# SOME FACTORS AFFECTING THE SOLUBILITY OF SOIL PHOSPHORUS IN STANDARD SOIL TESTING EXTRACTANTS.

by

JOHN DAVID DONNELLY

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ORIGINALITY OF THESIS.

This is a statement to certify that, except for the assistance acknowledged, the experimentation and analysis, interpretation and presentation of the results are my own original work.

J.D. Donnelly

J.D. DONNELLY.

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## SUMMARY.

A study of the effects of variation in soil composition on the P values obtained by a range of standard soil testing procedures is described.

In a preliminary study P test values were obtained for a range of 44 soils from eastern Australia and the soils were characterized by a series of standard analyses for Fe, Al, Mn, Ti, Ca, Mg, K, Na, C, clay, pH and P fractions. The relationships between P test values were then examined by fitting regression models to the data. The importance of the characterizing analyses to these relationships was then assessed by analyses of variance of the regressions. The more important soil analyses for explaining the relationships between the P test values were oxalate (Tamm)-soluble Fe and Al, total Ca and Mg, or organic C.

More extensive studies were then carried out on 145 soil samples with characterizing soil analyses selected on the basis of the preliminary studies.

P test values determined by the $H_2SO_4$-P, Acetic-P and Truog-P procedures were very highly correlated with each other but only moderately correlated with P values determined by other test procedures. However, with any of these 3 dilute acid test P values as dependent variable, the relationships with other P

test values were greatly improved by allowing for the effects of exchangeable Ca or Mg. These analyses apparently represent a source of P dissolved more by $H_2SO_4$-P, Acetic-P and Truog-P extraction procedures than by the other extractions. Smaller effects of oxalate-Fe and Al on the relationships were attributed to resorption of P during acid extraction. That these effects did not occur with the other tests indicated that either a blocking agent (fluoride, lactate or citrate anions) or an alkaline pH was inhibiting resorption during these extractions.

The alkaline tests, Bicarbonate-P and NaOH-P, were shown to be affected by the oxalate-Fe and Al analyses, thus suggesting these tests dissolve more of the Fe and Al bound P than the acidic tests.

The Citric-P relationships suggest this test dissolves P from sources represented by both Ca and Mg analyses and Fe and Al analyses.

Bray-P and Lactate-P values were closely related to each other but not to the other test values, nor were any of the present series of analyses able to improve these relationships substantially.

The implications of these results to the development of soil testing for P fertilizer requirements is discussed.

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# I. INTRODUCTION.

Phosphorus is the most important soil nutrient element restricting plant growth in Australia, as evidenced by the widespread use of phosphatic fertilizers. For example, for the year ended 30th June 1968 3·6 million tons of phosphatic fertilizers were used in Australia (Bureau Census and Statistics, 1969) and this amount is much greater than that for any other fertilizer. The P fertilizer requirements of individual paddocks are usually estimated on the basis of fertilizer experiments carried out within districts (for example: Beare, 1968) and also on the basis of the farmer's personal experience of responses, the paddock history, the traditional dressings of the district or farm and the availability of finance (Donald, 1964).

In order to obtain more specific estimates of the P fertilizer requirements of individual paddocks chemical soil analyses for readily soluble P, termed soil tests, are often used.

The standard P tests differ with respect to composition of the extracting solution, soil:solution ratio, time and temperature of extraction, etc. (Williams, 1952), ranging from soil extractions that give P values approaching a total P analysis, such as hot 0·1N NaOH (Saunder, 1956), to very mild extractions such as water or weak salt solutions (for example: Aslyng, 1954, used 0·01M $CaCl_2$). No single P test is consistently superior on all soils, the relative usefulness of different tests varying

with the type of soil. The reasons for variability in the usefulness of the P tests amongst different soils are not properly understood. In general the solubility of soil P in different P test extractions is affected by soil composition, the effects of particular constituents depending on the nature of the extraction. The experimental study reported in this thesis examines the relationships between the P test values obtained by a series of procedures and the extent to which these relationships can be explained by soil composition.

The study is described in two sections. Firstly a preliminary study was carried out with a selection of 44 contrasting soils to determine the most important soil constituents affecting the relationships between P test values by different procedures. This was followed by a more extensive study involving 145 soils to establish more representative relationships.

# II. LITERATURE REVIEW.

## 1. Forms of soil phosphorus.

The forms of soil P are of interest because the result of any P test can be expected to depend on their relative solubility under the experimental conditions of the P test procedure. The P forms may be identified in various ways. Thus one may attempt to identify all the inorganic P minerals present in the soil and organic P compounds. Another approach is to partition the soil P into solubility fractions.

### 1.1 Mineral forms.

In most soils few P minerals can be easily identified because many are present as complexes of iron, aluminium, manganese, titanium, calcium, magnesium and barium. The common P minerals known to occur in soils are Ca phosphates, such as hydroxyapatite and fluorapatite, Fe phosphates, such as vivianite and strengite and Al phosphates such as wavellite and variscite (Black, 1957; Huffman, 1962).

P minerals may be prepared under laboratory conditions supposedly similar to conditions in soil (Haseman *et al.*, 1950; Kittrick and Jackson, 1956). Haseman *et al.* (1950) synthesized taranakite and three other groups of similar minerals, the formulae of which suggest extensive isomorphous substitution with

a consequent wide range of solubilities. These forms of P may not, however, occur in soils (Norrish, 1968). Similarly, evidence of the existence of a number of these P minerals in soils from solubility product data (for example: Wright and Peech, 1960) cannot be considered conclusive since the situation is very complicated (Larsen, 1967).

Studies by Machold (1963), Murrmann and Peech (1968) and Roth (1968) suggest that amorphous Fe and Al phosphate complexes are more important sources of P to plants than crystalline compounds, such as strengite and variscite. Further, many of the crystalline forms cannot be identified in the surface horizons of Australian soils (Norrish, 1968).

### 1.2 Chemical solubility forms.

Inorganic soil P may be characterized into chemical forms according to solubility in particular reagents. Such classifications are simpler than the direct determination of the mineral forms, and for this reason are more popular.

Early schemes (Ghani, 1943; Williams, 1950) made no attempt to specify the nature of the compounds yielding the P within each fraction, and used such simple terms as "acid-soluble P" and "alkali-soluble P". The fractionation procedure of Chang and Jackson (1957) was claimed by its originators to be a departure from previous methods in that it enabled a

> "... fractionation of inorganic soil phosphorus into the total amount of each discrete chemical form ... ".

Under the extracting conditions specified by Chang and Jackson the P soluble in neutral ammonium fluoride is called "aluminium-bound P", in sodium hydroxide solution "iron-bound P", and in sulphuric acid "calcium-bound P". Following these successive extractions the remaining P in the soil residue may be further fractionated into P occluded in iron oxides ("reductant-soluble Fe-P") and either "occluded Al-P" or "occluded Al-Fe-P".

The scheme has been subjected to a number of criticisms (Khin and Leeper, 1960; Bromfield, 1967; Khanna and Uhlrich, 1967), and has, in turn, been improved by a number of modifications, such as the scheme devised by Williams et al., (1967). The main difficulty lies in ensuring that extraction of each P form is substantially complete while only negligible quantities of other forms are dissolved. Although the procedure of Williams et al., (1967) includes many precautions against, and allowances for, such errors, there remains some uncertainty when working with soils very different from those used in the establishment of the extraction procedures. For example, Bromfield (1967) has shown the difficulty of distinguishing between aluminium phosphate and the P of recently phosphated iron oxides, since the latter can be fairly soluble in the ammonium fluoride reagent used to selectively extract aluminium phosphates.

The use of chemical extractions to characterise forms of soil P is in dispute not only on grounds of technique but also

on grounds of principle. Norrish (1968) argued that as extraction is an indirect method of identification it is inherently inferior to X-ray diffraction, which is more direct. However, extraction methods may not only be easier than X-ray techniques, but more suitable in that their estimate includes P in the form of adsorbed monolayers and metal-humate complexes.

When Chang and Jackson (1957) first presented their scheme they suggested it would have applications in the fields of classification, genesis and fertility of soils. They used the scheme themselves to support the hypothesis that in weakly weathered soils most of the inorganic P is present as Ca-bound P, and in moderately weathered soils the principal form is P sorbed as films on aluminium and iron oxides. As weathering proceeds an increasing proportion of P occurs inside iron oxide precipitates (Chang and Jackson, 1958). Cho and Caldwell (1959) found alkaline soils were abundant in the Ca-bound forms of P, whereas in soils of low pH the Fe- and Al-bound forms were predominant. In soils of neutral reaction all forms were equally abundant. Other similar studies (for example: Hawkins and Kunze, 1965; Westin and Buntley, 1966) have generally provided results consistent with these.

### 1.3 Organic Phosphorus.

The importance of organic forms of soil phosphorus to

plant growth is dependent on the rate at which they can be mineralized. In temperate climates mineralization is considered to be too slow to provide sufficient P for rapid plant growth (Williams, 1966; Russell, 1961, p.496) and so soil tests have been designed only to take account of inorganic P. In fact evidence that a soil test may be dissolving organic P has been used to discredit the test (Van der Paauw, 1959). As the situation in tropical regions can be quite different, with a flush of mineralized P being produced under suitable conditions (Russell, 1961, p.496), it may be appropriate to examine incubation procedures as a basis for P testing in the tropics. Since the work embodied in this thesis was carried out on soils from a temperate region, and since the classical soil tests are of inorganic P, organic phosphorus has not been included in this study.

## 2. The availability of soil phosphorus to plants.

The immediate source of P for crops growing in a soil is probably that of the inorganic phosphate ions in the soil solution (Russell, 1961, p.489). The word "intensity" is commonly used to describe the concentration or activity of this immediately available P. One such measurement is simply the concentration of P in the soil solution or in a suspension of soil and water. Another is the mono-calcium phosphate potential: $\frac{1}{2}$ p Ca + p($H_2PO_4$)

where the p notation is analogous to pH. It has been suggested (Schofield, 1955; Aslyng, 1954) that the availability of soil P to plants is mainly determined by the mono-calcium phosphate potential in the soil solution, together with the soil's capacity to maintain this potential during periods of P withdrawal by plant roots. The practical usefulness of P potential measurements has not yet been clearly demonstrated (Quirk, 1966). Their usefulness has been shown in a glasshouse pot trial by Barrow (1967), but Wild (1964) has shown their estimation may not be superior to simple concentration of P.

The P potential concept has been criticised on theoretical grounds (Wilson, 1968) and its measurement is undoubtedly beset by many practical problems (Larsen, 1967). Nevertheless, the evidence is that some measurement of the intensity of P supply, (such as P concentration with or without transformation for potential, complex formation, activity coefficients or orthophosphate ion species) can give useful information on the availability of soil P (Larsen, 1967). Asher and Loneragan (1967) have shown that, for a wide variety of species growing in solution culture, there was a marked response to increments of solution P concentration until a certain level (characteristic of each species, but usually in the range 1 to 5 $\mu$M) was reached. Above this level there was little or no yield increase with increasing P concentration.

The value of soil P intensity measurements can be improved by allowing for variation in other soil parameters. Soil P capacity, the ability to supply P to the soil solution, has already been mentioned as a parameter required in addition to potential, according to Schofield (1955). One measure of capacity used by Olsen and Watanabe (1963) is described below. A number of factors can limit this supply of P: (i) the quantity of readily soluble P present, (ii) the rates of dissolution of the various P fractions and (iii) the rate of P diffusion through the soil micropores. Further parameters can be derived by combining some of these. For instance, the slope of the line relating labile P (quantity of P readily exchangeable with $^{32}P$) to concentration of P in solution has been called the phosphate capacity by Olsen and Watanabe (1963). These authors found that most of the variation in the rate of P uptake by corn seedlings could be explained by variation in the term b D, where b is the phosphate capacity and D is a phosphate diffusion coefficient. Using a quantity/intensity relationship (a sorption isotherm), Ozanne and Shaw (1968) estimated the quantity of P required to raise the concentration of the equilibrium solution to 0·3 ppm. They found this sorption parameter to be a useful indicator of phosphate fertilizer requirement. Cooke (1966) found the rate of release of P to a "sink" (an ion exchange resin) was more important in determining crop uptake of P than the equilibrium P concentration. Thus

intensity, quantity, rate and diffusion measurements are all implicated in the description of soil P availability.

As with many soil properties, these parameters are themselves inter-related to some extent. For example Phillips et al. (1968) found the magnitude of the phosphate diffusion coefficient in a range of clays and soils was a function of the capacity of the soil or clay to sorb P. Because of this intercorrelation of properties Larsen (1967) considered it unnecessary to obtain data on all the relevant P supply parameters. He quoted the results of Gunary and Sutton (1967), who found 80 to 85 percent of the variation in P uptake from a range of soils could be accounted for by an intensity factor (log P concentration) and a quantity factor (the 'L-value', a pot trial assessment of soil P status using $^{32}P$ to include soil P reserves not utilized during the period of plant growth).

In spite of this moderate success it still appears to be a difficult task to predict responses to fertilizers, and thus fertilizer requirements, particularly over a wide range of soils and under field conditions. Further refinements in our understanding of soil-plant relationships will be helpful. For instance, an assessment of the importance of root exudates in modifying the chemical environment immediately adjacent to the plant root is needed, as these excretions may facilitate the displacement of sorbed P from colloidal interfaces (Quirk, 1966).

## 3. Soil tests for phosphorus fertilizer requirement.

### 3.1 Introduction.

The usual aim of soil testing is to determine fertilizer requirement and the value of soil tests is usually assessed by the magnitude of their correlation with yield response to fertilizer. Other crop measures, such as P uptake, although less easily related to economic fertilizer requirement than is yield response to fertilizers, are also often used for the valuation of P tests.

It might be thought possible to devise a universally suitable soil test from an understanding of the behaviour of soil P as outlined in the previous sections of this review. The test would have to represent both the quantity of soil P available to plants and the effects of soil factors on the availability of added P fertilizer. The test must also provide a measure of the importance of these factors throughout the growing season. The difficulty inherent in the theoretical approach is that a very complex situation is involved and it is doubtful that a single measurement could accurately allow for all the variables involved. The success of the simple soil test measurements depends on the extent to which they represent all of the soil factors affecting the availability of P to plants. The soil tests are conveniently considered under headings related to their

chemical nature. Procedures for the more common standard P tests are summarized in Table 1, and the abbreviated notation for these P tests contained in the first column of Table 1 will be used in the remainder of the thesis.

3.2 Acid extractants.

A series of soil test procedures has been based on extraction of soil P by various dilute acid solutions. These solutions have often been chosen on theoretical grounds such as that plant roots excrete acids (Dyer, 1894; Truog, 1930). Extraction with 0·2N acid has been proposed because this dissolves various calcium phosphates and only slowly attacks the iron and aluminium phosphates (Kurtz, 1953). This assumption that calcium phosphates were the source of P to plants has been ".... commonly believed, though on no good evidence ...." (Russell, 1961, p.495). Examples of acid extractants are 0·01N sulphuric acid (the $H_2SO_4$-P test, Table 1), a standard test in Queensland, and 2·5% acetic acid (Acetic-P, Table 1), a standard test in Scotland. Many other acid tests, some as strong as 0·3N HCl, have been used successfully (see reviews by Mattingly and Talibudeen, 1967, and Nelson et al., 1953).

It is now generally recognized that acid reagents extract calcium phosphates from soil and this is the reason for the use of 0·5N sulphuric acid reagent for the fractionation of

TABLE 1.

Some Standard P tests.

| Title | Reference | Reagent | Soil:Solution | Shaking Time |
|---|---|---|---|---|
| Truog-P | Truog (1930) | 0·002N $H_2SO_4$ +$(NH_4)_2SO_4$,pH 3·0 | 1:200 | 30 min |
| Acetic-P | Williams and Stewart (1941) | 2·5% acetic acid, pH 2·6 | 1:200 | 16 hr |
| $H_2SO_4$-P | Kerr & Von Stieglitz (1938) | 0·01N $H_2SO_4$,pH 2·2 | 1:200 | 16 hr |
| Citric-P | Dyer (1894) | 1% citric acid, pH 2·1 | 1:10 | 16 hr |
| Bray No.1-P | Bray & Kurtz (1945) | 0·03N $NH_4F$, 0·025N HCl | 1:7 | 1 min |
| Bray No.2-P | Bray & Kurtz (1945) | 0·03N $NH_4F$, 0·1N HCl, pH 1·7 | 1:7 | 40 sec |
| Bray No.3-P | Bray & Kurtz (1945) | 0·5N $NH_4F$, pH 7·0 | 1:50 | 1 hr |
| CaLactate-P | Egner *et al.* (1938) | 0·02N Ca lactate+0·01N HCl, pH 3·7 | 1:50 | 2 hr |
| D.Lactate-P | Kosanovic *et al.* (1962) | 0·04N Ca lactate+0·02N HCl, pH 3·7 | 1:50 | 2 hr |
| $NH_4$Lactate-P | Egner *et al.* (1960) | 0·1N $NH_4$ lactate+ 0·4N acetic acid, pH 3·8 | 1:20 | 4 hr |
| Olsen-P | Olsen *et al.* (1954) | 0·5M $NaHCO_3$, pH 8·5 | 1:20 | 30 min |
| NaOH-P | Saunder (1956) | 0·125N NaOH | 1:200 | 5 min, boiling |
| Morgan-P | Morgan (1941) | 3% acetic acid+10% Na acetate, pH 4·8 | e.g. 1:5 | e.g. 30 min |

Ca bound phosphates in the P fractionation scheme of Chang and Jackson (1957). Strongly acid extractants may also dissolve appreciable quantities of Fe and Al bound P (Williams, 1952), so in the Chang and Jackson fractionation these forms of P are removed before the 0·5N sulphuric acid extraction. P extracted by the dilute acid Truog-P and $H_2SO_4$-P tests (Table 1) has usually been shown to correlate more highly with the Chang and Jackson "Ca-bound P" fraction than with "Fe-bound P" or "Al-bound P" (Grigg, 1965; Chang and Juo, 1963; Misra and Ojha, 1969), although Truog-P has also been related to "Al-bound P" as well as "Ca-bound P" (Suzuki et al., 1963). Not all soils are suitable for using acid tests since these sometimes measure high amounts of P which are apparently unavailable to plants (Nelson et al., 1953). In England 0·3N HCl was found frequently ineffective on calcareous soils (Mattingly and Talibudeen, 1967). This may be because some calcium phosphates, at least in the apatite series, have poor availability to plants (Lamm et al., 1963; Chu and Chang, 1966).

A feature of the more dilute acid extractants is that resorption can take place since their final pH, usually in the range 3 to 5, is close to the anion sorption capacity of most soils (Williams, 1952). Many studies have shown that under acid conditions P is sorbed mainly by the Fe and Al minerals in the soil (for example, reviews by Wild, 1950; Hemwall, 1957; Smith,

1965). Thus, the P dissolved from Ca phosphates may not all appear in the final solution due to resorption during extraction. The resulting concentration will then represent the net effect of the dissolution-resorption processes and will vary with time of extraction, often showing a maximum followed by a decrease as resorption becomes more important (Williams, 1952; Askinazi and Guinsbourg, 1957). The extent of resorption depends not only on extraction time but also on the soil:solution ratio, temperature of extraction and nature of the anion. Thus some workers, attempting to reduce resorption of extracted P, have advocated a short extraction time, a low soil:solution ratio or incorporation of reagents to block resorption sites.

The extent of resorption also depends, of course, on the soil's content of sorbing material. It has already been indicated that Al and Fe minerals are the main sites of P sorption under acid conditions, but the relative importance of these minerals remains a matter of controversy. Smith (1965) reviewed considerable evidence favouring either Fe or Al minerals and concluded that both could be active sorbers under appropriate conditions but what conditions favoured sorption by Fe rather than Al and vice versa were not clear. Fried and Dean (1955) found that while resins coated with Fe or Al sorbed similar quantities of P in separate systems, the Fe-resin sorbed much more P than the Al-resin in a system where the two resins were mixed. This

shows the difficulty of extrapolating results obtained in pure systems to the complex system that is soil. Important factors in sorption of P are the degree of hydration and crystallinity of the sorbing minerals, with the more hydrated and amorphous forms having greater sorbing capacity. However, the mechanism of sorption may be similar, as shown for gibbsite and kaolinite (Muljadi et al., 1966). The results of Humphreys and Lambert (1965) suggest that exchangeable Al may account for most of the relation of other, stronger extractions of "active" Al to P sorption. Organic matter may sorb P but usually it has been possible to relate this to the content of Al or Fe in the organic matter as a metal-humate complex (Kaila, 1959; Weir and Soper, 1963; Larsen et al., 1959; Williams, 1960). P sorption by such complexes has actually been reduced by the addition of humic acid (Larsen et al., 1959) and sorption of P by oxide minerals was reduced by the addition of fulvic acid (Leaver and Russell, 1957). Apart from Fe and Al, other sites of P sorption are Mn and Ti minerals (Ghani and Islam, 1957; Beckwith and Little, 1963). Ghani and Islam found that although in acetic acid medium Mn and Ti oxides sorbed less P than equivalent (equal surface areas) amounts of Fe and Al oxides, the Mn and Ti sites were less easily blocked by complexing anions such as selenate.

