

Amounts, Forms, and Solubility of Phosphorus in Soils Receiving Manure

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ABSTRACT

Continually land-applying manure at rates exceeding crop removal can change soil P chemistry and increase soil P to levels that are of environmental concern. To assess the effect of long-term manure application on soil P forms and solubilities, we determined water-extractable P, Mehlich-3 P, Hedley-P fractions, and crystalline Ca-P minerals in surface soil (0–5 cm) from 20 locations in New York ($n = 6$), Oklahoma ($n = 8$), and Pennsylvania ($n = 6$), which received dairy, poultry, or swine manure (40–200 kg ha⁻¹ yr⁻¹) for 10 to 25 yr. For all untreated and manured soils, the pH averaged 5.9 and 6.6; exchangeable Ca, 0.9 and 6.2 g kg⁻¹; organic C, 15.7 and 32.6 g kg⁻¹; and total P, 407 and 2480 mg kg⁻¹, respectively. As Mehlich-3 P increased (64–2822 mg kg⁻¹), the proportion that was water extractable (14–3%) declined as exchangeable soil Ca increased ($R^2 = 0.81$). Results suggest that addition of manure to soils shifts P from Al- and Fe- to Ca-P reaction products, accounting for the relatively greater Mehlich-3 but lower water extractability of soil P. This shift has implications to environmental soil P testing. For instance, the fact that Mehlich-3 P has been shown to overestimate potential losses of P in overland flow from heavily manured soils may be explained by dissolution of Ca-P minerals not soluble in water.

IN THE LAST 20 yr, crop and livestock operations have specialized into spatially separate production systems (Evans et al., 1996; Kellogg et al., 2000). Since 1990, beef, dairy, pig, and poultry numbers in the USA have increased 10 to 30%, while the number of farms on which they were reared has decreased 40 to 70% (Gardner, 1998). This intensification has been driven by a greater demand for animal products and improved profitability. Intensification has also resulted in a major transfer of P from grain-producing areas to animal-producing areas, where localized surpluses and land application of manure rich in P can occur, increasing soil P concentration (Lander et al., 1998; Lanyon, 2000). These farming system developments have taken on greater significance, in terms of manure management, with the recent adoption of P-based nutrient management strategies to address water quality impairment by accelerated eutrophication (U.S. Department of Agriculture and U.S. Environmental Protection Agency, 1999; U.S. Environmental Protection Agency, 2000, 2001).

Many studies have shown an increase in soil P, usually documented as soil test P, with continual land application of manure at rates above crop requirements (Sharpley et al., 1993). Research has also demonstrated that in-

creases in overland flow P concentrations are directly related to an elevation in soil test P concentration of surface (0- to 5-cm depth) soil of both noncalcareous and calcareous soils (Fang et al., 2002; Pierson et al., 2001; Pote et al., 1999; Torbert et al., 2002). However, tests designed for one set of soil properties may give erroneous results if applied to other soils. For example, the ammonium fluoride and acid based soil tests of Bray and Kurtz (1945) are recommended for use in acid soils but not for calcareous soils due to the dissolution of CaCO₃ and precipitation of F by Ca interfering with the extraction of P (Smillie and Syers, 1972).

Adding manure can cause an increase in soil pH (Eghball, 2002; Iyamuremye et al., 1996; Kingery et al., 1994), due to input of large amounts of Ca (up to 60 g Ca kg manure⁻¹) and the buffering effects of added bicarbonates and organic acids with carboxyl and phenolic hydroxyl groups (Sharpley and Moyer, 2000; Whalen et al., 2000). This suggests that not only the amounts but also form and relative availability of P for crop uptake and release to overland flow can change with manure application (Wang et al., 1995). Hence, a clearer understanding of the forms and solubility chemistry of P in manured soils is needed to refine soil test methods and develop soil test P thresholds for crop response, environmental risk assessment, and manure management recommendations in general.

The aim of this study was to determine the effect of continual long-term (>10 yr) manure applications on the forms and solubilities of P in soil. Soils from Oklahoma, New York, and Pennsylvania that had received dairy, poultry, or swine manure (40–200 kg P ha⁻¹ yr⁻¹ for 10–25 yr) were used along with untreated analog soils.

MATERIALS AND METHODS

Site Management and Soil Collection

The classification, location, and management history of 20 sites and soils selected in New York (6 sites), Oklahoma (8 sites), and Pennsylvania (6 sites) are presented in Table 1. Soils are from LeFlore and McCurtain Counties of eastern Oklahoma, Steuben County of south central New York, and Lancaster and Northumberland Counties of southeastern and central Pennsylvania, respectively. Land and nutrient management at all sites are typical of these regions, dominated by concentrated animal feeding operations. Annual rainfall in eastern Oklahoma is about 1200 mm, in south central New York about 1000 mm, and in central and southeastern Pennsylvania about 1100 mm. All sites are on gently sloping areas

Abbreviations: Acid IP, hydrochloric acid extractable inorganic soil P; Bicarbonate IP, sodium bicarbonate extractable inorganic soil P; Bicarbonate OP, sodium bicarbonate extractable organic soil P; DCP, Dicalcium phosphate dehydrate; Hydroxide IP, sodium hydroxide extractable inorganic soil P; HA, Hydroxyapatite; Hydroxide OP, sodium hydroxide extractable organic soil P; Mehlich-3 P, Mehlich-3 extractable soil P; OCP, Octocalcium phosphate; Resin P, resin membrane extractable inorganic soil P; TCP, tricalcium phosphate.

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Table 1. Site location, soil type, management, and manure applied to soils used in this study.†

| Soil‡ | Classification | Management | Manure application | | |
|---------------------|--------------------|---|--------------------|--|-----------------|
| | | | Type | Rate kg P ha ⁻¹ yr ⁻¹ | Duration§ yr |
| New York | | | | | |
| Morris, sl | Aeric Fragiaquepts | fescue pasture¶ | dairy manure | 75 | 25 |
| Morris, sl | Aeric Fragiaquepts | reduced till corn (<i>Zea mays</i> L.) | poultry manure | 200 | 25 |
| Oquaga, sl | Typic Dystrudepts | reduced till corn | dairy manure | 150 | 25 |
| Oquaga, sl | Typic Dystrudepts | reduced till corn | poultry manure | 200 | 25 |
| Wellsboro, sl | Typic Fragiudepts | reduced till corn | dairy manure | 150 | 25 |
| Wellsboro, sl | Typic Fragiudepts | reduced till corn | poultry manure | 200 | 25 |
| Oklahoma | | | | | |
| Cahaba, vsl | Typic Hapludult | coastal bermudagrass# | poultry litter | 130 | 12 |
| Captina, sil | Typic Fragiudult | fescue pasture | swine slurry | 100 | 10 |
| Kullit, fsl | Aquic Paleudult | coastal bermudagrass | poultry litter | 130 | 12 |
| Muskogee, l | Aquic Paleudalf | coastal bermudagrass | poultry litter | 130 | 12 |
| Ruston, fsl | Typic Paleudult | coastal bermudagrass | poultry litter | 100 | 12 |
| Sallisaw, sl | Typic Paleudalf | fescue pasture | swine slurry | 80 | 15 |
| Shermore, fsl | Typic Fragiudalf | coastal bermudagrass | poultry litter | 90 | 20 |
| Stigler, sl | Aquic Paleudalf | conventionally tilled wheat | swine slurry | 40 | 10 |
| Pennsylvania | | | | | |
| Bucks, sil | Typic Hapludult | reduced till corn/barley | dairy manure | 120 | 10 |
| Bucks, sil | Typic Hapludult | reduced till corn/barley | poultry manure | 120 | 10 |
| Chester, sil | Typic Hapludult | pasture | dairy manure | 120 | 10 |
| Duffield, sil | Ultic Hapludalf | reduced till corn/soybean | dairy manure | 120 | 10 |
| Duffield, sil | Ultic Hapludalf | reduced till corn | poultry manure | 90 | 10 |
| Hagerstown, sil | Typic Hapludalf | reduced till corn/winter rye | poultry manure | 150 | 10 |

† Adjacent soils receiving no manure were all under idle native grass.

