EVALUATION OF PHOSPHORUS FERTILIZER MATERIALS ON TWO BENCHMARK SOILS OF THE TROPICS

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN AGRONOMY AND SOIL SCIENCE

DECEMBER 1983

By

David J. Harris

Dissertation Committee:

Goro Uehara, Chairman
Robert L. Fox
James A. Silva
Tung Liang
Gary R. Vieth

We certify that we have read this dissertation and that, in our opinion, it is satisfactory in scope and quality as a dissertation for the degree of Doctor of Philosophy in Agronomy and Soil Science.

DISSERTATION COMMITTEE

Goro Uehara
Chairman

Robert L. Fox

James A. Silva

Tung Liang

Gary Vieth

ACKNOWLEDGEMENTS

I wish to acknowledge the financial support recieved during my graduate program, initially from the National Science Foundation Graduate Fellowship Program and subsequently from the US Agency for International Development (USAID) and from the International Fertilizer Development Center (IFDC) through the Benchmark Soils Project. Dr. Tej Gill at USAID and Drs. W.D. Bishop and L.L. Hammond at IFDC deserve special mention.

Also, I wish to express my gratitude to the staff members of the Department of Agronomy and Soil Science and the Benchmark Soils Project at the University of Hawaii for their support and collaboration. To Dr. Goro Uehara, my major advisor, I give special thanks for the interaction which lead to the design of this study and for his confidence which gave me the independence to carry it out. I thank Dr. J.A. Silva, Principal Investigator of the Benchmark Soils Project and member of this disseration committee for his support and assistance. To Dr. G.Y. Tsuji, Project Manager, I express my apprecitation for administrative and logistical support, which were essential for this study. To Drs. R.L. Fox, T. Liang and G.R. Vieth, members of the dissertation committee, I am grateful for their time and efforts in reading and making suggestions for improving this dissertation. I thank Mrs. Ada Chu of the Benchmark Soils Project Lab for the soil analyses and Mr. Ernest Okazaki of the University of Hawaii, Agricultural Service Center for plant tissue analyses.

I wish to thank the staff of each of the collaborating institutions, the Philippine Council for Agricultural and Resources Research and Development (PCARRD), Los Banos, Philippines, and the Center for Soil Research (CSR), Bogor, Indonesia, for their collaboration which made this work in their countries possible. To the in country project leaders, Mr. R.G. Manuelpillai in Indonesia and Dr. M.E. Raymundo in the Philippines, I express my sincere appreciation. A special thanks is due to the on-site staff at Naga; Mr. P.R. Vicente, Ms. Anchie Pago, Mr. Alberto Borromeo, Mr. Jaime Gibe, Mr. Rogelio Arco, and Mr. Edgardo de la Torre; and to the on-site staff in Nakau; Ir. Soleh, Ir. Sugijono, Rum Harayitno, and Agus Tarman. Without their collaboration the field experiments could not have been conducted.

Finally, I express my gratitude to my wife, Susan and children, John and Jenny, for their support and encouragement during my graduate program and for their patience and understanding during the extended absences that were necessary to conduct and complete this study.

ABSTRACT

One possible strategy for improving the economic attractiveness of P fertilization on acid P-deficient soils in the tropics was investigated agronomically in two field experiments on sites of the Benchmark Soils Project in the Philippines and Indonesia. The specific strategy is the use of phosphate rock for direct application or partially acidulated or thermally altered phosphate rock in place of acidulated phosphates, e.g., superphosphate. The experiments were conducted on Hydric Dystrandept soil on a site near Naga City, Camarines Sur, Philippines and on a Typic Paleudult on a site located near Kotabumi, Lampung on the island of Sumatra, Indonesia. The experiments compared crop response (primarily maize) to one highly reactive phosphate rock (North Carolina, NC) and one moderately reactive phosphate rock (Central Florida, CF), which were used because they are well characterized with respect to reactivity. These two P-sources were used in finely-ground form and also each was used in a different minimally altered form. For the North Carolina rock, a minigranular form was used form, to determine if the minigranulation process can be used to overcome the handling and transportation problems of the dusty, finely-ground form without reducing agonomic effectiveness. For the Central Florida rock a minigranular form which was 20% partially acidulated with phosphoric acid was used as the minimally altered form to determine if partial acidualtion of moderately reactive phosphate rocks could adequately improve agronomic effectiveness on acid soils.

Comparing the results for the two soils sites in the first crop, a large difference between sources is seem on the Hydric Dystrandept, while no significant differences are seen between sources on the Typic Paleudult. In the second crop, fresh applications of superphosphate were made on former control plots on both sites and the other treatments were left as residuals. On the Hydric Dystrandept significant differences between sources are seen in the residual effects. On the Typic Paleudult, soybeans were planted, and no significant differences are seen between residual effects of the sources.

The higher P requirement evidenced by the Hydric Dystrandept as compared to the Typic Paleudult, made reapplication necessary at all rates for the third crop on the Hydric Dystrandept, whereas for the Typic Paleudult, reapplication of all sources was made only on the 10 kg/ha plots, on which 70 kg P/ha were applied to permit comparison with the residual 80 kg P/ha treatments. The third season yield results again show no significant differences between sources on the Typic Paleudult, even for the reapplications of 70 kg P/ha, whereas some significant differences are seem for the reapplication on the Hydric Dystrandept.

With respect to rock modifications on the Hydric Dystrandept, where differences between sources are detected, minigranulation of the NC rock did not reduce its effectivesness, thus confirming the agronomic viability of the process. Also on the Hydric Dystrandept, partial acidulation did improve the performance of the CF rock, but not sufficiently to make it equal to superphosphate or the NC forms.

In summary, these results indicate that the Typic Paleudult is well suited for direct application of phosphate rocks of moderate and possibly lower reactivity, whereas the Hydric Dystrandept requires phosphate rocks of high reactivity to obtain yields comparable to those of superphosphate. This difference in performance of phoshpate rock between the two soils can be related to the slightly lower pH of the Typic Paleudult and also, its lower P-sorption capacity, in comparison to the Hydric Dystrandept.

The results from the post harvest P soil test analyses indicate that neither the modified Truog nor the Bray P I procedure can be satisfactorily used to predict residual P in the Hydric Dystrandept when P-sources varying in solubility are used. In the Typic Paleudult there is some indication that the Bray I procedure underestimates residual P from the CF sources; however, it appears that minor modification of the procedure by increasing the solution to soil ratio could overcome this problem. This is considered to be a worthwhile area for research since direct application of phosphate rock over the complete range of solubility appears to be an agronomically advisable practice for the Typic Paleudult and similar soils.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

Figure Page

LIST OF ABBREVIATIONS

AID	Agency for International Development, US
ACS	Absolute Citrate Solubility
BLSD	Baysian Least Significant Difference
BSP	Benchmark Soils Project
CFf	Central Florida finely ground phosphate rock
CFpam	Central Florida Partially acidualted minigranular phosphate rock
CA	Carbonate Apatite
FA	fluorapatite
FAO	Food and Agriculture Organization, UN
FMP	Fused Magnesium Phosphate
H.D.	Hydric Dystrandept
IFDC	International Fertilizer Development Center
LSD	Least Significant Difference
NAC	Neutral ammonium citrate
NCf	North Carolina finely ground phosphate rock
NCm	North Carolina minigranular phosphate rock
SCS	Soil Conservation Service, USDA
SSP	Simple superphosphate
T.P.	Typic Paleudult
TSP	Triple superphosphate
TVA	Tennessee Valley Authority
USDA	United States Department of Agriculture

CHAPTER I

INTRODUCTION

The ever growing demand for food by a rapidly increasing world population is well recognized. The greatest increase, both in population and in demand for food, is occurring in the developing countries of the tropics. Further, the segment of the population most in need of additional food is also that segment with the fewest resources for either its purchase or production.

The potential for increased food production does exist in much of the tropics and can be realized by increasing agricultural yields on currently used land and by opening new lands. However, large areas of currently cultivated or potentially arable land in the nonarid upland regions are occupied by soils for which phosphorus deficiency is the factor most limiting crop production. Thus, finding economical methods for overcoming phosphorus (P) deficiency is an integral part of any solution to the problems of food and agricultural development in most developing countries of the tropics.

One of the basic concepts of soil chemistry is that phosphorus applied to the soil reacts with the mineral constituents and to a lesser extent enters the organic matter cycle of the soil. In either case, P availability to plants is affected. Thus, phosphorus requirements for plant growth are a function of soil properties. Furthermore, the form in which P is applied affects both its reactions with the soil and its availability to plants. As a result, soils of widely different properties necessitate different strategies of P fertilization when cultivated.

In addition to the soil and plant factors, the following economic points must be considered in any effort to overcome P deficiency by input of phosphorus fertilizer:

1) At the national level, limited foreign exchange is a major constraint in most developing countries. As a result, it is desirable to develop indigenous sources of phosphate fertilizers to reduce the need for foreign exchange. Development of indigenous phosphate sources also promotes internal economic development. In developing the use of indigenous sources, it is desirable to seek processes which efficiently use the phosphate resource while avoiding excessive capital outlay, since capital is also often scarce on a national level.
2) At the farmer level, scarcity of capital for fertilizer purchase is a constraint in the agricultural production sector, particularly for small farmers who are in the segment of the population most in need of improved nutrition and increased income. Thus, phosphorus fertilizer materials which are effective and economical are needed, as well as, methods for efficiently utilizing limited quantities of fertilizer.

The best phosphorus source and method for its use depend on the available resources, the soil, the crop management system, and ultimately, the economic environment. Thus, the basic agronomic information about P materials and their use in a given soil and cropping system is integral information required for planning phosphorus fertilizer strategies. The experimental work described in this dissertation is an agronomic study of crop response, primarily maize, to P fertilizer materials on two P deficient soils in the tropics.

The published literature contains numerous studies designed to explore methods of improving the efficiency of applied P, that is, reducing the amount of phosphorus needed to obtain a given yield level. Among these are use of amendments such as lime and silicates or the utilization of microbes such as mycorrhiza and P-dissolving bacteria. In this study, the strategy investigated involves only the P material applied and its management, considering the possibility of direct application of phosphate rock and minimally altered phosphate rock materials in place of conventionally acidulated phosphate, i.e., superphosphate.

The two sites used for the experiments reported in this study are part of the University of Hawaii Benchmark Soils Project (BSP) network of soil families of the tropics as described by the Benchmark Soils Project (1978). The Benchmark Soils Project is an AID-funded, research contract officially entitled "Crop Production and Land Capabilities of a Network of Tropical Soil Families." The principal objective of the Benchmark Soils Project is "to determine scientifically the transferability of agroproduction technology among tropical countries" (Benchmark Soils Project, 1976). Soil classification at the family level in the USDA Soil Taxonomy (Soil

Survey Staff, 1975) is proposed as the principal basis for transfer. To test the transfer hypothesis the network of experimental sites on three selected tropical soil families was established. The experiments reported in this study were conducted on these two sites as "management experiments" within the overall objectives of the Benchmark Soils Project. The general objectives for "management experiments" were:

1. Provide local governments with information on ways to increase production by improved utilization of resources; and
2. Provide farmers who have limited resources with basic information indicating how they can best increase yields (Benchmark Soils Project, 1976).

Management experiments are the kind of locally relevant activity an agricultural experiment station would undertake after obtaining by "horizontal transfer" (Benchmark Soils Project, 1978) the basic information on major factors limiting production. In the case of these soils, the basic transferable information is high capacity to sorb P and also base saturation and pH sufficiently low to suggest potential suitability for alternate, non-acidulated P-source materials. The International Fertilizer Development Center (IFDC), Muscle Shoals, Alabama, based on its mandate to assist "the goal of increasing agricultural productivity in developing countries through the use of improved fertilizer and fertilizer know-how" (Stangel, 1979) provided partially support for this study and supplied experimental phosphate fertilizer materials.

CHAPTER II

LITERATURE REVIEW

HISTORY OF PHOSPHORUS FERTILIZATION

Addition of phosphorus by man to cultivated soil probably dates back to ancient times when ashes, kitchen waste, and plant residues were disposed of around inhabited areas. Bear (1938) reports the development of P use in agriculture in more modern times as follows. Literature from England indicates the application of bones to soils in the mid 1600's. By the eighteenth century, grinding machines had been developed for processing bones before application. This practice was widely enough adopted that English agents were buying bones on the European continent in the 1800's. The famous German agricultural researcher, Justus Liebig, charged the English with robbing Europe of its P resources, including the the remains from the graves of the battles of Leipzig, Waterloo, Crimea, and the catacombs of Sicily.

In 1840 Liebig first suggested treating bones with sulfuric acid to produce soluble phosphate. However, the Englishman, John B. Lawes, of Rothamsted secured the first patent for the method in 1842 using mineral phosphates, i.e. phosphate rock, in place of bones. Discovery of phosphate rocks in England, Spain, and France in the 1840's, and in Florida in 1887, permitted the continued growth of P application in agriculture in the form of acidulated phosphate rocks or superphosphate.

In Germany in the 1880's, the value of basic slag as a fertilizer material was recognized. Basic slag is also known as Thomas slag since it is a by-product of the Thomas process for refining iron from ores with high P contents, which were the predominant type of ore found in Europe. Basic slag, which, in addition to phosphorus, contains calcium and silicate in substantial amounts, was widely used in Germany because the country did not have large phosphate rock deposits. Basic slag was produced and used as a fertilizer and amendment in other parts of Europe and the Americas, but it never attained such importance ouside of Central Europe because superphosphate was readily available.

Bear (1938) also notes that "Ground phosphate rock . . . is being used in certain portions of the world because of the cheapness of the local supply or as in the case of Illinois, because of very active propaganda in its favor." However, he noted that in the period of the 1920's and 30's, quantities of phosphate rock for direct application were small on a world scale compared to quantities of superphosphate, basic slag, and bone meal.

PHOSPHATE ROCK AS A DIRECT APPLICATION FERTILIZER

As indicated in the historical review above, directly-applied phosphate rock never was the predominate P fertilizer in world-wide use. IFDC/UNIDO (1979) cites FAO statistics for 1976 indicating that about 5% of the world P fertilizer consumption of 116 million tons of rock was in the form of directly applied phosphate rock. Over 70% of this use was in the U.S.S.R., and unreported use in China would probably increase the 5% figure. However, interest in the use of phosphate rock has been sufficient to make its direct application the subject of a significant number of studies (For a recent review see Khasawneh and Doll, 1978). Such studies have shed light on the effect soil properties have on P availability from phosphate rock. Also, phosphate rocks have been found to vary widely in mineralogy. This affects the chemical and physical propertiesof the rocks and results in wide differences in reactivity and P availability. These subjects are discussed below.

Effect of phosphate rock characteristics on solubility and effectiveness as a fertilizer

Early researchers working on the use of phosphate rock as fertilizer had little knowledge of the range in mineralogical properties of the rocks. Lipman *et al.* (1916) refer to phosphate rock as tricalcic phosphate, even though Schaller (1912) had named five different apatites as the minerals found in natural phosphorites. Many published reports on the use of phosphate rock as fertilizer did not cite the source or composition of the rock used. A relatively recent example of this is Chu *et al*. (1962). An understanding of phosphate rock mineralogy and crystal structure has emerged over the years. Particularly in the last ten to twenty years, this has led to an understanding of the relationship of rock properties to solubility and effectiveness as a fertilizer.

Chemical composition and mineralogy:

Naturally occurring phosphate deposits can be divided into three classes, which represent a natural weathering sequence (McClellan and Gremillion, 1980). The largest and most economically important group of phosphate deposits are the calcium phosphates, which belong to the apatite mineral group. Apatite is the tenth most abundant mineral in the earth's crust and occurs in rocks of sedimentary, metamorphic, and igneous origin (McClellan and Lehr, 1969). This is the class of deposits from which most of the phosphate rock used for direct application comes.

The other two classes of phosphate deposits (Ca-Fe-Al phosphates and Fe-Al phosphates, which are sequential weathering products of the Ca phosphates) are generally not used for direct application. However, low temperature calcination processes are now in use for producing direct application fertilizers from the Senegal Fe-Al phosphate (Anon, 1975) and the Christmas Island Ca-Fe-Al phosphates (Doak *et al*., 1975). These types of materials were not included in the study reported here and, therefore, will not be reviewed in greater detail.

In one of the early studies in which the effectiveness of a series of six phosphate rocks was related to composition, Bartholomew (1935) observed that as fluorine (F) content of the rocks increased, yield of sudan grass decreased. This effect was observed for the first cutting, but by the second cutting the effect disappeared. Bennett *et al*. (1957) studying a series of seven sources of which only two were common to those studied by Bartholomew, found no relationship between fluorine content and availability.

Arminger and Fried (1957) reported on pot trials with buckwheat and alfalfa on three soils, comparing ten phosphate rock sources which had been chemically and physically characterized by Caro and Hill (1956) in a coordinated study of rock properties and agronomic effectiveness conducted by the Soil and Water Conservation Research Branch, USDA, Beltsville, Maryland. This coordinated study showed a good correlation between agronomic effectiveness and phosphate rock solubility in either citric acid or neutral ammonium citrate. The citric acid method had initially been developed for evaluating the quality of basic slags and the neutral ammonium citrate method, for evaluating the completeness of reaction in acidulated phosphate production (IFDC/UNIDO, 1980). The effect of fluorine was again not clear in the USDA study, although the rocks with the highest F content were found to be the most reactive. The chemical constituent of the ten phosphate rocks that showed the best relationship to agronomic effectiveness of the ten sources was "bound carbonate content." Bound carbonate is carbonate in the apatite crystal structure, as opposed to free carbonate occurring in impurities mixed with apatite in the phosphate rock deposit, such as calcite. Bound carbonate content of phosphate rock samples is determined after removing free carbonates by extraction with triammonium citrate (Silverman et al., 1952).

The discovery of the correlation of bound carbonate with agronomic effectivness, along with research in the fields of geology and dentistry, set the stage for breakthroughs in understanding the interrelationships of chemical composition, reactivity, and agronomic effectiveness. Natural apatites can be divided into three groups (hydroxy-, chlor-, and fluorapatite), defined by the main anion other than phosphate in the crystal structure (McClellan and Lehr, 1969). The generalized formula is $Ca_{10}(PO_4)_6X_2$, where X stands for OH, Cl or F. Hydroxy- and chlorapatite rarely occur in nature, whereas fluorapatite in near stoichiometric form, $Ca_{10}(PO_4)_6F_2$, does occur in igneous and metamorphic deposits. The sedimentary phosphate rock deposits which comprise the major deposits in the southeastern and western U.S., North Africa, and Latin America differ from the pure hydroxy- and fluorapatites due to a continuous range in substitution of carbonate for phosphate, and also of other cations for calcium (McClellan and Lehr, 1969). This explains the structural location of bound carbonate, which had been shown by Arminger and Fried (1957) to affect reactivity. Lehr and McClellan (1972), working at the Tennessee Valley Authority (TVA), used chemical, crystallographic, and statistical procedures to characterize 560 phosphate rocks. They identified the following general formula for the carbonate-substituted fluorapatite, known mineralogically as the francolite series:

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{2+0.4x}$$

The substitution of planar, divalent carbonate for tetrahedral, trivalent phosphate results in partial substitution of F^- in the vacant O^{2-} site. Monovalent Na^+ substituting for Ca^{2+} corrects for most of the resulting charge imbalance. The maximum observed value for x was about 1.4.

This substitution of CO_3^{2-} for PO_4^{3-} and the associated substitutions were found to change the crystal structure, as indicated by unit cell dimensions, and to decrease individual crystal size. The crystal size decrease is presumably due to incompatibilities in the structure that prevent the growth of large crystals. The net effect of incompatibilities in the crystal structure and small crystal size is increased chemical reactivity (Lehr and McClellan, 1972).

Chemical reactivity in solvent solutions:

Using the relationships developed between crystallographic dimensions and chemical composition of apatite, Lehr and McClellan (1972) proposed a reactivity measurement for carbonate-substituted fluorapatites called Absolute Citrate Solubility (ACS). The ACS of phosphate rock is the percentage of the theoretical P_2O_5 content of the apatite in the rock that is soluble in neutral ammonium citrate. The theoretical P_2O_5 content of the apatite can be determined from the crystallographic a-dimension using the statistical relationships also determined by Lehr and McCellan (1972). They reasoned that the absolute expression would remove the effect of non-apatitic accessory minerals on P_2O_5 content of rocks when ranking rocks as to solubility. Since both the reactivity and the P_2O_5 content of the apatite are related to the degree of carbonate substitution in the apatite, Lehr and McClellan (1972), using regression, developed an equation relating ACS to the a-dimension (a_o) determined by x-ray diffraction:

$$ACS = 421.4\ (9.369-a_o).$$

Engelstad et al. (1974) observed a better relationship between agronomic effectiveness and ACS than was found with neutral ammonium citrate in flooded rice experiments. However, Chien and Hammond (1978) comparing six solubility evaluation methods with seven rocks for predicting agronomic effectiveness for guinea grass on an Oxisol and for beans on an Andept, found four methods to be superior to neutral ammonium citrate or ACS. One of the superior methods (2% citrate extraction) is used in Brazil and, as cited earlier was originally developed for evaluating basic slag. Another method giving higher correlation (2% formic acid) is the standard in the European Economic Community. The third method (ammonium citrate, pH3) was researched by IFDC-TVA. The fourth method showing a higher correlation to crop performance than ACS or neutral ammonium citrate was a second extraction following an initial extraction with ammonium citrate. The second extraction in sequence better reflected the relative reactivity of the rocks because the first extraction removed the reactive free carbonates in one of the seven rocks in the study, permitting the second extraction to reflect the reactivity of the apatite.

Chien and Hammond (1978) further concluded the chemical extraction methods are superior to the ACS method because physical effects of crystalline intermixing with gangue minerals, such as silica, on rock solubility are better taken into account in extractions. Also, the ACS method is limited to use with the carbonated-substituted fluorapatites (francolites). Thus, it is not useable with rocks which contain significant hydroxide substitution for fluoride, such as the Christmas Island, Curacao, and Sechura, Peru deposits.

Chemical composition and the dissolution process:

Applying the Le Chatelier principle of chemical equilibrium indicates that processes which reduce the activities of Ca^{2+}, Na^{+}, Mg^{2+}, $PO_4{}^{3-}$, $CO_3{}^{2-}$, F^{-} and OH^{-} in solution provide the driving force for dissolution of phosphate rock.

$$Ca_tNa_uMg_v(PO_4)_w(CO_3)_xF_y(OH)_z \Rightarrow$$

$$tCa^{2+} + uNa^{+} + vMg^{2+} + wPO_4{}^{3-} + xCO_3{}^{2-} + yF^{-} + zOH^{-}$$

The recognition of the importance of acidity to the dissolution of phosphate rock stems from the work of Liebig in Germany and Lawes in England, in the early 1800's (as discussed earlier with regard to the invention of the superphosphate process). The reason that acidity promotes dissolution is that the protonated forms such as $H_2PO_4^-$, $HCO_3{}^-$, HF, and H_2O act as sinks for the constituent anions, thus drawing the equilibrium further to the right in the above equation. Paauw (1965) reported that a soil pH in KCl of 4.2 was needed for effective response to Gafsa rock (a high reactivity rock by the McClellan and Lehr analysis) whereas, a pH in KCl of 3.8 was needed for Florida rock (a medium reactivity rock). This result points out the effect of rock properties on solubility and the role of acidity in overcoming low reactivity.

Wier et al. (1971) determined the solubility product constant (pK) for hydroxyapatite, and Chien and Black (1975) determined the pK for a carbonate apatite (Florida phosphate rock) in dilute acid solutions over a range of pH's. For both materials a range in solubility was observed such that the more material that was dissolved in the process of determining the solubility, the lower the ion activity product. The range in the values of the negative logarithm of the ion-activity products (pK) for Florida phosphate rock was from 110.8 to 120.7. The existence of a range in solubility is consistent with the fact that sedimentary phosphate rocks are poorly crystalline. Solubilities were, however, essentially constant in the pH range from 4 to 6. Chien and Black (1976) applied the free energy of formation concept to the range in francolite formulas provided by McClellan and Lehr (1972). Chien and Black (1976) derived the coefficient for the molar carbonate substi- tution as +130.2 kcal/formula weight in the free energy of formation equation. This demonstrates thermodynamically that substitution of of carbonate makes the free energy of formation less negative, thus making carbonate-substituted apatite less stable.

Chien (1977) calculated that the free energy of dissolution of apatites is always positive, and for the purpose of that paper he assumed that the free energy of dissolution was not a function of carbonate substitution. However, he showed that free energy of neutralization (reaction with hydrogen ion) is negative and becomes more negative with either carbonate substitution for phosphate or hydroxide substitution for fluoride in the fluorapatite structure. Thus, the free energy of reaction in acid, which is the sum of the free energies of dissolution and neutralization, is also negative and becomes more negative with increasing carbonate or hydroxide substitution. The decrease calculated by Chien (1977) in free energy of reaction with the substitution of one mole of carbonate is 6.1 kcal/mole, compared to 14.8 for substitution of one mole of hydroxide. This indicates that hydroxide substitution for fluoride has an effect that is about three times greater than carbonate substitution for phosphate in increasing the reactivity of fluorapatite. However, there is no experimental evidence to confirm this.

From this discussion it is clear that thermodynamic solubility studies confirm the expectation raised by the x-ray crystallographic studies, i.e., that substitution increases the reactivity of fluorapatite. The work of Chien and Black (1976) demonstrated the effect of crystallographic substitution on the solubility product constant. The effect of substitution on the free energy of reaction calculated by Chien (1977) is, however, independent of the crystallographic effect, since he assumed the free energy of dissolution of carbonate apatites to be a constant, i.e., not a function of the degree of carbonate substitution. Thus, two factors increase the equilibrium solubility in acid solution of carbonate substituted apatites:

1. Increasing ion solubility product constant (K) (e.g., decreasing pK) with increasing CO_3^{2-} and ^-F substitution;
2. Increasingly negative free energy of neutralization as a result of CO_3^{2-} and F^- substitution.