In view of the effects discussed above it is not surprising to find that P values obtained by some of the standard

dilute acid test extractants have been affected by the soil content of clay (Hamdi et al., 1958) and citrate-soluble Al (Franklin and Reisenauer, 1960). Since the standard P test procedures vary considerably in such conditions as extract pH, extraction time, etc., these effects could explain differences between P tests.

### 3.3 Complexing extractants.

The sesquioxides (hydrous oxides of Fe, Al, Mn and Ti) in soil may react with the anions of some extractants to form stable complexes, thus releasing P. P held to organic matter via metal ions may also be released in the same way. These anions can at the same time serve to block sites of possible resorption of P during acid extractions. Several studies have been made of relative abilities of various anions to displace P from soils and block the sorption of added P. These have usually shown citrate, selenate, oxalate and fluoride to be very effective, 8-hydroxy-quinoline to be less effective, though still useful, and anions such as sulphate, nitrate and chloride, which do not complex with metal cations, to be least effective (Williams, 1952). The relative effectiveness of the complexing anions has been found to differ according to soil type, extract pH and the initial level of P (Deb and Datta, 1967). Recent studies of the mechanism of the sorption of anions by goethite and gibbsite have shown that

competition between anions, including phosphate and the organic acid anions, is dependent more on the relative ability of the species to increase the negative charge on the colloid surface than on simple anion exchange (Nagarajah et al., 1968; Hingston et al., 1968).

Among the standard P tests containing complexing anions are (see Table 1) Citric-P, $NH_4$ Lactate-P and several due to Bray. Bray and Kurtz (1945) claimed fluoride displaced from the soil colloid surfaces adsorbed P which was not fully extracted by acid action alone. Tandon et al. (1967) found that more Fe and Al, as well as P, were extracted by acid fluoride than by acid alone, which indicates fluoride to be a rather strong reagent. Further evidence of this was provided by the studies of Huang and Jackson (1965), who found neutral ammonium fluoride attacked the clay structure, not just exchanging with surface hydroxyls but also dissolving lattice iron (III) and aluminium ions with stoichiometric release of hydroxyl. It was realized long ago that fluoride might attack difficultly soluble forms of P but it was thought this could be counteracted by using a very short period of extraction (Williams, 1952).

From the action of complexing anions these extractants could be expected to dissolve mainly Al and Fe bound P, but since most of them are acidic they may also dissolve some Ca bound P. Fluoride, however, tends to suppress the solubility of phosphate

both in soils containing free calcium carbonate and those carbonate-free soils whose cation exchange capacity is nearly saturated with calcium and magnesium (Smith et al., 1957; Tandon et al., 1967). Studies correlating P test values with the Chang and Jackson P fractions have shown Bray No.1-P, $NH_4$ Lactate-P and D.Lactate-P values to be correlated with "Al-bound P" (Payne and Hanna, 1965; Werner, 1969; Pratt and Garber, 1964) and for Bray No.2-P and $NH_4$ Lactate-P to be correlated with both "Al-bound P" and "Ca-bound P" (Suzuki et al., 1963; Grigg, 1965). These results may, however, be biased to whichever form of P is predominant in the soils studied.

### 3.4 Alkaline extractants

Strong alkalis dissolve both iron and aluminium phosphates. In the Chang and Jackson fractionation 0·1N sodium hydroxide is used to dissolve Fe bound P after the Al bound P is dissolved by ammonium fluoride. Hot 0·1N sodium hydroxide has also been used to remove "adsorbed P" (Piper, 1942). In fact the only phosphate forms definitely insoluble in sodium hydroxide are those of the apatite type (Kurtz, 1953).

Several alkaline soil test extractants were listed by Nelson et al. (1953), including 0·5N NaOH, 1% $K_2CO_3$, and solutions of calcium bicarbonate and potassium bicarbonate. Others shown in Table 1 use 0·1N NaOH or 0·5M sodium bicarbonate (Olsen-P). The

Olsen-P test was originally recommended as a simple and quick measure, the results of which correlated with "surface phosphate", the latter being considered a good indicator of P fertility but requiring radioisotopic measurements (Olsen, 1953). Extraction of soil P with bicarbonate has proved in many cases to be as good as, or better than, other methods of predicting plant responses to P fertilizer (for example: Olsen et al., 1954, in U.S.A.; Colwell, 1963, in Australia; Yurtsever et al., 1965, in Turkey). In their review of soil P, Mattingly and Talibudeen (1967) state:

"Sodium bicarbonate, unlike acid reagents used for soil analysis, removes measurable amounts of phosphate from the 'labile pool' without dissolving either soil phosphate that is not isotopically exchangeable or mineral and bone phosphates that are unavailable to plants in neutral soils."

This does not indicate whether the release of P from the soil is due mainly to the displacement with bicarbonate or hydroxide ions or some other mechanism. Williams and Knight (1963) considered the high soil:solution ratio (1:20) and short shaking time (30 minutes) of the Olsen-P method contributed to its relative success, but the test has also proved successful when used with a low ratio (1:100) and a comparatively long shaking time (16 hr) (Colwell, 1963; Grigg, 1968). In accordance with the above discussion, studies with the Chang and Jackson P fractionation scheme have usually shown Olsen-P values to be unrelated to "Ca-bound P", but to be highly correlated with either "Al-bound P" or "Fe-bound P" or both. Grigg (1968) found the extraction of

"Fe-bound P" increased with extraction time. Less P is likely to be resorbed from alkaline extracting solutions than acid, but nevertheless some resorption may occur if calcium clays predominate (Kurtz, 1953; Pratt and Garber, 1964).

3.5 Mild extractants.

Although the preceding methods are popular and useful they have been frequently criticized. For example, Larsen (1967) has drawn attention to the "uncontrolled" redistribution of P compounds during extraction with "strong" reagents. Extraction with water is a comparatively mild treatment and should leave the soil P forms relatively unaltered. However, results so obtained are greatly affected by the level of soluble salts present in the soil. For example, P is generally more soluble in the presence of sulphate than chloride (Kurtz et al., 1946; Olsen et al., 1960) and KCl increases the solubility of the alkaline earth phosphates but decreases the solubility of iron and aluminium phosphates (Nelson et al., 1953). These salt effects have been explained by Mattson et al. (1950) on the basis of Donnan equilibrium effects. A practical difficulty with water extraction is that many soils do not give clear filtrates. The use of neutral salt solutions, such as 0·01M calcium chloride, effectively standardises the electrolyte concentration and by flocculating the soil colloids gives clear extracts for analysis. If a long extraction time is used microbial activity may be a problem, mainly through

production of $CO_2$ which would reduce the pH of unbuffered solutions (Larsen, 1967). In practice water and neutral salt solutions have not proved any more successful than the more commonly used standard extractants described in previous sections (Nelson et al., 1953; Andersen and Mogensen, 1962; Moser et al., 1959).

Anion exchange resins have been used to extract P from soils and the values obtained have often been well correlated with other measures of plant available P (Mattingly and Talibudeen, 1967). The results are dependent on salt concentration and very dependent on temperature, varying about 4% per degree at 20°C according to data of Cooke and Hislop (1963).

The radioisotope phosphorus-32 has been used to determine readily exchangeable P in soil by isotopic dilution. The strict application of isotopic dilution equations requires the attainment of equilibrium between the soil P and added P. This is seldom, if ever, achieved in practice. One reason is the time involved - Gunnarson and Fredriksson (1953) waited 14 days without reaching equilibrium. The other reason for not waiting for equilibrium is that it appears most inorganic P fractions will exchange with added P, though at different rates, and some very slowly, so that eventually even difficultly soluble P of low plant availability may be included in the result. Isotopic exchange reactions depend on the crystal structure and surface

area of all the solid compounds, the nature of the chemical bonds involved and the chemical reactions which may take place with the solution components. Thus addition of carrier P with the $^{32}P$ will upset the equilibrium, possibly with the formation of a new solid phase (Lamm et al., 1963). For this reason equilibrium should be approached more rapidly with carrier-free $^{32}P$ and this should be the preferred technique. However, the use of carrier-free $^{32}P$ has been criticized, especially for strongly phosphate-fixing soils (McConaghy et al., 1966; Amer et al., 1969), mainly on the grounds that the results seem to be over-estimates of the quantity of plant-available P in these soils. One reason for this could be a rapid initial fixation of added P (including $^{32}P$), giving erroneously high values of exchangeable P if measurements are made before equilibrium is approached (Amer et al., 1969). Another possible reason is that some of the P that is isotopically exchangeable may be retained by the soil with greater energy than can be overcome by plants (Russell et al., 1957).

Another procedure for determining fertilizer requirement of soils is to allow for the P sorbing properties of soils, such as by estimating the absorption maximum from fitting a Langmuir-type isotherm to the data (Thompson et al., 1960; Woodruff and Kamprath, 1965). Similar procedures have been suggested in Australia (Beckwith, 1965; Ozanne and Shaw, 1968). Although some success has been obtained these procedures have not been widely

adopted.

3.6 Conclusions.

The above discussion has indicated the solubility of soil P in extracting solutions may be affected by the presence of compounds of Fe, Al, Ca, Mg, etc. The extent of these effects depends not only on the nature of the reagent but also the extracting conditions. For example P values determined in standard extractants have been shown to vary with soil:solution ratio (Stelly and Ricaud, 1960), time of extraction (Askinazi and Guinsbourg, 1957) and temperature (Golden, 1962). These variations in P solubility may give rise to poor correlations between P test values determined by different standard procedures. For example, for a group of 8 soils P values by the Morgan-P and Bray No.2-P tests were found to be highly correlated ($r = \cdot 97$, Candussio and Romanin, 1960). In contrast, for another group of 15 calcareous soils, P values by these two tests were not significantly related ($r = -\cdot 124$, Sen Gupta and Cornfield, 1963). Thus it seems likely that poor relationships between P tests would be explicable in terms of the factors affecting P solubility discussed above, and this is the basis of the experimental study reported in this thesis.

# III. MATERIALS AND METHODS.

## 1. The soils.

### 1.1 Sampling technique and sample preparation.

Each soil sample was taken from the 0-10 cm surface layer, air dried, sieved (discarding the > 2 mm diameter fraction) and then thoroughly mixed and stored in glass jars.

### 1.2 Sample description.

The soil profile was examined at each sampling-site to determine the Great Soil Group classification (Stace et al., 1968) and, where possible, the parent material. At some sites this was done by pedologists from the Division of Soils, C.S.I.R.O., Canberra. Because only the surface horizons were sampled the differences between Great Soil Groups were not always evident in the samples. The Great Soil Group classification, parent material and locality of origin of each sample are recorded below, for the 44 soils used in the preliminary studies (Table 2) and for the extra 101 soils used in later studies (Table 3).

## 2. Chemical methods.

### 2.1 Phosphorus analyses.

The phosphorus determinations were based on the ascorbic acid reduction of molybdenum blue (Murphy and Riley, 1958). This procedure has proven high sensitivity and relative freedom from

TABLE 2. The Great Soil Group, parent material and locality of the 44 soil samples used in the preliminary studies. N.D. = not determined.

| Sample No. | Great Soil Group | Parent Material | Locality |
|---|---|---|---|
| E1 | Krasnozem | Basalt | Robertson |
| E2 | Krasnozem | Basalt | Cootamundra |
| E3 | Krasnozem | Laterite | Little Plain |
| E4 | Red Earth | Basalt | Ben Lomond |
| E5 | Red Earth | Sandstone | Robertson |
| E6 | Yellow Podzolic | Sandstone | Nowra |
| E7 | Yellow Podzolic | Granite | Breadalbane |
| E8 | Yellow Podzolic | Granite | Breadalbane |
| E9 | Red Earth | Colluvium | Stockinbingal |
| E10 | Red Earth | Colluvium | Stockinbingal |
| E11 | Red Brown Earth | Colluvium | Collingullie |
| E12 | Red Podzolic | Sandstone | Nowra |
| E13 | Yellow Podzolic | Shale | Carabost |
| E14 | Siliceous Sand | Fossil desert sand dune | Darlington Point |
| E15 | Siliceous Sand | Fossil coastal sand dune | Sussex Inlet |
| E16 | Grey, Brown Clay | Colluvium | Condobolin |
| E17 | Black Earth | Basalt | Breeza |
| E18 | Grey, Brown Clay | Colluvium | Willbriggie |
| E19 | Yellow Podzolic | Sandstone | Boggabri |
| E20 | Grey, Brown Clay | N.D. | Boggabri |
| E21 | Grey, Brown Clay | N.D. | Boggabri |
| E22 | Grey, Brown Clay | N.D. | Narrabri |
| E23 | Grey, Brown Clay | N.D. | Crooble |
| E24 | Grey, Brown Clay | N.D. | Milguy |
| E25 | Black Earth | Basalt | Tamworth |

TABLE 2. (ctd).

| | | | |
|---|---|---|---|
| F1 | Krasnozem | Basalt | Glen Innes |
| F2 | Grey, Brown Clay | N.D. | North Star |
| F3 | Grey, Brown Clay | N.D. | North Star |
| F4 | Black Earth | Basalt | Graman |
| F5 | Black Earth | Basalt | Graman |
| F6 | Grey, Brown Clay | N.D. | Croppa Creek |
| F7 | Red Earth | Trachyte | Dorrigo |
| F8 | Red Earth | Trachyte | Dorrigo |
| F9 | Red Earth | Trachyte | Dorrigo |
| F10 | Krasnozem | Basalt | Dorrigo |
| F11 | Grey, Brown Clay | N.D. | Coolamon |
| F12 | Grey, Brown Clay | N.D. | Coolamon |
| F13 | Yellow Podzolic | Shale | Bethungra |
| F14 | Yellow Podzolic | Shale | Goulburn |
| F15 | Terra Rossa | Limestone | Bungonia |
| F16 | Krasnozem | Basalt | Mt. Russell |
| F17 | Alpine Humus | Granite | Point Lookout |
| F18 | Yellow Podzolic | Shale | Yass |
| F19 | Yellow Podzolic | Shale | Canberra |

TABLE 3. The Great Soil Group, parent material and locality of 101 soil samples. N.D. = not determined.

| Sample No. | Great Soil Group | Parent Material | Locality |
|---|---|---|---|
| B1 to B20 | Terra Rossa | Limestone | Buchan (Vic.) |
| C1 | Grey, Brown Clay | Alluvium | Ardlethan |
| C2 | Red Brown Earth | Alluvium | Binya |
| C3 | Red Brown Earth | Alluvium | Binya |
| C4 | Red Earth | Alluvium | Erigolia |
| C5 | Red Earth | Alluvium | Rankin Springs |
| C6 | Red Brown Earth | Alluvium | Grong Grong |
| C7 | Red Brown Earth | Alluvium | Grong Grong |
| C8 | Red Earth | Alluvium | Coolamon |
| C9 | Yellow Podzolic | Shale | Ladysmith |
| C10 | Yellow Podzolic | Alluvium | Ladysmith |
| C11 | Grey, Brown Clay | Alluvium | Ardlethan |
| C12 | Red Earth | Alluvium | Ardlethan |
| C13 | Red Earth | Alluvium | Ardlethan |
| C14 | Red Earth | Shale | Coolamon |
| C15 | Red Brown Earth | Alluvium | Temora |
| C16 | Red Brown Earth | Shale | Temora |
| C17 | Grey, Brown Clay | Alluvium | Barmedman |
| C18 | Grey, Brown Clay | Alluvium | Barmedman |
| C19 | Yellow Podzolic | Shale | Boorowa |
| C20 | Yellow Podzolic | Alluvium | Boorowa |
| C21 | Yellow Podzolic | Quartz porphyry | Yass |
| C22 | Red Earth | Quartz porphyry | Canberra |
| C23 | Yellow Podzolic | Shale ? | Yass |
| C24 | Red Earth | Quartz porphyry | Canberra |
| C25 | Red Brown Earth | Alluvium | Boree Creek |

TABLE 3. (ctd)

| | | | |
|---|---|---|---|
| C26 | Red Brown Earth | Sandstone | Boree Creek |
| C27 | Grey, Brown Clay | Alluvium | Boree Creek |
| C28 | Grey, Brown Clay | Alluvium | Boree Creek |
| C29 | Red Brown Earth | Alluvium | The Rock |
| C30 | Red Brown Earth | Alluvium | The Rock |
| C31 | Red Brown Earth | N.D. | Boree Creek |
| C32 | Red Brown Earth | N.D. | Boree Creek |
| C33 | Grey, Brown Clay | Alluvium | Boree Creek |
| C35 | Red Brown Earth | Alluvium | Binya |
| C36 | Red Brown Earth | Alluvium | Binya |
| C37 | Red Earth | Alluvium | Kamarah |
| C38 | Red Earth | N.D. | Kamarah |
| C39 | Grey, Brown Clay | N.D. | Ardlethan |
| C40 | Grey, Brown Clay | N.D. | Ardlethan |
| C41 | Red Earth | N.D. | Coolamon |
| C42 | Red Earth | N.D. | Coolamon |
| C43 | Yellow Podzolic | N.D. | Ladysmith |
| C44 | Yellow Podzolic | N.D. | Ladysmith |
| C46 | Red Earth | Quartz Porphyry | Canberra |
| C47 | Red Earth | N.D. | Cootamundra |
| C48 | Red Earth | N.D. | Cootamundra |
| C49 | Red Brown Earth | Alluvium | Ariah Park |
| C50 | Red Brown Earth | Alluvium | Ariah Park |
| C51 | Grey, Brown Clay | Alluvium | Barmedman |
| C52 | Grey, Brown Clay | Alluvium | Barmedman |
| C53 | Yellow Podzolic | Shale | Tarago |
| C54 | Yellow Podzolic | Shale | Tarago |

TABLE 3. (ctd)

| | | | |
|---|---|---|---|
| C55 | Yellow Podzolic | Shale | Yass |
| C56 | Yellow Podzolic | N.D. | Yass |
| C57 | Yellow Podzolic | N.D. | Boorowa |
| C58 | Yellow Podzolic | Shale | Boorowa |
| N1 to N13 | Black Earth | Basalt | Nimmitabel |
| R1 to R12 | Krasnozem | Basalt | Robertson |

interference by ions commonly found in soil extracts (for example, John, 1970; Watanabe and Olsen, 1965). Aluminium and ferric ions at 100 ppm in the final solution did not depress the molybdenum blue colour and therefore interference from this source was most unlikely. It was necessary, however, to take precautions against interference by some of the extracting reagents. This was usually a pH effect, overcome simply by neutralizing the extract prior to colour development. The Bray-P reagent contains ammonium fluoride which interferes severely with colour development. This interference was overcome by the addition of boric acid (Bray and Kurtz, 1945). Citric acid and ammonium lactate as used in the Citric-P and Lactate-P test reagents were found to reduce sensitivity unless diluted, but sensitivity was always adequate after dilution and standards contained equal quantities of these reagents and were always diluted in the same proportions as the unknown samples, so destruction of organic matter was unnecessary.

With the exception of solutions containing fluoride, whose colour development was read on a Unicam SP600 spectrophotometer, all solution P analyses were carried out on the Technicon AutoAnalyzer. The manifold for Bicarbonate-P has been described by Colwell (1965) and other manifolds were similar but did not have to allow for the removal of $CO_2$. Auto-analysis of NaOH-P extracts was difficult due to the large amount of dark-coloured organic matter extracted from many soils. Satisfactory

analyses were obtained by incorporating in the manifold a dialyser which excluded this organic matter.

P test procedures and abbreviated nomenclature. The P test procedures used are described and named in Table 4, below.

