) to 7.9 (calcareous soil on Bridgets in Hampshire), and annual rainfall ranged from 1,150 mm (Trawscoed) to 550 mm (Boxworth, Cambridgeshire). Four crops were grown each year, and all experiments tested superphosphate, Gafsa phosphate, basic slag, and dicalcium phosphate dihydrate. These and other experiments discussed in this section supplement our limited information on long-term residual values.

Williams, Boyd, and Farrar (1971) reported on results up to 1964 (when totals of the mean dressings applied were 326 and 652 kg/ha P_2O_5). Trawscoed soil was very poor in soluble P, and rock phosphate was as effective in the first year as superphosphate for swedes. This soil "fixed" phosphate more severely than other soils, and the residues of Gafsa phosphate were superior to residues of the other forms for potatoes, barley, and swedes. On two calcareous soils (pH 7.7, 7.9) rock phosphate had little or no direct or residual value. At Gleadthorpe Farm (pH 6.7) and Boxworth (pH 7.4) residues of rock phosphate were as effective as superphosphate residues for potatoes and barley. At Rosemaund (pH 5.9) rock phosphate residues were more effective than superphosphate for kale but had little value for potatoes and barley. No explanation could be given for the value of residues of rock phosphate on slightly calcareous Boxworth soil or for their failure to be useful for two crops on acid soil at Rosemaund Farm.

A later report on these experiments by Boyd et al. (1972) described tests of fresh fertilizer made in 1967 to value the residues of dressings applied from 1951 to 1964 which had totaled 0.32 and 0.65 t/ha. The crops were potatoes (High Mowthorpe and Trawscoed) or kale (Bridgets and Rosemaund). At Rosemaund (pH 5.9) and High Mowthorpe (pH 7.7) dicalcium phosphate residues gave best yields, and rock phosphate was poorest. At Trawscoed rock phosphate residues were as effective for potatoes as residues of any other form.

One quarter of each of four of the experiments was continued until 1971 when the total amounts applied had become 0.0, 0.5, and 1.0 t/ha of P_2O_5. Sparrow and Russell (1977) reported the last work done on these sites in 1973 to value residues. Potatoes were grown and the residues in the soil were compared with fresh dressings of superphosphate supplying 37.5 and 75.0 kg P_2O_5/ha. On the three sites having soils with pH 6.7, 7.7, and 7.9, rock phosphate residues were quite inactive and had no value even after 20 years; the other phosphates had similar residual effects. On the fourth site (Rosemaund Farm) on soil with pH 5.9, rock phosphate had left sufficient soluble P in the soil for full yield without fresh phosphate; its residual effect was superior to those from superphosphate or dicalcium phosphate.

Grassland--Mair (1962) described an experiment on permanent grassland where Gafsa phosphate (29% P_2O_5, 80% through 100-mesh sieve) was applied for 6 consecutive years and was tested against basic slag and superphosphate. The pH of the soil was 5.3 when the experiment began, but the soil was limed when the fertilizers were applied. Basic slag was equivalent to superphosphate for raising yield and for promoting P uptake by herbage. Even after 8 years rock phosphate had no effect on herbage yields, and it was less effective than superphosphate in raising herbage uptake of P. It seems that the initial liming inactivated the rock phosphate although the soil was initially very acid and the rainfall was high.

Archer (1978) reported more recent experiments on eight sites on permanent grassland. Superphosphate was applied at 81 and 162 kg P/ha. Basic slag and coarse and fine (150μ and 40μ) Gafsa rock phosphate were tested at the lower rate. Soil pH ranged from 4.6 to 6.3. In the first season after application rock phosphate was inferior to soluble phosphate; measurements were continued for six more seasons and rock phosphate increased in value. Rock was most effective where soils were very acid at the time the phosphate was applied; it was less useful when soil pH was greater than about pH 6.0 or where lime had recently been applied. On these latter sites it tended to become more effective with time. Low soil pH appeared to be more important than high rainfall in securing high efficiency

for rock phosphate. In general, Gafsa phosphate was rated as a satisfactory source of P for grassland with soil pH below 6.0; it was much less efficient and slower acting on soils with higher pHs or where lime had been applied. Fine grinding (to 300-mesh [50μ]) was not worthwhile.

Work At Levington

Devine, Gunary, and Larsen (1968) investigated residual effects by pot experiments 3 years after mixing soil and rock phosphate. On calcareous soils ground north African phosphate was inert even after 3 years. On soils with pH 5.7-6.5 rock phosphate dissolved too slowly and was not as effective as residues from superphosphate or basic slag. With soil of pH 4.7, rock phosphate dissolved quickly and left residues superior to those from superphosphate or basic slag.

Recent Annual Experiments on Swedes Made by ADAS

Jones (1975) described eleven annual experiments made from 1966 to 1971; swedes were grown in Wales in a high rainfall area (1,200-1,500 mm) on acid soils (pH 5.6-6.9).

The phosphates were tested at 28 and 56 or 44 and 88 kg P/ha. On some sites Gafsa phosphate was equivalent to the same amount of P supplied as basic slag or superphosphate; at other sites Gafsa phosphate was much less useful. Jones commented that inconsistent results detracted from the overall usefulness of rock phosphate. There was no advantage from "fine" (80% through 300-mesh [50μ] sieve) over "coarse" (60% through 100-mesh [150μ] sieve). In seven of the experiments Moroccan phosphate was tested and found to be inferior to material from Gafsa.

Finely Ground Rock Phosphates in Scotland

Williams and Reith (1973) reported briefly experiments where four rock phosphates were ground to 10 μm and to less than 1 μm and were compared with the same materials in the "normal" (50-150 μm) size range. In pot experiments on oats in acid soil,

fine grinding improved the effectiveness of Gafsa phosphate, but less available rock phosphates were not greatly improved. Including 10% of sulfur further improved the fine Gafsa so that in several tests the 1-μm product was as good as soluble phosphate. Irrespective of particle size, effectiveness depended on soil pH. In field experiments on potatoes and swedes the effects of fine grinding and of added sulfur "were generally smaller and often inconclusive." For potatoes fine grinding improved the effect of the rock phosphates, but they were still inferior to soluble phosphate. Results with swedes were more variable, but Gafsa products "were occasionally comparable with soluble phosphate especially on the basis of phosphorus uptake."

Leaching of Phosphates

Phosphate fertilizers are not readily leached from soils with more than a few percent of clay, but they are lost from sandy soils nearly devoid of clay and from peats containing little mineral material.

Mattingly (1970) described pot and laboratory work to measure the fate of P fertilizers applied at 3.6 g P/m^2 for each of 6 years to a sandy Podzol. Residues of basic slag, Gafsa phosphate, and superphosphate were equivalent in the first years. The experiment was then continued for 8 more years, applying 9-11 g P/m^2 annually; basic slag and Gafsa phosphate then gave larger labile P values which were more effective for ryegrass in pot experiments than superphosphate did. The percentages of the applied P recovered from the surface soils were respectively 7%, 40%, and 65% of the totals applied as superphosphate, basic slag, and Gafsa in the 8 years. Residues of basic slag were in the <20-μ fraction of soil, rock phosphate was retained in the sand fraction (20μ to 200μ), 90% of the P in superphosphate had leached from the surface soil, and 60%-70% of the P in basic slag was leached and only 50% of that in rock phosphate.

Experiments on acid blanket peats in Northern Ireland (McConaghy et al., 1971) showed that less phosphate was leached when rock phosphate was used than when superphosphate was applied.

Experiments on Phosphal

Phosphal is a heat-treated aluminum phosphate from west Africa. Ryan, Smillie, and McAleese (1973) reported the results of a pot experiment made in Ireland testing this material on six soils (pH 4.2-7.4) for Italian ryegrass. Superphosphate was generally superior to basic slag and this, in turn, was superior to phosphal. On average phosphal had only one-third of the efficiency of superphosphate; it tended to be superior to basic slag on soils with high pH.

ADAS is doing experiments on a product of this type, and Davies (1977) has reported that calcined calcium aluminum phosphate was of very little use.

Mixtures of Rock Phosphate with Basic Slag

Because basic slag of traditional type and of high solubility in citric acid solution is no longer made by the British steel industry, replacements are needed for acid grassland. Mixtures of lower grade basic slags with Moroccan rock phosphate are therefore being tested (Davies, 1977). Mixtures of "super slag" (with 80%-85% of basic slag with 9%-12% P_2O_5) behave as the basic slag from which they are made. "Phosphated slag" ("Europhos") is made from very low-grade (2% P_2O_5) basic slag with Gafsa or Moroccan rock phosphate; it behaves as straight rock phosphate being useless on soils containing free lime and, even on acid soils, being less efficient than superphosphate for swedes.

Mode of Action of Rock Phosphates

Relatively little work has been done in the United Kingdom on the ways in which rock phosphates interact with soil and with plant roots and on the uptake of the phosphate ions released. There are many "openended" questions which need more research.

Mattingly and Widdowson (1956) showed that rock phosphates often have a higher value, relative to superphosphate, when assessed by amount of P taken up by the crop rather than by yield of dry matter.

They suggested that this was because the phosphate potential in the soil around particles of rock phosphate is higher in the later stages of growth than around superphosphate particles because diffusion away from the particles of rock is slower. In the later stages phosphate may be taken up preferentially from these zones of high potential.

The behavior of rock phosphates in certain calcareous soils is a related question. Although the evidence from pot experiments and the vast majority of field experiments is overwhelming--rock phosphates being practically useless on calcareous soils--there are a few experiments in the series reported earlier in this paper when rock phosphate was active in soils containing free calcium carbonate. Edwards (1956) reported two experiments on soils containing 4.3% and 5.5% $CaCO_3$ where rock phosphate increased yields of brassicae crops. Whether such effects are due to the presence of acid pockets in a soil containing fragments of hard limestone which dissolve slowly is not known.

Similarly, little has been done to determine the effects of soil factors other than pH on the availability of rock phosphate. The possible role of organic matter has received little attention in Britain. Wilkinson (1960) has suggested that soil temperature is an important factor; he considered that rock phosphate was more active in the west and south where soil temperatures in spring are higher than in the northeast. Soils which warm up quickly because they are well drained, are sandy in texture, or have dark colors may enhance the activity of rock.

Conclusions

Types of Rock Phosphate

Of the types tested in the U.K. experiments, only rocks from north Africa and Curacao are active enough to merit use for direct application. Gafsa (Tunis) phosphate has proved the best of the north African materials.

Climate

In the U.K. rock phosphates have been most effective in wetter areas (but these also have more

acid soils). There have been suggestions that they are more effective in areas where soils are warmer in winter and spring than in colder areas.

Mixtures

There is no good reason for making mixtures of rock phosphate with other, more soluble, phosphates. Each type should be applied for the purposes for which it is most suitable.

Potential for Rock Phosphates in Britain

Arable Land--There is no potential use for rock phosphates over most of the arable areas of England. Cash crops sensitive to soil acidity (notably sugar beet and barley) are widely grown, and soils are limed to maintain them near pH 7. Farming in these areas is intensive, and high yields are needed to repay large costs. Soil phosphate is maintained above the level at which large responses are likely, and farmers cannot afford the risk of yield losses caused by inadequate levels of soil P or by fertilizer phosphate which may be uncertain in action.

There is more potential for rock phosphate in the west and north, and particularly in Scotland, where arable land is used for animal feed crops (notably kale, swedes, turnips) and many soils are acid.

Grassland--The results of a random survey of soil pH values in England and Wales, made by ADAS, are summarized below.

	pH 5.9 and below	pH 6-6.9	pH 7 and over
	- - - Percentage of all fields- - -		
Arable land	7	29	65
Grass-arable (rotations)	17	42	41
Grassland	33	55	13

While very little arable land has soil below pH 6, a third of the grassland is acid, and good quality

rock phosphate may be a suitable fertilizer. Unfortunately, there are no corresponding soil pH data for Scotland. In addition, the United Kingdom has 6 million ha of rough grazing, some of which is suitable for improvement, and rock phosphate could be used to maintain better grass on this land.

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VIEWPOINTS ON THE UTILIZATION OF ROCK PHOSPHATE FOR DIRECT APPLICATION

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Introduction

This subject, dealing with the application of phosphate rock as a fertilizer, will be discussed and outlined in relation to the agricultural situation in the Federal Republic of Germany at present. A short outlook at the near future development of this product within the phosphate fertilizer market (straight and compound fertilizers) will be attempted.

Phosphate rock (phosphorite) as an important raw material for the production of P-fertilizers has been utilized in Europe since about 1840. It was applied directly and successfully in the twentieth century, especially as a typical fertilizer for acid peaty soils.

The phosphate rocks used were in the form of cryptocrystalline lattice-structure of apatite and were rich in the content of active lime. This natural product, when used for the above-mentioned soils, increased the yield of the crop very distinctly and was economical because of its low price.

As peaty soils in the German agriculture only represent a small part of the total acreage, the amount of this fertilizer for consumption was negligible.

Development in the Utilization of Ground Phosphate Rock During the Last 25 Years

During the early 1950s, phosphate rock was officially registered under the name of "Hyperphosphate" as a special fertilizer for peaty and acid humic soils as well as grassland. Some years later, after it was proven in numerous field experiments, hyperphosphate was also admitted for use on acid mineral soils. In 1962 the Fertilizer Regulations Act was passed, and this fertilizer was listed in the Schedules to the Regula-

tions as a special type of P-fertilizer with the following criteria:

(a) Satisfactory fineness exists when 100% of the product passes through a standard sieve of 0.125-mm mesh width;

(b) At least 90% must pass through a standard sieve of 0.063-mm mesh width;

(c) At least 65% of the total P-amount should be soluble in 2% formic acid;

(d) The fertilizer should be evaluated on the basis of total P-units.

The consumption rate for finely ground phosphate fertilizers was not more than 2%.

This percentage--annual fluctuations not being considered--has changed little since then. There was an augmentation due to a steady increase in the fertilizing rates per unit of area (table 1).

The main reasons for the small role of the ground phosphate rock before World War II may be explained due to its unsatisfactory effects on the growth of the plants as compared with those phosphates which were thermally or chemically processed and highly soluble such as Rhenania and superphosphate and also because of the strong position held by basic slag (Thomas phosphate) in the German fertilizer market.

In 1949-50 the phosphate consumption for agricultural purposes was 60% Thomas phosphate, 15% superphosphate, and 11% Rhenania phosphate. About 10% of phosphate consumption was as compound fertilizers, mainly NPK, and only the very small remainder was phosphate rock.

Its preferable use on acid, peaty soils is based on humic and fulvic acids, which attack the apatites and make them more soluble and available for the plant root. In addition to this, its inexpensive price was an attractive factor for applying this kind of fertilizer. On the other hand, many results of field experiments on most of the cropped soils did not justify the utilization of phosphate rock because of the low P-status of the soils.

The soluble phosphates, processed by thermal or chemical reactions, as well as the basic slag offered more chances (even at pretime application in autumn or winter) to satisfy the demand of the plants, especially cereals and root crops.

In order to feed both the unsaturated soil and the crop, relatively high dressings of soluble phosphates have been applied--normally 1.5-2.5 fold of the P-amount removed by cropping. As a consequence the P-status of the soil was continuously rising.

At present, this process in most German agricultural and horticultural soils has reached such a level that a further augmentation of available P reserves seems not to be very profitable (table 2).

Due to this high level of available phosphorus in many soils, the utilization of finely ground phosphate rock for direct application, as a base dressing in autumn or winter, became attractive for more farmers because the price per unit P_2O_5 was relatively low (table 3).

In the early 1960s there was a high increase in the rate of labor costs, bringing forth the idea of recommending phosphate dressings in advance for several years. This policy, followed by many farmers, was responsible for a remarkable increase in phosphate rock consumption because the price was still low.

By this, the high-soluble phosphates were losing part of the straight fertilizer market and the position as soil-improving substances. Superphosphate was utilized more for the production of compound fertilizers, mainly NPK. Rhenania phosphate was combined with potash and entered the market as PK fertilizer with increasing success (table 4).

In accordance with these changes in the pattern of the phosphates used, the market was opened to new phosphorus products: the partly wet-processed (underacidulated) phosphates such as Novaphos, Carolon phosphate, and others.

In these fertilizers the slow-releasing effect of the ground phosphate rock was combined with the high solubility of superphosphate. The result was consider-

able savings in sulfuric acid and in the costs of chemical processing, thus making these fertilizers profitable for use.

The consumption of ground phosphate rock also has risen due to a continuous reduction in the offer of basic slag caused by a fundamental change in the iron ore smelting process with the consequence that more and more iron ore poor in phosphorus is preferred by the steel industry (table 5). Thus, the market was open for other commercial phosphates as substitutes, especially for those having properties and behaviors similar to Thomas phosphate as a slow-release fertilizer, applicable in the autumn and winter and also in advance for several years.

The decrease in the production of basic slag as a percentage of straight phosphates and compound PK fertilizers in the consumption of phosphorus since 1960 is shown in table 6.

Despite the steadily decreasing trends in the use of straight phosphates and PK fertilizers together, the PK fertilizers, the ground rock phosphates, and the underacidulated phosphates have received preference by the declining offer of basic slag. The negative effect resulting from the drastically raised prices for oil and important raw materials in 1974 (phosphate consumption dropped from 916,740 tons in 1973-74 to 779,684 tons in 1975-76) did not cause a real proportional change between the various phosphates within the N-free group; the reduced production of basic slag was the more limiting factor.

In 1973-74 Thomas phosphate still held 44.3% of the P fertilizer market without N, followed by PK fertilizers. Two years later this position was lost to the PK chemicals. Up to now there has been no change in this tendency.

In this process of substitution finely ground phosphate rock played a role of straight fertilizer as well as complex fertilizer (by mixing with potash).

Another considerable part of the market went over to triple phosphate which was imported from the United States, countries of the "Eastern block," and others. This highly concentrated P fertilizer, produced by the

phosphoric acid treatment of phosphate rock, was offered at a very low price, which was caused by economical difficulties (loss of purchasing power) in other foreign markets.

Viewpoints on the Further Development in the Utilization of Phosphate Rock for Direct Application in German Agriculture

At present it is very difficult to forecast any tendency in the change of the fertilizer market especially dealing with phosphates among which the competition between the producers and the dealers is very strong. Price and effectiveness of the various phosphates with respect to the already reached P-status of the soil are considered and compared by the farmer more thoroughly than before.

From the viewpoint of the plant producer two important considerations may mark future development. First, amount of phosphate used per unit area, as a consequence of the already reached high P-status in most of the agricultural soils in the Federal Republic of Germany, needs an adjustment. Because such soils are replenished satisfactorily with available P-reserves, as shown by the standard extraction methods (table 2), the real demand for additional dressings will be determined mainly by the growth and yield of the crop (Hagin, 1961).

As a result of these findings, the annual dressings of phosphate per unit area should not be increased further. This is already a fact in the Federal Republic of Germany.

Second, with the increasing yield based on the high-yielding potential of present cultivated crops, the demand of the plant must be satisfied by considerable amounts of available nutrients during its main growth period. Because protein synthesis is a fundamental process in the formation of the yield, much phosphorus is needed, especially in strong connection with the other major nutrient, nitrogen. Therefore, the combination of both in compound/complex fertilizers such as NP or NPK will cause further progress in the near future.

The farmer of today is more interested in feeding the plant instead of the soil on which he has operated for many decades when large amounts of phosphate were cheap. Under those conditions, dressings of phosphate and potash during autumn or winter have been the normal procedure in the past when the yield was relatively low. Now the farmer is confronted with very high demands for the high-yielding varieties for plant food. Therefore, time of application must be shifted to the beginning of the growth period in the spring. Mid-season dressings by splitting or foliar application may be more interesting for the future (Welte, 1978).

For these reasons, the amount of major nutrients needed can no longer be calculated only on the basis of the total quantity for the expected yield; additionally, the daily rate of uptake becomes more important (figure 1).

High-yielding varieties need much more plant food within the same growth period as compared with a low-yielding level one. Therefore, high flow rates of available phosphorus in the soil must be secured during the growing season (Welte, 1973). The fast-growing plant needs phosphorus in combination with nitrogen which is the real driving power for growth and yield and by this an eminent regulator for the P-uptake. The higher the net production of assimilates is, the more important are a sufficient offer of available phosphorus in the soil and the procedure to protect fertilizer phosphorus from being fixed or strongly absorbed by the soil.

The increase in the consumption of N-containing phosphates as NP or NPK fertilizers is not only a result of economical techniques and processing or savings in labor costs (distribution, transport, application, etc.) but also a result of the enormous demand of the high-yielding varieties during a very short period.

Despite this distinct shift in tendency of phosphorus toward nitrogen, as is shown by the increasing production of NP and NPK fertilizers, the P-status of the enriched soils should not be neglected. In order to keep an adequate P-level, after-season applications of phosphate may still be an economical procedure beside the necessary offer of available P together with N at the beginning of the growth. Only where erosion may occur should soils not be fertilized when they are un-

covered in order to protect the natural waters against additional eutrophication of agricultural origin.

With respect to price per unit of P_2O_5, finely ground phosphate rock along with basic slag is very well qualified to provide the soil with phosphate during the nongrowing season. Only on soils where Ca-dynamic prevails or free lime exists should the thermally or chemically processed soluble phosphates be preferred.

Even after the rise in prices for oil and phosphate rock in 1974, it is still favorable in comparison with other commercial P-fertilizers as shown in table 7.

To take advantage of the price situation, the general policy for using phosphate rock must agree with favorable climate conditions and good soil properties in order to get the same effectiveness as with the use of thermally or chemically processed phosphates. This requires the utilization of scientific results and practical experiences with phosphate rock under various ecological conditions (Laske, 1956a; Laske, 1956b; Amberger, 1957; Selke, 1964; and Vetter, 1976).

The main viewpoints which should be considered by the extension service may be pointed out as follows:

1. Solubility and solubilization of phosphate rock--Despite the standard methods for the evaluation of phosphate rock, there still exists a wide range in the properties of solubility and solubilization in the materials originating from various natural sources (Hofmann and Mager, 1952; Gisiger and Pulver, 1953; Avnimelech, 1961; Timmermann, 1972; and Timmermann 1973). The variations in relation to effectiveness are caused often by a different crystal-lattice structure of the P-minerals, the proportion between the hydroxyapatite and the fluorapatite, and the structural integration of the accompanying $CaCO_3$.

   The raw material used by manufacturers is mostly Gafsa phosphate rock or a provenance of the same quality.

   For the evaluation of this rock material the analytical method of Hoffmann and Mager (1953) is best. Using 2% formic acid, the

first extraction will be followed by a second extraction of the insoluble remainder of the first.

Compared with the manifold reaction possibilities which the thermally and chemically processed phosphates are undergoing in the various soils, the change of the cryptocrystalline structure of the apatites in phosphate rock will be very low because of their equilibrium conditions in relation to the soil phosphates, especially within a pH range of 5.5-7.0. Under these conditions the solubility and-solubilization of phosphate rock will be positively influenced by an increasing H^+-potential and the concentration of chelating substances.

2. Influence of soil on the effectiveness of rock phosphate--The most important parameters in the soil, influencing the effectiveness of phosphate rock, are as follows: soil moisture, pH value, free $CaCO_3$, humus, biological activity, and the P-status of the soil.

Because the "product of solubility" of all kinds of apatites is very low, soil moisture has a strong influence. Increasing water content in soil enlarges the solution volume and thus improves conditions for the uptake of phosphorus by roots.

A good soil structure, which affords an optimal water-holding capacity and aeration, is a basic requirement for the storage of available plant precipitation. This exerts beneficial effects on the P-flux of slowly soluble phosphate rock.

The role of the pH in the solubility of apatites has been well known for many years. Soils with a high H^+-potential, such as acid-humic and acid-mineral soils, represent favorable prerequisites for an acid treatment of phosphate rock by nature. Therefore, in these cases phosphate rock will be more efficient than superphosphate.

Soils of neutral reaction often show good results also with phosphate rock if biological activity is high. A more or less high production of CO_2 originates from the respiration of microorganisms and roots. This accelerates the solubilization of cryptocrystalline apatites and/or tertiary Ca-phosphates, if present.

The humus of the soil exerts additional positive effects by solving reactions of hydroxy and carboxyl groups and also by chelating substances.

Only on those soils where the soil solution is rich in Ca-ions or free $CaCO_3$ prevails, does phosphate rock not react very effectively.

The high Ca-potential reduces the solubility, especially when CO_2 pressure is low as is often the case in cultivated fields. On the contrary, grassland, even when high in Ca potential, reacts more aggressively against phosphate rock by reason of strong CO_2 pressure in the rooted soil layers.

The higher the biological activity in soils of neutral or alkaline reaction and the more the content of convertible organic matter, the greater the probability that phosphate rock will show the same effectiveness as the highly soluble phosphates.

This phenomenon may be explained by very intensive metabolic processes in the soil as well as in the root with the result of a high production of CO_2, organic acids, chelates, etc., and the conversion of the phosphorus from mineral into organic compounds (nucleotides, phosphatides, phytates, etc.).

A further positive influence on the effectiveness of phosphate rock can be found on those soils which have been enriched by phosphate fertilization for many decades. This accumulating effect, based on the residues of the former applications, has considerably improved the P reserves and their availability for the roots.

The enrichment of P in the soil reduces the effectiveness of P dressings in the year of application as is shown in figure 2.

The increase of P reserves which have mobile and partly mobile character by enrichment procedures is responsible for a nearly instantaneous replacement of phosphate ions which have been taken up from the soil solution by the roots. In this way, the saturation value is always reached so that the plant is well provided with available phosphorus if soil moisture is sufficient.

The difference in solubility of finely ground phosphate rock and highly soluble P fertilizers, when both are applied as after-season dressings, does not play a role because of the high P status in the P-enriched soil.

The efficiency of this P-releasing system, therefore, cannot be distinctly improved by application of soluble phosphates because rock phosphate may give the same effect, especially in the biologically active soils (Cooke, 1961).

3. Disintegration power of the plant--It is well known that on grassland the conditions for all economical utilization of phosphate rocks are favorable. The main reasons for this have been mentioned (CO_2 concentration, organic acids, chelates, etc.). This ecological system, improving the solubility and solubilization processes, works particularly well if legumes and herbs play an essential part in the composition of the sward, realized mainly on meadow soils. Pastures, if wet enough, are also suitable for phosphate rock dressings. The effectiveness of the fertilizer can be increased by bursting the sward with a harrow in the spring.

Among the arable crops the legumes and also the crops of the brassica family (rape, mustard, etc.) are known for their capability to utilize the slowly soluble phosphate reserves of the soil much better than other crops. Intensity and depth of rooting are

further factors which influence the flow-rate of phosphorus in the soil.

Enrichment by plowing in phosphates may stimulate the penetration of roots into deeper layers by reasons of chemotactical reactions and improve the resistance against drought. Field experiments have shown that deep-rooting crops, such as sugar beet and lucerne, react in this manner. Ground phosphate rock is qualified for this kind of treatment.

An additional positive effect on the utilization of slowly soluble phosphates can also be obtained by combination with green manuring (Ramirez, 1977 and Mahdi, 1977). This helps in different ways. The crops--mainly grass-clover mixtures, rape, etc.--utilize the phosphate according to their very efficient disintegrating power, make the soil a better place for plants to grow, and supply the following crop with P by decomposition and mineralization of soil-borne organic matter. Also ground phosphate rock may be added to farmyard manure or other suitable organic wastes with a benefit to P-availability.

Finally, the influence of the mycorrhiza on the release of phosphorus from phosphate rock and other slowly soluble P sources should be mentioned. Fungi and actinomyces similar to bacteria are capable of utilizing such materials as have been found in many trials and experiments (Trolldenier, 1971). This holds true for microorganisms also which live in symbiosis with higher plants (ecto-trophic and endotrophic mycorrhiza). To be effective they must be sufficiently provided with carbohydrates by the roots which is only possible when the crop grows well and photosynthesis products are plenty.

Disintegration of minerals by mycorrhiza is a special reaction of biological activity and one of the many aspects of the geobiochemical weathering processes of rocks and minerals which occur in the soil.

As a final conclusion, it may be said that, above all, pH value, biological activity, and the P status of soil are the most important factors which decide the effectiveness of phosphate rock when the water regime is optimal. If soils are chosen with reference to these factors, there will still be a fair chance for finely ground phosphate rock in the market if the preference in price can be maintained.

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Table 1. Increase of P-Fertilizer Use Per Unit Area in the Federal Republic of Germany During the Last 25 Years

Year	Consumption	
	1,000 tons P_2O_5	kg P_2O_5/ha
1935-38	376	25.7
1949-50	342	24.2
1954-55	519	36.4
1959-60	730	50.9
1964-65	816	57.7
1969-70	857	62.9
1974-75	877	65.7

Table 2. Development of the P-Status on Agricultural Soils in the Federal Republic of Germany in Percent

Year	Quantity of Samples	Low	Satisfactory	High
1955-56	632,811	37.6	32.2	30.2
1960-61	564,723	24.0	33.0	43.0
1960[a]	518,353	19	30	51
1972	453,097	16	28.9	54
1975[b]	501,086	15.9	36.0	48.1

a. Change of evaluation scale by raising of the limiting values.
(After LUFA)

b. Change of methods.

Table 3. Average Prices for Phosphate Fertilizers Up to 1973-74 (DM/ton P_2O_5)[a]

Types of Fertilizers	1959-60	1964-65	1969-70	1971-72	1973-74
Superphosphate	826	826	890	931	1,175
Thomas phosphate	558	544	584	605	720
Rhenania phosphate	752	752	765	829	1,083
Finely ground rock phosphate	429	482	564	641	916

a. Before the rise in prices for oil and phosphate rock.
(After Stat. Bundesamt)

Table 4. Development of Compound Fertilizers in the Federal Republic of Germany Calculated on P_2O_5 Terms as Percent of Total Phosphate Consumption

	1949-50	1954-55	1959-60	1964-65	1969-70	1974-75
P_2O_5 in compound fertilizers	10.0	19.2	30.4	45.2	59.4	64.6

Table 5. Production of Thomas Phosphate (Basic Slag) in the Last 25 Years

	1,000 tons		1,000 tons
1951-52	1,630	1966-67	2,614
1956-57	2,524	1971	2,025
1961-62	3,366	1976	1,014

Table 6. Development of N-Free Phosphate Fertilizers (straight and PK) as Percent of the Phosphate Consumption in the Federal Republic of Germany Since 1960

Type of Fertilizer	1959-60	1966-67	1973-74	1976-77
P straight[a]	89.3	76.4	59.9	54.2
PK	10.7	23.6	40.1	45.8
Both types as percentage of total phosphate consumption	78.0	67.0	63.3	56.9

a. Superphosphate, Thomas phosphate, Rhenania phosphate, Rochling phosphate, finely ground rock phosphate, underacidulated rock phosphate.

