Chapter 6

Soil testing for phosphate rock application

Soil testing for phosphorus (P) has been a subject for extensive research. Numerous extractants ranging from strong acids to alkalis and various organic and inorganic complexing agents have been developed to evaluate P bioavailability with certain crops and soils. The most widely used soil P tests are Bray I (Bray and Kurtz, 1945), Mehlich I (Nelson *et al.*, 1953), and Olsen (Olsen *et al.*, 1954). Other common tests include Bray II, Mehlich II and III, and resin (Fixen and Grove, 1990). However, all these soil tests are mainly for recommendations with water-soluble P fertilizers such as di-ammonium phosphate (DAP), single superphosphate (SSP) and triple superphosphate (TSP). Reports have shown that these conventional acid or alkaline soil tests do not work well in soils fertilized with phosphate rock (PR) (Perrott *et al.*, 1993; Menon and Chien, 1995; Rajan *et al.*, 1996). Thus, there is a need to develop appropriate soil tests that reflect closely P uptake from PR over a wide range of PR sources, soil properties, and crop varieties. Furthermore, the soil tests should be suitable for PR and for water-soluble P fertilizers. This issue has become more important because of the increasing interest in the use of PR for direct application in developed and developing countries, e.g. Australia, New Zealand, Brazil, Indonesia, Malaysia and countries in sub-Saharan Africa.

This chapter provides an overview of the soil tests that have been used to measure available P from soils treated with PR and water-soluble P fertilizer. It provides an introduction to the nature of the reactions of PR and water-soluble P fertilizer in soils. It then discusses the use of the ^{32}P isotopic exchange kinetic method in relation to soil-available P measurement.

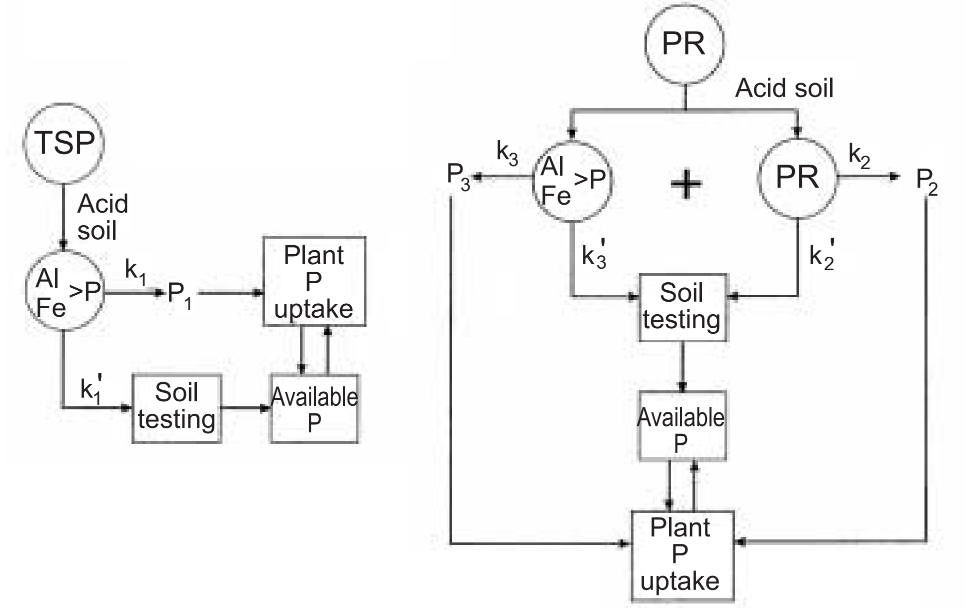
SOIL PHOSPHORUS REACTION AND SOIL TESTING

When a water-soluble P fertilizer, e.g. TSP, is applied to acid soil containing oxides of iron (Fe) and aluminium (Al), reaction products in the form of Fe-Al-P are the sources of available P through desorption/dissolution processes for uptake by the plant (Figure 14). If the amount of available P extracted by a soil test (k_1') is proportional (i.e. good correlation) to the amount of P absorbed by the plant (k_1) or the crop yield, then this soil test is suitable for calibration for fertilizer-rate recommendations of water-soluble P.

When a PR is applied to an acid soil (Figure 14), dissolution of the PR releases P to the soil solution. The plant roots can absorb directly part of the released P, and part of the released P forms reaction products (above). These can also provide available P later through the desorption process (unlike water-soluble P, soil solution P concentration from PR dissolution is too low to precipitate Fe-Al-P compounds). Thus, both the reaction products and undissolved PR can provide available P to the plant (Chien, 1978). The degree of relative P availability from undissolved PR versus Fe-Al-P depends on: PR reactivity, soil P-fixing capacity, and the duration of the PR reaction with soil. Although the reaction products of PR dissolution may be assumed to be the same as that of TSP dissolution, i.e. $k_3/k_3' = k_1/k_1'$, the P mineral in PR is calcium (Ca) P.

