1985

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Recommended Citation

Ali, Mohamed, "Comparison of Two Phosphorus Tests on Calcareous Soils of Eastern South Dakota" (1985). *Electronic Theses and Dissertations*. 5689.
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COMPARISON OF TWO PHOSPHORUS TESTS ON CALCAREOUS SOILS OF EASTERN SOUTH DAKOTA

by

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A thesis submitted in partial fulfillment
of the requirements for the degree
Master of Science,
Major in Agronomy
South Dakota State University
March 1985

COMPARISON OF TWO PHOSPHORUS TESTS ON CALCAREOUS SOILS OF EASTERN SOUTH DAKOTA

This thesis is approved as a creditable and independent investigation for the degree, Master of Science, and is acceptable as meeting thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

[redacted]

Dr. Paul Fixen Date
Thesis and Major Advisor

[redacted]

Dr. Maurice L. Horton Date
Head, Plant Science Department

وَجَعَلْنَا مِنَ الْمَآءِ كُلَّ شَيْءٍ حَيٍّ

We made every living thing of water."

(21:30)

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. Paul Fixen for advice, guidance, encouragement and assistance given while serving as major advisor. Dr. Fixen was always available when I needed help or direction. The author also wishes to extend his gratitude to Dr. Robert Kohl, whom he started out with. Appreciation is also extended to the other members of my graduate committee: Dr. Jerry Myers and Dr. Ruth Foreman.

The author wishes to acknowledge the following people who assisted him in this research: Paul Carson, Ron Gelderman, Dara Islam, Brian Hilton, Brad Farber, Dale Sorenson, Bob Nettleton, Lauri Mattinen, Phil Hansen, Rose Neal, Marcia Casper, and Lu Ann Anderson. Special appreciation to the staff and students of the Plant Science Department as a whole.

The author is also grateful to Kathy McKinley at the Graduate School for the help she gives to International students. Special thanks goes to Cathy Haan for finishing the typing on so short a notice.

I would also like to thank my mother, brother and his wife, and first cousin all in Riyadh, Saudi Arabia, for their patience, encouragement and support throughout my studies.

BROOKINGS IS SOMEPLACE SPECIAL.

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CHAPTER 1

INTRODUCTION

Phosphorus is an important nutrient in crop production, since many soils in their native state do not contain sufficient available phosphorus to maximize crop yield. Now, more than ever, the importance of an adequate supply of plant nutrients to insure sufficient crop production is being recognized. Soil scientists and agronomists are continually striving to overcome nutrient deficiencies as well as use improved management practices in order that yields may more nearly approach the genetic limit of crop plants.

Phosphorous forms sparingly soluble compounds with divalent and trivalent cations in soils. Therefore, the amount of P in the soil solution at any one time is very small. Plants growing in the soil apparently absorb P only from the soil solution. The limiting soil factor in P uptake by plants is likely to be renewal of the P in the soil solution near the plant roots by processes of dissolution, desorption and diffusion. The factors involved in renewal of soil solution P are the amount of P which can be solubilized, solubility, and the rate of P diffusion from the solid surface to the plant root surface.

Thus, unless the soil contains adequate P or P is supplied to soil from external sources, plant growth will be restricted. South Dakota soils are frequently low in P due to crop removal and low indigenous levels. A successful and reliable soil testing method is, therefore, essential for predicting P need before crops are seeded.

Several Midwest soil testing laboratories base their P fertilizer recommendations on the modified Bray & Kurtz 1 (weak acid) soil test. The Olsen method is also frequently used for P determination for more alkaline soils. These tests have been evaluated in many states and several countries; results of greenhouse studies varied from no difference between tests (2, 53, 106, 109) to significant advantage for the Bray & Kurtz-1 (67) or in other studies significant advantage for the Olsen test (93).

Much less work under field conditions has been reported. In such cases, correlations have generally been quite low. Olsen et al. (71) reported correlation coefficients of 0.63 and 0.58 for Bray & Kurtz-1 and Olsen tests respectively with percent yield increase for 40 wheat experiments in Nebraska.

Research with calcareous soils shows that widening the soil to solution ratio of the Bray & Kurtz (Bray) extracting reagent results in higher correlations with yield response. In other instances grouping the soils by genetic origin has increased the resulting correlations (57). Consideration of climatic factors has also improved the correlation between these soil tests and yield response (17, 68, 74).

Fixen and Carson (28) compared the Bray (soil to solution ratio of 1:7, 1:10, 1:20, and 1:50) and Olsen P. Results of 74 South Dakota small grain field experiments over a 13-year period indicated the modified Bray, 1:50, was the soil test most highly correlated with yield response.

The objectives of this study were:

(1) To determine the influence of P additions under field conditions on Bray and Kurtz-1 and Olsen test levels for alkaline soils in eastern South Dakota.

(2) To determine the effects of various soil factors on P extracted by the two tests.

(3) To determine the relationship between P extracted and crop yield response in alkaline soils of eastern South Dakota.

CHAPTER 2

REVIEW OF LITERATURE

Phosphate deficiency is of world-wide importance as a factor limiting crop production. Methods for determining soil P and its various forms and plant availability have been essential for understanding the nature and behavior of P in the soil system. The total P content in soils is relatively low. The P contained in the plow depth of soil ranges normally between 0.025 and 0.125 %, with an average of about 0.06 % (9). According to Jackson (42) the P content of most mineral soils falls between 0.02 and 0.5 % P. An average of 0.05 % (0.12 % P_2O_5) frequently is representative of soils compared to an average of 0.12 % in the earth's crust. About 50% of the soil P occurs in combination with organic matter in surface soils, and the remainder occurs in mineral or inorganic combinations.

The amount of total P in the soil is not necessarily a good measure of the amount that is available for growth because a large proportion of the P may exist in forms that are difficult to utilize. When P is added in dilute solution or in salts of near neutral pH, there appears to be an initial adsorption of phosphate ions by a number of different solids. These may include $CaCO_3$, Fe and Al oxides and clay minerals. Soil phosphate reacts with soil to form less soluble products almost immediately. With time these products become even more insoluble, reacting with Ca in calcareous soils and with Al and Fe in neutral to acid soils.

A. Phosphate Minerals and their Stability

The reactions of phosphates in soils have been studied intensively and almost continuously since chemistry began to play its role in soil science. Knowledge of the chemistry of P in soils is a requirement for knowledge of its utilization by plants, and explanations of soil-plant relations will be clear only when the forms and properties of soils are known.

Soil P is considered primarily under two classes, organic and inorganic, depending on the nature of the compounds in which it occurs. The organic fraction is found in humus and other organic materials which may or may not be associated with it. The inorganic fraction, which we are going to emphasize in this study since it is generally the prediction measurement in the laboratory, almost without exception, exists as salts of orthophosphoric acid. These salts can be classed generally as fluoro-, oxy- and hydroxy-phosphates of iron, aluminum, calcium, titanium, magnesium, and manganese (36). The calcium phosphates constitute a series, ranging from the relatively soluble mono- and di-calcium phosphates, which are present only in small amounts, to relatively insoluble hydroxyapatite and fluorapatite. Iron and aluminum phosphates probably exist in soils largely as basic compounds such as in the minerals variscite and strengite, which are insoluble except under neutral or alkaline conditions. There is also evidence that some inorganic P in soils may be combined with clay minerals.

In general, solubility studies have shown that the inorganic phosphates of iron and aluminum tend to accumulate in acid soils whereas calcium phosphates are predominant in neutral or alkaline soils.

Much research has been done to learn how P behaves in soils and how it is affected by the different degrees of acidity in the soil (expressed in terms of pH). In general, P is more available at a pH of 6.0 to 6.5 than at higher or lower pH values. At a soil pH above 6.5, fertilizer P tends to be precipitated by calcium and magnesium. At a soil pH of 5.0 or below, fertilizer P is precipitated with aluminum and iron.

1. Phosphate Species in Soil Solutions

The amount of phosphate present in the soil solution is very low in comparison with adsorbed phosphate. Adsorbed phosphate exceeds the phosphate of the solution by a factor of 10^2 to 10^3 (64). The phosphate concentration of the soil solution itself is very dilute and in fertile arable soils is about 0.3 to 3 ppm P. Phosphate ion concentrations are affected by the presence of several cations which favor the formation of a series of compounds of varying solubility (Table 1).

It has been shown that orthophosphate is the stable form of P in soils. For this reason orthophosphoric acid provides a good starting point for considering P reactions in soils. The dissociation reactions of orthophorphoric acid are given by Reactions 1 through 5 of Table 1. The relative abundance of the different orthophosphoric acid species as a function of pH is plotted in Figure 1.

Table 1. Equilibrium constants for various phosphate reactions at 25°C (Lindsay, 1979).

Reaction #	Equilibrium Reaction	log K
	Orthophosphoric Acid	
1	$H_3PO_4^\circ \rightleftharpoons H^+ + H_2PO_4^-$	−2.15
2	$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$	−7.20
3	$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	−12.35
4	$H_2PO_4^- \rightleftharpoons 2H^+ + PO_4^{3-}$	−19.55
5	$2H_2PO_4^- \rightleftharpoons (H_2PO_4)_2^{2-}$	−0.35
	Orthophosphate Complexes	
6	$Fe^{2+} + H_2PO_4^- \rightleftharpoons FeH_2PO_4^+$	2.70
7	$Fe^{3+} + H_2PO_4^- \rightleftharpoons FeH_2PO_4^{2+}$	5.43
8	$Fe^{2+} + H_2PO_4^- \rightleftharpoons FeHPO_4^\circ + H^+$	−3.60
9	$Fe^{3+} + H_2PO_4^- \rightleftharpoons FeHPO_4^+ + H^+$	3.71
10	$Ca^{2+} + H_2PO_4^- \rightleftharpoons CaH_2PO_4^+$	1.40
11	$Ca^{2+} + H_2PO_4^- \rightleftharpoons CaHPO_4^\circ + H^+$	−4.46
12	$Ca^{2+} + H_2PO_4^- \rightleftharpoons CaPO_4^- + 2H^+$	−13.09
13	$Mg^{2+} + H_2PO_4^- \rightleftharpoons MgHPO_4^\circ + H^+$	−4.29
	Calcium Phosphates	
14	$Ca(H_2PO_4)_2 \cdot H_2O$(MCP) $\rightleftharpoons Ca^{2+} + 2H_2PO_4^- + H_2O$	−1.15
15	$CaHPO_4 \cdot 2H_2O$(brushite) $+ H^+ \rightleftharpoons Ca^{2+} + H_2PO_4^- + 2H_2O$	0.63
16	$CaHPO_4$(monetite) $+ H^+ \rightleftharpoons Ca^{2+} + H_2PO_4^-$	0.30
17	$Ca_4H(PO_4)_3 \cdot 2.5H_2O$(octacalcium phosphate) $+ 5H^+ \rightleftharpoons 4Ca^{2+} + 3H_2PO_4^- + 2.5H_2O$	11.76
18	α-$Ca_3(PO_4)_2$(c) $+ 4H^+ \rightleftharpoons 3Ca^{2+} + 2H_2PO_4^-$	13.61
19	β-$Ca_3(PO_4)_2$(c) $+ 4H^+ \rightleftharpoons 3Ca^{2+} + 2H_2PO_4^-$	10.18
20	$Ca_5(PO_4)_3OH$(hydroxapatite) $+ 7H^+ \rightleftharpoons 5Ca^{2+} + 3H_2PO_4^- + H_2O$	14.46
21	$Ca_5(PO_4)_3F$(fluorapatite) $+ 6H^+ \rightleftharpoons 5Ca^{2+} + 3H_2PO_4^- + F^-$	−0.21
	Magnesium Phosphates	
22	$MgHPO_4 \cdot 3H_2O$(newberryite) $+ H^+ \rightleftharpoons Mg^{2+} + H_2PO_4^- + 3H_2O$	1.38
23	$MgKPO_4 \cdot 6H_2O$(c) $+ 2H^+ \rightleftharpoons Mg^{2+} + K^+ + H_2PO_4^- + 6H_2O$	8.93
24	$MgNH_4PO_4 \cdot 6H_2O$(struvite) $+ 2H^+ \rightleftharpoons Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O$	6.40
25	$Mg_3(PO_4)_2$(c) $+ 4H^+ \rightleftharpoons 3Mg^{2+} + 2H_2PO_4^-$	24.51
26	$Mg_3(PO_4)_2 \cdot 8H_2O$(bobierrite) $+ 4H^+ \rightleftharpoons 3Mg^{2+} + 2H_2PO_4^- + 8H_2O$	14.10
27	$Mg_3(PO_4)_2 \cdot 22H_2O$(c) $+ 4H^+ \rightleftharpoons 3Mg^{2+} + 2H_2PO_4^- + 22H_2O$	16.01

Table 1. (continued)

Reaction #	Equilibrium Reaction	log K
	Aluminum Phosphates	
28	$AlPO_4$(berlinite) + $2H^+ \rightleftharpoons Al^{3+} + H_2PO_4^-$	0.50
29	$AlPO_4 \cdot 2H_2O$(variscite) + $2H^+ \rightleftharpoons Al^{3+} + H_2PO_4^- + 2H_2O$	−2.50
30	$H_6K_3Al_5(PO_4)_8 \cdot 18H_2O$(K-taranakite) + $10H^+ \rightleftharpoons 3H^+ + 5Al^{3+} + 8H_2PO_4 + 18H_2O$	−22.30
31	$H_6(NH_4)_3Al_5(PO_4)_8 \cdot 18H_2O$($NH_4$-taranakite) + $10H^+ \rightleftharpoons 3NH_4^+ + 5Al^{3+} + 8H_2PO_4 + 18H_2O$	−19.10
	Iron Phosphates	
32	$FePO_4$(c) + $2H^+ \rightleftharpoons Fe^{3+} + H_2PO_4$	−5.37
33	$FePO_4 \cdot 2H_2O$(strengite) + $2H^+ \rightleftharpoons Fe^{3+} + H_2PO_4^- + 2H_2O$	−6.85
34	$Fe_3(PO_4)_2 \cdot 8H_2O$(vivianite) + $4H^+ \rightleftharpoons 3Fe^{2+} + 2H_2PO_4^- + 8H_2O$	3.11

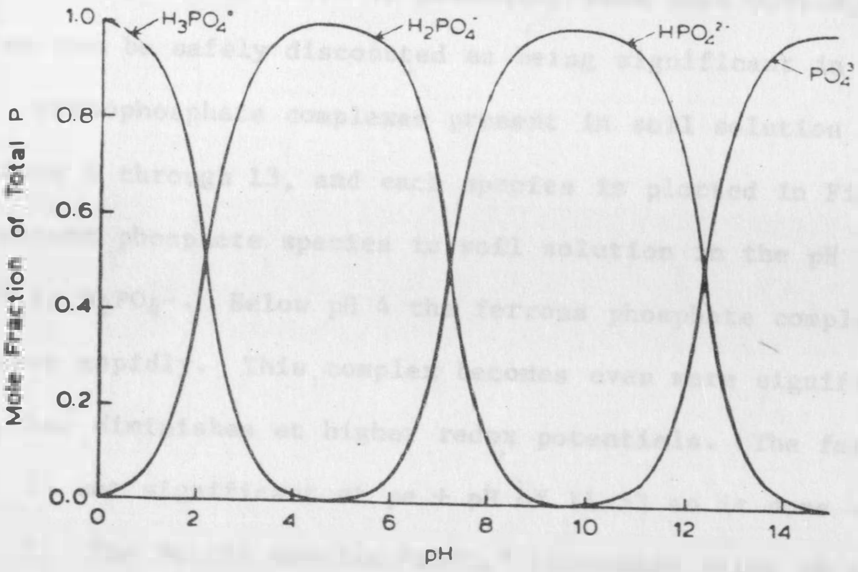

Figure 1. Effect of pH on the distribution of orthophosphate ions in solution.