Table 7. Prices of Phosphate Fertilizers in the Federal Republic of Germany in the Fertilizer Year 1977-78

(After Heller and Landmann)

Delivery: in bulk free station of destination[a]

Type of Fertilizer	Net Price[b] DM/kg P_2O_5 Time of Delivery (period) First Period	Last Period
Superphosphate (granulated, 18% P_2O_5)	1.217	1.358
Rhenania phosphate (finely granulated, 28%/30% P_2O_5)	1.158	1.328
Hyperphosphate (granulated, 26%/29% P_2O_5)	1.000	1.160
Basic slag (Thomas phosphate) (ground, 15% P_2O_5)	0.707	0.782
Freight additional f.i. for a distance of 100 km	+ 0.125	
300 km	+ 0.270	
500 km	+ 0.360	

For comparison: PK-Fertilizers

	DM/ton Extra Charge for Mixing[c] Included	
RHE-KA-PHOS (finely granulated, 15% P_2O_5/ 25% K_2O)	29.90 (1.76)	34.05 (1.53)
Hyperphos-Kali (granulated, 15% P_2O_5/25% K_2O)	28.30 (2.53)	32.80 (2.80)

a. Thomas phosphate + freight from basic station Volklingen/Saar.
b. Without sales tax (11%).
c. Calculated cost for mixing in ( ) on comparable basis of price for the single nutrient P_2O_5 or K_2O.

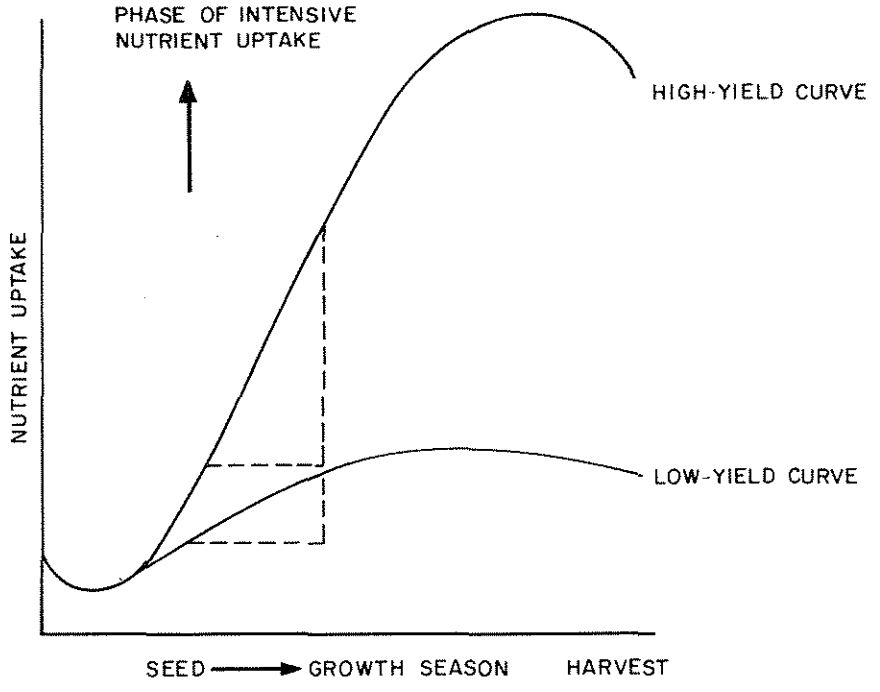

Figure 1. Nutrient Requirement as a Function of Time and Yield Level.

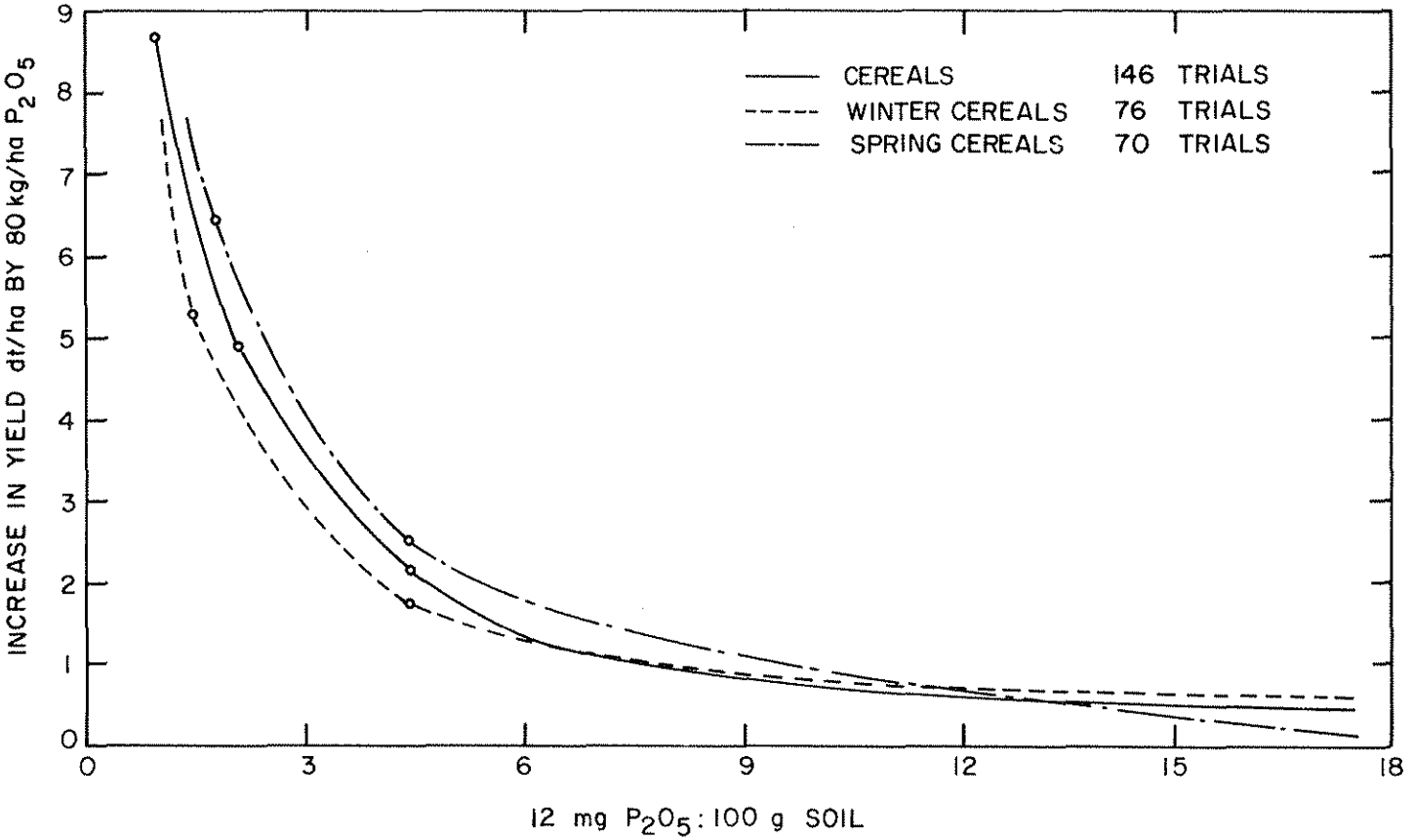

Figure 2. Relation Between the Effectiveness of P-Fertilizer Dressings and the P-Status of the Soil.

ROLE OF PHOSPHATE ROCKS IN THE PHOSPHATIC FERTILIZATION OF FRENCH SOILS

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Introduction

The presence of phosphatic iron ores in northeastern France, the deposits of which extend into Luxembourg, West Germany, and Belgium, provides these western European countries with an indigenous source of phosphatic fertilizers, that is, basic slags, a byproduct of the iron smelting industry.

For over one century industrial tradition has allowed the P fertilizer industry to hold an important part in supplying the national market, as the first French bone superphosphates were produced around 1860 and the first chemical superphosphates in 1876.

These two facts explain the minor role played by phosphate rocks in the phosphatic fertilization of French soils. Just before World War II, phosphate rocks accounted for 16% of the phosphorus applied to French soils. This percentage gradually decreased to 8% in 1972-73, the year preceding the world economic crisis which brought about a considerable increase in the cost of phosphate rocks and petroleum. This increase in cost led to social and economic upsets, especially in countries like France which did not have such raw materials.

Since this crisis, phosphate rocks have made up an increasingly larger role of French phosphatic fertilizer consumption and at present account for 12%-14%.

This recent relative increase observed in the use of phosphate rocks is undoubtedly linked to the depletion of slags, a result of the recession in the French iron smelting industry, as well as the reduction of imports of slags because of unfavorable prices. This partial substitution of slags by phosphate rocks appears very sensible since both types of fertilizers have similar preferred areas of

use on acid soils as deduced by the results of cultural experiments carried out in France for the last few decades and more recent results obtained in our pot trials.

Experimental Results

Pot trials are very suitable for studying relative efficiency of phosphatic fertilizers. They enable close control of both water and mineral (other than P) alimentation as well as the creation of well aerated growth media by using coarse particles and the settlement of root systems. By carrying out successive trials, the use of perennial grasses enables the kinetics of absorption and depletion of phosphate, provided by the soil and fertilizer, to be followed.

Experimental Procedure

Under these conditions, we have compared the relative efficiency of finely-ground north African phosphate (95% minus 0.063 mm-mesh size and formic acid solubility of 73.8%) with other forms of phosphatic fertilizers in five representative soils taken from the Massif Central. These five soils were:

- two calcimagnesimorphic soils--one a Rendzina and the other a calcareous clay soil; and
- three acid soils--a Brown soil, a leached Brown soil, and a humic andosoil.

Two levels of fertilizers were mixed in each soil: 100 and 200 ppm of phosphorus (200 and 400 ppm in the case of the andosoil because of its extremely high fixing capacity).

Immediately after mixing and after the addition of ^{32}P to the soils, a series of samples were used to grow Italian ryegrass until the phosphate of the medium was used up.

A second growth of Italian ryegrass was conducted 3 years later under the same conditions using another series of the same soil samples which had been submitted to thermal and aqueous cycles to bring on fertilizer aging.

From these treatments carried out twice each we determined:

- Phosphorus uptake by the ryegrass (including roots)
- Labile phosphorus or L value and for those samples which had been subjected to aging:
- "Assimilable" phosphorus in the soil, determined according to conventional French methods (Dyer method for acid soils, Joret-Hebert method for basic soil)
- Isotopically exchangeable phosphorus or E value
- Fractionation of phosphorus according to the Chang and Jackson method (only in the case of the most enriched soils).

Discussion

Despite the low number of replicates, the results are relatively meaningful both in the case of phosphorus uptake by the plant and in the case of the L values.

The L values represent the total labile pool of the soil and the phosphorus of the fertilizer included in the soil. In the presence of easily soluble fertilizers, such as superphosphate, the variation of L in the course of the first growth tests corresponds fairly well to the phosphate included in the five soils that were studied. This showed that under these conditions the fertilizer is not affected by the nature of the soil. The same is not true after the fertilizers have aged for 3 years.

In the two calcareous soils (Nos. 1 and 2) the phosphate rock used shows either weak or null efficiency regardless of the control test. However, in the least carbonated soil, a tendency for increase of phosphorus uptake and L value is observed. The aging of the superphosphate resulted in a loss of lability of approximately 50% in the Rendzina soil and a more distinct drop in the case of the clay-soil but only in the case of the higher dose which brought on considerable precipitation in basic phosphates.

In the three acid soils (Nos. 3, 4, and 5) the role of the phosphate rock in providing phosphorus to

the ryegrass became more important since 30%-50% of the fertilizer applied was absorbed by the plant and the aging treatment did not seem to affect this relationship very much except in the andosoil which was characterized by an extremely high fixing capacity. The E value confirmed that a significant part of the fertilizer was dissociated into labile ions except in the Brown soil which had a pH of 6.4.

In the case of superphosphate, however, the relative efficiency decreased perceptibly after 3 years of contact with the soil, thus demonstrating that the availability of the superphosphate ions became more difficult, especially in the presence of the strong fixing capacity of the andosoil which is also responsible for the fall in the L value.

This behavior during aging of phosphate rock and superphosphate is due to the components of the major processes which govern the dynamics of phosphorus transfer in the soil and absorption by the plant, particularly the phenomenon of dissolution or precipitation as related to the respective solubilities of the fertilizers and the chemical environment of the soil. Furthermore, near the roots, the main factors are the competition imposed on the phosphate ions by the soil's fixing capacity and the metabolism of the plant since they influence the rhizosphere directly or indirectly.

In the presence of phosphate rock, the competition of the soil's fixing capacity is reduced by the fact that a portion of the fertilizer remains as it is even after aging but at the same time is relatively accessible to the roots as is shown by the L value and the P uptake. This occurs especially in soil No. 3 which is weakly acidic as the low variation of E value and the fractionation according to the Chang and Jackson method showed, at the same time remaining relatively accessible to the roots as is shown by the L value and the P uptake.

In the case of a soil which is strongly acidic and has a very high phosphate ion-fixing capacity after 3 years of contact with the soil (as in the case of soil No. 5), there is a sort of compensation between the high intrinsic activity of the superphosphate ions which are nevertheless actively blocked by the fixing

capacity of the soil and the slow release of phosphate rock which is less affected by this soil-fixing capacity. Our results show that in the short term ryegrass makes much better use of the superphosphate than the phosphate rock, and in the medium term this difference is considerably reduced.

Finally, our results show that, starting from comparable labile pools, P uptake by the plant is inversely proportional to the fixing capacity of the soil. The same is true for the three acid soils where andosoil offers a phosphate ion flux which is distinctly less than that of the leached Brown soil and even less than that of the Brown soil.

Conclusion

These tests confirm the conclusions made in field tests carried out in agronomic experiment stations in France, especially the most recent ones on carbonate or neutral silts in northern France (Hebert) and calcareous clay soils from the Charentes (Courpron et al.).

Finely ground phosphate rocks have either no efficiency or negligible efficiency in carbonate-containing soils even after 10-12 years.

The more acid the soil the more readily labile ions will be set free. Under these conditions, they can be used very well to maintain the phosphate fertility of the soil when this has been brought up to a sufficient level to satisfy the plant's needs over an intermediate term. On the other hand, because of their slow-release action they are not as good as soluble or hyposoluble forms when needed to improve soil fertility quickly.

These trials also show that directly after application of phosphate rocks the availability to plant growth can be estimated more closely by the L value than by the E value as the former takes the "rhizospheric" effect into account.

Finally, they confirm that the flux of ions actually available to the plant is a function not only of the labile or exchangeable phosphate ions

quantities but also of the soil's fixing capacity (Gachon, 1966).

As far as the use of phosphate rocks in fertilization of French soils is concerned, it is likely that their use will continue to increase, but this increase will be strongly affected by developments in the French iron smelting industry which produces slag. There are about 20 million ha of acidic agricultural land in France where phosphate rocks could be used. Much of this land is at the present time relatively under-fertilized, but we will be surprised if the consumption of phosphate rocks in France goes above 500,000 tons of P_2O_5/year by 1985. This tonnage would correspond to doubling the present consumption and would be about a quarter of the present phosphatic fertilization.

EXPERIENCES WITH SOFT ROCK PHOSPHATES FOR DIRECT FERTILIZER APPLICATION

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Introduction

Hard rock phosphates, crystalline apatites from the earth magma with about 15% P, are the most important raw material for manufacturing phosphate fertilizers by chemical or thermochemical decomposition. Fine crystalline or amorphous phosphorites of marine, especially biological origin--so-called "soft rock phosphates"--can be used for direct fertilizer application, depending on P-content, solubility in specific organic acids, and an extremely fine grinding.

In order to find a proper criterion for distinguishing these two types of raw material, some organic acids like formic, citric, tartaric acid, etc., were tested in a concentration of 2%, which is roughly adequate with the ability of plant roots to dissolve phosphates and make them available for uptake.

As a result, 2% formic acid was agreed upon as a conventional solvent for differentiation (table 1). Citric acid does distinguish very well between soft rock phosphates on one hand and chemical, especially chemothermically manufactured, fertilizers on the other hand, but it does not between soft and hard rock phosphates. The formic acid, however, differentiates best between the three groups of phosphate fertilizers, and these differences correspond very well with the different plant response. Corresponding with the German fertilizer code, the European community adopted the criteria for the type of "soft rock phosphate," which has to fulfill the following postulates:

Total P-content must be at least 11%.

At least 55% of P-content must be soluble in 2% formic acid. With respect to grinding fineness, at least 99% has to pass the 0.125-mm mesh screen.

At least 90% has to pass the 0.063-mm mesh screen.

In the case of granulation, the whole fertilizer has to decompose completely as influenced by moisture.

Whereas the hard rock phosphates consist to a very great extent of fluorine apatite, the soft rock phosphates contain predominantly carbonate apatite with various amounts of free calcium carbonate but only to a small extent fluorine apatite.

From the diagram (figure 1) it follows that fluorine apatite has an extremely low solubility, especially at pH above 7; whereas, hydroxylapatite is much more soluble, especially in the very acid or light acid field.

At the Institute of Plant Nutrition of the Technical University of Munich, we have carried out many investigations and plant experiments for 30 years, especially with North Africa, especially Gafsa, phosphates. On the basis of these results, we can make some recommendations for the direct application of soft rock phosphates.

Weihenstephan, near Munich, lies 467 m above sea level at the edge of tertiary hill land with a yearly average temperature of 7.7° C and a July average temperature of 17° C. The yearly amount of sunshine is 1,840 hours, and the rainfall is 810 mm/year, fairly well distributed over the year with maximum during June, July, and August (figure 2).

As a result of these experiments the effectiveness of direct application of soft rock phosphates depends on different factors.

Efficiency and the Residue Effect of Renophosphate

The objective of the following pot experiment was to compare the efficiency and the residue effect of renophosphate, which is a Gafsa phosphate, to that of basic slag on a sandy soil, poor in phosphate on different pH levels (pH 4.3-5.0-6.5) with and without lime, with ryegrass for 4 years on two phosphate levels (0.45 and 1.35 g P_2O_5/6.2 kg soil) and optimal N + K doses yearly (figures 3 and 4).

As a result of the cumulative P removals, the soft rock phosphate gives better response on lower

than on higher pH values. High doses of basic slag are more effective than those of renophosphate on this soil, having low levels of available phosphate.

P-Form Trial - Pettenbrunn

The experiment started in 1952 on a pseudogley Brown Earth (silty loam), pH 4.9, poor in phosphate (~3 mg CAL - P_2O_5/100 g soil). The data of table 2 show the total dry-matter production and P-removal of hyperphosphate (a Gafsa phosphate) and basic slag on different pH-levels (without and with lime). This location is characterized by a relatively low biological activity and P-transformation; for 16 years no organic manure was applied (table 3).

In the block "without lime" there is a very good response on mineral P-fertilizers; by liming without P-application the total dry-matter production and P-removal has been increased considerably as a result of mobilizing soil-P, which is strongly absorbed on Fe- and Al-oxides, as well as improvements in soil structure and biological activity. Consequently, in the block "with lime," a smaller response of P-fertilizers compared with P_0 is given. In the whole period basic slag represents slightly better results (between +1% and +9%) concerning yields and P-removals.

The differences are highest with low P doses in the limed block and are accentuated especially in case of intensive crops (barley, maize, sugar beets, etc.) with short vegetation periods, respectively, low root activity. However, both P-forms reached practically equal results with wheat, rape, beans, and oats (table 4).

For the following 3 years no mineral phosphates were applied in order to prove the residue effect of both fertilizers. However, the plots were supplied with optimal N + K doses and all the disposable organic material (straw, leaves, etc.) to improve biological activity (table 5). At low pH there are no differences between hyperphosphate and basic slag; only in the limed block high doses of basic slag show a better residue effect than hyperphosphate.

In conclusion, the overall effectiveness of directly applied soft rock phosphates on acid soil is nearly as

great as that of basic slag and is only a little lower at pH 6.2. Small differences between hyperphosphate and basic slag exist on this soil which is low in phosphates especially with P-intensive crops.

P-Form Trial - Weihenstephan

The location Weihenstephan is a Brown Earth developed from loess loam on tertiary material (clayey sands and sands), pH (KCl) 6.2 with a good biological activity. The total P content is high enough (84 mg) with a good rate of available phosphates (18 mg P_2O_5/ 100 g soil). During the last 14 years the tested question was: Is hyperphosphate able to hold equal yields and P-removals like the chemically treated P-fertilizers?

From table 2 it follows that all the proved P-fertilizers obtained nearly the same results of dry-matter production, P removal, and P utilization. Superphosphate and basic slag showed only a little better tendency (however the differences are still in the statistical error), which results from potatoes and other P-intensive crops but not from wheat, sugar beets, etc. (table 6).

Soil investigations done in 1972 represent remarkable differences in the P fractions, according to Chang and Jackson between the controls and the plots with mineral phosphates. NH_4Cl-P, which is available to plants, is fairly high in all P-fertilized plots. Besides that, the NaOH-extractable fraction is higher after long-term superphosphate and basic slag application; however, H_2SO_4-extractable Ca-phosphates prevail in the hyperphosphate plots (table 7). Thus, on a good P-level the soft rock phosphates attained practically the same results as chemically or chemothermically treated P fertilizers on a light acid soil.

P-Form Trial - Hohenbachern

In previous field experiments we always used hyperphosphate in the granulated form. In the following 2 years' field experiment the granulated hyperphosphate was compared with the powdered form on an acid Brown Earth of very low biological activity and extremely poor in available phosphates (table 8).

As the results show, there is a good response of wheat and barley to P fertilizing. However, on this soil, poor in total and available phosphate, there are evident differences between basic slag and superphosphate on one hand and the granulated soft rock phosphate on the other hand. The granulation of hyperphosphate slows down its effectiveness. Under these conditions it takes longer for the roots to meet granular phosphate and make use of it than in case of the powdered material well distributed in the root zone.

In conclusion, in soils poor in phosphates the granulated form is definitely of lower effectiveness than the powdered form, especially with P-intensive crops.

Biological Activity

It is known from the literature that both plant roots and microorganisms are active in mobilizing soil-P by excreting organic acids which, in part, produce a chelating effect. Humic acids will be produced during microbial decomposition of organic material. In that way mineral calcium phosphates can be dissolved up to a certain extent. This was demonstrated in an old but still relevant model experiment (table 9) done by Flieg. Also microscopic investigations done by E. Konig provide evidence that fungi and other microorganisms develop a close network of mycelia around phosphate particles and are able to decompose them.

In connection with direct application of soft rock phosphates, two points should be stressed. Microorganism activity depends very much on pH and is best around neutral reaction. However, with increasing pH of the soil, the chemical solubility of calcium phosphates decreases. Therefore, acid soils should be limed carefully up to pH 6.0-6.5 maximum. High amounts of organic material should be brought into the root zone very near the granular fertilizer in order to make phosphates available to microorganisms and plants.

Negev Phosphates

Concerning Negev phosphates (Arad 3 and Arad 3a), we have made some pot experiments in the past

year with maize and ryegrass on two sandy loams of pH 5.7 and 6.3 with the following results (figures 5 and 6). On pH 5.7 next to the dicalcium phosphate curve is hyperphosphate, which attained a very similar P removal. Then follows Arad 3, which is finer ground than the less effective Arad 3a. On pH 6.3 the distance between dicalcium phosphate and the soft rock phosphates is larger; however, there are nearly no differences between hyperphosphate and Arad 3. Again, the coarser ground Arad 3a is of lower effectiveness.

Zinc Content of Soft Rock Phosphates

As a result of our recent investigations, some soft rock phosphates are rich in some microelements, especially zinc (∿500 ppm Zn probably in the form of zinc carbonate). It is known that zinc uptake is critical on soils with high P-level, especially in the case of high phosphate applications. Therefore, the idea was: a slower phosphate delivery from hyperphosphate (compared with superphosphate) could probably promote the zinc uptake from the soft rock phosphate at low pH by plant root excretions (table 10). On the acid humic sand, poor in phosphate and zinc, the control plants suffered from both P- and Zn-deficiency symptoms. On P-rich loamy sand, Zn-deficiency was obvious. Hyperphosphate obtained the same or nearly the same dry-matter production as dicalcium phosphate + $ZnSO_4$ but, on humic sand, a lower P- and Zn-removal.

Thus, hyperphosphate proved an effective phosphate fertilizer with available zinc, which facilitates Zn uptake by plants as a consequence of slower phosphate delivery.

Effectiveness of Aluminum Phosphate

From one of the first graphs it can be followed that Fe- or Al-phosphates may also become available to plants under specific conditions. The effectiveness of mineral phosphates depending on different soil pH is shown in table 10.

At low pH the dry-matter production is the same in case of hyperphosphate and chemothermic phosphate but not the P removal. Al-phosphate (with its low

solubility under these conditions) gives only a very low response. On the contrary, at high pH the soft rock phosphate shows nearly no effect, but Al-phosphate approaches the chemo-thermic phosphate at least with respect to yields but not to P removals.

In conclusion, mineral phosphates show different solubility and effectiveness depending on soil pH. This point has to be respected in phosphate fertilizer use.

Summary

The effectiveness of direct application of soft rock phosphates depends on several factors.

I. Concerning the product:

1. The solubility in 2% formic acid as a conventional method must be at least 55% of total P.
2. Grinding is required to produce extremely fine particles (99% through 0.125-mm screen).

II. Concerning the location:

1. Soft rock phosphates should be used only under favorable climatic conditions with enough rainfall.
2. They act best at low pH, depending on the solubility of calcium phosphates (<6.5 pH).
3. A high biological activity (organic manure) is necessary for the breakdown of minerals by microorganisms and plant roots.
4. Crops with a long vegetation period (wheat, sugar beet) and high root activity (leguminosae) are very convenient; this is not the case with P-intensive crops or those with a short growth period (barley, potatoes).

Under suitable conditions, directly applied soft rock phosphates give nearly as good results as chemically or chemothermically manufactured phosphate fertilizers.

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Comments From the Discussion

1. The formic acid differentiates better between hard and soft rock phosphates than citric acid; this is in accordance with our plant experiments.
2. The sample Arad phosphate 3a is not as finely ground as Arad 3; this explains the different results.
3. Content and availability of zinc in rock phosphates differ according to the deposits' respective locations.

Table 1. Solubility of Soft and Hard Rock Phosphates

Phosphates	Total P Content	Soluble P from Total P in 2% Citric Acid	Formic Acid
		%	
Gafsa	12.5-13	35-41	54-73
Morocco		20-31	43-62
Constantine		33	58
Florida	13.7-14	22	22
Kola		8	7
Basic slag	5.0-7.7	90	85
Thermic phosphate	10.3	92	86

According to Hofmann and Mager.

Table 2. P-Form Trial-Weihenstephan

Fertilizer (Yearly) N + K Optimal P = 74 kg P_2O_5/ha	Σ 1953-68 Dry-Matter Production, dt/ha	Removal kg P/ha	P-Utilization %
P_0	934	453	-
Superphosphate	1,156	641	17.5
Thermic phosphate	1,115	613	14.3
Basic slag	1,163	642	15.9
Hyperphosphate	1,128	611	15.2

Soil data: Brown Earth (sandy clay loam)-pH ($CaCl_2$) 6.2
Exchangeable capacity (T) 14.2 mval/100 g soil
Total-C 0.72%; Total-N 0.09%; Total-P 84 mg/100 g soil

Table 3. P-Form Trial-Pettenbrunn

Fertilizer (yearly) N + K optimal P_1=60 kg P_2O_5/ha	Ca_0-pH 4.9 Σ 1953-65 Dry-Matter Production, dt/ha	Removal kg P/ha	Ca_1-pH 6.2 Σ 1953-65 Dry-Matter Production, dt/ha	Removal kg P/ha
P_0	715	94	945	142
P_1 hyperphosphate	1,044	155	1,103	187
P_1 basic slag	1,060	169	1,203	201
P_2 hyperphosphate	1,069	184	1,154	198
P_2 basic slag	1,160	208	1,212	229

Soil data: Pseudogley Brown Earth (silty loam)
Exchangeable capacity (T) 11.2 mval/100 g soil
Total-C 1.18%; Total-N 0.14%; Total-P 68 mg/100 g soil

Table 4. P-Form Trial-Pettenbrunn

Fertilizer	Ca_0-pH ($CaCl_2$) 4.9			Ca_1-pH ($CaCl_2$) 6.2		
	Wheat	Barley	Maize	Wheat	Barley	Maize
	grains (14% H_2O) dt/ha					
P_0	43	29	34	47	39	54
P_1 hyperphosphate	51	37	53	50	42	60
P_1 basic slag	52	41	53	52	44	63
P_2 hyperphosphate	53	39	60	51	45	62
P_2 basic slag	53	41	67	52	46	69

Average yields: wheat--4 years
barley--4 years

Table 5. P-Form Trial-Pettenbrunn, P-Residue Effect

Fertilizer	Ca_0-pH ($CaCl_2$) 4.9 Σ 1966-68		Ca_1-pH ($CaCl_2$) 6.2 Σ 1966-68	
	Dry-Matter Production, dt/ha	Removal kg P/ha	Dry-Matter Production, dt/ha	Removal kg P/ha
P_0	103	48	152	76
P_1 hyperphosphate	130	68	152	85
P_1 basic slag	134	69	152	83
P_2 hyperphosphate	141	78	153	86
P_2 basic slag	143	80	166	98

Table 6. P-Form Trial-Weihenstephan
Different crops 1970-75 (dt/ha)

Fertilizer	Grains (14% H_2O), Beets, and Tubers (fresh)					
	Potatoes 1970	Wheat 1971	Sugar Beets 1972	Wheat 1973	Potatoes 1974	Wheat 1975
P_0	274	52	380	45	194	41
Superphosphate	343	56	501	53	288	48
Thermic phosphate	306	56	511	53	256	43
Basic slag	303	56	508	54	250	44
Hyperphosphate	306	56	524	52	228	45

Table 7. P-Form Trial-Weihenstephan (soil investigations, 1972)

Fertilizer	Total P mg/100 g Soil	NH_4Cl	NaOH	H_2SO_4
		ppm P		
P_0	67	2	166	102
Superphosphate	85	13	281	133
Thermic phosphate	81	-	-	-
Basic slag	80	19	260	145
Hyperphosphate	84	13	218	160

Table 8. P-Form Trial--Hohenbachern

Fertilizer (NK optimal)	1976, 75 kg P_2O_5/ha Wheat Yields (86% H_2O) dt/ha	Removal kg P/ha	1977, 100 kg P_2O_5/ha Barley Yields (86% H_2O) dt/ha	Removal kg P/ha
P_0	42.0	11.6	27.1	5.8
Hyperphosphate, powdered	50.0	15.9	39.2	11.5
Hyperphosphate, granulated	46.0	14.6	36.3	9.4
Basic slag	54.0	17.2	40.8	12.3
Superphosphate	53.0	16.9	40.7	12.3

Soil data: Brown Earth, pH ($CaCl_2$) 5.6
Exchangeable capacity (T) 9.2 mval/100 g soil
Total P 43 mg, CAL-P_2O_5 1 mg/100 g soil

Table 9. Effect of Humates on Phosphate Mobilization (according to Flieg)

P-Form	Humate Without	With
	mg P_2O_5/100 ml Filtrate	
Morocco phosphate	1.0	182
Constantine phosphate	0.8	237
Hard rock phosphate	1.3	109
Fluorine apatite	0.7	61
Bone powder	0.9	159

Experiment: shaking 20 g phosphates in ammonium humate solution (pH 7.8) for 8 days

Table 10. P-Zn Experiments with Hyperphosphate
1975 + 1976 maize (green) + oats (green) + maize (green)

Fertilizer, N+K optimal g/pot	Humic Sand pH 4.2 (KCl) 1 mg P_2O_5/100 g Soil (CAL) 5 ppm Zn (EDTA)			Loamy Sand pH 6.6 (KCl) 90 mg P_2O_5/100 g Soil (CAL) 21 ppm Zn (EDTA)		
	Dry-Matter Production g/pot	P mg/pot	Zn mg/pot	Dry-Matter Production g/pot	P mg/pot	Zn mg/pot
P_0-Zn_0	182	197	5.7	319	986	13.8
P_0-5 mg Zn as $ZnSO_4$	178	187	5.7	396	1,113	18.0
3 g P_2O_5 hyperphosphate	270	385	6.5	423	1,198	16.2
5 mg Zn						
3 g P_2O_5 as dicalcium phosphate	222	506	6.3	339	1,111	12.0
3 g PO as dicalcium phosphate 5 mg Zn as $ZnSO_4$	271	608	11.4	446	1,368	15.6

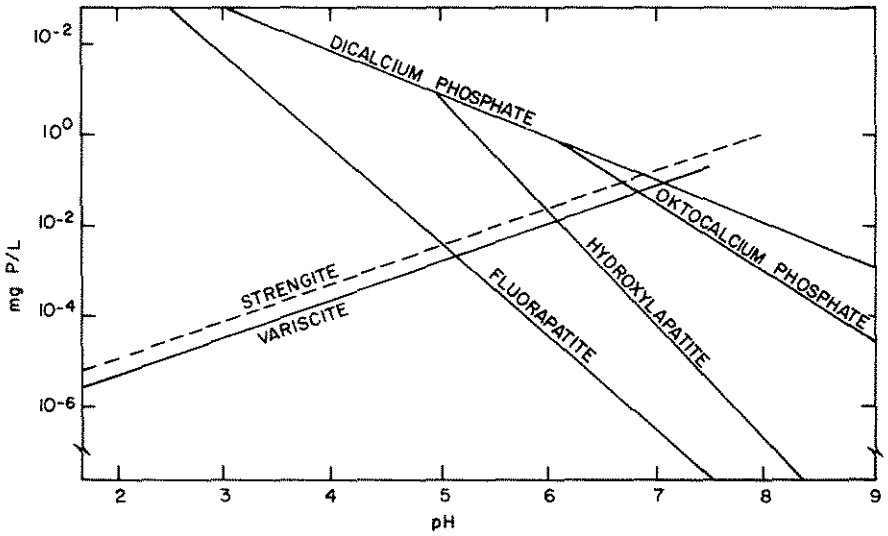

Figure 1. Solubility of Phosphates as Influenced by pH at 25°C (acc. to Schachtschabel).