FIGURE 14

Relationship between plant P uptake and soil available P from TSP and PR applied to acid soil



This differs from the reaction products of TSP in the form of Fe-Al-P. Thus, the proportionality of k_1/k_1' for TSP may or may not be the same as that of k_2/k_2' for PR with a given soil test. If $k_2/k_2' > k_1/k_1'$, the soil test will underestimate the available P from PR with respect to TSP. If $k_2/k_2' < k_1/k_1'$, the soil test will overestimate the available P from PR with respect to TSP. If $k_2/k_2' = k_1/k_1'$, then the soil test will be applicable to both PR and TSP.

As Figure 14 shows, as long as the undissolved PR is the primary source for providing available P to the plant, there will be two separate calibration curves with a given soil test (one for PR and one for TSP) if k_2/k_2' ^{1} k_1/k_1'. When most of the PR is dissolved and the reaction products of PR are the main sources of available P to the plant, both TSP and PR will follow the same calibration curve if $k_3/k_3' = k_1/k_1'$ within a given soil test. However, there is some evidence to suggest that the reaction products of PR with soil and their availability to plants may differ from those obtained with soluble P fertilizers, i.e. $k_3/k_3' \neq k_1/k_1'$, owing to the slow-release nature of PR dissolution (Chien *et al.*, 1987a). Therefore, whether a soil test is applicable to both TSP and PR depends on: the chemical nature of the test (acidic, alkaline, etc.); the amount of undissolved PR; and the amount and nature of the reaction products formed from PR dissolution.

CONVENTIONAL SOIL TESTS

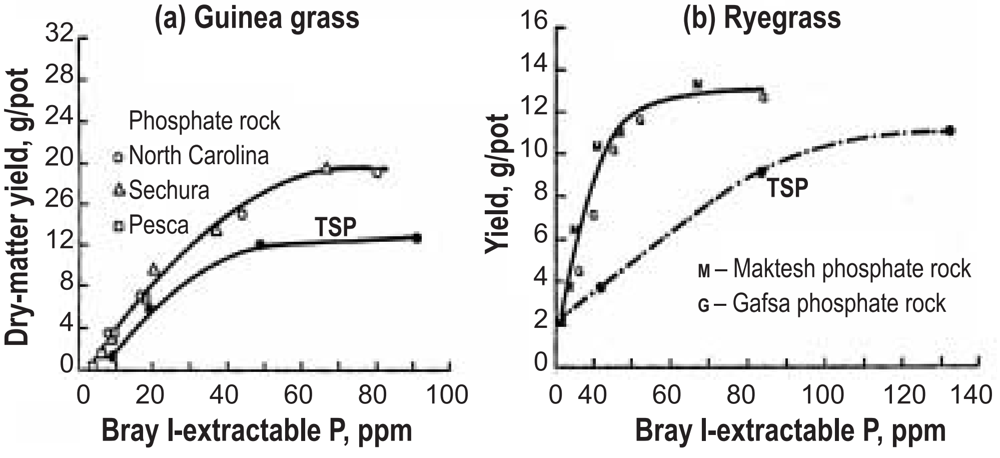
Bray I test

The Bray I solution (0.03 M NH_4F + 0.025 M HCl) developed by Bray and Kurtz (1945) has been employed widely to determine the available P in soils. It has given results that are highly correlated with crop response to P fertilization. The combination of weak HCl and NH_4F is designed to remove soluble forms of P by the acid and precipitation of CaF_2, largely Ca-P other than apatite, and a portion of Fe-Al-P by complexing cations with fluorine (F) ions. Therefore, many researchers have assumed that the P extracted by Bray I from soils treated with PRs is the available P derived from the reaction products of PRs rather than from the undissolved PRs in the soils. However, Chien (1978) found that Bray I was able to dissolve PRs in an acid soil at time zero, i.e. before the soil reacted with PRs. The amounts of Bray I-P extracted from the soil treated with PRs before and after incubation (three weeks) correlated well with PR solubility and P rate. Thus, Bray I can help predict crop response to various sources of PR applied at different P rates without comparing with water-soluble P fertilizers. Numerous reports support this statement (Barnes and Kamprath, 1975; Smith *et al.*, 1957; Smith and Grava, 1958; Howeler and Woodruff, 1968; Hammond, 1977; Mostara and Datta, 1971). However, the question arises as to whether Bray I can be used to compare available P in soil treated with PR to that with water-soluble P fertilizers in terms of crop response to P.