‡ vsl, fsl, sl, sil, sl, and l represent very fine sandy loam, fine sandy loam, sandy loam, silt loam, and loam texture, respectively, for the surface 5 cm of the soil profile.

§ Approximate minimum number of years manure applied.

¶ Fescue pasture was intermittently cut and grazed for hay.

Cut for hay.

(0–2% slope), so any changes in soil properties due to erosion are expected to be minimal.

Information on the rate and duration of manure application at each site was obtained from landowners. Soils receiving no manure or fertilizer (untreated) were all under idle native or introduced grasses and adjacent to fields receiving manure (treated). Native and introduced grasses were big (*Andropogon gerardii* Vitman) and little [*Scizachyrium scoparium* (Michaux.) Nash] bluestem, tall dropseed [*Sporobolus drummondii* (trin) Vasey-Fernald], side oats grama [*Bouteloua curtipendula* (Michaux.) Torrey], meadow fescue (*Festuca elatior* L.), purple love grass [*Eragrostis spectabilis* (Pursh) Steud.], and switchgrass (*Panicum virgatum* L.).

At each site, six surface soil samples (0- to 5-cm depth) were collected from an approximate 0.5-ha area within each field. Samples were air-dried, sieved (2 mm), and subsamples (equal weights) of the six sampled soils from each site composited. Sample mixing was done after air-drying, to avoid any confounding effects of P readsorption during mixing field-moist samples (Maguire et al., 2002). All individual and composited samples were stored in airtight containers for later analysis. Water- and Mehlich-3 extractable soil P was determined on individual subsamples, while all other analyses (i.e., pH, texture, organic C, P sorption capacity, P fractionation, and ion-activity products) were conducted on composited samples for each site.

Chemical Analyses

Soil Analysis

Particle-size analysis was conducted by hydrometer method after dispersion with sodium hexametaphosphate (Gee and Bauder, 1986). Organic C was determined by combustion using a Leco C/N analyser¹ (Leco Corp., St. Joseph, MI) and pH

¹ Mention of trade names does not imply endorsement by the USDA.

measured with a glass electrode at a 1:2.5 soil/water ratio (w/w). Exchangeable Ca was determined by shaking 10 g of soil in 50 mL of 1 M CH₃COONa (buffered to pH 4.8) for 15 min (Lathwell and Peech, 1964). Concentrations of Ca in filtered extracts (0.45 μm) were determined by inductively coupled plasma-mass adsorption spectroscopy.

Water-extractable soil P was measured by shaking 2 g of soil with 20 mL of deionized water end-over-end for 30 min (Kuo, 1996). This extraction method was found to closely represent soil P release to overland flow water (McDowell and Sharpley, 2001). Mehlich-3 extractable soil P concentration (Mehlich-3 P) was determined by shaking 1 g of soil with a 10 mL mixture of 0.2 M CH₃COOH, 0.25 M NH₄NO₃, 0.015 M NH₄F, 0.013 M HNO₃, and 0.001 M EDTA end-over-end for 5 min (Mehlich, 1984). Both water and Mehlich-3 extracts were centrifuged (2500 × g for 10 min) and filtered (0.45 μm) before determining P. Total soil P was determined following digestion of a 1-g sample with a semi-microKjeldahl procedure and filtration (Whatman No. 40 filter paper, Whatman Inc., Clifton, NJ) (Patton and Truitt, 1992). Each of these soil P measurements was conducted in duplicate. In all cases, P was determined on neutralized Mehlich-3 extracts and Kjeldahl digests by the colorimetric molybdenum-blue method of Murphy and Riley (1962). Solutions were neutralized using *p*-nitrophenol indicator (color change at pH 7.0) and dropwise addition of either 0.5 M H₂SO₄ or 1.0 M NaOH.

Soil P was fractionated according to the sequential extraction procedure of Hedley et al. (1982) by end-over-end shaking in triplicate 0.5 g of soil with: (Step 1) a 2-cm² anion-exchange resin membrane in 30 mL of 0.01 M CaCl₂; (Step 2) 30 mL of 0.5 M NaHCO₃ (pH 8.5); (Step 3) 30 mL of 0.1 M NaOH; and (Step 4) 30 mL of 1.0 M HCl each for 16 h. Between each fractionation step, extracts were centrifuged (2500 × g for 10 min) to separate soil from extracting solution, which was carefully decanted and filtered (0.45 μm). After the final extraction (HCl), the residual soil was digested with 18 M H₂SO₄ and 70% H₂O₂ (Step 5). Total P in the bicarbonate and hydrox-

ide extracts was determined following persulfate and concentrated H_2SO_4 digestion (Kuo, 1996).

After shaking the anion-exchange resin membrane square and soil (Step 1), the square was carefully removed after slow up-and-down movement of the square in the supernatant to remove adhering soil particles, thereby minimizing extraction of P from adhered soil as well as membrane P and any loss of soil particles for subsequent extraction. Phosphorus retained on the membrane was removed by shaking the strip end-over-end with 40 mL of 1 M HCl for 4 h. The membrane strip was removed, rinsed with deionized water, and shaken with an additional 40 mL of 1 M HCl for 4 h. Phosphorus in the two HCl extracts was measured separately and summed to give resin P (freely exchangeable inorganic P) (Tiessen and Moir, 1993).

Phosphorus in all filtered (0.45 μm) and neutralized extracts and digests was determined by the molybdenum-blue method (Murphy and Riley, 1962). The organic P content of bicarbonate and hydroxide extracts was calculated as the difference between total P and inorganic P contents. Inorganic P fractions determined in Steps 2, 3, and 4 are subsequently referred to as sodium bicarbonate extractable inorganic soil P (bicarbonate IP; biologically available inorganic P), sodium hydroxide extractable inorganic soil P (hydroxide IP; amorphous and some crystalline Al and Fe inorganic P), and hydrochloric acid extractable inorganic soil P (acid IP; relatively stable Ca-bound inorganic P). Organic P fractions determined from extracts in Steps 2 and 3 are subsequently referred to as sodium bicarbonate extractable organic soil P (bicarbonate OP; easily mineralizable organic P), and sodium hydroxide extractable organic soil P (hydroxide OP; chemically and physically protected organic P). Residual P determined in Step 5 is considered to be a resistant mixture of occluded inorganic P covered with sesquioxides and nonextracted stable organic P. These P fraction definitions follow those outlined by Hedley et al. (1982) and Tiessen and Moir (1993).