In concentrated phosphate solutions, two $H_2PO_4^-$ ions combine to form the dimer $(H_2PO_4)^{2-}$ according to reaction 5 of Table 1. For solutions containing 0.01 M H_2PO_4, the dimer constitutes 1% of the total P. Since total P in soils is generally less than 0.01 M, the dimer species can be safely discounted as being significant in soils.

Orthophosphate complexes present in soil solution are given by reactions 6 through 13, and each species is plotted in Figure 2. The predominant phosphate species in soil solution in the pH range of 3.5 to 7.0 is H_2PO_4-. Below pH 4 the ferrous phosphate complex, FeH_2PO_4, increases rapidly. This complex becomes even more significant at lower redox, but diminishes at higher redox potentials. The ferrous complex $FeHPO_4$ is not significant at pe + pH of 11.53 so it does not appear in Figure 2. The ferric complex $FeHPO_4^+$ increases below pH 4, whereas the line for FeH_2PO_4 barely touches the lower left-hand corner of this diagram.

At higher pH, calcium and magnesium complexes become important. In fact $CaHPO_4$ comprises 0.42 of the total phosphorus in solution at pH 7.8 compared to 0.24 for HPO_4^{2-} and 0.20 for $MgHPO_4$. At pH values above 8, $CaPO_4$- rapidly becomes important, but the presence of $CaCO_3$ (calcite) can be expected to reduce this ion.

It is obvious from Figure 2 that solution complexes must be considered in estimating phosphate activities from total phosphorus in solution. Computer programs can be developed to estimate solution complexes from elemental analyses of the soil solution. Ionic strength estimates also can be made to convert from concentrations to activities. To do this, it is necessary to recognize the major solution

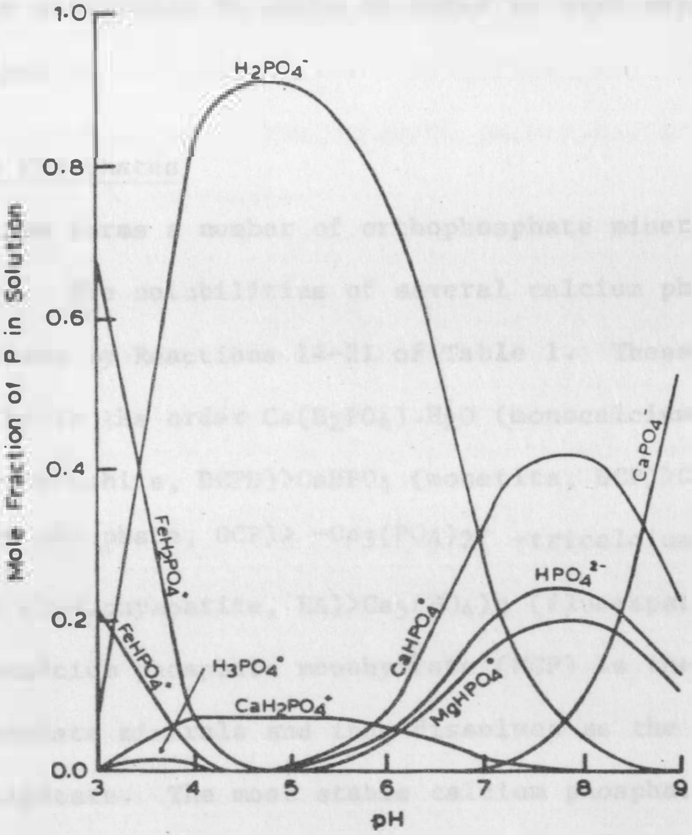

Figure 2. The effect of pH on the phosphate species in soil solution when $Ca^{2+} = 10^{-2.5}$ M, $Mg^{2+} = 10^{-3}$ M, Fe^{3+} is controlled by soil-Fe and redox is set at pe + pH of 11.53.

complexes and have reliable formation constants for them. Specific ion electrodes can be used to measure directly the activities of certain ions, but further investigations are needed to obtain reliable estimates of ion activities in soils in order to test important solubility relationships.

2. Calcium Phosphates

Calcium forms a number of orthophosphate minerals with varying solubilities. The solubilities of several calcium phosphates found in soils are given by Reactions 14-21 of Table 1. These generally decrease in solubility in the order $Ca(H_2PO_4).H_2O$ (monocalcium phosphate, MCP)> $CaHPO_4.2H_2O$ (brushite, DCPD)>$CaHPO_4$ (monetite, DCP)>$Ca_8H^2(PO_4)_6.5H_2O$ (octocalcium phosphate, OCP)> $-Ca_3(PO_4)_2$(-tricalcium phosphate, TCP)> $Ca_5(PO_4)_3OH$ (hydroxyapatite, HA)>$Ca_5(PO_4)_3$ (fluorapatite, FA).

Monocalcium phosphate monohydrate (MCP) is the least stable of calcium phosphate minerals and thus dissolves as the more stable compounds precipitate. The most stable calcium phosphate mineral in this group is fluorapatite, given that CaF_2 (fluorite) fixes F^- activity.

3. Magnesium Phosphates

Magnesium forms a number of orthophosphate minerals similar to those of calcium. The solubilities of several of these magnesium phosphates are given by Reactions 22-27 of Table 1. All of the magnesium phosphates represented here are more soluble than DCPD and OCP (52).

Magnesium phosphates have been found as initial reaction products of phosphate fertilizers in soils (53, 99, 97), but they later disappear as more stable minerals are formed. Magnesium phosphates can be discounted as permanent fixation products of P in soils. Instead, those phosphates should constitute useful fertilizers for supplying readily available P to plants. Struvite ($MgNH_4PO_4.6H_2O$) is readily available to plants (54). The other Mg phosphates are also expected to be highly available to plants.

4. Aluminum and Iron Phosphates

It is commonly believed that in soils below pH 5.0 soluble Al and Fe will react with added fertilizer P to form slightly soluble compounds. This reaction can be represented by this equation:

$$M^{3+} + H_2PO_4 + 2H_2O \longrightarrow M(OH)2H_2PO_4 + 2H^+$$

where M stands for Al or Fe.

Cole and Jackson (18) identified these compounds as aluminum/ferric dihydroxyl dihydrogen phosphate, variscite and strengite respectively. The solubilities of several of the Al and Fe phosphates are given in Reactions 28-34 of Table 1. The solubilities of the aluminum phosphate minerals decrease in the order $AlPO_4$ (berlinite $H_6N(NH_4)_3Al_5(PO_4)_8.18H_2O$ (NH_4-taranakite) > $H_6K_3Al_5(PO_4)_8.18H_2O$ (NH_4-taranakite) > $AlPO_4.2H_2O$ (variscite).

Lindsay (51) found that in some acid soils $AlPO_4.2H_2O$ (variscite) is the most stable mineral followed by $FePO_4.2H_2O$ (strengite, ST), $H_6K_3Al_5(PO_4)_8.18H_2O$ (potassium taranakite), and $H_6(NH4)3Al_5(PO_4).18H_2O$ (aluminum taranakite), respectively.

B. Mechanisms of Phosphate Fixation

The fixation of phosphate by soils has been demonstrated by many researchers. Fixation of plant nutrients in soils may be defined as the process whereby readily soluble plant nutrients are changed to less soluble forms by reaction with inorganic or organic components of the soil. The result is a decrease in mobility in the soil and a decrease in availability to the plant.

The types of reactions by which P becomes fixed can be placed in three general groups: adsorption, isomorphous replacement, and double decomposition involving solubility product relations. In all of the reactions the P is involved as one or more of the ionic forms into which orthophosphoric acid may disassociate. All phosphate reactions are fundamentally influenced by the hydrogen ion activity in the systems.

1. Adsorption Reactions

Phosphate adsorption is taken to mean the retention of phosphate at a surface. Davis (24) stated that phosphates penetrate the liquid-solid phase interface to form new compounds with the hydrated minerals that are in equilibrium with the hydrated minerals and phosphate compounds.

According to Kurtz et al. (47) the amount of P taken up by soils is proportional to the P concentration. Low and Black (56) found that the degree of adsorption was increased by increasing temperature.

Pissarides et al. (79) suggested that P is retained by adsorption on the surface of clay minerals, most likely on the edge surfaces.

The exchangeable cations influenced the extent of P adsorption by controlling the accessibility of the edge clay surfaces to phosphate ions.

Scarseth (86) studied the mechanism of phosphate retention by bentonite as a function of pH in the presence of calcium or sodium cations. Maximum retention occurred between pH 5.2 and 6.1 when Ca ions were the exchangeable cations and at about pH 6.1 when the Na ions were present. The Ca ions greatly increased the phosphate sorption capacity of the clay. The explanation given to this was that the phosphate ions were held by the Ca present as exchangeable Ca.

The retention of P by the exchange or substitution of phosphate ions has been suggested by many researchers (86, 92, 44, 45, 65, 81). An increase in pH accompanies the disappearance of phosphate ions from solution when the clay suspension and a phosphate solution of similar pH are mixed.

2. Retention by Absorption

Phosphate absorption is taken to mean the retention of phosphate within a solid phase. Many researchers have suggested phosphate sorption on soil colloids by displacement of silicon (56, 59, 85, 102). However, none of these studies explained whether the released silicon had existed as adsorbed or structural silicon. Other researchers working with allophane (amorphous aluminosilicate) clay samples have found that phosphate displaces the adsorbed and structural silicon at low and high P concentrations, respectively (81, 83).

3. Retention by Precipitation

Precipitation of phosphates refers to the removal of phosphate ions from solution and their chemical bonding in the solid phase. The reactions of phosphate with the sesquixodes of iron and aluminum, either by solution or chemical precipitation or by surface adsorption, have long been considered important factors in the fixation of P in acid soils (25, 41, 45).

Results from a study of potentiometric titrations by Swenson et al (94) indicate that for each metal ion two hydroxyls and one phosphate ion reacted to give a basic phosphate represented by the formulas $Al(H_2O)_3(OH)_2H_2PO_4$ and $Fe(H_2O)_3(OH)_2H_2PO_4$ at the pH range of acid soils dominated by $H_2PO_4^-$.

Cole and Jackson (19) concluded that the capacity of acid soils to retain P is largely due to precipitation of variscite. Hsu (41) instead suggested that phosphate is fixed as variscite or strengite-type compounds only in the vicinity of a fertilizer particle due to localized high acidity and high phosphate concentration. The precipitated phosphate cannot be considered stable, and upon dilution by soil moisture, will become adsorbed by amorphous aluminum hydroxides and iron oxides which are more stable.

Haseman et al. (34) studied the rate of fixation of P by individual clays and hydrous oxides of Fe and Al under various conditions of temperature, pH and concentration of phosphate. They demonstrated the capacity of concentrated solutions being released by dissolving fertilizers to attack clays and oxides of Fe and Al with the formation of various phosphates of Fe and Al. Lindsay and Stephenson (54) showed that monocalcium phosphate dissolves in soils and precipitates to form $CaHPO_4.2H_2O$, $H_6K_3Al_5(PO_4)8.18H_2O$ $H_8K(Al, Fe)3(PO_4)6.6H_2O$, and $CaHPO_4$.

Buehrer (16), studying the physico-chemical relationships of soil phosphates, concluded that the phosphate concentration is directly proportional to the hydrogen ion concentration and inversely proportional to the calcium ion concentration. Boischot et al. (12) demonstrated a surface sorption of P on $CaCO_3$ particles at low concentrations, and a precipitation reaction at higher concentrations. They concluded that in calcareous soils phosphate precipitates are formed initially in the neighborhood of soluble fertilizer granules, but that these precipitates redissolve and the P gradually becomes distributed over the surfaces of $CaCO_3$ particles. Cole et al. (20) indicated that when soluble phosphate fertilizers are added to calcareous soils, the reactions with $CaCO_3$ consist of rapid monolayer sorption on $CaCO_3$ surfaces and, at high phosphate concentrations, the precipitation of dicalcium phosphate.

Chang and Jackson (18) showed that when phosphate fertilizer is added to calcareous soils calcium aluminum phosphates are more likely to be formed than iron phosphates. This is attributed to the relatively higher activities in the soil of calcium and aluminum ions than iron ions, which are controlled by the activities of the respective cations of calcium carbonate, alumino-silicates and gibbsite, and iron oxides.

C. Soil Properties and Phosphate Sorption

Evidence has been presented that soils have several different sorption surfaces for phosphate (36, 107). These sorption surfaces include the iron and aluminum oxides and hydroxides, the calcium and magnesium minerals (mainly in calcareous soils); iron and aluminum on the exchange sites of clay minerals silica hydrogel of quartz, manganese, and titanium; and iron, aluminum, and calcium ions associated with the organic matter.

1. Free Sesquioxides and P Sorption

The retention of phosphate by soil has been demonstrated by many researchers and is affected by many factors. These factors include the mechanical composition of the soil, phosphate concentration, temperature, time of reaction, and effect of salts (107). Kittrick and Jackson (45) suggest that formation and growth of separate-phase phosphate precipitates of varying composition controlled by solubility product principles provides a unified theory of phosphate fixation of phosphate reactions in Fe, Al, and Ca soil systems.

Bache (6) in a study on the sorption of phosphate on to gibbsite and hydrous ferric oxide has shown three stages to the reaction: (i) a high energy chemiosorption of small amounts of phosphate by both Al and Fe hydrous oxides occurs over a wide pH range without precipitating Al_3+ and Fe_3+ ions; (ii) with the larger amounts of phosphate, Al_3+ and Fe_3+ ions are precipitated as insoluble phosphates; (iii) when the activities of these ions are reduced by very low values increasing additions of phosphate are sorbed at low energy, which may be physical adsorption onto a phosphate saturated surface, or may replace phosphate ions which diffuse into the solid. The composition of the precipitated product is likely to be $(Al, Fe)(H_2PO_4)_n(OH)_{3-n}$, where $n = 1$ at pH values below 3.5 for the Al system, and below 1.5 for the Fe system, but is less than 1 at higher pH values.

2. Calcium Carbonate and P Sorption

Phosphorous in calcareous soils and the reactions of phosphate fertilizers with these soils are the objects of considerable study to help determine (1) economical levels of P fertility to be established under different cropping systems, (2) the best way to establish and maintain this fertility and (3) a reliable chemical method for evaluating P fertility.

Calcium carbonate, through its effects on soil reaction (pH), its reactive surface, and as a source of the common ion, exerts a dominant effect on the nature and properties of phosphate in calcareous soils. Much conflicting evidence has been presented regarding the effects of calcium carbonate on phosphate fertility. The conclusion that calcium carbonate depressed the solubility and plant availability of phosphate is generally accepted.

The reactions that take place when phosphate fertilizers are applied to a soil are of scientific and practical value in the production of crops. In calcareous soils numerous chemical reactions and physical changes take place that render soluble phosphate fertilizers unavailable for plant use. According to McGeorge and Breazeale (61), fixation of phosphates in calcareous soils is due, in many instances, to formation of compounds more basic than tricalcium phosphate, and calcium, as calcium carbonate, is a definite part of the molecule. McGeorge (60) has reported that Arizona soils have a strong fixing power for soluble phosphates because of the large amount of solid-phase calcium carbonate present and the high pH. Hinkle (37) found by chemical analysis that calcareous soils are well supplied with total P, but that the amount available to the crop during the growing season is often small.

The level of available P maintained in calcareous soils when water-soluble type phosphate fertilizers were added was higher than that maintained by the citrate-soluble types (49). The time of application of the water-soluble type fertilizers, if previous to crop growth, was not important in calcareous soils. Some benefit was shown when more available fertilizer was present during the early stages of growth on soils where no incubation had taken place.