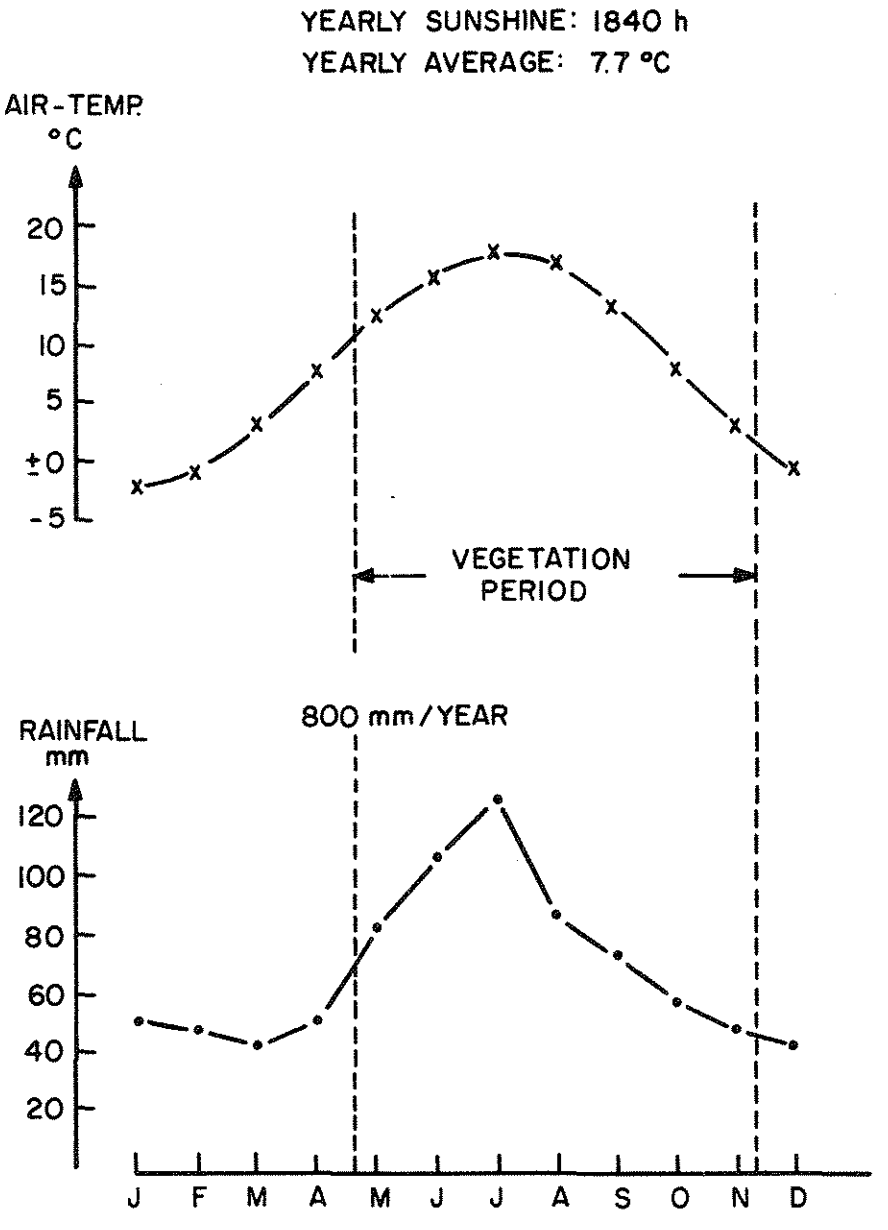

Figure 2. Dates of Climate-Weihenstephan.

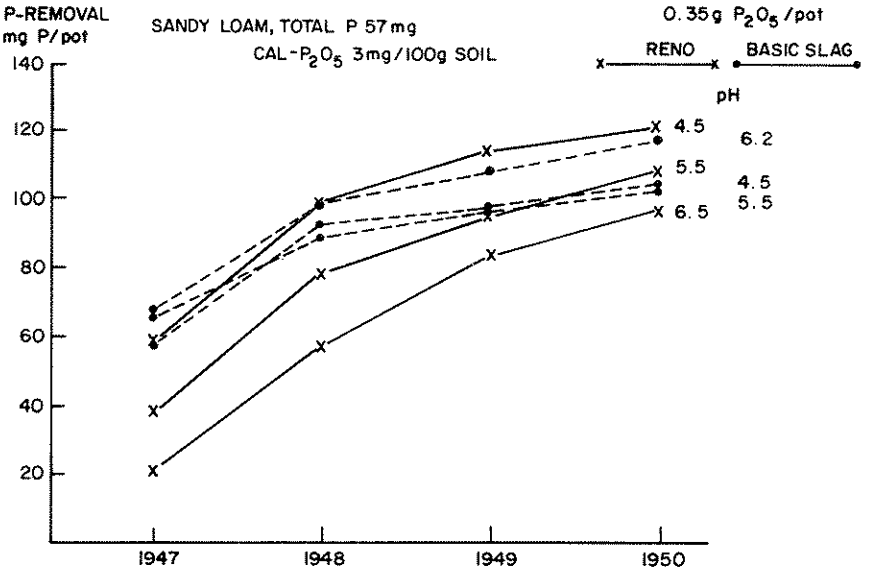

Figure 3. Effect of Renophosphate with Ryegrass on Different pH Levels (pot experiment 1947-1950).

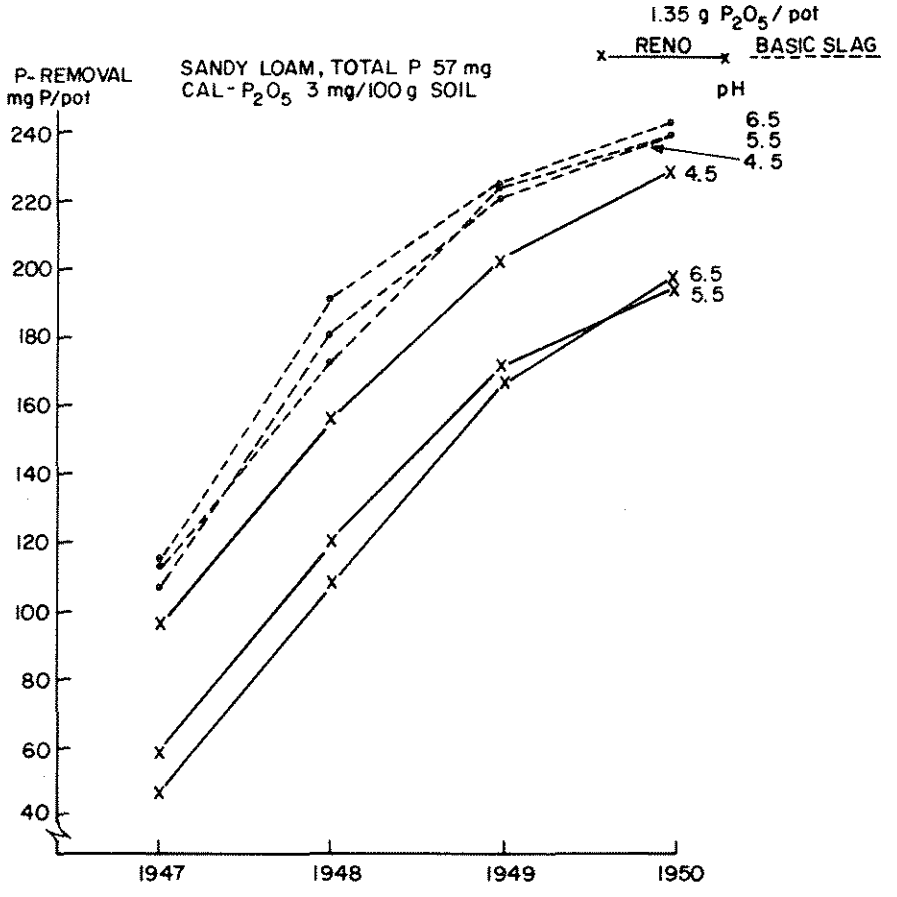

Figure 4. Effect of Renophosphate with Ryegrass on Different pH Levels (pot experiment 1947-1950).

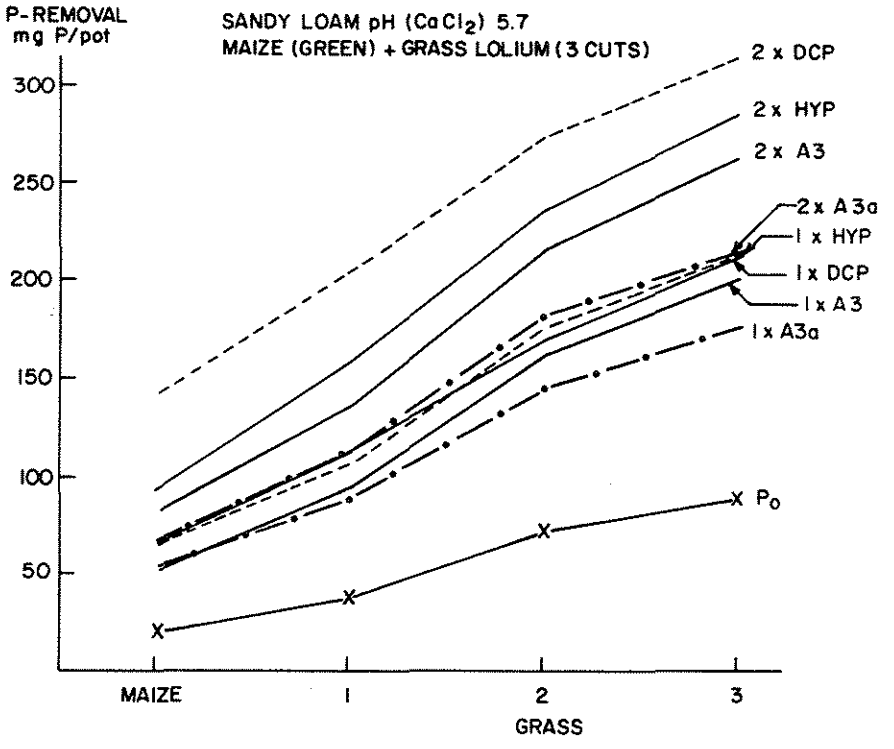

Figure 5. Trials with Negev Phosphates.

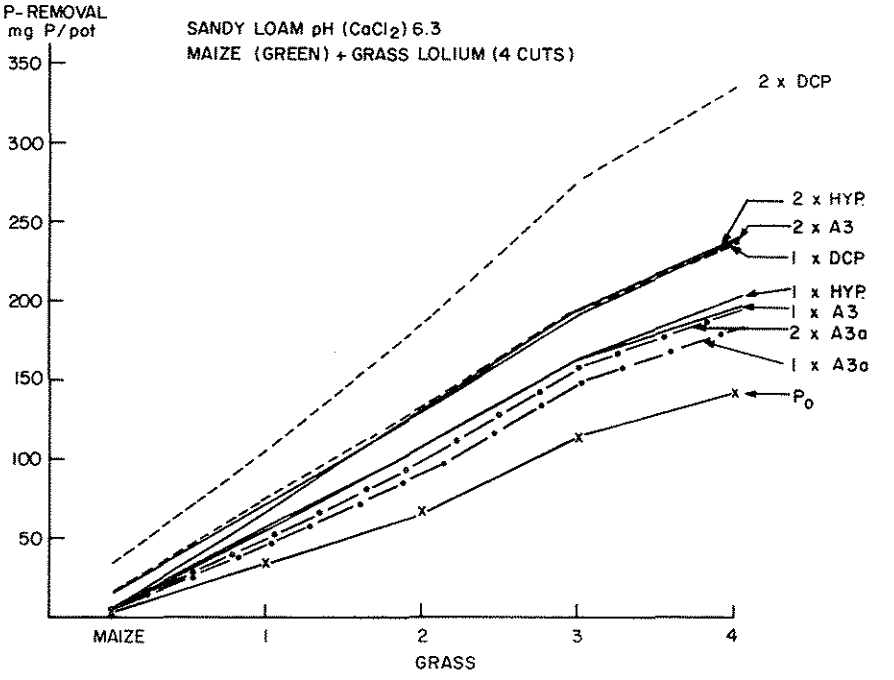

Figure 6. Trials with Negev Phosphates.

MINIGRANULATION--A METHOD FOR IMPROVING THE PROPERTIES OF PHOSPHATE ROCK FOR DIRECT APPLICATION

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Summary

One of the main obstacles inhibiting the use of ground phosphate rock for direct application is the troublesome problem of handling finely ground, dusty material. Bench- and pilot-scale tests are being performed by the International Fertilizer Development Center (IFDC) to evaluate a method for producing very small, dust-free granules (minigranules) that would exhibit favorable handling and crop response characteristics. For the initial phase of work, a particle size range of minus 50- plus 200-mesh (Tyler) was established for minigranules.

A spherical, nondusty minigranulated product was produced in small- scale tests using a pin-type mixer. Finely ground rock, together with a small amount (about 5%) of binder, was processed in the mixer. The need for a drying step depends on the type of binder used. Preliminary tests indicate that phosphate rock can be minigranulated, and agronomic tests are being made of several products by IFDC. Further tests are planned in batch and continuous equipment to determine the effects of variables and the technical and economic feasibility of the process.

Introduction

Finely ground phosphate rock is difficult to handle in equipment generally used for traditional pulverized and granular bulk fertilizer materials. Furthermore, the dustiness of finely ground rock during handling is troublesome and expensive to control. Also, when dry, finely ground rock is used as a direct application phosphate fertilizer; uniform distribution on the soil is hard to obtain using manual

or mechanical methods. In general, agronomic tests show that finely ground phosphate rock is necessary for most food crops when a relatively high initial crop response is needed. IFDC is studying methods to improve the properties of phosphate rock to enhance its value and attractiveness for direct use as fertilizer. One such method is to granulate the finely ground rock to improve its handling and application characteristics, and at the same time, obtain a product having suitable agronomic properties. This paper discusses preliminary data on a new process being developed by IFDC for preparing very small granules (minigranules) in the size range of minus 50- plus 200-mesh from finely ground (minus 200-mesh) phosphate rock. The development of the process is at the exploratory bench-scale stage, but pilot-plant tests are planned. An application for an IFDC patent has been filed, and some others related to the pin-type mixer are shown in the references.

The minigranulation process converts finely ground phosphate rock into small spherical granules using a granulation aid or binder. Several types of binders are being evaluated, including soluble salts, mineral acids, and some organic materials. Process conditions and the chemical composition of the product may vary depending on the specific binder used. For example, when a soluble salt is used as a binder, a drying step is needed, while the use of an acid may not require drying. At present, the use of an intensive, pin-type mixer is being evaluated for minigranule production; however, other types of equipment probably can be used and will be tested. Preliminary results are limited to small-scale tests, and no estimate of the investment or operating costs for the process has been made. Phosphate rock granulation processes are considered appropriate technology for developing countries because the processes are simple, and investment and operating costs are relatively low. IFDC has a special interest in the development of appropriate technology for transfer to developing countries where indigenous phosphate resources can contribute to their fertilizer needs.

From both a technical and economic viewpoint, minigranulation is a compromise approach for improving phosphate rock for direct application. The agronomist wants a finely ground material to achieve

maximum soil-phosphate contact, while the engineer wants a granular, easy-to-handle, nondusty product which does not disintegrate during handling. Some desirable engineering features of granular phosphate rock, such as uniformity in particle size, also help the agronomist in obtaining a uniform application to the soil. The process of minigranulation shows potential for obtaining some of these objectives.

IFDC will continue to work on minigranulation using both batch and continuous processes. The primary purposes of the present tests are as follows:

1. To determine the effect of factors such as rock:binder ratio, type of rock and binder, moisture content, mixer tip speed, and retention time on the process and product characteristics.
2. To evaluate the product's characteristics, such as particle-size distribution, surface area, abrasion resistance, and other handling and storage factors.
3. To determine the agronomic performance of the various products in the soils laboratory, the greenhouse, and the field. One especially interesting study is underway to determine the effect of particle size on the initial and residual phosphate yield response.

Reports on these activities will be forthcoming as the experiments are completed. Results given in this paper must be considered preliminary, but they indicate positive technical results.

Experimental Procedure

The batch mixer used by IFDC has a capacity of about 3 kg of finely ground phosphate rock. Although pin-type mixers have been used for over 30 years primarily for compaction and granulation of carbon black, apparently IFDC is the first to apply the equipment to minigranulation of phosphate rock. This mixer is based on a design using a high-velocity horizontal shaft containing an arrangement of radial rods or pins. This shaft rotates inside a stationary housing having a length-to-diameter ratio in the range of 2 to 5. A diagram of a typical unit is

shown in figure 1. A simplified flowsheet of the process is shown in figure 2.

Only two phosphate rocks have been used in minigranulation tests to date, North Carolina and Pesca (Colombia). The quantity of finely ground rock added to the batch mixer depended upon the bulk density of the material. A rock charge that filled about one-fifth of the mixer housing was found to be about optimum. This volume was equivalent to about 3 kg of phosphate rock. Shaft speeds ranged from 630 to 825 rpm. From one-third to two-thirds of the binder solution was added initially along with the rock. The cover was closed, and the unit was operated for 15-90 seconds. Following this period of operation, the mixture was checked visually to determine the approximate size distribution and degree of compaction and to determine if more binder solution needed to be added. After two or more repetitions of this procedure, depending upon test objectives, the material was removed and oven dried at temperatures ranging from 85° to 120° C. Binders prepared from water solutions of soluble salts, such as urea, potassium chloride, and magnesium sulfate, have been used in tests to date. The liquid phase (binder salt plus water) content in the mixer ranged from 11% to 19%. This level of moisture required a separate drying step to produce a dry, free-flowing, minigranulated product. Typically, the dry product contained about 4% binder salt. With good operation, a large fraction (70%-80%) of the dried product was in the desired particle-size range of minus 50- plus 200-mesh.

Acid binders may offer two advantages. Acid attacks the rock and converts some of the phosphate to water-soluble and/or available forms which should improve initial crop response. Also, at certain levels the acid serves as a binder and drying agent, eliminating the separate drying step. Insufficient data are available to fully evaluate the elimination of drying, but tests with 54% wet-process acid have demonstrated that this is possible. The laboratory-scale mixer being evaluated is made of mild steel, and a wide range of acid concentrations and acid: rock ratios could not be tested. However, it appears that almost any acid could be used, and further tests are planned. A major disadvantage of using partial

acidulation is that the process becomes more complicated and capital intensive because of required acid production, transportation, storage, and handling considerations.

Results And Discussion

Material obtained from the minigranulation process was in the form of well-rounded, hard granules and was free flowing and relatively nondusty as shown in figure 3. In some tests up to 80% of the product was in the size range of 50- to 200-mesh. At present, sufficient data have not been collected to make a statistical study of variables affecting product quality. No doubt a number of variables such as mixer speed, type and quantity of binder, retention time, liquid phase in the mixer, type and time of drying, and several other factors affect the quality and agronomic suitability of the product. Of course, the type of rock is expected to have a major effect on the agronomic performance, and only two types (North Carolina and Pesca) have been tested. Both seemed to minigranulate equally well in the range of conditions tested. Some typical test results with these two rocks are shown in table 1.

Due to the limited number of tests at this time only very tentative and limited statements can be made on some variables. Some points are as follows:

1. Shaft speed: Two shaft speeds were tested equivalent to a pin tip speed of 9 and 12 m/second. The higher speed gave better results. A wider range and further testing are needed to confirm this.

2. Retention time: A retention time of 90 seconds gave a higher fraction of the desired particle-size range (minus 50- plus 200-mesh) than did 60 or 45 seconds. In general, the longer time was necessary to reduce initial lumping and obtain the spherical, minigranular form of product.

3. Moisture content: Liquid phase expressed as weight percent of salt plus water was in the range of 11%-19%, which is not too different from that in conventional granu-

lation. The optimum liquid phase no doubt depends upon such factors as the type of binder and the fineness of the rock. At these moisture levels the product must be dried after minigranulation to obtain a free-flowing material, especially if there is no chemical reaction between the rock and binder. It is important to note that material produced in tests with 54% phosphoric acid and liquid phase contents of 16%-18% in the mixer appeared to be dry and was free flowing at the mixer discharge. If phosphoric acid or other acids were available, they could be used as a binder for minigranulation, probably without drying. At the same time, some of the rock phosphate could be converted to an available form, thus improving initial crop response. Decreasing or eliminating the need for drying could be important in some situations where energy is in short supply or not available. However, the use of acid complicates the process, and materials of construction become more important. The use of acid is an interesting and potentially useful aspect of this process that will be investigated.

4. Type and Amount of Binder: Soluble salt binders, such as urea, potassium chloride, and magnesium sulfate, were satisfactory. The salt increases the strength of the product and should also help to cause the particles to disintegrate when they are exposed to soil moisture. When acid is used as a binder, especially sulfuric acid, some of the particles appeared to be quite hard and probably will not disintegrate and solubilize rapidly in the soil solution. More tests (production and crop response) are required to determine the impact of various binders on the product characteristics.

As can be seen, IFDC has only begun a preliminary study of the intensive mixers and their use for minigranulation. The equipment and process appear to be applicable for developing countries seeking simple and appropriate technology. A number of other potential uses for the application of minigranulation technology in the fertilizer industry

can be envisioned in addition to that of phosphate rock for direct application. Such diverse applications as granulation of phosphate slimes, sewage or fly-ash sludge, cattle-feed additives, and use as an intensive mixer in concert with a pan- or drum-type granulator are just a few examples.

IFDC will continue studies of the minigranulation of phosphate rock and other materials employing batch and continuous processes. Some of the effects of production and raw material variables will be determined. Alternative equipment systems will be evaluated for use in the minigranulation process. Products will be produced for agronomic studies in greenhouse and field-level tests. Small samples of these experimental materials can be made available to agronomic investigators by requests to IFDC.

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Table 1. Typical Results of Minigranulation of Phosphate Rock[a]

Test No.	Mixer Speed Pin-Tip Speed rpm	Mixer Speed Pin-Tip Speed m/sec	Binder Type	Binder % of Product Dry Basis	Operating Time, sec	Product Size Tyler Mesh, % +50	Product Size Tyler Mesh, % -50+200	Product Size Tyler Mesh, % -200	Liquid Phase, Water + Binder, %	Total P_2O_5, % (Dry)
			North Carolina Phosphate Rock (30.6% P_2O_5 @ 80% -200 Tyler Mesh)							
1	620	9	none	-	90	83	11	6	14.7	30.6
2	825	12	none	-	90	12	64	24	15.4	30.6
3	620	9	urea	4.3	90	54	40	6	19.0	29.3
4	825	12	urea	4.3	90	7	69	24	14.2	29.3
5	825	12	KCl	4.3	60	80	16	4	13.4	29.3
6	825	12	KCl	3.8	90	17	76	7	13.4	29.4
7	825	12	$MgSO_4 \cdot 7H_2O$	4.4	60	15	76	9	13.2	29.3
8	500	7	phosphoric acid (54%)	16.0	90	20	57	23	18.2	36.2
9	825	12	sulfuric acid (60%)	8.9	90	13	30	57	13.9	26.9
			Pesca Phosphate Rock from Colombia (20.4% P_2O_5 @ 70% -200 Mesh)							
10	825	12	KCl	2.9	90	12	75	13	11.3	19.8
11	825	12	phosphoric acid (54%)	14.8	90	36	40	24	16.8	23.9[b]
12	825	12	sulfuric acid (45.3%)	6.6	90	15	84	1	13.5	19.2[c]

a. Using about 2,300 g of ground rock per batch.
b. Sample also contained 9.5% water-soluble P_2O_5.
c. Sample also contained 0.5% water-soluble P_2O_5.

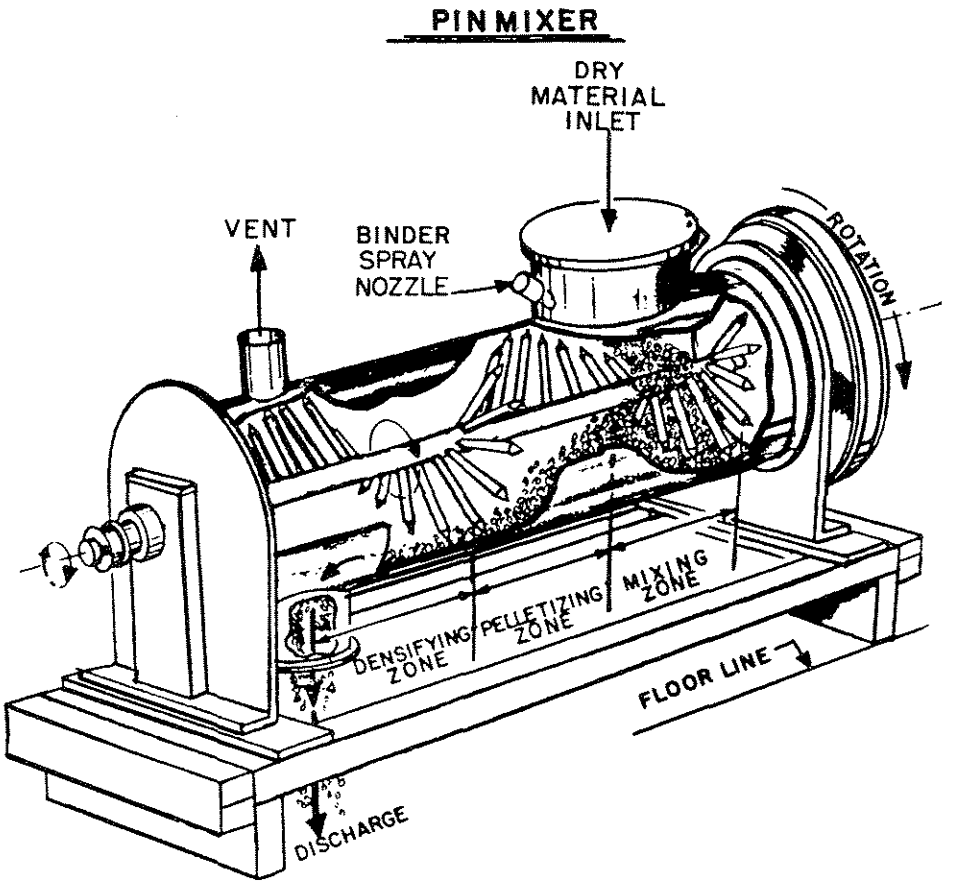

Figure 1. Perspective View of Pinmixer Used for Minigranulation of Phosphate Rock.

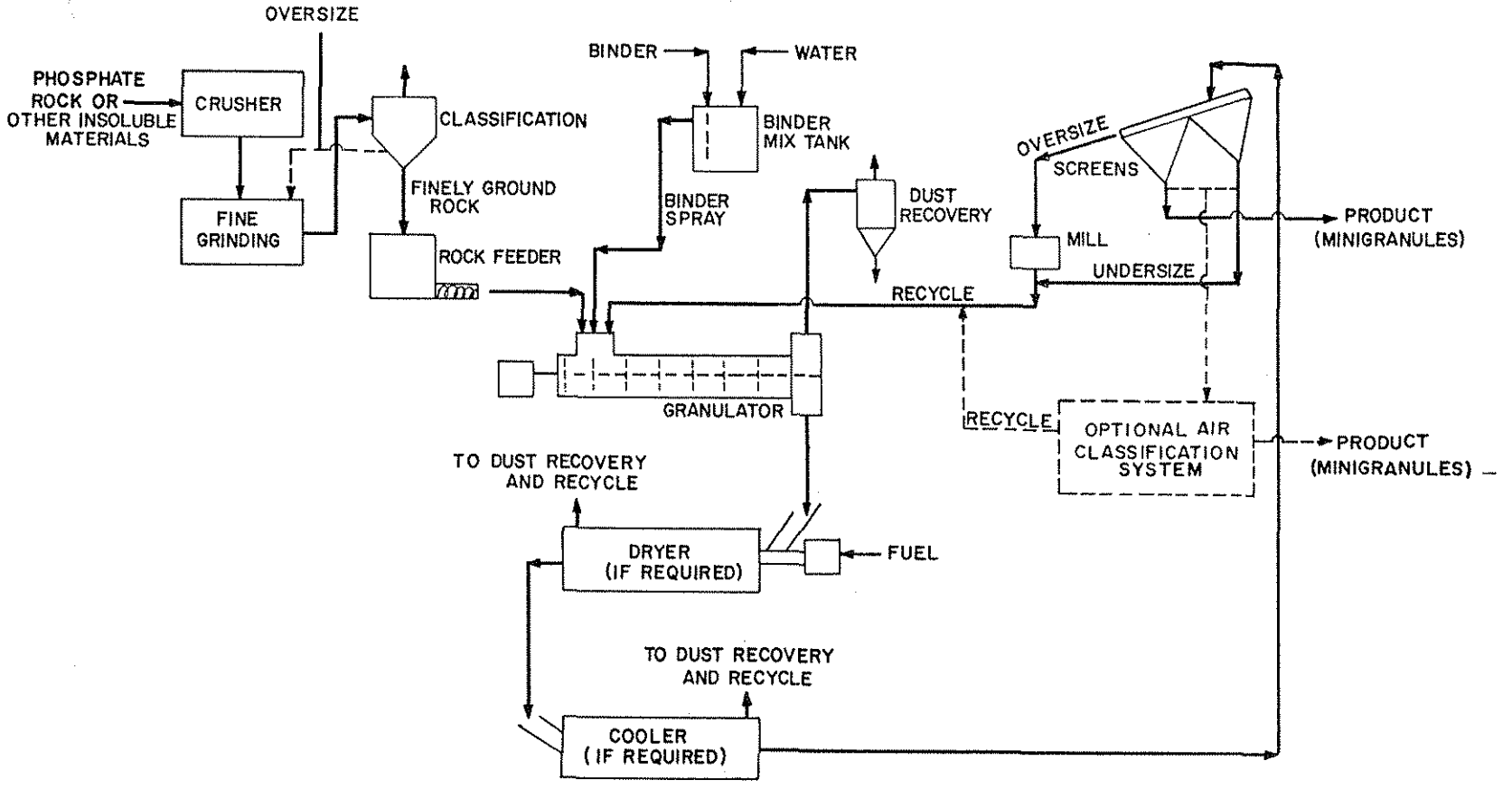

Figure 2. Process for Minigranulation of Phosphate Rock or Other Insoluble Materials.