Ion-Activity Products

Ion activity products were determined from chemical activities generated from ion concentrations in solution and calculated using the MINTEQA2 chemical speciation model (Allison et al., 1991). For each manure type, ion-activity products for three soils were determined: for dairy manure—Bucks (fine-loamy, mixed, active, mesic Typic Hapludult), Morris (coarse-loamy, mixed, active, mesic Aeric Fragiaguet), and Wellsboro (coarse-loamy, mixed, active, mesic Typic Fragiudult); for poultry litter—Kullit (fine-loamy, siliceous, semi-active, thermic Aquic Paleudult), Muskogee (fine-silty, mixed, active, thermic Aquic Paleudalf), and Shermore (fine-loamy, siliceous, semiactive, thermic Typic Fragiudalf); for poultry manure—Duffield (fine-loamy, mixed, active, mesic Ultic Hapludalf), Hagerstown (fine, mixed, semiactive, mesic Typic Hapludalf), and Oquaga (loamy-skeletal, mixed, superactive, mesic Typic Dystrudept); and for swine slurry—Captina (fine-silty, siliceous, active, mesic Typic Fragiudult), Sallisaw (fine-loamy, siliceous, superactive, thermic Typic Paleudalf), and Shermore. Duplicate samples of each soil (10 g, <2 mm air-dried) were suspended in 50 mL of 0.01 M $CaCl_2$ (to provide an equilibration matrix of fixed ionic strength). After shaking for 16 h, suspension pH was determined, then centrifuged and filtered (0.45 μm). Nitrate, P, SO_4 , F, and Cl were measured using a Dionex ion chromatograph (Dionex, Sunnyvale, CA). Magnesium, Al, and Fe were determined using atomic absorption spectroscopy. Calcium was also measured by atomic absorption spectroscopy and the data confirmed that no Ca from the background matrix of 0.01 M $CaCl_2$ was adsorbed by any

of the soils. Sodium and K were determined by flame photometry and ionic strength estimated from electrical conductivity (Griffin and Jurinak, 1973).

Manure Analysis

Manure samples were collected before applying to land at each location (i.e., 2002 in New York, 1993 in Oklahoma, and 2001 in Pennsylvania). Five 2-L plastic containers of dairy manure and swine slurry were collected from a concrete storage pit and manure spreader, respectively, before applying to land. Ten samples of poultry manure (1 kg) and poultry litter (500 g) were collected from the layer- and broiler-house floor, respectively, on the same day as clean out at each location. All individual samples of each manure type were combined, thoroughly mixed, subsampled, and stored at 4°C for approximately 2 d until analyzed. All analyses were conducted in triplicate on field-moist manures. The pH of manures was measured by a glass electrode at a 5:1 water/manure ratio (weight/dry-matter weight). Organic C was determined by dry combustion using a Leco C/N analyzer (Nelson and Sommers, 1996). The concentration of Ca in manure was measured by ICP on microwave-assisted digestion with concentrated nitric acid (Peters et al., 2003). Total P and N concentrations of the manures were determined by a modified semimicro-Kjeldahl procedure (Patton and Truitt, 1992). The procedure used a 1.133-g mixture of K_2SO_4 and $CuSO_4$ (100:3 weight ratio), concentrated H_2SO_4 (4 mL), and fresh manure (equivalent to 0.25 g of dry material), digested at 180°C for 60 min and 375°C for 120 min. Moisture content of the manures was determined by gravimetric analysis (35°C basis), which was used to correct organic C, Ca, P, and N concentrations to a dry-weight basis (Table 2) (Kleinman et al., 2002).

Statistical Analysis

Statistical analyses (*t* tests, means and standard errors) were performed with SPSS v. 10.0 on individual (noncomposited) soil sample analyses, which included water and Mehlich-3 extractable soil P (SPSS Inc., 1999). Differences between analyses conducted in composited samples of untreated and manured soils were not statistically compared. Treatment differences discussed in the text are significant at $p \leq 0.05$.

The presence of a Mehlich-3 P threshold, at which there is no change in water extractability of soil P, was determined using a segmented quadratic-linear regression, using a modified version of SAS's nonlinear segmented regression (NLIN; SAS Institute, 2001). The quadratic and linear models were evaluated by least squares regression. The NLIN procedure requires initial estimation of quadratic ($a + b\text{Mehlich-3 P} + c^2\text{Mehlich-3 P}$) and linear ($d + e\text{Mehlich-3 P}$) model parameters (a , b , c , d , and e), and solves for the threshold between the quadratic and linear regressions by iterative re-evaluation of the equation (SAS Institute, 2001). Above the threshold

Table 2. Properties of the manures applied in the year of soil sampling (New York, 2002; Oklahoma, 1993; Pennsylvania, 2001).

| Manure type | Dry matter | Organic C | Total P | Total N | Total Ca |
|---------------------|------------|---------------------------------------|---------|---------|----------|
| | % | g kg ⁻¹ (dry-weight basis) | | | |
| New York | | | | | |
| Dairy manure | 33 | 326 | 9.8 | 45.3 | 21.9 |
| Poultry manure | 47 | 332 | 25.2 | 67.4 | 82.6 |
| Oklahoma | | | | | |
| Poultry litter | 82 | 413 | 15.5 | 45.8 | 60.3 |
| Swine slurry | 7 | 281 | 29.7 | 60.1 | 23.2 |
| Pennsylvania | | | | | |
| Dairy manure | 16 | 351 | 3.5 | 18.9 | 24.8 |
| Poultry manure | 53 | 364 | 27.8 | 50.2 | 108 |

Mehlich-3 P value, the linear model has a slope of 0 (i.e., e is equal to 0), such that there is no change in water extractability of soil P with an increase in Mehlich-3 P.

The Mehlich-3 P threshold was also determined by a split-line model (McDowell and Sharpley, 2001) that describes two segmented linear relationships, with significantly different slopes ($p < 0.05$) on either side of a threshold value (Genstat, 1997). Below the threshold;

$$\text{Water extractability of soil } P = m_1(\text{Mehlich-3 P}) + c \quad [1]$$

and above the threshold value;

$$\text{Water extractability of soil } P = m_1(\text{threshold value of Mehlich-3 P}) + m_2(\text{Mehlich-3 P} - \text{threshold value of Mehlich-3 P}) + c \quad [2]$$

where c is the intercept, m_1 is the slope of the linear relationship for values of Mehlich-3 P less than the threshold value, and m_2 is the slope after the threshold. The four parameters (m_1 , m_2 , Mehlich-3 P threshold value, and c) were estimated by nonlinear regression, using the method of maximum likelihood in Genstat v. 5.0 (Genstat, 1997).