Khasawneh and Doll (1978) using the solubility constant relationship from Chien and Black (1976) produced solubility diagrams for phosphate as a function of pH and pCa for hydroxyapatite, fluorapatite, and the carbonate-substituted fluorapatites. Their calculations show that not only does solubility increase more per unit decrease in pH with increasing carbonate substitution in fluorapatite, but also, that the solubility increase per unit decrease in calcium activity is also greater as carbonate substitution increases. This latter fact is due to the lower calcium content resulting from concurrent Mg^{2+} and Na^{+} substitution for Ca^{2+} as $CO_3{}^{2-}$ substitutes for $PO_4{}^{3-}$.

Plant factors affecting P availability from phosphate rocks

Truog (1916) introduced his "theory regarding the feeding power of plants." Using sand culture he observed that plant species that had high calcium content were better able to use phosphate rock than species with lower Ca contents. Bauer (1921) showed that sweet clover had a much better "feeding power" for P from phosphate rock than did cereals. He thus concluded that sweet clover was an excellent crop to include in rotation with cereals, not only because it fixed nitrogen but also because it increased P availability.

Cook (1935) tested various crop species in sand culture fertilized with phosphate rock, to which either H-saturated or Ca-saturated exchange material (bentonite or organic matter) had been added. He found that buckwheat performed equally in the presence of either Ca- or H-saturated material, whereas cereal grains (oats, maize, and millet) used phosphate rock effectively only in the presence of H-saturated exchange material. Thus, species clearly differed with regard to the effect of Ca on availability of P from rock. Drake and Steckel (1955) demonstrated that crop species that were more effective users of P from phosphate rock had root systems with high cation exchange capacities. These plants could thus promote dissolution of phosphate rock by providing a sink for Ca, without Ca necessarily being assimulated into tissue.

Cooke (1956) suggested that crops best suited to use P from phosphate rock are those with well-developed fibrous root systems. This conclusion, however, conflicts with the observations that cereals, which have fibrous root systems, are inefficient users of P from phosphate rock. Tinker (1975) examined the effect of mycorrhizal association on phosphate rock availability. He concluded that mycorrhiza enhance P uptake from rock but that mycorrhiza alone cannot explain differences among crops with regard to phosphate rock use.

The discussion in the preceding section on the solubility of phosphate rock demonstrated that rock solubility increases as pH decreases. This would in general result in increased P availability from phosphate rocks in soil as pH decreases. However, decreased pH in soil also increases solubility of the elements aluminium and manganese, both of which can be toxic to plants if concentrations exceed certain limits. Foy (1976) stated that aluminum toxicity has been reported at soil pH values of 5.5, but it is particularly severe below pH 5.0. He further stated that, in well-drained soil, Mn toxicity occurs at pH 5.5

or below. There is, however, diversity among and within species with regard to the level of tolerance to these toxic elements. Ellis *et al.* (1955) conducted experiments with oats in sand culture in which a pH range from 4.9 to 7.4 was obtained by adding 1% bentonite suspensions which had been washed with HCl and then titrated with $Ca(OH)_2$ to the various pH values. Yields in the treatments with Florida phosphate rock were lowest at pH 4.9, increased to a maximum at pH 5.5, and then decreased at pH's above 6. Thus, there was an apparent Al toxicity that reduced yield at pH 4.9, even though rock solubility would be expected to be higher at this pH.

Foy and Brown (1964) demonstrated that plant species differed in their tolerance of aluminium. This indicates that species can be expected to differ in their suitability for fertilization with phosphate rock at the acid soil pH's which are most conducive to rock dissolution.

Soil factors affecting P availability from phosphate rock

The phosphorus in acidulated phosphate fertilizers is nearly 100% water soluble. Lindsay and Stephenson (1959) demonstrated the rapid dissolution of monocalcium phosphate monohydrate (triple superphosphate) in soil with the formation of a concentrated solution of phosphate and calcium that is very acid. The high acidity of the solution is due to noncongruent dissolution, resulting in precipitation of dicalcium phosphate. Phosphorus concentration exceeded 1 mole per liter or 30,000 ppm within 15 mm of the fertilizer granule in Hartsells fine sandy loam, and pH was depressed in excess of 3 pH units near the granule. As this concentrated solution moved through the soil, it dissolved Fe, Al, Mn and Ca, all of which began with time to reprecipitate as phosphate compounds. Phosphate rock, on the other hand, is not water soluble and depends on reaction with the soil and also plant roots for dissolution. Only then is it available for plant uptake. After dissolution the phosphate from phosphate rock reacts with the soil in processes that remove it from solution. However, these reactions take place at much lower concentrations than in the case of superphosphate. These factors, which affect the dissolution and reactions of phosphate rock in soil, are discussed in the following sections.

Considering again the Le Chatelier principle, the soil properties that govern the dissolution of phosphate rock in an acidic environment in the pH range from 4 to 6 can be enumerated:

$$Ca_tNa_uMg_v(PO_4)_w(CO_3)_xF_yOH_z + sH^+ \Rightarrow$$
$$tCa^{2+} + uNa^+ + vMg^{2+} + wH_2PO_4^- + xH_2CO_3 + yF^- + zH_2O$$

As discussed previously, any reaction which reduces the activity of the component ions of phosphate rock will enhance dissolution. In brief, the possibilities are:

1) Protonation of the anion species. This is dependent on soil pH and exchangeable acidity.
2) Removal of the cation species, particularly Ca, from solution by cation exchange reactions. This is dependent on the exchange properties of the soil, such as, cation exchange capacity and base saturation.

3) Reduction of Ca activity in solution through formations of ion pairs.

4) Decomposition of H_2CO_3 to CO_2 and water can further reduce CO_3^{2-} activity.

5) F can react with soil constituents such as Ca, Al, and Si.

6) Removal of phosphate from solution by precipitation with Al or Fe, or by sorption reactions on the surface of soil minerals.

Thus, sinks exist in the soil for all of the constituents of phosphate rocks. It is, first, the extent of these reactions that determines the dissolution of phosphate rock in soil, and this dissolution is essential for the availability of the nutrients in phosphate rock to plants. However, the degree of reversibility of the processes that remove nutrients (primarily, P and Ca) from solution determines their availability to plants. Thus, extremes of soil properties that favor the dissolution process may not favor nutrient availability in the final analysis.

Protonation reactions:

The protonation equilibria of the anion species reduces the activity of the component anions without removing them from solution. Thus, protonation of anions is a process which promotes dissolution of the rock and also leaves the ions in a more available form than the original crystalline apatite. The tendency for protonation reactions to take place is a function of the respective equilibrium constant and the pH, which is a measure of the H^+ activity. However, the extent to which acidulation of the rock continues depends on the buffer capacity of the soil with respect to pH. The pH buffer capacity is a soil property which is not routinely measured but is related to KCl extractable acidity in some soils. Thus, the most obvious soil properties related to phosphate rock dissolution are pH, pH buffer capacity and exchangeable acidity.

Removal of cation species from solution:

Truog (1916) recognized the importance of soil acidity to phosphate rock dissolution and he attributed the effect to the removal of calcium carbonate and bicarbonate by the soil. The importance of the Ca sink is clear from the fact that phosphate rocks contain on a molar basis about 60% more Ca than P as indicated by the formula, $Ca_{10}(PO_4)_6X_2$. The removal of Ca from solution is expected to take place primarily by cation exchange reactions. These same reactions can also take place for the minor amounts of Na, Mg and other cation constituents of phosphate rock. The soil properties that relate to these reactions are cation exchange capacity, base saturation, and the selective affinity of the exchange complex for the specific cations. The fact that exchange complexes differ in affinity for Ca was demonstrated by Graham (1955) using a series of natural and artificial exchange complexes in 2.5% suspensions, all with 50% Ca saturation. He found that the systems with the lowest energy of exchange for Ca dissolved the most P from rock. He used this to point out the importance of the calcium sink to phosphate rock dissolution. However, the energy of exchange for Ca was correlated to pH, pointing out the difficulty of separating the relative importance of individual properties of acid soils with regard to phosphate availability.

In another example of the combined effect of Ca concentration and pH on P availability from rock, Ellis *et al.* (1955) found that incubating phosphate rock with acid soil for one month before liming gave much better plant response than when the order was reversed.

Ion pair formation:

Ca has a distinct tendency to form ion pairs in solution. Khasawneh and Doll (1978) considered $CaH_2PO_4^+$ and $CaHPO_4$ to be important in the $Ca-PO_4-H$ system in the 4.5 to 7.5 pH range. $CaSO_4$ has been shown to be an important ion pair in the soil solution (Adams, 1974). Thus, for the case of phosphate rock dissolution, the presence of sulfate could provide a sink for Ca in solution and promote dissolution.

Decomposition of H_2CO_3 to CO_2:

At pH's below 6, H_2CO_3 is the predominate form of carbonate in soil solution in equilibrium with ambient atmospheric CO_2 (Lindsay, 1979). The log K of the decomposition reaction to CO_2 is 1.46, indicating the positive tendency of the equilibrium. Since soil is a porous medium, it must be considered an open system with regard to carbonate, since CO_2 is free to diffuse through the soil to the atmosphere. The atmosphere provides a huge sink for carbonate released from apatites in acid soils.

Fluoride reactions with soil constituents:

The flouride anion forms coordination complexes with Al and Fe (Lindsay, 1979). Fluorite, CaF_2, has been considered to be the solid phase controlling F activity in soil (Lindsay, 1979). Fluoride can also attack siliceous minerals to form other compounds. Thus, numerous sinks exist in the soil for F dissolving from phosphate rock.

Phosphate removal from solution by precipitation and sorption:

The reactions which remove P from solution and thereby promote the dissolution of phosphate rock can be precipitation reactions with Al and Fe (Wright and Peech, 1960), and also sorption on mineral surfaces (Rajan and Fox, 1975). Precipitation reactions form crystalline compounds, such as $AlPO_4$ and $FePO_4$ at various levels of hydration. Sorption reactions involve the substitution of $H_2PO_4^-$ for OH^-, coordinated with Al or Fe on the surfaces of sesquioxides or clay minerals. The relative importance of these two suggested mechanisms is in fact very difficult to separate in a real soil system. Precipitation and sorption reactions are not distinguishable by the Chang and Jackson (1957) fractionation method. Harris (1975) demonstrated that both mechanisms would appear to follow solubility product relationships. Considering the mixed system of the soil, including organic matter and the possibilities of isomorphous substitution, it is unlikely that clearly definable crystalline phases are of major importance.

These phosphate reactions, unlike the protonation reactions, are of the type that promote rock dissolution, but since the resulting phases are more stable than the original apatite (Khasawneh and Doll, 1978), the reactions leave phosphate in forms that are chemically less soluble and therefore, less available than the apatite. However, these reaction products are more widely dispersed in the soil than the original apatite and, therefore, may be more available by virtue of closer proximity to the plant root system.

Rate processes of dissolution in soil:

The earlier discussions on dissolution have been based on equilibrium principles. In fact, in soil, dissolution takes place from the surface of phosphate rock particles and the process then continues as the constituent ions diffuse away from the particle along concentration gradients. The concentration gradients are induced by the reactions of the constituents with the soil acting as the sink. Also, a decreasing H^+ gradient toward the particle results, due to consumption of H^+ in the protonation reactions.

The solubility diagram given by Khasawneh and Doll (1978) for the two end members of the carbonate-substituted apatite series, fluorapatite and carbonate apatite with 1.5 moles of carbonate per formula weight, show the total concentration of P in solution at equilibrium in apatite-fluorite-Ca^{2+}-H^+ systems. Examining Table 2.1, the concentation of P in solution at equilibrium varies from 0.02 ppm (fluorapatite) and 0.17 ppm (carbonate apatite) at pH 5.5 to 1.1 ppm (fluorapatite) and 120 ppm (carbonate apatite) at pH 4.5 under solution conditions which could exist in soil. Fox *et al.* (1974) indicated that maize yields of approximately 90% of maximum yield are obtained at a P in solution concentration of 0.02 ppm, as determined by

Table 2.1 -- Total phosphorus concentration in solution, $[P_T]$, for fluor-apatite (FA) and carbonate apatite (CA) at equilibrium over a range of pH's. Ionic strength set at 0.01 M and pCa at 2.6. $[P_T]$ is the calculated sum of HPO_4^{2-}, PO_4^{3-}, $CaH_2PO_4^+$, and $CaHPO_4$. Adapted from graph by Khasawneh and Doll (1978), Figure 3, p. 173.

pH	Fluorapatite	Carbonate apatite
	------$[P_T]$, ppm------	
4.5	1.1	120.
5.0	0.11	1.9
5.5	0.02	0.17
6.0	0.003	0.05

the isotherm method. Even the low reactivity fluorapatite can maintain this concentration at pH 5.5 in a Ca^{2+}-H^{+} system. This suggests that the lower effective- ness of low reactivity phosphate rocks as compared to superphosphate in soil with pH less than 5.5 is not due to the inherent low solubility of apatites, but to soil factors which affect the P concentration maintained by apatite in soil. There are at least two possible ways in which soil factors could reduce P solubility below that found in a simple Ca^{2+}-H^{+} system. First, pH and/or Ca concentration could increase at the surface of the apatite particle. This could well happen in the case of Ca due to a low Ca sorption capacity in the soil. Second, since the dissolution process involves the movement of components from the less stable apatite to stable reaction phases, concentration in solution in soils could remain well below that predicted for equilibrium solubility due to the fact that diffusion through the soil and reaction to new phases is much more rapid than dissolution at the surface of apatite. This points out clearly the importance of rate processes in soil with regard to P availability from phosphate rock.

Thus, the process of P supply from phosphate rock is clearly a dynamic, kinetic one. Khasawneh and Doll (1978) indicated that research on the kinetics of phosphate rock dissolution in solution was sparse and that research on the process in undisturbed soil was nonexistent. They reasoned that since differences in phosphate rock are in fact observed in soils, the limiting factor is not diffusion in the soil but is diffusion across the stagnant solution layers "on the surface of the solid particles." It seems equally plausible to argue that since a rock varies in rate of dissolution in different soils (Smyth and Sanchez, 1982) that the diffusion process in the soil can be limiting. In either case the conclusion is the same, i.e., the kinetics of phosphate rock dissolution in soil is important and needs to be researched.

In summary of this discussion of the processes that promote phosphate rock dissolution in soil, Table 2.2 shows commonly measured soil properties and the phosphate rock dissolution processes to which they relate. As revealed by the discussion of the dissolution process, none of the commonly measured soil properties clearly relates to any (not to mention all) of the components of the dissolution process. Furthermore, many of these properties are correlated with each other to some extent, making it difficult to isolate the importance of individual properties. Relationships have been observed in the literature between rock effectiveness and properties such as pH, exchangeable Ca, or P sorption capacity and are reviewed below.

Soil pH:

Joos and Black (1950) showed that the increase in extractable P from phosphate rock, incubated with a series of bentonite suspensions, was greatest at low pH. However, they concluded that the problem is more complex than a simple relationship between the solubility of phosphate rock and pH. Ellis et al. (1955), working in sand culture with 1% bentonite suspensions having a range of pH's from 4.9 to 7.4,

Table 2.2

Soil Properties Related to Principal Phosphate Rock Dissolution Processes

Phosphate rock dissolution processes	Soil properties
Protonation of anions	pH Exchangeable acidity
Ca sink	CEC Exchangeable Ca Base saturation
Phosphate sink	Extractable Al Free iron oxide P sorption capacity

found the highest yield of oats at pH 5.5 with yields decreasing with increasing pH. The lowest yield, observed at pH 4.9, was probably the result of Al toxicity. Peaslee _et al_. (1962) found a high correlation between soil pH and both extractability coefficients and availability coefficients of P from rock, relative to superphosphate. With the assumption that the rock constituent was hydroxyapatite and using the corresponding solubility relationship with pH 6.3 and pCa 3.8, they calculated that the total P in solution was 460 times more sensitive to change in H concentration than to change in Ca concentration.

Soil Ca:

Bennett _et al_. (1957) compared phosphate rocks on two soils: Cecil, which contained predominately kaolinite in the clay fraction and Eutaw, in which montmorillonite and kaolinite predominated. The natural pH of both soils was 5.0; however, phosphate rock was more effective on the Cecil soil than the Eutaw. This could be explained by the fact that Ca saturation was much higher on the Eutaw soil.

In an effort to separate the pH and Ca effects of liming on phosphate rock availability, Khasawneh and Doll (1978) compared liming with $CaCO_3$ or $SrCO_3$. Above pH 5.2, $CaCO_3$ had a greater effect in reducing effectiveness of phosphate rock than $SrCO_3$.

Depending on mineralogy, pH, and organic matter content, soil cation exchange complexes can differ in charge density. The charge density affects the relative affinity of soils for ions, depending on their hydrated charge density (Bohn _et al_., 1979). Thus, minerals with a higher charge density have a greater affinity for divalent cations than for monovalent cations. Exchange complexes with very low charge density have a greater affinity for monovalent cations. Thus, an increase in pH, in variable charge systems, will increase affinity for Ca, since negative surface charge increases.

P sorption capacity:

Soils vary widely in their P sorption capacity and this variation is primarily related to soil texture and mineralogy (Fox, 1978). These differences, which are on the order of a 1000 ppm in extreme cases, greatly affect the size of the P sink in soils, and this in turn, affects the extent and rate of phosphate rock dissolution.

Reaction of phosphorus with Al and Fe in acid soils, as opposed to reaction with Ca, was stressed by Hsu and Jackson (1960). The rapid increase in exchangeable Al as soil pH decreases indicates the high reactivity of aluminum in acid soils. Chu et al. (1962) showed that the Al-phosphate formed from phosphate rock reaction in a number of soils correlated with the exchangeable Al content of the soils, but that nonexchangeable Al was also involved in reactions. They also found that the Fe-phosphate formed from reaction of phosphate rock with five soils was related to the free iron content. The Davidson soil, which had a free-iron content of 4%, decomposed 20 to 30% of the phosphate rock added, over the pH range 6 to 5.5. All other soils in the study had free-iron contents of less than 2% and required pH values about one unit lower in order to decompose the same percent of the phosphate rock as the Davidson soil. Smyth and Sanchez (1982) also observed the effect of high free-iron content on the rate of dissolution of phosphate rocks. Both of these studies demonstrate the effect of the Fe-phosphate sink on dissolution of phosphate rock, but they do not indicate the final effect on P availability from phosphate rock.

Phosphorus reaction with Al and Fe, whether by precipitation or sorption on oxide surfaces, is pH dependent. In the case of precipitation, Al and Fe activity in solution are generally considered to be controlled by the solubility of the respective hydroxides (Wright and Peech, 1960). Considering the reaction,

$$3H^+ + Al(OH)_3 = Al^{3+} + 3H_2O$$

and the solubility product relations,

$$K = \frac{(Al^{3+})}{(H^+)^3} \quad ,$$

$$pK = pAl - 3pH \quad ,$$

$$pAl = pK + 3pH \quad ,$$

it is demonstrated that Al activity decreases three orders of magnitude for each unit increase in pH. The same effect holds for Fe^{3+}. Thus, increases in soil pH greatly decrease the importance of precipitated Al- and Fe-phosphate as P-sinks in the phosphate rock dissolution process.

Phosphorus sorption on sesquioxides is related to soil pH. Two mechanisms have been proposed. Hingston et al. (1972) suggested that decreased sorption with increased pH was due to competition between OH^- and $H_2PO_4^-$ for sorption sites. Uehara and Gillman (1981) postulated that the effect was due to increased negative surface charge with increased pH.

Returning to the Al solubility question, Lindsay (1979) showed that, depending on silica activity, mineral species other than aluminum sesquioxides can control Al activity. Thus, Al solubility is not a function of pH alone. This pertains not only to the phosphate reactions with Al but also to pH levels at which Al is toxic to plants. The pH level at which Al is toxic to plants depends not only on the plant's tolerance, as discussed in the section on plant factors, but also on the suite of minerals present and activity of constituents such as silicate. Uehara and Gillman (1981) gave an example of three soils for which KCl extractable Al increased as soil pH increased. They explained this by the fact that montmorillonite content increased as pH increased in this series of three soils.

With regard to P sorption or "fixation capacity" of soil and availability of P from fertilizers varying in solubility, McLean and Logan (1970) reported that soils with high fixing capacity yielded best with partially acidulated phosphate rock, whereas soils with lower fixing capacities yielded best with 100% acidulated rock, i.e., superphosphate. Similarly, Dynia (1977) reported a positive correlation between effectiveness of Gafsa rock (relative to powdered superphosphate) and phosphate sorption requirement to attain 0.2 ppm in solution. In soils with the highest sorption requirements, Gafsa rock had a relative effectiveness ranging up to 150%. Both of these studies were, however, conducted with only one rate of applied P per experiment. Particularly in the study of Dynia (1977) the rates applied were suboptimum on the high-P-fixing soils, resulting in a maximum yield about 20% of that obtained on the low-fixing soil. This suggests that effectiveness of phosphate rock relative to superphosphate could be related to the position on the response curve. Specifically, in the highly responsive, lower part of the curve on very responsive soils, less soluble sources could produce higher yields. However, as the rate is increased and the yield plateau approached, soluble sources may be more effective. This phenomenon bears similarity to the crossover effect observed in P-placement (de Wit, 1953) and suggests that a major effect of low solubility may be restricted placement, i.e., decreased volume of soil fertilized.

Effect of liming:

It has generally been accepted that liming decreases P-fixation in temperate soils (Ford, 1932). In soils dominated by permanent surface charge materials, liming would reduce exchangeable Al, thereby decreasing this sink for P. Also, exchangeable Ca is increased by liming, which reduces the sink for Ca from phosphate rock (Khasawneh and Doll, 1978). These two changes are in addition to the increase in pH which reduces the protonated anion sink. Some workers have related the differential effect of lime in different soils on phosphate rock availability to its effect on P-sorption capacity. Ford (1932), working with a group of acid Kentucky soils, found that lime increased P uptake on all soils treated with superphosphate, but that when phosphate rock was applied some soils responded positively and others negatively to lime. He found that a negative effect of liming on phosphate rock availability occurred in soils with a high capacity to fix P, whereas, soils with a positive effect of liming on phosphate rock had low P-fixing capacity. Ford concluded that the negative effect of lime was due to the fact that in high-fixing soils, lime is not sufficiently effective in preventing transformation of P to relatively unavailable forms to offset the decrease in phosphate rock solubility due to the increased pH and Ca concentration.

In contrast to this effect is the finding of Amarasiri and Olsen (1973) that liming increased the phosphorus sorption capacity of an Oxisol from Colombia. They suggested that the effect may be due to sorption of P by freshly precipitated Fe and Al hydroxide caused by the increased pH after liming. Wann and Uehara (1978) demonstrated in a variable charge soil system, that when present in high concentration, calcium was absorbed into the Stern layer. This could result in positive charge at the interface of the Stern and diffuse layers that would promote sorption of the negatively charged phosphate ions.

Conclusion on soil properties and phosphate rock availability:

The above discussion shows that the relationship between soil properties and phosphate rock dissolution and subsequent P availability is a complex one. Current knowledge of the processses is not adequate to model and thus, predict the effectiveness of phosphate rock based on the chemical, physical, and biological processes involved. Within groups of soils that are basically similar in properties (e.g., mineralogy and organic matter) but have a range in a few chemical properties (for example, pH), it may be possible to relate phosphate rock effetiveness to one or two commonly measured soil properties, such as pH or Ca saturation. However, over all soils in the world or subsets of soils with a broad range in many properties (mineralogy, organic matter, pH etc.), predicting phosphate rock performance based on commonly measured soil properties becomes a futile exercise. The practical solution to this problem is to group soils into categories with similar properties using Soil Taxonomy and within these groups it should be possible to identify relationships between phosphate rock performance and commonly measured soil properties.

Physical and chemical alterations of phosphate rock

In addition to the effects of cyrstal chemical properties, physical properties, such as particle size, affect reactivity. Also destruction of the apatite crystal by acidulation and thermal processes alter P availability. These effects are discussed below.

Particle size and granulation:

Partical size would be expected to have an effect on the effectiveness of phosphate rock because decreasing particle size implies increasing surface area, which should favor dissolution.

Joos and Black (1950), in a greenhouse experiment using bentonite as the growth medium, observed a difference in effectiveness between two phosphate rock particle size fractions, less than 400 mesh and 150 to 300 mesh. Khasawneh and Doll (1978) demonstrated a larger effect of grinding Tennessee rock to clay size (< 2 um) than for North Carolina rock. This can be related to the fact that the North Carolina rock, which has higher carbonate substitution than the Tennessee rock, also has a smaller crystal size and greater porosity.

However, in general, the major reviews on particle size conclude that grinding to 80% to 90% passing 100 mesh is adequate (Cooke, 1956; Khasawneh and Doll, 1978). Two factors that decrease the effect of particle size on effectiveness are high rates of P application and high soil acidity. Thus, under conditions favorable to phosphate rock use, particle size is less important than when other conditions for use are marginal.

Granulation also affects interaction of phosphate rock with the soil environment. The reason for interest in granulation is that it improves physical handling characteristics (Livingston, 1978). However, granulation results in a _de facto_ placement effect which limits chemical interaction with the soil and thus, limits dissolution. Terman _et al_. (1969) and Engelsted _et al_. (1972) observed that granualating phosphate rock to conventional fertilizer granule size greatly reduced effectiveness. Because of the possibility that small granules made with water soluble binders might improve the physical handling characteristics of phosphate rock without significantly reducing rock interaction with the soil, the International Fertilizer Development Center (IFDC) developed a minigranule process (Livingston, 1978). The granule size produced by IFDC was in the range of 50 to 200 mesh (0.3 to 0.1mm) using salts such as KCl as the binder.