EVALUATION OF GRANULATED PHOSPHATE ROCK FOR DIRECT APPLICATION

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Abstract

Greenhouse experiments were performed with two phosphate rocks from the Negev area of Israel. One of them, Maktesh, was granulated with $MgCl_2$, $MgSO_4$, KCl, $(NH_4)_2SO_4$, and H_2SO_4 in the range of 5- to 10-mesh; the second, Arad, was granulated with KCl and $MgSO_4$ in the range of 5- to 10-mesh and 20- to 40-mesh. North Carolina and central Florida phosphate rocks were granulated with $MgCl_2$ to obtain 6- to 16-, 16- to 48-, and 48- to 150-mesh granules. Clover, oats, ryegrass, and alfalfa, cut several times, were grown on acid soils from Ireland, Germany, Turkey, and England. The following factors were evaluated: granule size, binder materials, methods of placement, and influence of consecutive cropping. Results of greenhouse experiments showed an improved efficiency of granulated phosphate rock with consecutive cropping, especially so with larger granules. Placing granules on soil surface proved more efficient than mixing into the whole soil volume. Nature of binder material had only a slight influence on the availability of granulated phosphate rock.

Introduction

Phosphate rocks for direct application are usually ground to pass a 100-mesh sieve or finer, in order to increase their availability for crops. The resulting fine material is dusty and difficult to handle. There is considerable interest in granulating phosphate rock, as one method for improving its handling and application characteristics. However, it is believed that granulation influences negatively the agronomic effectiveness of phosphate rocks. Some improvement in availability of the granulated phosphate rock could be achieved by adding small amounts of sulfur, pyrite, or H-resin or by

granulating it with mineral acids (Fenster and Attoe, 1967; Kittams and Attoe, 1965; Terman et al., 1964, and Terman et al., 1969). The purpose of the reported work was to test some of the factors influencing availability of granulated phosphate rock. Several greenhouse experiments were performed considering the following factors: granule size, character of binder materials, soil properties, length of time of contact of granules with soil prior to sowing, methods of placement, and influence of consecutive cropping.

Granulation of phosphate rock affects presumably its availability by reducing its dissolution rate due to a reduced surface area in contact with the soil and by diminishing the root and fertilizer contact due to localized phosphate application (Bouldin and Sample, 1959; Lawton and Cook, 1978; Moreno, 1959; Terman, 1956; and Van Burg, 1963).

Binder materials used to granulate phosphate rock may form a hard surface skin, preventing soluble phosphate diffusion into the soil from the interior of granules. Soluble-salt binders may affect both positively or negatively uptake of P by roots coming into contact with the granules (Barber, 1977).

It is generally agreed that P diffuses in soil very slowly and to a small distance and that roots have to come in close contact with P sources in order to ensure maximum supply (Barber, 1977; Jungk and Barber, 1975; Engelstad and Moreno, 1965). This implies that the fertilizer must be thoroughly mixed with the soil.

Thus, it may be expected that granulated phosphate rock will be less effective than the powdered one at the beginning of the growing period. However, the possibility exists that the granulated rock will become more available as the root system develops and reaches a larger number of fertilized zones. Field observations on grassland in a wet climate indicate that surface application of granulated phosphate rock may enhance its effectiveness (Personal communication by J. Ankorion).

Materials and Methods

Phosphate sources in greenhouse experiments were Maktesh and Arad phosphate rocks, both from the Negev area in Israel, and North Carolina and central Florida phosphate rocks supplied in granulated form by the International Fertilizer Development Center (IFDC). The Maktesh rock was granulated with H_2SO_4, $MgCl_2$, $MgSO_4$, KCl and $(NH_4)_2SO_4$ and the Arad rock with KCl and $MgSO_4$. They were prepared by Fertilizers and Chemicals, Ltd., Haifa, Israel. The North Carolina and central Florida rocks were granulated with $MgCl_2$.

Dry- and wet-sieving average diameters of the granules were determined according to the U.S. Department of Agriculture (USDA) Handbook No. 60 (1954). Stability to water was measured by the number of water drops, falling from a height of 30 cm, necessary to destroy the granules.

Dry and wet sieving and disintegration by water drops showed that granules prepared with H_2SO_4 were the most stable ones; those bound with $(NH_4)_2SO_4$ and $MgSO_4$ were less stable; those granulated with $MgCl_2$ and KCl were the least stable (table 1).

Some characteristics of experimental materials are summarized in table 1. Other characteristics of the nongranulated phosphate rocks and of superphosphate may be found in the paper by Hagin et al., "Comparison of Finely Ground Phosphate Rocks as P Sources to Plants," in these Proceedings.

Soils for the greenhouse experiments were imported from Ireland, Germany, Turkey, and England. Some of their characteristics are given in table 2.

Organic carbon was determined by the wet combustion method and potentiometric titration of dichromate residues (Raveh and Avnimelech, 1972). Measurements of pH were done in a soil paste by glass-calomel electrodes. Moisture at field capacity was measured on vertical soil columns open at both ends. Enough water was added to wet the upper half of the column. After 24 hours, the moisture content

of the layer at 5-10 cm depth was determined. Texture of soil was determined by the sedimentation and decantation method (Black, 1965) and available P by the Bray P_1 method (Black, 1965).

The soil from Ireland was sterilized by dry heat and later limed to pH 5.2 and inoculated with a manure extract.

Soils were placed in 3-liter pots. Phosphate materials were mixed with the whole soil volume, except in the placement experiment, where part of the treatment was surface applied. K_2SO_4 was applied to supply 0.5 g K/pot, except for those pots receiving the granulated phosphate rock with a KCl binder. There the amounts of K were adjusted according to those supplied in the granules. NH_4NO_3 was given to supply 1 g N/pot; again the amounts given to treatments receiving granulated phosphate rock with $(NH_4)_2SO_4$ were adjusted accordingly. Microelements were applied in a solution to supply 0.3 mg Mg, 1.3 mg B, 0.7 mg Zn, 0.2 mg Cu, 1.7 mg Fe, 2.5 mg Mn, and 0.01 mg Mo/pot. The pots were watered frequently to "field capacity" by weighing.

In greenhouse experiments with North Carolina, central Florida, and Maktesh phosphate rocks yields of one cut of clover (Trifolium alexandrinum), two cuts of oats (Avena sativa), and two cuts of ryegrass (Lolium perenne) were obtained. In one experiment with Maktesh phosphate rock, one cut of clover (Trifolium alexandrinum) and three cuts of alfalfa (Medicago sativa) were measured. Whereas in those with Arad phosphate rock, clover (Trifolium alexandrinum) was harvested three times.

Relative agronomic effectiveness (RAE) of the various P sources was calculated from the dry-matter yields data (Engelstad et al., 1974).

$$RAE = \frac{Y_F - Y_C}{Y_R - Y_C} \cdot 100, \text{ where,}$$

Y_F - maximum yield obtained in treatments that received the tested fertilizer,
Y_C - yield in the control treatment, and
Y_R - maximum yield obtained in treatments that received a reference fertilizer (ground rock

phosphate or concentrated superphosphate [CSP]).

The maximum yield was estimated from freehand yield curves drawn for each crop, cut, or fertilizer.

Results and Discussion

Dry-matter yields resulting from mixing North Carolina and central Florida granulated phosphate rocks and CSP into the whole soil volume of soil from Ireland are reported in table 3. Analysis of variance showed that differences due to treatments were statistically significant at a 0.01 level for all yields, except the second cut of oats where they were significant at a 0.05 level. Relative agronomic effectiveness of these P sources, based on estimated maximal yields, with CSP as reference material was calculated and presented in figure 1. Results in table 3 and figure 1 show that for the North Carolina phosphate rock, which is a more reactive one, the finer granules were nearly as effective P sources as concentrated superphosphate; the coarser granules were rather ineffective for the first crop and their effectiveness improved with consecutive cropping to about the same level as that of the finer granules. The availability of P from granulated central Florida phosphate rock, a less reactive phosphate, was about nil to the first crop, and it improved with consecutive cropping. The rate of improvement was faster with the finer granules than with the coarser ones.

Dry-matter yields of clover obtained in an experiment with Arad phosphate rock in soil from Ireland are presented in table 4. Differences due to treatments were statistically significant at a 0.01 level. Calculations of RAE were based on estimated maximal yields and related to Arad phosphate rock in powder form (minus 200-mesh). They are plotted in figure 2. Results in table 4 and figure 2 indicate a higher effectiveness of finer granules than that of coarser ones, a parallel agreeing with the one observed in the experiment with North Carolina phosphate rock. However, only effectiveness of finer granules incorporated into the whole soil volume improves with consecutive cropping. Surface-applied granules are considerably more effective, especially for the second and third harvest than the ones mixed

into the soil. The results do not show a clear preference in performance of the $MgSO_4$ or KCl binders.

The influence of binders on availability of phosphate rock as a P source to plants was tested in another experiment with Maktesh phosphate rock, again on soil from Ireland (table 5). Analysis of variance showed that differences due to treatments were significant at a 0.01 level for all yields except for the second cut of oats where they were significant at a 0.05 level. Relative agronomic effectiveness was calculated in the same way as for data in figure 1, and results are plotted in figure 3. Again, it may be seen that the relative effectiveness of granulated materials increases with consecutive cropping. No significant difference between binding materials may be observed, except for the sulfuric acid which by partial acidulation improves the effectiveness of the granulated phosphate rock.

Improved performance of granulated phosphate rock with consecutive cropping is additionally illustrated by data from an experiment with Maktesh phosphate rock on three soils (table 6), where differences due to treatments were statistically significant at a 0.01 level.

Conclusions

The experiments performed indicate that method of placement of the larger phosphate rock granules influences strongly their effectiveness as P sources to plants. Surface-applied granules are more effective than those mixed into the soil volume. It seems that the dispersion of material from granules embedded in the soil volume is inhibited by physical constriction, whereas those on the soil surface disperse gradually with continuing irrigation. Frequent watering probably enables root development in the upper soil layers. A combination of these factors would provide a better contact of roots with phosphate rock in the surface placement than in the other one. The method of placement of granulated phosphate rock seems to be an important factor in determining its availability to plants. Additional studies for understanding the phenomenon are necessary.

Influence of granule size on effectiveness is more pronounced with the more reactive phosphate rocks, where finer granules show a greater effectiveness than the coarser ones to the first crop. This difference was not observed with the less reactive phosphate simply because all granule sizes were a very poor phosphate source to the first crop.

The effectiveness of phosphate rock granules improves with consecutive cropping, and it may reach the same level of effectiveness as the finely ground materials. It seems that with continuous cropping a denser net of roots develops around the granules, enabling an improved P uptake. This explanation needs additional experimental work and clarification.

No clear influence of granule binder materials on their availability was observed in those experiments, except for sulfuric acid, which produced more available granules, probably because of partial acidulation.

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Table 1. Some Characteristics of Granulated Phosphate Rocks

Phosphate Rock	Binder Material	Specified Size Range	Average Diameter Dry Sieving	Average Diameter Wet Sieving	Stability to Water, No. of Drops
		(mm)			
Maktesh	5% $MgSO_4$	2-4	1.67	0.30	39
	10% KCl	2-4	1.47	0.25	14
	5% $(NH_4)SO_4$	2-4	2.18	0.67	220
	5% $MgCl_2$	2-4	1.92	0.26	12
	14% H_2SO_4	2-4	2.35	1.94	>450
Central Florida	10% $MgCl_2$	1.2-3.3	1.39	0.23	14
		0.3-1.2	-	-	-
		0.1-0.3	-	-	-
North Carolina	10% $MgCl_2$	1.2-3.3	1.55	0.31	41
		0.3-1.2	-	-	-
		0.1-0.3	-	-	-
Arad	5% KCl	2-4	-	-	14
		0.8-0.4	-	-	-
	5% $MgSO_4$	2-4	-	-	50
		0.8-0.4	-	-	-

Table 2. Some Characteristics of Experimental Soils

	Ireland	Germany	Turkey	England
Texture	clay loam	clay loam	clay	clay
pH	4.6	6.1	5.4	5.3
C, organic, %	2.0	1.0	0.8	2.2
Bray P_1 soil, µg P/g	20.0	30.5	1.1	7.6
Moisture at field capacity, %	29.4	19.2	27.7	25.1

Table 3. Effect of Granule Sizes of North Carolina and Central Florida Phosphate Rocks on Soil from Ireland--Dry-Matter Yields (g/pot) in Greenhouse Experiment

P Source and Granule Size Mesh	P Applied, g/pot	First Crop, Clover	Second Crop, Oats		Third Crop, Ryegrass		Accum. Yields
			1st Cut	2d Cut	1st Cut	2d Cut	
Central Florida 6/16	0.2	0.59	3.12	6.01	2.24	2.05	14.01
	0.5	0.57	3.29	6.22	2.55	2.13	14.76
	1.0	0.47	3.54	6.23	3.00	2.37	15.61
	4.0	0.68	3.18	5.50	3.60	2.89	15.85
Central Florida 16/48	0.2	0.55	3.20	6.24	2.05	1.72	13.76
	0.5	0.58	3.48	6.54	2.50	1.80	14.90
	1.0	0.69	3.60	6.46	2.60	2.06	15.41
	4.0	0.35	3.03	5.41	3.81	2.84	15.44
Central Florida 48/150	0.2	0.51	3.16	5.90	2.41	1.68	13.66
	0.5	0.65	3.44	6.45	2.70	1.88	15.12
	1.0	0.56	3.82	6.92	2.82	1.98	16.10
	4.0	0.77	4.58	6.67	3.37	2.13	17.52
North Carolina 6/16	0.2	0.45	4.30	7.33	2.23	1.41	15.72
	0.5	0.23	4.81	6.48	3.12	1.89	16.53
	1.0	0.79	5.63	7.17	3.53	1.99	19.11
	4.0	1.05	4.84	6.47	4.42	3.63	20.41
North Carolina 16/48	0.2	0.61	4.88	7.21	2.35	1.40	16.45
	0.5	1.13	5.46	6.71	2.94	1.79	18.03
	1.0	0.88	5.71	6.89	3.61	2.27	19.36
	4.0	2.07	5.11	6.40	4.52	3.84	21.94
North Carolina 48/150	0.2	0.87	4.77	7.55	2.25	1.44	16.88
	0.5	1.36	5.39	6.33	2.95	1.83	17.86
	1.0	2.46	5.92	6.47	3.62	2.28	20.75
	4.0	1.83	4.78	6.43	4.03	3.74	20.81
CSP	-	0.75	3.81	7.45	2.80	2.25	17.06
	0.1	1.15	4.64	7.07	2.30	1.50	16.66
	0.2	1.93	5.60	6.25	2.90	1.90	18.58
	0.5	2.31	5.87	7.32	3.70	2.50	21.70
	1.0	2.59	6.25	6.85	4.80	3.80	24.29

Table 4. Effect of Granule Size, Placement and Binder Materials of Arad Phosphate Rock in Soil from Ireland--Dry-Matter Yields (g/pot) in Greenhouse Experiment

Binder Material	Placement	Size (Mesh)	P Applied g/pot	Clover 1st Cut	Clover 2d Cut	Clover 3d Cut	Accum. Yields
KCl	mixed	5-10	0.2	0.35	0.29	0.67	1.31
			0.5	0.43	0.18	0.31	0.92
			1.0	0.47	0.60	0.55	1.62
			2.5	0.61	0.71	0.80	2.12
KCl	mixed	20-40	0.2	0.46	0.44	0.20	1.10
			0.5	0.57	0.75	0.69	2.01
			1.0	0.98	1.98	2.08	5.04
			2.5	2.11	5.78	6.06	13.95
KCl	surface	5-10	0.2	0.54	0.55	0.75	1.84
			0.5	1.15	3.25	3.54	7.94
			1.0	1.79	5.81	6.97	14.57
			2.5	2.53	7.18	7.55	17.26
$MgSO_4$	mixed	5-10	0.2	0.44	0.28	0.20	0.92
			0.5	0.49	0.42	0.36	1.27
			1.0	0.54	0.35	0.32	1.21
			2.5	0.78	1.34	1.74	3.86
$MgSO_4$	mixed	20-40	0.2	0.47	0.29	0.09	0.85
			0.5	0.65	0.90	0.76	2.31
			1.0	1.19	2.58	3.31	7.08
			2.5	1.99	5.26	6.29	13.54
$MgSO_4$	surface	5-10	0.2	1.02	1.91	1.46	4.39
			0.5	1.85	4.01	4.88	10.74
			1.0	2.55	6.18	7.45	16.18
			2.5	2.96	7.17	7.74	17.87
	mixed	-200	-	0.25	0.21	0.21	0.67
			0.2	0.58	0.85	0.95	2.38
			0.5	1.28	1.89	2.39	5.56
			1.0	3.21	6.31	7.65	17.17
			2.5	4.54	8.56	8.88	21.98

Table 5. Effect of Binder Materials of Granulated Maktesh Phosphate Rock (5-10 Mesh) Mixed in Soil From Ireland--Dry-Matter Yields (g/pot) in Greenhouse Experiment

Binder Material	P Applied, g/pot	First Crop, Clover	Second Crop, Oats		Third Crop, Ryegrass		Accum. Yields
			1st Cut	2d Cut	1st Cut	2d Cut	
$MgSO_4$	0.2	0.37	3.20	5.97	1.96	1.95	13.45
	0.5	0.48	3.93	7.30	2.43	1.74	15.88
	1.0	0.29	4.20	6.96	3.03	2.23	16.71
	4.0	0.60	4.63	7.14	4.20	3.78	20.35
KCl	0.2	0.27	3.71	6.66	2.28	1.90	14.82
	0.5	0.47	3.51	6.60	2.73	2.58	15.89
	1.0	0.44	3.80	6.80	3.52	3.00	17.56
	4.0	0.35	2.45	4.45	4.44	5.98	17.67
$(NH_4)_2SO_4$	0.2	0.52	3.65	6.62	1.94	1.66	14.39
	0.5	0.36	4.32	7.25	2.67	2.12	16.72
	1.0	0.36	4.33	7.92	2.78	2.31	17.70
	4.0	0.48	4.43	8.01	4.17	3.57	20.66
$MgCl_2$	0.2	0.35	3.84	7.31	1.88	1.70	15.08
	0.5	0.40	4.15	7.44	2.78	1.97	16.74
	1.0	0.73	4.15	7.75	2.85	2.33	17.81
	4.0	0.51	3.91	6.67	3.71	4.13	18.93
H_2SO_4	0.2	0.65	4.18	6.71	2.48	2.07	16.09
	0.5	1.02	5.18	6.90	2.62	1.76	17.48
	1.0	1.01	4.97	6.64	3.88	2.85	19.35
	4.0	1.04	4.90	7.22	5.03	4.19	22.38
(-200 mesh)	0.2	0.67	3.94	7.16	2.12	1.69	15.58
	0.5	1.18	4.85	6.79	2.60	1.92	17.34
	1.0	1.40	5.37	7.43	2.89	1.82	18.91
	4.0	1.49	5.05	7.44	4.56	3.68	22.22

For CSP treatments see table 3.

Table 6. Effect of Maktesh Phosphate Rock Granulated With $MgCl_2$ and Mixed Into Soil--Dry-Matter Yields (g/pot) in Greenhouse Experiment

Origin of Soil	Mesh Size	P Applied, g/pot	Dry Matter Yield: First Crop, Clover	Second Crop, Alfalfa: 1st Cut	2d Cut	3d Cut	Accum. Yields
England	-	0.0	0.79	0.17	0.08	0.48	1.52
	-200	4.0	3.03	5.33	7.10	8.05	23.51
	5-10	4.0	0.89	4.09	5.21	6.55	16.74
Turkey	-	-	0.40	0.15	0.07	0.20	0.82
		0.2	0.59	0.35	0.09	0.37	1.40
	-200	1.0	2.35	3.55	4.45	6.34	16.69
		4.0	4.00	6.95	6.63	7.23	24.81
	5-10	0.2	0.38	0.63	0.53	0.82	2.36
		1.0	0.44	1.61	2.25	2.97	7.27
		4.0	0.78	4.33	5.25	6.37	16.73
Germany	-	-	0.70	0.76	0.65	1.38	3.49
		0.1	1.02	2.05	1.83	2.96	7.86
		0.2	1.22	2.93	3.21	5.49	12.85
	-200	0.5	1.44	5.46	5.52	7.73	20.15
		1.0	1.91	4.34	4.94	7.36	18.55
		4.0	2.96	6.82	5.72	7.46	22.96
	5-10	0.1	0.96	1.22	1.06	2.75	5.99
		0.2	1.05	1.46	1.60	3.30	7.41
		0.5	0.96	2.82	3.45	6.18	13.41
		1.0	0.97	3.98	4.40	7.13	16.48
		4.0	0.99	5.25	5.45	7.50	19.19

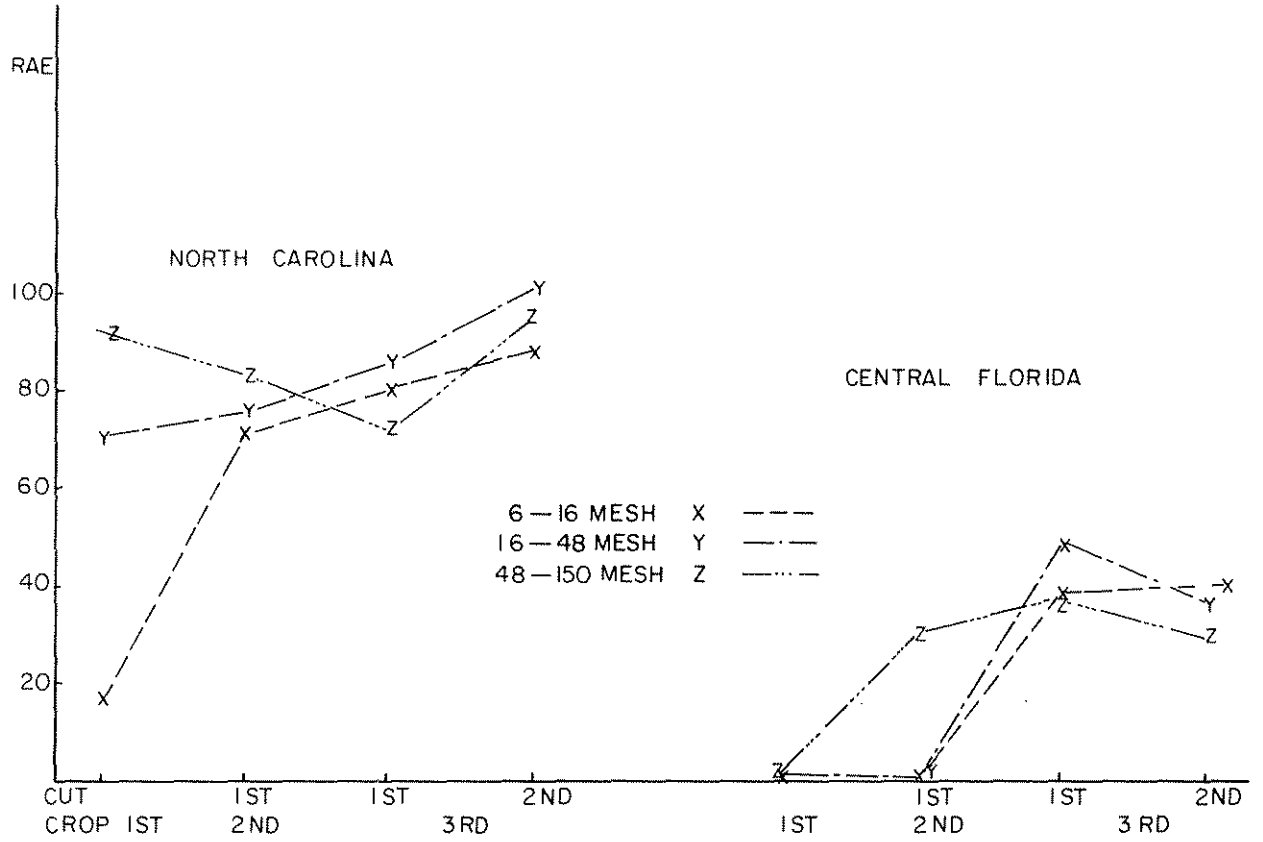

Figure 1. Influence of North Carolina and Central Florida PR Granule Size on Their Relative Agronomic Effectiveness (RAE).

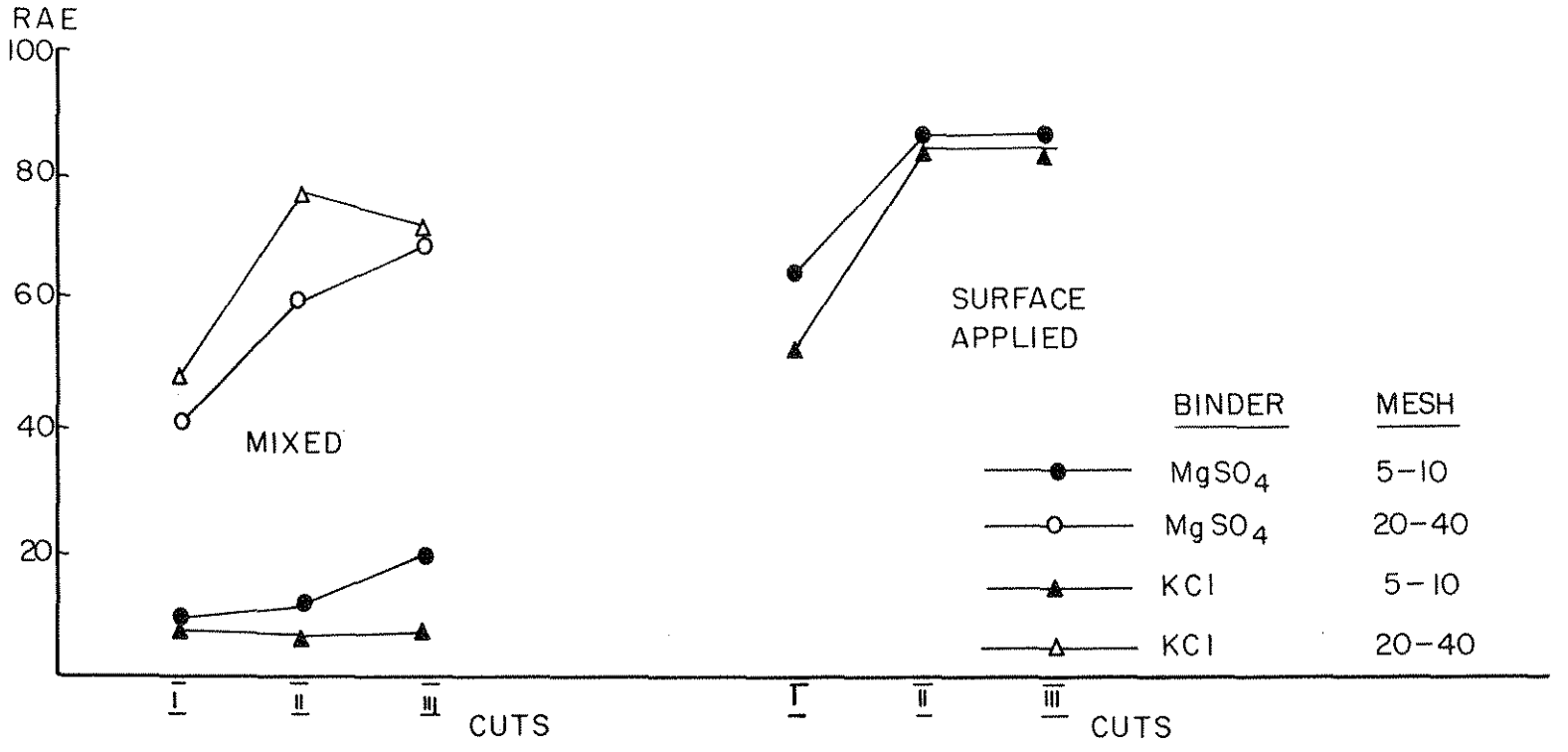

Figure 2. Influence of Arad Phosphate Rock Granule Size and Method of Placement on Its Relative Agronomic Effectiveness (RAE).

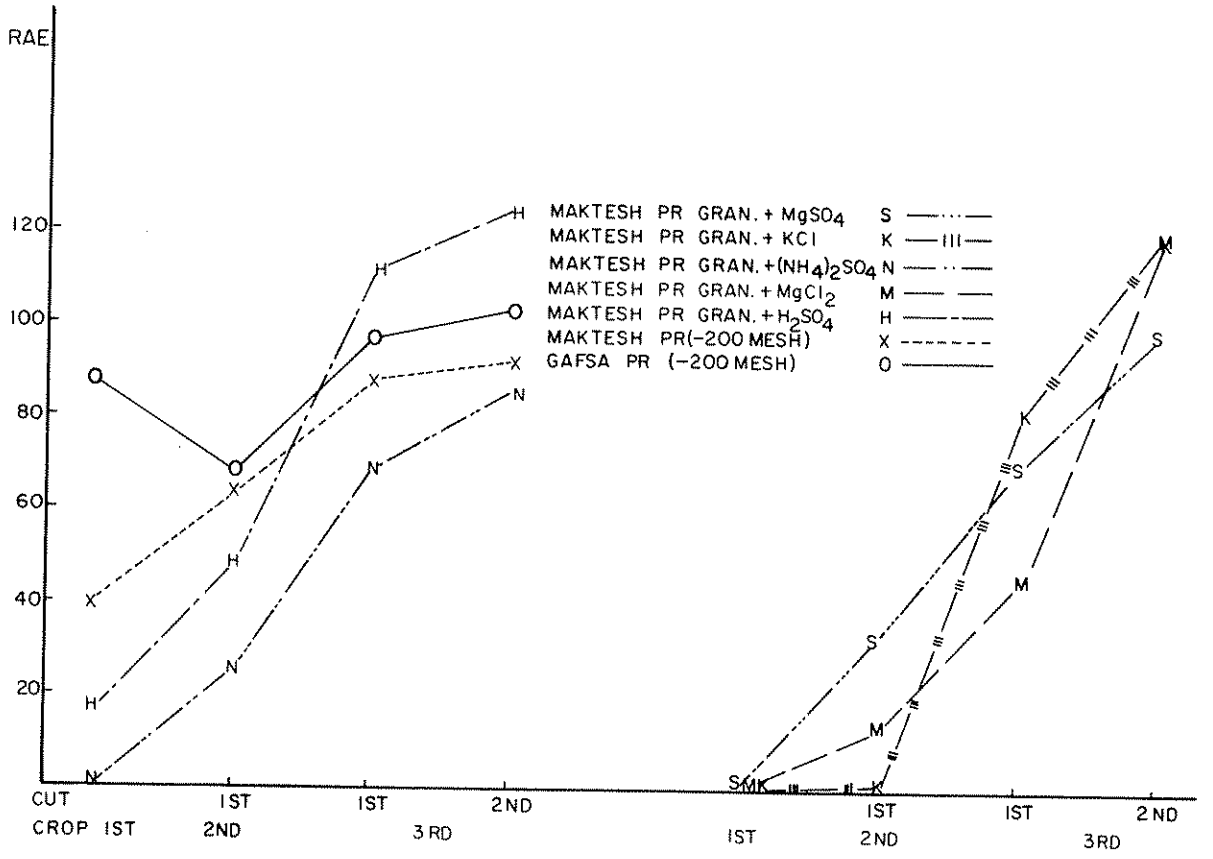

Figure 3. Influence of Maktesh PR Granule Binders on Relative Agronomic Effectiveness (RAE).