RESULTS AND DISCUSSION

Soil Properties

Soils with histories of receiving manure differed greatly from those with no manure application history. Soil pH was significantly greater in manured soils than in untreated soils, with differences ranging from 1.5 units in Muskogee (poultry litter added) to 0.4 units in Stigler (swine slurry added) (Table 3). Manured soils also had significantly more organic C, exchangeable Ca, and total P than untreated soils (Tables 3 and 4), reflecting the large additions of these elements in manure (Table 2). The most dramatic increases between untreated and manured soils were observed in Mehlich-3 P (64 mg kg⁻¹ for Stigler to 2822 mg kg⁻¹ for Oquaga receiving poultry

Table 3. Selected mean physical and chemical properties of the 0- to 5-cm depth of untreated (Unt.) and manured (Tr.) soils.

| Soil | pH | | Clay | | Organic C | | Exch. Ca | |
|-----------------------|-------|-----|------------------------|-----|-----------|------|----------|------|
| | Unt. | Tr. | Unt. | Tr. | Unt. | Tr. | Unt. | Tr. |
| | — % — | | — g kg ⁻¹ — | | | | | |
| Dairy manure | | | | | | | | |
| Bucks | 6.8 | 7.6 | 15 | 17 | 8.2 | 15.4 | 1.06 | 5.58 |
| Chester | 5.6 | 6.5 | 26 | 23 | 9.3 | 19.4 | 1.23 | 3.62 |
| Duffield | 6.2 | 6.9 | 21 | 18 | 7.7 | 16.2 | 0.77 | 3.49 |
| Morris | 6.4 | 7.1 | 15 | 19 | 18.2 | 44.9 | 0.85 | 3.34 |
| Oquaga | 6.2 | 6.9 | 17 | 16 | 16.5 | 33.4 | 1.08 | 3.47 |
| Wellsboro | 6.3 | 6.9 | 13 | 19 | 15.3 | 32.5 | 1.21 | 2.62 |
| Poultry litter | | | | | | | | |
| Cahaba | 5.5 | 6.3 | 13 | 18 | 24.1 | 43.9 | 1.15 | 4.67 |
| Kullit | 4.8 | 5.8 | 8 | 16 | 17.0 | 55.6 | 0.58 | 11.0 |
| Muskogee | 5.6 | 7.1 | 14 | 10 | 33.6 | 59.6 | 0.64 | 20.7 |
| Ruston | 5.8 | 6.1 | 9 | 12 | 23.7 | 33.7 | 0.97 | 9.02 |
| Shermore | 5.1 | 5.7 | 14 | 10 | 21.6 | 56.8 | 1.02 | 3.54 |
| Poultry manure | | | | | | | | |
| Bucks | 6.6 | 7.4 | 13 | 15 | 7.1 | 17.3 | 0.96 | 6.53 |
| Duffield | 5.9 | 7.1 | 22 | 20 | 7.8 | 16.4 | 1.01 | 7.02 |
| Hagerstown | 6.2 | 6.7 | 18 | 22 | 8.5 | 22.4 | 0.87 | 2.81 |
| Morris | 6.4 | 6.7 | 15 | 14 | 17.2 | 33.6 | 0.85 | 3.90 |
| Oquaga | 6.2 | 7.0 | 17 | 16 | 15.1 | 30.5 | 0.96 | 9.90 |
| Wellsboro | 6.3 | 6.9 | 13 | 17 | 16.4 | 31.1 | 0.84 | 8.82 |
| Swine slurry | | | | | | | | |
| Captina | 5.0 | 5.9 | 14 | 16 | 15.4 | 22.6 | 0.48 | 5.20 |
| Sallisaw | 5.4 | 5.9 | 11 | 13 | 16.9 | 33.6 | 0.52 | 4.23 |
| Stigler | 5.6 | 6.0 | 15 | 17 | 13.9 | 32.2 | 1.24 | 5.26 |

Table 4. Water extractable, Mehlich-3 extractable, and total P concentration of the 0- to 5-cm depth of untreated (Unt.) and manured (Tr.) soils.

| Soil | Water-extractable P | | Mehlich-3 P | | Total P | |
|-----------------------|-------------------------|-----|-------------|-------|---------|--------|
| | Unt. | Tr. | Unt. | Tr. | Unt. | Tr. |
| | — mg kg ⁻¹ — | | | | | |
| Dairy manure | | | | | | |
| Bucks | 2.1 | 53 | 17 | 1 300 | 373 | 4 790 |
| Chester | 2.7 | 48 | 20 | 886 | 627 | 3 140 |
| Duffield | 4.0 | 41 | 31 | 676 | 461 | 1 960 |
| Morris | 4.1 | 24 | 31 | 360 | 480 | 1 900 |
| Oquaga | 2.4 | 37 | 16 | 592 | 554 | 1 790 |
| Wellsboro | 2.5 | 38 | 22 | 539 | 529 | 1 310 |
| Poultry litter | | | | | | |
| Cahaba | 1.6 | 22 | 11 | 292 | 159 | 926 |
| Kullit | 0.8 | 11 | 5 | 128 | 122 | 1 280 |
| Muskogee | 1.1 | 16 | 7 | 197 | 571 | 1 510 |
| Ruston | 1.7 | 30 | 12 | 386 | 240 | 1 120 |
| Shermore | 2.9 | 25 | 25 | 240 | 206 | 1 250 |
| Poultry manure | | | | | | |
| Bucks | 4.8 | 39 | 40 | 626 | 525 | 2 460 |
| Duffield | 6.0 | 32 | 64 | 691 | 494 | 2 030 |
| Hagerstown | 4.9 | 27 | 44 | 336 | 563 | 1 530 |
| Morris | 3.0 | 34 | 25 | 857 | 424 | 3 100 |
| Oquaga | 2.2 | 85 | 18 | 2 840 | 496 | 6 770 |
| Wellsboro | 3.3 | 74 | 24 | 1 940 | 520 | 10 800 |
| Swine slurry | | | | | | |
| Captina | 0.8 | 14 | 5 | 121 | 273 | 766 |
| Sallisaw | 0.6 | 18 | 4 | 147 | 226 | 486 |
| Stigler | 2.5 | 11 | 18 | 82 | 302 | 736 |

manure; Table 4). For untreated soils, Mehlich-3 P was 1 to 13% of total P, while in manured soils it was 10 to 42% of total P.

Soil Phosphorus Extractability

Soil P extracted by water was closely related to that extracted as Mehlich-3 P ($R^2 = 0.94$; Fig. 1). The relationship was curvilinear, with the proportion of P extractable by water declining with increasing Mehlich-3 P (Fig. 2). For example, an Oquaga silt loam with a history of no manure applied had a Mehlich-3 P of 18 mg kg⁻¹ of which 14% was water extractable. In contrast, another Oquaga silt loam known to have received poultry manure had a Mehlich-3 P concentration of 2840 mg kg⁻¹, only 3% of which was water extractable. Similar trends in water extractability of soil P with increasing Mehlich-3 P were observed across all four manure types.

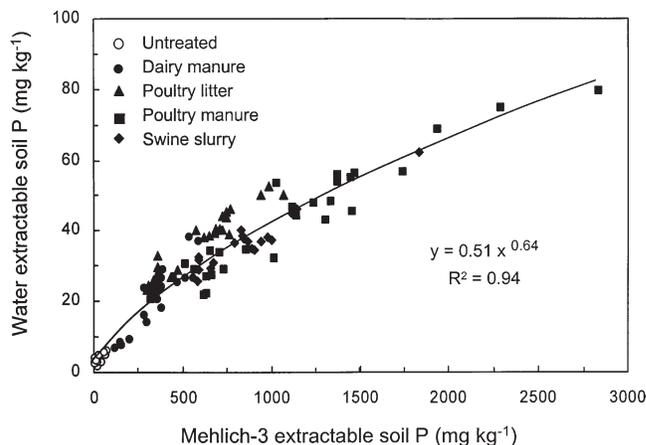


Fig. 1. Relationship between water and Mehlich-3 extractable soil P for untreated and manured soils from New York, Oklahoma, and Pennsylvania.