Partial acidulation:

Superphosphate is produced by adding a sufficient quantity of acid (sulfuric acid, in the case of simple super or phosphoric acid, in the case of triple super) to convert all of the phosphate in the phosphate rock to monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2 \cdot H_2O$.
If less than this required quantity of acid is added, the resulting product is partially acidulated phosphate rock. McLean and Logan (1970) indicated that phosphate rock, 20% partially acidulated with H_3PO_4, outyielded 100% acidulated materials on soils with high fixing capacity. These comparisons were made at a single rate per experiment. Terman and Allan (1967), on the other hand, showed partially acidulated phosphate rock to be inferior to TSP in greenhouse experiments. As discussed in the section on P sorption, these discrepancies are probably due to differences in rock solubility and soil properties, and as is usually the case, no all-inclusive conclusion can be drawn.

The economic factor that favors the production of partially acidulated material is its lower cost because the acid requirement is lower than for superphosphate. McLean and Logan (1970) estimated that the first 20% increment of H_3PO_4 converts about 10 times as much P in phosphate rock to citrate plus water soluble forms as the last 20% increment needed to produce TSP. Thus, under conditions where rock is available and acid is expensive, partial acidulation may hold an economic advantage.

Fused Magnesium Phosphate:

An alternative process to acidulation for increasing the P solubility of phosphate rock is fusion with Mg and Si compounds to produce fused magnesium phosphate (FMP). This process was described by Walthall and Bridges (1943). They found that fusing phosphate rock at 1450 to 1550°C with MgO and SiO_2 in the ratio of 1:0.28:0.28 and then quenching the molten mix in water yielded a noncrystalline glass material. The P and Mg in the product were 99% and 90% soluble in citrate solution, respectively. A similar product can be prepared using olivine or serpentine, both of which contain Mg and Si. The common total composition of FMP is 22% P_2O_5 (10% P), 10% Mg, 22% Ca, and 15% Si.

Walthall and Bridges (1943) reported FMP to be essentially as effective as superphosphate in greenhouse experiments on two soils of pH 6.0 and 6.3. Soils were prelimed with dolomite so that magnesium in FMP would not contribute to the response. Among other advantages, Walthall and Bridges (1943) cited the following advantages: the FMP process did not require expensive acid, the Mg silicate minerals were cheap, and the soluble Mg may be beneficial as an additional plant nutrient.

FMP has been produced in Japan on a commercial scale since 1950 (Ando, 1959). The discovery that rice responds to silicate has contributed to its popularity as a fertilizer (Slack, 1968). Response to silicate by other crops, principally of the grass family, has been shown on tropical soils in Hawaii (Plucknett, 1972). Fox et al. (1967) attributed the following benefits to silicate in crop production:

1) greater solubility of soil P;
2) decreased fertilizer P fixation;
3) correction of Ca or Mg deficiencies;
4) increased soil pH;
5) decreased P requirement within the plant;
6) prevention of the accumulation of toxic concentrations of manganese in the plant;
7) enhanced efficient use of water in the plant;
8) improved resistance to damage by insects and fungus diseases;
9) strengthening of tissue, decreased lodging and promotion of more efficient use of sunlight; and
10) benefiting the plant in some essential role.

In addition to the benefits from P, Si, Ca, and Mg, FMP has a lime equivalence of 0.5 to 0.7 ton $CaCO_3$/ton FMP, and supplies micronutrients, depending on the source of raw materials used.

CHAPTER III

MATERIAL AND METHODS

SOILS

The soils at the sites used in this study have been classified according to Soil Taxonomy: A Basic system of soil classification for making and interpreting soil surveys (Soil Survey Staff, 1975) as reported by Ikawa (1979). Ikawa (1979) reports the profile descriptions and the chemical and physical analyses by horizon. The site in the Philippines is located on the campus of the Philippine Union College (PUC) in the municipality of Panicuasan, which is located approximately 15 km east of the city of Naga, Camarines Sur, Luzon, Republic of the Philippines. The coordinates are approximately 13°40'N, 123°18'E. The site is located on the lower slopes of the extinct volcano Mt. Isarog at an elevation of approximately 250 m above sea level. The soil is classified as a thixotropic, isohyperthermic Hydric Dystrandept (H.D.), based on the criteria in Soil Taxonomy (Soil Survey Staff, 1975). This soil is, as are most Andepts, derived from parent material of volcanic origin. Operationally, the volcanic ash origin is defined by a bulk density of the fine earth fraction of less than 0.85 grams per cm^3 in the epipedon. The formative element, Dystr-, in the name indicates that the soil has a base saturation of less than 50% (by the ammonium acetate, pH7 procedure). Dystrandepts generally have a high capacity to fix phosphorus. The Hydric modifier of the subgroup indicates that the soil intergrades to the Hydrandept great group. The Hydric Dystrandept, like the Hydrandept, has a subhorizon that is thixotropic and dehydrates irreversibly into particles that are sand size. The thixotropic property relates to the consistency of the soil. In the identification of the sites in the Benchmark network, the thixotropic property was recognized in the field when, under "strong to moderate pressure between the thumb and the fingers, the soil material becomes smeary and changes to material containing appreciable amounts of fluid" (Ikawa, 1979). The thixotropic property is present in soils with exchange complexes dominated by amorphous clays, and is generally associated with a high capacity of the thixotropic subhorizon to sorb P (Soil Survey Staff, 1975). The isohyperthermic temperature regime indicates a mean annual soil temperature > 22°C at 50 cm depth and a difference between the coldest and warmest months of < 5°C. The Benchmark Soils Project (1980) indicates that the mean annual air temperature is approximately 25°C for this Philippine site. Since mean annual soil temperatures are within 1°C of the mean annual air temperature (Soil Survey Staff, 1975), the criterion for the isohyperthermic temperature regime is met.

The site in Indonesia, known as Nakau is located on the rubber estate NVPPP Nakau, 7 km southeast of Kotabumi, Lampung, Sumatra, Republic of Indonesia. The coordinates are approximately 5°S, 105°E. The site is located on a dissected plain with undulating topography at an elevation of approximately 50 m above sea level. The soil is classified as a clayey, kaolinitic, isohyperthermic Typic Paleudult (T.P.). Based on the criteria in Soil Taxonomy (Soil Survey Staff,

1975) the following description is given. The principal distinguishing properties of the Ultisol order to which this soil belongs are sufficient amounts of translocated silicate clays in the subhorizon to meet the criteria of an argillic horizon as defined by Soil Taxonomy (Soil Survey Staff, 1975) and a base saturation of < 35% (by the sum of the cations procedure). The Udults are humus-poor Ultisols. They also have well- distributed rainfall as required for a udic moisture regime, i.e., the moisture control section is not dry in any part for more than 90 cumulative days in most years. The formative element Pale- of the great group name identifies this soil with very old stable land surfaces. Weatherable minerals are nearly absent due to the high degree of weathering. The Typic subgroup of Paleudults are freely drained soils that have an ochric epipedon. The family modifiers "clayey, kaolinitic" indicate a fine earth fraction of > 35% clay of which 50% is 1:1 layer silicates. The isohyperthermic temperature regime indicates a mean annual soil temperature of > 22°C at 50 cm depth with a difference between mean monthly temperatures for the coldest and warmest months of < 5°C. Benchmark Soils Project (1980) indicates a mean annual air temperature of approximately 27°C for this Indonesian site.

Both sites had histories of previous cropping. The Hydric Dystrandept site probably had a long history of annual crops, such as upland rice and sugar cane intermixed with fallow periods. The Typic Paleudult site was located in an area which had been cleared from primary forest for a rubber plantation in the early part of the present century. The rubber trees had been cleared in the last 10 to 20 years and the area used for annual crops: upland rice, cassava, and maize, intermixed with grass fallow periods.

Table 3.1 presents the basic chemical properties of the surface soils at the two sites. The first set of data is from the sample taken for classification of the site. The second set of data is from samples taken after clearing the experimental area but before fertilizing or planting the first crop. The last set is from the P control plots sampled after harvest of the third crop. Thus, differences between the a and b pairs of data for each site reflect the effects of clearing of the grass cover and tillage. The third set, labelled c, reflects the effect of fertilization with N, K, Mg, S, and micronutrients and cropping for three season. The analyses of samples taken after the first crop are considered to be more representative of the chemical environment during the period of the experiments reported here than the classification samples. Both soils are acid as indicated by their pH values. All pH values for the Typic Paleudult are lower than those for the Hydric Dystrandept The Bray P I method (Chien, 1978) (standard 7:1 solution to soil ratio, 5 minute extraction) is used to compare extractable P. The value for the Hydric Dystrandept is much lower than for the Typic Paleudult

Both sites have well distributed rainfall; however, during the dry season at both sites, water was a limiting factor. To reduce the effect of natural water deficit on the crop growth, drip irrigation systems were installed. Tensiometers were installed to depths of 15 cm

Table 3.1
Chemical Properties of the Surface Soil at the Two Experimental Sites

	Hydric Dystrandept (Philippines)			Typic Paleudult (Indonesia)		
	a	b	c	a	b	c
Sampling interval (cm)	0-17	0-15	0-15	0-12	0-15	0-15
Exchangeable Bases (meq/100g) Ca	3.84	0.97	0.40	7.44	2.23	1.22
Mg	0.64	0.59	0.42	1.14	1.09	0.79
K	0.27	0.08	0.02	0.76	0.27	0.17
Sum	4.75	1.64	0.84	9.34	3.59	2.18
Extractable Al (meq/100g)	1.29	-	-	0.05	-	-
Al Saturation	21%	-	-	<1%	-	-
pH in H_2O	5.4	5.15	5.27	4.82	4.96	4.60
pH in KCl (1 N)	4.5	4.61	4.51	4.16	4.53	4.07
Delta pH	-0.9	-0.54	-0.76	-0.66	-0.43	-0.53
Extractable P (ppm)						
Modified Truog	-	4.1*	4.6	-	-	-
Bray I (7:1)	-	<0.2	-	-	1.4	2.1
Bray I (30:1)	-	7.5	2.4	-	-	-
P Sorption* (ug P/g) to attain						
0.01 ug P/ml		200			25	
0.2 ug P/ml		2650			350	

a) Classification samples taken before sites were cleared (Ikawa, 1979).
b) Mean values for samples taken after clearing the experimental area but before planting the first crop.
c) Mean values for three control plots after harvest of the third crop. Controls received basal nutrients but no P.

* Mean of three preplant composites by replication.

and 45 cm in one plot of each experiment to provide an index of water availability for scheduling irrigation. When the reading of the 15 cm tensiometer exceeded 40 cb, irrigation water was applied (if water was available and the water supply system functional).

P-SOURCE MATERIALS

The principal objective of the experiments reported here was to compare the effectiveness of a series of P-source materials in the two soils. The P fertilizer materials used are shown in Table 3.2 with data on their chemical and physical properties. A soluble, acidulated phosphate material was used as a standard in each case. In the Hydric Dystrandept experiment in the Philippines simple superphosphate (SSP) was used and in the Typic Paleudult experiment in Indonesia, triple superphosphate (TSP) was used, since these were the available materials in the respective local economies. Greater than 80% of the P in these materials is water soluble and approximately 95% is soluble in water and neutral normal ammonium citrate. Thus, superphosphates are considered to be sources of "readily available" P. The phosphate rocks used in the study were from North Carolina (NC) and Central Florida (CF). Both are chiefly composed of francolitic apatites, i.e., carbonate-substituted apatites and were chosen because they represent well-characterized rocks that have been used in other IFDC studies of direct application (e.g., Hammond, 1978). The North Carolina rock has a degree of carbonate substitution (Table 3.3) approaching the limit of 1.4 moles per apatite formula, as suggested by Lehr and McClellan

Table 3.2

Phosphorus Fertilizer Source Materials*

Fertilizer Material	Abbr.	Total P_2O_5 (%)	Water Solubility (---% of total P_2O_5---)	NAC** Solubility	Particle Size	Suppliers
Simple Superphosphate	SSP	18	83.7	11.8	Non-granular	Planters Products Philippines
Triple Superphosphate[†]	TSP	46			Conventional granular	P.T. Pusri Indonesia
North Carolina p.r.						
finely ground	NCf	29.5	nil	18.0	90% < 0.06 mm	IFDC
minigranular (3% KCl binder)	NCm	29.2	nil	19.5	0.1 - 0.3 mm	IFDC
Central Florida p.r.						
finely ground	CFf	32.9	nil	11.2	80% < 0.11 mm	IFDC
partially-acidulated (20% H_3PO_4) minigranular	CFpam	39.1	48.5	11.0	0.1 - 0.3 mm	IFDC
Fused Magnesium Phosphate	FMP	20	nil	36.5	< 0.9 mm	Japan via Planters Products
Guano 1[††]	G1				Finely ground	A.M. Briones, Philippines
Guano 2[††]	G2					

*Analyses courtesy of Dr. L. L. Hammond, International Fertilizer Development Center (IFDC)

**Neutral ammonium citrate, 1N 100 ml:1g of fertilizer. 65°C, 1 hour agitation.

[†] Assumed to meet international standards of > 80% water soluble and approximately 15% NAC soluble.

[††] No data available.

Table 3.3

Apatite Formulas For the Two Phosphate Rocks*

Phosphate Rock	Apatite Formula	CO_3/PO_4	Reactivity
North Carolina	$Ca_{9.53}\ Na_{0.34}\ Mg_{0.13}\ (PO_4)_{4.79}\ (CO_3)_{1.21}F_{2.48}$	0.25	High
Central Florida	$Ca_{9.74}\ Na_{0.19}\ Mg_{0.07}\ (PO_4)_{5.26}\ (CO\ )_{0.74}F_{2.30}$	0.14	Moderate

*Analyses courtesy of IFDC.

(1972). It is, therefore, a high reactivity rock. The Central Florida rock has an intermediate level of carbonate substitution (Table 3.3) and is, therefore, moderately reactive. Both rocks were used in a finely ground form (see Table 3.2, particle size). In addition, each rock was used in a modified form. The NC rock was used in a minigranular form, made from the finely ground material using KCl as the binding agent (Table 3.2). The objective was to determine whether minigranulation reduces agronomic effectiveness. The CF rock was also used in minigranual form, which was partially acidulated (20%, with phosphoric acid, H_3PO_4). The acidulation products acted as the binder. The objective was to determine whether partial acidulation adequately increased the effectiveness of this moderately reactive rock. In the Philippines, sufficient Fused Magnesium Phosphate (FMP) was obtained to include it at three of the four rates. Also in the Philippines, two local mineralized guano materials from the floor of a limestone cave were included. These apatitic materials were formed by the reaction of bat droppings with the limestone of the cave.

P-SOURCE EXPERIMENTS

General experimental design

In both the Hydric Dystrandept experiment (Philippines) and the Typic Paleudult experiment (Indonesia), a split-plot field design was used, with phosphorus rates as the mainplots and phosphorus sources as the subplots. For the first planting, most of the mainplots also contained a partial control. For subsequent replantings, these controls were selectively used for reapplication of superphosphate to provide a comparison with the residual effects of the sources, as detailed for each experiment below. Thus, for purposes of analysis of variance (ANOVA), a 4 rate (mainplots) by 5 source (subplots) factorial design was maintained throughout both experiments.

The crop planted was maize except in one case in Indonesia when soybeans were planted. To assure that nutrient deficiencies other than P would not limit yields, N, K, Mg, S, Zn, and B were applied as a blanket application for all experiments at the first planting. For subsequent plantings, primary nutrients were applied and the secondary and micronutrient elements were selectively applied as indicated for each experiment below.

Hydric Dystrandept experiment, Philippines

Design:

The field layout for the Hydric Dystrandept experiment is shown in Figure 3.1. A split-plot design with three replications and 28 treatments was used (see Table 3.4 for treatments). The principal sources were included at all rates; however, since sufficient material was not available, FMP was used at the first three rates only. The two samples of guano were used at the 120 kg P/ha rate only in place of the FMP and control treatments. The controls in the 15 kg/ha mainplots were maintained as controls throughout the experiment. The controls in the 30 and 60 kg/ha mainplots, and the guano treatments in the 120 kg/ha mainplot, were converted to other treatments during the second and third crops as shown in Table 3.4.

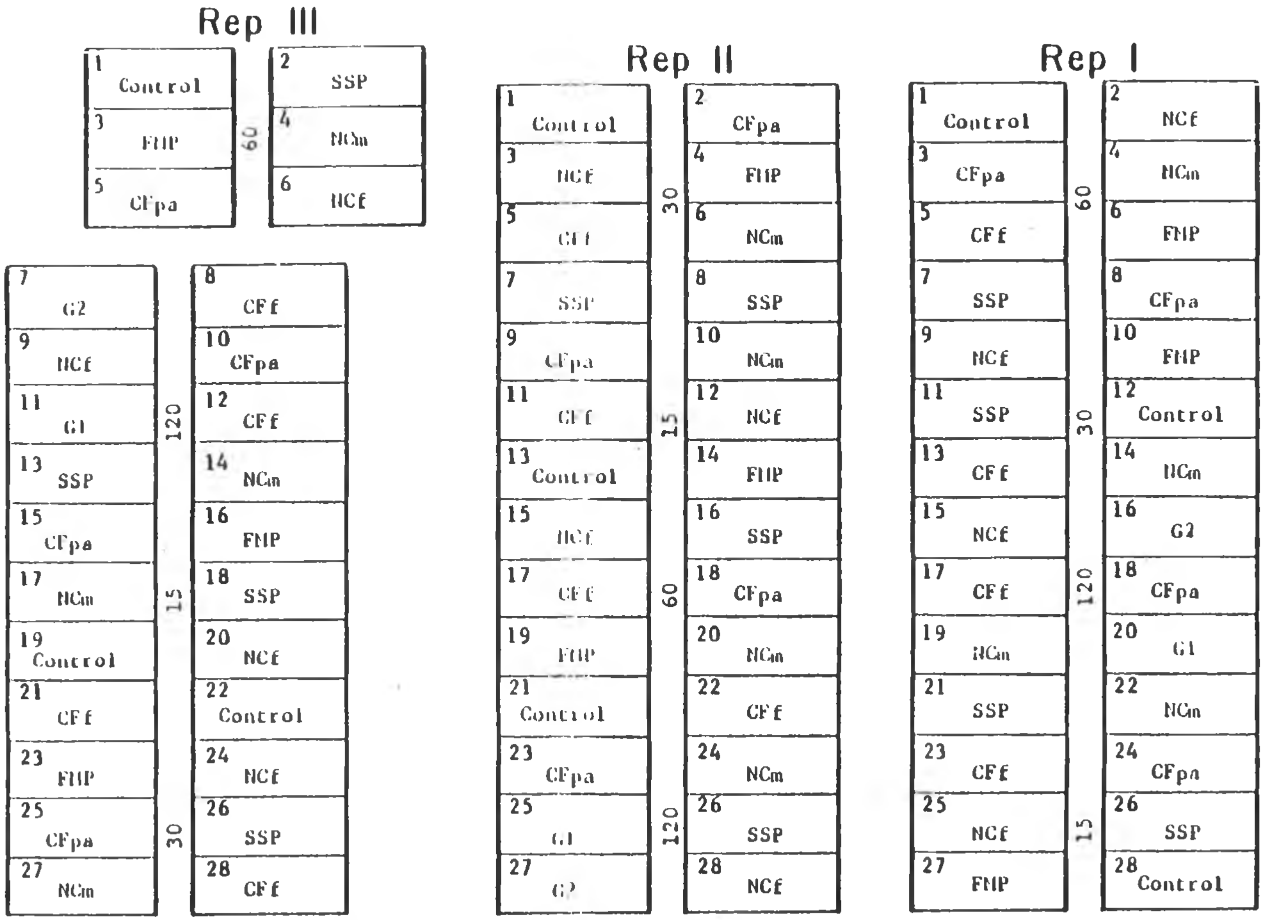

Figure 3.1 Field layout of the Hydric Dystrandept experiment, Philippines. Treatment abbreviations are shown in Table 3.2.

Table 3.4

P Treatments in the Hydric Dystrandept Experiment for 3 Crops
(See Table 3.2 for fertilizer abbreviations.)

Mainplots (kg P/ha)	Crop		
	First	Second	Third
	SSP	residual	reapplication*
	NCf	residual	reapplication
	NCm	residual	reapplication
15, 30, 60	CFf	residual	reapplication
	CFpam	residual	reapplication
	FMP	residual	reapplication
	Control[†]	SSP	residual
	SSP	residual	reapplication
	NCf	residual	reapplication
120	NCm	residual	reapplication
	CFf	residual	reapplication
	CFpam	residual	reapplication
	Guano 1	residual	FMP
	Guano 2	SSP	residual

*Reapplied means the original source was applied again at the same rate as in the first crop.

[†] In the 15 kg P/ha mainplots, control plots were maintained throughout the experiment.

Individual subplots were 8 m long by 3 m wide for an area of 24 m^2. Maize was planted in 4 rows, spaced at 75 cm, running the 8 m length of the plots. Two seeds were planted per hill, every 23 cm in the row. At 7 to 10 days after emergence, plants were thinned leaving one per hill. If a hill contained no plants at thinning, an adjacent hill was left with two plants. The resulting maize population was approximately 58,000 plants per hectare. At harvest, one meter was discarded from the end of each row and the two center rows with a planted total of 52 plants were harvested on 9 m^2 as the effective area.

Management:

Table 3.5 shows the basic information for each of the three crops including season and variety planted. Basal nutrients applied are shown in Table 3.6. For insect control, granular Furadan (3% active ingredient) was applied in the seed hole at planting of each maize crop at the rate of 1 kg active ingredient per hectare. A second application (at the same rate) of Furadan was made to each crop in the whorl 45-50 days after planting. Additional spray applications of Sevin and Thiodan were made at the manufacturer's recommended rates at intervals of 7 to 14 days, as needed for corn borer control. Weed control for the first crop was by hand weeding only. For the second and third crops, the herbicide, Lasso, was applied post-plant, preemergence at the rate of 3.5 quarts per acre, i.e., 20 ml per plot. Additional hand weeding was done as necessary.

Table 3.5

Basic Information on the Three Crops Planted in the Hydric Dystrandept Experiment, Philippines

Crop	First	Second	Third
Season	Dry	Wet to dry	Wet
Date planted	Jun. 8, '79	Oct. 29, '79	Jun. 24, '80
Date harvested	Oct. 15, '79	Mar. 10, '80	Oct. 30, '80
Maize variety	UPCA 1	UPCA 1	Pioneer X304C
Mean maximum temp. (°C)	30.3	29.5	30.9
Mean minimum temp. (°C)	21.4	20.1	21.9
Mean daily solar radiation (Langleys)	333	318	312
Cumulative rainfall (mm)	1753	1223	1270
Abnormalities	Typhoon Sept. 17-18 Corn borer	--	High winds Oct. 12
Maximum mean treatment yield (kg grain/ha)	2348	5549	5344

Table 3.6

Basal Nutrients Applied for the Three Crops Planted in the Hydric Dystrandept Experiment, Philippines

Crop	Basal Nutrients* (kg/ha)					
	N	K	Mg	Zn	S	B
First	180	120	75	15	107	2
Second	180	120	40	0	53	0
Third	180	120	40	7.5	57	1

*Basal nutrients were applied to all plots. N applied as urea, K as KCl, Mg as $MgSO_4 \cdot 7H_2O$, Zn as $ZnSO_4$, S from Mg and Zn sources, B as borax.

All nutrients (except N) applied in one application broadcast and incorporated before planting.

N applied in three equal applications:
1. Broadcast and incorporated before planting;
2. Side-dressed and covered at 30 days after planting;
3. Same method as 2, applied at tasseling.

Yield calculations:

Ears were harvested from the effective area of 9 m^2 of each plot and weighed. All harvested ears were shelled by a hand-powered corn sheller and the grain weighed. A subsample of the shelled grain was taken for moisture determination in a digital moisture meter. Grain yield was then calculated on a per hectare basis, adjusted to a standard moisture content of 15.5%.

Typic Paleudult experiment, Indonesia

Design:

The field layout for the Typic Paleudult experiment is shown in Figure 3.2. A split-plot design with three replications and 24 treatments was used (see Table 3.7 for treatments). The controls in the 80 kg/ha mainplots were maintained throughout the course of the experiment. The controls in the other mainplots were used for fresh applications of TSP in the second and third crops as shown in Table 3.7.