EFFECT OF GRINDING ON ARAD PHOSPHATE ROCK AVAILABILITY

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Abstract

In a greenhouse experiment on an acid soil, Arad phosphate rock, from the Negev area of Israel, was ground to various fineness and tested as a P source to plants. Phosphate rock in the range of 20- to 100-mesh was less effective than one ground to pass 100-mesh. Additional grinding (200-mesh) improved the effectiveness. The effectiveness of degree of grinding was reflected in phosphate rock solubility tests and in some soil analyses.

Introduction

Arad phosphate rock from the Negev area of Israel seems to be a rather reactive phosphate rock and suitable for direct application on acid soils. (Hagin et al., 1977). Information on the influence of fineness of grinding of this phosphate on its effectiveness as a P source to plants is important. Barnes and Kamprath (1975), in reviewing the influence of particle size of rock phosphate on its avaiiability, conclude that this effect was small in most investigations, although in most instances the smallest particle size used was 100-mesh. Hammond (1977) concludes in reviewing work done on fineness of grinding that grinding finer than 100-mesh is rarely justified. Caro and Hill (1956) found a relation between citric acid solubility of phosphate rocks and particle size.

Chien (1977) found an inverse relation between particle size and phosphate rock's solubility for a given time of reaction and concluded that particle size may affect the rate of dissolution rather than the maximum solubility. In an unpublished paper (S. H. Chien, 1975: Particle Size Effect on the Dissolution Rate of Phosphate Rock) limiting size of phosphate rock particles related to its solubility was calculated from a diffusion

equation, and it was concluded that particle-size effect may be a factor for short-term crop response and not significant in a long term.

Materials and Methods

Four size grades of Arad phosphate rock were prepared from one batch. The coarsest size grade, Sample A (plus 20- minus 100-mesh), was obtained by sieving the raw phosphate rock. The minus 100-mesh (Sample B) and minus 200-mesh (Sample D) grades were obtained by hand grinding in a mortar the above sample. An additional Sample C was ground in a jet mill. Some of the properties of the phosphate rock samples are given in table 1.

The soil from Ireland used in this experiment, the crop, greenhouse techniques, and plant and soil analyses are identical to those described in another paper in these proceedings: Hagin et al. "Comparison of Finely Ground Phosphate Rocks as P Sources to Plants."

Results

Yield of three cuts of ryegrass and P uptake are presented in table 2. Analysis of variance showed that differences due to treatments were significant at the 0.01 level. Total yields were plotted by freehand yield curves, and maximal yield was estimated. Relative agronomic effectiveness (see above paper), based on maximal yield, was calculated relative to the maximal yield obtainable by superphosphate. That, based on P-uptake, was related to North Carolina phosphate rock treatments. Data for both reference materials were taken from experiments reported in the above paper. Results of these calculations are listed in table 3.

The yield and P uptake data in table 2 and the relative agronomic effectiveness calculated in table 3 indicate that the effectiveness of Arad phosphate rock as a P source to plants increases with degree of grinding. The degree of grinding is also reflected in the solubility indices (table 1), where grinding increases the relative solubility.

Soil-phosphate mixtures were prepared parallel to those used for the greenhouse experiment. Soluble phosphate in them was determined shortly after the dry mixtures were prepared. Results of these measurements are given in table 4, and they represent the initial P status of the mixtures. As may be seen from table 4, rates of application are reflected in all P extraction results and somewhat in the pH values. The influence of grinding on extractable P can be determined by the water and Bray methods. Other methods of extraction do not effectively show the effect of grinding of the phosphate rock.

Soil samples were taken from greenhouse pots after the third cut of ryegrass. In the samples pH varied between 5.2 and 5.5, and the values are not reported (table 4). Results of P extractions are presented in table 5. These results represent the P status of the soil-phosphate mixture after some time of equilibration in the presence of plant roots. Again, levels of P application are well reflected in all extraction methods. All extraction methods used, except water extraction, differentiate between the coarser particle sizes (Sample A) of applied phosphate rock and between the finer ones (Samples B, C, and D), but they do not differentiate between degrees of grinding finer than minus 100-mesh.

Conclusions

Greenhouse experiment results indicate that the degree of fineness of Arad phosphate rock may somewhat influence its availability as a P source to plants. The indications are that a fineness of material to pass a 100-mesh sieve is necessary to ensure a relatively high availability to plants. A finer grinding down to minus 200-mesh may somewhat improve its availability.

Relative solubility of the variously ground phosphate rock in citric and formic acid and P extractability of fresh soil-phosphate rock mixtures produce similar indications. P solubility tests after a prolonged soil-phosphate rock contact in presence of plants do not differentiate between fineness of grinding below minus 100-mesh. These results are in agreement with observations of other authors reported in the Introduction.

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Table 1. Some Characteristics of Arad Phosphate Rock Ground to Various Degrees of Fineness

Sample	Nominal	Particle-Size Distribution % in Mesh Size									P_2O_5 Relative Solubility in 2% Acids	
		-200	-325	+20	(-20) +100	-100 +200	-200 +325	-325 +625	-625	Total	Formic	Citric
A	20/100	1.5	0.4	0.4	85.9	12.2	1.1	0.4	-	32.7	53.5	33.8
B	-100	54.5	38.5	-	2.0	43.5	16.0	11.0	27.5	34.0	59.7	35.4
C	-425	87.0	76.0	0.0	3.0	10.0	11.0	10.0	66.0	34.0	60.3	38.4
D	-200	91.4	80.6	0.0	1.4	7.3	10.7	80.6	-	33.1	61.1	38.9

Table 2. Yield of Ryegrass and P Uptake with Arad Phosphate Rock, Ground to Various Degrees of Fineness

Sample	P Applied, g/pot	Dry-Matter Yield, g/pot			P Uptake, mg P/pot		
		1st Cut	2d Cut	3d Cut	1st Cut	2d Cut	3d Cut
Check	0	5.26	4.84	4.30	10.5	7.6	5.1
A	0.2	6.01	5.63	4.35	10.3	9.9	5.7
	0.5	7.19	5.71	4.93	17.3	12.3	8.3
	1.0	7.73	6.16	5.17	21.6	16.3	10.7
	4.0	8.23	6.88	5.43	29.0	29.2	17.4
B	0.2	6.54	5.20	4.13	14.6	10.2	6.1
	0.5	7.90	6.19	5.33	22.7	17.8	9.8
	1.0	7.83	6.54	5.21	23.2	22.0	12.5
	4.0	8.29	7.33	6.08	31.2	38.4	22.9
C	0.2	6.95	5.37	5.39	16.1	12.7	7.8
	0.5	7.70	6.36	5.92	21.6	17.8	12.8
	1.0	7.40	6.76	6.47	25.5	26.5	16.0
	4.0	8.16	7.23	6.92	33.9	43.6	26.0
D	0.2	6.99	5.56	4.54	16.2	10.9	7.3
	0.5	7.88	6.41	5.52	21.1	16.1	9.9
	1.0	8.15	7.68	7.35	29.3	34.7	23.8
	4.0	8.16	7.30	7.71	32.6	36.5	27.1
Standard deviation		0.33	0.23	0.25			

Table 3. Relative Agronomic Effectiveness (RAE) of Arad Phosphate Rock Ground to Various Degrees of Fineness

Sample	RAE Based on Maximal Yield	RAE Based on P Uptake at 4 g P/pot
A	70.0	54.1
B	84.4	71.5
C	95.5	83.3
D	97.8	75.5

Table 4. Effect of Grinding of Arad Phosphate Rock on P Extracted from Freshly Prepared Soil-Phosphorus Mixtures

Sample	P Applied, g/pot	pH	Water, µg/ml	Bray P_1, µg/g	Double Acid, µg/g	Anion Resin, µg/g	Cation Resin, µg/g
A	0	5.2	0.08	24.6	10.5	24.0	10.8
	0.2	5.1	0.06	25.3	48.6	72.0	51.0
	0.5	5.1	0.06	30.3	140.0	184.0	100.4
	1.0	5.2	0.08	27.5	308.0	337.0	186.7
	4.0	5.3	0.13	36.7	856.7	536.0	534.2
B	0.2	5.2	0.09	26.8	61.3	74.6	60.2
	0.5	5.2	0.10	33.3	238.7	153.3	135.2
	1.0	5.2	0.10	29.6	186.7	126.6	127.1
	4.0	5.3	0.37	88.3	1,310.0	750.0	640.0
C	0.2	5.2	0.13	32.3	66.4	78.0	72.5
	0.5	5.2	0.25	38.6	161.3	128.0	181.7
	1.0	5.2	0.34	62.7	382.7	233.3	300.0
	4.0	5.4	0.59	136.7	1,546.7	546.6	675.0
D	0.2	5.2	0.09	36.0	62.1	76.0	75.8
	0.5	5.3	0.14	44.0	178.6	142.7	181.7
	1.0	5.3	0.30	67.0	465.3	253.3	320.0
	4.0	5.5	0.55	130.6	1,310.0	570.0	560.0
Standard deviation			0.02	2.2	29.3	16.4	9.1

Analysis of variance: differences due to treatments significant at the 0.01 level.

Table 5. Effect of Grinding of Arad Phosphate Rock on P Extracted from Soils Sampled from Pots After Three Cuts of Ryegrass

Sample	P Applied, g/pot	Water, µg P/ml	Bray P_1, µg P/g	Double Acid, µg P/g	Anion Resin, µg P/g	Cation Resin, µg P/g
A	0.2	0.04	20.3	61.3	40.4	37.0
	0.5	0.05	22.2	141.3	39.2	75.7
	1.0	0.08	17.6	189.3	96.6	149.2
	4.0	0.20	33.4	897.0	222.6	319.8
B	0.2	0.05	22.2	101.3	61.2	52.7
	0.5	0.05	27.2	184.0	106.4	129.7
	1.0	0.09	28.0	176.0	226.4	251.0
	4.0	0.10	32.8	1,260.0	364.0	460.0
C	0.2	0.05	20.8	65.6	67.3	65.7
	0.5	0.07	25.8	139.2	43.2	132.0
	1.0	0.10	28.4	264.0	184.0	158.3
	4.0	0.28	51.2	1,191.0	405.3	535.0
D	0.2	0	15.5	68.0	64.0	35.0
	0.5	0	21.0	141.0	96.0	142.0
	1.0	0.12	39.2	504.0	279.0	325.0
	4.0	0.18	34.4	940.0	342.7	415.0
Standard deviation		0.02	2.4	49.9	14.1	20.5

Analysis of variance: differences due to treatments significant at the 0.01 level.

EVALUATION OF THE BRAY P_1 METHOD FOR MEASURING PHOSPHATE ROCK AVAILABILITY IN SOILS

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Abstract

Phosphate rocks (Maktesh and Arad from Negev, Israel, and Gafsa from Tunisia) and concentrated superphosphate were added to two acid clay loam soils.

P extracted by the Bray P_1 method from greenhouse experiment samples was related to yields obtained. Two separate curves were obtained, one for rock phosphates and the other for concentrated superphosphate. Inorganic P fractionation in the same samples showed that most of the P in the rock phosphate treatments was in the Ca-P form, while that in the superphosphate treatment was in the Al and Fe-P forms.

Phosphate-treated soil samples were shaken in the Bray P_1 solution for 1, 5, and 60 minutes. The prolonged shaking did not increase the amounts of P extracted. Varying the soil-solution ratio from 1:5, 1:10, 1:20, and 1:50 to 1:100 did not change appreciably the amounts of P extracted from superphosphate treatments, but it influenced the amounts extracted from phosphate rock treatments. It was concluded that a wider soil-solution ratio than the standard one should be used for evaluating P availability in phosphate rock-treated soils.

Introduction

Extraction of P from soils by the Bray P_1 solution (0.03M NH_4F + 0.025M HCl) is used as a phosphorus availability index, mainly in acid soils (Olsen and Dean, 1965). In soils where rock phosphate and superphosphate were applied, two different curves relating plant response to extracted P were obtained for the two sources (Barnes and

Kamprath, 1975). Chien (1978) showed that P extracted by Bray P_1 solution from acid soils treated with phosphate rocks is partially derived from the unreacted phosphate rocks.

In this paper effects of extracting conditions on amounts and concentrations of P extracted from soils treated with superphosphate and rock phosphate are presented.

Materials and Methods

Greenhouse and laboratory experiments were performed in two soils. Some of their characteristics are presented in table 1.

Texture was determined by a sedimentation and decantation method (Black, 1965). In soil paste pH was measured at water saturation percentage or in solutions by glass calomel electrodes (Jackson, 1958). Organic carbon was determined by a wet combustion method and potentiometric titration of dichromate residues (Raveh and Avnimelech, 1972). Bray P_1 available was determined in a 1:10 ratio of soil to a dilute acid-fluoride solution or at the stated ratio. P in solution was determined by the method of Murphy and Riley (1962). The phosphate materials and some of their properties are listed in table 2. All materials were ground to pass a 200-mesh sieve. Total P was determined by the AOAC method (Horowitz, 1975).

Solubilities in 2% citric and 2% formic acid solutions were determined at a 1:100 solid:solution ratio and after one-half hour of shaking and filtration.[1] The greenhouse techniques and plant analyses were identical to those described in another paper in this Proceedings (Hagin et al. "Comparison of Finely Ground Phosphate Rocks as P Sources to Plants"). Bray P_1 available was measured in soil samples taken from the pots. In an experiment with the soil from

1. The methods follow: (1) Fertilizers-Methods of Analysis used in OEEC countries, Organization of European Economic Cooperation, Paris 16e, 1952; and (2) The Fertilizers and Feeding Stuff Regulation 1973, Her Majesty Stationary Office, p. 53.

Ireland, soil to solution ratios were 1:10 and 1:50, while in the soil from Germany the ratio was only 1:10. At the end of greenhouse experiments, fractionation of inorganic P (Petersen and Corey, 1966) was performed in some of the samples.

In the laboratory experiments, unlimed soil from Ireland was mixed with phosphate materials to provide 250, 500, 1,000, and 2,000 µg P/g soil. The mixtures were incubated 4 weeks with wet and dry cycles as described in another paper in these Proceedings (Reinhorn and Hagin. "Reactions of a Phosphate Rock with Soil"). The following extraction conditions were evaluated: at a 1:10 soil to solution ratio shaking periods were 1, 5, and 60 minutes, and at a shaking period of 5 minutes, soil to solution ratios were 1:5, 1:10, 1:20, 1:50, and 1:100.

Results

Dry matter yields obtained in a greenhouse experiment were related to amounts of P extracted by the Bray P_1 method. Dry matter yields were taken for the third crop obtained on soil from Germany (sum of two cuts) presented in table 3 of another paper in these Proceedings (Reinhorn et al. "Relation of Phosphate Rock Availability to Some Soil Properties and Cultivation Time"). The Bray P_1 available values were taken from table 8 of the same paper. The relation between yield and extracted P is presented in figure 1. Two separate curves can be distinguished: one for the concentrated superphosphate and the other curve for the phosphate rocks. At a given Bray P_1 value, the yield response to phosphate rock is higher than the response to superphosphate. This indicates that the extractable P and plant-available P are different for the two curves.

Results of fractionation of inorganic P in some of samples from the same pot experiment are presented in table 3. The fractionation of residual phosphates indicates that most of the Maktesh phosphate rock is still in the HCl-soluble fraction which is assumed to contain mainly Ca-P form, probably in the original form of apatite while the concentrated superphosphate is mainly in the NH_4F and NaOH soluble forms which contain mainly Al and Fe-P forms, respectively.

In the laboratory experiments, effects of extracting conditions on amounts of P extracted were studied. The amounts of P extracted after different periods of shaking are presented in table 4. These results indicate that the 5-minute period, which is used in the standard method, gave the maximal values. Increasing the shaking periods did not increase the amounts of P extracted, some decrease even occurred, and the same pattern was obtained for all P sources, the soluble and insoluble ones.

The P extracted, expressed as concentration on soil basis (µg P/g) or as percent of the applied P, and the mean values of measured pH in the resulting solutions at five ratios of soil to solution are presented in table 5. The amounts of P extracted from the superphosphate-soil mixture are fairly constant, independent of the volume of liquid phase. The percent of P extracted from these mixtures is not clearly affected by the amount of P applied, whereas the amounts of P extracted from the phosphate rock-soil mixture increase with the increasing volume of solution per gram of soil. The percent of P extracted from the soil treated with rock phosphate decreases greatly with the amount of P applied. The efficiency of the extraction as indicated by the percent of P extracted is higher for soils containing superphosphate than for those containing phosphate rock at all ratios, but the difference decreases with the soil to solution ratio.

In the resulting solutions pH was affected by the soil to solution ratio. The original pH of 3.1 increased with the ratio of soil to solution.

In figure 2 the change of P concentration in the solution versus volume of solution per gram of soil for some of the samples is presented. The concentrated superphosphate shows a steep decrease of concentration with increase of volume of solution per gram of soil for the narrower soil-solution ratios, whereas the curves for phosphate rock treatments show a slight decrease in concentration to a quite constant value.

Discussions and Conclusions

When applying a soluble source of P to an acid soil, most of the reaction products will be in the

aluminum and iron phosphate fraction (Russell, 1961) while when applying phosphate rock most of it will remain in the original form (Moschler et al., 1957). This is illustrated also by the results of fractionation of inorganic P (table 3). The Bray extracting solution removes P from reaction products and from unreacted phosphate rock also (Chien, 1978). In soils where superphosphate was applied, probably all the P extracted is from the reaction products. In soils where rock phosphates were applied, Chien (1978) showed that a large portion of the extracted P was from the unreacted phosphate rock. He also assumed that both forms of phosphate rock--unreacted and reaction products--contribute to the P removed by plants. We further assume that a larger amount of the unreacted phosphate rock is plant available than is extractable by this method.

This may be the reason for receiving two different curves for the reaction between plant response and P extracted: one for the phosphate rocks and one for the superphosphates (figure 1). Similar results were obtained by Barnes and Kamprath (1975). However, they assumed that some acidulation product from the phosphate rock is plant available but not extractable.

In order to measure the plant-available P from soils where phosphate rock was applied, the extraction method should be changed so that more of the unreacted phosphate rock becomes extracted. By increasing the extraction time from 1 minute to 5 minutes, a small increase was observed, similar to the results of Chien (1978), but increasing the extraction time to an hour did not increase the amounts of P extracted (table 4). By increasing the ratio of soil to solution, more P from the phosphate rock-soil mixtures could be removed, and only a small effect on the superphosphate-soil mixtures was observed (table 5).

Smith et al. (1957) found also that the 1:50 soil to solution ratio is preferable for evaluating availability of phosphate rock in soils.

An additional interesting finding is related to the change of the concentration of P in solution (figure 2). In the system containing superphosphate the decrease of concentration with decrease of soil to solution ratio can be explained by a dilution process. In the system

containing phosphate rock, probably two processes occur simultaneously: one is the dissolution of a slightly soluble P source and the other is the dilution of a solution containing soluble P. This would indicate the existence of two different fractions containing P in the phosphate rock-soil mixture: a readily soluble source which is diluted when more solution is used and a less soluble one which solubilizes at a quite constant concentration. The existence of different fractions of apatite in phosphate rock was proposed by Chien and Black (1975) as an explanation for a range of solubilities exhibited by the apatite.

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Table 1. Some Properties of Experimental Soils

Location of Sampling	Texture	pH	Organic C, %	Bray P Available, µg/g
Germany	clay loam	6.1	0.98	30.5
Ireland	clay loam	4.6	2.00	20.0

Table 2. Some Properties of Phosphate Materials

Material	P Total, %	P, % of Total P Soluble in	
		Citric Acid	Formic Acid
Maktesh	13.1	31.3	56.5
Gafsa	12.8	39.1	71.1
Arad	14.5	37.9	62.1
Concentrated superphosphate	20.7	-	-

Table 3. Fractionation of Inorganic P in Samples Taken at the Completion of the Greenhouse Experiments (Soil from Germany)

Phosphate Materials	P Applied, g/pot	P Fractions Soluble (µg/g) in Solutions of:			
		NH_4Cl	NH_4F	NaOH	HCl
-	0	2.5	39.0	115.0	70.0
Maktesh	4	6.5	74.0	135.0	1,090.0
Concentrated superphosphate	1	13.5	176.0	204.0	58.7

Table 4. Effect of Period of Shaking on P Extracted by Bray P_1 Solution From Different P Sources (at 1:10 Ratio to Soil Solution)

P Source	P Applied µg/g	P Extracted (µg/g) After Shaking Periods of: 1 min	5 min	60 min
-	0	26	29	15
Arad phosphate	250	44	66	40
	500	59	78	46
	1,000	77	91	65
	2,000	88	105	75
Maktesh phosphate	250	46	80	29
	500	56	78	43
	1,000	64	66	41
	2,000	80	85	57
Superphosphate	250	134	117	122
	500	248	315	228
	1,000	488	540	510
	2,000	906	1,100	1,040

Table 5. Effect of Soil-Solution Ratio in Bray Extraction on Amount of P Extracted and on pH of Resulting Solution

Soil-Solution Ratio	P Applied, ppm	P Source: Superphosphate P Amount, µg P/g	Superphosphate % of P Applied	Superphosphate pH	Arad Phosphate P Amount, µg P/g	Arad Phosphate % of P Applied	Arad Phosphate pH
1.5	0	15.3		3.70	-		3.90
	250	128.0	45.1		26.5	4.5	
	500	250.0	46.9		32.0	3.3	
	1,000	385.0	36.9		44.0	2.9	
	2,000	665.0	32.4		47.0	1.6	
1:10	0	29.0		3.47	-		3.65
	250	117.0	35.2		66.0	14.8	
	500	315.0	57.2		78.0	9.8	
	1,000	540.0	51.1		91.0	6.2	
	2,000	1,100.0	53.5		105.0	3.8	
1:20	0	36.0			-		3.35
	250	-			65.0	11.6	
	500	-			84.0	9.6	
	1,000	-			126.0	9.0	
	2,000	-			138.0	5.1	
1:50	0	34.0		3.10	-		3.10
	250	122.0	35.2		99.0	26.0	
	500	345.0	61.6		142.0	21.6	
	1,000	607.0	57.3		194.0	16.0	
	2,000	1,281.0	62.3		255.0	11.1	
1:100	0	48.7		3.10	-		3.10
	250	151.0	40.9		228.0	71.7	
	500	312.0	52.7		235.0	37.3	
	1,000	820.0	77.1		380.0	33.1	
	2,000	880.0	41.6		500.0	22.6	

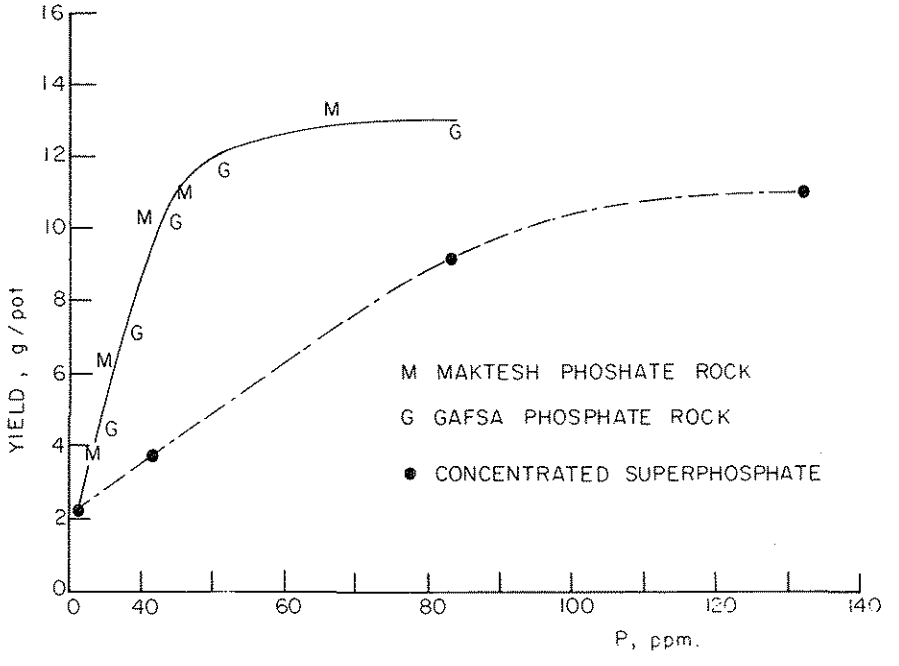

Figure 1. Relation Between Dry-Matter Yield of Third Crop and P Extracted by Bray Method Prior to Sowing That Crop (Soil from Germany).

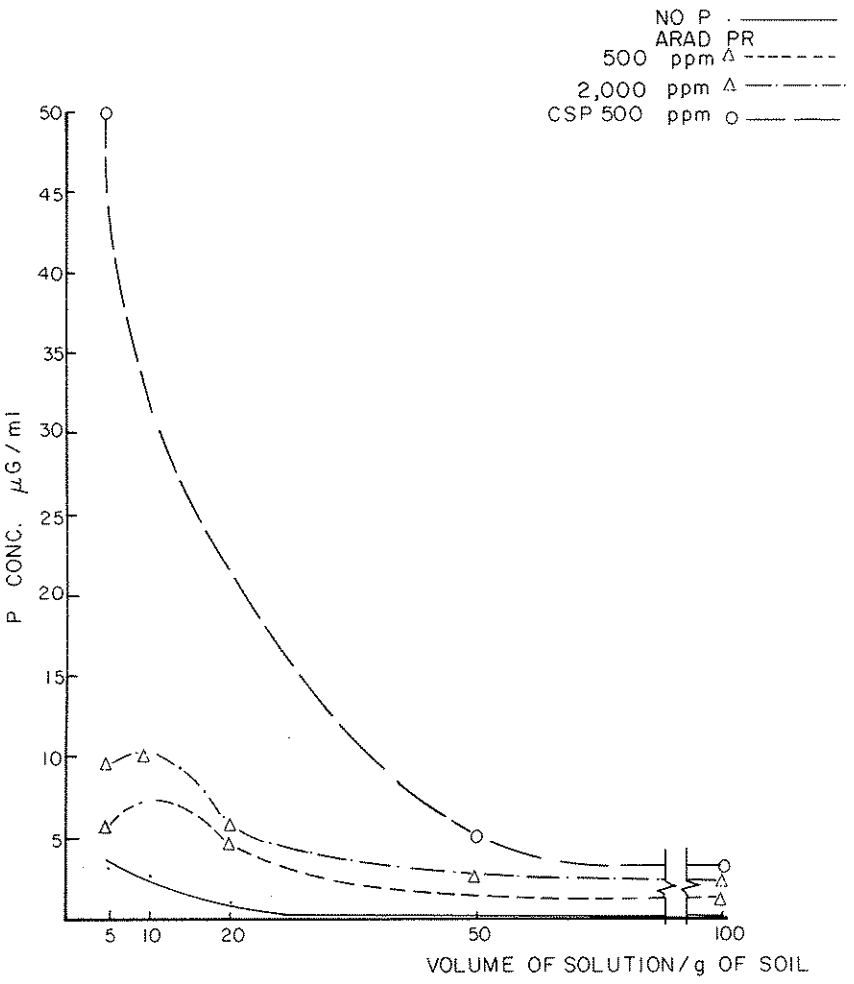

Figure 2. P Concentration in the Extracting Solution Versus Volume of Extracting-Solution/g Soil (Soil Samples Incubated 4 Weeks with CSP or Arad PR).

METHODS OF GRANULATION

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Negev Phosphates Ltd.

Summary

Effects of various parameters on the physical properties of granulated phosphate rock material were checked in order to get a granular product which can be handled and transported in bulk. It was found that by changing the drying process it is possible to increase the strength of granules which have the usual size distribution (2-4 mm) up to the desired crushing strength of 5-10 lb/granule. Another granular product which is already used in Brazil is minigranules made of phosphate rock powder bound with salt. The benefit of this material is high initial availability which is almost similar to the ground phosphate rock. Since the commercial material is weak it was necessary to look for a low-cost process which will strengthen the minigranules in order to eliminate dust problems during transportation. The suitable equipment was found to be the pinmixer which is already used in densification of carbon black powder.

Since those products had to be sent by bulk, it was necessary to study the effects of different salts on the moisture resistance of the material. It was found that the critical humidity of the granular product containing 3%-5% salt was much higher than the critical humidity of the pure salt. This was explained by the buildup of a moist layer on the surface of the pile which reached a certain depth--about 1 inch--blocking the way for more moisture to penetrate the pile even at relative humidities of 90%-95%. This was tried successfully with bulk storage, handling, and transportation of 15,000 tons of phosphate rock granules containing 5% $MgCl_2$ which were sent from Oron/Israel to Europe.

Methods

Effects of various process parameters on the physical properties of granular PR material were

checked in order to develop a product which will not be damaged during bulk handling and transportation and which will stand atmospheres of high humidities.

The conventional procedure of bagging after production increased the cost of the final product by 30%, eliminating the advantage of using a cheap raw material for direct application.

The laboratory tests were done at the International Fertilizer Development Center (IFDC) in Alabama, while the industrial part was carried out in the granulation plant at Oron, Israel. The flowsheet of the granulation plant at Oron is shown in figure 1.

Fine phosphate rock with recycle is fed batchwise to an Eirich mixer. The ratio of rock to recycle is 2. After a short mixing time, diluted $MgCl_2$ brine is added to the mixer through two full-cone nozzles. The total mixing time is 2 minutes. The wet blend is then transferred to a buffer silo which continuously feeds two 8-foot diameter pans by means of a table feeder.

After being dried in a rotary dryer, the granules are screened to a plus 2- minus 4-mm size. The undersize is transferred to the recycle silo, while the oversize (plus 4 mm) is rejected. The amount of oversize is usually 0.5% to 1.0% of the product.