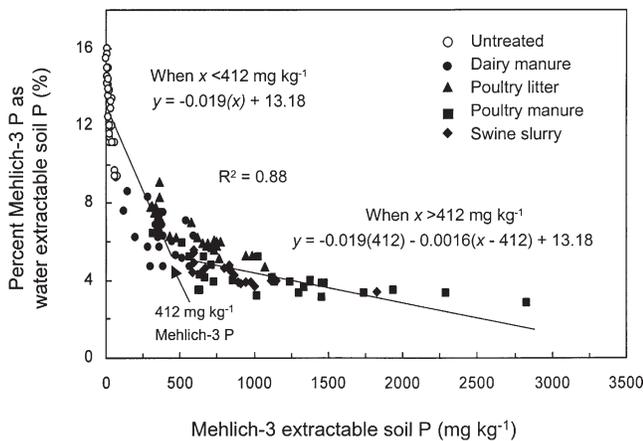


Fig. 2. Relationship between the percentage of Mehlich-3 P as water-extractable soil P and Mehlich-3 P for untreated and manured soils from New York, Oklahoma, and Pennsylvania. The arrow indicates the threshold value.

A threshold analysis was conducted on the relationship between the percentage of Mehlich-3 P as water-extractable soil P and Mehlich-3 P, by linear/linear models (split-line) and segmented quadratic/linear (NLIN SAS). The split-line model determined a Mehlich-3 P threshold of 412 mg kg^{-1} , below which the regression slope (-0.0187) was greater than above (-0.0016) the threshold (Fig. 2). Using the segmented quadratic/linear model, a similar threshold Mehlich-3 P concentration of 410 mg kg^{-1} was obtained, above which water extractability of Mehlich-3 P did not change ($p < 0.05$). This suggests that for the studied soils, a Mehlich-3 P threshold of about 400 mg kg^{-1} exists above and below the value which different relationships should be used to reliably estimate overland flow P from Mehlich-3 soil P. However, it must be made clear that Mehlich-3 P values of 400 mg kg^{-1} or greater are agronomically and environmentally unsustainable, being an order of magnitude greater than levels generally recommended for optimum crop yields (Beegle, 2001).

Several studies have reported greater regression slopes (as opposed to gradually decreasing) in the relationship of readily desorbable P and Mehlich-3 P. For example, Kleinman et al. (2000) found that the relationship between $0.01 \text{ M CaCl}_2 \text{ P}$ and Mehlich-3 P exhibited a significantly steeper regression slope above a Mehlich-3 P concentration of 141 mg kg^{-1} . Similarly, McDowell and Sharpley (2001), analyzing relationships between water-extractable soil P and Mehlich-3 P, observed a significantly steeper regression slope above Mehlich-3 P of 185 mg kg^{-1} . It is important to note that the maximum Mehlich-3 P concentration was 290 mg kg^{-1} for Kleinman et al. (2000). The maximum Mehlich-3 P concentration for McDowell and Sharpley (2001) was 624 mg kg^{-1} with most observations well below 500 mg kg^{-1} . When only those soils with Mehlich-3 P $< 400 \text{ mg kg}^{-1}$ were evaluated in the current study, a relationship similar to those reported by Kleinman et al. (2000) and McDowell and Sharpley (2001) was observed, with a Mehlich-3 P threshold of 201 mg kg^{-1} (Fig. 3).

Other studies have reported logarithmic plateaus in

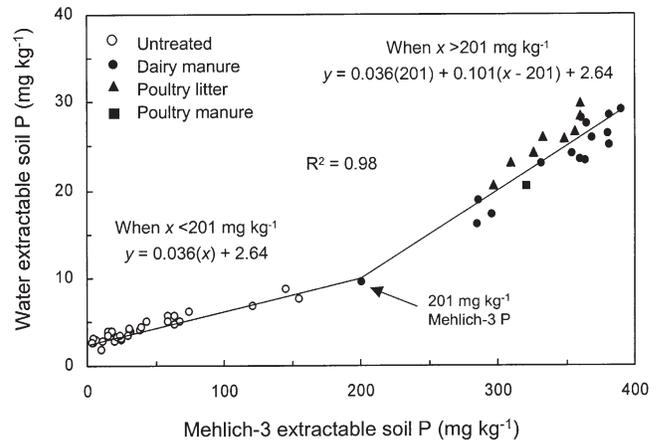


Fig. 3. Relationship between water- and Mehlich-3 extractable soil P for untreated and manured soils from New York, Oklahoma, and Pennsylvania with Mehlich-3 P less than 400 mg kg^{-1} . The arrow indicates the threshold value.

the proportion of Mehlich-3 P that is water extractable. Gaston et al. (2003) found water extractable soil P to be 13% of Mehlich-3 P (59 mg kg^{-1}) in a fine sandy loam under pasture that received poultry litter (9 Mg ha^{-1} for 1 yr), while only 5% of Mehlich-3 P (853 mg kg^{-1}) was water extractable when litter had been applied for 20 yr. Similarly, data presented by Torbert et al. (2002) shows that the proportion of Mehlich-3 P that was water extractable declined logarithmically with increasing Mehlich-3 P of two noncalcareous ($R^2 = 0.86$) and calcareous soils ($R^2 = 0.78$). To approximate the different water/soil ratios used by Torbert et al. (2002) (25:1) and the present study (10:1), water-extractable soil P values of Torbert et al. (2002) were multiplied by 2.5. Using this factor, water-extractable P was estimated as 8 to 13% of Mehlich-3 P in low P soils ($< 30 \text{ mg kg}^{-1}$ Mehlich-3 P) and 4 to 6% in high P soils ($> 300 \text{ mg kg}^{-1}$ Mehlich-3 P) (Torbert et al., 2002). These values are similar to those of the present study (Fig. 2).

The proportion of Mehlich-3 P that was water extractable was negatively related to exchangeable soil Ca ($R^2 = 0.89$; Fig. 4). Differences in exchangeable Ca among soils are likely a consequence of the large amounts of Ca added in each manure type (Tables 2 and 3), and a

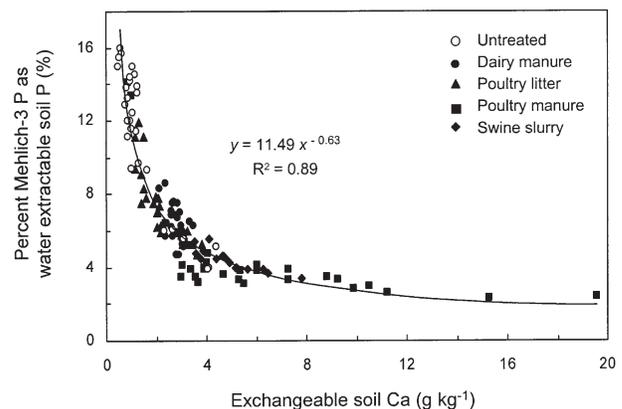


Fig. 4. Relationship between the percentage of Mehlich-3 as water-extractable soil P and exchangeable Ca for untreated and manured soils from New York, Oklahoma, and Pennsylvania.

key control of water solubility of soil P. For instance, Siddique and Robinson (2003) found that soil P solubility (0.01 M CaCl₂ extractable) decreased ($R^2 = 0.75$) with an increase in exchangeable soil Ca resulting from the application of poultry litter, poultry manure, and biosolid (each at 100 mg P kg⁻¹ soil) to five agricultural soils of pH 5.6 to 5.9 in Berkshire, UK. In that study, 100 mg kg⁻¹ of Ca was added in poultry litter, 137 mg kg⁻¹ in poultry manure, and 200 mg kg⁻¹ in biosolids. A similar effect of added Ca on soil P extractability may be expected with liming calcareous high P soils as a result of previous mineral fertilizer applications (Westermann, 1992).