Barnes and Kamprath (1975) reported that two distinct curves were obtained with a Bray I-P level from two PRs and TSP plotted against the dry-matter yield of maize. These curves indicated that the dry-matter yield of maize with a given Bray I-P level in a PR-treated soil was higher than the yield from the same Bray I-P level in the TSP-treated soil. Furthermore, Bray I-P extracted from the soils treated with PRs (Florida and North Carolina, the United States of America) correlated closely with plant yield and P uptake regardless of the changes in soil types, soil pH and source of PR. However, Barnes and Kamprath attempted to explain why two distinct curves were obtained when they plotted dry-matter yield of maize versus Bray I-P obtained with PRs and TSP. One explanation was that there are some ‘acidulation products’ from PR that the plant can utilize but the extractant cannot dissolve.

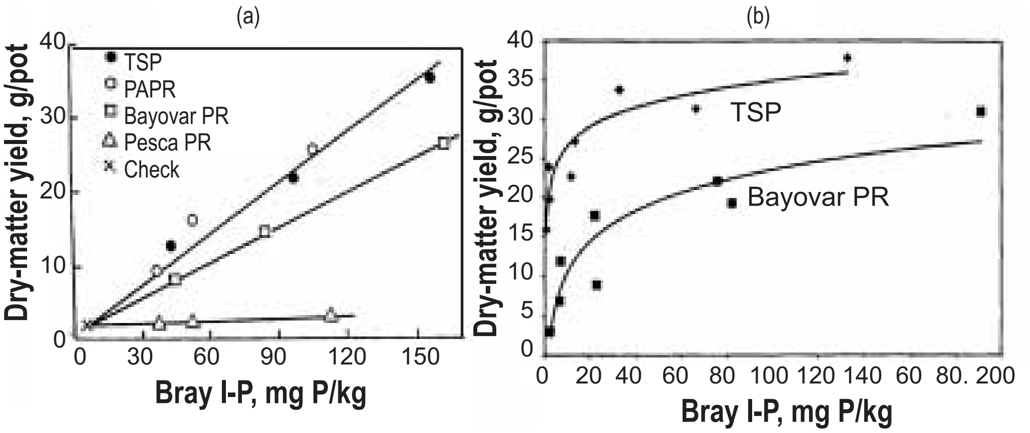
Figure 15 shows two more examples of the use of Bray I to evaluate available P of PRs as compared with TSP. These results show that the relationship between dry-matter yield and Bray I-P for various PR sources was the same, i.e. a single curve fitted all PR sources. Furthermore, the results show that the Bray I-PR curve was above the TSP curve. This suggests that Bray I underestimated available P from PRs with respect to TSP because a higher dry-matter yield was obtained with PRs than TSP at the same level of extractable Bray I. Apparently, the weak acidic Bray-I solutions extracted less P from apatite in the undissolved PR than the reactive

Figure 15
Relationship between dry-matter yield and Bray I-extractable P in soils treated with PRs and TSP



Sources: Data for (a) from Hammond (1977) and (b) from Reinhorn and Hagin (1978, unpublished data).

Figure 16
Relationship between dry-matter yield of maize with different P sources and Bray-I-P extracted from (a) acid sandy soil (pH 4.8) with low pH buffering capacity and (b) acid soil (pH 5.2) with high P-fixing capacity



Sources: Data for (a) from Chien *et al.* (1987b) and (b) from Hammond *et al.* (1986a).

products of TSP with respect to the relative P uptake by plants from PR versus TSP, i.e. $k_2/k_2' > k_1/k_1'$ (Figure 14).