Individual subplots were 3.75 m wide by 6 m long for an area of 22.5 m^2. Maize was planted in the first and third crop in 5 rows per plot spaced at 75 cm, running the 6 m length of the plots. Two seeds were placed per hill every 23 cm in the row and later thinned to one plant per hill. The resulting plant population was approximately 58,000 plants per hectare, the same as in the Hydric Dystrandept experiment. At harvest, one meter was discarded at the end of each row and the three center rows harvested, resulting in an effective area of 9 m^2. For the soybean crop planted in the second crop, the same 75 cm row spacing was used. Approximately 35 seeds were planted per

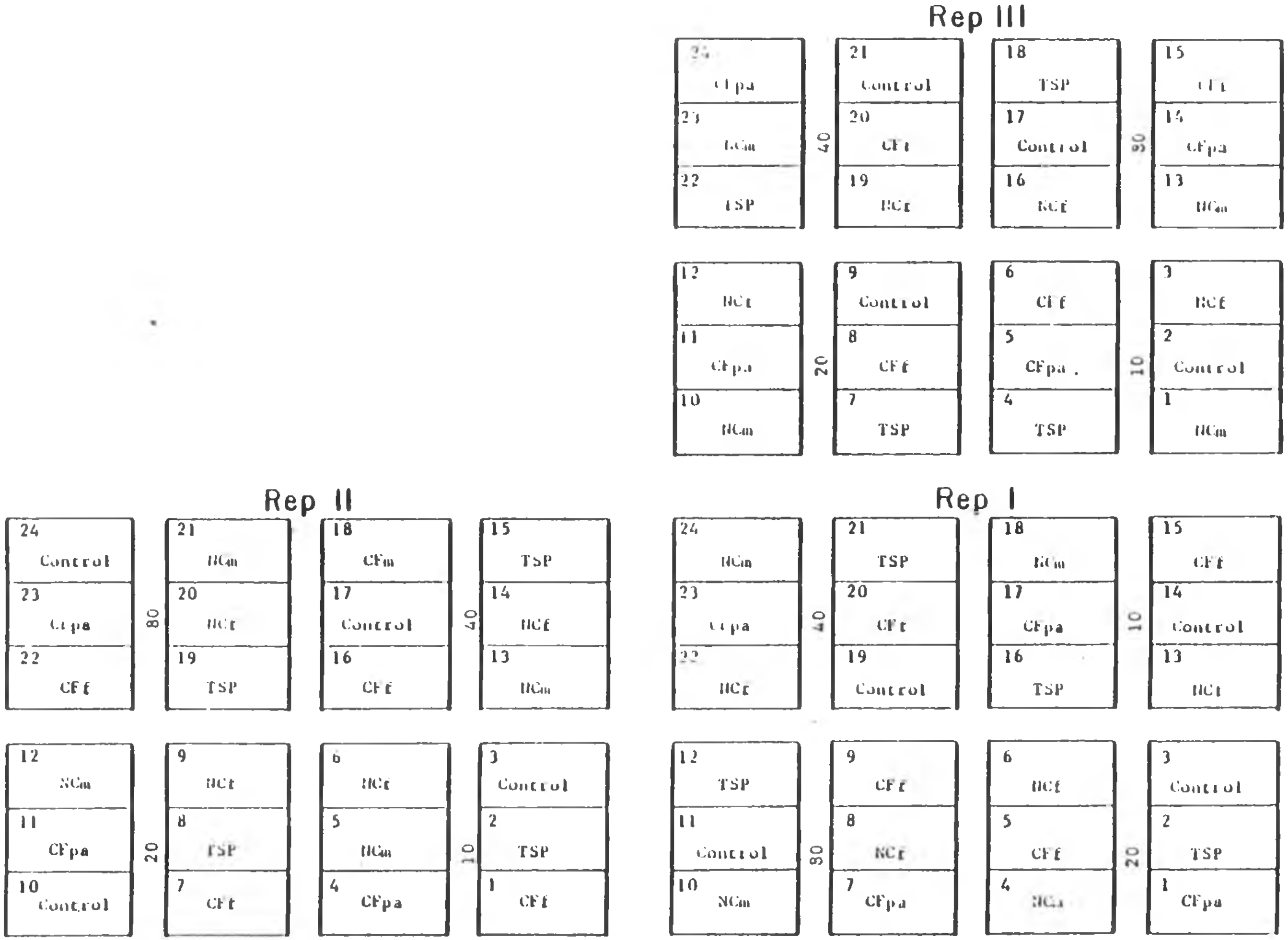

Figure 3.2 Field layout of the Typic Paleudult experiment, Indonesia. Treatment abbreviations are shown in Table 3.2

Table 3.7

P Treatments in the Typic Paleudult Experiment
For Three Crops
(See Table 3.2 for fertilzer abbreviations.)

Mainplots (kg P/ha)	Crop		
	First	Second	Third
10	TSP	residual	reapplication (70 kg P/ha)
	NCf	residual	reapplication (70 kg P/ha)
	NCm	residual	reapplication (70 kg P/ha)
	CFf	residual	reapplication (70 kg P/ha)
	CFpam	residual	reapplication (70 kg P/ha)
	Control	TSP*	TSP*
20 & 40	TSP	residual	residual
	NCf	residual	residual
	NCm	residual	residual
	CFf	residual	residual
	CFpam	residual	residual
	Control	TSP*	TSP*
80	TSP	residual	residual
	NCf	residual	residual
	NCm	residual	residual
	CFf	residual	residual
	CFpam	residual	residual
	Control	Control	Control

*Applications of TSP on controls were made at the corresponding P rate of the mainplot.

meter. The mean population at harvest was approximately 320,000 plants per hectare or 280 plants per effective area of 9 m^2.

Management:

Table 3.8 shows the basic information for each crop, including season and variety. Basal nutrient applications are shown in Table 3.9. The inoculant applied for the soybean crop was granular peat from Nitrigen Co., containing a mixture of three strains plus two additional strains which were supplied by the NifTAL project and mixed with the commercial inoculant.

For insect control Furadan was applied in the row at planting, for all three crops, at the rate of 1 kg active ingredient per hectare. Basudin (Diazanon) was applied at the recommended rate at regular intervals for insect control. Weed control was done manually.

In the first crop downy mildew affected approximately 40% of the maize. Affected plants were rogued resulting in reduced population. To avoid this disease, soybeans were planted in the second crop. For the third crop, maize was again planted, using Ridomil as a seed treatment at the manufacturer's recommendation rate to control the disease. The control was apparently 100% effective.

Yield calculations:

For the maize crops, ears were harvested from the effective area of 9 m^2 of each plot and weighed. Ten representative ears were selected from each plot for determination of shelling percentage. This shelling percentage was used to calculate grain yield per plot. The moisture content of a 200 g subsample of grain was determined on an

Table 3.8

Basic Information on the Three Crops Planted in the Typic Paleudult Experiment, Indonesia

Crop	First	Second	Third
Season	Dry	Wet	Wet
Date planted	May 4, '79	Oct. 1, '79	Feb. 13, '80
Date harvested	Sep. 5, '79	Jan. 11, '80	Jun. 6, '80
Crop variety	Maize, H-6	Soybean, Orba	Maize, Pioneer X304C
Mean maximum temp. (°C)	33.5	33.1	34.7
Mean minimum temp. (°C)	20.1	20.5	21.5
Mean daily solar radiation (Langleys)	366	422	423
Cumulative rainfall (mm)	598	856	815
Abnormalities	Downy mildew	Pod borer	---
Maximum mean treatment yield (kg grain/ha)	2949	1832	7709

Table 3.9

Basal Nutrients Applied for the Three Crops Planted in the Typic Paleudult Experiment, Indonesia

Crop	Basal Nutrients* ---(kg/ha)--- N	K	Mg	Zn	S	B	Mo
First	105	75	30	10	46	1	---
Second	50	75	--	--	--	1	0.3
Third	150	75	20	3.3	28	--	---

*Basal nutrients were applied to all plots. N applied as urea, K as KCl, Mg as $MgSO_4 \cdot 7H_2O$, Zn as $ZnSO_4$, S from Mg and Zn sources, B as borax.

All nutrients (except N) applied in one application broadcast and incorporated before planting.

N applied in three equal applications to maize crops:
1. Broadcast and incorporated before planting;
2. Side-dressed and covered at 30 days after planting;
3. Same method as 2, applied at tasseling.

For soybeans, N-sidedressed 40 days after planting. Mo sprayed as solution in the open planting furrows before planting.

electronic moisture meter and yield per hectare corrected to a standard moisture of 15.5%. Yield was calculated on a per area basis. No correction was made for reduced stand, since efforts to correct for missing plants resulted in increases in the coefficient of variation.

For the soybean crop, the same 9 m^2 effective area was harvested as for the maize crops. All pods were shelled manually and the total weight of grain per plot recorded. Moisture content of the grain was determined on a subsample using an electronic moisture meter. Grain yield was calculated on a per hectare basis for the 9 m^2 area, adjusting the moisture percentage to a standard 12% level.

SOIL ANALYSES

After the initial staking and soil preparation of the two experiments, but before applying any fertilizer, soil samples were collected from each plot of each of the two experiments. Eight subsamples were collected to a depth of 15 cm on each plot, thoroughly mixed in the field and a representative subsample taken in a plastic bag for each plot. In the case of the Hydric Dystrandept, the samples were passed through a 2 mm sieve and sealed in plastic bags so as to maintain the original moisture content at the time of collection. In the case of the Typic Paleudult, the samples were air dried; then ground by hand to pass through a 2 mm sieve and packed in plastic bags in the air-dry state. Similarly, following each harvest, samples were taken within 2 weeks of harvest on a plot-by-plot basis and processed in the same manner.

All samples were shipped by air freight to the Benchmark Soils Project laboratory at the University of Hawaii, Manoa campus, for analysis. A 5 g subsample of each sample was placed in an aluminum dish, and then dried for 24 hours in an oven at 105° C, for determination of the moisture content. Using this moisture factor, moist samples were weighed such that the calculated weight of moist soil taken gave the desired equivalent of oven-dry soil for each analysis.

Soil acidity was determined by two methods for all samples -- pH in a 1:1 soil to water ratio, and pH in a 1:1 soil to 1 N KCl solution ratio -- using a combination glass electrode and Corning digital pH meter. "Extractable aluminum" was determined by a 30 minute extraction of 10 g soil with 50 ml of 1 N KCl followed by leaching with an additional 50 ml of KCl solution in a Buchner funnel (SCS-USDA, 1972). The filtrate from this extraction was titrated with 0.05 N NaOH to the phenolphthalein endpoint. Then 10 ml of 1 N KF was added to form the aluminum fluoride complex and release the hydroxide which had reacted with Al. The solution was then titrated with 0.05 N H_2SO_4 to the colorless phenolphthalein endpoint. Al was calculated as the equivalents of H_2SO_4 to reach the second endpoint (SCS-USDA, 1972). The Al procedure was conducted on selected soil samples only.

The bases, Ca, Mg, and K were determined by extracting 25 g of dry soil or its moist equivalent with 1 N ammonium acetate, pH 7 followed by leaching in a Buchner funnel. Quantitative analysis of the bases was done by atomic adsorption.

A number of methods were used for soil P analysis. A modified Truog extraction consisting of 0.02 N H_2SO_4 and 0.3% $(NH_4)_2SO_4$ was used in a 100:1 solution to soil ratio, extracting for 30 minutes on a reciprocating shaker (Ayres and Hagihara, 1952). This procedure was used on the Hydric Dystrandept because the Bray I procedure gave very low values (<0.2 ppm) and was thus subject to unacceptable error. A Bray I extraction (0.025 N HCl and 0.03 N NH_4F) with a solution to soil ratio of 7:1, shaking for 5 minutes (Chien, 1978) was used for the Typic Paleudult. These two soil extraction methods, because differ in concentration and solution to soil ratio, also differ in equivalents of acid per unit of soil. These acidity to soil ratios, expressed in common terms, are 200 meq/100g (modified Truog) and 17.5 meq/100g (Bray 7:1). By this comparison the modified Truog method is more than 10 times as acid as the Bray method.

DATA ANALYSES

Calculations of results and statistical analyses were done by computer using the Statistical Analysis System (SAS) package (SAS Institute, Inc., 1979).

Data files

For each crop harvested from each experiment, a yield data file was set up containing a line entry for each plot in the experiment. Each entry contained the replication and plot number, history of P treatments applied, and all measurements of plant growth taken on the plot during the course of the crop, including all of the data used for yield calculations. For soil analyses for each experiment (Hydric Dystrandept and Typic Paleudult), a single data file was set up covering all three crops. Each line entry contained the replication and plot numbers, the treatment history, and the values for the selected analyses that were performed on the four sets of soil samples.

Statistical analyses

Analysis of variance was performed using the Procedure ANOVA of the SAS package for balanced data such as the yield results of the 4 rate by 5 principal P-sources (SSP, NCf, NCm, CFf, and CFpam) by 3 replication segment of each experiment. Since the field design used was split-plot in both experiments, the appropriate split-plot ANOVA was calculated using the error-a (Rep x Rate) to calculate the F to test the Rate (mainplot) effect, and using the error-b (the sum of Rep x P-source and Rep x Rate x P-source) to calculate the F for testing the subplot effects (P-source and Rate x P-source) (Helwig, 1979). The error-b, used to test the P-source effect, is also the correct value for the mean square for error (MS_e) for calculating the least significant differences to be used in testing differences between pairs of sources within each rate. For the cases in which the F value for the P-source effect was greater than 1, the Baysian Least Significant Difference (BLSD) at the 5% level was calculated on a hand calculator using the following formula:

$$\text{BLSD} = \sqrt{2 \cdot MS_e/3} \cdot 1.721 \cdot \sqrt{F/(F-1)}$$

In this formula 1.721 is the appropriate t value for the 5% test and the F value is that of the effect to be compared, in this case, the P-source effect (Duncan, 1965). If the appropriate F value for calculating a BLSD was less than 1, the conventional LSD (Steel and Torrie, 1960) was calculated using the following formula:

$$\mathrm{LSD} = t_{.05} \cdot \sqrt{2 \cdot MS_e/3}$$

If the F for an effect is less than 1, it is not possible to use the BLSD because it becomes an imaginary number. If the F test corresponded to a simple treatment comparison, an F value of less than 1 would suggest that comparisons of treatments by BLSD or LSD was not necessary, since the mean square for the effect is less than the mean square of the error. However, in the cases given here the P-source effect tested by the F test is the mean of four rates. As a result, even if the F test for the P-source effect is not significant or even less than 1, the existance of Rate by P-source interaction means that significant differences may exist between P-sources at some of the rates. For this reason, BLSD or LSD values were calculated in all cases. The resulting BLSD and LSD values are shown on the graphs of each crop (see Figures in Chapters IV and V) for use in comparing P sources. The SAS ANOVA procedure calculates an R^2 by dividing the corrected total sum of squares (SS) minus the error-b SS by the corrected total SS. This R^2, which I have designated the error-b R^2, indicates the proportion of the overall variation which is due to effects other than error-b. Similarly, an R^2, which I have designated the error-a&b R^2, can be calculated by dividing the corrected total SS minus the error-a SS, as well as minus the error-b SS, by the corrected total SS. This error-a&b R^2 appears to give a better measure of overall variation in the experiment. The coefficient of variation (C.V.) is commonly used as an index of variation in experiments. It is calculated by dividing the standard deviation ($\sqrt{MS_e}$) by the mean of all treatments in the experiment (Steel and Torrie, 1960). In the experiments reported, the response to treatments was great, and in most cases the yields of the controls were near zero. Since it was desirable to distribute the treatments over the entire response range, the low rate treatments had relatively low yields, resulting in a low overall mean for the experiments. The result of this low mean is that the C.V.'s are high. For this reason, in this type of response experiment, it is suggested that the R^2 values may be a more valid measure of variation than C.V.'s, since the R^2 values are less subject to the bias imposed by the range of the treatment variable (in this case, rate). The SAS Procedure General Linear Models (GLM) was used for unbalanced ANOVA (e.g., occurance of a missing plot) and for linear regression models and covariance. The SAS Procedure for Non-linear Models (NLIN) was used for combined analysis of multiple harvests from the same experiment. Within the NLIN procedure the Marquardt method for convergence was used. The NLIN procedure calculates an R^2 for each regression; however, it uses the uncorrected total sum of squares for the denominator. This always results in large R^2 values. For the models reported here an R^2 value was calculated using the corrected sum of squares and is designated as $R_c{}^2$. This corrected R^2 is considered to be a better measure of goodness of fit.

CHAPTER IV

RESULTS OF HYDRIC DYSTRANDEPT EXPERIMENT, PHILIPPINES

INTERPRETATION OF YIELD RESPONSES

First Crop (Maize)

In Figure 4.1, showing the grain yield response for the first crop of the Hydric Dystrandept experiment, a very marked difference in sources is noted. This experiment had a significant infestation of corn borers from tasseling onward and was hit by a typhoon during the later part of the growing season, resulting in low yields (less than 2500 kg/ha). The level of borer infestation is related to the difficulty of control during the wet season. The failure of the high rates to reach a yield plateau is attributed to these environmental factors, since other experiments on the site in normal seasons have reached plateaus with SSP rates of 60 to 120 kg P/ha (see the results for the second crop, fresh application of SSP in Figure 4.2, for example). In spite of these factors, the analysis of variance for the 4 mainplot by 5 principal source portion of the design (Table 4.1) shows an error-b R^2 of 0.88 and a significant P-source effect at the 0.0001 level. The rate effect is marginally significant since the probability is near 5%.

The only P-source which presents an inconsistency in performance over the 4 rates is NCm. At the 120 kg P/ha rate, the yield for NCm is much lower than would be predicted based on the yields of this source at the other three rates. The values for all three replicates of this

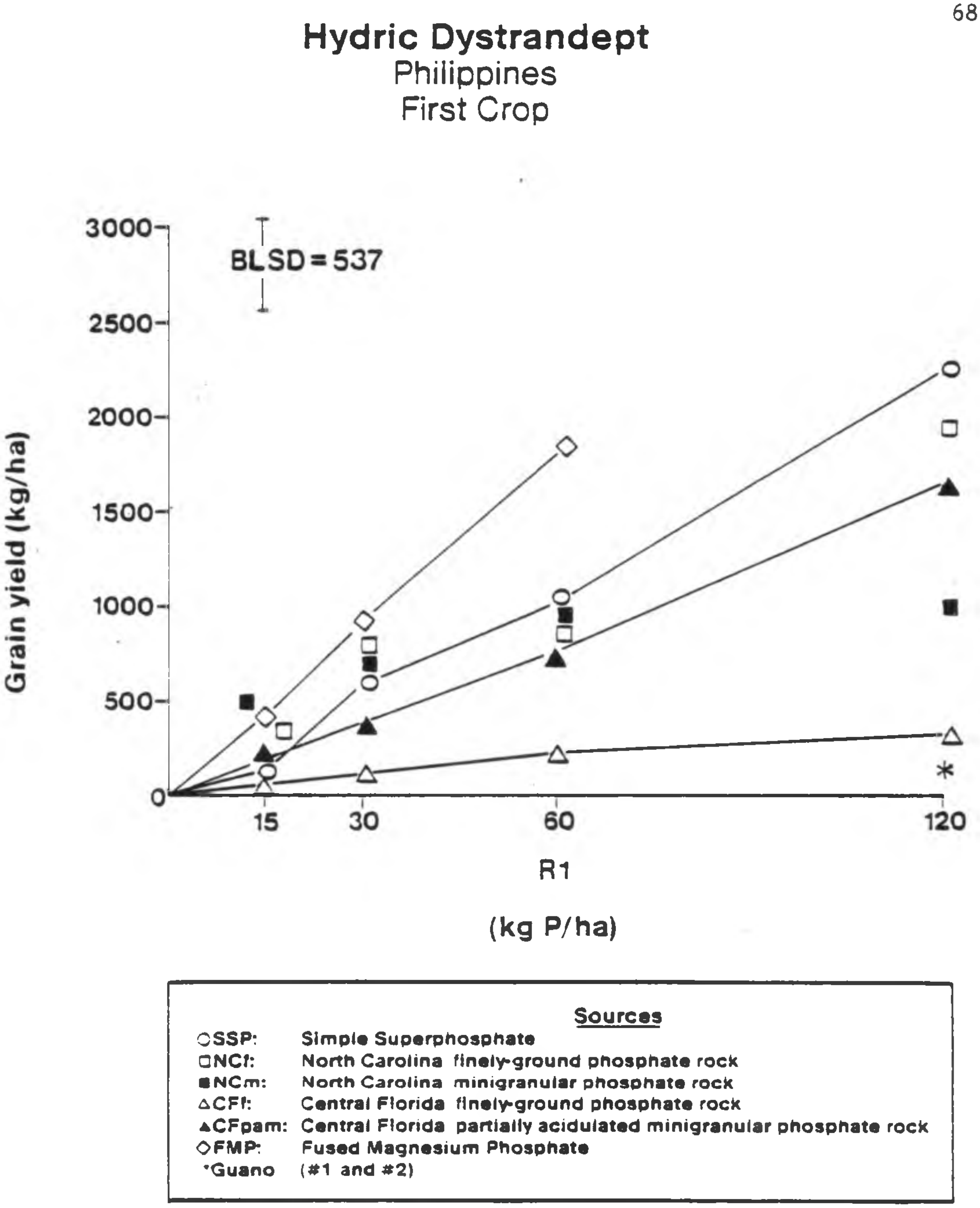

Figure 4.1 The grain yield response of maize to freshly applied P-sources at 4 rates in the first crop of the Hydric Dystrandept experiment, Philippines.

Table 4.1 -- Analysis of variance of grain yield for Hydric Dystrandept experiment, first crop covering 4 rate mainplots by 5 principal P-source subplots. See Materials and Methods for details.

Source of variation	DF	SS	F	PR>F
Rep	2	1,904,533		
Rate (R)	3	13,242,199	4.62	0.0530 N.S.
Rep x Rate (Error-a)	6	5,731,765		
P-source (S)	4	5,382,434	10.20	0.0001**
Rate x P-source	12	4,575,632	2.89	0.0082**
"Model" Total	27	30,836,562		
Error-b	32	4,222,590		
Corrected Total	59	35,059,152		

	BLSD	R^2	C.V.	Std.dev.	Yield mean
Error-b	537	0.880	48.6%	363	748
Error-a&b	-	0.716			

** Highly significant

N.S. Not significant

treatment are fairly consistent. At the other three rates, there is no significant difference between NCf and NCm. Also the lower yield of NCm at the 120 kg rate is not consistent with the plant height and stover yield measurements (data not shown) for this treatment. Considering this information, the lower grain yield is considered to be due to the variation caused by weather and insect stress rather than lower fertilizer effectiveness, and is therefore, not considered in the interpretation of these results which follows.

The sources, in order of effectiveness as shown in Figure 4.1, are FMP > SSP = NCf = NCm > CFpam > CFf > Guano #1 = Guano #2. Since Mg (in the form of epsom salts) was supplied at the rate of 75 kg Mg/ha to all treatments, the better performance of FMP is probably not due to a Mg effect. Also, the post-harvest pH of the FMP plots was not significantly higher than that of other plots, which suggests that the effect is due to P-availability, possibly caused by a Si effect.

The North Carolina rock was as effective as SSP in both the finely-ground and minigranular forms. This confirms the potential of minigranulation to improve handling characteristics of phosphate rock without reducing its effectiveness. Furthermore, the similarity in performance between SSP and the NC sources indicates the potential for using highly reactive phosphate rocks for direct application as an alternative to superphosphate on this soil. The moderately reactive Central Florida rock, on the other hand, gave extremely low yields over the entire range of rates. At the 120 kg/ha rate the yield for the CFf treatment was less than one-sixth of the yield for the SSP treatment.

The poor performance is presumably related to the lower reactivity of CF rock as compared to NC rock. Partial acidulation (20% with H_3PO_4) appears to largely overcome the low effectiveness of the CF rock, however, the yields for CFpam are generally lower than those for SSP and the NC sources. At the highest rate, the yield for CFpam was significantly lower than that for SSP.

The two guano sources performed very poorly and were not significantly different from each other. For this reason they are shown as a single point in Figure 4.1. These materials are apparently of too low a reactivity for successful use for direct application in this soil.

Considering the added stress factors which occurred during this crop, it is possible that the observed difference between sources were accentuated. The reason for this would be that initial differences between treatments which were expressed by differences in stages of maturity, would be further exaggerated by stress factors, since, for example, the factors would affect less- effective treatments before tasseling or silking and more-effective treatments in later stages of development. This would explain both the linear rather than curvilinear responses and also the great differences between sources.

Summary of the Hydric Dystrandept first crop:

Highly significant differences were observed between sources in this crop but it is believed that these differences were exaggerated by stress factors which acted differentially on treatments depending on their respective rates of development. Therefore, the results are considered valid for interpreting the relative effectiveness of sources but not the absolute differences in effectiveness. The order of relative effectiveness observed was FMP > SSP = NCf = NCm > CFpam > CFf > Guano #1 = Guano #2.

Second Crop (Maize)

The Hydric Dystrandept source experiment was replanted as a residual experiment as detailed in Table 3.4. The control plot in the 15 kg P/ha mainplot was maintained as a control while the control plots in the 30 kg and 60 kg P-rate mainplots were converted to freshly-applied SSP plots for comparison with the residual effects. The Guano #2 treatment, since it had shown yields similar to the control in the first crop, was also given a fresh application of SSP at the 120 kg rate.