Soil Phosphorus Fractionation

Fractionation of soil P revealed significant differences in the distribution of organic and inorganic P forms. Concentrations of P in inorganic fractions were significantly greater in soils receiving manures compared with untreated soil at all sites (Table 5). Organic fractions and residual P (i.e., occluded inorganic P and stable organic P) were also significantly greater in manured soils (Table 6). However, results revealed a relative increase in inorganic P forms compared with organic P in soils to which manure had been applied. In untreated soils, 43 to 74% of the total P was inorganic, compared with 49 to 80% in manured soils (Table 7). Several other studies have also shown more inorganic than organic P in soils that have received long-term applications (>10 yr) of different types of manures (Gale et al., 2000; Motavalli and Miles, 2002; Sharpley et al., 1998).

In untreated soils, most of the inorganic P was hydroxide IP (21–130 mg kg⁻¹) followed by acid IP, bicarbonate IP, and resin P (Table 5). However, in manured soils, most inorganic P was comprised of acid IP (193–5500 mg kg⁻¹). For example, hydroxide IP and acid IP averaged 49 and 22% of the inorganic P in untreated soils, while in manured soils 27% was hydroxide IP and 49% was

Table 6. Organic P fractions and residual P in the 0- to 5-cm depth of untreated (Unt.) and manured (Tr.) soils.

| Soil | Bicarbonate OP | | Hydroxide OP | | Residual P | |
|-----------------------|---------------------|-----|--------------|-----|------------|------|
| | Unt. | Tr. | Unt. | Tr. | Unt. | Tr. |
| | mg kg ⁻¹ | | | | | |
| Dairy manure | | | | | | |
| Bucks | 44 | 125 | 78 | 313 | 84 | 571 |
| Chester | 30 | 116 | 116 | 213 | 228 | 395 |
| Duffield | 22 | 83 | 97 | 173 | 165 | 256 |
| Morris | 48 | 82 | 119 | 228 | 104 | 340 |
| Oquaga | 32 | 85 | 112 | 192 | 198 | 387 |
| Wellsboro | 24 | 38 | 115 | 146 | 206 | 378 |
| Poultry litter | | | | | | |
| Cahaba | 12 | 68 | 44 | 216 | 57 | 189 |
| Kullit | 11 | 87 | 23 | 172 | 32 | 196 |
| Muskogee | 28 | 47 | 145 | 220 | 197 | 298 |
| Ruston | 24 | 56 | 40 | 65 | 89 | 207 |
| Shermore | 19 | 43 | 30 | 142 | 99 | 293 |
| Poultry manure | | | | | | |
| Bucks | 52 | 139 | 142 | 288 | 94 | 262 |
| Duffield | 44 | 120 | 133 | 184 | 147 | 243 |
| Hagerstown | 64 | 142 | 116 | 250 | 197 | 320 |
| Morris | 31 | 122 | 83 | 354 | 68 | 443 |
| Oquaga | 27 | 162 | 94 | 347 | 178 | 988 |
| Wellsboro | 46 | 150 | 96 | 472 | 160 | 1540 |
| Swine slurry | | | | | | |
| Captina | 14 | 22 | 35 | 39 | 129 | 166 |
| Sallisaw | 17 | 28 | 54 | 60 | 96 | 130 |
| Stigler | 14 | 23 | 65 | 91 | 99 | 134 |

acid IP (Table 7). Application of manure to soil appeared to have the greatest influence on acid IP relative to the other P fractions (Tables 5 and 7). For example, after 25 yr of poultry manure application (200 kg P ha⁻¹ yr⁻¹), the Wellsboro silt loam had an acid IP concentration of 5500 mg kg⁻¹, increasing from 30 to 64% of inorganic soil P. In fact, differences in acid IP between untreated and manured soils were exponentially related to differences in exchangeable Ca between untreated and manured soils ($R^2 = 0.89$; Fig. 5). The general shift in soil P chemistry with manure application from Fe- and Al- to Ca-reaction products likely resulted in a relatively greater extraction of P by the Mehlich-3 reagent.

Table 5. Inorganic P fractions in the 0- to 5-cm depth of untreated (Unt.) and manured (Tr.) soils.

| Soil | Resin IP | | Bicarbonate IP | | Hydroxide IP | | Acid IP | | Total inorganic P | |
|-----------------------|---------------------|-----|----------------|------|--------------|------|---------|------|-------------------|------|
| | Unt. | Tr. | Unt. | Tr. | Unt. | Tr. | Unt. | Tr. | Unt. | Tr. |
| | mg kg ⁻¹ | | | | | | | | | |
| Dairy manure | | | | | | | | | | |
| Bucks | 13 | 394 | 20 | 925 | 86 | 678 | 48 | 1780 | 167 | 3780 |
| Chester | 26 | 361 | 23 | 290 | 120 | 441 | 84 | 1320 | 253 | 2410 |
| Duffield | 15 | 321 | 10 | 174 | 103 | 441 | 49 | 510 | 177 | 1450 |
| Morris | 12 | 229 | 28 | 232 | 97 | 236 | 72 | 550 | 209 | 1250 |
| Oquaga | 16 | 161 | 13 | 143 | 98 | 264 | 85 | 559 | 212 | 1130 |
| Wellsboro | 20 | 79 | 15 | 149 | 86 | 212 | 63 | 309 | 184 | 749 |
| Poultry litter | | | | | | | | | | |
| Cahaba | 8 | 67 | 10 | 53 | 21 | 77 | 7 | 256 | 46 | 453 |
| Kullit | 6 | 146 | 8 | 126 | 32 | 194 | 10 | 359 | 56 | 825 |
| Muskogee | 15 | 124 | 17 | 104 | 106 | 269 | 63 | 446 | 201 | 943 |
| Ruston | 14 | 162 | 18 | 151 | 40 | 154 | 15 | 320 | 87 | 787 |
| Shermore | 12 | 108 | 7 | 93 | 29 | 220 | 10 | 355 | 58 | 776 |
| Poultry manure | | | | | | | | | | |
| Bucks | 29 | 382 | 20 | 293 | 123 | 295 | 65 | 802 | 237 | 1770 |
| Duffield | 22 | 283 | 29 | 174 | 88 | 322 | 31 | 708 | 170 | 1490 |
| Hagerstown | 14 | 184 | 39 | 141 | 34 | 127 | 99 | 370 | 186 | 822 |
| Morris | 16 | 403 | 14 | 284 | 130 | 680 | 82 | 814 | 242 | 2180 |
| Oquaga | 21 | 532 | 20 | 706 | 82 | 945 | 74 | 3090 | 197 | 5280 |
| Wellsboro | 17 | 757 | 28 | 1150 | 113 | 1210 | 60 | 5500 | 218 | 8610 |
| Swine slurry | | | | | | | | | | |
| Captina | 12 | 49 | 10 | 37 | 62 | 124 | 11 | 329 | 95 | 539 |
| Sallisaw | 10 | 53 | 9 | 46 | 30 | 76 | 10 | 193 | 59 | 368 |
| Stigler | 17 | 48 | 20 | 40 | 66 | 123 | 21 | 277 | 124 | 488 |