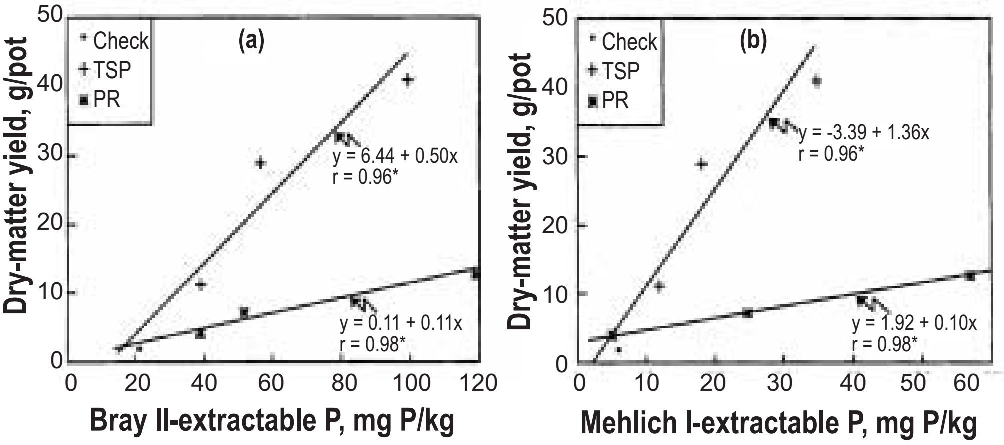
As Figure 16 shows, Bray I can also overestimate available P from PR with respect to TSP in acid sandy soil or high P-fixing soil. In sandy soils with relatively low pH buffering capacity, the pH of soil suspension can still be acidic during soil extraction. For example, the pH of Bray-I extract from the acid sandy soil (pH 4.8) shown in Figure 16(a) was 3.1, little changed from the pH of the Bray I solution (pH 3.0). Thus, the Bray-I solution can dissolve proportionally more P from PR than the reactive products of TSP with respect to P uptake from the two sources, i.e. $k_2/k_2' < k_1/k_1'$, as shown in Figure 14. In soils with relatively high pH buffering capacity, the acidity of the Bray-I solution can be neutralized partially by soil so that it is not strong enough to extract P from PR excessively. For example, the pH of Bray-I extract from an acid soil (pH 5.2) containing 34 percent clay was 4.6, higher than the pH of the Bray-I solution (pH 3.0). For these types of soil, Bray I frequently underestimates available P from PR with respect to TSP as shown in Figure 15.

In soils with relatively high P-fixing capacity, the plant-available P from PR dissolution in soil solution (i.e. k_2 in Figure 14) can be relatively low because P released from PR is fixed by the soil. However, the Bray-I solution can still extract P from PR during soil extraction (i.e. k_2' in Figure 14). Therefore, Bray I can overestimate available P from PR with respect to TSP in the soils with a high P-fixing capacity shown in Figure 16(b), i.e. $k_2/k_2' < k_1/k_1'$ in Figure 14.

Bray II and Mehlich I tests

Bray II (0.03 M NH_4F + 0.1 M HCl) and Mehlich I (0.05 M HCl + 0.0125 M H_2SO_4) are more acidic than Bray I because of relatively higher concentrations of HCl. These two soil tests are commonly used in tropical acid soils, e.g. Bray II in Malaysia and Colombia, and Mehlich I in Brazil. Because of the relatively strong acidic reagents of these two tests, they can dissolve a substantial amount of undissolved PR during soil extraction. Hence, they can overestimate

FIGURE 17
Relationship between dry-matter yield of maize and (a) Bray-II-extractable P, and (b) Mehlich-I-extractable P in soil treated with central Florida PR and TSP



Source: Data from Menon *et al.* (1989b).

PR availability with respect to water-soluble P (Barnes and Kamprath, 1975; Yost *et al.*, 1982; Bationo *et al.*, 1991). Figure 17 shows that both Bray II and Mehlich I extracted proportionately more P from PR than the reaction products of TSP with respect to P availability, i.e. $k_2/k_2' < k_1/k_1'$, as shown in Figure 14. Therefore, the Bray II and Mehlich I methods are not recommended for PR and water-soluble P as they can overestimate available P from PR as compared with water-soluble P.