Total-P. Determined by X-ray fluorescence analysis of ground soil samples less than 0·5 mm in diameter. The work was carried out by staff of the Division of Soils, C.S.I.R.O., Adelaide (Moore, 1967).

HCl-P. The P soluble in HCl (2 parts concentrated HCl to 1 part distilled water). The P was extracted by heating 5 g soil in a crucible for 1 hr at 500-550°C followed by boiling for 4 hr with 25 ml HCl (Beckwith and Little, 1963).

"Al-P", "Fe-P" and "Ca-P". These P fractions were determined by the method of Chang and Jackson (1957). Briefly, 1·000 g of soil was extracted successively by 50 ml 0·5 M $NH_4F$ for 1 hr, 50 ml 0·1 N NaOH for 17 hr and 50 ml 0·5 N $H_2SO_4$ for 1 hr, these dissolving "Al-P", "Fe-P" and "Ca-P" respectively. Because $NH_4F$ attacks glass "Al-P" was determined by conventional procedures using volumetric flasks rather than the AutoAnalyzer. The procedure used was that of Murphy and Riley (1962) except that 8 ml of 5% boric acid was placed in each 50 ml flask before addition of an appropriate aliquot (or P standard) and other reagents.

TABLE 4. The 8 standard P tests used in the present studies.

| Title | Reagent | Soil: Solution and Shaking Time | Reference and Comment |
|---|---|---|---|
| $H_2SO_4$-P | 0·01N $H_2SO_4$, pH 2·2 | 1:200, 16 hr | Kerr and Von Stieglitz (1938) |
| Acetic-P | 2·5% acetic acid, pH 2·6 | 1:200, 16 hr | Williams and Stewart (1941) |
| Truog-P | 0·002N $H_2SO_4$ + $(NH_4)_2$ $SO_4$, pH 3·0 | 1:200, 30 min | Truog (1930) |
| Bray-P | 0·03N $NH_4$ F + 0·1N HCl, pH 1·7 | 1:7, 40 sec | Bray and Kurtz (1945) |
| Lactate-P | 0·1N $NH_4$ lactate + 0·4N acetic acid, pH 3·8 | 1:10, 90 min | Andersen and Mogensen (1962), adapted from Egner et al. (1960). |
| Citric-P | 1% citric acid, pH 2·1 | 1:10, 16 hr | Dyer (1894) |
| Bicarbonate-P | 0·5M $NaHCO_3$, pH 8·5 | 1:100 16 hr | Colwell (1963), adapted from Olsen et al. (1954). |
| NaOH-P | 0·125N NaOH, boiling | 1:200, 5 min | Saunder (1956), from Piper (1942). |

## 2.2 Characterizing soil analyses.

The analytical procedures used to characterize the soils are summarized in Table 5 and the notation used in Table 5 will also be used to refer to these analyses throughout the remainder of the thesis.

Total analyses were determined by staff of the Division of Soils, C.S.I.R.O., Adelaide (Moore, 1967).

Fe in the oxalate extracts was determined colorimetrically using o-phenanthroline (Olson, 1965), buffering at pH 4·5 and suppressing oxalate interference by the addition of potassium aluminium sulphate to give a final concentration of 300 ppm Al. Al and Mn were determined by atomic absorption spectrophotometry using an acetylene-nitrous oxide flame for Al and air-acetylene for Mn (Raad et al., 1969).

Ca and Mg in the ammonium chloride extracts were determined by atomic absorption using an air-acetylene flame (David, 1960), and K and Na by flame emission photometry using an oxygen-propane flame.

TABLE 5. The characterizing soil analyses.

| Title | Procedure | Reference |
|---|---|---|
| Total-Fe | X-ray fluorescence spectrography. | |
| Total-Al | " | |
| Total-Mn | " | |
| Total-Ti | " | |
| Total-Ca | " | |
| Total-Mg | " | |
| Total-K | " | |
| Oxalate-Fe | 3 g soil extracted twice (2 x 1 hr) with 100 ml acid ammonium oxalate. | Tamm (1922) |
| Oxalate-Al | " | " |
| Oxalate-Mn | " | " |
| Ex.-Ca | 5 g soil extracted for 1 hr with 100 ml N $NH_4Cl$ (pH 7). | |
| Ex.-Mg | " | |
| Ex.-K | " | |
| Ex.-Na | " | |
| Org.-C | Digestion of soil in sulphuric acid -potassium dichromate solution. | Walkley and Black (1934) |
| pH | Glass electrode in soil:water (1:2·5) suspension. | |
| % Clay | Plummett balance. | Marshall (1956) |

# IV. RESULTS AND DISCUSSION.

## 1. Preliminary studies with 44 soils.

### 1.1 Introduction

It seemed likely on the basis of the knowledge reviewed in section II, that the relationships between P test values obtained by different extraction procedures would be affected by variations in soil composition, particularly with respect to hydrous oxides of Fe and Al and hydroxy carbonates of Ca and Mg, and to a lesser extent by compounds of Mn, Ti and K. The test values represent proportions of the total soil P dissolved from the soils by particular extraction procedures. If each of the different procedures extracted a constant proportion of the soil P, then the test values would be highly correlated, although differing in absolute magnitude. Because, however, the effects of soil constituents such as Fe, Al, Ca, and so on, vary with the extraction conditions and because the content of these constituents varies amongst soils, the proportions of soil P extracted vary both with extraction conditions and soil composition. These variations can lead to low correlations between P test values. Accordingly, a preliminary study was carried out on the 44 contrasting soils described in Table 2, to obtain information on the effects of a range of soil constituents, as measured by various methods of soil analysis, on the relationships between P test values. P test values were determined for the 44

soils by the 8 standard procedures listed in Table 4. The soils were analysed by the procedures listed in Table 5. The relative importance of these analyses as factors affecting the relationships between the P tests was then assessed using regression procedures.

1.2 Results.

(a) Correlations between P test values.

The amounts of P extracted by the different procedures cover a wide range of values (Table 6). The simple, direct relationships between the P values are indicated in Table 7 by correlation coefficients. Some P tests are highly correlated, such as Bicarbonate-P versus Citric-P ($r = \cdot 98$) and Bicarbonate-P versus NaOH-P ($r = \cdot 97$), whereas others are very poorly correlated, for example Acetic-P versus Bicarbonate-P ($r = \cdot 01$). The aim of this study is to explain such relationships in terms of variations in soil composition.

(b) The relationships of P test values to P fractions.

The relationships of the P test values to the Chang and Jackson soil P fractions (Chang and Jackson, 1957), "Fe-P", "Al-P" and "Ca-P", were examined to investigate the possibility that the P tests simply represent different fractions of the soil P and that this might explain the relative differences amongst the soil test values. Correlation coefficients for the relationships between the P tests and these P fractions are given in Table 8. Each of the P tests gave similar correlations with all of the P fractions,

TABLE 6a. Sample means, coefficients of variation (C.V.) and ranges of 44 values of 8 P tests. All analyses as ppm P.

| | Mean | Range | C.V. |
|---|---|---|---|
| $H_2SO_4$-P | 33·2 | 3·2 - 298·0 | 1·69 |
| Acetic-P | 14·8 | 0·8 - 208·0 | 2·10 |
| Truog-P | 11·3 | 0·8 - 41·0 | 0·83 |
| Bray-P | 12·2 | 0·6 - 61·0 | 0·99 |
| Lactate-P | 8·73 | 1·05 - 63·80 | 1·22 |
| Citric-P | 28·1 | 0·5 - 457·0 | 2·47 |
| Bicarbonate-P | 23·6 | 2·5 - 342·5 | 2·15 |
| NaOH-P | 223·0 | 9·3 - 4969·0 | 3·39 |

TABLE 6b. Sample means, coefficients of variation (C.V.) and ranges of 44 values of 3 Chang and Jackson P fractions, HCl-P and Total-P. Total P as percent; other analyses as ppm P.

| | Mean | Range | C.V. |
|---|---|---|---|
| "Al-P" | 53·9 | 1·8 - 1301·0 | 3·64 |
| "Fe-P" | 68·4 | 1·5 - 889·0 | 2·17 |
| "Ca-P" | 64·0 | 0·8 - 1663·0 | 3·92 |
| HCl-P | 491·0 | 35·2 - 3843·0 | 1·41 |
| Total-P | 0·09 | 0·00 - 1·24 | 2·15 |

TABLE 6c. Sample means, coefficients of variation (C.V.) and ranges of 44 values of soil characterizing analyses likely to affect P solubility. Org.-C and Total analyses as percent; other analyses (except pH) as ppm.

| | Mean | Range | C.V. |
|---|---|---|---|
| Oxalate-Fe | 3559 | 117 - 40000 | 1·71 |
| Total-Fe | 5·33 | 0·18 - 20·00 | 1·01 |
| Oxalate-Al | 3392 | 167 - 34778 | 1·90 |
| Total-Al | 6·87 | 1·17 - 19·00 | 0·66 |
| Oxalate-Mn | 941 | 5 - 4467 | 0·96 |
| Total-Mn | 1357 | 0 - 6100 | 1·05 |
| Total-Ti | 9418 | 400 - 31500 | 0·92 |
| Ex.Ca | 2229 | 10 - 11000 | 1·19 |
| Total-Ca | 4675 | 200 - 32700 | 1·29 |
| Ex.Mg | 459 | 26 - 2700 | 1·30 |
| Total-Mg | 4052 | 400 - 16700 | 0·99 |
| Ex.K | 355 | 40 - 1130 | 0·76 |
| Total-K | 7820 | 1100 - 22100 | 0·78 |
| Ex.Na | 41 | 0 - 510 | 1·98 |
| pH | 6·23 | 4·47 - 8·22 | 0·17 |
| Org.-C | 2·20 | 0·07 - 12·90 | 0·98 |

TABLE 7.

Correlation coefficients between 44 values obtained by 8 P tests.

| | Acetic-P | Truog-P | Bray-P | Citric-P | Lactate-P | Bicarb-P | NaOH-P |
|---|---|---|---|---|---|---|---|
| $H_2SO_4$-P | ·77 | ·70 | ·85 | ·75 | ·89 | ·63 | ·58 |
| Acetic-P | | ·45 | ·50 | ·17 | ·91 | ·01 | -·05 |
| Truog-P | | | ·87 | ·68 | ·72 | ·61 | ·49 |
| Bray-P | | | | ·80 | ·78 | ·72 | ·64 |
| Citric-P | | | | | ·47 | ·98 | ·94 |
| Lactate-P | | | | | | ·32 | ·23 |
| Bicarb-P | | | | | | | ·97 |

(Significance Rating: r = ·28, p = ·05; r = ·38, p = ·01; r = ·48, p = ·001.)

TABLE 8. Correlation coefficients between 44 values of "Al-P", "Fe-P" and "Ca-P" and 8 P tests.

| | "Al-P" | "Fe-P" | "Ca-P" |
|---|---|---|---|
| $H_2SO_4$-P | ·62 | ·53 | ·70 |
| Acetic-P | -·01 | -·08 | ·11 |
| Truog-P | ·54 | ·52 | ·55 |
| Bray-P | ·68 | ·60 | ·70 |
| Citric-P | ·97 | ·86 | ·98 |
| Lactate-P | ·27 | ·20 | ·37 |
| Bicarb-P | ·98 | ·92 | ·98 |
| NaOH-P | ·98 | ·95 | ·98 |

(Significance rating: r = ·28, p = ·05; r = ·38, p = ·01; r = ·48, p = ·001.)

TABLE 9. Correlation coefficients between 44 values of "Al-P", "Fe-P", "Ca-P", HCl-P and Total-P.

| | HCl-P | "Al-P" | "Fe-P" | "Ca-P" |
|---|---|---|---|---|
| Total-P | ·96 | ·92 | ·99 | ·93 |
| HCl-P | | ·80 | ·97 | ·81 |
| "Al-P" | | | ·88 | ·98 |
| "Fe-P" | | | | ·88 |

(Significance rating; r = ·28, p = ·05; r = ·38, p = ·01; r = ·48, p = ·001.)

thus suggesting that the differences between the P test values cannot be explained by their representing different P fractions. For example, $H_2SO_4$-P values gave correlation coefficients of ·53 ("Fe-P"), ·62 ("Al-P") and ·70 ("Ca-P"), thus not indicating a particularly outstanding relationship of the $H_2SO_4$-P to any one fraction. Similarly the Acetic-P gave non-significant correlations of -·01, -·08 and ·11 with "Al-P", "Fe-P" and "Ca-P" respectively, and so on for the other tests. Moreover, all the P fractions are highly correlated with each other, and with Total-P and HCl-P ($r > ·80$, Table 9), suggesting that they represent relatively constant proportions of the total soil P and as a consequence cannot explain the relative differences between P test values. For these reasons the use of the Chang and Jackson fractions of soil P to explain relative variations among the P test values obtained by different procedures seemed unpromising and fractionation by this procedure was not used for the more extensive study described below.

(c) The relationship of P test values to soil composition.

(i) Regression models.

The relationships between the P test values and the effects of soil composition were studied by fitting regression models to the data and carrying out appropriate analyses of variance (Draper and Smith, 1968).*

* The computer programmes used for these studies were provided by J.D. Colwell, C.S.I.R.O., Canberra.

Regression models of the form (1), (2), (3) and (4), below, were fitted to the data:

$$P_1 = a_o + a_1 P_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1),$$

$$P_1 = b_o + b_1 P_2 + b_2 P_2^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2),$$

$$P_1 = c_o + c_1 X + C_2 X^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (3),$$

$$P_1 = d_o + d_1 P_2 + d_2 P_2^2 + d_3 X + d_4 X^2 + d_5 P_2 X \ldots (4),$$

where $P_1$ = a P test, the dependent variable, $P_2$ = another P test as an independent variable and X = a characterizing analysis. The simple model (1) corresponds to the simple correlation coefficients, r, given in Table 7, and the goodness-of-fit of the model to the data can be judged by the coefficient of determination, $r^2$, or $r_1^2$ where the subscript refers to the model. The relationships between P tests are often curvilinear so that in general a better model is the quadratic (2), and again the goodness-of-fit can be judged by the coefficient of determination, $R_2^2$, where $R_2$ is the multiple correlation coefficient for model (2).

The characterizing chemical analyses can similarly be related to the P tests by model (3). Characterizing analyses may be related to P tests because they represent either a source of P or, alternatively, sites of sorption, reducing the P that has come into solution from some other source. Since the magnitude of these effects depends on the extraction procedure the characterizing analyses may explain differences between P tests.

The effect can be assessed by fitting model (4) to the data and determining the reduction in regression sum of squares due to the X, $X^2$ and $P_2$ X variables in the presence of $P_2$ and $P_2^2$. This is equivalent to comparing the magnitudes of $R_4^2$ and $R_2^2$.

The usefulness of the model

$$P_1/P_2 = e_o + e_1 X + e_2 X^2 \quad \ldots\ldots\ldots\ldots (5),$$

of the type used by Van der Paauw (1959) was also considered. This model is more restrictive than (4) as can be shown by writing it in the form,

$$P_1 = e_o + e_1 X P_2 + e_2 X^2 P_2,$$

and comparing it with (4). Model (5) does not allow for the possibility of a curvilinear relationship between the P tests $P_1$ and $P_2$. Further, it does not enable a direct comparison of the importance of $P_2$ relative to X, as factors determining $P_1$. It also does not indicate the relative importance of soil constituent X on the P tests. For example, the constituent X may be highly correlated with test $P_1$ and poorly correlated with test $P_2$. In such instances the significance of the relationship of model (5) could largely depend on the relationship of $P_1$ to X, and the conclusion that variations in $P_1/P_2$ are due to X may be misleading. For these reasons this model was not used.

The procedure adopted was to examine all the relationships shown by the small models (1), (2), (3) and (4).

This procedure defines, severally, the main general effects of soil constituents on the relationships between P tests and avoids problems associated with correlated variables. Statistical tests of significance on the contributions of variables to the regression sums of squares proved of little value in these studies since the large amount of data (44 sets of observations) and the usually low residual mean square in the analyses of variance, made most of the tests highly significant. Rather, consideration was given to the magnitudes of coefficients of determination, $R^2$, which is equal to (regression sum of squares)/(total sum of squares), (Snedecor and Cochran, 1967). This was a simple means for gauging the closeness of the relationships between P tests and the relative importance of improvements due to the various characterizing analyses. The application of the regression procedures is now described for each of the P tests.

(ii) P test relationships.

$H_2SO_4$-P

Values of $R_2^2$, where the subscript refers to the model, are given in Table 10 for $P_1$ = $H_2SO_4$-P and $P_2$ = each of the other P tests. The $R_2^2$ values, representing the direct relationship between P tests, cover a wide range (·35 for $P_2$ = NaOH-P to ·80 for $P_2$ = Lactate-P), in general being higher for the acidic tests than for the alkaline tests.

The extent to which the poorer relationships

TABLE 10. Coefficients of determination, $R_2^2$ (top line) and $R_4^2$, for $P_1 = H_2SO_4$-P, 44 soils.

| $P_2$ = | Acetic-P | Truog-P | Bray-P | Lactate-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|
| $R_2^2$ | ·59 | ·56 | ·74 | ·80 | ·69 | ·40 | ·35 |
| Oxalate-Fe | ·97 | ·60 | ·82 | ·98 | ·94 | ·45 | ·36 |
| Total-Fe | ·74 | ·56 | ·78 | ·97 | ·78 | ·43 | ·36 |
| Oxalate-Al | ·97 | ·59 | ·81 | ·98 | ·87 | ·42 | ·35 |
| Total-Al | ·63 | ·57 | ·77 | ·91 | ·74 | ·44 | ·39 |
| Oxalate-Mn | ·64 | ·58 | ·79 | ·96 | ·72 | ·43 | ·36 |
| Total-Mn | ·70 | ·58 | ·79 | ·96 | ·80 | ·43 | ·36 |
| Total-Ti | ·78 | ·56 | ·79 | ·97 | ·80 | ·43 | ·36 |
| Ex.-Ca | ·61 | ·60 | ·95 | ·85 | ·88 | ·47 | ·43 |
| Total-Ca | ·61 | ·91 | ·98 | ·82 | ·96 | ·92 | ·89 |
| Ex.-Mg | ·61 | ·69 | ·96 | ·82 | ·93 | ·47 | ·42 |
| Total-Mg | ·61 | ·81 | ·98 | ·81 | ·96 | ·66 | ·57 |
| Ex.-K | ·59 | ·59 | ·80 | ·80 | ·77 | ·45 | ·43 |
| Total-K | ·59 | ·57 | ·78 | ·85 | ·81 | ·47 | ·44 |
| Ex.-Na | ·60 | ·81 | ·95 | ·80 | ·96 | ·53 | ·54 |
| pH | ·63 | ·63 | ·88 | ·89 | ·90 | ·56 | ·48 |
| Org.-C | ·98 | ·61 | ·81 | ·98 | ·81 | ·42 | ·37 |
| % Clay | ·68 | ·57 | ·87 | ·85 | ·76 | ·43 | ·36 |

can be explained by variations in soil composition can be assessed, as described above, by comparing the magnitudes of $R_4^2$ and $R_2^2$ in Table 10. For at least one characterizing analysis the $R_4^2$ values are high ($R_4^2 > \cdot 89$) for each of the P tests substituted as $P_2$. Thus for $P_2$ = Acetic-P the characterizing analysis X = Org.-C gives $R_4^2 = \cdot 98$ and with X = Oxalate-Fe and Oxalate-Al $R_4^2 = \cdot 97$. Other analyses give little or no improvement over the $R_2^2$ value of ·59. This can be interpreted to indicate that the poor relationship of the $H_2SO_4$-P to Acetic-P test values is due to variations in soil Fe and Al as represented by the acid oxalate extraction.

Similarly, with $P_2$ = Truog-P the high $R_4^2$ values for X = Total-Ca, Total-Mg and Ex.-Na ($R_4^2 = \cdot 91$, ·81 and ·81 respectively) suggest that the poor relationship of the $H_2SO_4$-P to Truog-P test values is due to variations in these soil constituents. For the other P tests substituted as $P_2$ high $R_4^2$ values are obtained with Total-Ca, Total-Mg and Ex.-Mg ($P_2$ = Bray-P); Oxalate-Fe, Oxalate-Al and Org.-C ($P_2$ = Lactate-P); Total-Ca, Total-Mg and Ex.-Na ($P_2$ = Citric-P); Total-Ca, Total-Mg and pH ($P_2$ = Bicarbonate-P); and Total-Ca, Total-Mg and Ex.-Na ($P_2$ = NaOH-P). In general the more important analyses in this respect are Total-Ca, Total-Mg, Org.-C, Oxalate-Fe and Oxalate-Al.