Dicalcium phosphate dihydrate (DCPD), $CaHPO_4 \cdot 2H_2O$, and octocalcium phosphate (OCP), $Ca_8H_2(PO_4)6.5H_2O$, are the more stable P minerals formed as reaction products of P fertilizer applied to soils (53) and they exist in fertilized soils for various lengths of time (5, 105). Fixen et al. (29), studying the soil P solubility relationships on calcareous soils, concluded that OCP controlled solution P if the $NaHCO_3$- extractable P rose above 35 mg Kg^{-1} while tricalcium phosphate ($-Ca_3(PO_4)_2$, TCP) or a similar mineral phase dominated P intensity in the range of 10 to 25 mg Kg^{-1}. They also reported that OCP will form more readily and persist longer in some cultivated soils than in others.

Phosphorous sorption is very important in calcareous soils. Cole et al. (20) and Kuo and Lotse (46) concluded from laboratory experiments on pure calcite that monolayer adsorption, followed by precipitation reactions, occurs in the presence of increasing concentrations of P. Amer and Ramy (3) attempted to characterise the calcium phosphates formed from the reactions between reagent grade $CaCO_3$ and KH_2PO_4. They concluded from solubility measurements and from the ratios of surface Ca : surface P, measured by isotopic exchange, that octacalcium phosphate was present when the amounts of P retained exceeded 1360 mg/g $CaCO_3$.

The surface area of the calcite used by Cole et al. (20), measured by 45Ca exchange (39), was only 1.8 m^2/g, which is much smaller than the specific areas of $CaCO_3$ (16-500 m^2/g) in calcareous soils (39, 96). The calcites used by Cole et al. (20) must, consequently, be much less reactive than the $CaCO_3$ in soils. Moreover, soil carbonate surfaces are often modified by other cations and anions (48, 96), so that they may react differently than the surface of pure calcite.

Holford and Mattingly (39) studied the phosphate sorption on three Jurassic limestones whose surface areas ranged from 1.0 to 1.5 m^2/g $CaCO_3$. They reported that total sorption was due to (1) an initial chemisorption reaction at final P concentrations below 0.5 mg P/g; above this concentration most of the additional sorption was due to (2) physical adsorption which may occur in multilayers on the initial chemiosorbed layers, and (3) precipitation, probably of octacalcium phosphate, $Ca_8H_2(PO_4)6.5H_2O$, from solution and its deposition on the adsorbed layers. They also reported that the last two reactions probably overlap and cannot be distinguished from each other except by measuring sorption for a very short period (less than 60 seconds) by methods similar to those described by Kuo and Lotse (46) for pure calcite.

D. Phosphate Availability for Plants

Since the early days of applying mineral fertilizers to soils, phosphate fertilization has always been important. Indeed, vast areas of potentially good land are still agriculturally poor because of P deficiency. It must be remembered that soil phosphate can readily be rendered unavailable to plant roots, and that P is the most immobile of the major plant nutrients.

The term "available phosphate" is often used to indicate a soil P fraction that can be utilized by plants. Phosphorus uptake by plants grown in soil is affected by both soil and plant characteristics. The source of P is the soil, the medium of uptake is the soil solution, and the agent of uptake is the plant (30). Since at any one time the soil solution contains only a small fraction of the total P taken up by the plant, in order to maintain adequate growth the soil must continuously release P to the soil solution. Thus, the soil reaction of primary interest is the reversible release of P to the soil solution as shown in equation (1).

P soil → P solution (1)

The manner in which the P in the soil solution interacts with the other forms of P in soils is represented schematically in Figure 3.

Research has also clearly shown that the availability of P is influenced by soil acidity. It was shown that one pound of fertilizer P produced more pasture herbage at pH 6.3 than did three pounds at pH 5.2 (43). The pH level that is most conducive to plant growth is also the level that is most satisfactory for the growth of beneficial soil microorganisms.

The plant reaction of primary interest is the essentially irreversible uptake of P from the soil solution as shown in equation (2) (29).

P solution --> P (inside plant) (2)

As plant roots push their way through the soil they come in contact with the phosphate of the soil solution. Provided that the roots have a high demand for P, which is generally the case for growing plants, phosphate is absorbed by the roots at a high rate and the soil solution in the direct root vicinity is depleted of phosphate. This depletion creates a gradient between the phosphate concentration near the root surface and the phosphate concentration in the bulk soil (69). The concentration gradient regulates the rate of phosphate diffusion towards the plant root (7, 50). The importance of phosphate diffusion in supplying phosphate to plants has been demonstrated by Bhat and Nye (9) in experiments showing that the degree of P depletion around onion roots corresponds fairly well with P diffusion calcula-

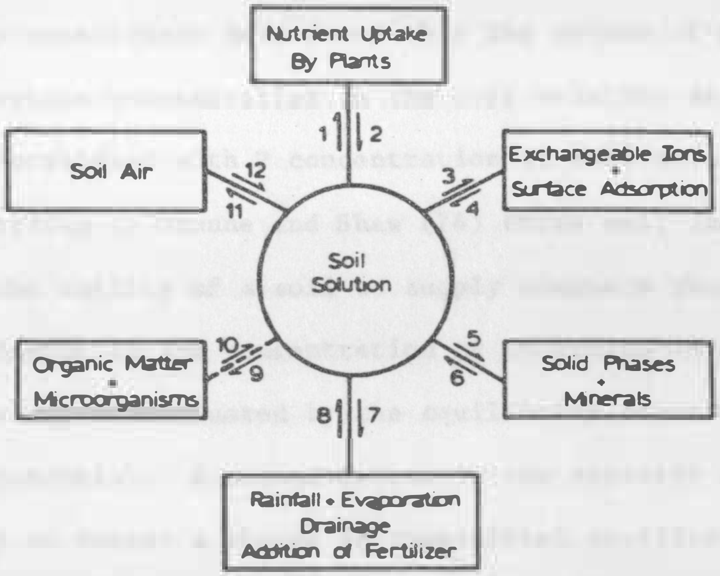

Figure 3. The dynamic equilibria that occur in soils (Lindsay, 1979).

tions. Mass flow can also play a part in the transport of phosphate, towards plant roots. Normally, however, its contribution is minimal since the phosphate concentration of the soil solution is so low (12).

Many researchers have found that the uptake of P is determined by the phosphate concentration in the soil solution and that P uptake is highly correlated with P concentration in soil solution (32, 67, 87, 107). According to Ozanne and Shaw (74) three soil factors probably determine the ability of a soil to supply adequate phosphate to plants. The first factor is the concentration of phosphate in the soil solution. This may be evaluated by the equilibrium concentration or the phosphate potential. A second factor is the capacity of the soil, or its ability to resist a change in the initial equilibrium concentration as phosphate is removed by plants. Thirdly, the rate of phosphate diffusion through the soil regulates the rate at which phosphate may move toward the plant root.

Generally phosphate availability to plants can be assessed by measuring the phosphate concentration in the soil solution and the ability of the soil to maintain the soil solution concentration (phosphate buffer capacity). Concentrations of about 10^{-4} M phosphate in the soil solution are considered high and present a high level of available soil phosphate (64). Phosphate concentrations of about 10^{-6} M in the soil solution are generally too low to supply crops adequately with P. Optimum soil solution phosphate concentrations probably differ for individual crops, cropping systems, and particular sites.

The quantity of P present in soil solution, even in soils with a fairly high level of available phosphate, is in the range of 0.3 to 3 kg P/ha (61). As rapidly growing crops absorb phosphate quantities of about 1 kg P/ha per day, it is clear that the soil solution phosphate must be replenished several times per day by mobilization of phosphate from the labile pool. The quantity of this fraction present in the top soil layer (20 cm) is in the range of 150 to 500 Kg P/ha. The rate of desorption is higher in soils with a higher P buffer capacity. According to experimental data of Olsen and Watanabe (70) the P concentration of the soil solution and the phosphate buffer capacity are the most important parameters controlling the phosphate supply to plant roots. The optimum P concentration of the soil solution may thus be low if the phosphate buffer capacity is high and vice versa. This relationship has been confirmed by investigations of Holford (39), who calculated P fertilizer requirements in relation to the P-concentration of the soil solution and the phosphate buffer capacity.

Considerable work has been done concerning the minimum concentration of phosphate required for maximum growth of plants in solution cultures. Hoagland and Martin (38) obtained satisfactory growth of barley in culture solutions containing 0.7 ppm PO_4, and a maximum growth at 1.1 ppm PO_4. Teakle (99) carried out an experiment on the growth of wheat plants in soil solutions with P concentrations varying from 0.15 to about 10 ppm P, and in solution cultures with P concentrations varying from 0.05 ppm to 50 ppm P. Absorption of phosphate was affected by the concentration of the soil or culture solution with respect to phosphate. Vigorous growth with tillering and high absorption of phosphate occurred between 1.0 and 50 ppm P in culture solution while small growth with greatly reduced tillering and low absorption of P occurred between 0.05 and 0.1 ppm P. The range most suitable for plant growth was between 0.1 and 1.0 ppm P.

Sommer (91) carried out solution-culture experiments to study the relationship of the PO_4 of the medium to the size and type of root system and time of maturity of several plant species. The P concentration varied from 0.1 to 0.8 ppm. Plants with larger root systems made better growth at low P concentrations than those with smaller root systems. Increasing P concentrations resulted in decreases of the root-shoot ratios. Plants in lower P concentrations matured the earliest. High P concentrations did not stimulate root development.

Houghland (40) studied the minimum P requirement of potato plants grown in solution cultures. Plants made excellent growth at a P concentration of approximately 1.5 ppm. At the low concentration of 0.5 ppm P, the height of the plants was only slightly reduced; dry matter production and the percentage of P in plants were definitely lowered. When the P concentration of the solutions was reduced to 0.1 ppm, however, the plants were much smaller, P-deficiency symptoms developed and there was a pronounced reduction in both dry matter and percentage of P. Tidmore (101) found that maximum growth of corn, sorghum and tomatoes was obtained at 0.5 ppm P in solution cultures, although some plants made a better growth in soils whose displaced solution contained from 0.02 to 0.03 ppm P than in culture solutions at 0.1 ppm P.

From studies with solution cultures, Andrew (4) reported that the approximate critical concentration of P in solution for optimum growth of legume species lies between 0.1 and 0.2 ppm. A concentration of about 0.2 ppm P was also calculated to be necessary for wheat (50).

E. Soil Tests for Available Phosphorus

The aims in soil testing are to assess the relative adequacies of available nutrients (or lime requirements) and to provide guidance on amounts of fertilizers (or lime) required to obtain optimum growth for plants. Such objectives are contingent upon securing representative samples of soil, analyzing them in an acceptable manner, and calibrating the effects on crop response (or increased soil test values) of added fertilizer (or lime) to soils at various initial levels of available nutrients.

Bray (13) described the requirements of a successful soil test as follows:

1) The extracting solution and procedure used should extract the total amount (or a proportionate part) of the available form(s) from soils with variable properties whose variations in amount are responsible for significant variations in yield response to applied fertilizers;
2) The amount of nutrient in the extract should be measured with reasonable accuracy and speed;
3) The amounts extracted should be correlated with the growth and response of each crop to that nutrient under various conditions.

When selecting an extractant for a laboratory one should always consider the degree of correlation of the extractants with plant response to soil and fertilizer P. In other words, the extractant that the research has shown to be the most reliable index of the uptake or utilization of P from the types of soils that the laboratory will be testing should be used. We are now speaking of correlation which reflects the suitability of a soil test method for a range of soils. This is somewhat different from calibration which provides the information for making fertilizer recommendations from soil tests.

The determination of available soil phosphate is complicated, as phosphates of varying availability are present in the soil. In contrast to the available cationic nutrients, available phosphate is not only a measure of the exchangeable phosphate but of the solubility of soil phosphates (64). The most important soil phosphates are the Ca phosphates, phosphates adsorbed to soil colloids, and organic phosphates. The solubility of the inorganic soil phosphates depends on their chemical nature, the age and the surface area of the minerals. Generally, freshly precipitated phosphates are more readily soluble. On aging there is an increase in crystal size with a consequent decrease in surface area. Also as the phosphate minerals age some phosphates may diffuse into other minerals such as Fe and Al oxides and so becomes less available. The presence of other ion species in the soil solution may also affect the availability of phosphates (87). For the Ca phosphates, H^+ generally increases and Ca^{2+} decreases the solubility. The reverse is true for Al and Fe phosphates.

1. Methods for Phosphorus Determinations

Methods for determining P in soils have been discussed in the literature for more than a century. The purpose of these methods has been to characterize the P in the soil system. There are many methods varying in principle and technical detail. The selection of a suitable method requires a clear understanding of objectives that necessitate the measurement of soil P. Other considerations are the properties of soils involved, accuracy and reproducibility needed, and the facilities and personnel available.

Most soil P determinations have two distinct phases -- first, the preparation of a solution containing the soil P or fraction thereof, and second, the quantitative determination of the P in this solution. The choice of a method for determining P depends on the concentration of P in the solution, the concentration of interfering substances in the solution to be analyzed, and the particular acid system involved in the analytical procedure.

a. Determination of Phosphorus by Bray P-1 Extraction (Bray-1)

This method developed by Bray and Kurtz-1 (15) has been widely used as an index of available P in soils. The extracting reagent (0.03N NH_4F in 0.025 N HCl) is designed to remove easily acid-soluble forms of P, largely Ca phosphates, and a portion of the Al and Fe phosphates based upon the solubilization effect of the H^+ on soil P. The NH_4F dissolves Al^{3+} and Fe^{3+} phosphates by its complex ion formation with these metal ions in acid solution based on the ability of the F^- to lower the activity of Al^{+3} and to a lesser extent that of Ca^{2+} and Fe^{+3} in the extraction system. Though the Bray test was initially limited to soils with pH values of less than 6.8, it is now routinely used on more alkaline soils. Calcareous soils or high pH soils may be tested by this method, but higher ratios of extractant-to-soil are often used (28, 37, 42, 89).

The Bray-1 method yields a standard curve that is essentially linear to 10 ppm of P in the soil extract (approximately 200 Kg ha^{-1} of extractable P). The sensitivity is approximately 0.15 ppm in the extract (3 Kg ha^{-1} P in the soil).

The reproducibility of determinations by this procedure depends upon the extent to which the times of extraction, filtration, and color development are controlled. Reasonable control and thorough sample preparation should give a coefficient of variation of about 5%.

The extraction time and the solution-to-soil ratio in the original procedure were 1 minute and 7 ml of extractant to 1.0g soil, respectively. To simplify adaptation to routine laboratory work and to extend the range of soils for which the extractant is suitable, both the extraction time and the solution to soil ratio have been altered by various laboratories.

When a wide range of acid neutral and calcareous soils is found, the Bray extracting solution is still probably the best method for routinely determining available P. Fitts (27), in a study involving 74 samples from a wide variety of United States and Canadian soils, reported that the Bray extractant was least affected by soil properties. Peck (76) also concluded that the Bray test, when properly calibrated to the soil group, was probably the most practical test for available P where a large number of samples are processed. Van Diest

(103) found that the Bray method showed high correlation coefficients with soils having low and medium levels of labile P, but lower correlation when soils high in labile P were included.

Anamolous behavior has, however, been observed with calcareous soils. With high rates of phosphate fertilizers being applied, it has become increasingly difficult for soil testing laboratories to determine available P accurately in calcareous soils with the Bray extractant at a 1:10 soil-to-solution ratio (11, 31). Even after several years of uniform heavy phosphate applications on highly calcareous fields, the soil test values tend to vary greatly and, in many cases, low P values still occur (84). Although the soil test P seems to vary markedly on these soils, differential crop growth and yield responses to phosphate applications have not generally been shown. According to Cooke (21) some form of P fixation during the extraction of soils with very dilute acids is to be regarded as the rule rather than exception.