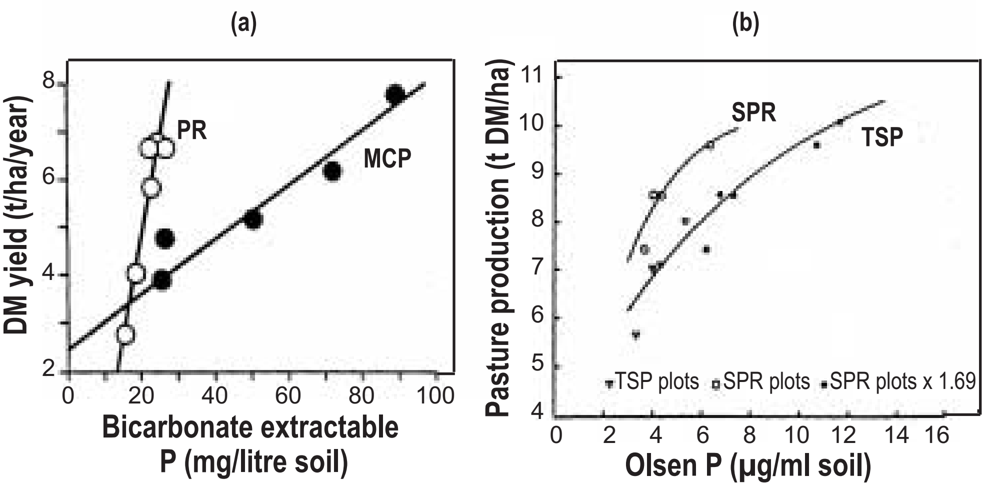
Olsen test

Olsen (0.5 M $NaHCO_3$, pH 8.5) is an alkaline reagent that extracts P from the reaction products of PR (i.e. k_3') in soil treated with PR similar to the reaction products of TSP (i.e. k_1') (Figure 14).

Although k_3/k_3' of PR may be similar to k_1/k_1' of TSP, the Olsen reagent does not extract P from undissolved PR (i.e. $k_2' = 0$). However, undissolved PR can be a more important P source than its reaction products for providing available P to the plant, especially the initial P effect. In this case, the Olsen test usually underestimates available P from PR as compared with that from TSP with respect to P uptake by the plant, i.e. $k_2/k_2' > k_1/k_1'$ (Figure 14). Therefore, the Olsen test frequently results in two curves with the PR curve above the curve of water-soluble P when crop yield or P uptake is plotted against Olsen-P (Figure 18).

In the study by Rajan *et al.* (1991b), the slope of the calibration curve for PR was very steep due to a narrow range of Olsen P (Figure 18(a)) that represented only the available P from the reaction products of PR but not from the undissolved PR. To have the same calibration curve for both PR and TSP, Perrott *et al.* (1993) used a correction factor (1.69) to multiply the Olsen P values of PR and moved the PR curve to the TSP curve (Figure 18(b)). However, this modification is an empirical approach and depends on several factors, e.g. time of PR dissolution, reactivity of PR source, soil properties, and crop species.

Figure 18
Relationship between pasture yield and Olsen P values in soils treated with Sechura PR and: (a) monocalcium phosphate, and (b) TSP



Sources: Rajan *et al.*, 1991b; Perrott *et al.*, 1993.

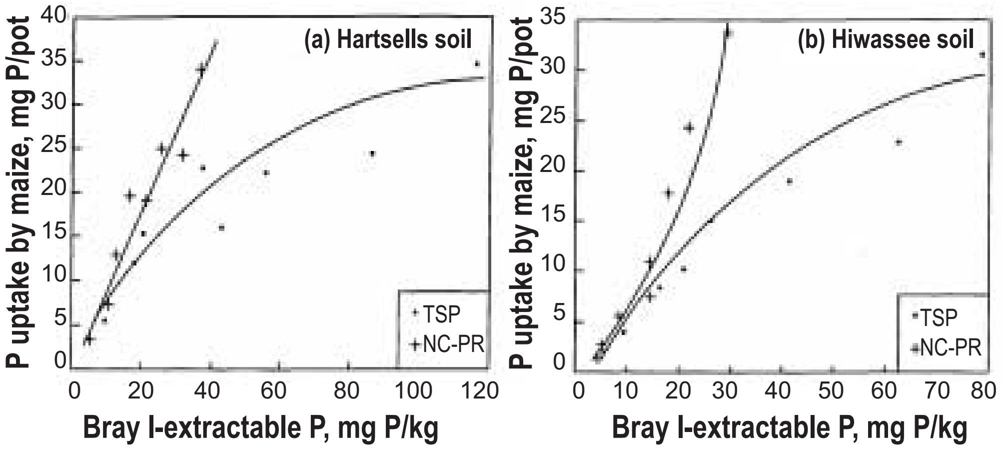
RECENTLY DEVELOPED SOIL TESTS

Iron-oxide-impregnated paper test

The iron-oxide-impregnated paper (P_i) strips test is a new approach for evaluating available P in soils (Menon *et al.*, 1989b; Menon *et al.*, 1990; Chardon *et al.*, 1996; Menon *et al.*, 1997). Instead of extracting solutions, the method uses P_i strips as a sink to sorb and retain P mobilized in a soil suspension, similar to anion exchange resin. However, unlike the anion exchange resin, the P_i strips show a preference for phosphate over other anions that are common in the soil (Van der Zee *et al.*, 1987). Moreover, the phosphate ions can be retrieved easily from the soil suspension. Furthermore, preparation of P_i strips is sufficiently simple and inexpensive as to enable almost all laboratories to produce them as opposed to purchasing expensive anion exchange resin from chemical companies (Menon *et al.*, 1989a). Unlike the reagents used in conventional soil tests, the P_i strips do not react with the soil but only sorb the P entering the soil solution. Thus, the method has potential for use in soils fertilized with water-soluble P and PR fertilizers.