Acetic-P

The relationships of Acetic-P were

considered by a similar procedure and corresponding $R_2^2$ and $R_4^2$ values are given in Table 11. Again the $R_2^2$ values cover a wide range (·01 for $P_2$ = NaOH-P to ·95 for $P_2$ = Lactate-P). High $R_4^2$ values for the different P tests, $P_2$, result from substitution of X = Oxalate-Fe, Total-Fe, Oxalate-Al, Total-Ti, pH and Org.-C ($P_2 = H_2SO_4$-P); Total-Ca, Ex.-Na, Total-Mg and Ex.-Mg ($P_2$ = Truog-P); Total-Ca, Total-Mg, Ex.-Ca and Ex.-Mg ($P_2$ = Bray-P); pH and % Clay ($P_2$ = Lactate-P); Total-Ca, Total-Mg and Ex.-Na ($P_2$ = Citric-P); Total-Ca, Total-Mg and pH ($P_2$ = Bicarbonate-P); and Total-Ca, Total-Mg and Ex.-Na (NaOH-P). Thus the more important analyses are Total-Ca and Total-Mg, with pH, Ex.-Mg, Ex.-Na and % Clay also important. For $P_2 = H_2SO_4$-P, however, several analyses, notably excluding Total-Ca and Total-Mg, are all equally useful.

The different $R_2^2$ and $R_4^2$ values obtained as different P tests are substituted successively as the dependent variable, $P_1$, in models (2) and (4) are due to the tests, $P_1$ and $P_2$, being related to different soil constituents. In the example above of Acetic-P as dependent and Bray-P as independent, Ca and Mg analyses contribute (Table 11), indicating their relationship to Acetic-P values. On the other hand, with Bray-P dependent and Acetic-P independent, Oxalate-Fe and Oxalate-Al contribute (Table 13). Thus the difference between Acetic-P and Bray-P tests is that Acetic-P values are affected more by Ca and Mg and Bray-P values by acid-oxalate-soluble Fe and Al.

TABLE 11. Coefficients of determination, $R_2^2$ (top line) and $R_4^2$ for $P_1$ = Acetic-P, 44 soils.

| $P_2$ | $H_2SO_4$-$P^4$ | Truog-P | Bray-P | Lactate-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|
| $R_2^2$ | ·63 | ·22 | ·29 | ·95 | ·41 | ·02 | ·01 |
| Oxalate-Fe | ·98 | ·38 | ·69 | ·98 | ·87 | ·12 | ·03 |
| Total-Fe | ·98 | ·32 | ·51 | ·97 | ·56 | ·08 | ·04 |
| Oxalate-Al | ·98 | ·32 | ·63 | ·98 | ·71 | ·05 | ·02 |
| Total-Al | ·90 | ·23 | ·33 | ·96 | ·47 | ·09 | ·09 |
| Oxalate-Mn | ·97 | ·29 | ·52 | ·97 | ·41 | ·04 | ·02 |
| Total-Mn | ·97 | ·34 | ·49 | ·97 | ·59 | ·06 | ·02 |
| Total-Ti | ·98 | ·33 | ·54 | ·98 | ·61 | ·07 | ·04 |
| Ex.-Ca | ·96 | ·55 | ·91 | ·98 | ·78 | ·18 | ·19 |
| Total-Ca | ·97 | ·95 | ·97 | ·98 | ·94 | ·90 | ·88 |
| Ex.-Mg | ·96 | ·64 | ·91 | ·98 | ·87 | ·17 | ·18 |
| Total-Mg | ·96 | ·70 | ·93 | ·97 | ·93 | ·52 | ·43 |
| Ex.-K | ·89 | ·29 | ·50 | ·97 | ·51 | ·10 | ·14 |
| Total-K | ·94 | ·36 | ·44 | ·96 | ·63 | ·12 | ·18 |
| Ex.-Na | ·96 | ·72 | ·86 | ·97 | ·92 | ·29 | ·41 |
| pH | ·98 | ·59 | ·82 | ·99 | ·84 | ·33 | ·24 |
| Org.-C | ·98 | ·36 | ·64 | ·98 | ·60 | ·06 | ·05 |
| % Clay | ·95 | ·35 | ·72 | ·99 | ·51 | ·05 | ·04 |

Other P tests.

High $R_4^2$ values are similarly obtained for the other P tests with the substitutions for X listed as follows:

Truog-P (Table 12); Total-Ca, Ex.-Ca, Total-Mg, Org.-C, pH and Total-Al,

Bray-P (Table 13); Oxalate-Al, Oxalate-Fe, Total-Mn, Org.-C, Total-Ca, Total-Mg and Total-K,

Lactate-P (Table 14); Total-Ca, Oxalate-Fe, Oxalate-Al, Total-Ti and Org.-C,

Citric-P (Table 15); Oxalate-Al, Oxalate-Fe, Total-Ca and Org.-C,

Bicarbonate-P (Table 16); Oxalate-Fe, Org.-C, Oxalate-Al and Total-Ti,

NaOH-P (Table 17); Oxalate-Fe, Org.-C, Oxalate-Al and Total-Ti.

## 1.3 Conclusions.

This preliminary study indicated that for at least some of the P test relationships compounds of Fe, Al, Ca and Mg may be responsible for the relative differences between P test values. For the Fe and Al relationships the Oxalate-Fe and Oxalate-Al values were often better than the more time consuming analyses, Total-Fe and Total-Al. Accordingly the Oxalate-Fe and Oxalate-Al analyses were chosen to characterize soils with respect to these constituents. Oxalate-Mn, which can be performed on the same extract as the Fe and Al analyses, was also chosen. Org.-C was of importance in many of the P test relationships and can be performed readily by automated

procedures (Dabin, 1966). It is also a common analysis used to characterize soils and it was therefore included in the general study described below. For Ca and Mg the total analyses were in general superior to Ex.-Ca and Ex.-Mg. The Ex.-Ca and Ex.-Mg analyses are, however, much more rapid and because of this it was decided to characterize soils simply by their exchangeable cations. A future study might be concerned with other routine methods of analysis for Ca and Mg, such as HCl-soluble Ca and Mg. As will be described later, the Ex.-Ca and Ex.-Mg analyses gave generally high $R_4^2$ values in the studies with 145 soils. Ex.-K was included since the analysis can be easily performed using the same extract as Ca and Mg. Soil pH was shown statistically to be related to some P tests and its measurement is simple and rapid. Other characterizing analyses were not statistically of great importance and in some cases (for example, % Clay) are cumbersome and time-consuming, and were therefore excluded from the subsequent studies.

TABLE 12. Coefficients of determination, $R_2^2$ (top line) and $R_4^2$, for $P_1$ = Truog-P, 44 soils.

| $P_2$ | $H_2SO_4$-P | Acetic-P | Bray-P | Lactate-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|
| $R_2^2$ | ·80 | ·58 | ·78 | ·82 | ·76 | ·59 | ·24 |
| Oxalate-Fe | ·82 | ·90 | ·80 | ·91 | ·77 | ·71 | ·27 |
| Total-Fe | ·82 | ·82 | ·80 | ·92 | ·77 | ·63 | ·31 |
| Oxalate-Al | ·85 | ·87 | ·85 | ·89 | ·78 | ·64 | ·27 |
| Total-Al | ·85 | ·71 | ·85 | ·94 | ·81 | ·67 | ·39 |
| Oxalate-Mn | ·82 | ·71 | ·82 | ·89 | ·77 | ·60 | ·25 |
| Total-Mn | ·83 | ·84 | ·84 | ·93 | ·78 | ·60 | ·33 |
| Total-Ti | ·82 | ·85 | ·80 | ·91 | ·76 | ·63 | ·26 |
| Ex.-Ca | ·89 | ·59 | ·86 | ·86 | ·84 | ·70 | ·47 |
| Total-Ca | ·89 | ·67 | ·88 | ·88 | ·84 | ·71 | ·49 |
| Ex.-Mg | ·88 | ·58 | ·85 | ·85 | ·82 | ·67 | ·36 |
| Total-Mg | ·89 | ·63 | ·86 | ·87 | ·84 | ·73 | ·41 |
| Ex.-K | ·83 | ·61 | ·80 | ·87 | ·81 | ·66 | ·46 |
| Total-K | ·82 | ·60 | ·79 | ·85 | ·77 | ·69 | ·43 |
| Ex.-Na | ·84 | ·58 | ·80 | ·83 | ·79 | ·67 | ·36 |
| pH | ·87 | ·59 | ·83 | ·85 | ·82 | ·75 | ·47 |
| Org.-C | ·83 | ·88 | ·80 | ·86 | ·77 | ·66 | ·33 |
| % Clay | ·87 | ·61 | ·84 | ·85 | ·82 | ·63 | ·30 |

TABLE 13. Coefficients of determination, $R_2^2$ (top line) and $R_4^2$ for $P_1$ = Bray-P, 44 soils.

| $P_2$ | $H_2SO_4$-P | Acetic-P | Truog-P | Lactate-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|
| $R_2^2$ | ·85 | ·46 | ·79 | ·80 | ·88 | ·60 | ·41 |
| Oxalate-Fe | ·96 | ·91 | ·84 | ·93 | ·89 | ·72 | ·47 |
| Total-Fe | ·96 | ·64 | ·80 | ·91 | ·92 | ·69 | ·48 |
| Oxalate-Al | ·96 | ·91 | ·85 | ·94 | ·91 | ·63 | ·43 |
| Total-Al | ·94 | ·52 | ·81 | ·88 | ·92 | ·63 | ·43 |
| Oxalate-Mn | ·96 | ·50 | ·81 | ·91 | ·88 | ·67 | ·43 |
| Total-Mn | ·96 | ·59 | ·81 | ·91 | ·93 | ·68 | ·42 |
| Total-Ti | ·95 | ·67 | ·80 | ·91 | ·92 | ·69 | ·45 |
| Ex.-Ca | ·95 | ·54 | ·83 | ·83 | ·88 | ·64 | ·45 |
| Total-Ca | ·95 | ·52 | ·89 | ·82 | ·89 | ·74 | ·55 |
| Ex.-Mg | ·95 | ·54 | ·82 | ·82 | ·88 | ·65 | ·43 |
| Total-Mg | ·95 | ·52 | ·83 | ·82 | ·88 | ·76 | ·46 |
| Ex.-K | ·95 | ·46 | ·80 | ·81 | ·92 | ·65 | ·52 |
| Total-K | ·94 | ·47 | ·80 | ·83 | ·91 | ·72 | ·59 |
| Ex.-Na | ·95 | ·48 | ·81 | ·80 | ·88 | ·65 | ·48 |
| pH | ·95 | ·55 | ·82 | ·86 | ·88 | ·65 | ·48 |
| Org.-C | ·95 | ·91 | ·85 | ·92 | ·88 | ·63 | ·48 |
| % Clay | ·95 | ·57 | ·84 | ·83 | ·90 | ·69 | ·44 |

TABLE 14. Coefficients of determination, $R_2^2$ (top line) and $R_4^2$, for $P_1$ = Lactate-P, 44 soils.

| $P_2$ | $H_2SO_4$-P | Acetic-P | Truog-P | Bray-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|
| $R_2^2$ | ·80 | ·88 | ·52 | ·63 | ·64 | ·16 | ·07 |
| Oxalate-Fe | ·96 | ·96 | ·64 | ·83 | ·92 | ·34 | ·11 |
| Total-Fe | ·96 | ·91 | ·60 | ·74 | ·79 | ·27 | ·08 |
| Oxalate-Al | ·95 | ·96 | ·59 | ·80 | ·84 | ·22 | ·08 |
| Total-Al | ·95 | ·88 | ·54 | ·65 | ·73 | ·23 | ·11 |
| Oxalate-Mn | ·94 | ·89 | ·57 | ·76 | ·65 | ·22 | ·08 |
| Total-Mn | ·95 | ·91 | ·63 | ·74 | ·83 | ·25 | ·07 |
| Total-Ti | ·96 | ·92 | ·61 | ·75 | ·81 | ·27 | ·08 |
| Ex.-Ca | ·91 | ·91 | ·63 | ·89 | ·76 | ·27 | ·19 |
| Total-Ca | ·92 | ·90 | ·95 | ·93 | ·88 | ·78 | ·66 |
| Ex.-Mg | ·91 | ·91 | ·68 | ·88 | ·82 | ·24 | ·16 |
| Total-Mg | ·91 | ·90 | ·75 | ·91 | ·86 | ·56 | ·33 |
| Ex.-K | ·87 | ·89 | ·53 | ·68 | ·73 | ·21 | ·17 |
| Total-K | ·95 | ·88 | ·63 | ·71 | ·81 | ·32 | ·26 |
| Ex.-Na | ·91 | ·89 | ·76 | ·87 | ·87 | ·32 | ·33 |
| pH | ·93 | ·91 | ·68 | ·86 | ·82 | ·39 | ·23 |
| Org.-C | ·94 | ·96 | ·60 | ·79 | ·73 | ·22 | ·10 |
| % Clay | ·90 | ·94 | ·55 | ·78 | ·65 | ·22 | ·08 |

TABLE 15. Coefficients of determination, $R_2^2$ (top line) and $R_4^2$, for $P_1$ = Citric-P, 44 soils.

| $P_2$ | $H_2SO_4$-P | Acetic-P | Truog-P | Bray-P | Lactate-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|
| $R_2^2$ | ·58 | ·04 | ·74 | ·92 | ·34 | ·96 | ·91 |
| Oxalate-Fe | ·98 | ·97 | ·97 | ·99 | ·99 | ·97 | ·92 |
| Total-Fe | ·98 | ·34 | ·85 | ·98 | ·93 | ·97 | ·93 |
| Oxalate-Al | ·99 | ·96 | ·98 | ·99 | ·99 | ·96 | ·91 |
| Total-Al | ·87 | ·14 | ·78 | ·94 | ·72 | ·96 | ·92 |
| Oxalate-Mn | ·97 | ·17 | ·89 | ·97 | ·92 | ·97 | ·92 |
| Total-Mn | ·98 | ·29 | ·84 | ·98 | ·92 | ·96 | ·92 |
| Total-Ti | ·97 | ·46 | ·87 | ·99 | ·94 | ·97 | ·92 |
| Ex.-Ca | ·97 | ·07 | ·82 | ·94 | ·54 | ·96 | ·93 |
| Total-Ca | ·98 | ·09 | ·78 | ·94 | ·43 | ·98 | ·94 |
| Ex.-Mg | ·98 | ·07 | ·76 | ·94 | ·45 | ·96 | ·92 |
| Total-Mg | ·98 | ·08 | ·76 | ·94 | ·37 | ·98 | ·92 |
| Ex.-K | ·91 | ·05 | ·79 | ·96 | ·36 | ·96 | ·94 |
| Total-K | ·91 | ·06 | ·82 | ·98 | ·54 | ·97 | ·93 |
| Ex.-Na | ·98 | ·05 | ·75 | ·93 | ·34 | ·96 | ·92 |
| pH | ·98 | ·12 | ·87 | ·96 | ·71 | ·97 | ·93 |
| Org.-C | ·98 | ·96 | ·96 | ·98 | ·97 | ·96 | ·94 |
| % Clay | ·97 | ·24 | ·80 | ·95 | ·59 | ·96 | ·92 |

TABLE 16. Coefficients of determination, $R_2^2$ (top line) and $R_4^2$, for $P_1$ = Bicarbonate-P, 44 soils.

| $P_2$ | $H_2SO_4$-P | Acetic-P | Truog-P | Bray-P | Lactate-P | Citric-P | NaOH-P |
|---|---|---|---|---|---|---|---|
| $R_2^2$ | ·43 | ·01 | ·65 | ·82 | ·25 | ·97 | ·96 |
| Oxalate-Fe | ·99 | ·96 | ·99 | ·99 | ·99 | ·99 | ·96 |
| Total-Fe | ·97 | ·39 | ·84 | ·95 | ·93 | ·98 | ·97 |
| Oxalate-Al | ·98 | ·95 | ·98 | ·98 | ·97 | ·98 | ·96 |
| Total-Al | ·82 | ·12 | ·70 | ·86 | ·67 | ·97 | ·97 |
| Oxalate-Mn | ·97 | ·19 | ·89 | ·95 | ·91 | ·98 | ·96 |
| Total-Mn | ·97 | ·30 | ·80 | ·93 | ·88 | ·98 | ·97 |
| Total-Ti | ·98 | ·49 | ·88 | ·96 | ·94 | ·98 | ·96 |
| Ex.-Ca | ·96 | ·03 | ·80 | ·91 | ·49 | ·98 | ·97 |
| Total-Ca | ·97 | ·06 | ·70 | ·90 | ·35 | ·98 | ·97 |
| Ex.-Mg | ·96 | ·03 | ·70 | ·89 | ·37 | ·98 | ·96 |
| Total-Mg | ·96 | ·06 | ·69 | ·89 | ·29 | ·98 | ·96 |
| Ex.-K | ·88 | ·02 | ·72 | ·90 | ·28 | ·97 | ·97 |
| Total-K | ·92 | ·03 | ·79 | ·94 | ·50 | ·98 | ·97 |
| Ex.-Na | ·96 | ·01 | ·65 | ·87 | ·26 | ·98 | ·96 |
| pH | ·97 | ·09 | ·87 | ·93 | ·69 | ·98 | ·97 |
| Org.-C | ·98 | ·96 | ·97 | ·97 | ·97 | ·98 | ·97 |
| % Clay | ·94 | ·21 | ·76 | ·90 | ·55 | ·98 | ·96 |

TABLE 17. Coefficients of determination, $R_2^2$ (top line) and $R_4^2$, for $P_1$ = NaOH-P, 44 soils.

| $P_2$ | $H_2SO_4$-P | Acetic-P | Truog-P | Bray-P | Lactate-P | Citric-P | Bicarbonate-P |
|---|---|---|---|---|---|---|---|
| $R_2^2$ | ·31 | ·00 | ·58 | ·79 | ·15 | ·94 | ·96 |
| Oxalate-Fe | ·99 | ·99 | ·99 | ·99 | ·99 | ·99 | ·99 |
| Total-Fe | ·96 | ·38 | ·80 | ·95 | ·89 | ·97 | ·97 |
| Oxalate-Al | ·98 | ·97 | ·98 | ·98 | ·98 | ·98 | ·99 |
| Total-Al | ·83 | ·14 | ·67 | ·87 | ·65 | ·97 | ·98 |
| Oxalate-Mn | ·96 | ·17 | ·87 | ·94 | ·88 | ·95 | ·96 |
| Total-Mn | ·94 | ·24 | ·74 | ·90 | ·81 | ·95 | ·96 |
| Total-Ti | ·97 | ·49 | ·84 | ·97 | ·92 | ·98 | ·98 |
| Ex.-Ca | ·93 | ·04 | ·77 | ·87 | ·46 | ·95 | ·97 |
| Total-Ca | ·94 | ·03 | ·66 | ·86 | ·28 | ·95 | ·96 |
| Ex.-Mg | ·92 | ·03 | ·64 | ·85 | ·31 | ·95 | ·96 |
| Total-Mg | ·92 | ·06 | ·65 | ·85 | ·19 | ·95 | ·96 |
| Ex.-K | ·84 | ·01 | ·69 | ·87 | ·20 | ·95 | ·97 |
| Total-K | ·90 | ·02 | ·73 | ·93 | ·39 | ·96 | ·97 |
| Ex.-Na | ·92 | ·01 | ·58 | ·83 | ·16 | ·94 | ·96 |
| pH | ·96 | ·09 | ·85 | ·91 | ·66 | ·96 | ·97 |
| Org.-C | ·99 | ·99 | ·99 | ·99 | ·99 | ·99 | ·99 |
| % Clay | ·91 | ·19 | ·70 | ·86 | ·50 | ·94 | ·96 |

## 2. Studies with 145 soils.

### 2.1 Introduction.

The preliminary study indicated that soil constituents represented by the standard analyses, Oxalate-Fe, Oxalate-Al, Ex.-Ca, Ex.-Mg, etc., affect the relationships between the different values obtained by different P test procedures. In order to obtain a more representative sampling of the region covered by the 44 soil samples, an additional 101 soil samples (Table 3) were collected and analysed by the same P test procedures and a selection of the characterizing analyses. The 145 samples represent several Great Soil Groups and many of the chemical analyses vary amongst these Groups, since they are identified on the basis of features such as texture, presence of calcium carbonate, colour and so on, which in turn are related to their chemical composition. Many of the regression relationships to be described depend on these variations amongst the samples and some of the differences may be associated with soil morphological classification groups. For this exploratory study all of the data has been regarded as homogeneous, ignoring soil groups, since there was no a priori information on the importance of the groups in this regard.

