Phosphorus Cycling in Unfertilized and Fertilized Agricultural Soils

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ABSTRACT

Surface soil samples (0–50 mm depth) were taken from several grassed and cropped, unfertilized and P-fertilized soils at monthly intervals for 2 yr, to investigate seasonal variations in amounts and forms of P and relative importance of inorganic and organic P as sources of plant available P. Although no consistent seasonal variation in inorganic P content was observed for the unfertilized soils, amounts increased after fertilizer P addition. Organic P content was higher in the winter (Oct.–Mar.) than spring months (May–June) for both unfertilized and fertilized soils. Consequently, mineralization of organic P during the growing season, which contributed similar amounts of P (20–74 kg P ha⁻¹) as added in fertilizer (13–100 kg P ha⁻¹), was not inhibited by fertilizer P addition. Organic P variation was mainly due to changes in moderately labile organic P, with more labile and resistant pools remaining constant. The most labile organic P pool was maintained at a constant level possibly by mineralization and formation from moderately labile organic P. Little change in P content of unfertilized subsurface soil (50–150 mm) was observed, although inorganic and available P contents increased slightly following fertilizer P application. Available P (Bray–1 P) was closely correlated with organic P in unfertilized soils and with organic P in fertilized soils. Slopes of these relationships were related to phosphatase enzyme activity and P sorption maximum for organic and inorganic P, respectively. The importance of organic P as a source of available P in both unfertilized and fertilized soils was demonstrated. The need to include organic P in soil-P fertility tests, especially with the increasing use of reduced-tillage practices, is emphasized.


Surface soil receives phosphorus (P) annually from plant residues and fertilizer materials. As these inputs and the removal of P by plant uptake vary with crop age and soil temperature and moisture, seasonal variations in the amount and distribution of P in both unfertilized and fertilized soils can occur. There is a lack of agreement, however, on these variations as reported in several studies. While a spring peak in the plant available P (AP) content of a grassed soil was observed by Gupta and Rorison (1975) (0.01 M CaCl₂-P), lower AP contents in the growing season than in fall months were found by Blakemore (1966) (0.01 M CaCl₂-P), Garbouchev (1966) (anion exchange-P), Haines and Cleveland (1981) (Bray–P), and Weaver and Forcella (1979) (Bray–P) for grassed, cropped, and forested soils. Furthermore, no distinct seasonal AP variations have been observed in grassed (Saunders and Metson, 1971) (anion exchange-P), cropped (Jesop et al., 1977) (bicarbonate-P), and forest soils (Peterson and Rolfe, 1982) (Bray-P) in other studies. In contrast, a decrease in organic P (OP) content during spring and early summer and increase in winter was reported by both Dormaar (1972) and Nguyen et al. (1969).

Although the importance of organic matter in the cycling of soil P is recognized (Dalal, 1977; Harrison, 1982; Stewart and McKercher, 1980), little information is available on the importance of OP as a source of AP in grassed or cropped soils under natural field conditions. Several researchers have fractionated soil OP and suggested that labile OP (Halm et al., 1972; Hedley et al., 1982), soluble OP (Dalal, 1979; Sekhon and Black, 1969), and inositol monophosphate (Van Diest and Black, 1959; Wild and Oke, 1966) make significant contributions to plant nutrition. Little information is available, however, on the relative contribution of different OP pools to seasonal OP variations.

Further information on seasonal variations in AP and OP content and on the relative importance of OP as a source of AP in unfertilized and P-fertilized soils is needed to improve the timing and reliability of soil-P fertility tests. This will be of increasing concern in the future, with the more frequent use of reduced-tillage systems resulting in the probable build-up of soil organic matter and OP. It is expected that this build-up will increase the importance of OP in supplying AP and should thus, be considered in soil P fertility tests (Abbot, 1978; Bowman and Cole, 1978a; Daughtrey et al., 1973).

The following study investigates seasonal variations in the amounts and forms of P in several grassed and cropped, unfertilized and P-fertilized soils during a 2-yr period under natural field conditions. The relative importance of organic P (IP) and OP as sources of AP in these soils is evaluated.