Menon *et al.* (1989b) reported on the use of P_i strips for available P in soils treated with a medium-reactive Florida PR or TSP before cropping with maize. Compared with other conventional soil tests, the P_i test had the highest correlation between dry-matter yield or P uptake and soil-available P when all the soils, P sources, and P rates were pooled. However, in the study, the ranges in plant yield or P uptake and P_i-P obtained with TSP were much wider than those obtained with Florida PR. Thus, statistically, it was not appropriate to run the same regression line between crop response (plant yield or P uptake) and P_i-P for both PR and TSP as the regression was dominated by TSP (although the correlation coefficient was highly significant). In order to evaluate critically whether PR and TSP follow the same relationship when crop response is plotted against P_i-P in soil, the ranges in crop response and P_i-P with PR and TSP should be approximately the same. Furthermore, the initially developed P_i test with 0.01 M $CaCl_2$ in soil extraction could have underestimated available P from PR with respect to TSP in the study by Menon *et al.* (1989b) because of Ca common-ion effect on PR dissolution, i.e. $k_2/k_2' > k_1/k_1'$ (Figure 14).

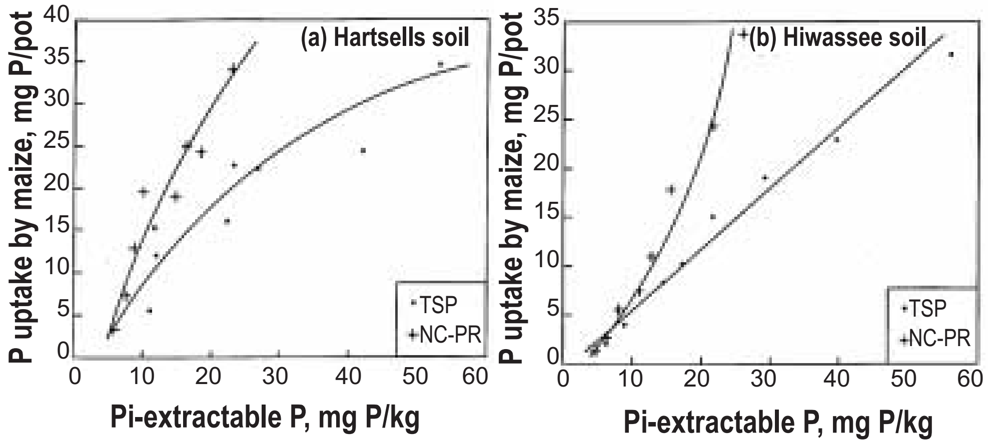
FIGURE 19
Relationship between P uptake by maize and Bray I-extractable P in soils treated with TSP and North Carolina PR



Source: Habib *et al.*, 1998.

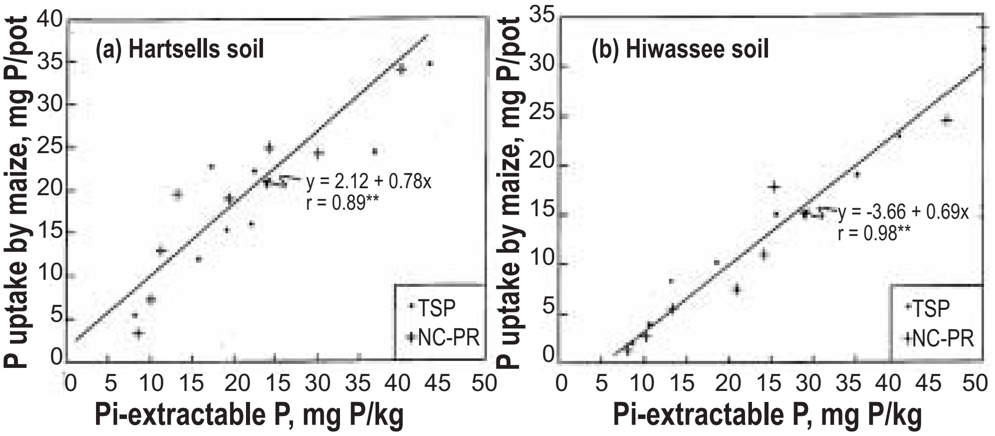
Habib *et al.* (1998) pre-incubated two acid soils with a highly reactive North Carolina PR and TSP followed by soil extractions for available P before cropping with maize. The ranges of crop response (dry-matter yield or P uptake) obtained with North Carolina PR were within 83–91 percent of TSP. The soil tests used were P_i strips with 0.01 M $CaCl_2$, P_i strips with 0.02 M KCl, and Bray I. The results showed that both Bray I and P_i strips with 0.01 M $CaCl_2$ underestimated available P from North Carolina PR (Figures 19 and 20), confirming $k_2/k_2' > k_1/k_1'$ (Figure 14). Available P estimated by P_i strips with 0.02 M KCl instead of 0.01 M $CaCl_2$ was related more closely to crop response for soils treated with North Carolina PR and TSP (Figure 21), i.e. $k_2/k_2' = k_1/k_1'$ (Figure 14). Less P was extracted from North Carolina PR by the P_i strips with 0.01 M $CaCl_2$ than with 0.02 M KCl (Figure 22) because $CaCl_2$ depressed