### 2.2 Results.

#### (a) Correlations between P tests

The P test values for the 145 soils are

summarized in Table 18 by their means, ranges and coefficients of variation. Full data are presented in Appendices 1 and 2A. There is a considerable variation amongst the P tests, reflecting contrasts in the various P test procedures. Simple correlation coefficients between P test values (Table 19) show that some are closely related, even though their absolute magnitudes differ. Thus the acid P tests, $H_2SO_4$-P, Acetic-P and Truog-P are all highly correlated ($r > \cdot 9$). In contrast, other tests are poorly correlated. The NaOH-P is poorly correlated with all other tests except Bicarbonate-P. The aim of the study is of course to explain these relationships.

(b) The characterizing soil analyses.

The characterizing analyses selected to explain the relationships between the P tests are listed in Table 20, together with the means, ranges and coefficients of variation for the results which are given in full in Appendices 1 and 2B. The analyses also show a wide range of magnitudes and varying degrees of correlation (Tables 20 and 21). It may be noted in particular that the Oxalate-Fe and Oxalate-Al analyses are highly correlated both with each other ($r = \cdot 93$) and with Org.-C ($r = \cdot 74$ and $\cdot 68$, respectively). Ex.-Ca, Ex.-Mg, Ex.-K and pH are also fairly closely correlated with each other ($r = \cdot 70$ to $\cdot 39$). These correlations may result from the normal processes of soil genesis and are important in that they affect the interpretation of the

TABLE 18. Sample means, coefficients of variation (C.V.) and ranges of the 145 values obtained by each of 8 P tests. All analyses as ppm P.

| | Mean | Range | C.V. |
|---|---|---|---|
| $H_2SO_4$-P | 76·9 | 3·2 - 858·0 | 2·11 |
| Acetic-P | 37·9 | 0·8 - 630·0 | 2·71 |
| Truog-P | 34·3 | 0·8 - 540·0 | 2·47 |
| Bray-P | 18·2 | 0·6 - 179·0 | 1·51 |
| Lactate-P | 14·7 | 1·1 - 304·0 | 2·10 |
| Citric-P | 41·1 | 0·5 - 457·0 | 1·91 |
| Bicarbonate-P | 34·6 | 2·5 - 343·0 | 1·33 |
| NaOH-P | 193·0 | 8·8 - 4969·0 | 2·52 |

TABLE 19. Correlation coefficients between sets of 145 values obtained by each of 8 P tests.

| | Acetic-P | Truog-P | Bray-P | Lactate-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|
| $H_2SO_4$-P | ·98 | ·96 | ·86 | ·73 | ·90 | ·65 | ·13 |
| Acetic-P | | ·97 | ·82 | ·70 | ·83 | ·52 | ·00 |
| Truog-P | | | ·80 | ·63 | ·84 | ·57 | ·05 |
| Bray-P | | | | ·89 | ·86 | ·66 | ·13 |
| Lactate-P | | | | | ·73 | ·46 | ·03 |
| Citric-P | | | | | | ·83 | ·47 |
| Bicarbonate-P | | | | | | | ·70 |

(Significance Rating: r = ·16, p = ·05; r = ·21, p = ·01)

TABLE 20. Sample means, coefficients of variation (C.V.) and ranges of the 145 values obtained for 8 characterizing analyses. Org.-C as percent; other analyses (except pH) as ppm.

| | Mean | Range | C.V. |
|---|---|---|---|
| Oxalate-Fe | 4693 | 117 - 40000 | 1·47 |
| Oxalate-Al | 3347 | 167 - 34778 | 1·70 |
| Oxalate-Mn | 1023 | 0·5 - 7170 | 1·03 |
| Org.-C | 3·03 | 0·1 - 12·9 | 0·84 |
| Ex.-Ca | 2312 | 17·0 - 8800 | 0·93 |
| Ex.-Mg | 503·0 | 10·0 - 3550 | 1·31 |
| Ex.-K | 431·0 | 55·0 - 1165 | 0·56 |
| pH | 6·01 | 4·5 - 8·3 | 0·14 |

TABLE 21. Correlation coefficients between sets of 145 values obtained for 8 characterizing analyses.

| | Oxalate-Al | Oxalate-Mn | Org.-C | Ex.-Ca | Ex.-Mg | Ex.-K | pH |
|---|---|---|---|---|---|---|---|
| Oxalate-Fe | ·93 | ·37 | ·74 | -·08 | -·01 | -·10 | -·33 |
| Oxalate-Al | | ·30 | ·68 | -·12 | -·07 | -·08 | -·30 |
| Oxalate-Mn | | | ·43 | ·20 | ·12 | ·05 | ·00 |
| Org.-C | | | | ·27 | ·00 | ·10 | -·21 |
| Ex.-Ca | | | | | ·62 | ·52 | ·70 |
| Ex.-Mg | | | | | | ·39 | ·45 |
| Ex.-K | | | | | | | ·52 |

(Significance Rating: r = ·16, p = ·05; r = ·21, p = ·01)

relationships between the P tests described below.

(c) The effects of soil composition on P test values

The effects of soil composition on P test values were examined by the same statistical procedures described for section IV-1, using the models (1), (2), (3) and (4) and comparing $R^2$ values.

$H_2SO_4$-P

Values of $r_1^2$, $R_2^2$, $R_3^2$ and $R_4^2$, for $P_1 = H_2SO_4$-P are given in Table 22. The $r_1^2$ and $R_2^2$ values range from high for $P_2$ = Acetic-P and Truog-P to low for the alkaline tests; and some of the relationships are curvilinear as indicated by the difference $R_2^2 - r_1^2$.

The characterizing chemical analyses, X, can also be related to the P tests similarly by model (3), $P_1 = c_o + c_1 X + c_2 X^2$, and $R_3^2$ values for this model are given in the first column of Table 22. Most of the $R_3^2$ values are very small compared with the $R_2^2$ values, indicating, as might be expected, much poorer relationships of $H_2SO_4$-P to non-phosphorus soil analyses. For X = Ex.-Mg, however, the $R_3^2$ value of ·576 is not small and is higher than the $R_2^2$ values for $P_2$ = Bicarbonate-P (·417) and $P_2$ = NaOH-P (·016), suggesting that the Mg analysis is more closely related than these P tests to the source of P dissolved by the $H_2SO_4$-P extractant.

TABLE 22. Coefficients of determination ($r^2$ or $R^2$) for regressions (1), (2), (3), (4) and (6), for $P_1$ = $H_2SO_4$-P. The largest $R_4^2$ values are underlined and the sign, + or -, refers to the general trend ($\partial P_1/\partial X$) in (4). X is the substitution for X used in (6).

| $P_2$ | X | $R_3^2$ | Acetic-P | Truog-P | Bray-P | Lactate-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|---|---|
| $r_1^2$ | | | ·965 | ·917 | ·745 | ·535 | ·807 | ·417 | ·016 |
| $R_2^2$ | | | ·970 | ·941 | ·767 | ·704 | ·835 | ·497 | ·019 |
| | Oxalate-Fe | ·043 | ·980 | ·944 | ·790 | ·727 | ·930- | ·640- | ·130 |
| | Oxalate-Al | ·004 | ·983 | ·946 | ·781 | ·728 | ·938- | ·618- | ·115 |
| $R_3^2$ | Oxalate-Mn | ·099 | ·972 | ·943 | ·778 | ·709 | ·903- | ·605- | ·055 |
| or | Ex.-Ca | ·170 | ·971 | ·946 | ·820+ | ·732+ | ·917+ | ·697+ | ·377+ |
| $R_4^2$ | Ex.-Mg | ·576 | ·974 | ·942 | ·938+ | ·931+ | ·957+ | ·829+ | ·630+ |
| | Ex.-K | ·109 | ·971 | ·941 | ·781 | ·740 | ·880 | ·565 | ·154 |
| | pH | ·056 | ·971 | ·947 | ·773 | ·712 | ·897 | ·720 | ·232 |
| | Org.-C | ·057 | ·983 | ·949 | ·779 | ·710 | ·924 | ·616 | ·102 |
| $R_6^2$ | | | | | ·946 | ·938 | ·958 | ·837 | ·646 |
| X | | | | | Mg | Mg | Mg | Mg | Mg |
| W | | | | | Fe | Fe | Fe | Ca | K |

As explained in the preliminary studies, characterizing analyses may be related to P tests because they are related to either a source of P, as in the above example, or sites of P sorption, reducing the P that has come into solution from some other source. These effects are assessed, as before, by comparing the magnitudes of $R_4^2$ and $R_2^2$, and this shows the extent to which the characterizing analyses explain the differences between P tests. Values of $R_4^2$ for each of the substitutions for X and for $P_2$ are given in Table 22, and are generally high ($R_4^2 > \cdot 8$) for at least one characterizing analysis. When $P_2$ = NaOH-P the highest $R_4^2$ is only ·630 but even this is a considerable improvement over the $R_2^2$ (·019), due largely to the effects of the Mg analysis as shown by the high $R_3^2$ value (·576). Analyses other than Ex.-Mg are also able, in many cases, to give $R_4^2$ values considerably higher than the corresponding $R_2^2$. For example, with $P_2$ = Citric-P the $R_4^2$ value for X = Oxalate-Al is ·938, which is almost as high as when X = Ex.-Mg ($R_4^2$ = ·957), even though the $R_3^2$ for X = Oxalate-Al is only ·004.

The variable X may have a positive effect, increasing $P_1$ relative to $P_2$ with increase in X, or a negative effect, decreasing $P_1$ relative to $P_2$ with increase in X. It is not always immediately obvious from the coefficients of the model (4) equations whether the effects are positive or negative. A simple method for distinguishing the direction of the overall

trend due to X is to determine whether the slope $\partial P_1/\partial X$ is positive or negative near the centre of the range of data. For major effects of X, that is where $R_4^2 - R_2^2$ is about 0·1 or more, this method always indicates a clear positive or negative effect of X. The direction of such clear effects is indicated in Table 22 by a + or - after the X, for Oxalate-Fe, Oxalate-Al, Oxalate-Mn, Ex.-Ca and Ex.-Mg, and, in a few cases of particular interest, for other analyses as well. An example of the calculation is given in Appendix 3 for $P_1$ = $H_2SO_4$-P, $P_2$ = Bray-P and X = Ex.-Mg. A positive effect of X can be interpreted to indicate the analysis X is related to either a source of P more soluble for the $P_1$ extraction than the $P_2$, or sites for P sorption which are less reactive under the conditions of the $P_1$ procedure than the $P_2$ procedure. A negative effect can similarly be interpreted to indicate either more sorption or less dissolution of P for the $P_1$ procedure relative to the $P_2$ procedure.

The $R_2^2$ values for $P_2$ = Acetic-P or Truog-P are quite high (·970 and ·941 respectively) and the corresponding $R_4^2$ values are only slightly higher for any substitution for X. This reflects the close relationship between these three acid P test values. For the other P tests, however, $R_4^2$ values are considerably larger than $R_2^2$, indicating sources of difference between the test values. The Ex.-Mg analysis is clearly outstanding, explaining much of the difference between $H_2SO_4$-P and the other

tests. The effect is positive, suggesting that the $H_2SO_4$-P values differ from these other P test values because the $H_2SO_4$-P procedure dissolves relatively more of a source of P represented by Ex.-Mg. The effect is particularly pronounced for $P_2$ = Bicarbonate-P and NaOH-P. For $P_2$ = Citric-P or Bicarbonate-P $R_4^2$ values are also substantially higher than $R_2^2$ for X = Oxalate-Fe and Oxalate-Al and the effect is in each case negative. This suggests that P is more strongly sorbed by Fe or Al constituents during the $H_2SO_4$-P procedure than during the Citric-P or Bicarbonate-P procedures.

Larger and more complicated models can be fitted to the data to allow for the effects of two or more characterizing analyses. For example both Ex.-Mg and Oxalate-Fe had substantial and opposite effects on the relationship of the $H_2SO_4$-P to Bicarbonate-P values (Table 22), so it is logical to investigate the value of both of these analyses simultaneously in a model such as,

$$P_1 = f_o + f_1 P_2 + f_2 P_2^2 + f_3 X + f_4 X^2 + f_5 P_2 X + f_6 W \quad \ldots(6),$$

where X = Ex.-Mg and W = Oxalate-Fe. For this model $R_6^2$ = ·830 which is only slightly greater than the value $R_4^2$ = ·829 for X = Ex.-Mg. In general it was found that if the substitution for X was that which gave the highest $R_4^2$ value, then any substitution for W in (6) gave $R_6^2$ values only slightly better than the corresponding $R_4^2$ value, as in this example. Enlarging the model (6) by adding

the terms $W^2$ and WP did not give any significant increases in $R_6^2$. The best of the $R_6^2$ values, with indicated substitutions for X and W, are given in Table 22. It may be noted regarding the above example that for $P_1$ = $H_2SO_4$-P, $P_2$ = Bicarbonate-P and X = Ex.-Mg, the best $R_6^2$ value was obtained with W = Ex.-Ca ($R_6^2$ = ·837) rather than with W = Oxalate-Fe. This suggests the Mg and Ca analyses together represent the source of P to the $H_2SO_4$-P procedure better than Mg alone. The superiority of Ex.-Mg over Ex.-Ca in this respect (as shown by higher $R_4^2$ values) may to some extent be due to the greater variability of the Mg analysis compared with Ca, (C.V. = 1·31 and ·93 respectively, Table 20) since this can affect the size of correlations. The $R_6^2$ values (Table 20) represent about the best relationships amongst many regression models, that were found with the data. In cases where $R_6^2$ is still low sources of variation other than those covered by the present range of characterizing analyses are apparently affecting the relationships between the P tests.

Acetic-P and Truog-P

The values of these P tests are closely correlated with the $H_2SO_4$-P values ($R_2^2$ > ·92, Tables 23 and 24) and show corresponding relationships to those described above. Thus the relationships with Bray-P, Lactate-P, Citric-P, Bicarbonate-P and NaOH-P are much improved by allowing for variations in Ex.-Mg, and similar though smaller improvements are obtained with Ex.-Ca

TABLE 23. Coefficients of determination ($r^2$ or $R^2$) for regressions (1), (2), (3), (4) and (6), for $P_1$ = Acetic-P. The largest $R_4^2$ values are underlined and the sign, + or -, refers to the general trend ($\partial P_1/\partial X$) in (4). X is the substitution for X used in (6).

| $P_2$ | X | $R_3^2$ | $H_2SO_4$-P | Truog-P | Bray-P | Lactate-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|---|---|
| $r_1^2$ | | | ·965 | ·950 | ·670 | ·487 | ·697 | ·272 | ·000 |
| $R_2^2$ | | | ·971 | ·951 | ·686 | ·632 | ·729 | ·381 | ·005 |
| | Oxalate-Fe | ·041 | ·980 | ·954 | ·717 | ·646 | ·906- | ·552- | ·009 |
| | Oxalate-Al | ·014 | ·982 | ·956 | ·721 | ·654 | ·919- | ·525- | ·090 |
| $R_3^2$ | Oxalate-Mn | ·030 | ·973 | ·956 | ·691 | ·635 | ·856- | ·507- | ·039 |
| or | Ex.-Ca | ·175 | ·973 | ·960 | ·769+ | ·679+ | ·865+ | ·611+ | ·318+ |
| $R_4^2$ | Ex.-Mg | ·649 | ·<u>986</u> | ·953 | ·<u>951</u>+ | ·<u>941</u>+ | ·<u>965</u>+ | ·<u>820</u>+ | ·<u>567</u>+ |
| | Ex.-K | ·094 | ·972 | ·952 | ·699 | ·665 | ·780 | ·462 | ·110 |
| | pH | ·071 | ·973 | ·<u>962</u> | ·708 | ·642 | ·837 | ·638 | ·194 |
| | Org.-C | ·063 | ·<u>986</u> | ·953 | ·717 | ·645 | ·909 | ·533 | ·082 |
| $R_6^2$ | | | | | ·953 | ·942 | ·968 | ·830 | ·680 |
| X | | | | | Mg | Mg | Mg | Mg | Mg |
| W | | | | | Ca | Ca | Fe | Ca | K |

TABLE 24. Coefficients of determination ($r^2$ or $R^2$) for regressions (1), (2), (3), (4) and (6), for $P_1$ = Truog-P. The largest $R_4^2$ values are underlined and the sign, + or -, refers to the general trend ($\partial P_1/\partial X$) in (4). X is the substitution for X used in (6).

| | X | $R_3^2$ | $H_2SO_4$-P | Acetic-P | Bray-P | Lactate-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|---|---|
| $P_2$ | | | | | | | | | |
| $r_1^2$ | | | ·917 | ·950 | ·639 | ·392 | ·703 | ·327 | ·002 |
| $R_2^2$ | | | ·922 | ·951 | ·669 | ·568 | ·738 | ·436 | ·010 |
| | Oxalate-Fe | ·049 | ·925 | ·957 | ·701 | ·590 | ·871- | ·590- | ·113 |
| | Oxalate-Al | ·011 | ·926 | ·967 | ·700 | ·596 | ·883- | ·564- | ·099 |
| $R_3^2$ | Oxalate-Mn | ·039 | ·926 | ·961 | ·677 | ·572 | ·818- | ·549- | ·045 |
| or | Ex.-Ca | ·151 | ·930 | ·962 | ·725+ | ·596+ | ·828+ | ·628+ | ·304+ |
| $R_4^2$ | Ex.-Mg | ·661 | ·957 | ·958 | ·949+ | ·902+ | ·963+ | ·864+ | ·689+ |
| | Ex.-K | ·092 | ·923 | ·952 | ·674 | ·587 | ·792 | ·513 | ·120 |
| | pH | ·059 | ·933 | ·967 | ·681 | ·589 | ·800 | ·643 | ·186 |
| | Org.-C | ·066 | ·928 | ·954 | ·694 | ·583 | ·879 | ·581 | ·093 |
| $R_6^2$ | | | | | ·950 | ·905 | ·964 | ·961 | ·709 |
| X | | | | | Mg | Mg | Mg | Mg | Mg |
| W | | | | | Fe | K | Fe | Ca | K |

($R_4^2$ values, Tables 23 and 24). The relationships to Citric-P and Bicarbonate-P are also improved by allowing for Oxalate-Fe. The regressions suggest, as with $H_2SO_4$-P, that the Acetic-P and Truog-P procedures extract more of a source of P represented by the Ex.-Mg analyses and comparatively less of Fe and Al sorbed P, than the other analyses.

Bray-P

The Bray-P test values are only closely correlated with Lactate-P values ($R_2^2$ = ·908, Table 25). The poorer relationships ($R_2^2$ ≤ ·776, Table 25) with the acid tests $H_2SO_4$-P, Acetic-P and Truog-P described above indicate a fundamental difference between these tests and Bray-P. This may be associated with the fluoride anion (which can complex with Fe and Al ions thereby enhancing release of P bound to these constituents and blocking them as sites of resorption), or the very short extraction period (40 seconds, Table 1) making the test sensitive to soil solution P that is sorbed during the other extractions. The highest $R_4^2$ values are obtained with X = Ex.-Mg or Ex.-K. For $P_2$ = $H_2SO_4$-P and Acetic-P the effect is negative, but with the other tests substituted as $P_2$ the effect is positive. This suggests the Bray-P procedure extracts less of the P associated with these analyses than $H_2SO_4$-P and Acetic-P, perhaps because of the short shaking time, but more than the other tests, perhaps because of the low pH of 1·7, (Table 1).