The batch units are controlled automatically from a central control board. The flow of material from the table feeder throughout the rest of the system is controlled manually.

The laboratory work was done in such a manner as to simulate the industrial plant operation as nearly as possible. It consisted of a kitchen mixer, 16-inch diameter pan, and 10-inch diameter rotary drum heated by an air gun heater. The laboratory tests were carried out batchwise.

The granulation of fine powder-like phosphate rock can be separated according to this flowsheet into three stages:

1. Mixing the fine powder and the recycle with brine--This is done mostly with pugmills or batch mixers. The product of this stage is small agglomerates which are very porous.

2. Granulation--This is primarily done in a pan or a drum. Relatively high forces are applied on the agglomerates, causing breakage and compaction. At the end of the granulation there is no more breakage, and the material is round and compact. The excess moisture is pushed to the granule's shell as the result of the compaction.

3. Drying--While the water evaporates, the dissolved salt crystallizes and binds the small particles of the powder together.

The first and the second stages determine the size distribution and the porosity of the granular product. The parameters involved are: size distribution of the powder, recycle/feed ratio, percent moisture, degree of premixing, residence time, and speed and angle of pan.

Besides the porosity which has some effect on the granule strength, the factors that dominate the strength are connected to the drying step.

The drying of granular materials involves three stages (D. M. Newitt et al., 1959):

A - B Constant rate--The shell of the granule is wet enough to saturate the boundary layer around the granule.

B - C Constant decrease in rate--The granule surface begins to dry. Moisture reaches the shell by capillary effect.

C - D Dry surface--The surface is completely dry. Moisture is driven to the shell by gas diffusion.

The relative length of stages B and C depends on the drying temperature. Low drying temperature lengthens line B - C, while high drying temperature lengthens line C - D. When using solution the dissolved salt moves toward the shell during stage B - C while it crystallizes in its place at stage C - D (figure 2).

The second effect of temperature is the crystallization move. Using high drying temperature accelerates the nucleation and, therefore, the crystal

size is small. Using low temperature leads to crystal growth.

In order to produce strong granules, it is desirable to have a uniform distribution of the salt throughout the granule and to have as many intra-granular bonds as possible by the creation of small crystals. This can be accomplished by using high temperatures during drying (figure 3).

Trying to establish this in the cocurrent dryer at Oron yielded an inferior product. Increasing the drying temperatures created excessive breakage due to thermal shock. Changing the operation from cocurrent to countercurrent eliminated the breakage and enabled achievement of good control on product strength.

The temperature profiles in three modes of drying show that the smallest thermal shock will occur in the countercurrent dryer (figure 4). Figure 5 gives the comparison between size distribution of two products which were made by using the same conditions of feed, percent moisture, size distribution of feed, etc. It is clear that the product of the counter-current dryer is superior. The crushing strength of that product was about 3-5 times higher than that of the product of the cocurrent operation.

Using the countercurrent dryer, it was possible to get the effects of drying temperature (expressed in % moisture of the product) and salt percentage on the crushing strength of the dried granules. Figure 6 summarizes 3 months of operation with the counter-current dryer. Choosing a certain concentration of salt (expressed as % Cl), the strength increases when % moisture decreases (or in other words, when the drying temperature increases).

It is possible to check a uniform distribution of the salt in the granule when correlating the crushing strength versus the diameter of the granule. When the salt is distributed uniformly, strength would increase as a linear function of the cross-section area of the granule (figure 7).

Using different salts as binders did not yield marked changes in strength (both at the laboratory

and at the plant). It was interesting to investigate the influence of the fine insoluble powder qualities on the bond between the crystallized salt and the insoluble particles. This can be seen in the granulation of a fine powder of soluble salt with a small amount of insoluble binders with different surface areas. The granulation was carried out in a manner similar to that of phosphate rock, and all parameters besides the binder type were the same (figure 8).

Using bulk transportation, the granular material should not absorb moisture from a relatively high humid atmosphere. At the range of 8%-10% moisture, the material loses its strength. It seems, therefore, that the salt used as a binder (3/1, $MgCl_2/CaCl_2$) was too hygroscopic. After some tests with potash as a binder, samples were compared using Tennessee Valley Authority (TVA) procedure--hygroscopicity (TVA report No. S-444, 1970). Beakers containing 5-inch depth of granular material were introduced into a constant humidity cell. Increase in weight with time in the range of 35%-80% relative humidity showed that there was no difference between the two binders (figure 9).

During the test of moisture penetration with time a layer of about 1 inch of affected material forms on the surface; thus, additional moisture penetration is prevented (figure 10). The same phenomena was observed with an 8,000-ton pile at Oron, Israel, which was exposed for several months in the winter. There was no penetration of moisture into the pile--more than 1 inch--even after light rains. Oil spraying is sometimes used to improve the moisture resistance of the granules. Using the same procedure, no difference was observed before and after spraying oil--as described in figure 11.

As a result of these tests, commercial trials in bulk transportation from Oron, Israel, to Europe were made during 1977. In these trials, 15,000 tons of phosphate rock granules containing 5% of $McCl_2$-$CaCl_2$ was stored, handled, and transported in bulk successfully.

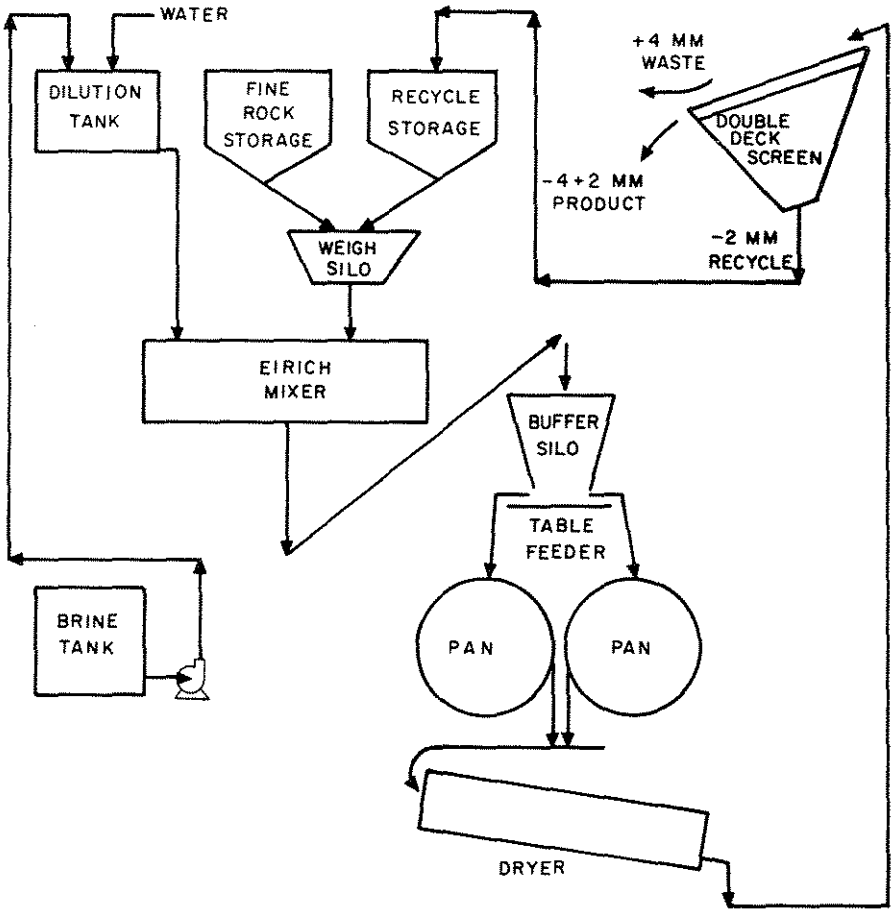

Figure 1. Flowsheet of Oron Granulation Plant.

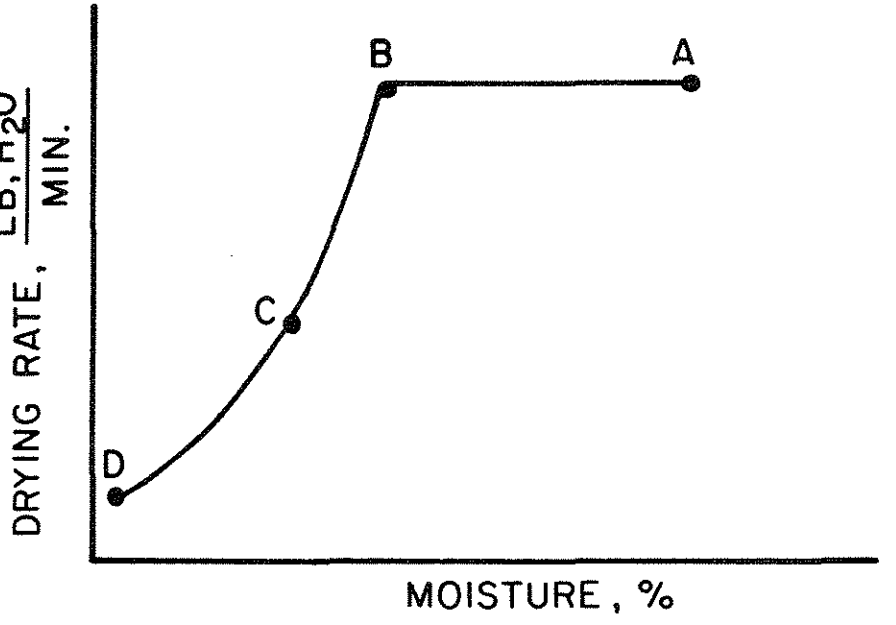

Figure 2. Stages of Drying Solid Granular Material at Constant Temperature.

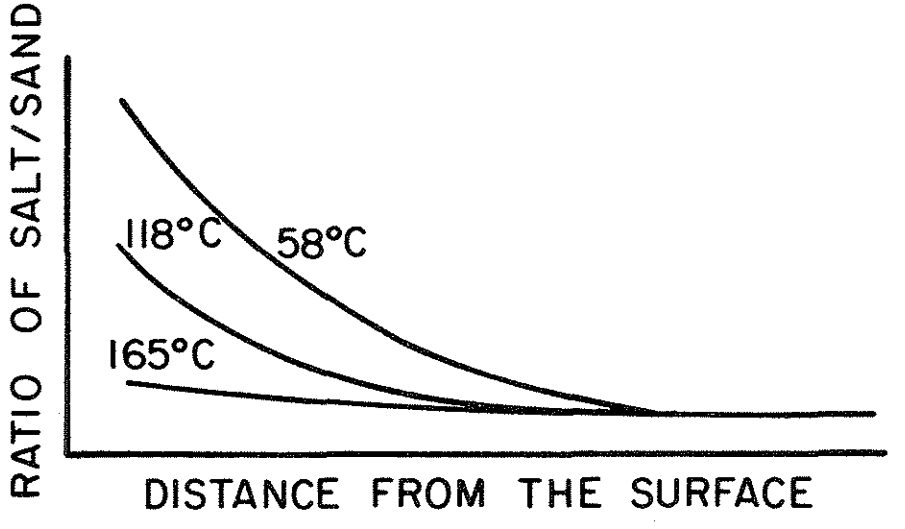

Figure 3. Effect of Temperature on Distribution of Salt in a Granule.

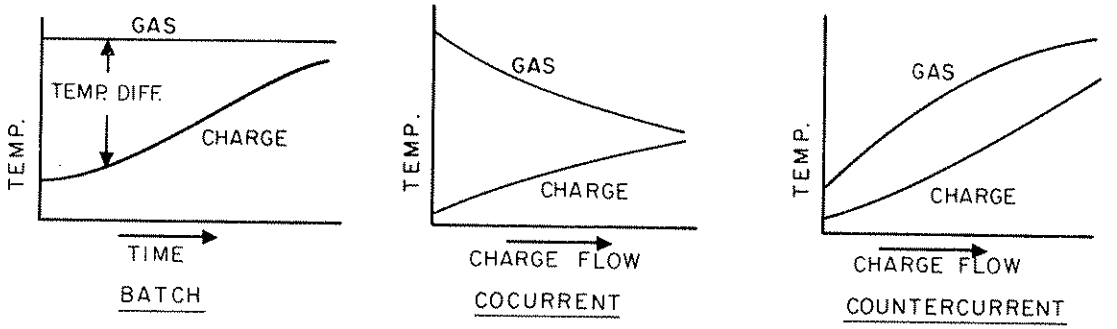

Figure 4. Temperature Differences in Three Types of Dryers.

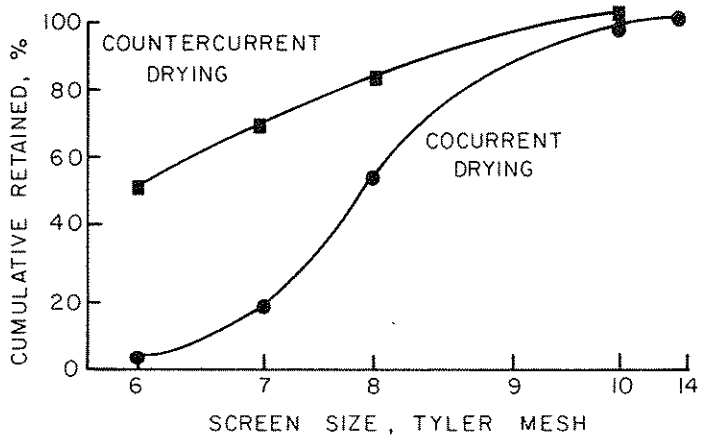

Figure 5. Size Distribution of Granules After Being Dried.

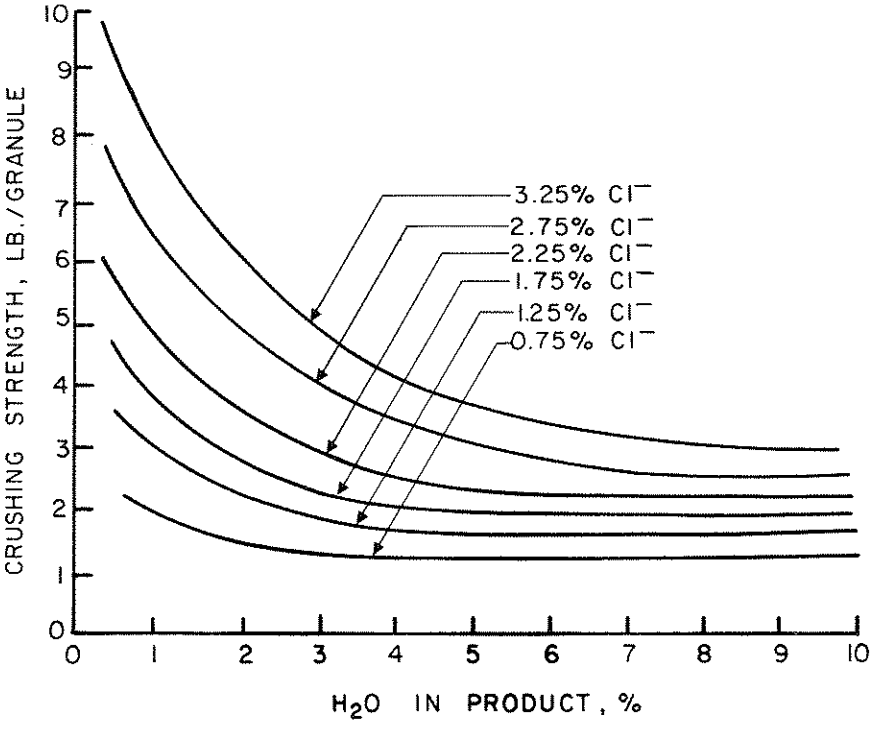

Figure 6. Relationship Between Strength and Moisture in Granules Containing Various Amounts of Salt.

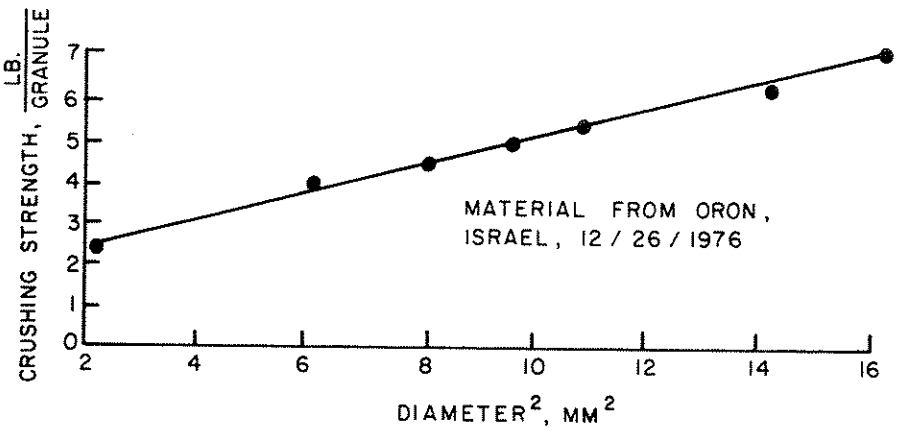

Figure 7. Relationship Between Strength and Diameter in Granules of Low Porosity.

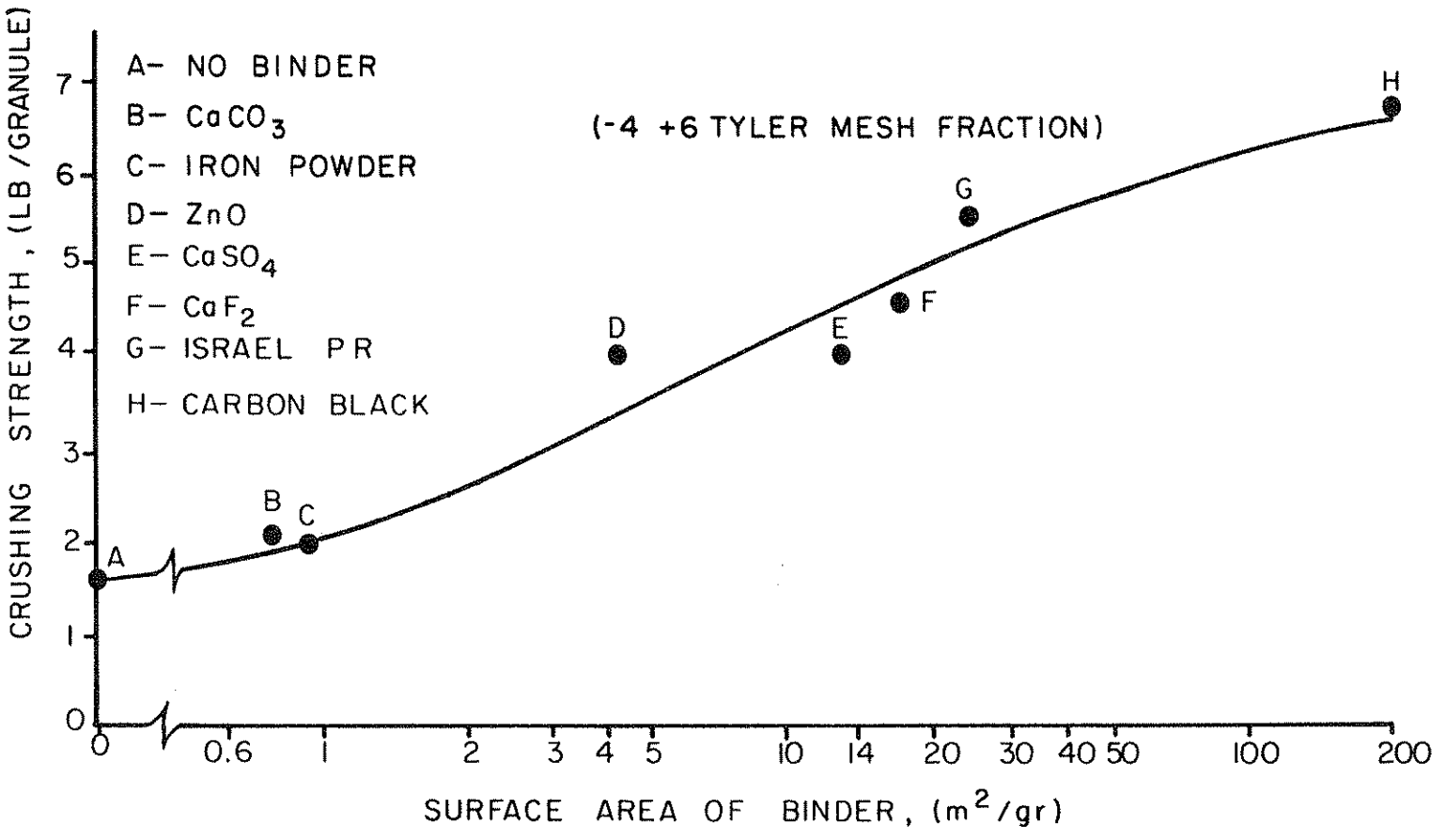

Figure 8. Effect of Binder Surface Area on Crushing Strength of Salt Granules (KCl Salt from IMC-Canada with 2% Binder).

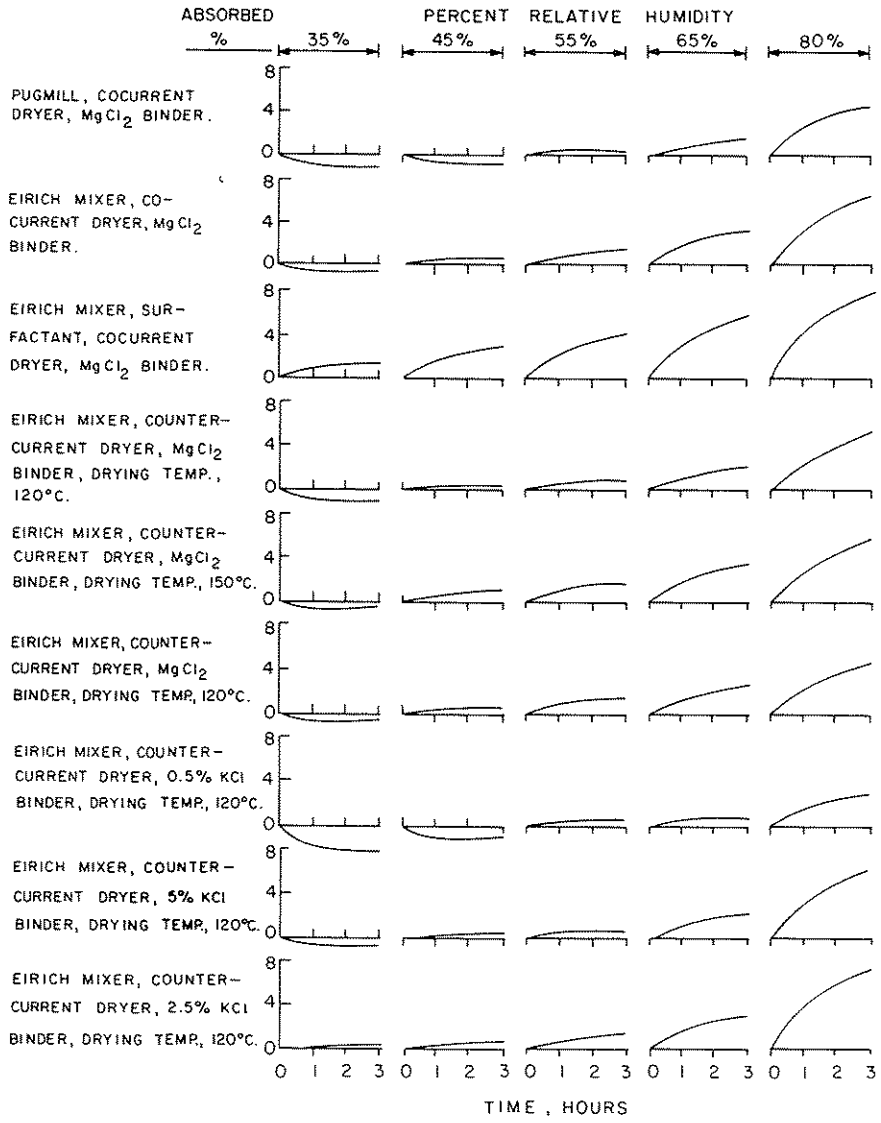

Figure 9. Moisture Absorbed by Granular Materials at Varying Relative Humidities.

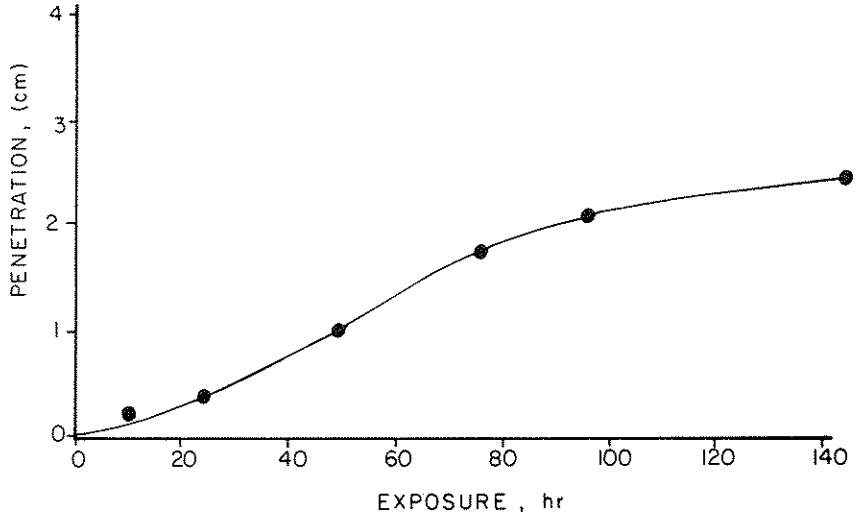

Figure 10. Moisture Penetration in Granular Product Exposed to 95% Relative Humidity.

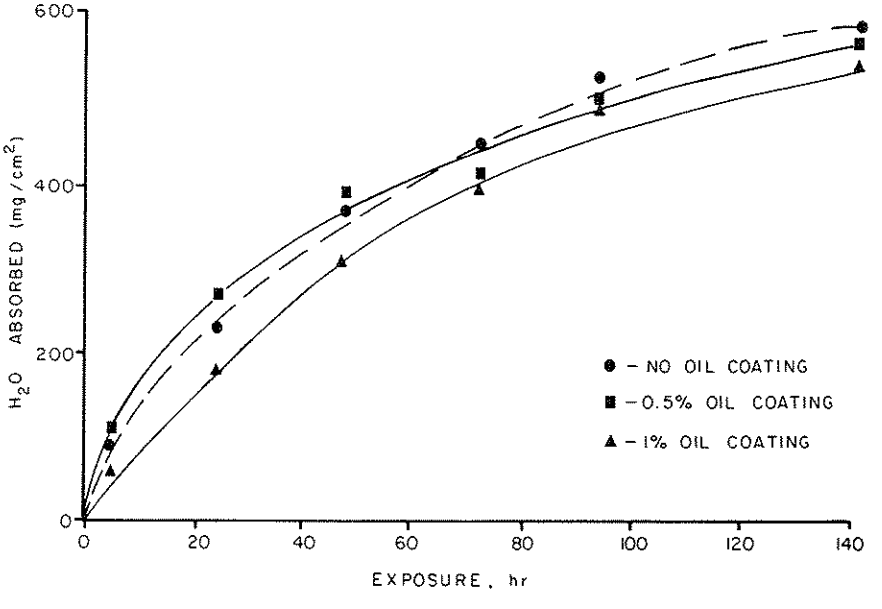

Figure 11. Moisture Absorbed by Oil-Coated Granules Exposed to 95% Relative Humidity.

VIEWS ON MARKETING OF PHOSPHATE ROCK FOR DIRECT APPLICATION

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Introduction

The possibilities for further expansion of the use of ground phosphate rock (GPR) and the existing obstacles from the agronomic and technical points of view are discussed. Current use and application forms are discussed based on various crops with guidelines for future research and recommendations.

Global Trends in Consumption of GPR for Direct Application

World consumption in the early 1970s (1971-72) reached almost 1.25 million mt P_2O_5 (excluding the People's Republic of China with additional estimated 400,000 mt P_2O_5). Out of this figure the Communist block in Eastern Europe consumed about 1 million mt P_2O_5 (equal to 80% of total world consumption), leaving another 320,000 mt P_2O_5 for international trade and other limited domestic use (equal to over 1 million mt of rock product). (More information can be found in "Ground Rock Phosphate Has Opportunities for Expansion" by British Sulphur Corporation, Ltd., Phosphorus and Potassium, No. 68, p. 19-23, November-December 1973, and in the current statistics of International Phosphate Industry Association (ISMA) or Food and Agriculture Organization of the United Nations (FAO).

In the mid-1970s (1974-75), the sharp rise in phosphate prices reduced the consumed quantities temporarily, but figures now have reached their normal level with a positive forecast for expansion in the 1980's.

A slow reduction is expected in the U.S.S.R. and the People's Republic of China due to increased capacity for production of water-soluble phosphate (WSP), and present changes in Vietnam and Cambodia

have, for the present time, halted further development of potential markets already prepared agronomically.

On the other hand, expansion of GPR use has already started in Europe, especially on behalf of the diminished basic slag. GPR either directly replaces basic slag or is mixed with low-grade slags in order to maintain a reasonable level of P_2O_5 (15%-16%) and try to keep its market share.

Another growing market is in Latin America, especially Brazil, with expected expansion in Colombia and Mexico.

Buildup and Further Development of New Markets

Potential market for further expansion of GPR usage exists in the tropics and southern hemisphere, but a buildup of agronomic knowledge is needed to support the expansion.

Latin America

Developed agronomic research is already in the advanced stages in Brazil, Colombia, and Mexico. Thus, new areas or additional crops will start using GPR. Additional work is required to prepare the background in Central America and the Caribbean (sugarcane, rice, coffee, and other suitable plantations).

Africa

Africa is still waiting for a more serious push in this regard. While preliminary research work was done in Nigeria, only primordial use exists in the francophone west African countries, especially on rubber plantations belonging to private companies (in Liberia and the Ivory Coast).

Training of extension services and improving of logistics of fertilizer handling might lead to greater usage. FAO/Fertilizer Industry Advisory Committee (FIAC) can contribute much to these efforts.

In east Africa the potential appears good in Kenya, Zambia, Malawi, etc., but nothing has been done to develop the use of GPR since the British

days when a traditional demand was created for WSP not only for short-term crops but also for perennials (tea, coffee, sizal, etc.).

Research work is required in order to convince local authorities to change their attitude in favor of GPR where its use is beneficial. Savings could be made in foreign currency spent today on importation of expensive fertilizers.

Southeast Asia

In addition to present traditional use of about 200,000 mt GPR on plantation crops in Malaysia, Indonesia, Sri Lanka, India, an additional quantity may be consumed by rice, sugarcane, and other tropical plantations in Burma, Thailand, the Philippines, and Bangladesh, subject to efficient market development in these countries.

"Indirect" Use of GPR for Direct Application

The statistics related to GPR do not count the "hidden" variations which might add considerable tonnage of phosphate rock as such.

Mixtures with Basic Slag

This method is already in practice in the United Kingdom, with final products, such as "super-slag" of Fisons, containing 15% GPR. This technique has a chance to be adopted in France and Germany as soon as further decline in slag quantity/ quality occurs.

PK Formulas (especially 0-20-20, 0-15-25, 0-24-12, etc.)