FIGURE 20
Relationship between P uptake by maize and P_i-P (0.01 M $CaCl_2$) in soils treated with TSP and North Carolina PR



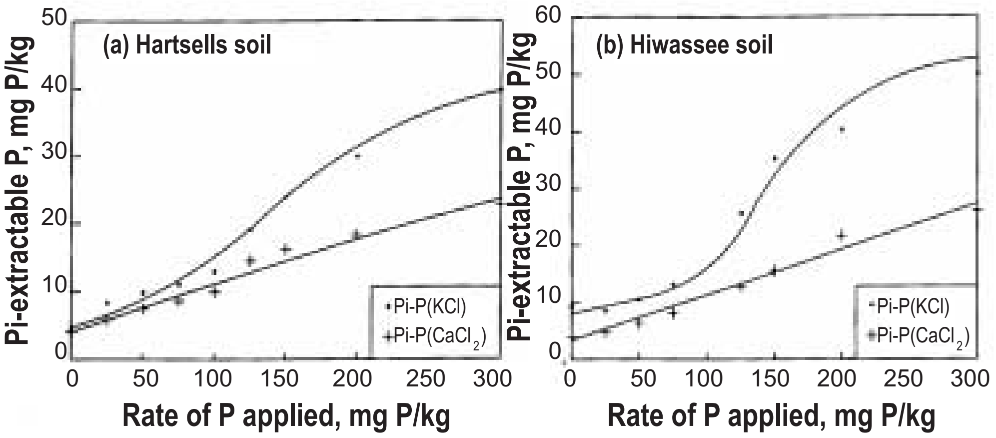
Source: Habib *et al.*, 1998.

Figure 21
Relationship between P uptake by maize and P_i-P (0.02 M KCl) in soils treated with TSP and North Carolina PR



Source: Habib *et al.*, 1998.

Figure 22
P_i-P with 0.01 M $CaCl_2$ or 0.02 M KCl in soils treated with North Carolina PR



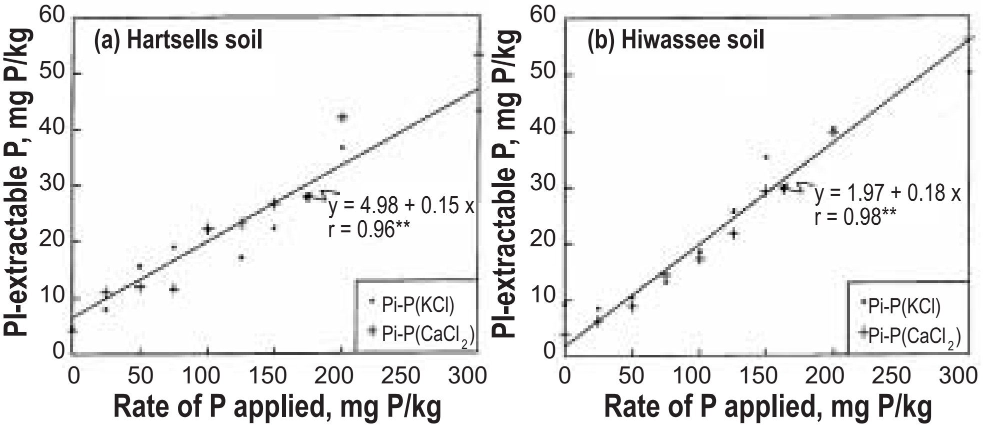
Source: Habib *et al.*, 1998.