TABLE 25. Coefficients of determination ($r^2$ or $R^2$) for regressions (1), (2), (3), (4) and (6), for $P_1$ = Bray-P. The largest $R_4^2$ values are underlined and the sign, + or -, refers to the general trend ($\partial P_1/\partial X$) in (4). X is the substitution for X used in (6).

| $P_2$ | X | $R_3^2$ | $H_2SO_4$-P | Acetic-P | Truog-P | Lactate-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|---|---|
| $r_1^2$ | | | ·745 | ·670 | ·639 | ·797 | ·741 | ·439 | ·018 |
| $R_2^2$ | | | ·758 | ·729 | ·776 | ·908 | ·753 | ·481 | ·018 |
| | Oxalate-Fe | ·005 | ·822 | ·816 | ·865 | ·915 | ·877- | ·746- | ·086 |
| | Oxalate-Al | ·003 | ·771 | ·814 | ·813 | ·916 | ·846- | ·647- | ·077 |
| $R_3^2$ | Oxalate-Mn | ·024 | ·812 | ·789 | ·844 | ·911 | ·868- | ·697- | ·038 |
| or | Ex.-Ca | ·115 | ·793 | ·766 | ·819+ | ·919+ | ·852+ | ·704+ | ·258+ |
| $R_4^2$ | Ex.-Mg | ·291 | ·869- | ·<u>864</u>- | ·<u>874</u>+ | ·<u>924</u>+ | ·813+ | ·626+ | ·<u>326</u>+ |
| | Ex.-K | ·177 | ·<u>882</u>- | ·862 | ·853 | ·911 | ·<u>926</u>+ | ·066 | ·221 |
| | pH | ·046 | ·814 | ·785 | ·865 | ·924 | ·868 | ·<u>803</u> | ·177 |
| | Org.-C | ·026 | ·766 | ·739 | ·790 | ·919 | ·835 | ·668 | ·086 |
| $R_6^2$ | | | | ·880 | ·881 | ·928 | ·937 | ·815 | ·379 |
| <u>X</u> | | | | Mg | Mg | Mg | K | pH | Mg |
| W | | | | K | K | Ca | Mg | Org.-C | K |

Lactate-P

The Lactate-P values give relatively poor correlations with all the other tests except Bray-P ($R_2^2$ = ·867 for Bray-P, $\leqslant$ ·577 for other tests, Table 26). However, the $R_4^2$ values are quite high ($R_4^2 > ·85$) except for the alkaline tests, with X = pH, showing that the differences between Lactate-P and the other acidic tests can be accounted for by this analysis. Soil pH is an expression of the effects of several soil constituents but combinations of the characterizing analyses as in model (6) with this data did not give $R^2$ values any higher than those obtained with pH alone. The high $R_4^2$ values for X = pH thus point to inadequacies in the present series of analyses for explaining the variations in Lactate-P values relative to the other P tests. The $R_4^2$ values with $P_2$ = Bicarbonate-P and NaOH-P are still low for any X, indicating fundamental differences between Lactate-P and the alkaline tests which are not explained by the present analyses.

Citric-P

The Citric-P values are fairly closely related to all of the tests ($R_2^2$ = ·656 to ·844, Table 27) except the NaOH-P ($R_2^2$ = ·225). For $P_2$ = $H_2SO_4$-P, Acetic-P, Truog-P, Bray-P and Lactate-P the relationship is improved substantially by allowing for variations in Oxalate-Fe or Oxalate-Al ($R_4^2$ = ·955 to ·840).

TABLE 26. Coefficients of determination ($r^2$ or $R^2$) for regressions (1), (2), (3), (4) and (6), for $P_1$ = Lactate-P. The largest $R_4^2$ values are underlined and the sign, + or -, refers to the general trend ($\partial P_1/\partial X$) in (4). X is the substitution for X used in (6).

| $P_2$ | X | $R_3^2$ | $H_2SO_4$-P | Acetic-P | Truog-P | Bray-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|---|---|
| $r_1^2$ | | | ·535 | ·487 | ·392 | ·797 | ·531 | ·209 | ·001 |
| $R_2^2$ | | | ·544 | ·557 | ·577 | ·867 | ·531 | ·262 | ·001 |
| | Oxalate-Fe | ·005 | ·680 | ·728- | ·720- | ·874 | ·747- | ·412- | ·021 |
| | Oxalate-Al | ·000 | ·583 | ·805- | ·642 | ·869 | ·711- | ·357- | ·022 |
| $R_3^2$ | Oxalate-Mn | ·013 | ·749- | ·768- | ·751- | ·894 | ·788- | ·380- | ·016 |
| or | Ex.-Ca | ·173 | ·783- | ·781- | ·774+ | ·920+ | ·830+ | ·492+ | ·<u>227</u>+ |
| $R_4^2$ | Ex.-Mg | ·216 | ·727- | ·800- | ·654+ | ·877+ | ·659+ | ·355+ | ·222+ |
| | Ex.-K | ·129 | ·656 | ·656 | ·618 | ·897 | ·739 | ·378 | ·135 |
| | pH | ·088 | ·<u>864</u>- | ·<u>854</u>- | ·<u>905</u>+ | ·<u>940</u>+ | ·<u>884</u>+ | ·<u>587</u>+ | ·144 |
| | Org.-C | ·031 | ·560 | ·563 | ·586 | ·871 | ·687 | ·344 | ·055 |
| $R_6^2$ | | | ·870 | ·862 | ·907 | ·943 | ·911 | ·588 | ·277 |
| X | | | pH | pH | pH | pH | pH | pH | Ca |
| W | | | Mg | K | K | Fe | Mg | Mg | K |

TABLE 27. Coefficients of determination ($r^2$ or $R^2$) for regressions (1), (2), (3), (4) and (6), for $P_1$ = Citric-P. The largest $R_4^2$ values are underlined and the sign, + or −, refers to the general trend ($\partial P_1/\partial X$) in (4). X is the substitution for X used in (6).

| | X | $R_3^2$ | $P_2$ | $H_2SO_4$-P | Acetic-P | Truog-P | Bray-P | Lactate-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|---|---|---|
| $r_1^2$ | | | | ·807 | ·697 | ·703 | ·741 | ·531 | ·697 | ·218 |
| $R_2^2$ | | | | ·844 | ·714 | ·770 | ·777 | ·656 | ·698 | ·225 |
| | Oxalate-Fe | ·114 | | ·931+ | ·865+ | ·895+ | ·<u>906</u>+ | ·834+ | ·741 | ·308 |
| | Oxalate-Al | ·121 | | ·<u>955</u>+ | ·<u>913</u>+ | ·<u>935</u>+ | ·886+ | ·<u>840</u>+ | ·727 | ·290 |
| $R_3^2$ | Oxalate-Mn | ·087 | | ·860 | ·737 | ·778 | ·853 | ·705 | ·732 | ·251 |
| or | Ex.-Ca | ·092 | | ·872 | ·723 | ·791 | ·778 | ·664 | ·756+ | ·503+ |
| $R_4^2$ | Ex.-Mg | ·400 | | ·885 | ·725 | ·782 | ·812 | ·747- | ·<u>831</u>+ | ·<u>678</u>+ |
| | Ex.-K | ·077 | | ·853 | ·717 | ·777 | ·818 | ·697 | ·710 | ·346 |
| | pH | ·014 | | ·859 | ·734 | ·790 | ·783 | ·695 | ·788 | ·392 |
| | Org.-C | ·076 | | ·910 | ·830 | ·871 | ·860 | ·741 | ·731 | ·294 |
| $R_6^2$ | | | | ·956 | ·914 | ·936 | ·935 | ·891 | ·833 | ·692 |
| <u>X</u> | | | | Al | Al | Al | Fe | Al | Mg | Mg |
| W | | | | Ca | Org.-C | Fe | Mg | Mg | Fe | K |

The trend for Oxalate-Fe and Oxalate-Al is positive indicating that the Citric-P procedure is more effective in extracting P from Fe or Al bound sources than are the other acidic tests. For the alkaline tests the largest $R_4^2$ values are for X = Ex.-Mg ($R_4^2$ = ·831 for Bicarbonate-P, ·678 for NaOH-P) and the trends are positive, indicating the superior ability of the Citric-P procedure to extract P related to this analysis.

Bicarbonate-P

The Bicarbonate-P values are in general not closely correlated with the other P tests, the best $R_2^2$ value of ·717 being for Citric-P (Table 28). For the acidic tests described above the highest $R_4^2$ values are for X = Oxalate-Fe or Oxalate-Al or, in the case of Citric-P, for X = Org.-C which is highly correlated with Oxalate-Fe and Oxalate-Al (Table 21). The trends with respect to X are positive, indicating the Bicarbonate-P procedure extracts Fe or Al bound P. The relationships are also improved by allowing for pH or, for $P_2$ = Citric-P, Ex.-Mg, and these trends are negative. The relationships with NaOH-P are all poor, the highest $R_4^2$ = ·739 being obtained with X = Ex.-Mg. This tend is positive, suggesting Bicarbonate-P does extract some P from a source represented by this analysis.

NaOH-P

The NaOH-P values show little or no relationship

TABLE 28. Coefficients of determination ($r^2$ or $R^2$) for regressions (1), (2), (3), (4) and (6), for $P_1$ = Bicarbonate-P. The largest $R_4^2$ values are underlined and the sign, + or -, refers to the general trend ($\partial P_1/\partial X$) in (4). X is the substitution for X used in (6).

| | X | $R_3^2$ | $H_2SO_4$-P | Acetic-P | Truog-P | Bray-P | Lactate-P | Citric-P | NaOH-P |
|---|---|---|---|---|---|---|---|---|---|
| $P_2$ | | | | | | | | | |
| $r_1^2$ | | | ·417 | ·272 | ·327 | ·439 | ·209 | ·697 | ·489 |
| $R_2^2$ | | | ·586 | ·350 | ·503 | ·552 | ·500 | ·717 | ·492 |
| | Oxalate-Fe | ·333 | ·826+ | ·701+ | ·808+ | ·<u>932</u>+ | ·<u>929</u>+ | ·892+ | ·571 |
| | Oxalate-Al | ·293 | ·<u>839</u>+ | ·<u>742</u>+ | ·<u>861</u>+ | ·831+ | ·888+ | ·883+ | ·571 |
| $R_3^2$ | Oxalate-Mn | ·189 | ·716+ | ·472+ | ·612+ | ·841+ | ·682+ | ·882+ | ·517 |
| or | Ex.-Ca | ·048 | ·713 | ·393 | ·610 | ·612 | ·552 | ·860- | ·734+ |
| $R_4^2$ | Ex.-Mg | ·156 | ·677 | ·358 | ·544 | ·565 | ·506 | ·868- | ·<u>739</u>+ |
| | Ex.-K | ·060 | ·593 | ·361 | ·507 | ·561 | ·517 | ·754 | ·619 |
| | pH | ·008 | ·720- | ·450- | ·619- | ·686- | ·660- | ·866 | ·609 |
| | Org.-C | ·250 | ·803 | ·627 | ·755 | ·867 | ·781 | ·<u>904</u>+ | ·564 |
| $R_6^2$ | | | ·862 | ·763 | ·874 | ·940 | ·931 | ·953 | ·754 |
| <u>X</u> | | | Al | Al | Al | Fe | Fe | Org.-C | Mg |
| W | | | Fe | Fe | Org.-C | Al | Al | Mg | K |

to the other P test values, the best being Bicarbonate-P ($R_2^2$ = ·636, Table 29), but are related to the Oxalate-Fe and Oxalate-Al results ($R_3^2$ = ·746 and ·814 respectively, top line of Table 29). Accordingly all of the relationships are improved very greatly by allowing for variations in Oxalate-Al ($R_4^2$ = ·959 to ·834) or Oxalate-Fe. These very marked improvements suggest that the NaOH-P procedure extracts Fe and Al bound P to a much greater extent than do the other tests.

TABLE 29. Coefficients of determination ($r^2$ or $R^2$) for regressions (1), (2), (3), (4) and (6), for $P_1$ = NaOH-P. The largest $R_4^2$ values are underlined and the sign, + or -, refers to the general trend ($\partial P_1/\partial X$) in (4). X is the substitution for X used in (6).

| | X | $R_3^2$ | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $P_2$ | | | $H_2SO_4$-P | Acetic-P | Truog-P | Bray-P | Lactate-P | Citric-P | Bicarbonate-P |
| $r_1^2$ | | | ·016 | ·000 | ·002 | ·018 | ·001 | ·218 | ·489 |
| $R_2^2$ | | | ·113 | ·000 | ·022 | ·081 | ·018 | ·277 | ·636 |
| | Oxalate-Fe | ·746 | ·854+ | ·749+ | ·779+ | ·929+ | ·848+ | ·939+ | ·955+ |
| | Oxalate-Al | ·814 | ·<u>940</u>+ | ·<u>834</u>+ | ·<u>906</u>+ | ·<u>930</u>+ | ·<u>916</u>+ | ·<u>952</u>+ | ·<u>959</u>+ |
| $R_3^2$ | Oxalate-Mn | ·163 | ·360+ | ·169+ | ·199+ | ·429+ | ·232+ | ·731+ | ·785+ |
| or | Ex.-Ca | ·026 | ·361 | ·038 | ·157 | ·208 | ·119 | ·742- | ·899- |
| $R_4^2$ | Ex.-Mg | ·008 | ·275 | ·015 | ·071 | ·174 | ·067 | ·721- | ·851- |
| | Ex.-K | ·008 | ·201 | ·010 | ·072 | ·161 | ·071 | ·586 | ·833 |
| | pH | ·103 | ·351 | ·120 | ·198 | ·280 | ·204 | ·741 | ·872 |
| | Org.-C | ·498 | ·649 | ·505 | ·537 | ·713 | ·544 | ·831 | ·882 |

## V. CONCLUSIONS.

These studies have shown that while some of the standard P tests seem to represent essentially the same fractions of soil P, as shown by their high correlations with each other, some other tests represent different fractions as shown by low correlations. The differences between the test values can be largely explained by the variations in soil composition represented by the characterizing soil analyses: Oxalate-Fe, Oxalate-Al, Ex.-Ca and Ex.-Mg. Since these constituents are known to vary in soils generally, the present results can be expected to apply to other regions.

The preliminary studies indicated Oxalate-Fe and Oxalate-Al were generally superior to Total-Fe and Total-Al analyses for explaining the differences between the P values obtained by different tests, probably because the oxalate analyses represent the P sorbing components of the soil (for example: Williams et al., 1958). The oxalate analyses are also more conveniently obtained than total analyses. The preliminary studies also showed the differences between P tests were better explained by Total-Ca and Total-Mg analyses than Ex.-Ca and Ex.-Mg, but in the studies with 145 soils Ex.-Ca and Ex.-Mg often accounted for much of the variation between P test values as shown by high values for $R_4^2$. Accordingly, other analyses such as Total-Ca, Total-Mg or even analyses not considered in these studies, are not likely to give

substantial improvements over Ex.-Ca, Ex.-Mg, Oxalate-Fe and Oxalate-Al. Further, Ex.-Ca and Ex.-Mg are more convenient soil analyses than Total-Ca and Total-Mg.

The three acid test procedures, $H_2SO_4$-P, Acetic-P and Truog-P, gave test values that were highly correlated with each other, and this is consistent with similarities in the nature of these extractants. These extractants are all essentially dilute acids, without any species capable of forming strong complexes with soil constituents. The absence of a complexing agent distinguishes these tests from the other acidic tests, Bray-P, Lactate-P and Citric-P, which contain the anions fluoride, lactate and citrate, which are known to complex with Fe and Al or Ca and Mg. The much lower soil:solution ratio of $H_2SO_4$-P, Acetic-P and Truog-P may also be a contributing factor. The P values obtained by $H_2SO_4$-P, Acetic-P and Truog-P are more strongly influenced by Ca and Mg than other tests, the P test values increasing as soil content of Ca and Mg increase. The alkaline tests, Bicarbonate-P and NaOH-P, are fundamentally different from the acidic tests, $H_2SO_4$-P, Acetic-P and Truog-P. Thus it has been shown that the alkaline tests are affected mainly by variations in Oxalate-Fe and Oxalate-Al and this suggests they extract mainly the P sorbed or precipitated as Fe and Al compounds, rather than that associated with the Ex.-Ca and Ex.-Mg. The Citric-P extractant apparently dissolves P from sources related to both the Ca and Mg analyses on

the one hand and the Fe and Al analyses on the other. This dual nature of Citric-P can be explained by its acidity, dissolving P associated with Ca and Mg, and its content of citrate which complexes with Fe and Al, thereby either releasing Fe and Al bound P or blocking these sites against resorption of P during the extraction. Bray-P and Lactate-P values were fairly closely correlated with each other but not with other test values, nor were these differences fully explained by the present series of soil analyses.

Application to soil testing.

The 145 soil samples used for these studies represent the diversity of soils that occur in a region of New South Wales where soil testing for P fertilizer requirements is done mainly by a single procedure (Bicarbonate-P), irrespective of soil type or soil composition. Since this test correlates with yield responses to P fertilizer (for example: Colwell, 1963) it may be assumed to correlate with the fraction of soil P that is available to plants. The other soil tests also correlate with yield response to P, at least on some types of soil, so that all may be assumed to correlate with available P to some extent. If then the available P could be measured directly as a P test it might be expected that it would be related to all of these P tests in much the same way that the P tests are related to each other. Thus this study suggests

that the soil features that affect the relationships of the different P tests to each other, that is, Oxalate-Fe, Oxalate-Al, Ex.-Ca and Ex.-Mg, may also affect the relationship of these tests to plant available P. Again, as with the P test interrelationships, the soil constituents most important in this regard would be determined by the nature of the respective extraction procedures. It is concluded therefore that P test calibration equations which relate soil test values to yield response to P fertilizer may be improved by adding variables for appropriate soil constituents. This conclusion is supported by the calibration study of Colwell and Esdaile (1968), who reported an improvement in a P test (Bicarbonate-P) calibration equation by adding variables for pH and Ex.-K. Other variables which this study suggests may prove of value are Ex.-Mg, Ex.-Ca, Oxalate-Fe and Oxalate-Al.

It has been shown that most of the P tests can be closely related to other P tests by regressions which include a term to allow for variation in soil composition, the chief exception to this result being the NaOH-P test. On this basis it can be expected that all of the P tests, with the possible exception of NaOH-P, should be equally useful for estimating P fertilizer requirements in this region if allowance is made for the effects of soil composition. Suitable analyses for this purpose would be Ex.-Ca, Ex.-Mg, Oxalate-Fe and Oxalate-Al.

As an alternative to allowing for the effects of variation

in soil composition by incorporating terms in calibration equations a region may be partitioned into districts of soil relatively uniform with respect to these variables. Calibrations of a convenient P test could then be carried out for each of the uniform districts. It is clear from the results of this study that it is undesirable to apply a single P test calibration to the wide range of soils covered by this study. Accordingly the feasibility of grouping soils into units that are relatively uniform with respect to Ex.-Ca, Ex.-Mg, Oxalate Fe and Oxalate-Al deserves investigation. Such a grouping would be practicable if it were found to correspond sufficiently closely to a grouping based on field morphology. If, however, it proved necessary to always have the analyses in order to obtain a grouping then it would be better to use the analyses in a general calibration equation.