MATERIALS AND METHODS

Surface soil samples (0–50-mm depth) were collected from several unfertilized and P-fertilized sites in Oklahoma and Texas (Table 1). Four samples were collected from each site at 30-d (monthly) intervals and composited. The samples were air-dried, sieved (2 mm), and stored at 4°C until chemical analysis. Classification of the major soil type at each site location (Table 1) was: Kirkland silt loam—fine, mixed, thermic Udertic Paleustolls; Houston Black clay—fine, montmorillonitic, thermic, Udic Pellusterts; and Woodward loam—coarse, silty, mixed, thermic, Typic Ustochrepts. The total and inorganic P contents were determined by extraction of ignited and nonignited samples, respectively, with 0.5 M H₂SO₄ (Walker and Adams, 1958). Organic P was calculated as the difference between TP and IP. Plant available P content (subsequently referred to as available P, AP) was determined by the Bray-1 procedure, where 2 g of soil was extracted with 20 mL of 0.03 M NH₄F and 0.025 M HCl for 5 min. Bray and Kurtz, 1945). The extracts were centrifuged (266 km s⁻¹ for 5 min) and filtered (0.45 μm). Soil phosphatase enzyme activity was assayed using p-nitrophenyl phosphate (Tabatabai and Bremner, 1969). The amount of P sorbed after shaking 1-g samples of soil with
25mL of 0.01 M CaCl₂, containing various amounts of P (0–10 mg L⁻¹), added as K₂HPO₄ and two drops of toluene, on an end-over-end shaker at 25°C for 40 h, was determined. The P sorption maximum was subsequently calculated using the Langmuir adsorption equation (Syers et al., 1973).

All analyses were carried out in duplicate. or alkali filtrates were neutralized prior to P determination. Twenty surface soil samples (0-50 mm) were taken from grid in October 1981, air dried and sieved as determined from spacial sampling.

Climate

Mean monthly rainfall and air temperatures at El Reno, Riesel, and Woodward locations are presented.

RESULT AND DISCUSSION

Mean monthly rainfall and air temperatures at El Reno, Riesel, and Woodward locations are presented.
ized soils. No consistent difference in TP, IP, or OP contents was apparent between sites or locations (Table 2).

**Total, Inorganic, and Organic P**

The TP and IP content of surface soil from the unfertilized sites remained fairly constant during the 2-yr sampling period (W1, Fig. 2). The OP content, however, was lower in the summer (June–Sept.) than winter months (Dec.–Mar.). W1 is given as an example, with the other unfertilized sites showing similar trends (data not shown). For the fertilized sites, TP and IP content content increased following the May fertilizer P application (Y, Fig. 2). As for the unfertilized soil, OP contents were greater in the winter than summer months. Similar changes were observed at the other fertilized sites (data not shown). No consistent seasonal variation in IP, OP, or AP content was observed for sub-surface soil samples (50–150 mm) collected from each unfertilized site at El Reno during 1984. A slight increase in IP and AP content of subsurface soil was observed following fertilizer P application. Consequently, only surface soil (0–50 mm) data is presented. The lack of any seasonal variation in P content of subsurface soil may be attributed to smaller fluctuations in soil temperature and moisture and, thus, microbial activity, and the low mobility of P in soil.

Spatial variability of surface soil IP and OP content was less than seasonal variability. For the 20 samples collected from FR-5 in October 1981 mean TP, IP, and OP contents were 376, 134, and 250 mg kg$^{-1}$, respectively, with coefficients of variation of 8, 6, and 10%, respectively. For the 12 samples taken at monthly intervals during 1981, mean TP, IP, and OP contents were 300, 101, and 216 mg kg$^{-1}$, respectively, with coefficients of variation of 17, 9, and 27%, respectively. Consequently, the observed seasonal variability can be accounted for by P cycling as well as spatial variability.

In both unfertilized and fertilized soils, OP changes cannot be accounted for solely by opposing changes in IP content. Consequently, the increase in OP content during the fall and winter months (Oct.–Feb.) results, in part, from an addition of fresh organic residues. In the warm, moist spring and early summer months (40–70% of annual rainfall fell during April and July), OP is mineralized and can be removed from the surface soil by plant uptake. Apparently, the formation and mineralization of OP was not inhibited by the application of fertilizer P (Y, Fig. 2). A similar decrease in OP content during spring and summer months, with maximum values in winter has been observed by Dormaar (1972) and Nguyen et al. (1969) in cropped surface soil.