Table 7. Percentage of inorganic P in resin, bicarbonate, hydroxide, and acid fractions and of total P as inorganic P (IP) in the 0- to 5-cm depth of untreated (Unt.) and manured (Tr.) soils.

| Soil | Resin IP | | Bicarbonate IP | | Hydroxide IP | | Acid IP | | Total IP | |
|-----------------------|----------|-----|----------------|-----|--------------|-----|---------|-----|----------|-----|
| | Unt. | Tr. | Unt. | Tr. | Unt. | Tr. | Unt. | Tr. | Unt. | Tr. |
| | % | | | | | | | | | |
| Dairy manure | | | | | | | | | | |
| Bucks | 8 | 10 | 12 | 24 | 51 | 18 | 29 | 47 | 45 | 79 |
| Chester | 10 | 15 | 9 | 12 | 47 | 18 | 33 | 55 | 40 | 77 |
| Duffield | 8 | 22 | 6 | 12 | 58 | 30 | 28 | 35 | 38 | 74 |
| Morris | 6 | 18 | 13 | 19 | 46 | 19 | 34 | 44 | 44 | 66 |
| Oquaga | 8 | 14 | 6 | 13 | 46 | 23 | 40 | 50 | 38 | 63 |
| Wellsboro | 11 | 11 | 8 | 20 | 47 | 28 | 34 | 41 | 35 | 57 |
| Poultry litter | | | | | | | | | | |
| Cahaba | 17 | 15 | 22 | 12 | 46 | 17 | 15 | 57 | 29 | 49 |
| Kullit | 11 | 18 | 14 | 15 | 57 | 24 | 18 | 44 | 46 | 64 |
| Muskogee | 7 | 13 | 8 | 11 | 53 | 29 | 31 | 47 | 35 | 63 |
| Ruston | 16 | 21 | 21 | 19 | 46 | 20 | 17 | 41 | 36 | 71 |
| Shermore | 21 | 14 | 12 | 12 | 50 | 28 | 17 | 46 | 28 | 62 |
| Poultry manure | | | | | | | | | | |
| Bucks | 12 | 22 | 8 | 17 | 52 | 17 | 27 | 45 | 45 | 72 |
| Duffield | 13 | 19 | 17 | 12 | 52 | 22 | 18 | 48 | 34 | 73 |
| Hagerstown | 8 | 22 | 21 | 17 | 18 | 15 | 53 | 45 | 33 | 54 |
| Morris | 7 | 18 | 6 | 13 | 54 | 31 | 34 | 37 | 57 | 70 |
| Oquaga | 11 | 10 | 10 | 13 | 42 | 18 | 38 | 59 | 40 | 78 |
| Wellsboro | 8 | 9 | 13 | 13 | 52 | 14 | 28 | 64 | 42 | 80 |
| Swine slurry | | | | | | | | | | |
| Captina | 13 | 9 | 11 | 7 | 65 | 23 | 12 | 61 | 35 | 70 |
| Sallisaw | 17 | 14 | 15 | 13 | 51 | 21 | 17 | 52 | 26 | 63 |
| Stigler | 14 | 10 | 16 | 8 | 53 | 25 | 17 | 57 | 41 | 66 |

Differences in inorganic P concentrations observed in this study are consistent with those reported elsewhere. Graetz and Nair (1995) found that the total P concentration of the surface A horizon (0–20 cm) of three Spodosols (Myakka, Immokalee, and Pomello fine sands) receiving dairy manure for 8 to 32 yr (1680 mg kg^{-1}), was about 50 times greater than untreated soils (34 mg kg^{-1}). This total P increase was concomitant with a general shift from Al- and Fe-P to Ca-P forms (Graetz and Nair, 1995). For example, hydroxide IP (Al- and Fe-bound P) was 49% and acid IP (Ca-P) was 9% of total P in untreated soils, while in manured soils 8% was hydroxide IP and 70% was acid IP.

Unlike inorganic soil P, P added in manure was evenly distributed across organic soil P fractions (Table 6). In untreated soils, bicarbonate OP and hydroxide OP accounted for 24 and 74% proportions of total organic P. In manured soils, bicarbonate OP and hydroxide OP accounted for 30 and 70% of total organic P (Table 6).

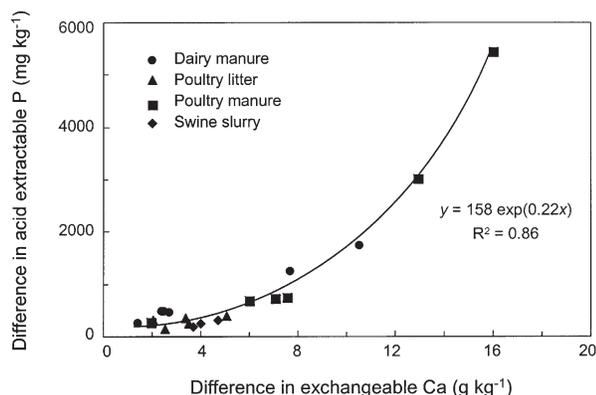


Fig. 5. Relationship between the acid extractable inorganic P difference in untreated and manured soils and exchangeable Ca difference in untreated and manured soils.

Siddique and Robinson suggested that soluble organic compounds of low molecular weight form complexes with Al, Fe, and Ca that increase soil P sorption capacity and, thus, decrease water extractability of soil P. The extent to which Ca in manure adds to the pool of exchangeable Ca in soil depends to a large degree on the nature of the bond between organic molecule and Ca in added manure (Siddique and Robinson, 2003; Wen et al., 1999). As organic compounds in fresh manures are of low molecular weight, the added Ca can readily contribute to the pool of exchangeable soil Ca (Siddique and Robinson, 2003).