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APPENDIX 1. Values of 8 P tests, 4 P solubility fractions, Total-P and 17 characterizing analyses for the 44 soils used in the preliminary studies. Total analyses, clay and Org.-C as percent, other results as ppm. All values are means of duplicates.

| Soil | $H_2SO_4$-P | Acetic-P | Truog-P | Bray-P | Lactate-P | Citric-P |
|---|---|---|---|---|---|---|
| E1 | 35·4 | 8·1 | 13·6 | 18·4 | 9·5 | 45·5 |
| E2 | 9·4 | 2·7 | 4·4 | 3·9 | 2·4 | 3·3 |
| E3 | 41·0 | 7·2 | 6·8 | 15·8 | 3·1 | 16·9 |
| E4 | 44·5 | 5·7 | 15·4 | 10·7 | 5·8 | 14·5 |
| E5 | 16·0 | 1·6 | 2·6 | 5·3 | 2·0 | 7·6 |
| E6 | 4·2 | 0·8 | 0·8 | 1·1 | 1·1 | 0·5 |
| E7 | 37·3 | 14·6 | 14·4 | 20·4 | 17·1 | 40·5 |
| E8 | 4·3 | 3·4 | 2·8 | 3·1 | 2·9 | 2·0 |
| E9 | 30·0 | 12·6 | 10·6 | 14·4 | 8·6 | 17·9 |
| E10 | 3·2 | 1·5 | 2·2 | 1·5 | 1·3 | 0·8 |
| E11 | 13·9 | 8·5 | 7·4 | 5·8 | 4·7 | 7·5 |
| E12 | 16·4 | 5·3 | 4·0 | 6·8 | 4·6 | 5·8 |
| E13 | 60·8 | 34·5 | 33·4 | 27·4 | 25·5 | 37·5 |
| E14 | 62·7 | 33·5 | 22·8 | 25·3 | 23·9 | 44·5 |
| E15 | 8·7 | 5·2 | 2·8 | 3·0 | 3·7 | 4·5 |
| E16 | 14·9 | 7·7 | 7·0 | 7·7 | 3·9 | 8·3 |
| E17 | 298·3 | 207·5 | 26·4 | 39·4 | 63·8 | 87·0 |
| E18 | 35·8 | 29·5 | 22·6 | 23·5 | 13·3 | 22·8 |
| E19 | 72·0 | 36·5 | 22·8 | 37·6 | 20·6 | 56·5 |
| E20 | 16·9 | 5·1 | 8·6 | 7·1 | 3·6 | 9·2 |
| E21 | 30·0 | 14·5 | 14·8 | 14·9 | 9·9 | 26·2 |
| E22 | 29·8 | 14·8 | 12·0 | 16·9 | 9·5 | 26·1 |
| E23 | 11·8 | 15·2 | 12·8 | 8·4 | 8·20 | 11·0 |
| E24 | 9·8 | 9·9 | 8·6 | 5·8 | 5·8 | 9·5 |
| E25 | 12·5 | 8·5 | 11·2 | 5·7 | 5·2 | 7·3 |
| F1 | 27·1 | 7·4 | 19·8 | 9·1 | 6·6 | 15·9 |
| F2 | 19·4 | 11·0 | 12·2 | 11·4 | 8·3 | 12·6 |
| F3 | 15·6 | 12·6 | 9·6 | 7·5 | 6·3 | 9·1 |
| F4 | 22·8 | 23·1 | 19·4 | 9·8 | 8·1 | 17·6 |
| F5 | 22·6 | 20·5 | 18·0 | 11·0 | 9·5 | 18·6 |
| F6 | 5·7 | 7·7 | 5·8 | 3·6 | 3·7 | 5·5 |
| F7 | 5·9 | 1·5 | 2·6 | 3·3 | 2·2 | 2·6 |
| F8 | 7·8 | 2·2 | 2·6 | 4·3 | 3·2 | 3·1 |
| F9 | 10·1 | 0·9 | 2·0 | 4·6 | 2·4 | 3·5 |
| F10 | 8·8 | 1·1 | 3·8 | 6·3 | 2·8 | 3·4 |
| F11 | 19·3 | 8·2 | 6·4 | 10·1 | 4·8 | 15·3 |
| F12 | 15·4 | 8·5 | 12·8 | 8·9 | 7·9 | 36·3 |
| F13 | 25·7 | 12·8 | 8·8 | 19·1 | 7·8 | 15·7 |
| F14 | 7·9 | 7·7 | 3·6 | 4·9 | 5·8 | 6·8 |
| F15 | 7·5 | 3·1 | 3·8 | 3·0 | 3·4 | 5·0 |
| F16 | 65·5 | 17·8 | 31·0 | 26·6 | 13·8 | 92·0 |
| F17 | 249·0 | 9·5 | 41·0 | 61·0 | 26·1 | 457·0 |
| F18 | 5·3 | 1·3 | 3·4 | 1·4 | 1·3 | 1·4 |
| F19 | 3·3 | 1·4 | 1·2 | 0·6 | 1·2 | 0·7 |

APPENDIX 1. (ctd)

| Soil | Bicarb-onate-P | NaOH-P | Total-P | HCl-P | "Al-P" | "Fe-P" |
|---|---|---|---|---|---|---|
| E1 | 38·0 | 1093·0 | 0·48 | 2172 | 89·8 | 350·8 |
| E2 | 6·0 | 72·9 | 0·06 | 432 | 7·4 | 30·6 |
| E3 | 15·8 | 398·0 | 0·15 | 877 | 205·0 | 88·5 |
| E4 | 31·7 | 543·0 | 0·28 | 1698 | 30·9 | 311·0 |
| E5 | 8·1 | 101·1 | 0·06 | 441 | 15·4 | 45·7 |
| E6 | 1·3 | 24·0 | 0·01 | 38·9 | 2·5 | 6·1 |
| E7 | 31·4 | 76·0 | 0·03 | 225 | 28·6 | 33·2 |
| E8 | 3·5 | 29·7 | 0·01 | 115 | 5·9 | 7·2 |
| E9 | 19·9 | 77·8 | 0·03 | 205 | 18·7 | 34·0 |
| E10 | 2·1 | 22·3 | 0·02 | 170 | 3·4 | 9·0 |
| E11 | 8·5 | 28·1 | 0·04 | 267 | 11·2 | 9·9 |
| E12 | 6·9 | 28·4 | 0·02 | 172 | 10·8 | 11·0 |
| E13 | 15·6 | 82·2 | 0·06 | 444 | 34·2 | 30·5 |
| E14 | 24·3 | 77·0 | 0·03 | 206 | 34·3 | 38·1 |
| E15 | 5·8 | 13·1 | 0·00 | 35·2 | 3·4 | 2·7 |
| E16 | 9·7 | 55·6 | 0·03 | 271 | 10·4 | 18·6 |
| E17 | 15·6 | 13·9 | 0·08 | 607 | 26·4 | 1·8 |
| E18 | 7·0 | 26·4 | 0·03 | 234 | 16·6 | 13·7 |
| E19 | 28·1 | 105·0 | 0·05 | 416 | 51·8 | 55·0 |
| E20 | 12·9 | 101·0 | 0·05 | 349 | 14·1 | 41·5 |
| E21 | 21·5 | 90·0 | 0·03 | 271 | 19·2 | 38·0 |
| E22 | 13·6 | 44·2 | 0·02 | 188 | 17·0 | 22·1 |
| E23 | 7·0 | 11·3 | 0·01 | 97 | 8·7 | 1·5 |
| E24 | 8·4 | 23·8 | 0·02 | 140 | 9·5 | 7·7 |
| E25 | 10·0 | 34·6 | 0·05 | 323 | 11·1 | 15·0 |
| F1 | 31·7 | 253·0 | 0·37 | 1717 | 32·8 | 208·0 |
| F2 | 7·5 | 26·1 | 0·02 | 218 | 11·2 | 9·4 |
| F3 | 8·5 | 9·3 | 0·02 | 230 | 8·3 | 1·9 |
| F4 | 19·5 | 22·8 | 0·05 | 319 | 19·7 | 17·2 |
| F5 | 22·6 | 28·2 | 0·05 | 264 | 18·2 | 19·2 |
| F6 | 5·0 | 11·1 | 0·01 | 64 | 4·7 | 4·4 |
| F7 | 6·0 | 63·5 | 0·04 | 254 | 12·3 | 19·3 |
| F8 | 7·1 | 50·5 | 0·04 | 240 | 13·3 | 16·9 |
| F9 | 13·3 | 327·0 | 0·13 | 737 | 22·0 | 150·7 |
| F10 | 12·2 | 296·0 | 0·16 | 502 | 19·4 | 128·0 |
| F11 | 11·0 | 54·3 | 0·03 | 219 | 11·2 | 23·3 |
| F12 | 30·5 | 69·4 | 0·04 | 307 | 14·5 | 53·0 |
| F13 | 15·0 | 50·8 | 0·03 | 218 | 25·4 | 17·3 |
| F14 | 6·7 | 22·3 | 0·01 | 101 | 7·9 | 6·7 |
| F15 | 5·6 | 26·9 | 0·03 | 242 | 5·0 | 9·9 |
| F16 | 46·2 | 256·0 | 0·20 | 1287 | 152·3 | 170·7 |
| F17 | 320·0 | 4969·0 | 1·24 | 3843 | 1301·0 | 888·8 |
| F18 | 6·5 | 54·9 | 0·02 | 254 | 4·7 | 28·8 |
| F19 | 2·4 | 52·5 | 0·02 | 184 | 1·8 | 13·8 |

APPENDIX 1. (ctd)

| Soil | "Ca-P" | Oxalate-Fe | Total-Fe | Oxalate-Al | Total-Al | Oxalate-Mn |
|---|---|---|---|---|---|---|
| E1 | 160·0 | 21667 | 14·60 | 18209 | 17·20 | 1075 |
| E2 | 13·3 | 1983 | 6·59 | 974 | 4·33 | 1124 |
| E3 | 54·1 | 8967 | 15·91 | 19375 | 16·76 | 1085 |
| E4 | 63·4 | 4200 | 17·11 | 3990 | 11·52 | 2030 |
| E5 | 11·4 | 3467 | 3·35 | 4930 | 5·74 | 2492 |
| E6 | 1·6 | 1400 | 2·01 | 1977 | 4·23 | 0 |
| E7 | 12·5 | 1750 | 0·77 | 339 | 2·03 | 175 |
| E8 | 3·2 | 933 | 1·81 | 1097 | 3·91 | 0 |
| E9 | 11·7 | 1050 | 2·04 | 380 | 3·23 | 190 |
| E10 | 4·0 | 837 | 2·57 | 614 | 4·04 | 130 |
| E11 | 12·0 | 1173 | 2·70 | 1064 | 5·56 | 1308 |
| E12 | 3·1 | 1667 | 1·19 | 2527 | 3·69 | 18 |
| E13 | 26·3 | 1350 | 2·55 | 1233 | 6·89 | 482 |
| E14 | 14·3 | 547 | 1·25 | 394 | 4·04 | 154 |
| E15 | 1·0 | 117 | 0·18 | 167 | 1·17 | 15 |
| E16 | 10·8 | 1400 | 2·76 | 850 | 5·15 | 842 |
| E17 | 251·7 | 887 | 4·74 | 1800 | 8·90 | 677 |
| E18 | 19·3 | 774 | 3·53 | 853 | 6·28 | 1027 |
| E19 | 33·4 | 1603 | 1·72 | 930 | 5·10 | 633 |
| E20 | 20·6 | 1314 | 1·74 | 900 | 4·52 | 1367 |
| E21 | 18·1 | 2190 | 2·61 | 827 | 3·59 | 1063 |
| E22 | 15·1 | 1107 | 0·98 | 467 | 1·69 | 510 |
| E23 | 12·0 | 627 | 2·59 | 1634 | 4·84 | 552 |
| E24 | 6·2 | 1067 | 2·20 | 880 | 4·26 | 1527 |
| E25 | 22·9 | 1597 | 5·44 | 1814 | 9·79 | 1103 |
| F1 | 52·4 | 6650 | 20·00 | 1667 | 6·06 | 4467 |
| F2 | 9·5 | 1004 | 1·72 | 583 | 3·94 | 529 |
| F3 | 19·8 | 1003 | 2·88 | 1474 | 5·38 | 477 |
| F4 | 18·5 | 2250 | 9·43 | 2834 | 9·45 | 900 |
| F5 | 15·3 | 2267 | 8·51 | 2694 | 8·79 | 1150 |
| F6 | 2·9 | 993 | 2·38 | 1230 | 4·10 | 1600 |
| F7 | 6·2 | 1843 | 4·63 | 5467 | 9·93 | 396 |
| F8 | 5·6 | 1557 | 3·85 | 4367 | 8·11 | 359 |
| F9 | 29·2 | 6850 | 13·23 | 5794 | 18·98 | 623 |
| F10 | 35·4 | 7734 | 14·56 | 4820 | 18·43 | 1244 |
| F11 | 11·1 | 1650 | 2·08 | 817 | 4·15 | 1662 |
| F12 | 17·7 | 5817 | 4·28 | 1500 | 8·36 | 1734 |
| F13 | 5·5 | 1143 | 2·24 | 1450 | 4·84 | 25 |
| F14 | 0·8 | 707 | 0·65 | 950 | 1·56 | 14 |
| F15 | 10·8 | 2617 | 4·66 | 867 | 3·71 | 2550 |
| F16 | 100·6 | 5900 | 11·33 | 7683 | 13·31 | 483 |
| F17 | 1662·5 | 40000 | 18·49 | 31778 | 12·32 | 2792 |
| F18 | 6·3 | 1553 | 3·16 | 987 | 4·65 | 817 |
| F19 | 3·7 | 1374 | 3·62 | 1165 | 7·55 | 0 |

APPENDIX 1. (ctd)

| Soil | Total-Mn | Total-Ti | Ex.Ca | Total-Ca | Ex.Mg | Total-Mg |
|---|---|---|---|---|---|---|
| E1 | 0·23 | 2·55 | 50 | 0·13 | 26 | 0·38 |
| E2 | 0·20 | 2·44 | 1060 | 0·31 | 170 | 0·23 |
| E3 | 0·18 | 2·13 | 2600 | 0·64 | 566 | 0·38 |
| E4 | 0·33 | 3·12 | 2570 | 0·50 | 660 | 0·65 |
| E5 | 0·29 | 0·56 | 520 | 0·11 | 112 | 0·08 |
| E6 | 0·00 | 0·36 | 10 | 0·03 | 98 | 0·07 |
| E7 | 0·02 | 0·41 | 370 | 0·19 | 52 | 0·10 |
| E8 | 0·00 | 0·47 | 90 | 0·08 | 146 | 0·20 |
| E9 | 0·02 | 0·56 | 430 | 0·10 | 44 | 0·12 |
| E10 | 0·02 | 0·56 | 820 | 0·13 | 160 | 0·16 |
| E11 | 0·13 | 0·59 | 2760 | 0·50 | 300 | 0·30 |
| E12 | 0·00 | 0·29 | 160 | 0·05 | 92 | 0·14 |
| E13 | 0·07 | 0·47 | 2080 | 0·41 | 196 | 0·25 |
| E14 | 0·02 | 0·19 | 580 | 0·33 | 52 | 0·20 |
| E15 | 0·00 | 0·04 | 250 | 0·08 | 68 | 0·04 |
| E16 | 0·08 | 0·46 | 1680 | 0·24 | 292 | 0·33 |
| E17 | 0·10 | 0·69 | 7900 | 3·27 | 1486 | 1·67 |
| E18 | 0·10 | 0·47 | 3280 | 0·55 | 720 | 0·64 |
| E19 | 0·06 | 0·29 | 1530 | 0·26 | 188 | 0·19 |
| E20 | 0·06 | 0·30 | 1310 | 0·28 | 132 | 0·21 |
| E21 | 0·14 | 0·76 | 1330 | 0·25 | 672 | 0·40 |
| E22 | 0·03 | 0·28 | 780 | 0·10 | 234 | 0·15 |
| E23 | 0·08 | 0·58 | 7125 | 1·22 | 1130 | 1·08 |
| E24 | 0·17 | 0·56 | 3020 | 0·44 | 600 | 0·34 |
| E25 | 0·13 | 0·63 | 6500 | 1·00 | 534 | 0·67 |
| F1 | 0·61 | 2·58 | 2600 | 0·55 | 484 | 0·48 |
| F2 | 0·05 | 0·42 | 1900 | 0·27 | 212 | 0·24 |
| F3 | 0·07 | 0·58 | 6965 | 1·54 | 1240 | 0·99 |
| F4 | 0·15 | 1·28 | 11000 | 1·79 | 2450 | 1·62 |
| F5 | 0·18 | 1·47 | 8600 | 1·47 | 2700 | 1·51 |
| F6 | 0·17 | 0·64 | 3450 | 0·44 | 1360 | 0·57 |
| F7 | 0·08 | 0·89 | 430 | 0·13 | 94 | 0·11 |
| F8 | 0·07 | 0·81 | 470 | 0·14 | 106 | 0·11 |
| F9 | 0·10 | 1·30 | 170 | 0·06 | 26 | 0·15 |
| F10 | 0·20 | 3·15 | 840 | 0·20 | 140 | 0·23 |
| F11 | 0·16 | 0·46 | 1080 | 0·22 | 280 | 0·23 |
| F12 | 0·21 | 0·54 | 3970 | 0·63 | 794 | 0·66 |
| F13 | 0·03 | 0·53 | 510 | 0·13 | 156 | 0·28 |
| F14 | 0·00 | 0·34 | 210 | 0·05 | 60 | 0·08 |
| F15 | 0·31 | 0·53 | 2640 | 0·48 | 100 | 0·24 |
| F16 | 0·54 | 1·90 | 3970 | 0·79 | 406 | 0·34 |
| F17 | 0·50 | 3·09 | 210 | 0·41 | 82 | 0·47 |
| F18 | 0·08 | 0·67 | 180 | 0·05 | 300 | 0·20 |
| F19 | 0·00 | 0·50 | 60 | 0·02 | 478 | 0·34 |

APPENDIX 1. (ctd)

| Soil | Ex.K | Total-K | Ex.Na | pH | Org.-C | % Clay |
|---|---|---|---|---|---|---|
| E1 | 110 | 0·17 | 15 | 4·95 | 6·5 | 30 |
| E2 | 410 | 0·85 | 0 | 6·25 | 1·4 | 19 |
| E3 | 686 | 0·30 | 30 | 6·38 | 4·4 | 23 |
| E4 | 494 | 0·30 | 20 | 5·69 | 5·4 | 56 |
| E5 | 162 | 0·19 | 15 | 5·62 | 2·9 | 34 |
| E6 | 60 | 0·11 | 15 | 5·53 | 1·2 | 20 |
| E7 | 142 | 0·75 | 15 | 5·06 | 1·78 | 4 |
| E8 | 94 | 0·69 | 20 | 5·02 | 1·8 | 19 |
| E9 | 288 | 0·97 | 0 | 5·51 | 0·8 | 22 |
| E10 | 326 | 0·91 | 0 | 6·20 | 0·9 | 25 |
| E11 | 842 | 1·42 | 25 | 7·58 | 2·1 | 12 |
| E12 | 140 | 0·39 | 30 | 4·98 | 2·9 | 14 |
| E13 | 334 | 1·71 | 0 | 6·24 | 3·3 | 14 |
| E14 | 148 | 2·11 | 0 | 6·88 | 0·4 | 5 |
| E15 | 40 | 1·06 | 0 | 5·16 | 1·0 | 0 |
| E16 | 882 | 1·10 | 10 | 6·24 | 1·2 | 34 |
| E17 | 668 | 1·51 | 150 | 8·22 | 1·5 | 46 |
| E18 | 834 | 1·82 | 95 | 7·79 | 0·9 | 47 |
| E19 | 558 | 2·21 | 0 | 6·60 | 1·4 | 26 |
| E20 | 530 | 2·18 | 10 | 6·19 | 0·9 | 37 |
| E21 | 248 | 0·40 | 146 | 6·20 | 1·2 | 37 |
| E22 | 240 | 0·21 | 52 | 6·38 | 0·8 | 23 |
| E23 | 300 | 0·23 | 30 | 8·04 | 0·9 | 52 |
| E24 | 170 | 0·15 | 40 | 6·87 | 1·1 | 9 |
| E25 | 476 | 1·00 | 20 | 8·06 | 1·4 | 51 |
| F1 | 572 | 0·37 | 5 | 6·79 | 3·6 | 41 |
| F2 | 460 | 1·02 | 30 | 7·46 | 0·9 | 29 |
| F3 | 362 | 0·50 | 70 | 8·08 | 1·6 | 49 |
| F4 | 340 | 0·34 | 80 | 6·87 | 1·5 | 79 |
| F5 | 476 | 0·34 | 84 | 6·86 | 1·6 | 76 |
| F6 | 180 | 0·13 | 510 | 6·92 | 0·5 | 58 |
| F7 | 114 | 0·16 | 36 | 5·50 | 3·4 | 45 |
| F8 | 136 | 0·15 | 10 | 5·41 | 3·7 | 30 |
| F9 | 88 | 0·13 | 10 | 4·95 | 4·0 | 50 |
| F10 | 126 | 0·17 | 10 | 5·25 | 4·2 | 44 |
| F11 | 446 | 0·95 | 32 | 5·91 | 1·1 | 27 |
| F12 | 892 | 1·49 | 36 | 6·49 | 1·7 | 64 |
| F13 | 380 | 1·00 | 12 | 5·02 | 2·5 | 22 |
| F14 | 92 | 0·38 | 0 | 4·47 | 2·7 | 18 |
| F15 | 156 | 0·96 | 5 | 7·24 | 2·3 | 32 |
| F16 | 1130 | 0·62 | 15 | 6·70 | 2·7 | 39 |
| F17 | 286 | 0·68 | 30 | 5·02 | 12·9 | 15 |
| F18 | 120 | 1·38 | 50 | 6·92 | 0·1 | 31 |
| F19 | 86 | 0·90 | 20 | 4·62 | 0·1 | 47 |