It is assumed that $CaCO_3$ is exerting a repressive effect on the extraction of P with the Bray solution (97), resulting in the extraction of less calcium phosphate (73). Blanchar and Caldwell (11) showed the Bray-1 extractable P to be inversely related to the amount of $CaCO_3$ present in the soil. However, the $CaCO_3$ equivalence was not related to the Bray-1 extractable P; consequently, only calcite lime repressed the extractable P. It was stated further by these investigators that in soils containing calcium carbonates the weak acid of the Bray extractant is rapidly neutralized by the carbonate rather than utilized in the dissolution of calcium phosphates. The repressing effect of the $CaCO_3$ on the extraction of P may involve two mechanisms: (a) neutralization of the dilute HCl by $CaCO_3$ and (b) deactivation of F^- ion by the Ca (11, 84).

Smillie and Syers (88) attributed the low Bray estimates for calcareous soils to the formation of CaF_2 when the dilute HCl is neutralized by $CaCO_3$. Syers et al. (95) in a study of the fractionation of inorganic P in calcareous soils has shown that the CaF_2 formed by the reaction of calcite with 0.5M NH_4F immobilizes an appreciable portion of the P released during this extraction.

The repressing effect of the carbonate on extractable P can be greatly reduced by increasing the soil to extractant ratio. Smith et al. (89) showed a soil-to-solution ratio of 1:50 to be superior to a ratio of 1:7 for estimating available P in calcareous soils. Al-Abbas and Barber (2) found that the amount of P extracted increased with widening of the soil/extractant ratio. Randall and Grava (84) indicated that available soil P from highly fertilized calcareous fields could be determined more accurately by using wider ratios of soil to Bray extractant. Fixen and Carson (28), in a study in South Dakota concluded that the 1:50 ratio was the most highly correlated ratio with yield response.

The amount of P extracted from soils by the Bray-1 extractant also can be dependent on shaking time. This dependence on shaking time has led to the use of different shaking times in soil test laboratories in different states. Hasett and Walker (35) found that a shaking time of 1 or 5 minutes resulted in extraction of a higher proportion of extractable P from soils with low P tests than from soils with high P tests.

b. Determination of Phosphorus by Olsen's Sodium Bicarbonate Extraction (Olsen P)

This extraction was first developed and described by Olsen et al. (73) and has been modified since (66, 104). The extractant is a 0.5M $NaHCO_3$ solution with a pH of 8.5. The solubility of Ca phosphate in calcareous, alkaline, or neutral soils is increased because of precipitation of Ca^{++} as $CaCO_3$. In acid soils, P concentration in solution increases when Al and Fe phosphates such as variscite ($AlPO_4 \cdot 2H_2O$) and strengite ($FePO_4 \cdot 2H_2O$) are present (53). Secondary precipitation reactions are reduced in acid and calcareous soils because Fe, Al and Ca concentrations remain low in the extract (69).

The molybdate complex obeys Beer's law (gives a straight line when plotting the log of % transmittance vs. concentration) up to a 2 ppm concentration of P in the final solution (66). The sensitivity of this method is 0.02 ppm of P in the extract. The coefficient of variation (cv) depends on the concentration of P in the extract. For routine analysis, the cv may vary from 5 to 10%.

Possible sources of variation in the analytical results in the $NaHCO_3$ extraction method are associated with the temperature of the extracting solution and the shaking speed (69). Data by Olsen et al. (73) were obtained at $25^{\circ} \pm 1^{\circ}$ C. The extractable P increased approximately 0.43 ppm for each degree rise in temperature between 20° C and 30° C, for soils testing between 5 and 40 ppm of P.

Plastic containers are preferable to glass for storing the extracting solution. If glass is used, a fresh solution should be prepared every month, since the pH tends to rise with time (69). This change causes higher values for extractable P.

If a Burrell wrist-action shaker is used, the shaking speed is set at 2. Other shakers may be used, but higher results will be found when the speed increases greatly from the above description.

The extractant and its modifications generally give best correlation with P uptake in calcareous soils (73, 80) and are adequate in evaluating available P in soils where no significant reserve of available P existed in organic form (1). However, there are exceptions to this generalization in calcareous soils. For instance, there was a poor relationship between plant response and $NaHCO_3$- extractable P for a wide range of calcareous Syrian soils (58). Correlation coefficients became significant when the soils were classified according to physical, chemical and mineralogical properties. It was suggested that the comparatively low coefficients for the limestone soils may be due to variation in the nature and form of the $CaCO_3$.

2. Calibration

To convert soil test values for P into fertilizer recommendations requires two sets of calibration information for each combination of crop-soil type-climate: (i) the soil test level for P that produces the maximum net return per acre for the overall input of production units, considering the individual farmer's economic risk situation and (ii) the quantity of fertilizer P that is required to reach that test level. The major advantage of what we will refer to as the "double calibration" approach is that the soil-fertilizer-extractant interaction and the plant-soil interactions are evaluated separately and can be taken into account more directly when making fertilizer recommendations.

The first component of calibration must be based upon crop yield response information from field studies and should indicate the soil test level of P beyond which no additional yield increments can be expected. For Kentucky, soils testing more than 20-30 ppm P (NH_4F-HCl, 1:10 ratio for 5 min) in the 15-cm layer normally will supply adequate P for most species (100).

Relatively little information has been published regarding the change in soil test values for P in the field as affected by varying rates of application. Peck et al. (77) reported that field application of 4 mg P Kg^{-1} soil was required to change the NH_4F-HCl extractable P by 1 ppm in Illinois soils. In Kentucky soils Thomas and Peaslee (100) found 3 to 6 ppm of P is required to change the soil test level 1 ppm (5-min extraction time), which is similar to the 2 to 4 reported by Griffin and Hanna (32) for New Jersey soils. These ratios have frequently been considered as constant, but the P adsorption characteristics of soils indicate that the ratio could decrease as the initial level of P is increased. For example, a soil initially having 5 ppm of extractable P may require 140 ppm of added P to reach the 40-ppm level, but a soil initially at the 40-ppm will likely require appreciably less than 140 ppm to reach 75 ppm of extractable P.

3. Interpretation

The conversion of soil test indices into rates of fertilization ideally should be based upon experimental evidence. Unfortunately, the diversity that occasionally may be seen among the rates suggested by different laboratories for identical crop and soil conditions probably reflects the general lack of research data necessary for the proper execution of this step in soil testing (100).

Many laboratories are abandoning the reporting of test levels of nutrients in "pounds per acre" (15 cm or 6 in depth) and are now reporting in terms of coded numerical indexes (1 through 10) or as ppm. The concentrations of extractable P that represent the generalized categories of "low," "medium," and "high" for both of the extractants discussed are presented in Table 2.

Table 2. Relative categorization of P concentrations into low, medium and high for Bray and Olsen soil testing extractants.

	Extractant	
Relative, Soil Level	0.03 N NH_4F^- 0.025 N HCl 1/	0.5 M $NaHCO_3$ 2/
	Extractable P in soil (Kg ha^{-1})	
Very low	< 6.7	
Low	6.7-16.8	0.0-10.0
Medium	16.8-28.0	11.0-21.0
High	28.0-44.8	22.0-33.0
Very High	>44.8	

1/ Fertilizers Recommendations Guide - 1984. South Dakota State University, Brookings.

2/ Crop production guide. 1984. North Dakota State University, Fargo.

A summary of this review points out an increasing need to compare the Bray and Olsen soil tests under field conditions on mildly calcareous soils. Therefore, the following study was undertaken to determine the influence of P additions on the P extracted by the two tests and the effects of various soil factors on the P extracted for alkaline soils in eastern South Dakota. The relationship between P extracted and crop yield response was also investigated.

MATERIALS AND METHODS

This study was conducted during 1983 and 1984 at five dryland sites and one irrigated site in eastern South Dakota (Figure 4). Site and soil characteristics are given in Table 3.

Field Methods

A single composited soil sample was taken in early 1983 to a depth of 0-15 cm and 15-61 cm from each site prior to P application. Again in June 1983 composited samples were taken from the 0-15 cm and 15-61 cm depths. Each composited sample was obtained by combining 15 cores from each plot from the 0-15 cm depth. Nine cores were composited from each site from the 15-61 cm depth. In July 1984 soil samples were taken from the 0-15 cm depth following the same procedure. All soil and plant analyses were performed by the S.D.S.U. Soil Testing Laboratory. The average soil test values for each site are presented in Table 4.

All study sites were laid out in a randomized complete block design with 4 replications. Six rates of P were broadcast prior to tillage in the spring of 1983. Phosphorus rates used were 0, 28, 56, 112, 224 and 448 Kg P/ha. Additional fertilizer applied, if any, is given in Table 5. Crops grown at each site from 1982 to 1984 are given in Table 6. Cultural practices were those followed by the individual cooperators. Precipitation for the growing season (April - September) and the annual total for 1983, 1984 and a 30-year average (1951 - 1980) are given in Tables 7-9.

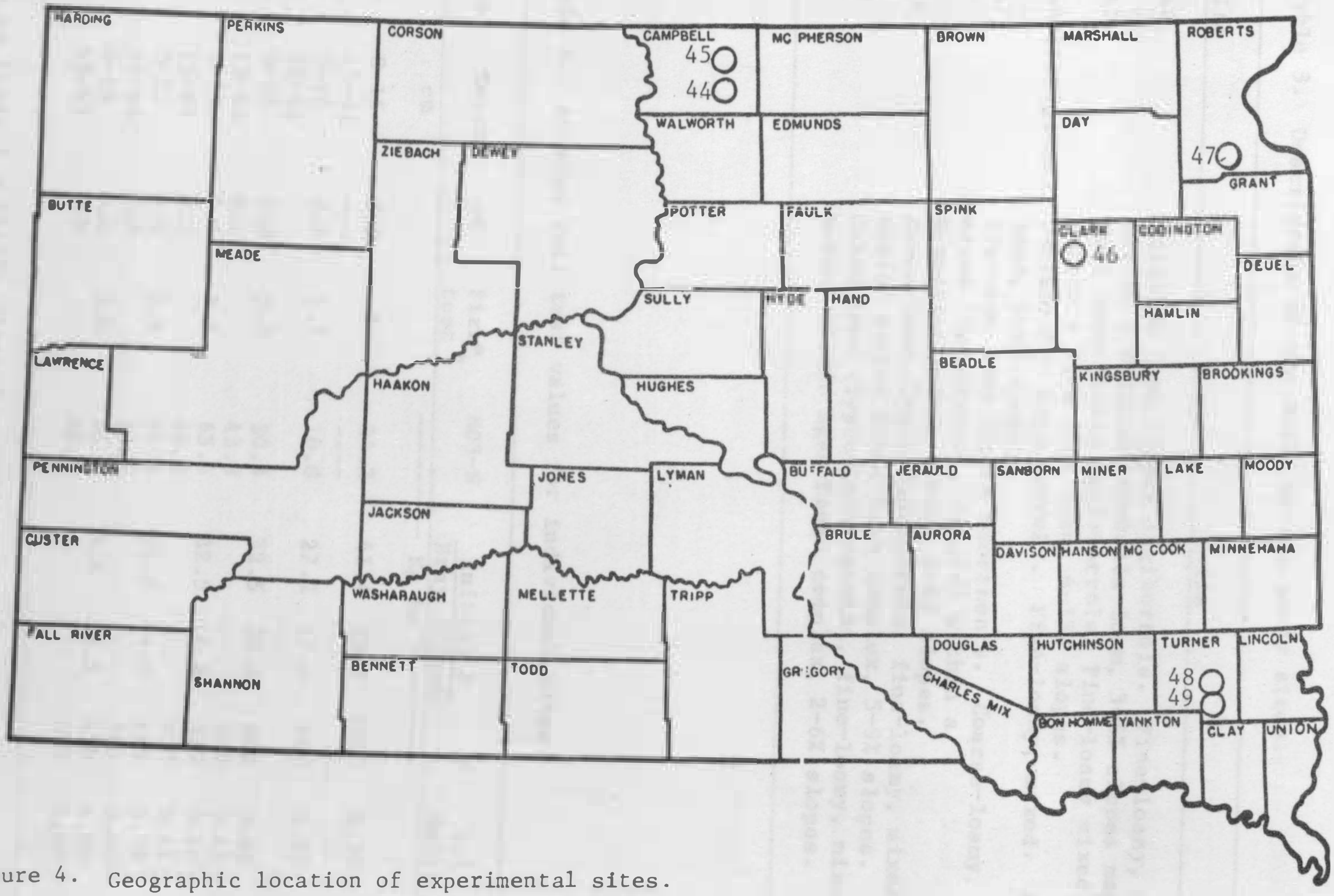

Figure 4. Geographic location of experimental sites.

Table 3. Description of the soils at the study sites.

Site	Soils
44	Williams loam (Typic Argiborrols. Fine-loamy, mixed) within a Williams-Bowbells loam, 3-6% slopes map unit.
45	Zahl loam (Entic Haploborrols, Fine-loamy mixed) within a Vida-Zahl loam, 6-15% slopes.
46 (irrigated)	Udorthentic Haploborrols. Fine-loamy, mixed. Buse loam, 0-4% slopes.
47	Sisseton loam (Typic Udorthents. Coarse-loamy, mixed 'Calcareous', frigid) within a Heimdal-Sisseton loams, 2-6% slopes.
48	Ethan loam (Typic Calciustols, fine-loamy, mixed, mesic) within Ethan-Egan complex, 5-9% slopes.
49	Ethan loam (Typic Calciustolls, fine-loamy, mixed, mesic) within Egan-Ethan complex, 2-6% slopes.

Table 4. Average soil test values for individual sites.

Site	Depth	pH	Fizz* test	NO3-N	Initial P		K	1:1	O.M
					Bray	Olsen		Salts	
	cm			--------- Kg ha^{-1} -------					%
44	0-15	6.8	0	14.3	41.4	29.7	1090	0.30	3.2
	15-61	---		----			---	---	---
45	0-15	7.8	1.7	10.0	27.2	17.4	860	0.30	2.7
	15-61								
46	0-15	8.0	2.3	30.3	32.5	20.2	690	0.40	2.8
	15-61	8.1		43.3			600	0.45	2.1
47	0-15	7.9	1.6	63.5	32.5	16.8	320	0.46	2.8
	15-61	8.2		48.4			420	0.41	1.4
48	0-15	8.0	2.9	22.2	35.6	44.0	420	0.39	3.7
	15-61	7.9		22.4			360	0.40	3.3
49	0-15	8.0	3.0	35.3	2.6	18.5	410	0.50	2.8
	15-61	8.0		40.0			290	0.50	1.6

*0 = no fizz; 1 = little fizz; 2 = moderate fizz; 3 = high fizz.

Table 5. Non-treatment fertilizer applied at each site in 1983 and 1984.

	Year	
Site	1983 N-P_2O_5-K_2O	1984 N-P_2O_5-K_2O
	Kg ha^{-1}	
44	101-0-0	None
45	101-0-0	None
46	None	16-18-0
47	None	None
48	188-0-0	18-20-17
49	None	18-20-17

Table 6. Crops grown at the different sites from 1982 to 1984.

	Crop		
Site	1982	1983	1984
44	Oats	Wheat	Corn
45	Wheat	Wheat	Barley
46	Corn	Corn	Soybeans
47	Corn	Corn	Oats
48	Oats	Corn	Oats
49	Soybeans	Soybeans	Corn

Table 7. Precipitation for the growing season (April-September) and the annual total at study sites for 1983.

	Site					
	44	45	46	47	48	49
	mm					
Precipitation for growing season (April-September)	382	382	385	337	543	543
Annual Precipitation	512	512	429	561	739	739

Table 8. Precipitation for the growing season (April-September) and the annual total at study sites for 1984.