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**Fig. 2.** Seasonal variation in total, inorganic, organic, and available P content of surface soil (0–50 mm depth) from an unfertilized (W1) and fertilized soil during 1981 and 1982.
Organic P Pools

The variation in OP content during the study period (Fig. 2) resulted from variations in moderately labile OP (Fig. 3). The amount of OP in more labile and resistant pools remained fairly constant. This was the case for both unfertilized (W1) and fertilized (Y) soils (Fig. 3). Similar variations were obtained at the other sites (data not presented). In contrast to the present study, Halm et al. (1972) reported that the labile OP content of a heavy clay soil under native grasses varied from 12.3 to 57.2 mg kg$^{-1}$, during a sampling period of approximately 1 yr.

As labile OP remained fairly constant, this pool could be the result of a dynamic equilibrium between mineralization and replenishment from moderately labile OP. This equilibrium is controlled by AP content. It is proposed that if AP falls below a certain level for a given soil, labile OP is mineralized supplying AP for plant uptake. The labile OP pool is then replenished rapidly by moderately labile OP. Similarly, Abbot (1978) and Dalal (1979) have suggested that solution or labile OP is readily mineralized and can constitute an important AP source.

The rates of these reactions will be a function of soil moisture and temperature, and possibly, pool sizes. As is the case for IP (Posner and Bowden, 1980), no distinct boundaries probably exist between the OP pools. The fractionation scheme used, however, does allow some distinctions to be made.

Available P

The AP content of unfertilized soil (W1) showed a slight increase in the fall months (Oct. and Nov.) from minimum values during the growing season of spring and summer (May–Sept.) (Fig. 2). Due to unfavorable soil conditions for biological activity during the winter months (Dec.–Feb.) (intermittently frozen and dry), OP mineralization and plant uptake of AP is minimal and, thus, AP content remained fairly constant (Fig. 2).

Fertilizer P application resulted in an immediate increase in AP content of surface soil (Y), (Fig. 2). Similar increases were obtained for the other fertilized soils. The AP content was not maintained at the high levels following fertilizer applications, however, with contents returning to the prefertilizer levels after approximately 21 to 28 d (Fig. 2).

Seasonal variability of the surface soil AP content was greater than spatial variability. The 20 samples collected from FR-5 in October 1981 had a mean value of 12 mg kg$^{-1}$ with a 40% coefficient of variation, whereas those collected at monthly intervals during 1981 had a mean of 22 mg kg$^{-1}$ and a 35% coefficient of variation. As for OP, seasonal AP variability can thus be accounted for by P cycling as well as spatial variability.

The AP content of surface soil during the study period was significantly related to the OP content of unfertilized soils and IP content of fertilized soils at most sites (Table 3). In fact, OP and IP content accounted for up to 81 and 88% of the AP variation in unfertilized and fertilized soils, respectively. Available P was not closely related to the OP content of fertilized and IP content of unfertilized soils (Table 3), emphasizing the importance of OP and IP in controlling the AP contents of unfertilized and fertilized soils, respectively.

The slope of the relationship between AP and OP content of the unfertilized soils (Table 3), represents the equilibrium constant for OP mineralization of the soil, such that as slope value increases, the potential for OP mineralization and AP production increases. For the fertilized soils, the slope of the relationship between AP and IP content (Table 3), represents the
P fixation potential of the soil, such that as slope value increases, the proportion of IP as AP increases.

Slope values of the AP-OP relationship for each unfertilized watershed (Table 3) were significantly related (0.1% level) to the phosphatase enzyme activity of a surface soil sample taken in March 1981 (Fig. 4). As phosphatase enzyme activity of surface soil increases, the potential for OP mineralization and subsequent AP production in these unfertilized soils is increased. Although enzyme activity was assayed under optimum soil conditions (Tabatabai and Bremner, 1969) and thus represents maximum activity, this potential will vary during the year as a function of OP content, soil temperature, moisture, and AP content. The close correlation between phosphatase enzyme activity and equilibrium constant for OP mineralization, as measured by the AP-OP conversion balance, substantiates earlier work by Halm et al. (1972) and Stewart et al. (1973), who suggested that rapid OP turnover was the result of high phosphatase activity.