PR dissolution, whereas no effect was observed with TSP (Figure 23) owing to the lack of a Ca common-ion effect on P extraction from its reaction products (Fe-Al-P). Therefore, it is recommended that the P_i test with 0.02 M KCl be used to estimate available P in soils treated with both PR and water-soluble P fertilizers. However, more research is needed, especially agronomic trials under field conditions, to test this modified P_i test.

Mixed anion and cation exchange resins

Since its introduction by Amer *et al.* (1955), anion exchange resin has been used widely in research work to evaluate soil-available P. Like the P_i test, anion resin is a non-destructive method that simulates the activity of plant roots. However, it is a time-consuming procedure involving

FIGURE 23
P_i-P with 0.01 M $CaCl_2$ or 0.02 M KCl in soils treated with TSP



Source: Habib *et al.*, 1998.

a two-step anion-exchange process (resin anion exchange with soil P, followed by exchange of resin P with anion). Moreover, the difficulty of separating the small resin beads from the soil and its cost have limited the use of this method to some countries, e.g. Brazil and Denmark.

Saggar *et al.* (1990) introduced a simplified resin membrane strip containing a mixture of cation (Na^+) and anion (HCO_3^-) to evaluate available P in the soils treated with PR and water-soluble P. The inclusion of Na^+-saturated resin will enhance P release from PR by removing Ca^{+2} associated with PR so that it does not underestimate PR availability but will not excessively dissolve PR to overestimate PR availability, i.e. $k_2/k_2' = k_1/k_1'$ (Figure 14). Saggar *et al.* (1990) simplified the procedure by shaking the P-retained strip directly with the colour-developed reagent for P and, thus, they omitted an elution step (traditional exchange of P-retained by resin with NaCl solution). The amounts of P extracted by the mixed resin procedure were in proportion to the amount and solubility of the P source applied to the soils. Subsequently, Saggar *et al.* (1992a, 1992b) compared the mixed cation-anion resin method with seven other soil tests and found the mixed method was best for assessing the available P status of soils treated with two PRs varying in reactivity. The method was also able to describe the relationship between crop yield and available P for both PR and TSP, whereas the Olsen test failed. However, more work is needed to evaluate the mixed resin membrane test for various crops grown on different soils treated with PR and water-soluble P fertilizers, especially under field conditions.

Compared with the P_i strip test, the mixed cation-anion resin membrane strip has the advantage that the strip can be regenerated for reuse. However, it is only available from commercial chemical companies, and it is probably considerably more expensive than the P_i paper strip, especially for laboratories in developing countries.

Isotopic ^{32}P exchange kinetic method

The isotopic ^{32}P technique provides quantitative data on P behaviour in the soil (Fardeau, 1996) and soil-plant system for evaluating the efficiency of P fertilizers (e.g. PR products) as influenced by management practices (Zapata and Axmann, 1995). The isotopic ^{32}P exchange kinetic method (IEK) provides a full characterization of soil-available P by determining four independent factors in a single experiment. The intensity factor is quantified by the measurement of the chemical potential of P ions in the soil solution (C_p). The quantity factor is estimated by the quantity of P ions being instantaneously isotopically exchangeable at 1 min (E_1). Two capacity factors, one 'immediate' and the other 'delayed', are determined simultaneously. These four characteristics permit the application of a functional and dynamic model for soil-available P (Fardeau, 1996).

Most extraction methods used in soil testing only allow the determination of a quantity factor, whereas water extraction measures only the intensity factor. Although the IEK method allows quantification of intensity, quantity and capacity factors, it cannot be used in routine soil analysis because of the radioactive nature of the ^{32}P isotope. However, the IEK method can be considered as the reference method for assessing the suitability of other soil tests in routine determination of soil-available P. Aigner *et al.* (2002) compared available P measured by the P_i test with the IEK method in soils varying widely in soil properties treated with and without Morocco PR. For soils that did not receive PR, a very high correlation ($R^2 = 0.94$) was found between the P extracted by the P_i test and the E_1 value determined by the IEK method. For soils treated with PR, the correlation was lower ($R^2 = 0.53$). One of the soils with the highest C_p value (from Hungary) showed that the E_1 value decreased from 9.4 mg of P per kilogram without PR to 6.8 mg of P per kilogram with PR addition, whereas P_i-P value increased from 19.3 to 31.1 mg of P per kilogram. No definitive explanation was given for this discrepancy. After excluding the soil from Hungary, the correlation between the P_i test and IEK method was very high ($R^2 = 0.92$). Therefore, it was concluded that the P_i test is a good alternative to the isotopic method in routine analysis, providing better estimates of soil-available P than other extraction methods.