	Site					
	44	45	46	47	48	49
	mm					
Precipitation for growing season (April-September)	338	338	464	500	550	550
Annual Precipitation	453	453	628	746	741	741

Table 9. Thirty-year average precipitation (1951-1980) for the growing season (April-September) and the annual total at study sites.

	Site					
	44	45	46	47	48	49
	mm					
Growing season precipitation (April-September)	350	350	366	417	461	461
Annual Precipitation	432	432	471	558	611	611

Laboratory Methods

a. Leaf Analysis

Fifteen leaf samples from each corn plot were collected at the silking stage for leaf analysis. Samples were dried in paper bags at 40-50° C in a forced-air dryer. They were then ground to pass a 60-mesh stainless steel screen using a Wiley ED-5 mill and stored in paper envelopes. They were redried overnight at 65-70° C just prior to analysis.

A wet digestion procedure was used for both P and Zn. One gram of ground plant material was placed in a 25 mm x 15 mm test tube. Five ml of nitric acid was added to each flask and allowed to stand overnight. Tubes were placed in blocks and heated at 130° C until reddish flames were gone. Two and a half ml of perchloric acid were added and heat was carefully increased to 180° C. When digestion was completed a colorless liquid developed. Solution was filtered using No. 31 filter paper into 50 ml volumetric flasks.

Phosphorus content was determined colorimetrically using Barton's reagent. Zinc was determined by atomic absorption spectrophotometry.

b. Soil Analysis

1. Bray and Kurtz-P procedure (Bray)

This procedure is an adaptation of the Bray and Kurtz No. 1 method. It has been correlated to field response found in P fertilizer trials throughout the state. One gram of 2 mm crushed soil was measured into a set of 50 ml Erlenmeyer flasks in a rack. Ten milliliters of the extracting solution (0.03 N NH_4F,0.025N HCl) was added to each flask. The racks were shaken for 2 minutes at 200 OPM and filtered immediately into marked filter tubes through S + S No. 597 filter paper. Filtrate above the 5 ml mark on the tube was removed by means of an aspirator connected by tygon tubing to a thin glass tube. One quarter milliliter each of molybdate reagent and of the reducing reagent (sulfonic acid) were added to each tube and mixed with the vortex mixer. Fifteen minutes were allowed for color development. The tubes were then inserted into a spectrophotometer that had been set at 655 nm and had been adjusted at the 0 percent T with the light blocked off and the 100% T with distilled water. The spectrophotometer reading was determined and the amount of P per unit area was obtained directly from a calibration curve (ppm P in filtrate x 17.9 = Kg P/ha in soil).

2. Olsen-P procedure

Two grams of soil were measured into a set of 50 ml Erlenmeyer flasks. Forty milliliters of extracting solution (0.5 M $NaHCO_3$ with a pH of 8.5) were added to each flask and shaken at 200 OPM for 30 minutes. The mixture was filtered using Whatman No. 2 filter paper. Extracts had an organic color. Five millimeters of the extractant were transferred into a 50 ml Erlenmeyer flask. Fifteen milliliters of distilled water and five milliliters of ascorbic acid were added to each flask, and the mixture was agitated on a shaker for 2 minutes. Filtrate readings were determined on a probe colorimeter and converted to P content per unit area in soil (ppm P in filtrate x 35.7 = Kg P/ha in soil).

Harvest Methods

Harvesting of corn and soybeans was done by hand. In corn, three meters of the four center rows were harvested, while in soybeans three meters of the two center rows were harvested. In small grains an area of 24 m x 76 m per plot was harvested with a small plot combine.

Statistical Methods

Statistical analyses were performed on the S.D.S.U. computer using a Statistical Analysis System developed by North Carolina State University (8).

RESULTS AND DISCUSSION

The results will be presented in three major sections: (A) soil test analysis, (B) plant analysis, and (C) yield.

A. Soil Analysis

The Bray and Kurtz No. 1 (Bray) method and the Olsen method have been used to estimate available soil P in South Dakota and the former test has been correlated to the response found in P fertilizer trials throughout the state.

1. Bray & Kurtz-P No. 1 Soil Test

The Bray soil test indicated that five of the six sites contained high to very high amounts of extractable P for both years for almost all the rates of P_2O_5 applied (Figure 5). All the sites contained more extractable P in 1983 than in 1984 except sites 46 and 48 where the individual cooperators applied P fertilizer in 1984. Site 49 did not show this same trend, although P fertilizer was also applied in 1984. In both years, site 49 was low in extractable P. This site was the most eroded and had the highest fizz test of all the sites.
The high fizz test indicates that this soil either had more carbonate minerals or more reactive carbonate minerals than the other soils, which could have caused neutralization of the HCl and complexing of the fluoride in the extracting reagent (28). Figure 6 clearly shows the effect of the fizz test on the Bray-P availability. As the fizz test increased, Bray-P level dramatically decreased.

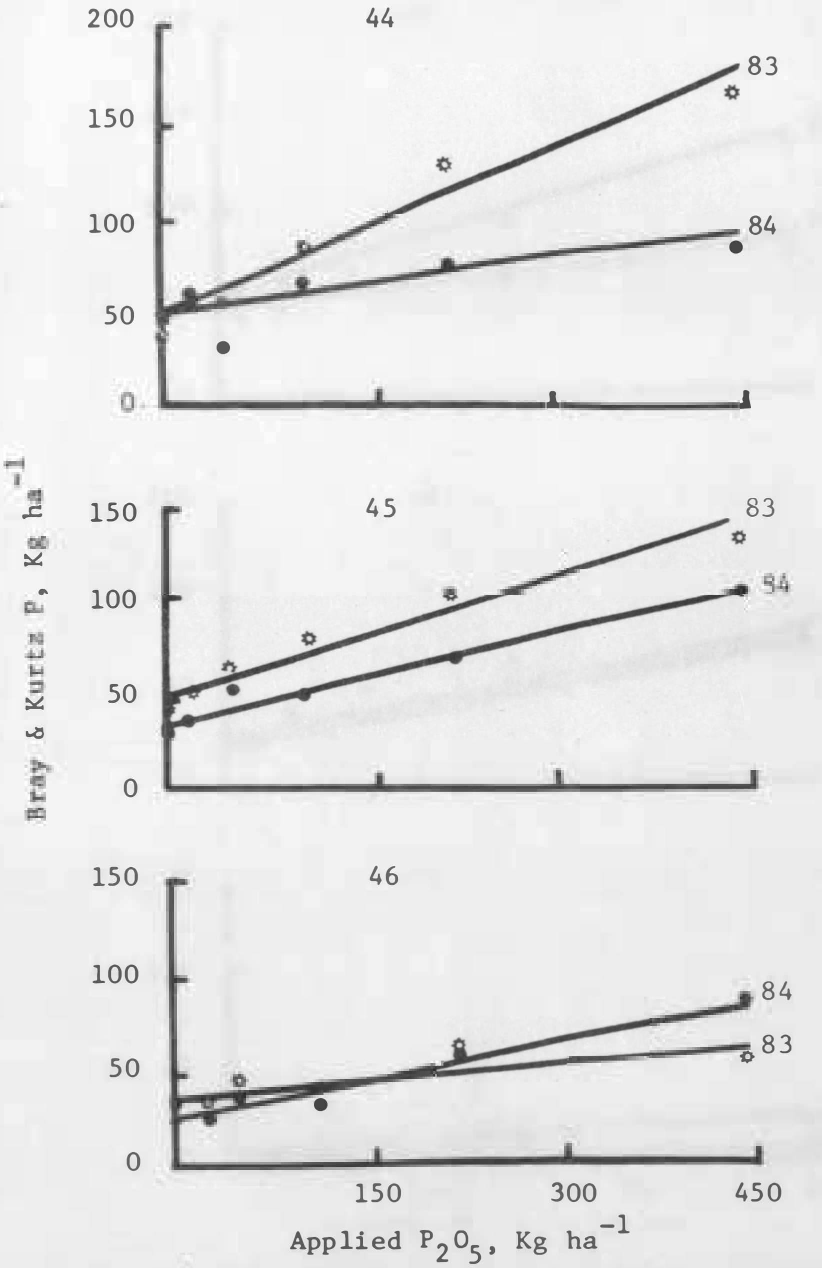

Figure 5. Relationship between Bray I soil P test results and applied P_2O_5 at individual sites for 1983 and 1984.

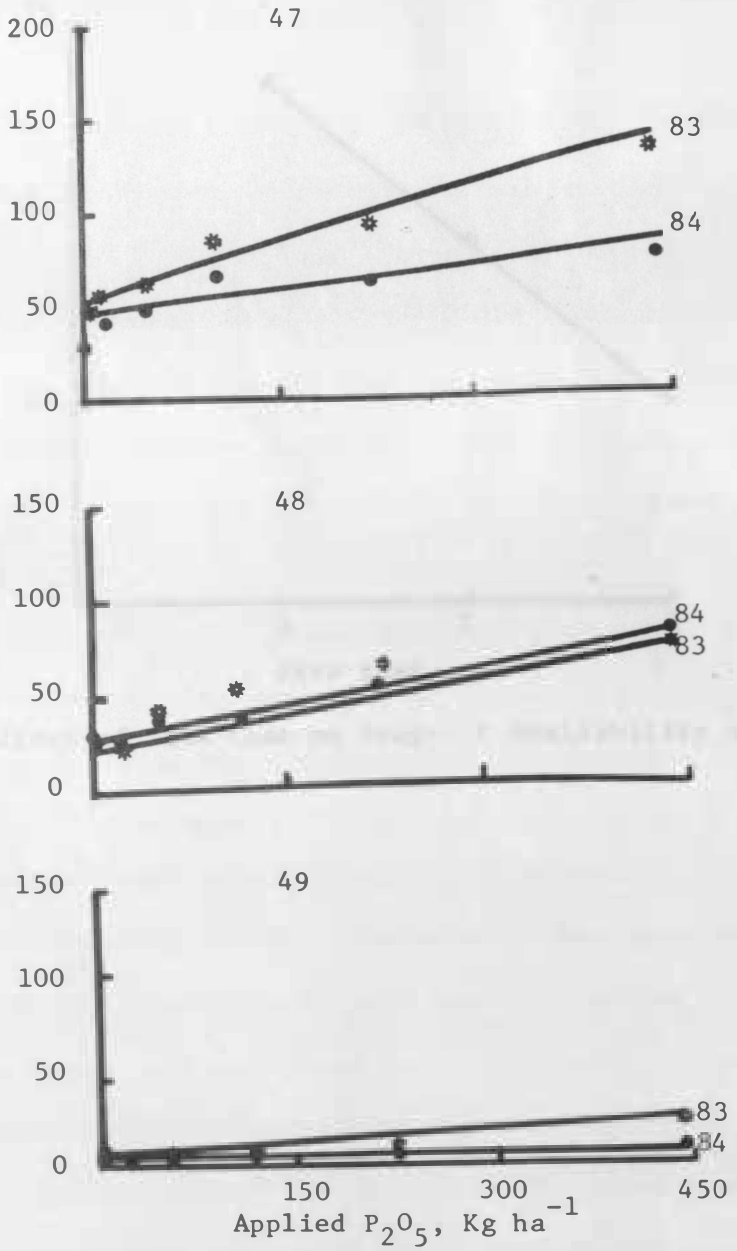

Figure 5 (continued). Relationship between Bray soil P test results and applied P_2O_5 at individual sites for 1983 and 1984.

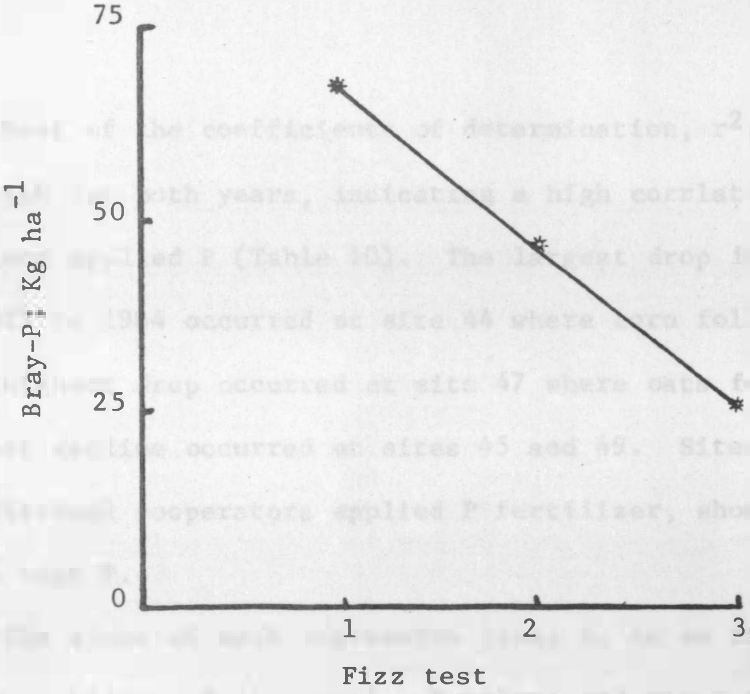

Figure 6. Effect of fizz test on Bray-1 P availability at site 47.

Most of the coefficients of determination, r^2, for the sites were quite high for both years, indicating a high corrlation between Bray P and applied P (Table 10). The largest drop in soil test level from 1983 to 1984 occurred at site 44 where corn followed wheat. The second highest drop occurred at site 47 where oats followed corn. Less soil test decline occurred at sites 45 and 49. Sites 46 and 48, where the individual cooperators applied P fertilizer, showed a slight gain in soil test P.

The slope of each regression line, b, is an indicator of the buffering ability of that soil. B values and other pertinent soil characteristics are given in Table 11. The lower the b value, the higher the buffering capacity of the soil and the greater the amount of P_2O_5 that must be applied to change the soil test level by 1 unit. The lowest Bray b value (0.02) and highest fizz test were observed at site 49. At least two factors could have caused this low b value. As discussed earlier, soil carbonate could have neutralized the extracting solution and resulted in low extractable P levels even though considerable plant available P was present. The second possibility is that the soil at this site had a higher fixing capacity for P and a greater amount of P_2O_5 had to be applied to change the soil test level. The highest slope was observed at site 45, indicating that the soil at this site had the lowest P buffering capacity.

An attempt was made to evaluate the relationship between b and several soil factors. Factors evaluated were the fizz test, pH and the initial soil P test level. There was no statistical relationship

Table 10. Regression equations for predicting Bray P level from applied P fertilizer.

Site	Year	Equation	r^2	Sign.
44	83	$50 + 0.22\ P_2O_5$	0.96	0.01
	84	$46 + 0.11\ P_2O_5$	0.77	0.05
45	83	$51 + 0.20\ P_2O_5$	0.98	0.01
	84	$35 + 0.15\ P_2O_5$	0.95	0.01
46	83	$37 + 0.06\ P_2O_5$	0.61	NS
	84	$28 + 0.13\ P_2O_5$	0.97	0.01
47	83	$57 + 0.18\ P_2O_5$	0.97	0.01
	84	$44 + 0.08\ P_2O_5$	0.70	0.05
48	83	$32 + 0.11\ P_2O_5$	0.84	0.01
	84	$31 + 0.11\ P_2O_5$	0.71	0.05
49	83	$4 + 0.04\ P_2O_5$	0.71	0.05
	84	$2 + 0.02\ P_2O_5$	0.62	NS

NS -- Not significant at 0.05 probability level.

Table 11. Bray b for 1984 and other pertinent soil characteristics across the sites.

Site	pH	Fizz test	Initial P $-\text{kg ha}^{-1}-$	Bray b '84
44	6.8	0	46.4	0.11
45	7.8	1.7	30.5	0.15
46	8.0	2.3	36.4	0.13
47	7.9	1.6	36.4	0.08
48	8.0	2.9	40.0	0.11
49	8.0	3.0	2.9	0.02

between the fizz test level or pH and the b value for Bray (Figure 7 and 8). In Figure 9, as the initial soil test P increased, b tended to decrease. The entire relationship, however, was due to site 49.