For the fertilized soils, the slope of the relationship between AP and IP (Table 3) was significantly related (0.1% level) to the Langmuir P sorption maximum of a surface soil sample taken in March 1981 (Fig. 5). With an increase in sorption maximum a smaller portion of the applied fertilizer P will remain as AP. The net mineralization of OP during the period of maximum crop growth was calculated as the decrease in OP during spring and early summer (Feb.–June) of both 1981 and 1982 (Table 1). Since net OP mineralization was calculated as the difference in surface soil OP content between 2 sampling dates, an approximate coefficient of variation of these values will be 20%, that is twice the coefficient of variation for OP spatial variability, discussed earlier. Consequently, similar amounts of AP were added to surface soil from OP mineralization as from fertilizer P at all sites (Table 1). It is apparent, however, that OP was mineralized even with the addition of fertilizer P. For the unfertilized soils, net OP mineralization contributed from 14 to 37 kg P ha⁻¹ during February to June, averaged for 1981 and 1982. As soil OP will be formed by plant residue incorporation during this period, the calculated amount of OP mineralized (Table 1), will be an underestimate of the actual value. As no net reduction in OP content of either unfertilized or fertilized soil was observed during the study period, OP mineralized during this period was replaced through plant residue incorporation. The importance of OP as a source of AP in the unfertilized soils is thus demonstrated. In addition, OP mineralization can supply as much P in fertilized soils as applied in fertilizer material.

The amounts of OP mineralized during the growing season in the present Southern Plains soils (Table 1), are slightly greater than amounts mineralized (0.5–8.5 kg ha⁻¹ yr⁻¹) in several English soils (Chater and Mattingly, 1980). The maximum mineralization rate of 8.5 kg P ha⁻¹ yr⁻¹ measured by Chater and Mattingly (1980) represented approximately half the seasonal P requirements of an average cereal crop. In other studies, Greb and Olsen (1967) and Dormaar (1972) found that 10-15 and 18-51 kg P ha⁻¹, respectively, was made
available for alfalfa uptake by OP mineralization during a growing season in several calcareous soils of Colorado and dark brown Chernozems of southern Alberta.

CONCLUSIONS

In both the unfertilized and fertilized soils, the pool of AP can be rapidly replenished from OP and fertilizer P pools, as a function of phosphatase enzyme activity and P sorption maximum, respectively. As labile OP remained fairly constant, it can be hypothesized that mineralization of this pool and replenishment from moderately labile OP occur simultaneously and at similar rates. Available P content of the unfertilized soils, however, exhibited an approximate two-fold seasonal variation. Consequently, estimates of AP for soil-P fertility tests should be made as close to planting as possible. With the probable increase in organic matter content in reduced-tillage practices, which conserve soil organic matter, may not result in a direct increase in soil P fertility. Consequently, agricultural management practices which maintain or increase OP content, however, may not result in a direct increase in OP content with cultivation of Fargo silty clay loam soil for 60 yr, and Tiessen et al. (1982) when cellulose plus fertilizer P was added. Consequently, differing soil-P reactions, which include Ca- and Fe-dominated processes, had little effect on the importance of IP and OP as sources of AP.

Several studies have shown that soil OP content can decrease during long-term cultivation (approximately 50 yr) (Adeputa and Corey, 1977; Haas et al., 1961; Thompson et al., 1954; Williams and Lipsett, 1961). For example, Sharpley and Smith (1983) found a 73% decrease in OP content with cultivation of Fargo silty clay loam soil for 60 yr, and Tiessen et al. (1982) a 29% decrease with cultivation of Bradwell sandy loam for 65 yr. As OP mineralization can supply large amounts of AP in both unfertilized and fertilized soils, a decrease in soil OP content will result in a reduction in soil P fertility. Consequently, agricultural management practices which maintain or increase OP contents are advantageous for long-term (up to 50 yr) soil fertility maintenance. The incorporation of plant residues in surface soil and increase in soil organic matter content, however, may not result in a direct increase in OP content. Chauhan et al. (1981) and Halm et al. (1972) have shown that cellulose addition to surface soil (Ap horizon) increased microbial activity and subsequently the amount of microbial OP and IMobilized. In a P deficient subsurface soil (Bm horizon), however, an increase in OP was only observed when cellulose plus fertilizer P was added. Consequently, the application of fertilizer P to reduced-tillage practices, which conserve soil organic matter, may not only increase AP content directly, but may also stimulate OP production. This process will also be particularly important for soils in which P fixation and occlusion maintain AP at low levels. Under these conditions, therefore, fertilizer P application may increase both immediate and long-term soil fertility.