The grain yield results for the second crop are shown in Figure 4.2. Note that the yields for this crop are much higher than those observed in the first crop due to the absence of the stress factors which were present in the first cropping season. A yield exceeding 5500 kg/ha was obtained at the highest rate of fresly applied SSP and the highest yielding residual treatments were between 4000 and 5000 kg/ha. The analysis of variance for the 4 rate by 5 residual P-source segment of the design is presented in Table 4.2 and can be used for comparison of the residual treatments. Note that the error-b standard deviation, 393, is greater than that observed in the first crop, 363 (Table 4.1); however, because of the higher mean yield, the C.V. based

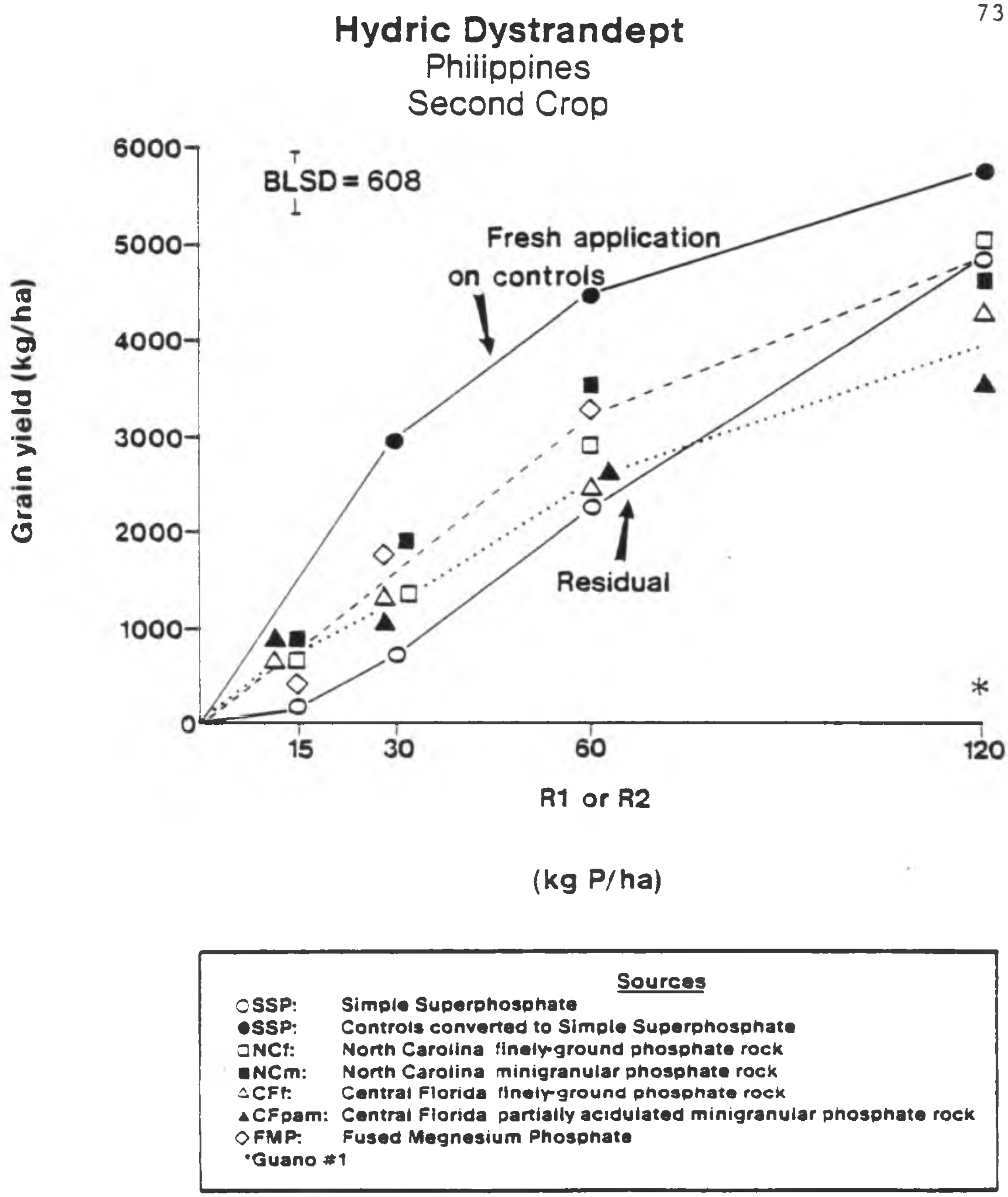

Figure 4.2 The grain yield response of maize in the second crop of the Hydric Dystrandept experiment, Philippines, to residual treatments of the 5 principal P-sources and fresh applications of SSP on three former control treatments. R1 is the P rate applied in the first crop to treatments that are residual in this crop. R2 is the P rate for SSP applied to former controls at the time of planting of this crop. Solid lines connect the points in both the fresh and residual SSP treatments. A dashed line connects the means of the two forms of the NC rock. A dotted line connects the means of the two forms of the CF rock.

Table 4.2 -- Analysis of variance of grain yield for Hydric Dystrandept experiment, second crop covering 4 rate mainplots by 5 principal P-source subplots. See Materials and Methods for details.

Source of variation	DF	SS	F	PR>F
Rep	2	665,314		
Rate (R)	3	150,403,543	204.66	0.0001**
Rep x Rate (Error-a)	6	1,469,816		
P-source (S)	4	3,456,385	5.60	0.0016**
Rate x P-source	12	4,186,113	2.26	0.0327*
"Model" Total	27	160,181,171		
Error-b	32	4,940,125		
Corrected Total	59	165,121,296		

	BLSD	R^2	C.V.	Std.dev.	Yield mean
Error-b	609	0.970	17.9%	393	2194
Error-a&b	-	0.961			

* Significant

** Highly significant

on the error-b is 17.9% compared to 48.6% for the first crop. The low variation in the results for this crop is indicated by the error-b R^2 of 0.97 compared to 0.88 in the first crop and the error-a&b R^2 of 0.96 compared to 0.716 in the first crop. The BLSD for comparing P-sources within each rate is 609 for the residual treatments. The analysis of variance for the balanced factorial segment of the design containing the three rates which received fresh SSP applications is shown in Table 4.3. Interestingly, although this ANOVA covers a slightly different set of treatments than those covered in Table 4.2 and although the standard deviations and the R^2's are different for the two ANOVA's, the BLSD's are essentially identical. With regard to the significance of effects, the two ANOVA's lead to the same conclusions. In both ANOVA's the rate and P-source effects are both highly significant (< 1% level) and the rate-by-P-source interaction is significant at the 5% level.

This significant rate-by-source interaction is evidenced in Figure 4.2 by the change in the position of the residual SSP treatments relative to the other P-sources as rate changes. This change in relative position which results in a cross-over of SSP and the CF sources near the 60 kg/ha rate indicates that it is not possible to rank the sources across all rates for their residual effects. At the low rates, all four of the residual rock sources outyielded residual SSP (see Figure 4.2), but SSP "catches up" with the other sources at the highest rate. This is evidenced by the fact that the residual SSP curve has a sigmoidal tendency, whereas, the phosphate rock sources

Table 4.3 -- Analysis of variance of grain yield for Hydric Dystrandept experiment, second crop covering 3 rate mainplots (30, 60 and 120) by 6 P-source subplots (5 principal sources plus SSP fresh application). See Materials and Methods for details.

Source of variation	DF	SS	F	PR>F
Rep	2	525,299		
Rate (R)	2	90,853,963	154.08	0.0002**
Rep x Rate (Error-a)	4	1,179,328		
P-source (S)	5	22,079,878	24.56	0.0001**
Rate x P-source	10	4,116,691	2.29	0.0389*
"Model" Total	23	118,758,759		
Error-b	30	5,395,046		
Corrected Total	53	124,153,805		

	BLSD	R^2	C.V.	Std.dev.	Yield mean
Error-b	608	0.957	13.8%	424	3066
Error-a&b	-	0.947			

* Significant

** Highly significant

tend to have curves with continuously decreasing slopes. In residual effect, NCm was comparable to NCf, again confirming the potential of minigranular forms. At the three rates at which it was used, FMP gave a residual effect comparable to the NC sources. The beneficial effects from partial acidulation of CF, which were evident in the first crop, have disappeared in this residual crop, resulting in comparable yields for CFf and CFpam, except at the highest rate, where CFf actually out-yielded CFpam. This equal to better performance of CFf when compared to CFpam, could be explained by concluding that the more available P in the partially acidulated form was taken up by the last crop or has reacted with the soil leaving the reactions of the apatitic component, which is identical to that of CFf, to control the residual solubility. Particularly at the highest rate, differential uptake between the two sources in the first crop could also be considered as a factor contributing to the higher yield from CFf. However, if the BLSD is applied, the residual effects of the two forms of the NC phosphate rock are not significantly different from each other over the entire response curve. Similarly for the CF phosphate rock, differences between the two forms are not significant. Thus, for comparison with the residual effect of SSP, the two NC forms will be considered together, as will the two CF forms. Response curves for the two pairs and SSP are shown in Figure 4.2.

Examining the residual response curves in Figure 4.2, the CF forms show their best residual effect relative to the other sources at the lowest rate. As rate increases, the residual effectiveness of the CF forms relative to the other sources decreases progressively. Likewise for the NC forms, their residual effectiveness relative to residual SSP decreases continuously. These observations support the conclusion in the Literature Review that lower reactivity is advantageous at suboptimum fertilizer rates and that as rates increase, more reactive or soluble sources have the advantage.

The question of differential uptake between the NC sources and SSP in the first crop should be considered. Since the NC sources at the 30 and 60 kg P/ha rates produced yields essentially equal to those for SSP in the first crop (see Figure 4.1), it is reasonable to assume that the uptakes were also approximately equal. However, in the second crop the residual effects of NCf and NCm were both greater than that of SSP at these same rates. If the residual effects are examined graphically (Figure 4.2), the average yield produced by NCf and NCm at 30 and 60 kg P/ha can be seen to be equal to that produced by about 50% more SSP, i.e., 45 and 90 kg P/ha on the response curve. Thus, with essentially equal uptake in the first crop, the residual effect of NC sources is greater than that of SSP in the second crop at the intermediate rates. This raises the possibility that differential uptake will, in the course of a few crops, cause the residual effects of the NC sources and SSP to again approach each other. However, the notable effect observed here is that a highly reactive rock, which essentially equals SSP in effectiveness in the first crop, shows a much greater residual effect in the second crop.

The difference between CFf and the NC sources which was evident in the first crop is greatly diminished in this second crop. The effect of differential uptake could contribute to this change. Probably more important is the absence of the stress factors which were present in the first crop and were previously argued to have exaggerated the differences in the first crop. A third contributing factor could be that with the passage of time the apatite has reacted with the soil and P has diffused away from the rock particles increasing the availability.

Summary of the Hydric Dystrandept second crop:

In the residual response no significant difference is observed between the two NC forms or between the two CF forms. They are, therefore, discussed together as their respective pairs. The residual SSP response demonstrates a sigmoidal tendency, whereas, the phosphate rock sources both show curves with continuously decreasing slope. This effect is evidenced in the statistical analysis by the significant rate x P-source interaction, which precludes a ranking of sources by effectiveness as was done for the first crop. Rather the conclusion which is reached is that at low rates (well below the yield plateau) the low reactivity of phosphate rock has its greatest residual advantage. As rates increase and the yield plateau is approached, the rocks decrease in effectiveness relative to the residual SSP effect.

Third Crop (Maize)

The Hydric Dystrandept source experiment was replanted in the wet season 1980. Since in the second crop, yields in the residual treatments had dropped to about one-half of those for the fresh applications of SSP on the former control plots, it was deemed necessary to reapply the original P-sources to the experiment. Had no reapplication been made, the continuation of this trend would have caused the residual treatments at 15 and 30 kg P/ha to approach zero yield and the two higher treatment levels, 60 and 120 kg P/ha to produce yields of less than one-half of the maximum yield obtainable with reapplication. The actual yield decline would probably have been much greater since yields were so much higher in the second crop than the first, that the P-uptake would have caused a greater reduction in residual levels. Also since three months time (end of dry season and beginning of wet season) elapsed between harvest of the second crop and planting of the third, reactions in the soil could be expected to reduce the residual effect. Therefore, to assure a complete response curve for the comparison of sources, reapplications were made of all of the original treatments applied in the first crop, except for the guano treatments (see Table 3.4). Guano #1 had been the more effective in terms of plant height of the two guanos applied for the first crop, however, in the second crop the yield was not significantly different from that of the control. For this reason the Guano #1 treatment at 120 kg P/ha was converted to FMP at the same rate for the third crop. This provided a fourth point on the FMP curve, however, the history of the treatment necessitates assumptions for its inclusion in the analysis with the other FMP treatments, as discussed later.

The grain yield response to total P applied is shown in Figure 4.3. The analysis of variance for the 5 principal P-sources (residual SSP, control and FMP excluded) is shown in Table 4.4. As in the residual data of the second crop, a difference is evident between sources, particularly at the intermediate rates. The ANOVA (Table 4.4) indicates a highly significant rate effect and also a highly significant P-source effect. In contrast to the second crop residual effect, the interaction between rate and P-source is not significant.

Using the BLSD derived from this ANOVA, no significant difference between the two forms of the NC sources are found at any of the four rates. Thus, as with the second crop (residual), the minigranule is shown to be as effective as the finely ground North Carolina rock.

Although there is a tendency for the two NC sources to outyield SSP at the lower rates which was also evident in the first two crops, the differences are not significant in the third crop. Thus, the three sources, SSP, NCf, and NCm can be considered to be equal in this crop which received reapplication.

The Central Florida sources are not significantly different from SSP at the low rates, but at the higher rates they do tend to have lower yields and CFf is significantly lower than SSP at the two highest rates and is significantly lower than the two NC sources at the highest rate. This suggests that CFf may have a lower potential maximum yield than the other sources, which would be related to its lower solubility. Partial acidulation improves the performance of the CF rock, but does not appear to totally overcome the problem of lower solubility.

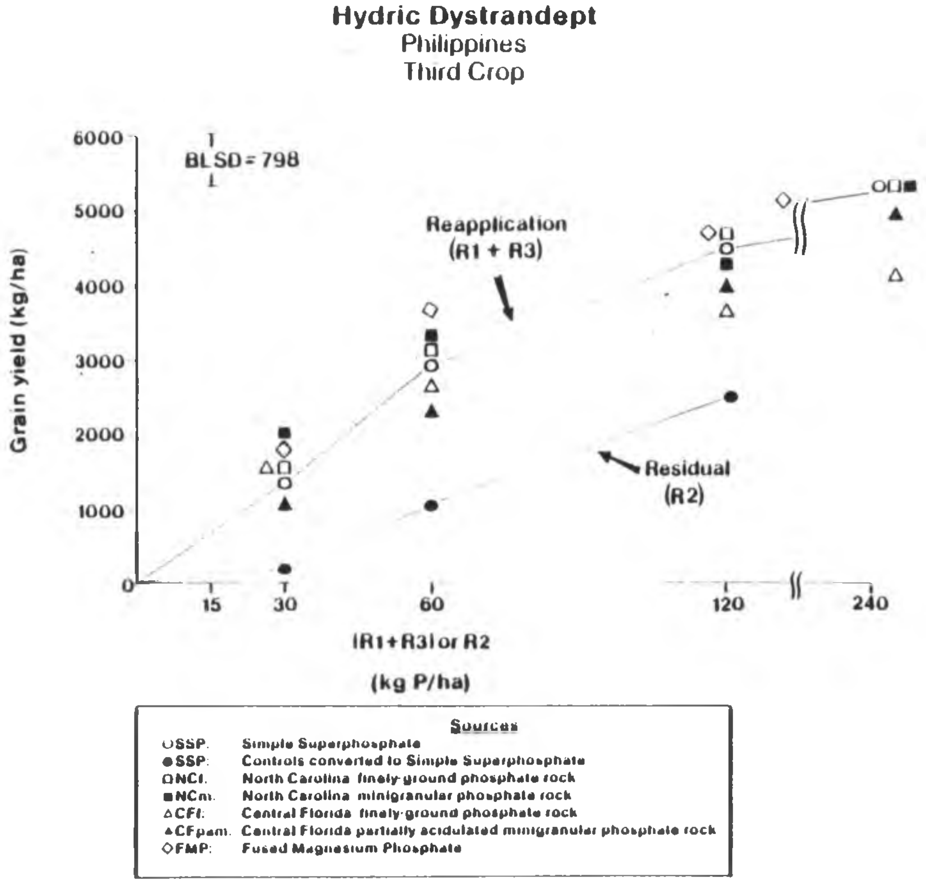

Figure 4.3 The grain yield response of maize in the third crop of the Hydric Dystrandept experiment, Philippines, to reapplications of the 5 principal sources and FMP and also, the residual response to SSP applied for the second crop. R1 + R3 is the cumulative P rate applied in the first and third crops. R2 is the P rate applied to the SSP fresh applications in the second crop. The solid lines connect the points in both SSP reapplication and residual treatments.

Table 4.4 -- Analysis of variance of grain yield for Hydric Dystrandept experiment, third crop covering 4 rate mainplots by 5 principal P-source subplots. See Materials and Methods for details.

Source of variation	DF	SS	F	PR>F
Rep	2	544,165		
Rate (R)	3	103,040,223	255.03	0.0001**
Rep x Rate (Error-a)	6	808,061		
P-source (S)	4	6,330,952	5.91	0.0011**
Rate x P-source	12	3,561,637	1.11	0.3867 N.S.
"Model" Total	27	114,285,038		
Error-b	32	8,564,877		
Corrected Total	59	122,849,916		

	BLSD	R^2	C.V.	Std.dev.	Yield mean
Error-b	798	0.930	15.1%	517	3418
Error-a&b	-	0.924			

** Highly significant

N.S. Not significant

The yields from the FMP treatments are superior to those from SSP at the rates which received reapplications of FMP and using the BLSD, the difference is significant at the rate of 60 kg P/ha total. As noted above, the FMP treatment at 120 kg P/ha was applied on the treatment which previously received 120 kg of Guano #1. Examining the yield of this Guano treatment in the second crop (Figure 4.2), it is seen that the yield was approximately the same as the 15 kg/ha FMP treatment. For this reason the effect of the Guano #1 treatment at 120 kg P/ha is considered to be equivalent to 15 kg P/ha FMP applied for the first crop, and therefore, for the third crop with the fresh application of 120 kg P/ha, FMP is graphed on the X-axis of total P applied as 135 kg P/ha (R1 + R3 = 15 kg P/ha FMP equivalent + 120 kg P/ha FMP). Graphed in this manner, FMP outyields SSP all along the response curve. If the FMP treatment at 120 kg P/ha were graphed at 240 kg P/ha, it would coincide with SSP, NCf, and NCm. This would lead to the conclusion that the same maximum yield was obtainable for all four sources, which is probably true. However, FMP can still be considered more effective at the lower rates than the other sources. The higher efficiency of FMP should not be attributable to Mg response since all treatments received 75 kg Mg/ha for the first crop and 40 kg Mg/ha for both the second and third crop as epsom salts (see Table 3.6). The leaf tissue analysis shown in Table 4.5 supports the conclusion that additional nutrients in FMP are not the cause of the higher yield in the FMP treatment at the 30 kg P reapplication rate. At this rate, the P content of the FMP leaf samples is slightly higher

Table 4.5 -- Comparison of earleaf analyses of FMP and SSP treatments for the Hydric Dystrandept experiment, third crop. Analyses conducted on the University of Hawaii quantometer.

	P Rate for the Third Crop (kg P/ha)									
	15		30		60		120			
	FMP	SSP	FMP	SSP	FMP	SSP	FMP	SSP	BLSD	Critical levels[1]
P(%)	0.170	0.173	0.207	0.203	0.240	0.233	0.257	0.227	0.036	0.25-0.40
Mg(%)	0.303	0.290	0.243	0.253	0.237	0.237	0.247	0.237	0.026	0.21-0.40
Si(%)	2.22	2.20	2.12	2.21	2.03	2.01	2.01	2.11	0.20	---

---

[1] Based on Ohio State University Plant Analysis Lab sufficient nutrient concentration ranges.

than that for SSP, but not significantly so. The concentrations of the two constituents found in substantial quantities in FMP but not in SSP, Mg, and Si, are lower in the FMP samples than in the SSP samples, although the differences are also not significant. The tissue data thus confirms that the greater efficiency of FMP is not attributable to the principal secondary constitutents in FMP, and is, therefore, likely to be due to superior P availability alone.

The yields from the residual effects in the third crop of the three fresh application rates of SSP in the second crop are also shown in Figure 4.3. Again as was observed in the second crop, the yields from the residual treatments are dramatically below the yields of the SSP treatments which received reapplication, indicating the rapid rate at which the residual value of SSP declines in this soil. Also the sigmoidal tendency is again evident. This effect will be further discussed in a combined examination of the second and third crop results.

Summary of the Hydric Dystrandept third crop:

With reapplication, the two NC rock forms and SSP are not significantly different. FMP gave significantly higher yield at the intermediate rate of 30 kg P/ha reapplied, demonstrating it to be a source with superior effectiveness in the Hydric Dystrandept The yields from the CF sources were lower than those from all other sources, particularly at the highest rates. Partial acidulation does not appear to adequately overcome the lower solubility of the apatite. The residual effect of SSP with no reapplication declined much more from the second to the third crop than in the first to second crop period. This could be due to the much higher yields and thus, uptake in the second crop and also, the 3 month follow period before planting the third crop made necessary by the dry season.

A COMBINED ANALYSIS OF THE HYDRIC DYSTRANDEPT CROPS

The preceding discussions of the three crops grown on the Hydric Dystrandept source experiment point out the need for a combined treatment of the results. The first crop has been argued to be quantitatively unrepresentative of the response that is expected from fresh applications of the P fertilizer materials because of the stress factors which acted during that season. However, the yields obtained in that first season affect the residual performance of the sources in the subsequent seasons and, thus, cannot be ignored. Examination of the response to the application of SSP made in the second crop and the reapplication made to the third crop (Figure 4.4) shows that the response curves are almost identical. The fact that the two response curves are so nearly identical suggests that the residual effect of SSP over this range of rates up to 120 kg P/ha after two seasons of cropping (the first crop to the third crop, one year of elapsed time) is essentially nil. Furthermore, since the two responses are essentially identical, it can be argued that the two crops can be considered together in a single regression type model. This will first be done for SSP in a graphic analysis and then in a more comprehensive way using nonlinear regression for all sources.

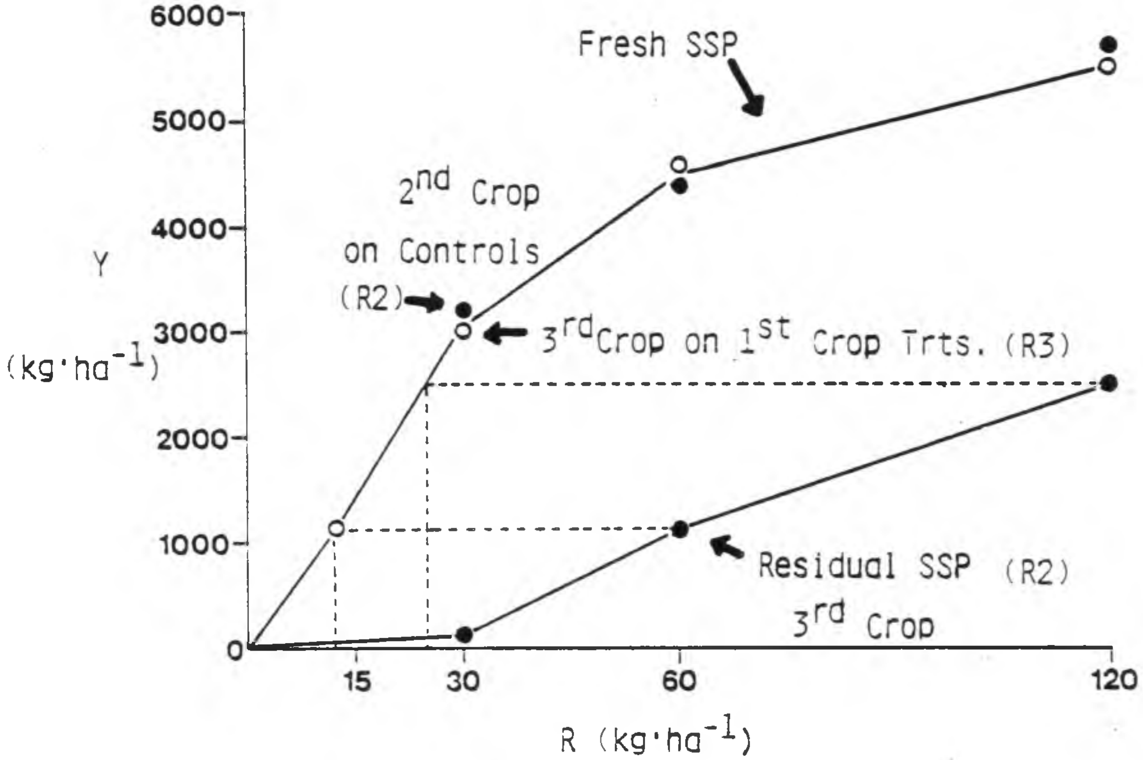

Figure 4.4 Maize grain yield response to freshly applied SSP for the second and third crops and to residual SSP for the third crop. Dotted lines demonstrate the graphical deterimination of equivalent freshly applied rates for the residual treatments. These equivalent freshly applied rates are called effective residual rates.

Graphical analysis of SSP residual effect

Figure 4.5 shows together on a single graph the response curves for the equivalent residual SSP treatments in the second and third crops. The marked difference between the two responses (especially when contrasted with the similarity of the fresh application responses Figure 4.4) indicates the importance of including the previous seasons response in any attempt to model the response curves. That is to say that the much lower residual effect after one season for the third crop compared to the residual effect of the equivalent treatments in the second crop is, at least in part, related to the higher yields and thus, depletion of applied P by uptake in the second crop as compared with the first crop.