2. Olsen-P

The Olsen-P soil test indicated that the sites contained a medium to very high amount of soil P for both years for all the different rates of P_2O_5 applied (Figure 10). In this test all the sites contained more P in 1983 than 1984. As was the case using the Bray test, site 49 had the lowest amount of Olsen-P especially for 1984 although it still tested in the medium category. Site 49 apparently had a higher fixing capacity for P since the carbonate content of the soil would not have interfered with P extraction by this test. Unlike for the Bray test, the fizz test did not affect the Olsen-P levels at site 47.

The coefficients of determination, r^2, were high for most of the sites indicating a high correlation between the Olsen-P and applied P (Table 12). Overall, the coefficients of determination were generally greater in the Olsen test than in the Bray test. The regression coefficients, b values, were lower at all the sites in 1984 than 1983 due likely to the additional mixing of soil and fertilizer caused by tillage. This mixing usually speeds the conversion of soluble fertilizer reaction products to less soluble minerals.

As already mentioned, the slope of the regression line, b, is an indicator of the buffering ability of the soil. B values and other pertinent soil characteristics are given in Table 13. The lowest

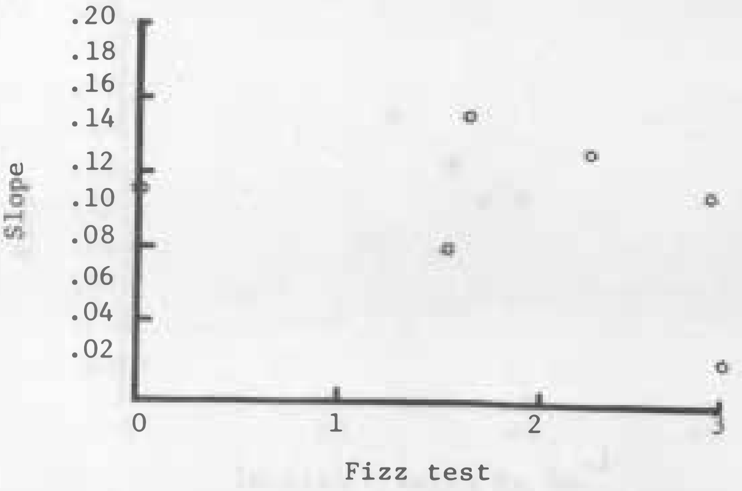

Figure 7. Relationship between the change in Bray for a unit P and the fizz test.

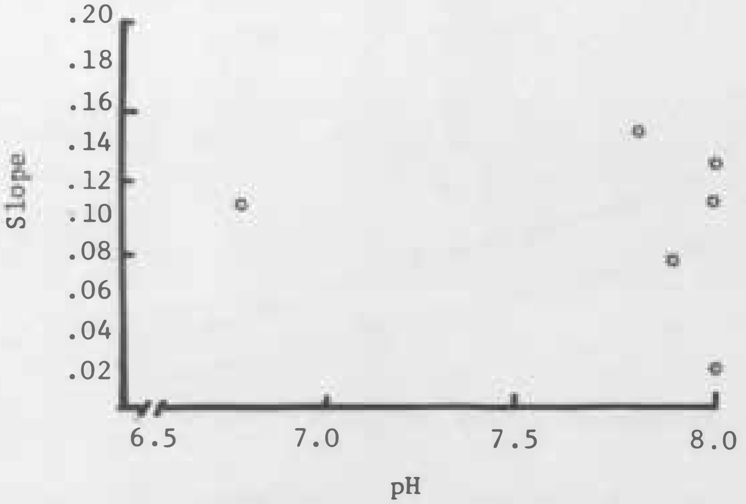

Figure 8. Relationship between the change in Bray for a unit P and pH.

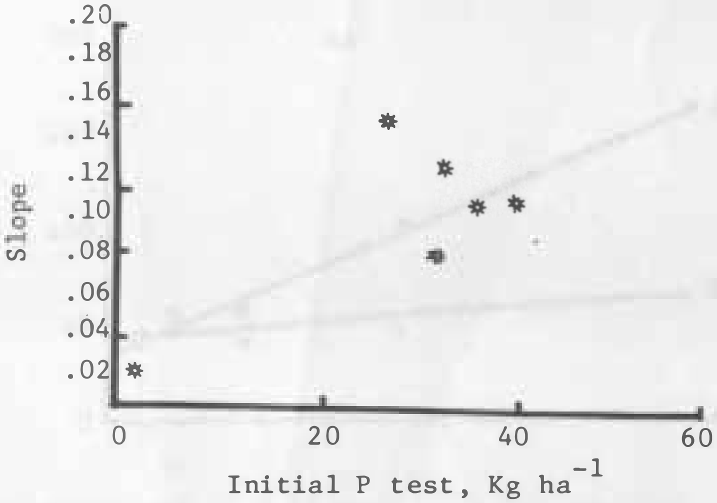

Figure 9. Relationship between the initial Bray test and the change in Bray for a unit P.

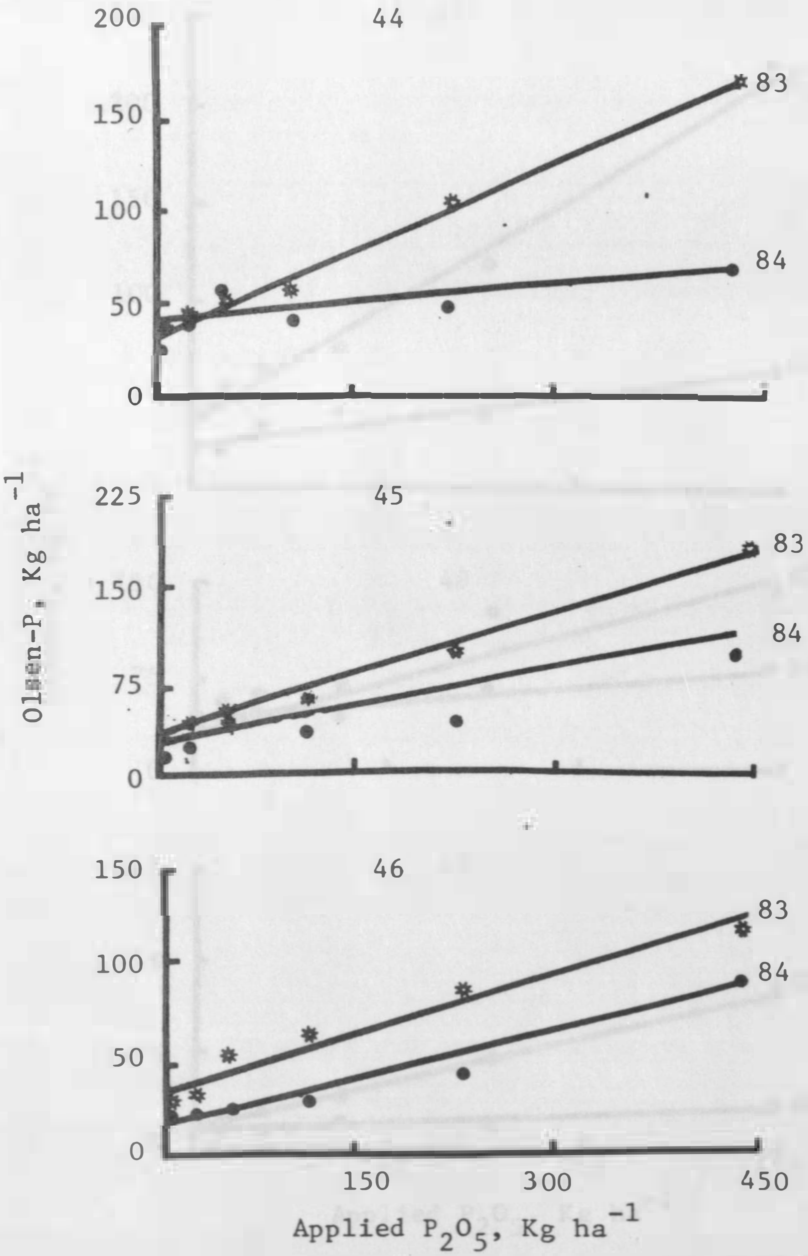

Figure 10. Relationship between Olsen-P soil test results and applied P_2O_5 at individual sites for 1983 and 1984.

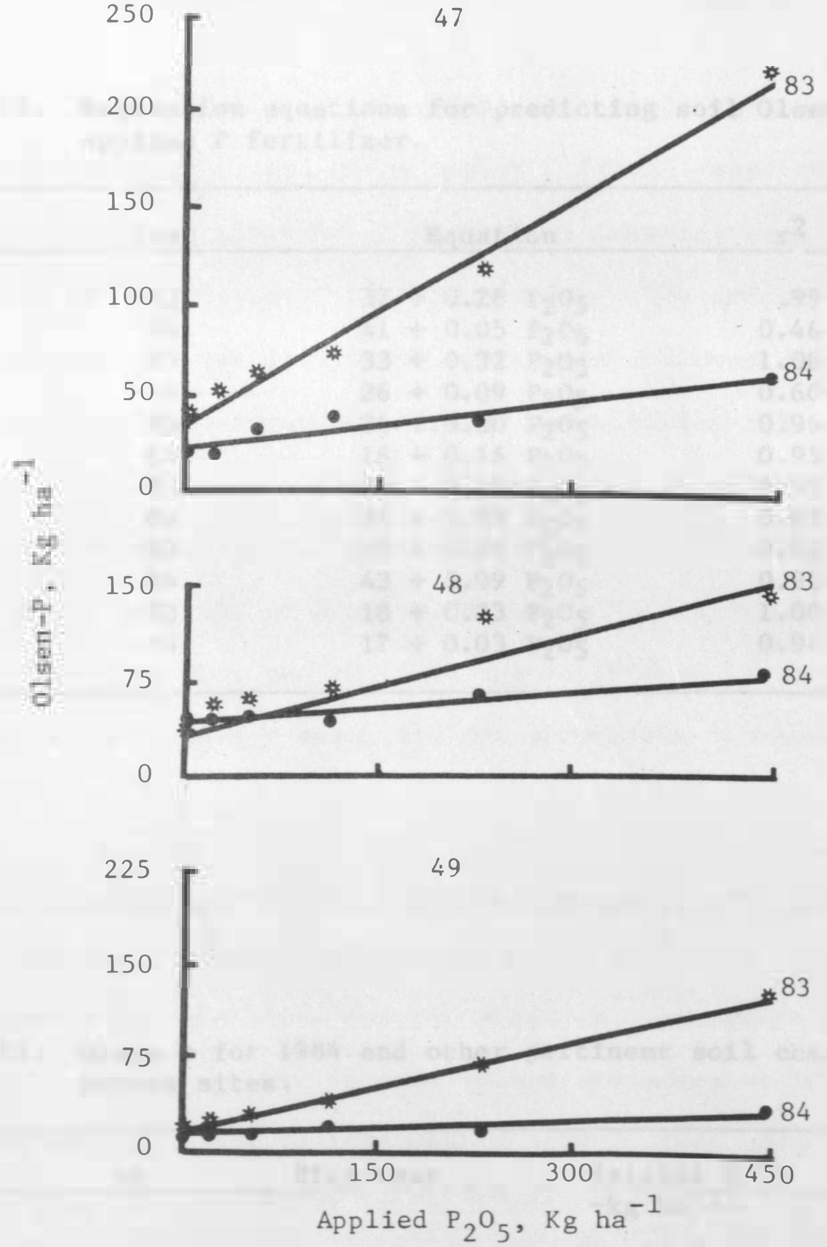

Figure 10 (continued). Relationship between Olsen-P soil test results and applied P_2O_5 at individual sites for 1983 and 1984.

Table 12. Regression equations for predicting soil Olsen-P test from applied P fertilizer.

Site	Year	Equation	r^2	Sign.
44	83	$37 + 0.28\ P_2O_5$	.99	.01
	84	$41 + 0.05\ P_2O_5$	0.46	NS
45	83	$33 + 0.32\ P_2O_5$	1.00	.01
	84	$26 + 0.09\ P_2O_5$	0.60	.01
46	83	$36 + 0.20\ P_2O_5$	0.96	.01
	84	$16 + 0.16\ P_2O_5$	0.95	.01
47	83	$34 + 0.41\ P_2O_5$	0.99	.01
	84	$24 + 0.09\ P_2O_5$	0.85	.01
48	83	$49 + 0.24\ P_2O_5$	0.92	.01
	84	$43 + 0.09\ P_2O_5$	0.95	.01
49	83	$18 + 0.23\ P_2O_5$	1.00	.01
	84	$17 + 0.03\ P_2O_5$	0.94	.01

Table 13. Olsen b for 1984 and other pertinent soil characteristics across sites.

Site	pH	Fizz test	Initial P -kg ha^{-1}-	Olsen b '84
44	6.8	0	33.3	0.05
45	7.8	1.7	19.5	0.07
46	8.0	2.3	22.6	0.16
47	7.9	1.6	18.8	0.09
48	8.0	2.9	49.3	0.09
49	8.0	3.0	20.7	0.03

b values (0.03) and highest fizz test were again observed at site 49, indicating that this soil had a higher P fixing capacity. The highest b value (0.16) was observed at site 46, indicating that for this test, this soil had the lowest P fixing capacity. The greatest drop in slope from 1983 to 1984 was at site 47 where oats followed corn. Site 44 where corn followed wheat and site 45 where barley followed wheat were second and third, respectively, in the change of soil-P. The change in soil-P was similar for the remaining sites.

As in the case of Bray, there was no statistical relationship between the fizz test and pH and b values (Figure 11 and Figure 12). The initial soil test P level did not affect the b values for Olsen P (Figure 13).

3. Relationship between the Bray and Olsen soil test levels.

The relation between Bray and Olsen soil test results for both years across all the sites for the different treatments is presented in Figures 14 and 15. There is less spread and somewhat better correlation for the two tests in 1984 than in 1983. This could be due to the greater time the fertilizer products were in the soil and to the additional tillage operations that increase the mixing of fertilizer reaction products and soil.

For both years the Bray test did not reflect fertilizer additions at site 49. The factors involved in lack of response by the Bray test were probably the high reactivity of the carbonates and the rapidity of the soil fixation process of this site. Olsen test results were much lower in 1984 than in 1983 at site 49 due to the more intimate

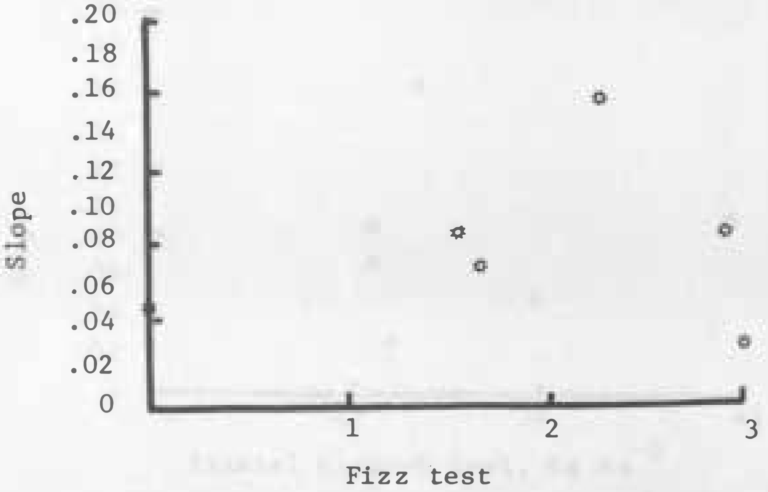

Figure 11. Relationship between the change in Olsen for a unit P and the fizz test.