APPENDIX 2A. P extracted by 8 P tests from the 101 soils described in Table 3. All values are means of duplicates, expressed as ppm.

| Soil | $H_2SO_4$-P | Acetic-P | Truog-P | Bray-P | Lactate-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|---|
| B1 | 18·0 | 3·4 | 4·3 | 2·95 | 3·3 | 8·0 | 18·2 | 53·8 |
| B2 | 16·6 | 4·1 | 5·8 | 3·15 | 4·0 | 6·1 | 17·2 | 51·7 |
| B3 | 23·3 | 6·5 | 10·0 | 5·55 | 6·2 | 13·4 | 28·0 | 66·3 |
| B4 | 30·0 | 9·5 | 9·5 | 6·58 | 7·5 | 15·1 | 29·8 | 26·4 |
| B5 | 13·5 | 3·0 | 17·9 | 2·27 | 3·7 | 9·9 | 20·0 | 46·4 |
| B6 | 48·8 | 11·5 | 6·9 | 13·15 | 8·4 | 14·5 | 35·5 | 32·7 |
| B7 | 16·0 | 3·9 | 7·0 | 2·95 | 4·5 | 9·7 | 22·9 | 50·1 |
| B8 | 22·2 | 4·3 | 22·0 | 5·21 | 4·4 | 7·4 | 19·7 | 66·7 |
| B9 | 35·8 | 15·3 | 22·0 | 15·14 | 16·9 | 33·5 | 50·0 | 56·6 |
| B10 | 80·0 | 33·2 | 42·0 | 34·66 | 26·1 | 44·5 | 72·0 | 68·8 |
| B11 | 45·0 | 10·6 | 17·0 | 11·72 | 8·0 | 21·1 | 33·5 | 79·4 |
| B12 | 27·5 | 8·2 | 14·3 | 9·25 | 7·9 | 15·2 | 26·7 | 46·8 |
| B13 | 20·2 | 5·3 | 8·8 | 5·00 | 4·3 | 4·9 | 17·0 | 28·9 |
| B14 | 22·7 | 4·8 | 7·8 | 3·70 | 4·2 | 6·1 | 19·6 | 40·2 |
| B15 | 42·5 | 14·4 | 17·5 | 9·59 | 7·5 | 16·2 | 22·4 | 35·2 |
| B16 | 23·8 | 9·4 | 10·9 | 6·03 | 7·4 | 7·4 | 21·5 | 35·6 |
| B17 | 74·9 | 28·5 | 23·5 | 18·15 | 19·6 | 23·4 | 36·3 | 33·6 |
| B18 | 39·8 | 11·6 | 12·4 | 8·91 | 9·1 | 17·4 | 31·3 | 69·9 |
| B19 | 61·0 | 22·3 | 21·4 | 13·29 | 15·0 | 18·6 | 36·5 | 43·8 |
| B20 | 32·7 | 9·3 | 9·8 | 6·10 | 6·5 | 13·3 | 23·4 | 68·8 |
| C1 | 31·8 | 11·3 | 4·8 | 2·88 | 7·2 | 5·3 | 6·5 | 8·8 |
| C2 | 23·0 | 5·8 | 10·0 | 12·88 | 4·9 | 7·5 | 13·6 | 45·5 |
| C3 | 22·0 | 6·5 | 7·6 | 10·55 | 4·8 | 8·7 | 12·8 | 43·0 |

APPENDIX 2A. (ctd)

| Soil | $H_2SO_4$-P | Acetic-P | Truog-P | Bray-P | Lactate-P | Citric-P | Bicarbonate-P | NaOH-P |
|---|---|---|---|---|---|---|---|---|
| C4 | 44·2 | 8·6 | 10·2 | 9·86 | 5·8 | 7·0 | 10·8 | 33·5 |
| C5 | 24·0 | 4·4 | 7·8 | 8·91 | 4·1 | 5·2 | 8·7 | 33·8 |
| C6 | 30·4 | 6·9 | 10·4 | 17·81 | 6·4 | 11·6 | 19·1 | 74·2 |
| C7 | 29·8 | 7·0 | 11·2 | 15·76 | 6·2 | 16·8 | 17·8 | 51·0 |
| C8 | 28·0 | 8·1 | 11·2 | 15·34 | 6·2 | 18·2 | 14·8 | 52·0 |
| C9 | 34·6 | 10·6 | 7·6 | 15·21 | 9·2 | 20·5 | 16·4 | 37·0 |
| C10 | 40·0 | 10·6 | 11·6 | 22·06 | 10·5 | 48·0 | 32·6 | 98·8 |
| C11 | 25·6 | 7·8 | 6·8 | 4·11 | 4·9 | 7·3 | 7·7 | 17·5 |
| C12 | 14·8 | 3·0 | 5·4 | 5·07 | 3·1 | 7·0 | 6·6 | 40·1 |
| C13 | 14·2 | 2·6 | 3·6 | 6·58 | 2·5 | 5·2 | 7·9 | 49·1 |
| C14 | 24·5 | 6·5 | 8·8 | 10·62 | 5·7 | 18·2 | 18·6 | 60·5 |
| C15 | 38·6 | 10·6 | 11·4 | 18·50 | 8·3 | 22·5 | 24·4 | 65·0 |
| C16 | 22·0 | 7·6 | 6·0 | 9·59 | 4·9 | 11·7 | 13·4 | 47·5 |
| C17 | 38·2 | 11·6 | 12·0 | 13·02 | 7·7 | 12·1 | 13·4 | 23·8 |
| C18 | 34·0 | 13·0 | 11·2 | 12·00 | 9·5 | 14·0 | 13·8 | 28·0 |
| C19 | 13·6 | 2·4 | 3·8 | 8·22 | 5·8 | 12·5 | 13·2 | 39·5 |
| C20 | 15·6 | 7·9 | 6·2 | 18·50 | 7·6 | 13·2 | 11·8 | 28·0 |
| C21 | 13·0 | 4·8 | 5·0 | 8·49 | 5·0 | 10·5 | 9·6 | 29·3 |
| C22 | 16·0 | 5·0 | 6·0 | 8·22 | 5·4 | 9·5 | 13·4 | 50·8 |
| C23 | 25·0 | 6·3 | 5·4 | 16·58 | 8·0 | 8·9 | 15·3 | 37·3 |
| C24 | 15·0 | 2·6 | 3·4 | 7·54 | 3·9 | 9·1 | 13·1 | 55·0 |
| C25 | 22·0 | 7·6 | 6·0 | 9·59 | 4·9 | 11·7 | 13·4 | 47·5 |
| C26 | 20·0 | 5·9 | 8·0 | 9·32 | 4·9 | 9·2 | 11·6 | 43·3 |
| C27 | 39·6 | 13·8 | 14·4 | 11·23 | 9·3 | 10·3 | 11·0 | 11·3 |
| C28 | 32·0 | 11·0 | 10·2 | 5·89 | 6·5 | 7·2 | 7·7 | 12·0 |
| C29 | 32·9 | 7·8 | 14·2 | 16·23 | 7·4 | 19·4 | 21·7 | 72·0 |

APPENDIX 2B. Results for 8 characterizing analyses of the 101 soils described in Table 3. All values are means of duplicates, expressed as ppm except Org.-C (percent) and pH.

| Soil | Oxalate-Fe | Oxalate-Al | Oxalate-Mn | Org.-C | Ex.-Ca | Ex.-Mg | Ex.-K | pH |
|---|---|---|---|---|---|---|---|---|
| B1 | 8333 | 2136 | 833 | 5·82 | 3240 | 452 | 305 | 5·7 |
| B2 | 5834 | 2200 | 4192 | 5·09 | 4000 | 365 | 434 | 6·0 |
| B3 | 4667 | 2153 | 468 | 5·29 | 3720 | 445 | 283 | 5·8 |
| B4 | 4500 | 2756 | 2677 | 9·2 | 5760 | 405 | 525 | 6·2 |
| B5 | 5417 | 2633 | 7170 | 5·54 | 2780 | 378 | 387 | 5·8 |
| B6 | 2567 | 4323 | 3292 | 6·09 | 6580 | 280 | 670 | 5·7 |
| B7 | 6000 | 2673 | 7117 | 5·21 | 2600 | 423 | 228 | 5·6 |
| B8 | 4250 | 1433 | 1020 | 3·88 | 2630 | 138 | 135 | 5·6 |
| B9 | 5100 | 1107 | 717 | 5·67 | 2290 | 381 | 335 | 5·5 |
| B10 | 3067 | 2353 | 1174 | 5·80 | 5380 | 292 | 693 | 6·7 |
| B11 | 4300 | 3266 | 1577 | 5·55 | 5080 | 287 | 395 | 5·8 |
| B12 | 6133 | 1410 | 490 | 4·50 | 2500 | 126 | 190 | 5·5 |
| B13 | 6250 | 3201 | 894 | 7·40 | 7080 | 380 | 420 | 6·3 |
| B14 | 3435 | 3213 | 2067 | 6·10 | 6400 | 295 | 243 | 6·3 |
| B15 | 4034 | 2215 | 694 | 7·00 | 5760 | 282 | 570 | 6·4 |
| B16 | 5800 | 1600 | 395 | 8·49 | 5220 | 394 | 487 | 6·5 |
| B17 | 2000 | 1656 | 574 | 9·80 | 6180 | 324 | 1075 | 6·9 |
| B18 | 5067 | 1800 | 514 | 6·48 | 4430 | 255 | 815 | 5·9 |
| B19 | 2650 | 1904 | 657 | 9·12 | 7160 | 300 | 970 | 6·9 |
| B20 | 6000 | 1993 | 1000 | 5·98 | 4570 | 254 | 578 | 6·1 |
| C1 | 1240 | 1700 | 437 | 1·20 | 7280 | 840 | 499 | 8·3 |
| C2 | 594 | 620 | 147 | 1·01 | 965 | 177 | 568 | 5·6 |
| C3 | 870 | 757 | 510 | 1·13 | 1180 | 313 | 768 | 5·9 |

APPENDIX 2B. (ctd)

| Soil | Oxalate-Fe | Oxalate-Al | Oxalate-Mn | Org.-C | Ex.-Ca | Ex.-Mg | Ex.-K | pH |
|---|---|---|---|---|---|---|---|---|
| C4 | 940 | 1334 | 484 | 1·53 | 2500 | 403 | 901 | 7·0 |
| C5 | 794 | 700 | 500 | 1·26 | 1380 | 203 | 562 | 6·3 |
| C6 | 1034 | 857 | 169 | 1·31 | 945 | 212 | 540 | 5·5 |
| C7 | 940 | 723 | 507 | 1·07 | 820 | 238 | 442 | 5·8 |
| C8 | 637 | 667 | 400 | 1·38 | 903 | 106 | 328 | 5·4 |
| C9 | 600 | 294 | 433 | 1·16 | 432 | 33 | 242 | 5·6 |
| C10 | 2557 | 527 | 883 | 1·90 | 658 | 92 | 366 | 4·8 |
| C11 | 1400 | 834 | 800 | 1·47 | 2545 | 775 | 644 | 6·8 |
| C12 | 1034 | 465 | 500 | 0·60 | 1050 | 134 | 291 | 6·3 |
| C13 | 784 | 457 | 163 | 0·63 | 750 | 116 | 285 | 5·8 |
| C14 | 904 | 672 | 684 | 1·36 | 810 | 138 | 360 | 5·2 |
| C15 | 1667 | 844 | 317 | 1·55 | 830 | 233 | 255 | 5·3 |
| C16 | 1784 | 802 | 334 | 1·61 | 905 | 266 | 519 | 5·5 |
| C17 | 1400 | 977 | 1034 | 1·46 | 3330 | 935 | 956 | 7·5 |
| C18 | 1614 | 967 | 1200 | 1·28 | 2575 | 883 | 826 | 6·8 |
| C19 | 1917 | 459 | 490 | 1·63 | 268 | 57 | 245 | 4·8 |
| C20 | 614 | 223 | 557 | 1·10 | 323 | 34 | 263 | 5·3 |
| C21 | 1164 | 275 | 93 | 1·17 | 395 | 70 | 167 | 5·8 |
| C22 | 1117 | 667 | 1210 | 1·31 | 624 | 107 | 321 | 5·4 |
| C23 | 1277 | 400 | 1 | 1·21 | 275 | 60 | 79 | 5·3 |
| C24 | 1360 | 760 | 1274 | 1·39 | 538 | 89 | 336 | 5·0 |
| C25 | 1403 | 670 | 430 | 1·44 | 1055 | 308 | 402 | 5·5 |
| C26 | 984 | 572 | 300 | 1·35 | 935 | 256 | 373 | 5·8 |
| C27 | 1114 | 1407 | 550 | 0·88 | 4745 | 906 | 649 | 7·8 |
| C28 | 1260 | 1190 | 517 | 1·03 | 4263 | 924 | 544 | 7·6 |
| C29 | 2093 | 964 | 177 | 1·57 | 700 | 162 | 453 | 5·3 |

APPENDIX 2B. (ctd)

| Soil | Oxalate-Fe | Oxalate-Al | Oxalate-Mn | Org.-C | Ex.-Ca | Ex.-Mg | Ex.-K | pH |
|---|---|---|---|---|---|---|---|---|
| C30 | 1850 | 1060 | 277 | 1·49 | 760 | 150 | 503 | 5·6 |
| C31 | 1000 | 780 | 184 | 1·05 | 720 | 158 | 473 | 6·1 |
| C32 | 1597 | 730 | 454 | 1·52 | 860 | 157 | 448 | 5·6 |
| C33 | 1850 | 1620 | 440 | 0·71 | 3910 | 820 | 568 | 7·5 |
| C35 | 997 | 913 | 430 | 1·05 | 1160 | 275 | 680 | 6·0 |
| C36 | 1217 | 1044 | 560 | 1·22 | 1200 | 370 | 632 | 5·9 |
| C37 | 987 | 1020 | 567 | 0·66 | 1320 | 210 | 409 | 6·2 |
| C38 | 600 | 747 | 94 | 0·72 | 1160 | 160 | 341 | 6·5 |
| C39 | 1064 | 1044 | 533 | 1·69 | 3340 | 557 | 744 | 7·3 |
| C40 | 867 | 1024 | 762 | 1·20 | 3900 | 560 | 705 | 7·6 |
| C41 | 1120 | 807 | 750 | 1·25 | 940 | 105 | 440 | 5·6 |
| C42 | 990 | 1097 | 424 | 1·37 | 920 | 105 | 558 | 5·1 |
| C43 | 997 | 587 | 847 | 1·07 | 300 | 10 | 240 | 5·2 |
| C44 | 1834 | 633 | 525 | 1·41 | 230 | 10 | 103 | 4·8 |
| C46 | 1384 | 733 | 953 | 1·19 | 415 | 34 | 372 | 5·1 |
| C47 | 1333 | 1203 | 927 | 1·86 | 1200 | 125 | 656 | 5·8 |
| C48 | 1750 | 1180 | 1167 | 2·29 | 1200 | 160 | 348 | 5·2 |
| C49 | 1394 | 753 | 217 | 1·32 | 880 | 223 | 388 | 5·8 |
| C50 | 1417 | 710 | 190 | 1·38 | 920 | 260 | 385 | 5·4 |
| C51 | 2650 | 1037 | 1208 | 1·13 | 1840 | 700 | 470 | 6·6 |
| C52 | 3334 | 960 | 1320 | 1·25 | 1530 | 760 | 554 | 5·8 |
| C53 | 1710 | 567 | 592 | 1·64 | 480 | 94 | 255 | 5·3 |
| C54 | 1154 | 543 | 394 | 1·52 | 435 | 91 | 100 | 5·5 |
| C55 | 1540 | 497 | 182 | 2·53 | 1070 | 145 | 200 | 5·9 |
| C56 | 834 | 564 | 294 | 2·70 | 830 | 122 | 565 | 5·7 |
| C57 | 1817 | 547 | 710 | 1·96 | 480 | 50 | 270 | 5·2 |

APPENDIX 2B. (ctd)

| Soil | Oxalate-Fe | Oxalate-Al | Oxalate-Mn | Org.-C | Ex.-Ca | Ex.-Mg | Ex.-K | pH |
|---|---|---|---|---|---|---|---|---|
| C58 | 1597 | 527 | 617 | 1·66 | 380 | 24 | 195 | 4·9 |
| N1 | 14883 | 2364 | 1477 | 5·75 | 4360 | 1595 | 285 | 6·4 |
| N2 | 6750 | 2884 | 1590 | 3·00 | 4150 | 1750 | 489 | 6·0 |
| N3 | 4917 | 3250 | 1214 | 2·20 | 5120 | 2890 | 670 | 6·4 |
| N4 | 4000 | 2134 | 1247 | 4·07 | 5320 | 1350 | 1150 | 7·1 |
| N5 | 1917 | 1926 | 707 | 3·07 | 7820 | 1750 | 729 | 8·0 |
| N6 | 4507 | 2506 | 1127 | 2·98 | 5040 | 2160 | 725 | 6·7 |
| N7 | 3934 | 2934 | 1047 | 3·93 | 6000 | 2680 | 735 | 6·7 |
| N8 | 5317 | 2630 | 1164 | 3·42 | 4780 | 2070 | 790 | 6·5 |
| N9 | 9167 | 2567 | 1630 | 4·70 | 4000 | 2050 | 470 | 6·2 |
| N10 | 8584 | 2900 | 1830 | 4·71 | 5380 | 1840 | 553 | 6·2 |
| N11 | 9017 | 2600 | 1593 | 4·74 | 4760 | 1430 | 846 | 6·0 |
| N12 | 7250 | 3006 | 1440 | 3·47 | 4080 | 3550 | 460 | 6·3 |
| N13 | 9067 | 2887 | 2237 | 3·89 | 4160 | 2100 | 605 | 5·8 |
| R1 | 21066 | 19125 | 1477 | 10·07 | 1280 | 262 | 448 | 4·9 |
| R2 | 23334 | 19750 | 1477 | 7·78 | 435 | 85 | 218 | 4·5 |
| R3 | 20000 | 16734 | 2125 | 6·48 | 800 | 214 | 276 | 5·3 |
| R4 | 19000 | 18084 | 2167 | 8·63 | 1790 | 312 | 500 | 5·3 |
| R5 | 16400 | 20771 | 1855 | 7·73 | 2300 | 425 | 610 | 5·6 |
| R6 | 24167 | 14750 | 1230 | 6·05 | 425 | 99 | 182 | 5·1 |
| R7 | 23334 | 17042 | 1537 | 6·30 | 580 | 82 | 265 | 5·1 |
| R8 | 23767 | 14108 | 1860 | 6·35 | 630 | 98 | 250 | 5·0 |
| R9 | 25234 | 20175 | 1667 | 5·25 | 360 | 48 | 160 | 4·7 |
| R10 | 36000 | 26367 | 2363 | 10·00 | 805 | 175 | 373 | 4·9 |
| R11 | 17000 | 10583 | 1107 | 6·77 | 1360 | 332 | 418 | 5·2 |
| R12 | 15834 | 13200 | 1470 | 5·63 | 1390 | 250 | 468 | 5·5 |

APPENDIX 3. An example of the calculation of the sign, positive or negative, for the general trend with respect to X ($\partial P_1/\partial X$) in regression (4).

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Consider $P_1 = H_2SO_4$, $P_2$ = Bray-P and X = Ex.-Mg for this example.

Differentiate equation (4) with respect to X:

$$P_1 = a_o + a_1 P_2 + a_2 P_2^2 + a_3 X + a_4 X^2 + a_5 P_2 X \quad \ldots\ldots(4)$$

$$\partial P_1/\partial X = a_3 + 2 a_4 X + a_5 P_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)'.$$

From the regression equation:

$$a_3 = -2{\cdot}65657 \times 10^{-2}$$

$$a_4 = 1{\cdot}11805 \times 10^{-5}$$

$$a_5 = 2{\cdot}77653 \times 10^{-3}$$

Also, mean of Ex.-Mg = 503 ppm, and

mean of Bray-P = 18·2 ppm.

Substituting these values in (4)',

$$\partial P_1/\partial X = -2{\cdot}657\times10^{-2}+(2)(1{\cdot}118\times10^{-5})(503)+(2{\cdot}777\times10^{-3})(18{\cdot}2)$$

$$= (6{\cdot}18\times10^{-2})-(2{\cdot}66\times10^{-2}),$$

which is clearly positive.

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