For this discussion the assumption is made that "normal" growing seasons, such as those of the second and third crop, could be expected to predominate over time. With this assumption the fresh application response to SSP in the second crop, the corresponding residual response in the third crop and the reapplication response in the third crop could be considered as the necessary information to describe the response to fresh and residual SSP (See Figure 4.4). Thus, for fresh applications the response would be as in the second crop. The residual response in the following season is that shown in the third crop. Interpreting graphically, the residual effects of 30 kg is essentially zero in the subsequent season. Likewise, 60 kg P/ha drops to approximately 13 kg P/ha and 120 kg P/ha drops to 26 kg P/ha. As discussed above, the comparison of the results for the reapplication in

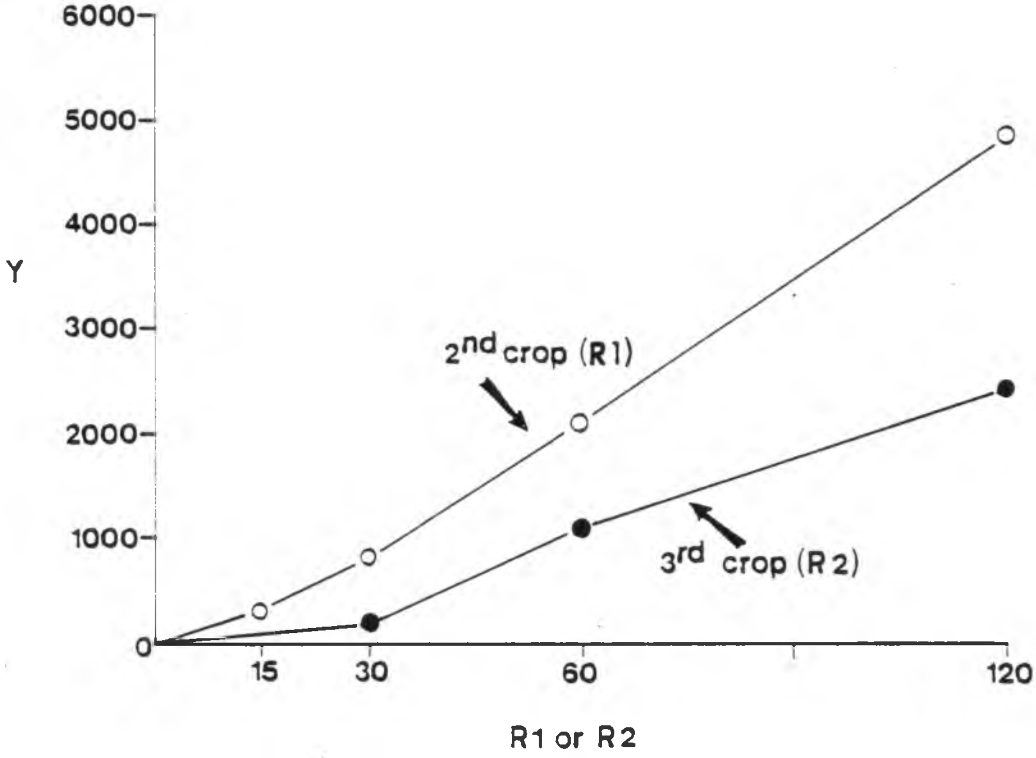

Figure 4.5 Comparison of the yield responses to the residual SSP treatments in the second and third crops. Rates designated R1 were applied for the first crop and those designated R2 were applied for the second crop. Y and R are expressed in kg per ha.

the third season to the fresh application in the second leads to the conclusion that, were a second residual crop to be planted, the effective rates would be nil over this range of rates. This information, which is summarized in Table 4.6, can be expressed in simple mathematical relationships. The effective rate for the first residual effect (R1RE) can be expressed as a function of the previous rate (R1R) as follows:

$$R1RE = 1.53 \cdot (R1R-30)^{0.63} \ . \qquad [1]$$

The effective rate for the second residual effect (R2RE) in terms of the rate applied two seasons previously (R2R) is even simpler:

$$R2RE = 0 \cdot R2R. \qquad [2]$$

These expressions are both limited to the rate range from which they were derived, i.e. 0 to 120 kg P/ha. Assuming linear additivity for residual effects and fresh applications, the following expression describes the total effective rate (REFF).

$$REFF = RF + 1.53 \cdot (R1R-30)^{0.63} + 0 \cdot R2R, \qquad [3]$$

where RF is the freshly applied rate. Since the last term is equal to zero it can be dropped, yielding:

$$REFF = RF + 1.53 \cdot (R1R-30)^{0.63} \ . \qquad [4]$$

This same strategy cannot be followed for describing the residual effects of the other sources in the experiment since independent residual effects are not available in the third crop as they are for SSP. The only available residual data for the phosphate rock sources is the second crop, which is not considered characteristic because of the first crop results. However, if the first crop results could be

Table 4.6 -- Rate of P applied as SSP (R), the apparent residual effect in the first residual crop (R1RE), and the apparent residual effect in crop two seasons after the original application (R2RE).

R	R1RE	R2RE
---------------	kg P/ha	---------------
30	0	0
60	13	0
120	26	0

taken into consideration in a model, it may be possible to develop a generalized model describing response to fresh application and also response to residual applications after one season. For SSP the argument has already been made that by the third crop no residual effect of the first crop applications remained. To proceed with the development of a combined model it is necessary to also assume that the residual effects of the phosphate rock sources are negligible by the third crop. This at first consideration seems improbable in light of the general belief of the long residual effect of phosphate rock when compared with superphosphate. However, examination of the reapplication response curves in the third crop (Figure 4.3), shows in general the same order of effectiveness for the sources relative to SSP as observed in the first crop. For example, CFpam is at no point more effective than SSP. If a significantly greater residual effect from CFpam compared to SSP existed, the yields from the combined effects of effects of residual CFpam in the third crop and the new application could have resulted in a higher yield for the CF source. Based on this line of reasoning, for the purposes of model development the assumption will be made for the range of rates under consideration (0 to 120 kg P/ha) that no significant residual effect remains by the third crop for any of the P-sources. This is clearly an assumption based on indirect reasoning and thus, is not strictly valid. However, the principal objective of this combined analysis is not the interpretation of these results, but rather the development of a method for combined consideration of initial and residual effects. This method will have the potential to be used in analysis of future data obtained in new experiments.

Non-linear analysis for all P-source

It is possible to carry out the simple exercise above for SSP because only two non-zero yields points occur for the residual SSP treatments in the third crop. For the residual effects of the 5 principal sources in the second crop, 4 non-zero yield points exist for each source (see Figure 4.2). Thus, a statistical procedure is desirable. In addition, it is desirable to estimate the residual effectiveness of the sources in the context of a yield response model which smooths out some of the variation in the response curve of the freshly applied treatments, as opposed to the graphical method used in Figure 4.4.

The response model chosen for this analysis is the Mitscherlich equation (Mitscherlich, 1909):

$$Y = A\ (1-e^{-cx})$$

where Y is yield
A is the asymptotic yield
c is a slope parameter
x is the independent variable, for this model the total effective P rate

The Mitscherlich equation describes a response curve with continuously diminishing returns. This type of response curve is capable of fitting the normal response to a freshly applied P-source in this soil (such as those in Figures 4.2 and 4.3). The upper curve in Figure 4.6 is the response curve to freshly applied SSP and the lower curve is the residual response to SSP. Because the residual response to SSP shows a

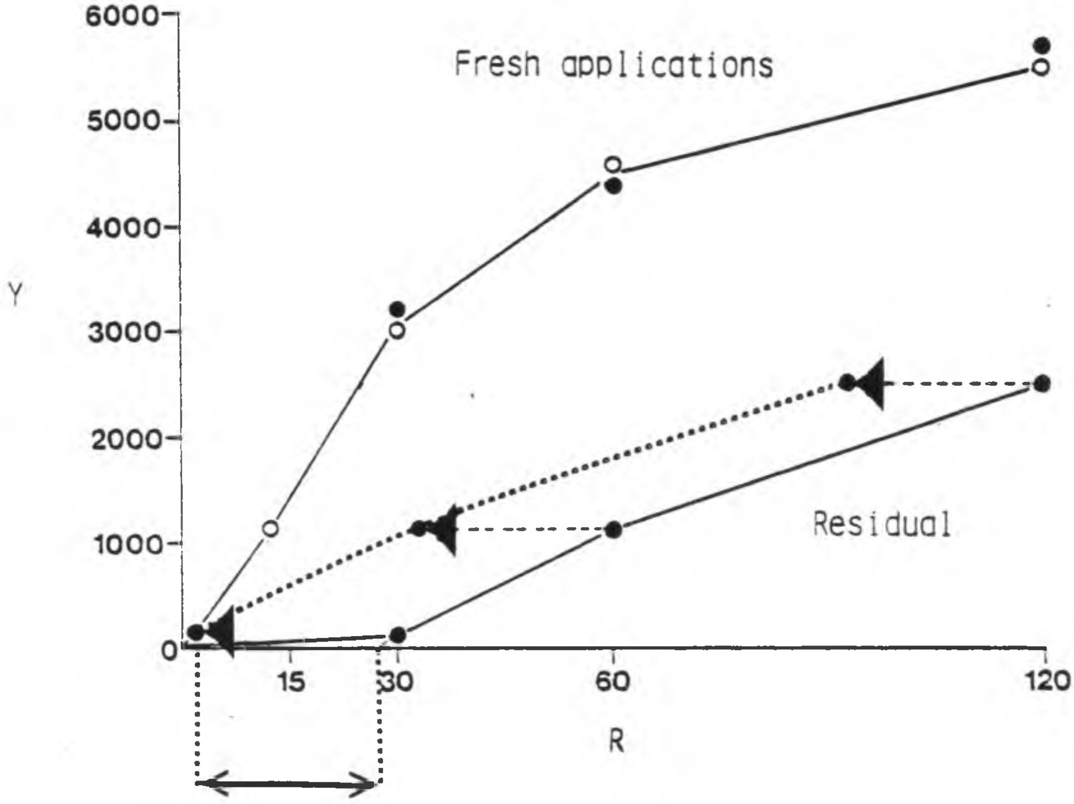

Figure 4.6 Graphical illustration of the removal of the sigmoidal tendancy in the residual response by subtracting a term from all points. Y and R are expressed in kg per ha.

sigmoidal tendency, it is not possible to fit it directly with the Mitscherlich equation. It is necessary to convert the residual values into their equivalents of freshly applied rates. This is what is accomplished with the non-linear regression as explained below.

First it is necessary to define terminology.

Y = Yield of current crop
Y_{1R} = Yield of previous crop
R_F = Freshly applied rate for current crop
R_{1R} = Residual rate applied to previous crop
R_{ER} = Effective Residual Rate
R_{TE} = Total Effective Rate ($R_F + R_{ER}$)

The next step is to define a term for the effective residual rate (R_{ER}). The sigmoidal effect could be handled by a number of methods; however, since only a few points make up the response curve, complex methods of handling the sigmoidal effect would result in over parameterized models. Therefore, it is handled in as simple a manner as possible. In the example shown in Figure 4.6, subtracting a single parameter, L from all of the residual rates removes the sigmoidal effect, transforming all the residual yield points to the left. Another term which should be subtracted from previously applied rates is the calculated uptake in the previous crop. This term can be calculated for each point by multiplying the P content (k) by the yield in the previous crop (Y_{1R}). The subtraction of the constant L parameter and the term, $k \cdot Y_{1R}$, which increases with Y_{1R}, is not generally sufficient to completely transform the residual rate, R_{1R}, into its freshly applied equivalent, R_{ER}. The simplest way, again avoiding over parameterization, is to multiply the resulting term by a fractional term (K_{1R}) which completes the transformation. The resulting expression for effective residual rate (R_{ER}) is

$$R_{ER} = K_{1R} \cdot (R_{1R} - k \cdot Y_{1R} - L).$$

Thus, the total effective rate (R_{TE}) becomes

$$R_{TE} = R_F + R_{ER}$$

Substituting the expression for R_{ER} yields

$$R_{TE} = R_F + K_{1R} \cdot (R_{1R} - k \cdot Y_{1R} - L).$$

Expressing the Mitscherlich equation in terms of the composite independent variable, R_{TE}, its form is

$$Y = A \cdot (1 - e^{-c \cdot R_{TE}}).$$

Substituting the expression for R_T gives

$$Y = A \cdot (1 - e^{-c[R_F + K_{1R} \cdot (R_{1R} - k \cdot Y_{1R} - L)]})$$

For this example the mean P content the grain removed was 0.19% P. Using the finding of Hanway (1962) that at harvest approximately 75% of the P is in the grain and 25% in the stover, the P content in the grain was multiplied by 1.33 to estimate the total P removed in the grain and stover. Therefore, 4 parameters remain to be solved in the model. They are A and c which describe the response curve in crops that received fresh applications. The other two terms, K_{1R} and L, describe the loss in effectiveness of the residual treatments.

The SAS NLIN procedure, as described in Materials and Methods (Chapter III), was used to solve for the four parameters for each P-source using a data set combining the second and third crops in a single analysis. Table 4.7 shows the solution of these 4 parameters

Table 4.7 -- The solution value of the four parameters in the combined non-linear model for the initial and residual response of maize to the six P-sources.

Source	A	c	K_{1R}	L	R_c^2
SSP	6058	0.021	0.73	21	0.95
NCf	5790	0.026	0.64	12	0.92
NCm	5237	0.032	0.69	10	0.93
CFf	4541	0.027	0.68	11	0.91
CFpam	5805	0.017	0.57	6	0.95
FMP	5486	0.035	0.64	12	0.96

for the 6 P-sources in the Hydric Dystrandept experiment. All of the values of the corrected coefficient of determination, R_c^2, are greater than 0.90, indicating acceptable regression fits. Examination of the paired values of A and c shows a tendency for a negative correlation between these parameters, i.e., high values of A correspond to low values of c. This makes separate interpretation of these parameters ambiguous. To overcome this problem, they are graphed against each other in Figure 4.7. The A and c pair for SSP has been chosen as the standard of comparison. Iso-yield lines have been calculated for three different P rates (1, 60, and 120 kg P/ha) covering the locus of combinations of A and c values that would give the same yield as the A and c values of SSP. This permits a classification of the phosphate rock sources with respect to their effectiveness relative to SSP over the response curve. The two CF forms lie to the left of the 1 kg P/ha iso-yield line. This means that at no rate do the yields from these P-sources exceed the yield from SSP. The other three sources (NCf, NCm, and FMP) fall between the 60 and 120 kg P/ha iso-yield lines. This means that up to a rate falling in this range (60 to 120), the yields for these sources exceed that for SSP. Above these "crossover" rates, the highest yields are obtained with SSP.

Table 4.7 also shows paired values of K_{1R} and L for each of the sources. As discussed, L is a measure of the sigmoidal tendency of the residual response curve. The larger the value of L, the greater the sigmoidal tendency. As is evident in Figure 4.2, the greatest

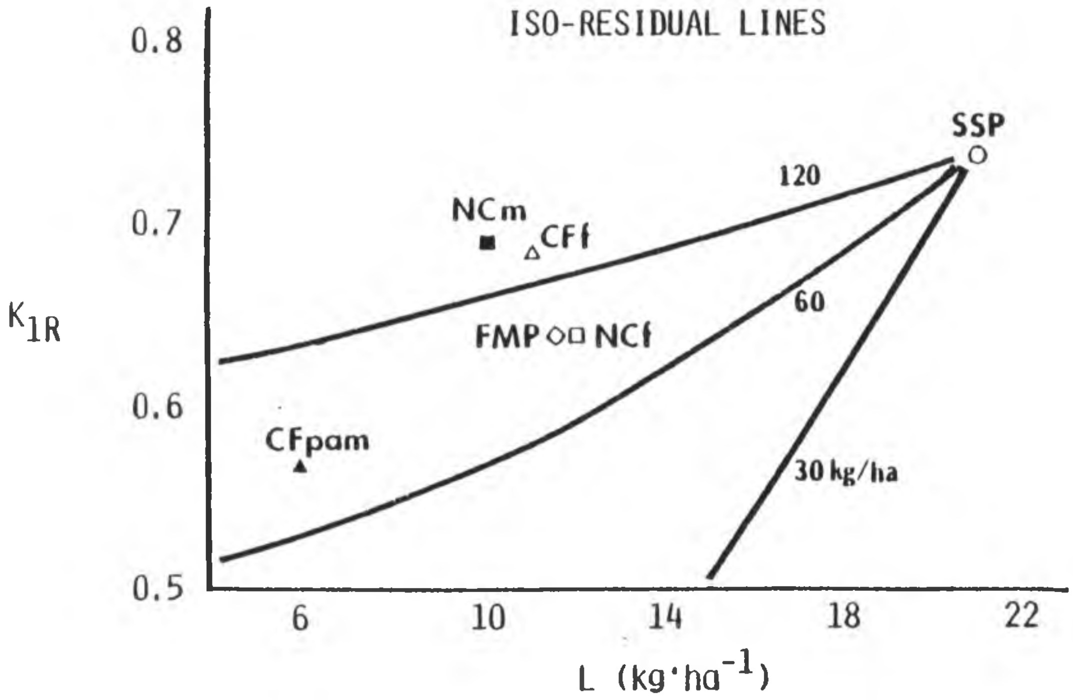

Figure 4.7 Plot of the A and c parameters of the nonlinear models for the six P-sources. The iso-yield lines at three rates of P permit comparison of the five alternative P-sources to the standard source, SSP.

sigmoidal tendency is observed for SSP and this is confirmed by the fact that SSP has the largest L value in Table 4.7. The parameter K_{1R} is a fraction that completes the transformation of the residual rate to its corresponding fresh equivalent, after removal of the terms for crop removal and sigmoidal effect. As with the A and c pairs, there is a tendency for the L and K_{1R} parameters to be correlated. However, in this case the correlation is positive, i.e., the larger the value of the L parameter, the larger the corresponding K_{1R} value. The problem of interpretation presented by this correlation can also be dealt with by a graphical method. Figure 4.8 shows a graph of the pairs of K_{1R} and L values for the six P-sources in Table 4.7. Again SSP is chosen as the standard of comparison. Iso-residual lines are graphed at 3 rates (30, 60, and 120 kg P/ha). These iso-residual lines cover the locus of K_{1R} and L pairs that would have the same relative residual effectiveness at each of the three rates as the K_{1R} and L pair for SSP. This residual effectiveness is relative to the response to the freshly applied corresponding P-source. This point is clearer if we examine the form of the Mitscherlich equation being used. The K_{1R} and L values act in the equation in the context of the overall response described by the A and c pairs for each P-source. Thus, the K_{1R} and L values describe the form of the residual response relative to the form of the initial response as described by the A and c values for each source. In Figure 4.8, CFpam, FMP, and NCf lie between the 60 and 120 kg P/ha iso-residual lines of SSP. This indicates that up to rates in the range of 70 to 90 kg P/ha the

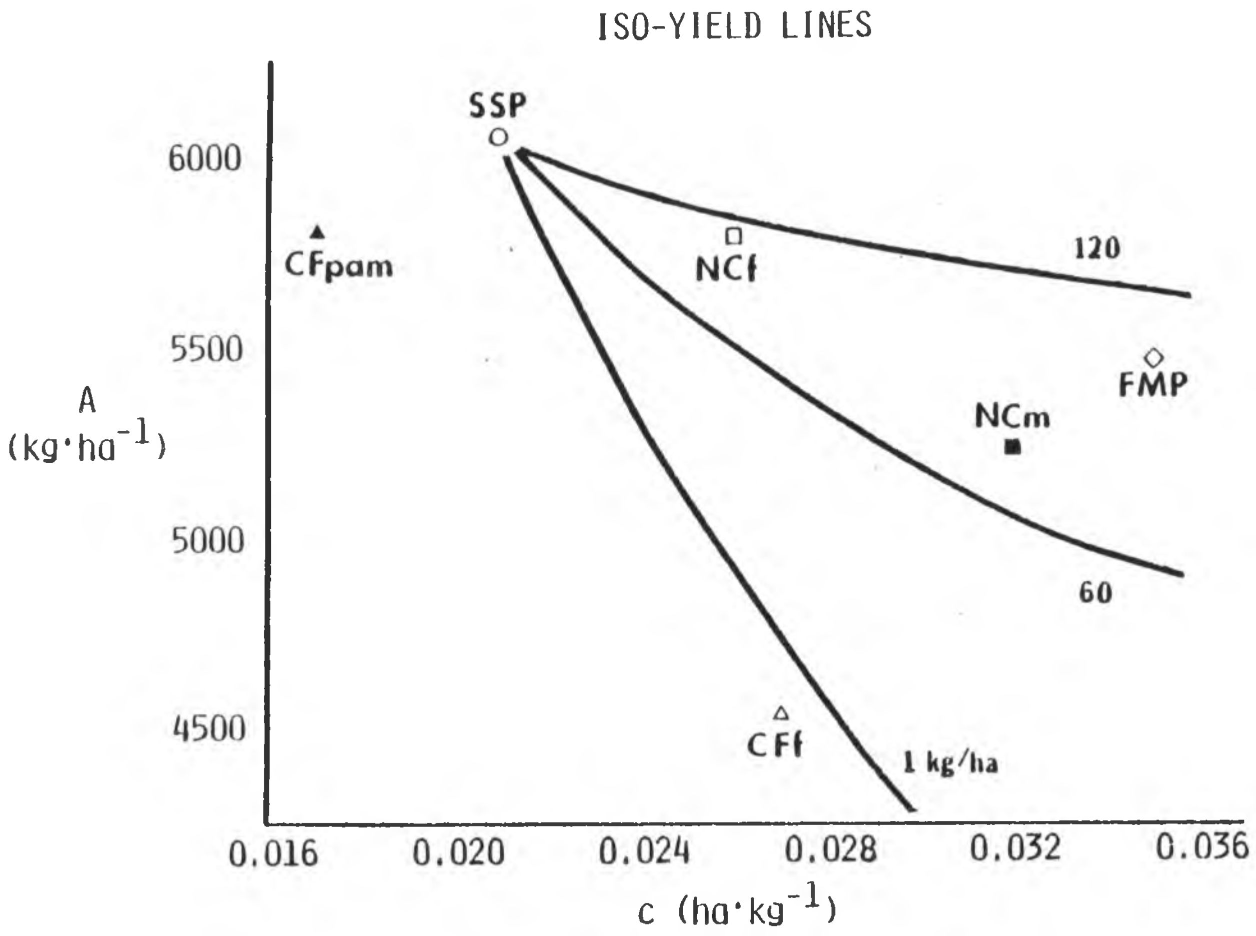

Figure 4.8 Plot of the residual parameters, K_{1R} and L, of the nonlinear models for the six P-sources. The iso-residual lines at three rates of P permit comparison of the five alternative P-sources to the standard, SSP, in terms of residual effectiveness relative to initial effectiveness.

relative residual values of these sources is greater than that of SSP. Above these rates, the relative residual values of these sources is less than that of SSP. In Figure 4.8, NCm and CFf lie above the 120 kg P/ha iso-residual line. This indicates that these two sources show a greater relative residual effect than SSP over the entire range of rates used in the experiment. This effect may be related to the slower rate of reaction of these sources in the soil due to lower reactivity in the case of CFf and due to the slight placement effect of minigranulation in the case of NCm.

Conclusions of the combined analysis of the Hydric Dystrandept crops:

The nonlinear regression model presented can be used to combine the initial response curve, which has a continuously decreasing slope for all sources, with the residual response curve, which has varying degrees of sigmoidal tendency for the six sources. With this model the initial and residual responses are defined by a total of four parameters. The A and c parameters primarily describe the initial response curve. The K_{IR} and L parameters describe the decline in the residual effectiveness relative to the initial effectiveness. The graphical techniques of iso-yield and iso-residual lines developed here permit the use of these pairs of parameters to compare P-sources. With data from a more complete set of experiments, i.e., experiments in which initial and residual responses were obtained in the same season and which tested the additivity of the effects of residual and freshly applied P fertilizer, this kind of model could be used to develop a comprehensive comparative production economic analysis of P fertilizer source materials.

POST HARVEST P SOIL TEST VALUES OVER THE THREE CROPPING SEASONS

Soil samples were taken after each of the three harvests. Modified Truog analyses were run on all samples. Bray P I analyses were run on the first and second crop post-harvest samples only and not on the third, since values obtained were extremely low. The results of the Truog P analyses are shown in Table 4.8 and the Bray P I analyses in Table 4.9. The BLSD values shown are calculated from the ANOVA error-b of the 4 rate by 5 principal P-source balanced segment of the experiment and can be used to compare the mean values between the 5 principal sources within each P rate.

Modified Truog analyses

The analyses in Table 4.8 show a continuous increase with rate for all sources as would be expected. However, this rate of increase within each crop is greater for the phosphate rock sources than for SSP. Within the phosphate rock sources, the rates of increase with respect to added P levels is lower for the NC sources than for the CF sources. Within the two NC sources, there is a consistent tendency for NCf to have a higher value than NCm at the highest rate, but the differences are not significant. However, in the case of the CF sources, the differences at the high rates are significant, with CFpam always higher than CFf. This difference is hard to explain since partial acidulation has converted part of the CF rock in CFpam to

Table 4.8 -- Modified Truog P levels of samples taken after harvest of the respective crops of the Hydric Dystrandept P-source experiment. Values are means of the three replications of each treatment.

First Crop, initial application

P rate

Control 4.7 ppm

	SSP	NCf	NCm	CFf	CFpam	FMP	Controls
-kg/ha-				ppm			
15	5.7	5.0	5.6	6.3	6.6	5.1	--
30	6.5	6.1	7.2	7.8	8.5	7.2	5.6
60	7.8	7.5	9.1	10.7	12.2	9.0	5.5
120	11.0	13.1	10.7	17.6	22.7	--	5.7

BLSD (error-b) = 2.1

Second Crop, residual

P rate

Control 5.0 ppm

	SSP	NCf	NCm	CFf	CFpam	FMP	(Fresh)
-kg/ha-				ppm			
15	5.9	5.3	5.5	5.7	5.6	5.0	--
30	6.6	6.1	7.3	6.5	9.4	6.8	6.9
60	8.0	7.3	9.0	10.6	10.3	10.7	11.1
120	10.3	12.5	10.2	12.0	17.8	--	14.3

BLSD (error-b) = 2.0

Third Crop, reapplication

P rate

Control 4.6 ppm

	SSP	NCf	NCm	CFf	CFpam	FMP	(Residual)
-kg/ha-				ppm			
15	5.1	5.1	5.5	5.6	5.6	5.0	--
30	6.5	6.3	6.9	7.5	8.1	6.1	5.6
60	8.5	9.4	9.7	10.7	12.4	10.8	5.9
120	14.2	17.6	16.8	22.3	25.5	12.0	8.7

BLSD (error-b) = 2.8

monocalcium phosphate and possibly some to dicalcium phosphate. Since monocalcium phosphate is the principal constituent of SSP, the extractable level of P in the CFpam treatments might be expected to lie between the values for CFf and SSP. In fact the CFpam values lie above the range set by SSP (on the low end) and CFf.