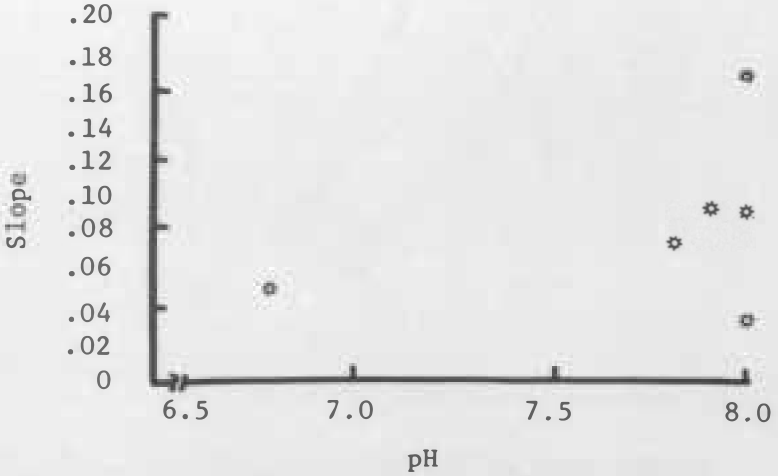

Figure 12. Relationship between the change in Olsen for a unit P and pH.

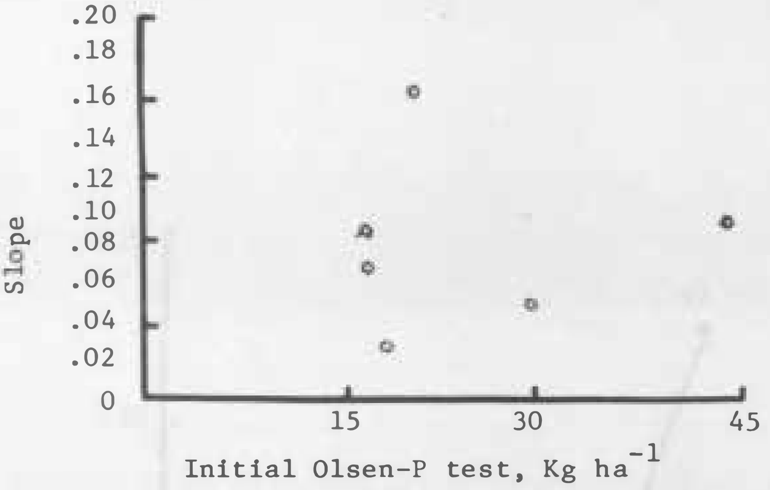

Figure 13. Relation between the initial Olsen-P test and the change in Olsen for a unit P.

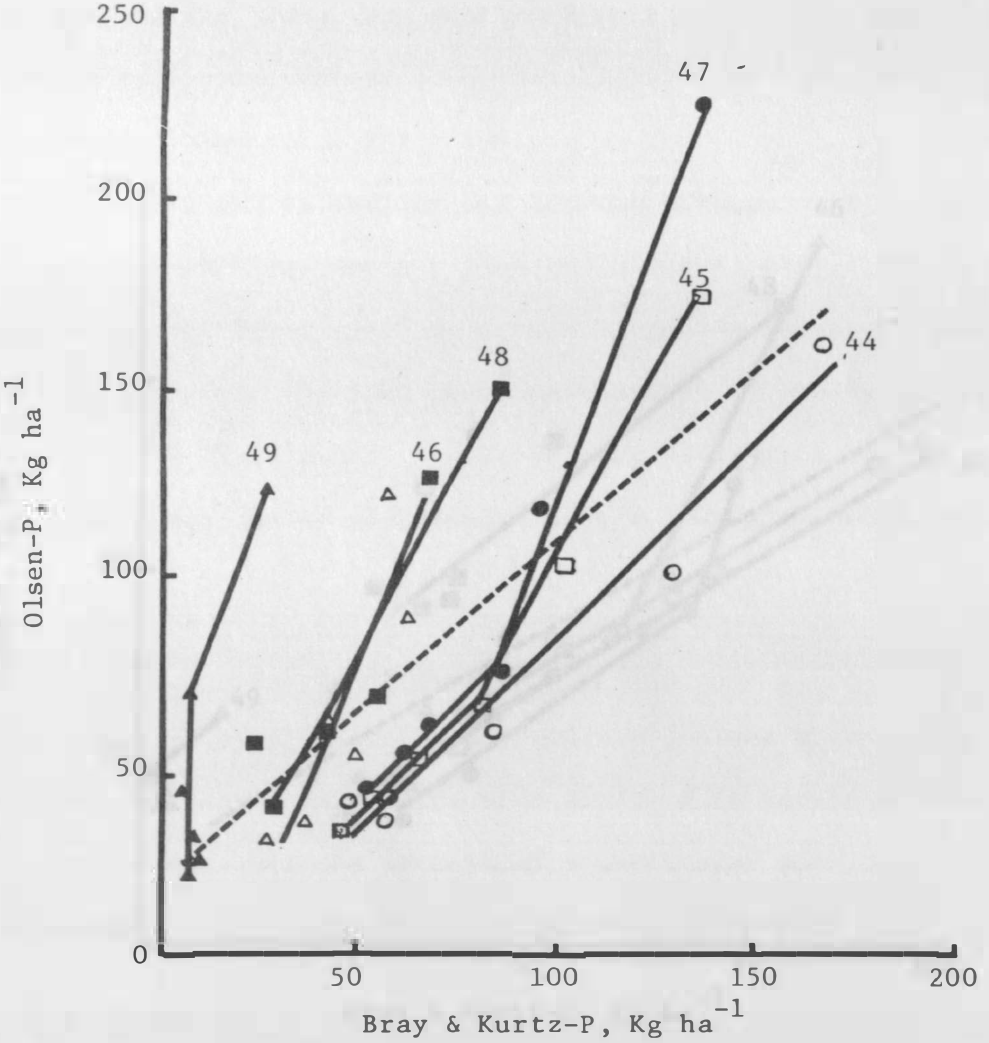

Figure 14. Relationship between Bray and Olsen soil P test level for 1983.

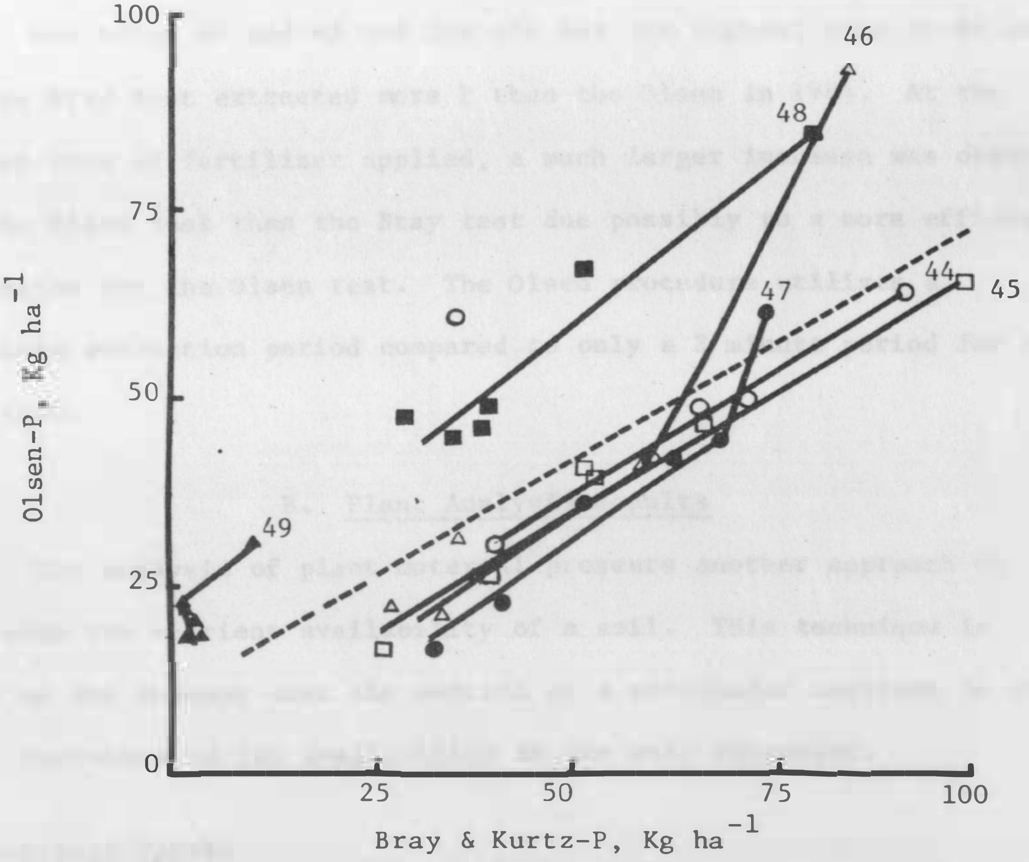

Figure 15. Relationship between Bray and Olsen soil P test level for 1984.

mixing of fertilizer reaction products and soil by the tillage operations.

At site 48 the Olsen test extracted more P than the Bray, due likely to the calcareousness of the site. At site 44 both tests extracted similar amounts of P for 1983.

For sites 44 and 45 and for all but the highest rate at 46 and 47, the Bray test extracted more P than the Olsen in 1984. At the highest rate of fertilizer applied, a much larger increase was observed for the Olsen test than the Bray test due possibly to a more efficient extraction for the Olsen test. The Olsen procedure utilizes a 30-minute extraction period compared to only a 2 minute period for the Bray test.

B. Plant Analysis Results

The analysis of plant material presents another approach to determine the nutrient availability of a soil. This technique is based on the concept that the content of a particular nutrient in the plant increases as its availability in the soil increases.

1. Nutrient Uptake

Leaf samples taken at the silking stage on 3 sites where corn was grown in 1983 were analyzed for P and Zn. The analytical results are given in Table 14 and graphed in Figure 16. Corn leaves in the investigated sites showed a high content of P ranging from 0.228% to 0.325%. Applied P caused minor changes in leaf P content. Zinc content varied from 9.9 to 15.9 mg kg^{-1} and generally decreased as the

Table 14. Plant analysis results from corn sites, 1983.

P_2O_5 Applied	Site 46		Site 47		Site 48	
	P	Zn	P	Zn	P	Zn
lbs A^{-1}	%	ppm	%	ppm	%	ppm
0	0.235	15.9	0.261	13.1	0.231	14.4
25	0.228	12.1	0.292	13.0	0.246	14.4
50	0.272	14.1	0.289	13.8	0.240	14.9
100	0.235	11.1	0.289	12.8	0.234	15.0
200	0.235	11.4	0.257	13.3	0.248	13.5
400	0.253	10.4	0.325	9.9	0.255	13.4

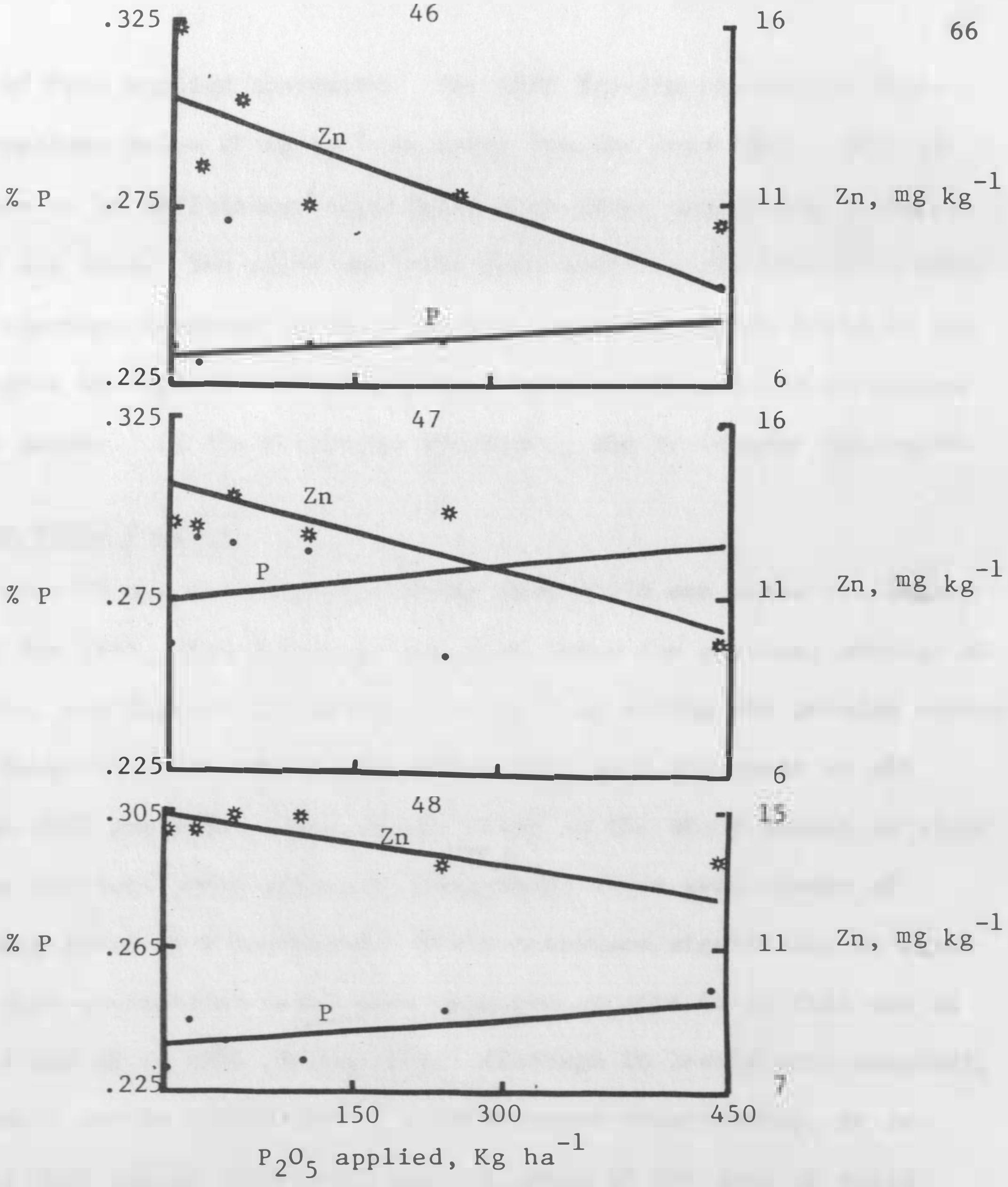

Figure 16. Relationship between P and Zn content of corn to applied P_2O_5.

amount of P_2O_5 applied increased. The SDSU Testing Laboratory cites concentrations below 20 mg kg^{-1} as being low for corn (22). Corn is sensitive to Zn deficiency, especially when large quantities of P fertilizer are used. The plant analysis data confirms the visual Zn deficiency symptoms observed on early growth, particularly at sites 46 and 47. Figure 16 depicts the relationship between % P and the Zn content of corn leaves. As the P content increased, the Zn content decreased.

C. Crop Yield Results

Site 45 was the only site where crop yield was below the county average for 1983. Precipitation was also below the seasonal average at this site, and Hessian fly larvae were spotted during the growing season.

Table 15 shows crop yield results for each treatment at all sites in 1983 and 1984. Most of the sites in the study showed no yield response for both years although, generally, there were trends of increasing yield as P increased. Yield responses significant at least at the 0.20 probability level were observed at site 48 in 1983 and at sites 45 and 49 in 1984 (Figure 17). Although Zn levels were marginal, since there was no indication of a Bell-shaped relationship, it is unlikely that the Zn deficiency was the cause of the lack of yield response.

Table 15. Crop yield results by treatments at individual sites for 1983 and 1984.