Consumption is estimated at almost 90,000 mt P_2O_5 (equal to 450,000 mt product based on 0-20-20). Use of these types is mainly in France and Germany with lesser quantities used in the United Kingdom and Finland.

Hybrids (mixtures of WSP and GPR with or without potash)

Various combinations are very popular in France with impressive development during the last 2-3 years from 1-2 million mt of product.

Partially Acidulated GPR

"Novaphos" (50% of the P_2O_5 is WSP) and "Carolonphosphate" (25% of the P_2O_5 is WSP) are produced and marketed within West Germany.

Phosphate rock with high P_2O_5 content and high reactivity is required in order to receive a concentrated end-product with good residual effect of the unacidulated remainder.

Phosphate Sources Suitable for Direct Application

Nature's "wisdom" is the one to be blamed for the location of most of the important phosphate deposits in arid or semiarid areas, while the typical use of GPR is subjected to humid climate or countries with considerable amounts of rainfall.

The idea of trying to find good sources in or near areas of consumption is blessed though not always practical for various reasons, such as:

- Deposits may be uneconomical for commercial exploitation (small, deep, low P_2O_5 in the ore, etc.).
- Rock is not good enough for direct application according to current standards based on solubility (reactivity).
- Local transportation may be costly versus reasonable ocean freight of imported rock of high suitability.
- Hardness of rock, limited grinding capacity, and negative balance of demand/supply leave enough room for importation of good phosphate rock from well-known deposits either as a raw, ground, or granulated material.

Table 1 shows some characteristics of various phosphate sources. Most of them are well known today for their efficiency, and their potential share in world trade is discussed hereunder.

Basic Slag

Basic slag is limited to the European market where its quantity/quality is under sharp decline and cannot supply its natural traditional market.

North Carolina PR

This is an efficient source but not freely available for international trade.

Gafsa PR

Gafsa PR has been exported from Tunisia to Europe and Latin America in reasonable quantities for the past 30 years. At present, the "historical" 29.5% P_2O_5 rock is no longer available, and 26%-28% low grades are now traded, hence lowering its importance as a future world supplier.

Christmas Island PR

Christmas Island was the main supplier in Southeast Asia for many years. Now reserves are diminishing, and present traded rock for direct application is lower grade than the "historical" 35%-36% P_2O_5.

As ferro-alumo phosphate, like some phosphates of Senegal, it is less effective on acid soils and gives better results on basic soils, after calcination in 500°-600°C ("calciphos" - Christmas Island or "phospal" - Senegal).

Arad PR

Arad PR rock from Negev Mines, Israel, seems to be very promising for future world trade. It is a soft rock, easily ground, with good performance in agronomic tests, high P_2O_5 content (minimum 32.5%), and high solubilities in formic/citric acids. Arad phosphate is ready for immediate exploitation, and an efficient basis for exportation already exists. Yield comparisons and plant uptake of P from Gafsa and Arad GPR are shown in table 2 and figures 1, 2, and 3.

Concentration of PR as an Additional Commercial Criterion After Agronomic Effectiveness

Agronomic efficiency of PR, as compared and based on equal P_2O_5 basis in field or greenhouse trials, is the main criterion for evaluating PR. But,

we must not forget that P_2O_5 concentration in the rock has significant importance in establishing its commercial basis.

After all, the application recommendations are not always very sensitive and, for instance, calling for spreading of 300 kg GPR/ha means having 12 kg P_2O_5/ha more in case of Arad (32% P_2O_5) compared with Gafsa (28% P_2O_5). There is about a 15% difference in favor of Arad over Gafsa, beyond their similar agronomic efficiency as expressed on an equal P_2O_5 basis.

Crop Suitability and Practice in Use of GPR

It is quite well accepted that the optimal conditions for agronomic use of GPR combine acid soils under pH 6.0, perennial crops, and rainy/humid climate. The situation in major "consumer" crops is discussed below.

Grassland

In the temperate climate of Europe and South America, this crop consumes over 80% of the total usage of GPR, a classical grassland fertilizer. In most cases the GPR is topdressed to established grassland in either powdered or granulated form.

Grassland is a major crop in the relevant countries (United Kingdom, Ireland, France, Germany, Austria, and Latin American countries such as Argentina, Uruguay, and Brazil) where more than 30% of the total arable land is subjected to this crop.

Larger maintenance dressings of comparatively inexpensive GPR can increase soil P reserves and thereby reduce the need for high-priced P compounds. One would hope that this would also encourage more legume growth in grassland and reduce the requirement for N fertilizers.

Forestry

GPR is well known in commercial forestry in Western Europe (United Kingdom, Ireland, and France) and Scandinavia. The U.K. Forestry Commission is recommending the use of unground

Gafsa rock (or equivalent). Thus, a combination of rather economic fertilizer with long-lasting effect required by forestry meets the possibilities of air spreading. (GPR and basic slag are too dusty while granulated phosphate rock is too expensive.)

In the U.K. about 10,000-20,000 mt PR (about 1/3 as PK 0-20-20) is annually consumed by this crop, and about 5,000 mt PR is consumed in Ireland. An estimated 5,000-10,000 mt PR is consumed annually in France. In Scandinavia, application of P is limited to organic soils (peat soils). These soils also need K; therefore, PK formula (0-20-20) is most suitable. In Finland, almost 60,000 mt granulated 0-20-20 is annually consumed while in Sweden present consumption is only about 1,000 mt PR with expectations of reaching 5,000 mt in the future.

The new Arad phosphate (Negev, Israel) is very promising for application as unground PR by aerial spreading to forestry due to its high agronomic effectiveness and P_2O_5 concentration.

Sugarcane

The sugarcane belt in the tropics is a potentially important user of GPR. Research from Hawaii and Mauritius shows good response of this crop to GPR.

Rice (Paddy)

Field trials in Thailand showed good response as do further trials now being conducted by the International Rice Research Institute (IRRI) in the Philippines. The problem anticipated is how to reach the small farmer with his small area unit.

Rubber

Rubber is a good traditional consumer of GPR in Malaysia governed by the Rubber Research Center in Malaysia and south Thailand. Only small tonnage is used on rubber plantations in west Africa (Liberia and Ivory Coast). Additional potential can be utilized by developing this area.

Oil Palm and Coconut

Palm and coconut are using GPR in Malysia and

Indonesia, but more information is required on research results, recommendations, etc., in these important crops.

Tea

The use of GPR mixed with N is a common practice in Sri Lanka. More developing work should be done in Kenya (with the Tea Research Center) and Turkey in the Black Sea acid soil belt.

Coffee/Cocoa

These are potential major crops for use of GPR in the tropics. Research work should be carried on with the relevant institutes in Brazil, Colombia, and Kenya for coffee and cocoa in the Ivory Coast and Brazil.

Soya

Good response was noticed in field observations in Paraguay with "Phosmak" GPR on acid soils. Field trials are now being carried out by Fecotrigo, the large cooperative of Soya/wheat growers in south Brazil. As a legume, soya might be a good exploiter of GPR; hence, we would recommend applying it before soya is planted since it has a lasting effect which favors the successive wheat in the two-crops-per-year rotation practiced in that area.

Corn

In southern France (Bordeaux) the use of GPR as such or in PK forms is quite common among corn growers on acid soils. Good response was noticed in field observations in Paraguay with "Phosmak" GPR on acid soils.

A 2-year field trial with "Phosmak" was included in the International Potash Institute (IPI) research plan in Turkey (Black Sea acid soil belt). Results are shown in table 3. The GPR and TSP were applied at the same P_2O_5 recommended levels used for WSP while the GPR was spread and incorporated 6 months before planting date. First-year results showed a remarkable increase in yields versus control though lower efficiency compared with TSP. In the following year the gap was closed, and both TSP and

GPR treatments were identical as was expected in this high fixing soil. (A pot trial with this soil is also presented in these Proceedings by Hagin et al.)

The Obstacle of the Limiting Recommendations

The usual recommendation for phosphorus fertilization in Western European grassland is narrowing the application season to autumn/winter. While this is true in the case of fast-acting, expensive P fertilizers, there does not appear to be any agronomic reason why PR fertilizers should not be applied year round for the maintenance of soil phosphate levels where there is not an acute deficiency and where soil and weather conditions are suitable for the use of GPR. In fact, there are also practical, logical reasons for this. Due to weather conditions or farmers' hesitation, the real autumn/winter season is only 2-3 months. (Dry summer--farmers hesitate and delay spreading. Wet season--No technical possibility for spreading, etc.)

We believe that the mode of action of natural phosphates allows for widening the spreading season over the regular use of water solubles, giving the farmer an alternative solution when "missing the season." GPR can stand criticism where its efficiency is questionable, but it should be credited more where its nature has some advantages over WSP.

GPR versus TSP

During the past 2 years, substantial quantities of TSP were imported into Europe and Southeast Asia. Unreasonably low prices in 1976-77 created a ridiculous condition in Germany where a unit of P_2O_5 in TSP was more economical than in GPR. It seems that the European Economic Community (EEC) will avoid future uncontrolled importation of that kind in order to support local producers. We have to keep in mind that, in Western Europe, normal sales of GPR are possible when keeping at least 20% price reduction per unit P_2O_5 versus WSP.

In Southeast Asia, TSP is now highly requested in tenders by Indonesia, Sri Lanka, Bangladesh, and Burma. The last favorable prices of September-

October 1977 showed $158,C+F, for bagged TSP in Sri Lanka and Bangladesh. At this price level GPR, either in powder or granulated form, is still cheaper per unit of P_2O_5 (30%-20% saved, respectively) and, for the suitable conditions of soil/crop/climate which are optimal in these countries, the use of GPR can be very efficient with a big savings in foreign currency for the local governments or importers in this area. Therefore, we see no justification to run into the high figures tendered for TSP when GPR can economically solve a great part of the phosphorus consumption in those countries.

Traditional and Tailor-Made Tenders in GPR Trade

Since certain PRs have been marketed for many years, some patterns were established and created a traditional use which now raises some difficulties in changing from one source of PR to another.

For instance, the Christmas Island PR was well established in the Far East and Southeast Asia. Tenders up to now called for 35%-36% P_2O_5 in PR, not taking into account the following facts:

1. Such a rock no longer exists due to depletion of Christmas Island deposits.
2. There are more effective PRs, even though lower in P_2O_5. Researchers and decision-makers should be aware of these alternatives and be open for additional standards which better suit their agronomic effectiveness.

Another example can be shown in forestry fertilization in the United Kingdom which traditionally calls for unground Gafsa rock. Since Gafsa rock traded now is of low-grade P_2O_5 concentration, it is logical to allow other suitable reactive and higher P_2O_5-containing phosphates to participate in those tenders, without "tailoring" them to a certain rock.

Topdressing Versus Incorporation of Granulated PR

Previous criticism on efficiency of granulated PR derived from unsuitable testing procedures or avoiding the understanding of the main practical use and/or the expectations from this kind of fertilizer.

The mode of action of GPR requires good contact of the fine particles with the soil in the root feeding

area. Hence, best results are obtained by mixing GPR with the soil volume in pot trials. Of course, trying to do the same with granulated material fails to give the same results, and usually only about 50% of the GPR response can be obtained in the first crop (figure 4).

We must not forget that for quick response we always have the WSP fertilizers. Usually GPR is given for the maintenance of soil phosphate levels, acting in the long run as a slow-release P fertilizer. Gillon et al. (in these Proceedings) found that when granulated PR is incorporated and mixed with the soil, there is a steady trend toward improving response in the following cuts/crops.

In order to gain further improvement in the short run, the idea of using minigranules was raised. This will have to obtain farmers' acceptance when the trend is toward bigger granules in the range of 2-5 mm which fits perfectly into common centrifugal spreaders.

Incorporation of minigranules is expected to give better agronomic performance than larger granules but is less effective than with powdered material (figure 4). One must keep in mind that the majority of the perennial crops treated with GPR are topdressed (established grassland, forestry, tropical plantations) with quite good results and without successive incorporation.

Pot trials treated with granulated PR resulted in better response of clover to topdressing rather than to granule incorporation (table 5 and figure 4).

An easy disintegration of topdressed PR granules during the first irrigations (rain) may create approximate conditions to powder application which is reflected sooner or later (depends on nature of the granule) in results of the following harvests of the tested ryegrass.

Grassland fields in the rainy areas of Ireland, France, and England are often soaked with water, and optimal conditions for root development exist in the upper soil layer; therefore, good P uptake occurs from the soil surface, especially in a wet year.

The problem is how to treat new plantings (either perennial or annual) when short-run response is re-

quired. Considering the above-mentioned results and mode of action, it seems that suitable agro-technical recommendations should be adopted rather than changing granule type. A possible recommendation might be to apply GPR several months before planting date and leave it on the surface until it is broken down by rain. It should be incorporated into the soil just before planting by discing, harrowing, etc., during seedbed preparation.

Too Many Standards for Checking GPR Solubility and the Search for Equal Basis for Comparison

The various methods used today in different regions or countries do not allow comparison among alternative phosphate sources on an equal basis. It would be quite helpful to adopt an international standard according to which the agronomic efficiency of different phosphates can be compared (such as ferro-alumo phosphates, carbonate-apatites, high calcite-containing phosphate rock, etc.).

It seems that a first step was made by the EEC in adopting the 2% formic acid procedure. The International Fertilizer Development Center (IFDC) suggests another genuine standard based on acid ammonium citrate solution at pH 3.0 (presented in these Proceedings). We do hope one of these standards or both of them would be spread worldwide to eliminate the above-mentioned obstacle.

A Potential Solubility Index (PSI)

The common standard solubility tests are qualitative in nature, using procedures which limit the solubility either by time of reaction or narrow ratio of rock sample to acid solution. Therefore, the results have direct projection on the short-term agronomic period. Since GPR is applied mostly for its long-term effects, we need an additional measure for estimating quantitative values.

The PSI value shows solubilities in optimal conditions and may be an important quantitative criterion for evaluating the total efficiency of any tested PR in the long run (taking into account also the lasting effect).

Variations in the common Wagner method such as changing reaction time, ratio of solid to liquid, successive extractions, etc., show that PR can contribute much more than obtained in the official Wagner test, with clear variance between various rocks. This can be seen in table 1. It seems that optimal solubilities may be achieved by using a ratio of 1:250 or 1:350 of rock to 2% formic/citric acid solution with marginal differences at these levels. Therefore, we can choose either of them to express the PSI of certain PR, and we can select several groups as follows.

1. Group I: Highly reactive PR having PSI values of more than 90%-95% (table 1). In this group we may find North Carolina, Gafsa, Arad, Machtesh, and Sechura phosphate rock.

2. Group II: Less reactive PR with medium PSI of about 60%. In this group we find Christmas Island and Senegal (ferro-alumo phosphates).

3. Group III: Low reactive PR with low PSI value of up to 50% such as Florida rock.

4. Group IV: Really ineffective PR with PSI under 20% like Kola phosphate.

Another advantage gained by using the PSI value is that the small differences resulting from interaction with the complementary minerals such as calcite in carbonate-apatites are eliminated, while in the ordinary Wagner method they produced some masking effect on the true capability of the apatite to release P.

Fineness of Grinding--Where is the Border?

This subject is still under discussion, and there are differing opinions. The recommendation in the United Kingdom and Ireland mentioned that further grinding under 100-mesh is not necessary since the additional agronomic benefit is marginal. On the other hand, Reno claims fineness of almost 300 tamis (50 microns) is needed based on experience with Gafsa rock. The new legislation of the EEC is somewhere between those figures, 230-mesh (63 microns).

According to our experience with Negev rocks, further grinding under 200-mesh does not add any substantial agronomic benefit, and one must keep in mind that for any given PR there might be a different point from which additional grinding does not pay. Therefore, we believe that 200-mesh fineness is quite reasonable for most reactive rocks, and further grinding seems to have more "commercial" than agronomic appeal.

Liming Effect of GPR

Carbonato-apatite (phosphorite) has a certain liming effect which might be slightly higher when containing calcite as a complementary mineral to the apatite. In evaluating the liming effect in greenhouse trials at Technion of Haifa, Israel, on various acid soils from Germany, Ireland, and Turkey, Hagin et al. found about 1% addition of PR mixed into the soil induced an increase of about 0.5 pH units. Since field application is on the top layer, a certain liming effect can be locally achieved. Of course, this is not sufficient to make a big change where usually 4-5 tons of lime is used per hectare for amending soil pH, but it can keep the soil from further deterioration and replace acidic WSP fertilizers which contribute to quicker acidifying of acid soils.

General Agronomic Recommendations

In conclusion to the agronomic aspects raised in this paper, we suggest keeping the following in mind:

- Small annual applications of GPR, when compared with WSP on deficient soils and based on common recommendations (as probably practiced in that area), might lead to a failure to reach equalization between the two fertilizers if the soil is not of the high fixing type. In this case, a huge amount of cheap PR applied once per several years may be better when compared with annual small amounts of more expensive WSP.
- If the soil is of the high fixing capacity, a regular comparison based on annual equal applications of P_2O_5 can bring the two treatments to equalization in a few years

due to cumulative buildup of active reserves in the case of GPR versus continuous quick fixation of WSP.

- In case of crop rotation, PR treatment should be applied to the "best exploiter" so as to achieve maximum short-term effect and allow the residuals to serve the following crops.
- In the case of granulated PR, it should be applied as such but incorporated (or not) only after its disintegration by rain/ irrigation.

Table 1. Selected Characteristics of Some Phosphate Materials

Sample	Total P_2O_5, %	CO_2, %	Soluble P_2O_5 mg			Soluble P_2O_5--Percentage of Total P_2O_5		
			1 g/100 ml	1 g/250 ml	1 g/350 ml, PSI	1 g/100 ml	1 g/250 ml	1 g/350 ml, PSI
					2% Formic Acid			
North Carolina	29.6	5.9	202	268	281	68.2 (20.2)	90.5	94.9
Basic slag	11.7	1.9	98	100	104	83.7 (9.8)	85.5	88.9
Arad 0712	31.9	5.3	202	306	308	63.3 (20.2)	95.9	96.5
Arad mine	33.1	5.1	211	287	321	63.7 (21.1)	86.7	97.0
Gafsa	29.5	6.3	226	285	288	76.6 (22.6)	96.3	97.6
Sechura	31.1	4.4	206	244	300	66.8 (20.6)	88.8	95.5
Machtesh	30.5	7.6	174	287	286	57.0 (17.4)	94.0	93.8
Christmas Is.	36.3	2.0	118	196	223	32.5 (11.8)	54.0	61.4
Florida	32.7	n.d.	69	142	174	21.1 (6.9)	43.4	53.2
					2% Citric Acid			
North Carolina	29.6	5.9	112	219	254	37.8	74.0	85.8
Basic slag	11.7	1.9	110	112	115	94.0	95.7	98.3
Arad 0712	31.9	5.3	122	264	277	38.2	82.7	86.8
Arad mine	33.1	5.1	127	279	293	38.4	84.7	88.5
Gafsa	29.5	6.3	120	240	265	40.7	81.3	89.3
Sechura	31.1	4.4	153	281	299	49.2	90.3	96.1
Machtesh	30.5	7.6	97	223	251	31.7	73.1	82.3
Christmas Is.	36.3	2.0	111	193	218	30.5	53.2	60.0
Florida	32.7	n.d.	67	127	167	21.1	38.8	51.1

Notes: Samples pass 200-mesh sieve; dissolution determined after 1/2-hour agitation with Wagner apparatus at room temperature, using folded filter--no vacuum. PSI is potential solubility index. Figures in parentheses relate to soluble P_2O_5 as percentage of total rock sample.

Table 2. Response of Ryegrass to Phosphate Sources in a Pot Experiment[a]

P Source[b]	P_2O_5, g/pot	Ryegrass Yield, g/pot[c] Medium Clay, pH 4.5	Heavy Clay, pH 6.1	Loamy Sand, pH 6.7
Control	-	16.3	16.6	16.9
Basic slag	0.1	25.0	23.7	22.1
Basic slag	0.2	30.9	26.0	23.1
Basic slag	0.3	31.1	27.8	23.7
Granphos 1975	0.2	23.0	21.9	20.5
Arad rock	0.2	27.5	23.7	20.7
Gafsa rock	0.2	28.4	23.9	21.7
LSD (0.05)		2.42	2.22	1.34
(0.01)		3.23	2.96	1.79
CV %		6.89	6.99	4.48

a. Pot experiment conducted at Fisons-Levington Research Station, United Kingdom, 1977.
b. The analysis of the phosphate sources is:

Material	Total P_2O_5 (W.B.)	2% Citric Acid-Soluble P_2O_5, %	% of Total P_2O_5 Citrate Soluble
Basic slag	12.50	10.20	81.6
Granphos 1975 (granulated RP)	28.20	9.70	34.4
Ground Arad rock	31.70	12.60	39.7
Ground Gafsa rock	28.20	12.70	45.0

c. Total dry-matter yield from eight cuttings during 4.5 mo. Topdressing to established ryegrass.

Table 3. Response of Corn to Phosphate Sources in Field Trials at Samsun, Turkey, 1976 and 1977

P Source	Yield, kg/decar 1976	1977
TSP (granulated)	452	375 a
Phosmak (dust) (30%)	408	367 a
Phosmak (granulated) (30%)	360	339 a
Check	298	270 b
		Standard deviation - 14.3
		LSD - 63

Notes: Trials were conducted by Dr. Agme of International Potash Institute and Dr. Basaran of Topraksu Arastirma Institute, Samsun, on a clay loam soil with a pH of 5.4. TSP was broadcast at planting time in May. "Phosmak" was broadcast in the fall or winter and incorporated prior to planting time. Plots were harvested in mid-October each year. Decar = 1/10 ha (3,000 corn plants).

Table 4. Response of Ryegrass in Pot Experiments to Phosphate Sources when Topdressed or Incorporated into Soils[a]

Applied P_2O_5		Dry-Matter Yield, g/pot[c]		
Source[b]	Rate, g/pot	pH 4.6 Sandy Clay Loam	pH 5.0 Medium Clay	pH 7.3 Loam
Incorporated				
Basic slag	0	7.31	7.28	7.88
Basic slag	0.1	13.22	13.57	14.65
Basic slag	0.2	16.48	17.26	16.97
Basic slag	0.3	17.64	19.79	20.22
Gafsa rock	0.2	15.52	14.86	9.89
Phosmak (powder)	0.2	12.65	10.80	8.93
Granphos	0.2	7.79	8.35	7.97
LSD (0.05)		2.08	1.67	2.13
(0.01)		2.78	2.23	2.84
Topdressed				
Basic slag	0	7.76	9.80	8.04
Basic slag	0.1	12.09	14.51	9.77
Basic slag	0.2	13.94	16.67	9.96
Basic slag	0.3	14.96	17.18	9.32
Gafsa rock	0.2	10.56	14.18	7.82
Phosmak (powdered)	0.2	9.85	11.68	7.77
Granphos	0.2	10.60	13.51	7.76
LSD (0.05)		1.41	1.73	1.58
(0.01)		1.88	2.32	2.12

a. Experiments were conducted by J. R. Devine, Fisons-Levington Research Station, United Kingdom, 1975.

b. Phosphate Sources

Material	Total P_2O_5, %	2% Citric Acid Soluble P_2O_5, %	Citrate Soluble % of Total P_2O_5
Basic slag	14.20	13.70	96.5
Gafsa rock	28.89	12.00	41.5
Phosmak (powdered)	31.70	10.20	32.2
Granphos (granulated RP)	28.20	11.50	32.3

c. Incorporated: yield from six cuttings during 4 mo. Topdressed: yield from five cuttings during 5 mo.

Table 5. Clover Yield Response to Arad Phosphate Rock as Affected by Placement, Particle Size, Granule Binder, and P Rate in a Soil from Ireland

Binder Material	Placement	Size (mesh)	P rate, g/pot	Dry Matter Yield, g/pot 1st Cut	2d Cut	3d Cut
KCl	mixed	5-10	0.2	0.35	0.29	0.67
			0.5	0.43	0.18	0.31
			1.0	0.47	0.60	0.55
			2.5	0.61	0.71	0.80
KCl	mixed	20-40	0.2	0.46	0.44	0.20
			0.5	0.57	0.75	0.69
			1.0	0.98	1.98	2.08
			2.5	2.11	5.78	6.06
KCl	surface	5-10	0.2	0.54	0.55	0.75
			0.5	1.15	3.25	3.54
			1.0	1.79	5.81	6.97
			2.5	2.53	7.18	7.55
$MgSO_4$	mixed	5-10	0.2	0.44	0.28	0.20
			0.5	0.49	0.42	0.36
			1.0	0.54	0.35	0.32
			2.5	0.78	1.34	1.74
$MgSO_4$	mixed	20-40	0.2	0.47	0.29	0.09
			0.5	0.65	0.90	0.76
			1.0	1.19	2.58	3.31
			2.5	1.99	5.26	6.29
$MgSO_4$	surface	5-10	0.2	1.02	1.91	1.46
			0.5	1.85	4.01	4.88
			1.0	2.55	6.18	7.45
			2.5	2.96	7.17	7.74
	mixed	-200 (powder)	-	0.25	0.21	0.21
			0.2	0.58	0.85	0.95
			0.5	1.28	1.89	2.39
			1.0	3.21	6.31	7.65
			2.5	4.54	8.56	8.88

Reference: "Evaluation of Granulated Phosphate Rock for Direct Application," Gillon et al. (paper in these Proceedings), table 4.

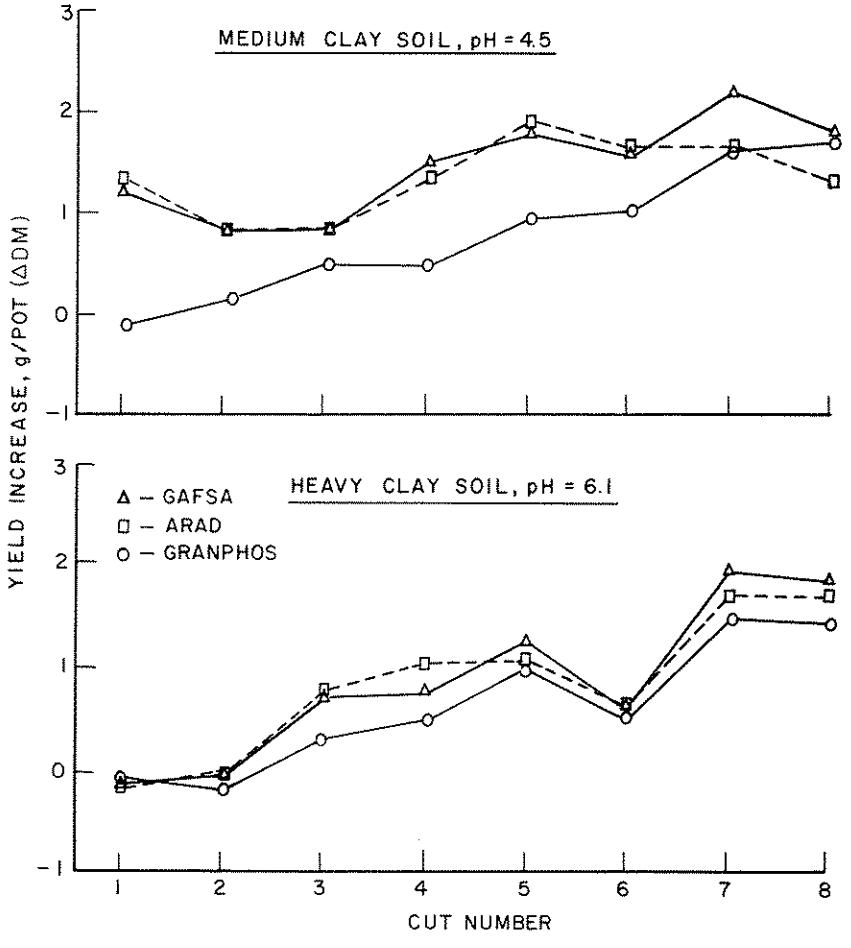

Figure 1. Ryegrass Yield Response During 8 Cuttings to Phosphate Sources on 2 Soils in Pot Experiments.[1]

[1] Experiments conducted at Fisons-Levington Research Station, United Kingdom, 1977. (See also table 2 herewith.)

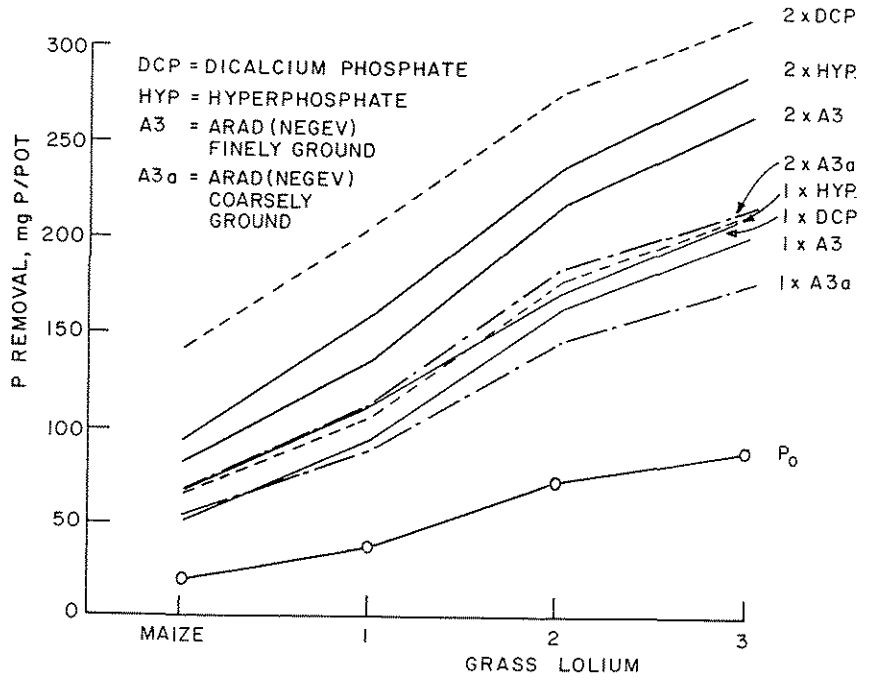

Figure 2. Comparison of Plant Uptake of P from Phosphate Sources in a Sandy Loam Soil (pH 5.7) (A. Amberger, Inst. Plant Nutrition, Tech. Univ. of Munich-Weihenstephan, W. Germany).