Ion-Activity Products

There was a difference in the dominant form of crystalline Ca-P minerals in manured compared with untreated soils as shown by Ca-P double function plots of solubilities of three soils for each manure type (Fig. 6). Hydroxapatite was the main mineral form of Ca-P in all untreated soils (Fig. 6). In manured soils, crystalline Ca-P forms were dominated by more soluble tricalcium P and octocalcium P minerals (Fig. 6). This infers that as more P and Ca are introduced into the system, P is increasingly precipitated in more soluble Ca-P forms. Furthermore, the general decrease in water-extractable P compared with Mehlich-3 P suggests that while these minerals are not extractable by water, these compounds are readily dissolved in the acid buffered matrix of the Mehlich-3 solution. Tran and Simard (1993) point out that the Mehlich-3 soil test has the advantages of being less neutralized by CaCO_3 and is less aggressive toward solubilizing apatite and other Ca-P compounds than more acidic soil P tests (e.g., Bray-1 or Mehlich-1). However, our data would suggest that the Mehlich-3 soil test still solubilizes Ca-P compounds that limit water-

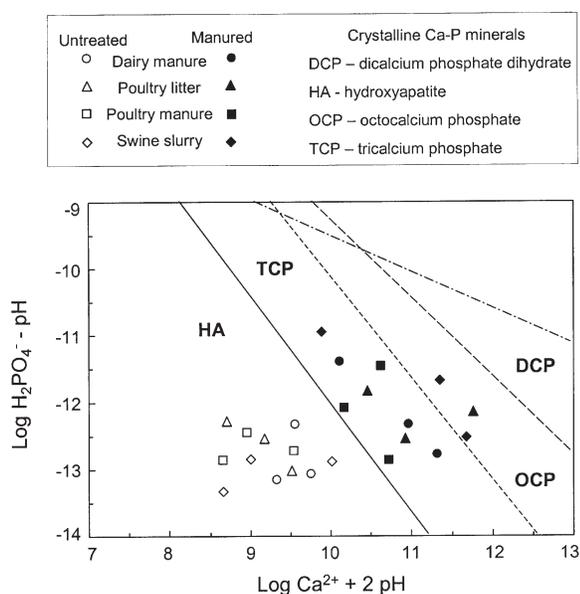


Fig. 6. Calcium phosphate double function plot of solubilities for untreated and manured surface soil (0- to 5-cm depth) in relation to dicalcium phosphate dihydrate, DCPD; octocalcium phosphate, OCP; tricalcium phosphate, TCP; and hydroxyapatite, HA.

extractable P and therefore, may overestimate P loss potential if based on a soil test alone.

Implications to Soil Testing

The change in P concentration, form, and solubility with application of manure has important implications to soil P testing. In fact, there are two processes that could influence soil test P results and recommendations. First, the dramatic increase in Ca-bound P (acid IP) in manured soils can result in a relatively greater dissolution of P by the acidic Mehlich-3 extractant than in untreated soils (Mallarino, 1997; Sen Tran et al., 1990). This could result in an overestimation of plant available P as determined by this soil test method. This is not of agronomic concern due to the fact that the high Mehlich-3 P levels (up to 2840 mg kg⁻¹) are considerably greater than optimum Mehlich-3 P levels for commonly manured crops (30–50 mg kg⁻¹ Mehlich-3 P; Beegle, 2001).

Second, and more important to environmental soil P testing of manured soils, is the diminishing proportion of water-extractable P with increasing Mehlich-3 P. Several recent studies have shown a leveling off of dissolved P concentrations in overland flow with continued increase in Mehlich-3 P (Torbert et al., 2002) and Bray-1 P (Davere de et al., 2003). For instance, Torbert et al. (2002) observed less of an increase in dissolved P concentration of overland flow when surface soil (0–2.5 cm) Mehlich-3 P was greater than about 100 mg kg⁻¹ compared with below this value, for two calcareous (Houston Black and Purves) and one noncalcareous (Blanket) soil in Texas. These soils had been amended with dairy manure to achieve target Mehlich-3 P levels of 60 to 360 mg kg⁻¹, 6 mo before overland flow. Further, Torbert et al. (2002) found that dissolved P concentration was significantly less ($P < 0.05$) in overland flow from the calcare-

ous (0.23 and 0.34 mg L⁻¹) than noncalcareous soils (0.70 and 1.37 mg L⁻¹) at a given Mehlich-3 P (200 mg kg⁻¹).

The implications of this change in water extractability relative to Mehlich-3 P in environmental soil P testing are highlighted using published data relating water extractable and Mehlich-3 P to dissolved P in overland flow, from four Pennsylvania soils (McDowell and Sharpley, 2001), four Arkansas soils (Pote et al., 1996, 1999), and four Texas soils (Torbert et al., 2002). The combined data gave the overland flow dissolved P vs. soil P regression equations ($p < 0.01$) shown below:

$$\text{Overland flow dissolved } P = 0.0031 \times \text{Mehlich-3 soil } P + 0.129 \quad R^2 = 0.64 \quad [3]$$

$$\text{Overland flow dissolved } P = 0.0294 \times \text{Water extractable soil } P + 0.124 \quad R^2 = 0.73 \quad [4]$$

where the units of overland flow P are milligrams per liter (mg L⁻¹) and Mehlich-3 and water extractable soil P are milligrams per kilograms (mg kg⁻¹). The data used to develop Eq. [3] and [4] ranged in Mehlich-3 P from 15 to 775 mg kg⁻¹ and in water-extractable P from 1 to 56 mg kg⁻¹. Using Eq. [3] and measured Mehlich-3 P for a low (22 mg kg⁻¹) and high P Wellsboro soil (539 mg kg⁻¹) from the present study, overland flow dissolved P can be estimated. The Wellsboro was selected because Mehlich-3 P for the untreated (22 mg kg⁻¹) and manured soil (539 mg kg⁻¹) was within the range of values used to develop Eq. [3], and was close to our previously discussed Mehlich-3 P threshold value of 400 mg kg⁻¹. If overland flow occurred from these soils, the dissolved P concentration predicted from Mehlich-3 P using Eq. [3] was 0.197 mg L⁻¹ for the low and 1.80 mg L⁻¹ for the high P soil. For the low P soil, overland flow dissolved P predicted from water-extractable soil P (2.5 mg kg⁻¹) using Eq. [4], was 0.198 mg L⁻¹, which is similar to that predicted from Mehlich-3 P (0.197 mg L⁻¹). For the high P soil, however, an overland flow dissolved P concentration of 1.24 mg L⁻¹ was predicted from water-extractable P (38 mg kg⁻¹), which is lower than that predicted from Mehlich-3 P (1.80 mg L⁻¹).

Assuming water-extractable soil P reflects the extent of P release from surface soil and provides a more reliable estimate of overland flow dissolved P than Mehlich-3 P (McDowell and Sharpley, 2001; Pote et al., 1999), use of Mehlich-3 P may overestimate the potential of heavily manured soils to enrich overland flow with P. This overestimation may explain the plateau in the relationship between Mehlich-3 P and overland flow dissolved P observed by Torbert et al. (2002). Thus, at high soil P levels, Mehlich-3 P is likely extracting some P that may not be immediately released from manured surface soil to overland flow.

CONCLUSIONS

The long-term application of manure can result in an accumulation of large amounts of P, particularly as Mehlich-3 and acid-IP. There is an overall change in P chemistry with inorganic P comprising 26 to 57% of total P in untreated soils, increasing to 49 to 80% of

total P in manured soils. This change in soil P form with manuring, is also accompanied by a shift in P chemistry and reaction products from Al- and Fe-dominated complexes (49% of inorganic P in untreated soils) to Ca minerals (49% of inorganic P in manured soils), as well as an average 0.7 unit increase in soil pH.

Results of the present study show that there is a change in extractability and dominant forms of P in soils with long-term application of manures. Overall, P extractability and solubility in heavily manured soils tended to be dominated by Ca reaction products. This has important implications to environmental recommendations for agricultural P management if routine acid-based soil test extractants, such as Mehlich-3 P are used. It is suggested that for the New York, Oklahoma, and Pennsylvania soils used in this study, an environmental threshold of about 400 mg kg⁻¹ exists for Mehlich-3 P, where above and below this value different relationships should be used to estimate the potential P enrichment of overland flow by soil P release.

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