			Yield by P_2O_5 applied						Sign. of
Site	Year	Crop	0	28	56	112	224	448	F
			---------- Kg ha^{-1} ----------						
44	83	Wheat	1440	1440	1470	1520	1480	1510	NS1/
	84	Corn	1620	1510	1720	1700	1520	1460	NS
45	83	Wheat	1400	1350	940	1160	1250	1200	NS
	84	Barley	5180	5430	4710	4900	5340	5490	0.1
46	83	Corn	9900	9780	9890	9420	8980	10000	NS
	84	Soybeans	2760	2790	3060	2950	2990	2900	NS
47	83	Corn	3560	3030	2600	2700	3030	2940	NS
	84	Oats	----	----	----	----	----	----	--
48	83	Corn	5300	5110	5050	5170	5600	5500	0.17
	84	Oats	2710	2560	2470	2860	2760	2740	NS
49	83	Soybeans	2420	2320	2420	2390	2370	2590	NS
	84	Corn	6750	5790	6800	6510	7120	6870	.05

1/ Nonsignificant at 0.20 probability level.

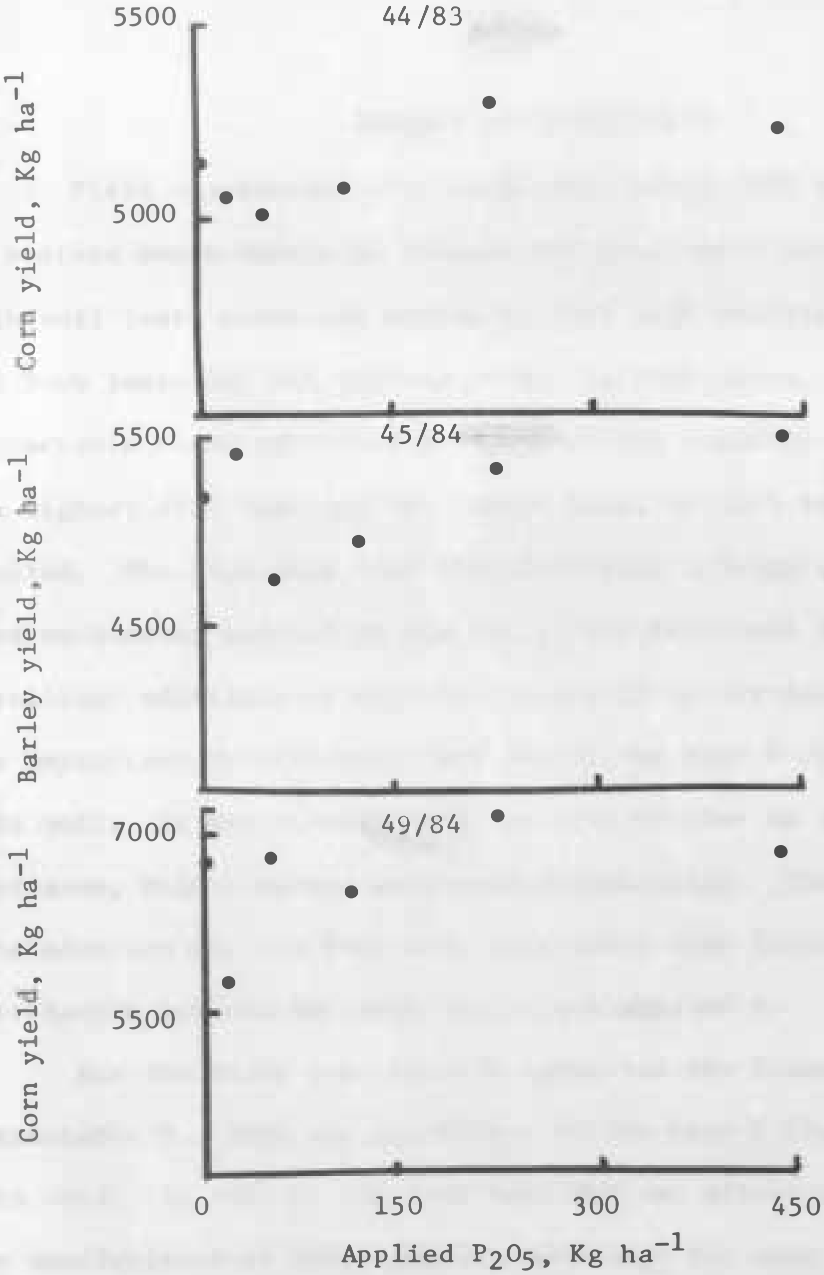

Figure 17. Effect of P_2O_5 on grain yield at the 3 most responsive sites.

SUMMARY AND CONCLUSION

Field experiments were conducted during 1983 and 1984 at 6 sites in eastern South Dakota to compare the Bray and Olsen soil P tests. Both soil tests predicted medium to very high amounts of available P for both years for all but one site. In both years, site 49 was low in extractable P and exhibited a high P fixing capacity. This site had the highest fizz test and the lowest slope of soil test level versus P applied. The high fizz test that indicates a large quantity of reactive carbonates existed in the soil. The Bray test did not reflect the fertilizer additions at site 49 due likely to partial neutralization of the extractant by carbonates and due to the high P fixing capacity of this soil. It was clearly shown at site 47 that as the fizz test increased, Bray-P levels decreased dramatically. The coefficients of determination for the Bray test were quite high indicating a high correlation between the soil test P and applied P.

For the Olsen test site 49 again had the lowest amount of extractable P. This was likely due to the high P fixing capacity of this soil. At site 47 the fizz test did not affect the Olsen-P levels. The coefficients of determination were high for most of the sites, indicating a high correlation between the Olsen-P and applied P.

The relationship between the Bray test and the Olsen test was evaluated. In 1983 both tests were predicting similar amounts of extractable soil P except at site 49, where the Bray test was not reflecting fertilizer additions. The Olsen test at this site reflected the fertilizer additions to a limited extent, especially in 1984. In

1984, the Bray test was predicting more available P than the Olsen test at all sites except one.

Other factors evaluated were the fizz test, pH, and initial soil P. For the Bray test no correlation was found between the slope of the regression equation and the fizz test or the pH. As the initial soil test P increased, the slope decreased.

Similarly, for the Olsen test, there was no statistical relationship between the fizz test and b values. Neither the soil pH or initial P test level affected the measured b values.

Although there were no significant yield responses, some trends of increasing yield with fertilizer additions occurred. Corn leaf samples taken at silking stage showed a correlation between P applied and Zn content. As the P content increased, the Zn content decreased. However, it is unlikely that Zn deficiency was the cause of the lack of the yield response to fertilizer P applied.

This study shows that generally both tests were predicting the available soil P content of eastern South Dakota alkaline soils and, thus, could be used as tools for predicting supplemental P requirements. Sites where the Bray test does not reflect fertilizer additions also appear to have high P fixing capacities. Thus, the Bray test may have some potential as a screening test for high P fixing soils.

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APPENDICES

Table 1. Bray-P soil test results (lbs A^{-1}) at site 44 for 1983 and 1984.

Replication	Year	Treatments 1	2	3	4	5	6
1	83	36	49	44	72	98	104
	84	28	34	34	62	76	98
2	83	52	51	40	113	135	180
	84	52	34	69	49	60	56
3	83	38	45	52	56	98	---
	84	28	42	—	60	69	86
4	83	42	58	62	63	124	153
	84	40	104	52	63	54	86

Table 2. Bray-P soil test results (lbs A^{-1}) at site 45 for 1983 and 1984.

Replication	Year	Treatments 1	2	3	4	5	6
1	83	42	38	44	56	98	120
	84	22	26	28	36	60	104
2	83	35	51	69	67	76	144
	84	28	30	30	51	54	54
3	83	47	48	69	67	98	80
	83	25	26	72	47	70	113
4	83	34	49	40	94	83	135
	84	22	52	60	65	54	88

Table 3. Bray-P soil test results (lbs A^{-1}) at site 46 for 1983 and 1984.

		Treatments					
Replication	Year	1	2	3	4	5	6
1	83	45	51	48	65	116	70
	84	32	42	35	48	63	62
2	83	25	47	06	56	36	88
	84	30	34	32	32	44	96
3	83	13	20	35	12	32	40
	84	30	22	34	12	47	113
4	83	17	05	88	13	34	09
	84	24	06	32	38	51	35

Table 4. Bray-P soil test results (lbs A^{-1}) at site 47 for 1983 and 1984.

		Treatments					
Replication	Year	1	2	3	4	5	6
1	83	38	40	76	80	08	164
	84	24	40	62	56	35	83
2	83	51	34	65	86	104	139
	84	32	25	48	49	88	65
3	83	49	52	56	69	102	160
	84	35	35	40	69	45	113
4	83	44	88	44	78	124	24
	84	25	51	32	67	56	07

Table 5. Bray-P soil test results (lbs A^{-1}) at site 48 for 1983 and 1984.

		Treatments					
Replication	Year	1	2	3	4	5	6
1	83	11	24	19	40	51	35
	84	17	22	09	40	24	14
2	83	40	12	12	49	72	88
	84	50	14	14	44	45	76
3	83	13	13	56	45	65	72
	84	15	19	56	24	65	113
4	83	45	32	60	56	40	78
	84	45	48	60	51	51	86

Table 6. Bray-P soil test results (lbs A^{-1}) at site 49 for 1983 and 1984.

		Treatments					
Replication	Year	1	2	3	4	5	6
1	83	08	05	08	04	04	05
	84	01	04	01	01	01	01
2	83	04	04	04	08	01	01
	84	06	02	01	01	02	08
3	83	01	02	08	01	11	09
	84	01	01	02	02	04	02
4	83	04	24	05	05	06	69
	84	01	07	02	01	01	26

Table 7. Bray and Kurtz soil P test results (lbs A^{-1}) for individual sites for 1983 and 1984.

		Treatment					
Site	Year	0	25	50	100	200	400
44	83	42	51	50	76	114	146
	84	37	54	32	59	65	82
45	83	40	47	56	71	89	120
	84	24	34	48	47	60	90
46	83	25	31	44	37	55	52
	84	29	26	33	33	51	77
47	83	46	54	60	78	85	122
	84	29	38	46	60	56	67
48	83	27	20	37	48	57	68
	84	32	26	36	35	46	72
49	83	4	9	6	5	6	21
	84	2	4	2	1	2	9

Table 8. Regression equations for predicting soil Bray & Kurtz-P test from applied P fertilizer (lbs A^{-1}).

Site	Year	Equation	r^2
44	83	$45 + 0.27\ P_2O_5$	0.96
	84	$41 + 0.11\ P_2O_5$	0.77
45	83	$45 + 0.20\ P_2O_5$	0.98
	84	$31 + 0.15\ P_2O_5$	0.95
46	83	$33 + 0.06\ P_2O_5$	0.60
	84	$25 + 0.73\ P_2O_5$	0.97
47	83	$51 + 0.18\ P_2O_5$	0.97
	84	$39 + 0.08\ P_2O_5$	0.70
48	83	$29 + 0.11\ P_2O_5$	0.84
	84	$77 + 0.11\ P_2O_5$	0.95
49	83	$4 + 0.04\ P_2O_5$	0.72
	84	$1 + 0.02\ P_2O_5$	0.63

Table 9. Olsen-P soil test results (lbs A^{-1}) at site 44 for 1983 and 1984.

		Treatments					
Replication	Year	1	2	3	4	5	6
1	83	30	38	35	53	80	85
	84	22	26	26	41	55	70
2	83	43	38	48	68	104	175
	84	38	28	53	38	43	44
3	83	36	40	55	49	82	190
	84	20	32	94	41	41	53
4	83	33	43	48	44	100	124
	84	26	63	41	46	33	59

Table 10. Olsen-P soil test results (lbs A^{-1}) at site 45 for 1983 and 1984.

		Treatments					
Replication	Year	1	2	3	4	5	6
1	83	28	35	32	41	94	124
	84	14	18	14	24	40	72
2	83	28	40	60	56	85	160
	84	16	22	24	38	36	36
3	83	33	41	64	63	89	124
	84	16	18	56	32	52	68
4	83	26	40	28	80	104	215
	84	16	36	44	49	36	55

Table 11. Olsen-P soil test results (lbs A^{-1}) at site 46 for 1983 and 1984.

		Treatments					
Replication	Year	1	2	3	4	5	6
1	83	36	44	43	56	111	94
	84	20	24	24	38	40	52
2	83	22	28	24	75	44	124
	84	16	18	24	28	33	82
3	83	33	24	35	46	80	128
	84	22	16	22	24	44	143
4	83	18	24	87	49	80	87
	84	14	24	20	24	28	55

Table 12. Olsen-P soil test results (lbs A^{-1}) at site 47 for 1983 and 1984.

		Treatments					
Replication	Year	1	2	3	4	5	6
1	83	41	35	85	80	102	160
	84	12	22	52	35	18	49
2	83	41	28	60	70	111	120
	84	18	12	35	30	68	41
3	83	36	46	41	53	94	205
	84	16	18	22	46	24	70
4	83	35	82	32	64	117	320
	84	14	30	16	41	35	59

Table 13. Olsen-P soil test results (lbs A^{-1}) at site 48 for 1983 and 1984.

Replication	Year	Treatments 1	2	3	4	5	6
1	83	30	53	49	55	94	156
	84	30	53	32	35	75	60
2	83	40	49	52	75	92	114
	84	56	32	40	43	60	68
3	83	36	49	59	70	132	128
	84	28	43	52	41	52	128
4	83	48	53	55	49	134	132
	84	43	40	48	46	53	85

Table 14. Olsen-P soil test results (lbs A^{-1}) at site 49 for 1983 and 1984.

Replication	Year	Treatments 1	2	3	4	5	6
1	83	20	22	30	32	40	128
	84	20	16	18	18	18	24
2	83	16	20	22	32	46	85
	84	16	16	14	20	26	32
3	83	20	22	28	40	59	117
	84	16	10	12	20	22	28
4	83	18	24	33	44	104	111
	84	14	20	16	20	16	28

Table 15. Olsen-P test results (lbs A^{-1}) for individual sites for 1983 and 1984.

		Treatment					
Site	Year	0	25	50	100	200	400
44	83	36	40	47	54	92	144
	84	27	37	54	42	43	57
45	83	29	39	46	60	93	156
	84	16	24	35	36	41	58
46	83	27	30	47	57	79	108
	84	18	21	23	29	36	83
47	83	38	48	55	67	106	201
	84	15	21	31	38	36	55
48	83	39	51	54	62	113	133
	84	39	42	43	41	60	76
49	83	19	22	28	37	62	110
	84	17	16	15	20	21	28

Table 16. Regression equations for predicting soil Bray & Kurtz-P test from applied P fertilizer (lbs A^{-1}).

Site	Year	Equation	r^2
44	83	$45 + 0.27\ P_2O_5$	0.96
	84	$41 + 0.11\ P_2O_5$	0.77
45	83	$45 + 0.20\ P_2O_5$	0.98
	84	$31 + 0.15\ P_2O_5$	0.95
46	83	$33 + 0.06\ P_2O_5$	0.60
	84	$25 + 0.73\ P_2O_5$	0.97
47	83	$51 + 0.18\ P_2O_5$	0.97
	84	$39 + 0.08\ P_2O_5$	0.70
48	83	$29 + 0.11\ P_2O_5$	0.84
	84	$77 + 0.11\ P_2O_5$	0.95
49	83	$4 + 0.04\ P_2O_5$	0.72
	84	$1 + 0.02\ P_2O_5$	0.63

Table 17. Amount of P_2O_5 applied to change the soil test level by one unit for 1984.

Site	Bray & Kurtz	Olsen
44	9.1	20
45	5.0	11.1
46	7.7	6.3
47	12.5	11.1
48	9.1	11.1
49	50	33.3
$\overline{x}$	15.6	15.2
$\overline{x}$ (excluding 49)	8.7	11.9