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REFERENCES


ALVARADO & BUOL: FIELD ESTIMATION OF PHOSPHATE RETENTION BY ANDEPTS

ALFREDO ALVARADO AND S. W. BUOL

ABSTRACT

In an attempt to develop a field method for soil surveyors and field agronomists to rapidly evaluate whether or not a particular site would retain a large amount of applied phosphate, 59 samples of Andepts from Costa Rica and Guatemala were incubated with rates of P, then analyzed. Phosphate retention ranged from 25 to 99% and correlated quite well with ammonium oxalate extractable Al concentration ($R^2 = 0.56$) in a linear model. In samples with $<2.4\%$ ammonium oxalate extractable Al, the amount of applied phosphate retained was related even better to this measurement, while at $>2.4\%$ oxalate extractable Al, retention was not influenced appreciably by oxalate extractable Al concentration. Phosphate retention was also correlated with pH in NaF. By the methods used, $>90\%$ phosphate retention was predicted by an oxalate extractable Al concentration of $>2.4\%$ or a NaF pH of $>10.7$. A quick test was devised to assess soils with extremely high phosphate retention. The method consisted of adding a few drops of 0.1 mol NaF L$^{-1}$ to approximately one gram of soil in a spot plate and, after 10 min, checking the pH with two drops of 0.04% thymolphthalein indicator. This technique was found to correctly identify 79% of the samples as having either $>90\%$ phosphate retention.

Additional Index Words: amorphous clays, Ando soils, allophane, phosphate fixation, volcanic ash soils.


ANDEPTS ARE KNOWN to retain large proportions of fertilizer phosphate in plant unavailable form (Fassbender 1968; 1969; Fox, 1974). Short range order silicates, Al- and Fe-humus complexes, imogolite and perhaps other materials are responsible for phosphate retention in Andepts. In addition to Al-OH and Fe-OH bonds the Al-OH-Al bonds (Theng et al., 1981) and Si-O-Al bonds (Veith and Sposito, 1977) have been identified as adsorption sites.

Phosphate retention in Andepts is related to the replacement of OH$^-$ from poorly ordered aluminosilicates and Al-humus by fluoride (Perrott et al., 1976a, b; Wada, 1980). The amount of OH$^-$ released from amorphous materials and Al-humus when NaF is added is proportional to the increase in pH of the supernatant solution, and is an indicator of the amount of these compounds in Andepts (Fieldes and Perrott, 1966; Shoji and Ono, 1978; Shoji and Fujiwara, 1984).

The objective of this study was to investigate the relationship between the phosphate retention capacity of Andepts and more easily measured properties such as NaF pH values in an attempt to develop a method suitable for identifying those Andepts with the greatest phosphate retention capacity during the course of field mapping.

MATERIALS AND METHODS

Samples and Sample Preparation

Fifty-nine soil samples representing A, B, and C horizons of Dystrandepts, Vitrandepts, Placandepts, and Andaquepts from Costa Rica and Guatemala were sampled by the senior author.

The samples were air dried at room temperature and ground to pass a 2-mm sieve. All chemical analyses were conducted on air dry samples but the results were calculated and reported on oven-dry weight basis.

Phosphate Retention

Phosphate retention was determined by equilibrating 3g soil samples at room temperature in 30 mL P solutions (KH$_2$PO$_4$), all 0.01 M with respect to CaCl$_2$. The P concentrations were 0, 35, 70, 140, 280, and 560 μg/mL. The samples were allowed to dry for 7 d and P was extracted from the dried samples with a modified Olsen solution (0.5 M NaHCO$_3$ + 0.01 M EDTA + 0.15 g Superlock/127 L) (International Soil Fertility Evaluation and Improvement Program, 1972) at a 1:10 ratio.

Percent phosphate retention was calculated as $\left(\frac{1-b}{100}\right)$ where $b$ is the slope of the linear regression of P-added on P-extracted for each soil.

Oxalate Extraction and NaF pH

Each soil sample was extracted with 10 mL of 0.2 M ammonium oxalate, pH 3, added to 0.5-g of soil. The samples were shaken in the dark for 2 h and then centrifuged. The amounts of Al, Si, and Fe in the supernatant were measured by atomic absorption spectrophotometry (McKeague and Day, 1966). The pH values in NaF were determined at two

2 Professor, Univ. of Costa Rica, San Jose, Costa Rica, and Professor, North Carolina State Univ., Raleigh, NC, respectively.