The modified Truog extractable P values would be of practical significance if they could be used to predict residual effectiveness of the P-sources. A comparison of the first crop post-harvest modified Truog values with the second crop residual yields provides a test of the predictive value. Figure 4.2 shows at the 120 kg P/ha rate that the relative residual effectiveness of the sources is NCf = NCm = SSP = CFf > Cfpam. Ranking the modified Truog values for the first crop post-harvest samples at the 120 kg rate gives the order CFpam > CFf > NCf > SSP = NCm, indicating a poor predictive capability of Truog values for residual effectiveness. In general an acid extractant used at a high solution to soil ratio (as is the case with the modified Truog method), might be expected to dissolve unreacted apatite and thus, give high values for the least effective P-sources. However, the, fact that the extractable values for CFpam are higher than those for CFf, even though CFpam gives higher yields indicates that there are factors affecting the extractability other than the amount of unreacted apatite remaining in the soil. In conclusion, the modified Truog extraction is not suitable for predicting the residual value of phosphate fertilizers if P-sources that differ in solubility have been applied to the soil.

Bray P I analyses

The analyses in Table 4.9 show very low values for the Bray P I extractions (7:1 solution to soil ratio, 5 minutes). These low values are subject to high error in determination. In fact some values decrease from the 15 kg to 30 kg rates and from the 30 kg to 60 kg rates. These low values can be attributed to the "amorphous" mineralogy of the Hydric Dystrandept, resulting in comsumption of F in reactions with silicates and aluminum oxides and causing an increase in pH due to release of OH^-. The only statistically significant differences are observed at the 120 kg rate. A casual correlation of the first crop analyses with the residual yields shown in Figure 4.2 shows a problem similar to the modified Truog analyses, i.e., CFpam shows the highest extractable P level but the lowest crop yield at the 120 kg P/ha rate. However, unlike the modified Truog case, in which the order of increasing extractable P is SSP < CFf < CFpam, the order for Bray I at the highest rat in the first crop is CFf < SSP < CFpam. This agrees with the expectation that less P from apatite should be extracted by the weaker Bray extractant. The fact that Cfpam has a higher value than SSP suggests, however, that the unreacted apatite may still be contributing to extracted P. The level of error in these determinations precluded conclusive interpretations.

Table 4.9 -- Bray P I levels of soil samples taken after harvest of the first and second crops of the Hydric Dystrandept P-source experiment.

First Crop, initial application

P rate

Control 0.16 ppm

	SSP	NCf	NCm	CFf	CFpam	FMP	Controls
-kg/ha-				ppm			
15	0.18	0.20	0.16	0.18	0.16	0.16	--
30	0.16	0.19	0.17	0.16	0.19	0.20	0.16
60	0.25	0.22	0.25	0.23	0.20	0.24	0.19
120	0.35	0.38	0.29	0.24	0.39	--	0.22

BLSD (error-b) = 0.07

Second Crop, residual

P rate

Control 0.21 ppm

	SSP	NCf	NCm	CFf	CFpam	FMP	(Fresh)
-kg/ha-				ppm			
15	0.19	0.22	0.19	0.18	0.20	0.20	--
30	0.18	0.21	0.21	0.18	0.25	0.22	0.25
60	0.24	0.22	0.24	0.17	0.17	0.15	0.23
120	0.30	0.30	0.29	0.23	0.26	--	0.41

BLSD (error-b) = 0.14

Conclusions from the extractable P analyses

Neither of the two extraction methods is suitable for evaluating residual P across P-sources in the Hydric Dystrandept. The modified Truog method, due to its high acid to soil ratio, presumably extracts large proportions of P from the unreacted phosphate rock, in addition to P which has reacted with the soil. This effect may be due to the fact that similar quantities of P are extracted from the unreacted apatite in the soil for both CFf and CFpam, even though a smaller quantity of unreacted apatite was applied in the partially acidulated product. The 7:1 Bray P I yields very low values in this soil and is, therefore, subject to high error. The performance of the Bray method is presumably due to the mineralogy of the Hydric Dystrandept. Thus, neither method is satisfactory in this soil for evaluating residual P across a range of sources. The P isotherm method (Fox and Kamprath, 1970) might be expected to give a better evaluation of residual effectiveness than either of these methods because it does not subject unreacted phosphate rock to acidic conditiions with pH values much lower than the natural soil pH. However, the isotherm method would take into account only the P which has already dissolved from the phosphate rock sources and would provide no measure of the P that could be expected to become available from the unreacted rock. Possibly a weak acid extractant such as the Bray I used at a higher solution to soil ratio such as 30:1 or 50:1 would extract sufficiently high levels to overcome the error problems of the 7:1 Bray I method but yet avoid the high dissolution of unreacted phosphate rock encountered with the modified Truog. Increasing the F concentration would probably also improve the Bray method for this soil; however, modification of the P determination method would be necessary to prevent interference by fluoride in the determination of P.

The problem of a suitable extractant would warrant further research if direct application of phosphate rock were a highly advisable practice, but the crop response results presented here indicate limitations to the efficiency of directly applied rocks of moderate or lower reactivity on the Hydric Dystrandept. IFDC (1982) is, however, advocating the use of partially acidulated phosphate rock in Andepts, and this is the material giving the most anomolous results with these extraction procedures. If partially acidulated rock is to be commercially recommended, research on an acceptable procedure for evaluating residual levels is necessary.

CHAPTER V

RESULTS OF THE TYPIC PALEUDULT EXPERIMENT, INDONESIA

INTERPRETATION OF YIELD RESPONSES

First Crop Yields

Triple superphosphate and the 4 principal P-source materials described in Table 3.2 were compared at 4 rates in this experiment using the split plot design indicated in Chapter III. Figure 5.1 shows the maize grain yield response for the first crop of the Typic Paleudult experiment and the analysis of variance is shown in Table 5.1. This experiment had up to 40% incidence of downy mildew resulting in maximum yields of less than 3000 kg/ha. However, the C.V. is less than 12% and the error-b R^2 is 0.758, indicating acceptable variation. The ANOVA shows a highly significant rate effect, but the P-source effect and the rate by P-source interaction are not significant. This contrasts strongly with the results of the Hydric Dystrandept experiment, particularly with regard to the P-source effect, and leads to the conclusion that this Typic Paleudult is well adapted to direct application of phosphate rock.

The variation caused by the downy mildew infestation definitely contributed to variation in this experiment. To remove some of this variation a corrected yield was calculated by removing the weight of abnormally small ears from each plot and adding in the average weight of ears with normal appearance for each abnormal ear. The resulting corrected yield showed lower variation than the uncorrected yield (C.V.

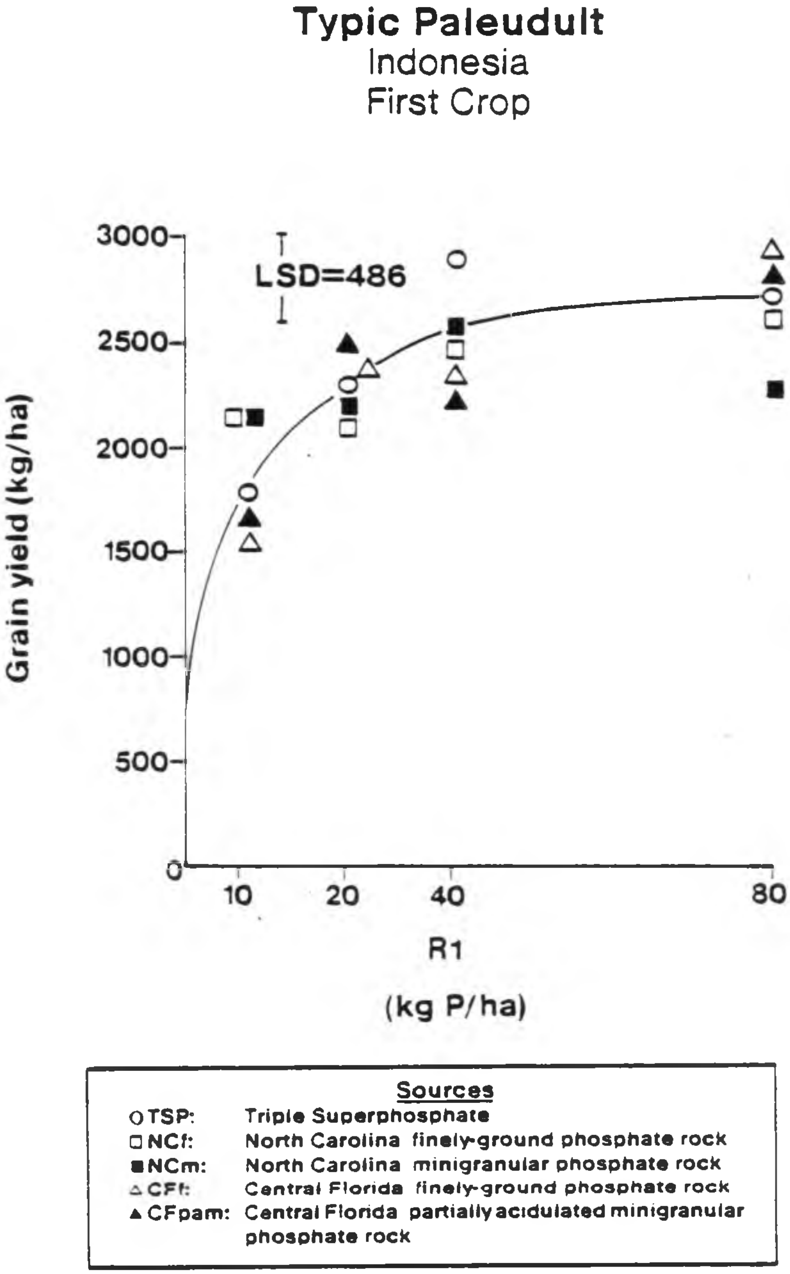

Figure 5.1 The grain yield response of maize to freshly applied P-sources at 4 rates in the first crop of the Typic Paleudult experiment, Indonesia. The solid line is a hand drawn fit to all points.

Table 5.1 -- Analysis of variance of maize grain yield for the Typic Paleudult experiment, first crop, covering all 4 rate mainplots by 5 P-source subplots. See Materials and Methods for details.

Source of variation	DF	SS	F	PR>F
Rep	2	429,803		
Rate (R)	3	6,293,432	20.37	0.0015**
Rep x Rate (Error-a)	6	618,027		
P-source (S)	4	36,819	0.11	0.9792 N.S.
Rate x P-source	12	1,233,594	1.20	0.3279 N.S.
"Model" Total	27	8,611,675		
Error-b	32	2,752,128		
Corrected Total	59	11,363,803		

	LSD	BLSD	R^2	C.V.	Std.dev.	Yield mean
Error-b	486	-	0.758	11.9%	293	2471
Error-a&b	-	-	0.703			

** Highly significant

N.S. Not significant

of 10.2% compared to 11.9%, error-b R^2 of 0.808 compared to 0.758). However, the F tests lead to the same conclusions, i.e., a highly significant rate effect and highly nonsignificant P-source and rate by P-source interaction.

Summary of the Typic Paleudult first crop:

The response to P is highly significant in the first crop but no significant differences occurred between sources, suggesting that this Typic Paleudult is well suited for direct application of phosphate rock.

Second Crop Yields

In replanting this experiment as a residual, soybeans were planted in place of maize to avoid further incidence of downy mildew. As in the Hydric Dystrandept experiment, three of the control subplots were converted to freshly applied TSP treatments for comparison with the residual treatments (see Table 3.7 for details).

Figure 5.2 shows the soybean grain yield response and Table 5.2 shows the analysis of variance of the balanced segment of the design (4 rates by 5 residual P-sources). The ANOVA shows a C.V. of 23.8% but the error-b R^2 is 0.911 and the error-a&b R^2 is 0.875. This is another case where the C.V. appears to be high because residual treatments have a low yield mean; however, the R^2 values suggest an acceptable level of variation. The conclusion from the F tests of the residual effects are the same as those for the first crop, i.e., the rate effect is highly significant but the P-source and rate by P-source effects are not significant. This supports the conclusion for the

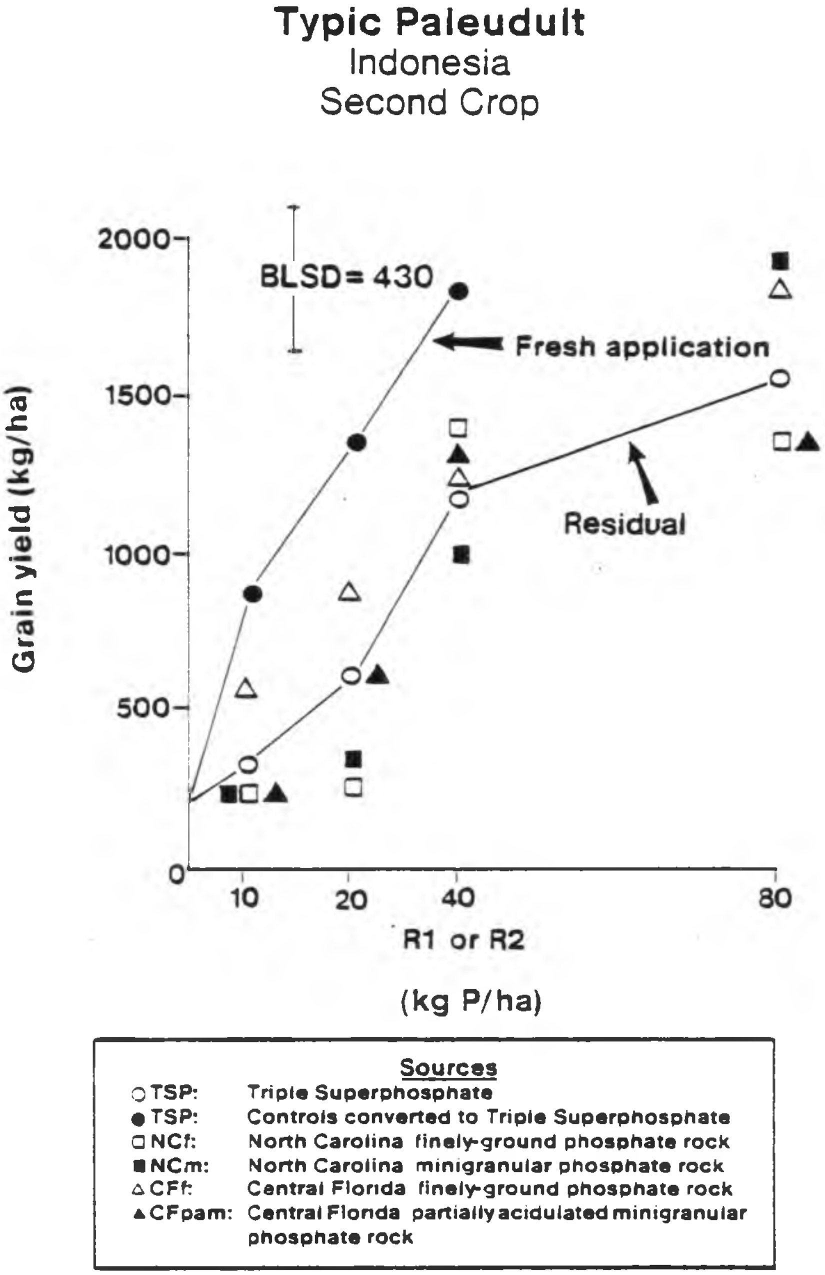

Figure 5.2 The grain yield response of soybean in the second crop of the Typic Paleudult experiment, Indonesia, to residual treatments of the 5 principal P-sources and fresh applications of SSP on three former control treatments. R1 is the P rate applied for the first crop to treatments that are residual in this crop. R2 is the P rate applied to former controls at the time of planting of this crop. The solid lines connect the points in both the TSP fresh and residual treatments.

Table 5.2 -- Analysis of variance of soybean grain yield for the Typic Paleudult experiment, second crop, covering all 4 rate mainplots by 5 P-source subplots. See Materials and Methods for details.

Source of variation	DF	SS	F	PR>F
Rep	2	223,726		
Rate (R)	3	13,990.973	45.45	0.0002**
Rep x Rate (Error-a)	6	615,700		
P-source (S)	4	403,726	2.06	0.1090 N.S.
Rate x P-source	12	712,105	1.21	0.3169 N.S.
"Model" Total	27	15,946,230		
Error-b	32	1,565,931		
Corrected Total	59	17,512,161		

	LSD	BLSD	R^2	C.V.	Std.dev.	Yield mean
Error-b	368	433	0.911	23.8%	221	931
Error-a&b	-	-	0.875			

** Highly significant

N.S. Not significant

first crop that this soil is well suited to direct application of phosphate rock.

Summary of the Typic Paleudult second crop:

The conclusion reached for the residual treatments is the same as that reached for the first crop, i.e., there is no difference between sources in this soil.

Third Crop Yields

For this crop on the Typic Paleudult, the 5 principal P-sources at the 20, 40, and 80 kg P/ha rates were maintained as residuals since the residual effects in the second crop suggested that adequate residual effects on yields could be expected to continue. However, because the yields at the 10 kg P/ha rate in the second crop had dropped to the level of the control treatments (see Figure 5.2), a reapplication of all P-sources in this mainplot was made for this crop at a rate of 70 kg P/ha. This raised the total P applied to 80 kg/ha for this mainplot and thus, permits comparison with the residual 80 kg/ha treatments. The former control plots, which had received applications in the second crop, received equal reapplications for the third crop. (The details of these treatment sequences are shown in Table 3.7.) Since an effective systemic fungicide for the control of downy mildew (Ridomil) had just become commercially available in Indonesia, it was again possible to plant maize in this experiment.

Figure 5.3 shows the maize grain yield response for the third crop and Table 5.3 gives the analysis of variance of the 4 mainplot by 5 P-source segment. A C.V. value of 11.9%, an error-b R^2 of 0.967, and

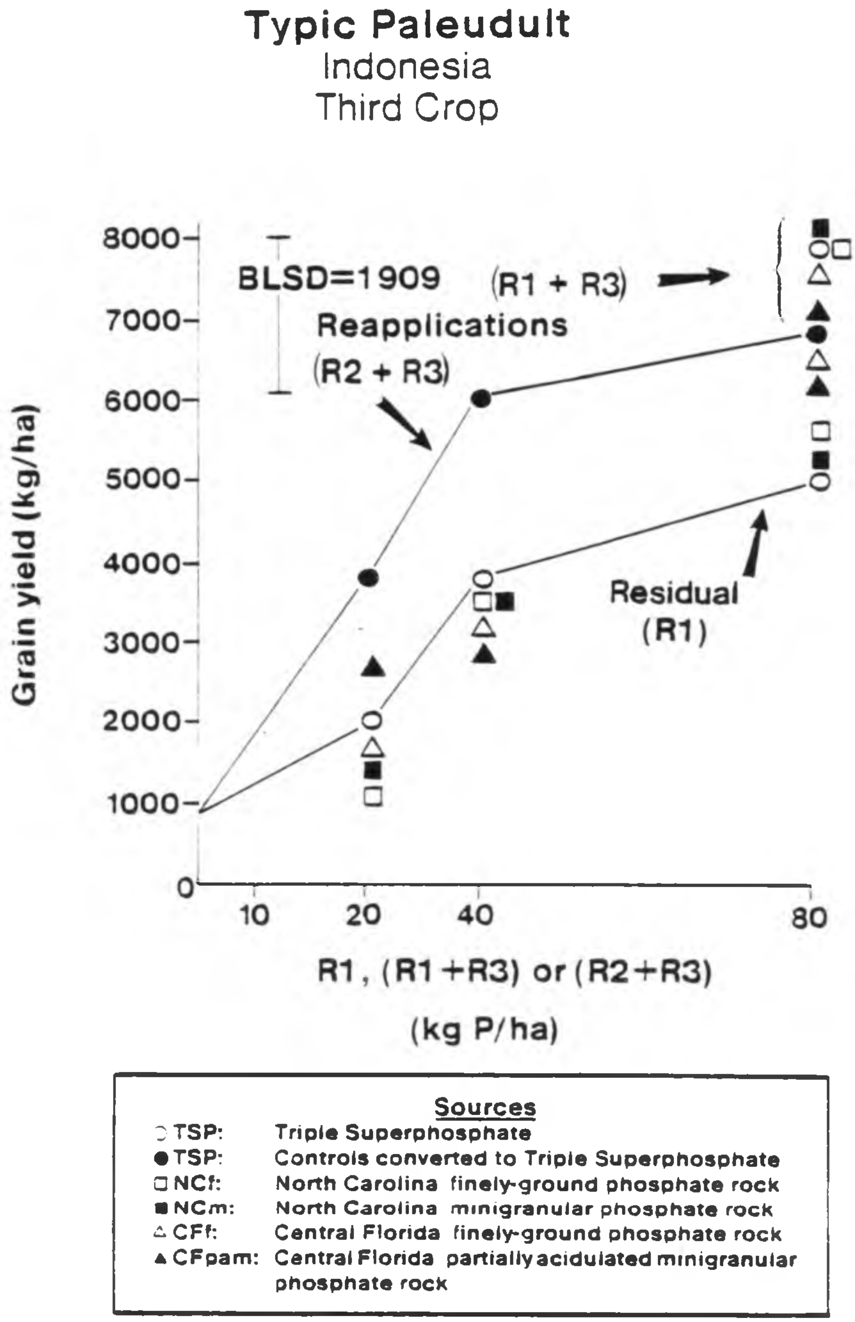

Figure 5.3 The grain yield response of maize in the third crop of the Typic Paleudult experiment, Indonesia, to residual and reapplication treatments. R1 is the P rate applied for the first crop. R2 is the TSP rate applied to former controls in the second crop. R3 is the rate applied for the third crop. Reapplications of 70 kg P/ha were made in this crop for all sources in the 10 kg P/ha mainplot, resulting in R1 + R3 treatments at 80 kg P/ha.

Table 5.3 -- Analysis of variance of maize grain yield for the Typic Paleudult experiment, third crop, covering all 4 rate mainplots by 5 P-source subplots. See Materials and Methods for details.

Source of variation	DF	SS	F	PR>F
Rep	2	481,336		
Rate (R)	3	305,823,922	226.22	0.0001**
Rep x Rate (Error-a)	6	2,703,803		
P-source (S)	4	1,704,123	1.23	0.3161 N.S.
Rate x P-source	12	8,716,000	2.10	0.0463*
"Model" Total	27	319,429,183		
Error-b	32	11,046,062		
Corrected Total	59	330,475,245		

	LSD	BLSD	R^2	C.V.	Std.dev.	Yield mean
Error-b	977	1909	0.967	11.9%	588	4923
Error-a&b	-	-	0.885			

* Significant

** Highly significant

N.S. Not significant

an error-a&b R^2 of 0.885 indicate low variation in this experiment. The yield mean is 4923 kg/ha and the maximum yields approach 8000 kg/ha. The ANOVA, as in the previous two crops, shows a highly significant rate effect and a nonsignificant P-source effect. For this crop the rate by P-source interaction is significant at the 5% level. An interpretation of this significant interaction is not evident in Figure 5.3. The continued nonsignificance of the P-source effect does have a clear interpretation, i.e., TSP, a highly reactive phosphate rock (NC) in either finely ground or minigranular form, and a moderately reactive phosphate rock (CF) are equally good sources in this soil. Obviously, neither full acidulation to TSP nor partial acidulation of the CF rock is necessary for agronomic performance. However, they do result in increased P content of the fertilizers, reducing shipping cost. The importance of the nonsignificant difference between P-sources is particularly clear in the treatments which received fresh applications of 70 kg P/ha. These treatments produced consistent, high yields of around 8000 kg/ha. This result conflicts with the statement of Khasawneh and Doll (1978) that phosphate rock "is not suitable for intensive agricultural production" and their paraphrase of Russel (1973) that phosphate rock "cannot maintain a sufficiently high concentration of P in soil solution for high yields of crops with high P requirements." This Typic Paleudult appears to have proper properties to permit high crop yields with both highly and moderately reactive phosphate rock. This raises the question of whether this soil and soils closely related to it in the Indonesian archipelago may not also be well adapted to direct application of indigenous sources of low reactivity.

Summary of Typic Paleudult third crop:

High grain yields were obtained in this crop and again the P-source effect was statistically nonsignificant while the rate effect was highly significant. The high yields with no significant difference between P-sources in the treatments which received fresh applications of 70 kg P/ha reconfirm the results of the first crop that even when freshly applied, the phosphate rock sources are equal to TSP. Furthermore, the residual treatments reconfirm the results of the residual treatments in the second crop that the P-source do not differ in residual effectiveness.

POST HARVEST P SOIL TEST VALUES OVER THE THREE CROPPING SEASONS

Soil samples were taken after each of the three harvests and Bray P I extractions (7:1 solution to soil ratio, 5 minute extraction per Chien, 1978) were run on all samples. The results are shown in Table 5.4. The BLSD values shown are calculated from the error-b of the GLM analysis of all applied P treatments and can be used to compare the mean values for all of the P-sources within each P rate.

Bray P I analyses

For the first crop, post harvest sample values in Table 5.4 vary from about 2 ppm for the controls to around 10 ppm for the highest P rate treatments. This contrasts sharply with the Bray P I results for the Hydric Dystrandepts (values of $<$ 0.2 ppm) shown in Table 4.9 and is

Table 5.4 -- Extractable P levels by the Bray I procedure after harvest of the successive crops of the Typic Paleudult experiment. Values are means of the three replications of each treatment.