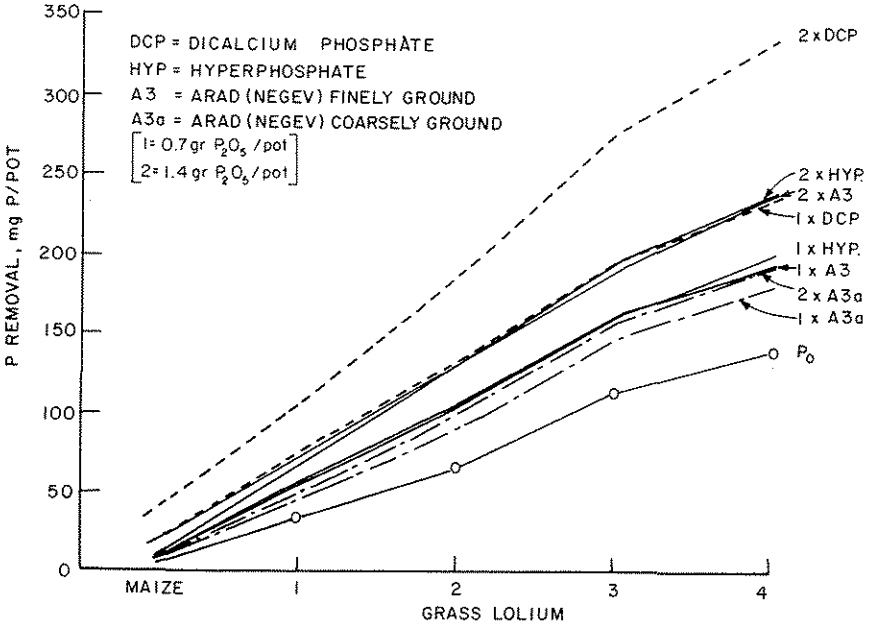

Figure 3. Comparison of Plant Uptake of P from Phosphate Sources in Sandy Loam Soil (pH 6.3) (A. Amberger, Inst. Plant Nutrition, Tech. Univ. of Munich-Weihenstephan, W. Germany).

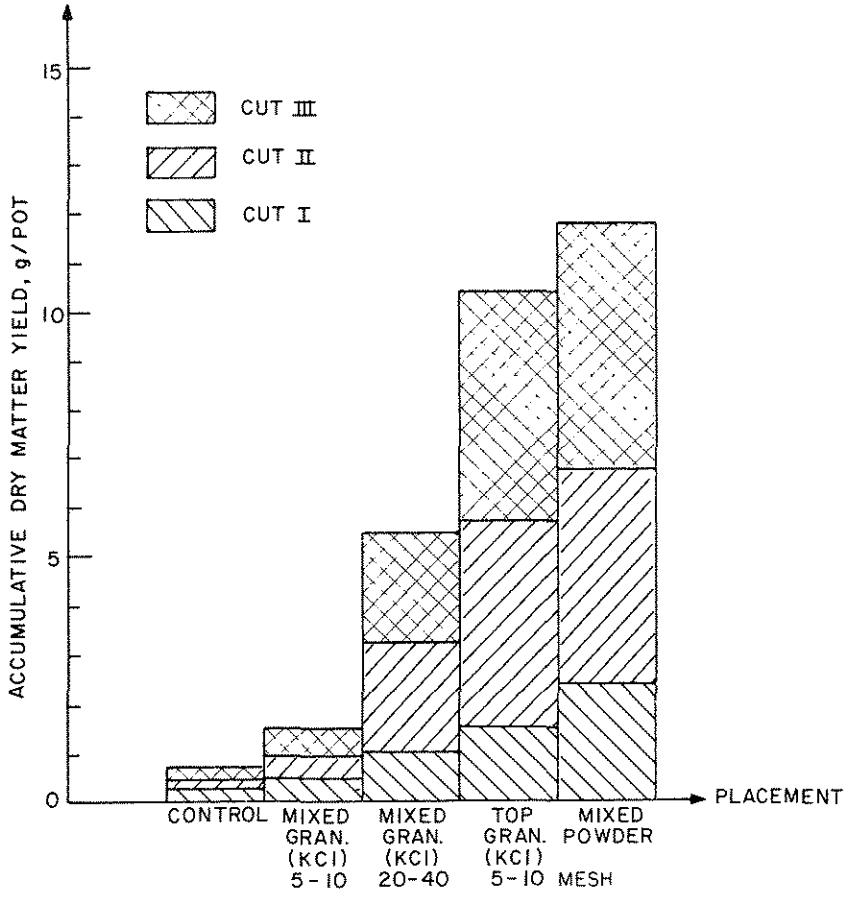

Figure 4. Influence of Particle Size and Method of Placement of Arad Phosphate Rock on Clover Yields (average of 4 rates) from a Greenhouse Experiment (Reference: table 5 herewith).

VIEWS ON MARKETING OF PHOSPHATE ROCK FOR DIRECT APPLICATION

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Introduction

The use of ground phosphate rock for direct application followed centuries after the use of other naturally occurring materials for soil fertility improvement and even after the use of single superphosphate. Calcined bones are thought to have been used as long as 2,000 years ago in China; fish and animal manures were used during the 17th century in Europe; and superphosphate was used in the mid-19th century. However, it was late 19th century before ground phosphate rock was used for direct application.

Early experimenters generally assumed that the phosphate component of phosphate rock was tricalcium phosphate, and later, fluorapatite. These over-simplifications were due to the failure to understand the complex chemistry of phosphate minerals, and the variations in mineralogy between phosphate rocks often led to inconsistent agronomic results. The indiscriminate use of various methods to estimate the available phosphate in rocks has led to further confusion.

It now appears that there is a close correlation among the various extractants used to estimate availability of most apatitic phosphate rocks even though the absolute values are very different (figure 1). It seems that these chemical extractants are useful to estimate the relative response of the first crop after application as well as the cumulative crop response during a series of crops (figures 2 and 3). However, it may not be possible to estimate the relative response of an individual crop within the series to residual phosphate from various sources of phosphate rocks. More research is needed to determine the accuracy of these generalizations. However, at the present time we can propose three categories of potential for phosphate rock for direct application based upon solubility and expected performance for the first crop after application (table 1).

Origin and Destination

Most internationally traded phosphate rock for direct application appears to come from Tunisia (table 2). Gafsa rock from Tunisia is one of the phosphate rocks with the highest citrate solubility. Other sources accounting for significant quantities in international trade are Morocco and the Christmas Islands, with Egypt, Israel, and Jordan supplying lesser quantities. Of these rocks Gafsa and some samples of Morocco and Israel rock have high potential, and the others have medium potential based upon their citrate solubility. It should be noted that solubilities may vary from one mine to another within a country and, therefore, the country of origin is not a reliable indication of potential.

Indigenous phosphates are used to a large extent in the U.S.S.R. The U.S.S.R. also supplies a significant quantity of rock to East European countries. In addition, the People's Republic of China and other centrally planned Asian countries appear to use large quantities of indigenous phosphate rock for direct application. British Sulphur Corp. (1973) estimated China may have use of up to 400,000 mt of P_2O_5 as phosphate rock in 1972. Thailand has recently started using indigenous rock. In Africa, Mali and Upper Volta are beginning small-scale exploitations of their deposits for use in direct application. South Africa, Morocco, and Senegal use indigenous phosphate rock for application; in South America, Brazil, Colombia, and Venezuela also use indigenous rocks. It appears likely that the United States uses 10,000-15,000 mt of P_2O_5 from phosphate rock (Mineral Industries Surveys, 1976).

The destinations of phosphate rocks for direct application in international trade (1972) are shown in table 3. Western Europe is the region of greatest consumption of imported phosphate rock (62%) with France consuming about 400,000 mt of product. Asia (mostly Malaysia) and Latin America (Brazil and Uruguay) each consume 18%-20% of the internationally traded phosphate rock for direct application.

Of the internationally traded and domestic phosphate rock used for direct application, eastern Europe uses almost 1 million mt (table 4). This is about 78% of the total consumed for direct application, excluding

the centrally planned Asian countries, and accounts for about 12.7% of the P_2O_5 used in the region. Other countries supplying a high percentage of their P_2O_5 from phosphate rock are Burma (64%), Malaysia (49%), Sri Lanka (46%), Argentina (26%), Senegal (15%), and Brazil (10%). However, only in Brazil does this account for as much as 100,000 mt of P_2O_5.

Total phosphate rock used for direct application appears to be between 1.6 and 2.2 million mt of P_2O_5 per year. However, as seen in tables 2-4, the statistics on use are variable depending upon the reporting source.

Processing and Use

In the strict sense, phosphate rock for direct application includes only apatitic rock which has not undergone a chemical reaction to solubilize the phosphate. However, it is unclear from the literature whether this criterion is always used. Calcined iron and aluminum phosphates (C-grade Christmas Island and Phospal from Thies, Senegal) are also used for direct application and may sometimes be counted in the statistics.

Phosphate rock for direct application may be processed by simply mining ore of small particle size or undergoing one or more additional steps of grinding, concentrating, and drying. Some suppliers also granulate the phosphate for ease in handling and application.

Other producers mix powdered phosphate rock with potassium chloride and/or ammonium sulfate, ammonium nitrate, or superphosphate. In addition, granular products containing potassium are commonly used in Western Europe. Several common formulations of phosphate rock used for direct application are shown in table 5.

It may be useful to look at other ways to handle and distribute phosphate rock for direct application. The finer phosphate rock is ground, the greater is the cost of grinding because of the increasing capital and energy costs. IFDC estimated equipment costs

and power requirement for dry grinding (7 mt/hr) are:

Fineness, mesh	Equipment Cost	Horsepower
80% < 100	$125,000	200
80% < 200	160,000	250
99% < 325	335,000	800

If the ground rock is acceptable as a 70% solids slurry in water, the horsepower requirement can be reduced. A mill to grind 7 mt/hr, open circuit, to 60%<200 (about equivalent to 80%<100) would require only 100 horsepower and cost $112,000. Tests by IFDC have shown that the rock slurry remains very easy to stir and resuspend after as long as 1 month's settling. Soluble P_2O_5 (MAP) can be added to the slurry to give early response if desired.

Costs have been estimated for mining rock in a developing country, and three processing and distribution cases were developed: (1) dry, grind, bag, and deliver through a series of warehouses to farm; (2) the same as (1) except granulated; and (3) the wet rock transported to a distribution center, wet ground, and delivered to farms as a slurry. Cost estimates were $103, $120, and $123/mt of PR for slurry, ground and bagged, and minigranules bagged, respectively.

Calculations indicate that the cheapest method of delivering rock to the farm is as a slurry. In most, if not all, situations in a developing country, the bulk facilities would be new. This method of distribution would be new and separate from any existing channels. It is likely most appropriate where the national interest is in increasing the level of soil fertility, primarily by correcting phosphorus deficiency. The nature of the national policy, as well as attitudes and physical conditions in individual countries, will dictate the appropriate method of handling and distribution.

No information was found concerning the quantities of phosphate rock used for specific crops; however, it appears quite obvious that in Malaysia, Brazil, and Sri Lanka, phosphate rock is used for plantation crops. In Europe, most appears to be used for pastures, and forestry use seems to be increasing.

Potential Advantages and Disadvantages

The low cost of phosphate rock in comparison with acidulated phosphate fertilizers is its principal potential advantage. Factors contributing to lower cost and other advantages include:

1. Very low capital investment is needed for processing, and equipment can be used for other purposes, e.g., cement industry.
2. No particular technical skills are required.
3. Energy requirement is small.
4. There is little or no loss in processing.
5. Rocks unsuitable for chemical processing are, in some cases, suitable for direct application.
6. The long delay involved in constructing chemical processing plants can be avoided.
7. Economy of scale and intermittent operation are relatively unimportant.
8. It has soil amendment benefits (liming effect) in addition to its phosphate and calcium contents.

Some potential problems for the use of phosphate rock as fertilizers are:

1. Different sources vary greatly in their chemical and mineralogical composition and hence in agro-economic value.
2. There is no universally standard laboratory method to estimate the relative agro-economic value.
3. In the finely ground state, it is dusty and difficult to handle and to apply uniformly.
4. Agronomic response is less than that of acidulated phosphates for the first crop following application.
5. The reactivity and residual relationship are not well defined.
6. It is less acceptable under some land tenure systems because a large part of the crop response is to residual phosphate.

Sales Concepts

Brochures promoting the sale of phosphate rock for direct application generally contain statements about the following factors to convince users to buy the product.

Acid Soils

It is widely known that phosphate rock is a better source of phosphorus in acid soils than in neutral or alkaline soils.

Less Reversion

This concept is not well understood or demonstrated to be true. The reversion to relatively insoluble iron and aluminum phosphate is certainly slower with phosphate rock than with soluble phosphates. But, this does not necessarily mean that plants will recover greater amounts of phosphorus from phosphate rock than from soluble phosphate. More research is needed on soils with high absorption capacity.

Availability to Crops

Phosphate rock is generally sold for the crop immediately following application and the following two to three crops. Research results demonstrate that crops do recover phosphorus from phosphate rock for more than one or two crops after application. However, particularly in soils of pH 5.0-7.0, crops similarly recover phosphorus from soluble phosphates.

Fine Particle Size

It is generally understood that grinding phosphate rock to a fine particle size increases the availability to crops. How fine this grinding should be is not well defined and may depend upon the rock characteristics as well as on the conditions under which it is used. It probably is not justifiable, based upon agronomic and economic considerations, to grind finer than 85%-90% through a 100-mesh screen for most rocks and uses.

Granules

Several companies are now granulating phosphate rock for direct application. Certainly the material is

easier to handle and apply than finely ground material. The companies comment that the granules disintegrate in soil. For small granules and high rates of application, the materials may give satisfactory crop responses. However, it appears very doubtful that 8- to 16-mesh granules will give satisfactory crop response even if they do disintegrate because the phosphate rock may not be adequately dispersed in the soil to be positionally available to roots. In these rice-growing areas where the phosphate is applied before puddling or for surface application on grassland, this effect will possibly be unimportant.

Liming Effect

Relatively few companies selling phosphate rock for direct application seem to recognize the potential liming effect for acid soils. However, they can improve the calcium status, decrease exchangeable aluminum, and partially offset the potential acidity of nitrogen fertilizers in acid soils. But, even the more reactive phosphate rocks seem to have little effect in increasing soil pH.

Micronutrients

Some companies accurately advertise that phosphate rock contains micronutrients. However, to have any value for the farmer, there must be a need for the micronutrients. In many soils and farming systems where phosphate rock is used, there may be no need to apply the micronutrients contained in the phosphate rock.

Potential Use

It was seen in an earlier section that in the mid-1970s phosphate rock for direct application probably supplied about 1.6 million mt of P_2O_5 or about 6% of the total P_2O_5 consumption. No official estimate exists of the area of soils suitable for the direct application of phosphate rock. However, if one assumes that only 25% of the land area in Africa, Latin America, and the noncentrally controlled economies of Asia planted to cereals, roots, tubers, and pulses is suitable for phosphate rock application and at an average application rate of 30 kg/ha/yr of P_2O_5, there would be a poten-

tial for 11.2 million tons of P_2O_5 from phosphate rock. This disregards plantation crops which account for most of the phosphate rock which is presently used in the above regions.

If prices for PR (32% P_2O_5) and TSP (45% P_2O_5) are \$30 and \$95/mt of product, f.o.b. producing country, the costs are \$94 and \$211/mt of P_2O_5 from PR and TSP, respectively. If transport, storage, handling, and marketing costs reach \$130/mt of material, delivered cost of each source is \$500/mt of P_2O_5. When those costs are \$45/mt of product, PR costs \$234/mt of P_2O_5, and TSP costs \$311/mt of P_2O_5 delivered to a farm, thus, making P_2O_5 from PR 75% of the cost of P_2O_5 from TSP. Therefore, the greatest economic advantage of PR will be found where indigenous PR is suitable for direct application and imported soluble phosphate would be the alternative. However, the advantage of PR in the initial cost of material is seriously eroded if the agro-economic value of PR is less than that of TSP.

Considering the potential new-market areas and their economic, political, and social systems leads to a question about the best marketing method for phosphate rock. Who is the customer? Is phosphate rock sold as a fertilizer or a soil amendment? What is the short- or long-term effect? The infrastructure in the market area, land tenure system, available financing at the farm level, the farmer's incentive to produce more per unit of land, and government policy dealing with increased crop production are some considerations in deciding upon a marketing method. In some cases, the customer may be the government or a crop production agency, and in others the customer may be the farmer. New marketing and delivery systems may be appropriate in the former case while traditional channels may be appropriate in the latter. There appears to be instances where each use is appropriate.

In particular, for land resettlement schemes where soils are known to be deficient in phosphorus, it might be practical to apply large doses of phosphate rock when the area is opened. The cost could be considered in the same way as the preparation of irrigation and drainage systems.

Conclusion

Even though much research has been conducted and a great deal of practical experience is available on the use of phosphate rock for direct application, there appears to be more needed to determine its place in efficiently supplying phosphorus to the world's agriculture. With the present understanding of the mineralogy and chemistry of phosphate rocks, the greatest research need is for long-term crop response data on different rocks under various environmental conditions, correlation of response with rock composition and reactivity, defining reactions with soil under various environmental conditions, and estimating economics of use under a range of conditions. Defining suitable economic handling and distribution systems is a key need which, however, must be preceded by a full study of the experiences from systems of the past and present. IFDC plans to conduct such a marketing study of phosphate rock for direct application. The study will cover production and use by origin, destination, and crops; methods and costs of processing and marketing including handling and distribution; determination of what has led to adoption or nonadoption in an area where tried; and projections of consumption.

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1. British Sulphur Corp., Ltd. 1973. "Ground Rock Phosphate Has Opportunities for Expansion," Phosphorus and Potassium, No. 68, p. 19-23.
2. Engelstad, O. P., J. G. Getsinger, and P. J. Stangel. 1972. Tailoring Fertilizers for Rice, TVA-NFDC Bulletin Y-52, Tennessee Valley Authority, Muscle Shoals, Alabama.
3. Food and Agricultural Organization (FAO). 1975. Annual Fertilizer Review, Rome.
4. International Superphosphate and Compound Manufacturers' Assn. (ISMA). 1977. Forecasts of Phosphate Fertiliser Consumption, A/F/77/105.

5. Phosphate Rock, Crop Year Annual. 1976. Mineral Industries Surveys.

6. Sidhu, Surjit S. 1978. "A Framework to Evaluate Phosphate Rock as an Alternative in Phosphate Fertilization," Paper presented at Seminar on Phosphate Rock for Direct Application, Haifa, Israel.

Table 1. Proposed Classification of Phosphate Rock for Direct Application Based Upon Solubility and Expected Initial Response

Rock Potential	Solubility, % of Rock		
	Neutral Ammonium Citrate	Citric Acid	Formic Acid
High	>5.4	>9.4	>13.0
Medium	3.2-4.5	6.7-8.4	7.0-10.8
Low	<2.7	<6.0	<5.8

Table 2. Origins of Phosphate Rock Traded for Direct Application, 1972

Country[a]	NAC Solubility[b]	Quantity of Rock[a]
		'000 mt
Tunisia	6.5 - 7.0	631
Morocco	4.0 - 6.0	225
Christmas Islands	3.1 - 3.8	149
Egypt	4.3 - 4.6	38
Israel	4.1 - 5.8	9
Jordan	4.2 - 4.6	3
Total		1,055

a. "Ground Rock Phosphate Has Opportunities for Expansion." British Sulphur Corporation, Ltd., Phosphorus and Potassium, No. 68, p. 19-23, November/December 1973.
b. Unpublished report of the International Fertilizer Development Center (IFDC), Muscle Shoals, Alabama 35660.

Table 3. Destinations of Phosphate Rock Traded for Direct Application, 1972[a]

Country	Quantity of Rock '000 mt
France	395
United Kingdom	113
Federal Republic of Germany	107
Austria	38
Uruguay	105
Brazil	98
Malaysia	126
Sri Lanka	41
Indonesia	23
Others	9
	1,055

a. "Ground Rock Phosphate Has Opportunities for Expansion," British Sulphur Corporation, Ltd., Phosphorus and Potassium, No. 68, p. 19-23, November/December, 1973.

Table 4. Estimates of Phosphate Rock Used for Direct Application

Region/Country	Phosphate Rock for Direct Application			Apparent Origin
	ISMA[a] '000 mt	FAO[b] '000 mt	ISMA[a] % Total P_2O_5	
Africa				
South Africa	20.5	15.0	5.6	Domestic
Morocco	2.8	1.3	4.2	Domestic
Senegal	2.7	-	15.0	Domestic
Others	0.9	0.4	0.3	?
	26.9	16.7	3.5	
Asia				
Malaysia	30.5	30.0	49.2	Christmas Islands
Burma	6.4	6.0	64.0	?
Indonesia	5.7	5.5	4.7	Jordan, Christmas Islands
Sri Lanka	5.5	12.0	45.8	Jordan, Egypt
Bangladesh	1.2	-	2.3	Jordan
India	-	10.0	-	?
Others	-	2.3	-	?
Total	49.3	65.8	1.2	
Europe				
France	46.0	35.0	2.8	Tunisia, Senegal
United Kingdom	17.5	15.7	4.5	Tunisia, Israel
Other Western Europe	6.2	7.9	0.2	?
U.S.S.R.	900.0	884.0	19.0	
Other Eastern Europe	84.0	-	2.8	?
Total	1,053.7	942.6	7.9	

(Continued)

Table 4. Estimates of Phosphate Rock Used for Direct Application (Continued)

Region/Country	Phosphate Rock for Direct Application			Apparent Origin
	ISMA[a] '000 mt	FAO[b] '000 mt	ISMA[a] % Total P_2O_5	
Latin America				
Brazil	101.3	106.8	10.2	Domestic, Tunisia, Morocco
Argentina	5.8	4.5	26.4	Tunisia
Venezuela	1.3	-	3.2	Domestic
Uruguay	-	28.0	-	Tunisia, Israel
Colombia	-	15.0	-	Domestic
Chile	-	13.0	-	?
Others	15.0	2.0	1.9	?
Total	123.4	169.3	41.7	
North America	1.0	8.9	<0.1	Domestic
Oceania	0.1	1.0	<0.1	?
World Total	1,255 (1,655)[c]	1,204.3	4.8	

a. Forecasts of Phosphate Fertilizer Consumption, ISMA, A/F/77/105 June 1977. (1975-76 statistics).
b. Annual Fertilizer Review, FAO, 1975 (1974-75 statistics).
c. Estimated 400,000 mt of P_2O_5 from phosphate rock in the People's Republic of China--"Ground Rock Phosphate Has Opportunities for Expansion," British Sulphur Corporation, Ltd., Phosphorus and Potassium, No. 68, p. 19-23, November/December 1973.

Table 5. Common Formulations of Phosphate Rock for Direct Application[a]

Powdered Products Formulation $N-P_2O_5-K_2O-MgO$, %	Granular Products Formulation $N-P_2O_5-K_2O-MgO$, %
0-(28-36)-0-0	0-(29-31)-0-0
0-14-30-0	0-15-25-0
0-16-26-0	0-20-20-0
0-20-20-0	0-24-12-0
0-24-12-0	0-23-0-7
0-16-8-6	0-15-0-0 + Basic Slag
	0-15-0-0 + Calcified Seaweed
	0-25-0-0 + Micronutrients

a. "Ground Rock Phosphate Has Opportunities for Expansion," British Sulphur Corporation, Ltd., Phosphorus and Potassium, No. 68, p. 19-23, November/December 1973.

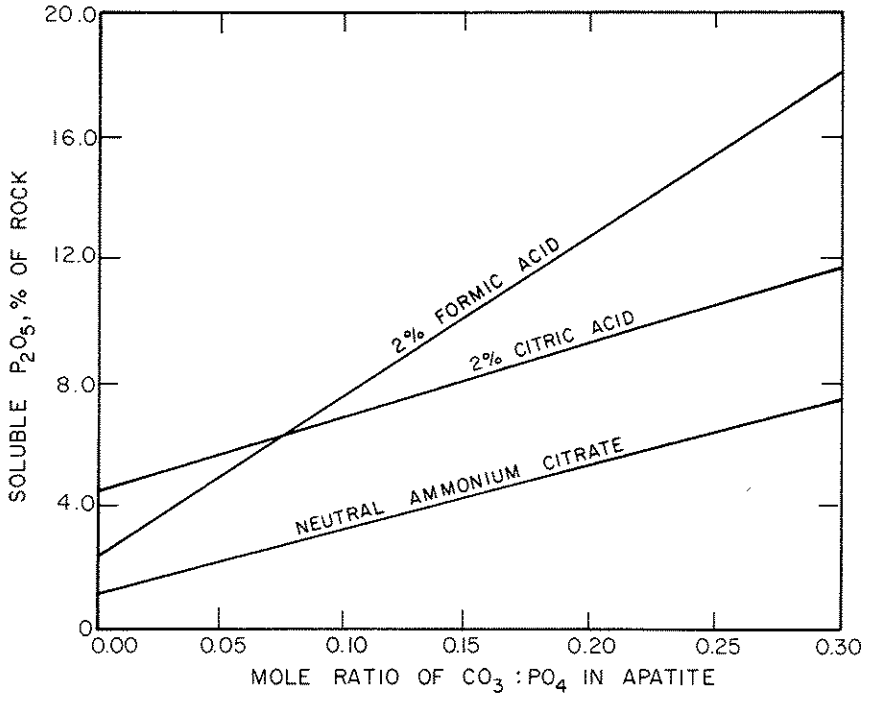

Figure 1. Solubility of Phosphate Rock in Various Solvents as a Function of Apatite Composition.

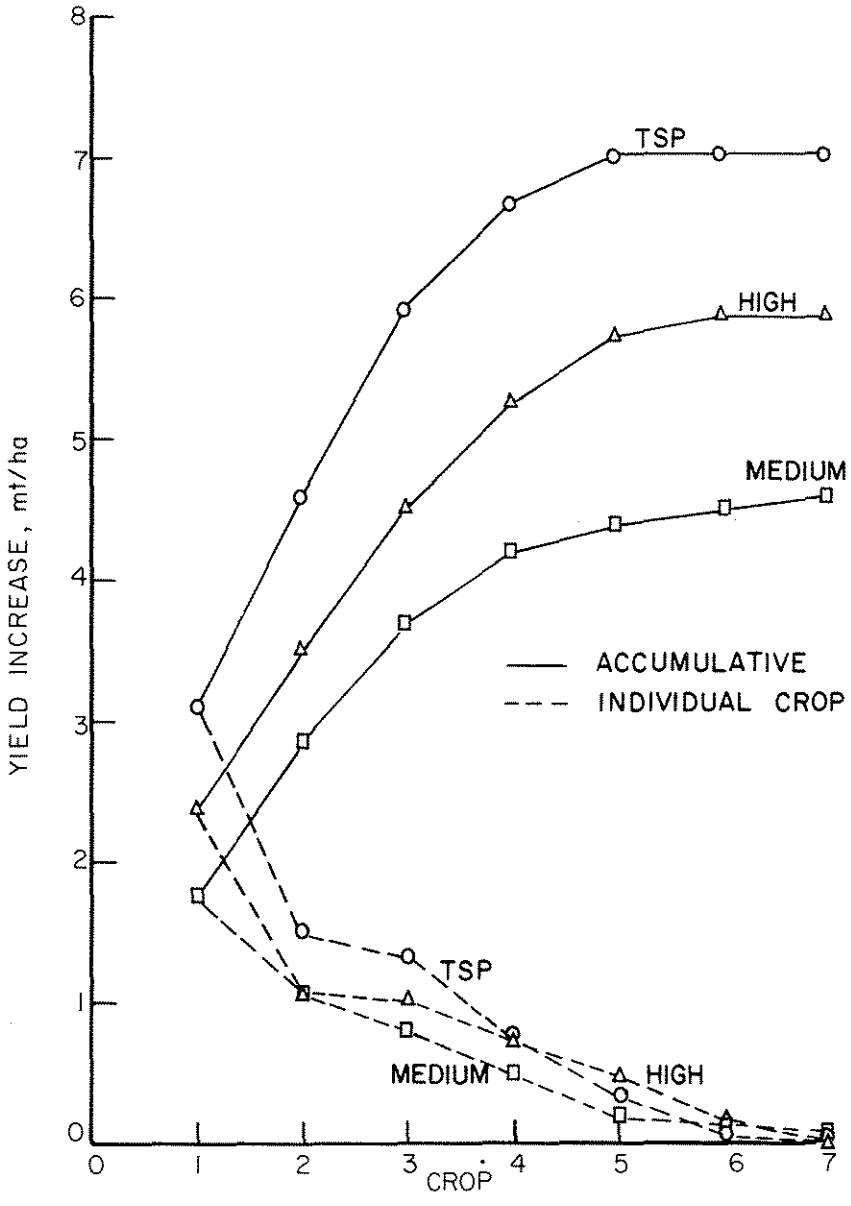

Figure 2. Accumulative and Individual Crop Response of Rice to Single Applications of Low Rates of P Sources in Thailand (TVA–NFDC Bulletin Y-52, 1972, and Sidhu, 1978).

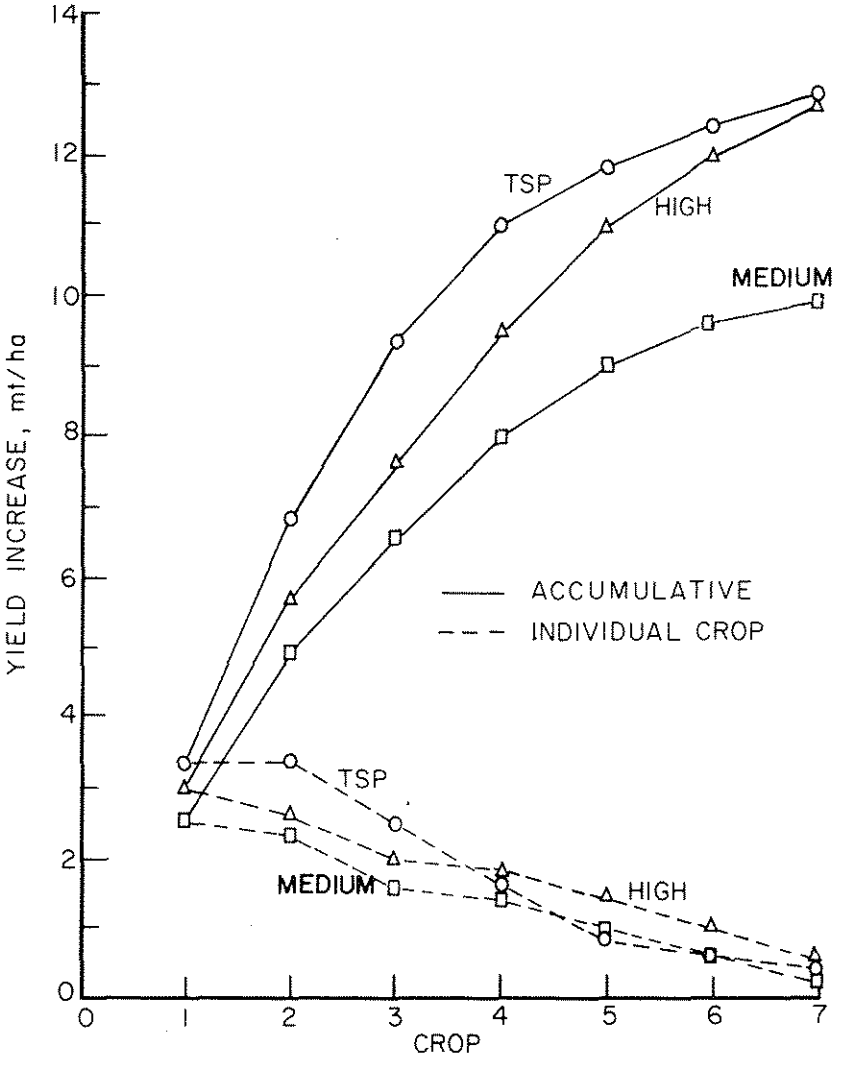

Figure 3. Accumulative and Individual Crop Response of Rice to Single Applications of High Rates of P Sources in Thailand (TVA–NFDC Bulletin Y-52, 1972, and Sidhu, 1978).

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