First Crop, initial application

Control 2.6 ppm

P rate	TSP	NCf	NCm	CFf	CFpam	Controls
-kg/ha-	ppm					
10	2.7	3.1	2.9	2.5	2.5	2.1
20	4.0	3.9	3.0	2.9	3.3	2.4
40	4.7	5.1	4.2	4.9	4.4	2.5
80	11.3	10.6	11.2	8.2	9.0	---

BLSD (error-b) = 1.1

Second Crop, residual

Control 1.7 ppm

P rate	TSP	NCf	NCm	CFf	CFpam	TSP (Fresh)
-kg/ha-	ppm					
10	1.9	2.3	2.1	1.9	2.3	2.4
20	2.6	2.8	2.5	2.3	2.9	2.7
40	3.8	2.9	3.4	3.0	2.8	3.3
80	6.8	5.9	6.4	4.3	4.9	---

BLSD (error-b) = 2.2

Third Crop, residual and reapplication

Control 2.1 ppm

P rate	TSP	NCf	NCm	CFf	CFpam	TSP (With Reapplication)
	ppm					
20	2.9	2.5	2.4	2.4	2.7	2.9
40	2.4	2.9	2.9	3.0	3.1	3.7
80	4.8	4.7	4.3	3.8	4.7	5.9
10+70	7.1	9.2	6.5	5.2	7.1	---

BLSD (error-b) = 1.4

due to the difference in mineralogy and chemical properties of the two soils. The Typic Paleudult is dominated by kaolinitic clay minerals that have a lower capacity to react with F and also, lower pH buffer capacity than the "amorphous" minerals of the Hydric Dystrandepts. Because of the smaller sinks for F^- and H^+ in the Typic Paleudult, the 7:1 Bray I procedure extracts sufficient levels of P to give a large range between the high and low treatments. Keeping in mind, however, that the yield analysis for these experiments shows the P-source effect to be nonsignificant, significant differences in Bray I values between P-sources are observed at the high rates, particularly in the first and and third crops for which initial and reapplications were made, respectively. In contrast with the modified Truog results for the Hydric Dystrandept experiment for which the CF sources had higher extractant values than the more soluble P-sources, in the Typic Paleudult experiment using the Bray extractant, the lowest values are obtained for CFf. The values for CFpam lie in the range between CFf and TSP as should be expected. However, although it is much less pronounced than with the Modified Truog method in the Hydric Dystrandept, the problem does exist in the Typic Paleudult that the Bray values are not well correlated with grain yield across P-sources. The fact that the CF extractable P values tend to be lower than those of the other sources, although yields are comparable, suggests that a more acidic extractant might overcome this problem by dissolving more of the unreacted apatite in the CF sources. This could be accomplished by an increase in the solution to soil ratio for this procedure, possibly in the range from 10:1 or 20:1. Because direct application of phosphate rock is agronomically advisable on these soils, further research to improve the predictive capabilities of P soil test procedures is warranted for the Typic Paleudult and related soils.

CHAPTER VI

CONCLUSIONS

YIELD RESPONSE COMPARISON

The absence of significant differences between P sources in the Typic Paleudult contrasts with the differences between sources observed in the Hydric Dystrandept. However, in both soils, both in the initial and residual responses, there are no significant differences between NCf and NCm, thus confirming the agronomic viability of the mini-granulation process. Partial acidulation of the CF phosphate rock improved its performance on the Hydric Dystrandept in the seasons with fresh application. There was still, however, some tendency for the partially acidulated CF rock to be inferior to the NC sources, as well as, SSP, suggesting that the reactivity of the apatite is still expressed in partially acidulated sources of moderate activity on the Hydric Dystrandept. The very poor performance of the low reactivity guanos indicates the complete range in the effect of apatite reactivity on fertilizer performance. On the Typic Paleudult, the absence of differences between TSP and the NC and CF sources over the three seasons suggests that even low reactivity sources may perform adequately on the Typic Paleudult. Lukman, et al. (1980) report for a maize and sorghum rotation at Tanjung Iman, Lampung (approximately 30 km from the Nakau site), that the low reactivity phosphate rock from Ciluar, Java, gave yields comparable to TSP and DAP at high rates in the first two seasons and at all rates in subsequent seasons. This suggests that further research with low reactivity phosphate rocks is warranted in the Typic Paleudult and related soils.

In examining the chemical properties which differ between the Hydric Dystrandept and the Typic Paleudult used in this study, pH and P sorption capacity (Table 3.1) are the two properties which most probably relate to the contrast observed in phosphate rock performance in the two soils. The lower pH and P sorption capacity of the Typic Paleudult suggest that dissolution of phosphate rock is faster due to the more acid environment and that the lower sorption capacity permits diffusion of dissolved P through a larger volume of the soil and permits high P in solution concentration levels. A conclusive elucidation of the properties responsible for the difference in performance will require future studies on a wider range of soils differing in measurable properties. As suggested in the conclusions in the Literature Review, the most fruitful method to follow is expected to involve classifying soils into similar groups and within these groups relating differences in performance to commonly measured properties, such as pH, Ca saturation, and P sorption capacity.

The contrast in effectiveness of P-sources between the two soils observed here is similar to that reported by the IFDC Phosphorus Project working in collaboration with the International Center of Tropical Agriculture (CIAT) in Colombia. The results of that project (IFDC, 1982) indicate significant differences between directly applied phosphate rock (moderately reactive Colombian sources) and TSP on an Andept near Popayan, Colombia, contrasted with smaller differences between directly applied phosphate rock and TSP on an Oxisol in the Llanos Orientales region of Colombia and an Ultisol in the interandean Cauca Valley.

RECOMMENDATIONS FOR SOIL TESTS

The results from the post harvest P soil test analyses indicate that neither the modified Truog nor the Bray P I procedure can be satisfactorily used to predict residual P in the Hydric Dystrandept when P-sources varying in solubility are used. In the Typic Paleudult there is some indication that the Bray I procedure underestimates residual P from the CF sources; however, it appears that minor modification of the procedure by increasing the solution to soil ratio could overcome this problem. This is considered to be a worthwhile area for research since direct application of phosphate rock over the complete range of solubility appears to be an agronomically advisable practice for the Typic Paleudult and similar soils.

Appendix 1. Grain Yield Means by Treatment for Three Crops in the Hydric Dystrandepts Experiment -- Philippines

Source			Rate			Grain Yield		
1	2	3	1	2	3	1	2	3
			------Kg/Ha-----			-------Kg/Ha-----		
			15 Kg P/ha Main Plot					
Cont.*	Cont.	Cont.	0	0	0	22	58	0
SSP	Res.**	SSP	15	0	15	151	123	1328
NCf	Res.	NCf	15	0	15	344	313	1682
NCm	Res.	NCm	15	0	15	363	445	2154
CFf	Res.	CFf	15	0	15	66	398	1573
CPpam	Res.	CFpam	15	0	15	168	458	1183
FMP	Res.	FMP	15	0	15	346	248	1834
			30 Kg P/ha Main Plot					
Cont.	SSP	Res.	0	30	0	0	3029	107
SSP	Res.	SSP	30	0	30	598	710	2846
NCf	Res.	NCf	30	0	30	690	1253	3245
NCm	Res.	NCm	30	0	30	670	1636	3331
CFf	Res.	CFf	30	0	30	124	1274	2606
CFpam	Res.	CFpam	30	0	30	395	1199	2306
FMP	Res.	FMP	30	0	30	945	1578	3881
			60 Kg P/ha Main Plot					
Cont.	SSP	Res.	0	60	0	13	4471	1179
SSP	Res.	SSP	60	0	60	1055	2262	4528
NCf	Res.	NCf	60	0	60	952	2945	4763
NCm	Res.	NCm	60	0	60	994	3544	4159
CFf	Res.	CFf	60	0	60	234	2328	3626
CFpam	Res.	CFpam	60	0	60	745	2384	3839
FMP	Res.	FMP	60	0	60	1789	3386	1179
			20 Kg P/ha Main Plot					
Guano 1	SSP	Res.	120	120	0	44	5548	2465
SSP	Res.	SSP	120	0	120	2348	4779	5343
NCf	Res.	NCf	120	0	120	1968	4980	5325
NCm	Res.	NCm	120	0	120	983	4653	5344
CFf	Res.	CFf	120	0	120	355	4387	4129
CFpam	Res.	CFpam	120	0	120	1747	3801	5030
Guano 2	Res.	FMP	120	0	120	85	270	5333
				BLSD (error-b)		537	609	798

*Control

**Residual

Appendix 2. Grain Yield Means by Treatment for Three Crops in the Typic Paleudults Experiment -- Indonesia

Source			Rate			Grain Yield		
1	2	3	1	2	3	1	2	3
			------Kg/Ha-----			-------Kg/Ha-------		
			15 Kg P/ha Main Plot					
Cont.	TSP	TSP	0	10	10	711	817	3591
TSP	Res.	TSP	10	0	70	1864	432	7541
NCf	Res.	NCf	10	0	70	2189	371	7606
NCm	Res.	NCm	10	0	70	2186	352	7709
CFf	Res.	CFf	10	0	70	1738	581	7483
CFpam	Res.	CFpam	10	0	70	1836	355	6868
			20 Kg P/ha Main Plot					
Cont.	TSP	TSP	0	20	20	861	1210	6098
TSP	Res.	Res.	20	0	0	2482	542	2099
NCf	Res.	Res.	20	0	0	2225	354	1426
NCm	Res.	Res.	20	0	0	2342	426	1659
CFf	Res.	Res.	20	0	0	2489	802	2554
CFpam	Res.	Res.	20	0	0	2558	561	2554
			40 Kg P/ha Main Plot					
Cont.	TSP	TSP	0	40	40	454	1778	6587
TSP	Res.	Res.	40	0	0	2928	1147	3772
NCf	Res.	Res.	40	0	0	2713	1292	3527
NCm	Res.	Res.	40	0	0	2735	916	3700
CFf	Res.	Res.	40	0	0	2620	1217	3492
CFpam	Res.	Res.	40	0	0	2576	1222	3137
			80 Kg P/ha Main Plot					
Cont.	Cont.	Cont.	0	0	0	720	268	811
TSP	Res.	Res.	80	0	0	2792	1600	5070
NCf	Res.	Res.	80	0	0	2767	1437	5672
NCm	Res.	Res.	80	0	0	2534	1832	5277
CFf	Res.	Res.	80	0	0	2949	1759	6457
CFpam	Res.	Res.	80	0	0	2888	1429	6153
				BLSD (error-b)		486	368	977

BIBLIOGRAPHY

Adams, Fred (1974) Soil Solution. In: E. W. Carson, ed. The plant root and its environment. Univ. of Virginia Press, Charlottesville, VA. p. 441-481.

Anonymous (1975) More phosphate from Thies. Phosphorus Potassium. 75:34-36.

Amarasiri, S. L. and S. R. Olsen (1973) Liming as related to solubility of P and plant growth in an acid tropical soil. Soil Sci. Soc. Am. Proc. 37:716-721.

Ando, J. (1959) Studies on fused calcium magnesium phosphate fertilizer. Chuo University, Tokyo, Japan, Faculty of Engineering, Reports. 30 pp.

Armiger, W. H. and M. Fried (1957) The plant availability of various sources of phosphate rock. Soil Sci. Soc. Amer. Proc. 12:183-188.

Ayres, A. S. and H. H. Hagihara (1961) Effectiveness of raw rock phosphate for sugarcane. Soil Sci. 91:383-387.

Barnes, J. S. and E. J. Kamprath (1975) Availability of North Carolina rock phosphate applied to soils. North Carolina Agricultural Experiment Station. Technical Bulletin No. 229. 23 pp.

Bartholomew, R. P. (1928) The unavailability of phosphorus in rock phosphate to some southern crops. J. Am. Soc. Agron. 20:913-920.

Bartholomew, R. P. (1935) Fluorine, its effects on plant growth and its relation to the availability to plants of phosphorus in phosphate rock. Soil Sci. 40:203-217.

Bartholomew, R. P. (1937) Availability of phosphate rock in soils of varying degrees of acidity. J. Amer. Soc. Agron. 29:293-298.

Bauer, F. C. (1921) The relation of organic matter and the feeding power of plants to the utilization of rock phosphate. Soil Sci. 12:12-41.

Bear, F. E. (1938) Theory and practice in the use of fertilizer S. (Second edition). John Wiley and Sons. New York, NY. 360 pp.

Benchmark Soils Project (1976) Annual Report 1975-1976. Hawaii Ag. Expt. St., Univ. of Hawaii, Dept. Paper No. 50, Honolulu, HI. 55 pp.

Benchmark Soil Project (1978) Research on agrotechnology transfer in the tropics based on the soil family. Progress Rept. No. 1. Univ. of Hawaii, Dept. of Agron. and Soil Sci and Univ. of Puerto Rico, Dept. of Agron. and Soils. 64 pp.

Benchmark Soils Project (1980) Annual Report 1979-1980. Dept. of Agron. and Soil Sci., Univ. of Hawaii, Honolulu, HI. 114 pp.

Bennett, O. L., L. E. Ensminger, and R. W. Pearson (1957) The availability of phosphorus in various sources of rock phosphate as shown by greenhouse studies. Soil Sci. Soc. Amer. Proc. 21:521-524.

Bohn, H., B. McNeal, and G. O'Connor (1979) Soil chemistry. John Wiley and Sons, New York, NY. 329 pp.

Bray, R. H. and L. T. Kurtz (1945) Determination of total organic and availalbe forms of phosphorus in soils. Soil Sci. 59:39-45.

Caro, J. H. and W. L. Hill (1956) Characteristics and fertilizer value of phosphate rock from different fields. J. Agr. and Food Chem. 4:684-687.

Cescas, M. P. and E. H. Tyner (1976) Rate of rock phosphate disappearance for the Morrow plots. Annales Agronomiques 27(5-6): 891-924.

Chavveri, J. G. and C. A. Black (1966) Theory of the solubility of phosphate rock. Iowa State J. Sci. 41:77-95.

Chien, S. H. (1977) Thermodynamic considerations on the solubility of phosphate rock. Soil Sci. 123:117-121.

Chien, S. H. (1978) Interpretation of Bray I extractable phosphorus from acid soil treated with phosphate rocks. Soil Sci. 126: 34-39.

Chien, S. H. and C. A. Black (1975) Activity concept of phosphate rock solubility. Soil Sci. Soc. Amer. Proc. 39(5):856-858.

Chien, S. H. and C. A. Black (1976) Free energy of formation of some carbonate apatites in phosphate rocks. Soil Sci. Soc. Amer. J. 40:234-239.

Chien, S. H. and L. L. Hammond (1978) A comparison of various laboratory methods for predicting the agronomic potential of phosphate rocks for direct application. Soil Sci. Soc. Am. J. 42:935-939.

Chu, C. R., W. W. Moschler, and G. W. Thomas (1962) Rock phosphate transformations in acid soils. Soil Sci. Soc. Amer. Proc. 26: 476-478.

Cook, R. L. (1935) Divergent influence of degree of base saturation of soils on the availability of native, soluble, and rock phosphate. J. Am. Soc. Agron. 27:297-311.

Dahnke, W. C., ed. (1980) Recommended chemical soil test procedures for the North Central Region. North Dakota State Univ., Fargo, ND. Bulletin No. 499 (Revised). 33 pp.

de Wit, C. T. (1953) A physical theory on placement of fertilizers. Verslagen van Landbouwkundige Onderzoekingen 59:4.

Doak, B. W., R. J. Gallaher, L. Evans, and E. B. Muller (1965) Low temperature calcination of "C"-grade phosphate from Christmas Island. N.Z. J. Agric. Res. 8:15-29.

Drake, M. and J. E. Steckel (1955) Solubilization of soil and rock phosphate as related to root cation-exchange capacity. Soil Sci. Soc. Amer. Proc. 19:449-450.

Duncan, D. B. (1965) A Baysian approach to multiple comparisons. Technometrics 7:171-222.

Dynia, J. F. (1977) Efeito do pH e da capacidade de retencao de fosforo dos solos na eficiencia de adubos fosfatados. M.S. Thesis, Univ. Federal do Rio Grande do Sul, Porto Alegre, Brasil. 61 pp.

Ellis, R., Jr., M. A. Quader, and E. Truog (1955) Rock phosphate availability as influenced by soil pH. Soil Sci. Soc. Amer. Proc. 19:484-487.

Englestad, O. P., A. Jugsujinda, and S. K. De Datta (1974) Response by flooded rice to phosphate rocks varying in citrate solubility. Soil Sci. Soc. Am. Proc. 38:524-529.

Ford, M. C. (1932) The distribution, availability, and nature of the phosphates in certain Kentucky soils. J. Am. Soc. Agron. 25: 395-410.

Fox, R. L. (1978) Studies on phosphorus nutrition in the tropics. In: C. S. Andrew and E. J. Kamprath, eds. Mineral nutrition of legumes in tropical and subtropical soils. pp. 169-187.

Fox, R. L. and E. J. Kamprath (1970) Phosphate sorption isotherms for evaluating the phosphate requirements of soils. Soil Sci. Soc. Amer. Proc. 34:902-906.

Fox, R. L., R. K. Nishimoto, R. S. Thompson, and R. S. de la Pena (1974) Comparative external phosphorus requirements of plants growing in tropical soils. Int. Congr. Soil Sci., Trans. 10th (Moscow) 4:232-239.

Fox, R. L., J. A. Silva, D. Y. Teranishi, M. Masuda, and P. Ching (1967) Silicon in soils, irrigation water and sugarcane of Hawaii. Hawaii Farm Sci. 16:1-4.

Foy, C. D. (1976) General principles involved in screening plants for aluminum and manganese tolerance. In: M. J. Wright, ed. Plant adaption to mineral stress in problem soils. Cornell Univ. Ag. Exp. Sta., Ithaca, NY. pp. 255-267.

Foy, C. D. and J. C. Brown (1964) Toxic factors in acid soils: II. Differential aluminum tolerance of plant species. Soil Sci. Soc. Am. Proc. 28:27-32.

Fried, M. and A. J. Mackenzie (1950) Rock phosphate studies with neutron irradiated rock phosphate. Soil Sci. Soc. Am. Proc. 14:336-231.

Graham, E. R. (1955) Availability of natural phosphorus according to energy changes. Soil Sci. Soc. Amer. Proc. 19:26-29.

Hammond, L. L. (1978) Agronomic measurements of phosphate rock effectiveness. In: Seminar on phosphate rock for direct application. IFDC, Muscle Shoals, AL. pp. 147-173.

Hanway, J. J. (1962) Corn growth in relation to soil fertility. II. Uptake of N, P, and K and their distribution in different plant parts in relation to stage of growth. Agron. J. 54:217-222.

Harris, D. J. (1975) Characterization of zinc and iron in limed Chalmers soil using synthetic chelates. Purdue Univ. Agronomy Dept., Lafayette, IN. M.S. Thesis. 80 pp.

Helwig, J. T. and K. A. Council, eds. (1979) SAS user's guide, 1979 ed., SAS Institute Inc., Cary, NC. 494 pp.

Hendricks, S. B., W. L. Hill, K. D. Jacob, and M. E. Jefferson (1931) Structural characteristics of apatite-like substances and composition of phosphate rock and bone as determined from microscopical and X-ray diffraction examinations. Indus. and Engin. Chem. J. 23:1413-1418.

Hingston, F. J., A. M. Posner, and J. P. Quirk (1972) Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. J. Soil Sci. 23:177-192.

Hsu, P. H. and M. L. Jackson (1960) Inorganic phosphate transformations by chemical weathering in soils as influenced by pH. Soil Sci. 90:16024.

IFDC (1982) Annual Reort, 1981. International Fertilizer Development Center, Muscle Shoals, AL.

Ikawa, H. (1979) Laboratory data and descriptions of soils of the Benchmark Soils Project, Vol. 1 - Hawaii Project. Haw. Ag. Expr. St., Mics. Pub. 165 (BSP Tech Rep. 1). 37 pp.

Joos, L. L. and C. A. Black (1950) Availability of phosphate rock as affected by particle size and contact with bentonite and soil of different pH values. Soil Sci. Soc. Amer. Proc. 15:69-75.

Khasawneh, F. E. and E. C. Doll (1978) The use of phosphate rock for direct application to soils. Adv. Agron. 39:159-206.

Lehr, J. R. and G. H. McClellan (1972) A revised laboratory reactivity scale for evaluating phosphate rocks for direct application. Tennessee Valley Authority, Muscle Shoals, AL. Bulletin 4-43.

Lindsay, W. L. (1979) Chemical equilibria in soils. John Wiley and Sons, New York, NY. 449 pp.

Lindsay, W. L. and H. F. Stephenson (1959) Nature of the reactions of monocalcium phosphate monohydrate in soils: I. The solution that reacts with the soil. Soil Sci. Soc. Amer. Proc. 23:12-18.

Lipman, J. G., H. C. McLean, and H. C. Lint (1916) Sulfur oxidation in soils and its effect on the availability of mineral phosphate. Soil Sci. 2:499-538.

Livingston, W. O. (1978) Minigranulation: a method for improving the properties of phosphate rock for direct application. In: Seminar on phosphate rock for direct aplication. IFDC, Muscle Shoals, AL. pp. 367-373.

Lukman Hakim S., Mursidi S., and Djoko Santoso (1980) Effectiveness of sources of phosphate and their residual effects. (In Bahasa Indonesia.) Center for Soil Research, Bogor, Indonesia.

McClellan, G. H. and L. R. Gremillion (1980) Evaluation of phosphatic raw materials. In: Khasawneh, F. E., E. C. Sample and E. J. Kamprath, eds. The role of phosphorus in agriculture. Am. Soc. Agron., Madison, WI. pp. 43-80.

McClellan, G. H. and J. R. Lehr (1969) Crystal chemical investigation of natural apatites. Am. Mineral. 54:1374-1391.

McLean, E. O. and T. J. Logan (1970) Source of phosphorus for plants grown in soils with different phosphorus fixation tendencies. Soil Sci. Soc. Am. Proc. 34:907-911.

Mitscherlich, E. A. (1909) Das Gesetz des Minimums und das Gesetz des abnehmenden Bodenertrages. Landwirtschaftliche Jahrbucher 38:537-552.

Paauw, F. (1965) Factors controlling the efficiency of rock phosphates for potatoes and rye on humic sandy soils. Plant Soil 22:81-98.

Peaslee, D. E., C. A. Anderson, G. R. Burns, and C. A. Black (1962) Estimation of relative value of phosphate and superphosphate to plants on different soils. Soil Sci. Soc. Amer. Proc. 26:566-570.

Plucknett, D. L. (1972) The use of soluble silicates in Hawaiian agriculture. Univ. of Queensland, Brisbane, Australia. Papers 1:203-223.

Rajan, S. S. S. and R. L. Fox (1975) Phosphate adsorption by soils. II. Reactions in tropical acid soils. Soil Sci. Soc. Am. Proc. 39:846-851.

Russell, E. W. (1973) Soil conditions and plant growth, 10th ed. Longman Group, Ltd., London. p. 587-588.

Sall, J. (1981) SAS regression applications. SAS Inst. Technical Report No. A-102 SAS Institute, Inc., Cary, NC.

Sanchez, P. A. and Goro Uehara (1980) Management considerations for acid soils with high phosphorus fixation capacity. In: E. C. Sample and E. J. Kamprath, eds. The role of phosphorus in agriculture. Am. Soc. Agron., Madison, WI.

Schaller, W. T. (1912) Mineralogical notes, Series 2. The composition of the phosphorite minerals. In: U. S. Geo. Surv. Bull. No. 509. p. 98.

SCS-USDA (1972) Soil survey laboratory methods and procedures for collecting soil samples. Soil Survey Investigation Report No. 1, U. S. Gov. Printing Office, Washington, DC. 63 pp.

Silverman, S. R., R. K. Fugat, and J. D. Weiser (1952) Quantitative determination of calcite associated with carbonate-bearing apatites. Amer. Mineral. 37:211-222.

Slack, A. V. (1968) Thermal and miscellaneous phosphate processes. In: Fertilizer developments and trends. Noyes Development Crop., Park Ridge, NJ. pp. 311-320.

Smyth, T. J. and P. A. Sanchez (1982) Phosphate rock dissolution and availability in Cerrado soils as affected by phosphorus sorption capacity. Soil Sci. Soc. Am. J. 46:339-345.

Soil Survey Staff (1975) Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA-SCS Ag. Hdbk. No. 436. U. S. Gov. Printing Of., Washington, DC. 754 pp.

Stangel, P. J. (1978) The IFDC phosphate program. In: Seminar on phosphate rock for direct application. IFDC, Muscle Shoals, AL. pp. 3-35.

Steele, R. G. D. and J. H. Torrie (1960) Principles and procedures of statistics. McGraw-Hill Book Co., Inc., New York, NY. 481 pp.

Terman, G. L. and S. E. Allen (1967) Response of corn to phosphorus in under acidulated phosphate rock and rock-superphosphate fertilizers. J. Agric. Food Chem. 15:354-358.

Terman, G. L., V. J. Kilmer, and S. E. Allen (1969) Reactivity of phosphate rock with acids in relation to effectiveness for crops. Phosphorus Agric. 54:1-9.

Tinker, P. B. (1975) Soil chemistry of phosphorus and mycorrhizal effects on plant growth. In: F. E. Sanders, B. Mosse, and P. B. Tinker, eds. Endomycorrhizas. Academic Press, New York, NY. pp. 353-371.

Truog, E. (1916) The utilization of phosphate by agricultural crops, including a new theory regarding the feeding power of plants. Wis. Agr. Exp. Sta., Res. Bull. No. 41.

Uehara, G. and G. Gillman (1981) The mineralogy, chemistry, and physics of tropical soils with variable charge clays. Westview Press, Boulder, CO. 170 pp.

Wann, S. S. and G. Uehara (1978) Surface charge manipulation in constant surface potential soil collids: I. Relation to sorbed phosphorus. Soil Sci. Soc. Am. J. 42:565-570.

Wier, D. R., S. H. Chien, and C. A. Black (1971) Solubility of hydroxyapatite. Soil Sci. 111:107-112.

Wright, B. C. and M. Peech (1960) Characterization of phosphate reaction products on acid soils by the application of solubility criteria. Soil Sci. 90:32-43.