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Long-Term Dynamics of Phosphorus Forms and Retention in Manure-Amended Soils

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Phosphorus (P) leaching from soils with elevated P levels due to manure applications is increasingly becoming a concern as a source of eutrophication of streams and lakes. This study investigates the relationship between organic and inorganic P in soil pools and equilibrium leachate along a chronosequence of poultry and dairy manure additions in New York state. Resin-extractable P (molybdate-reactive P, RP) and total soil P reached very high levels of 2330 and 7343 mg of P kg^{-1}, respectively, after more than 25 years of continuous manure applications. After long-term manuring, the ability of these soils to retain additional P was low (Langmuir maximum sorption potential of 51−59 g of P kg^{-1}) and equilibrium leachate concentrations of total dissolved P (TDP) were high (5.5−7.6 mg L^{-1}; saturated conditions, 0.15-m lysimeters in closed loop). Total dissolved P concentrations in equilibrium leachate increased linearly ($r = 0.737$) to a total soil P of 4500 mg kg^{-1} and increased to a greater extent above 4500−5500 g kg^{-1} (change point equivalent to about 1500 mg kg^{-1} Mehlich 3-extractable RP). The proportion of dissolved unreactive P (DUP) in equilibrium leachate decreased from 90% of TDP in fields with a short manure application history to 2% of TDP where mainly poultry manure had been applied for >25 years, while unreactive P (UP) in soil decreased from 44% to 6%. Dissolved RP (DRP) was less mobile than DUP in soils with short duration of manure applications ($p < 0.05$), while differences between DUP and DRP mobility disappeared with longer duration of manure application and greater total soil P. Organic P forms in NaOH/NaF extracts determined by ^{31}P NMR did not change with manure history, but sequential fractionation showed that the relative distribution of RP pools in soils changed. Dilute acid P_i increased from 10% to 62% with longer poultry manure additions, suggesting the formation of calcium phosphates as the soil pH increased from 4.1 to 6.0−7.2. The precipitation of P as calcium phosphates appeared to influence leachable P upon high and long-term applications of manure dominated by poultry litter.

Introduction

Animal manure as a waste product poses a widespread challenge in agricultural production systems in industrialized countries (*1*). Animal manures are a great source of plant-available P, but manures are often applied in excess of crop demands for P, resulting in increases in soil test P levels (*2*) and P losses from agricultural landscapes. Agriculture is now responsible for an estimated 48% of the water quality problems in rivers and streams (*3*). Phosphorus enrichment of our surface waters can lead to eutrophication that threatens fish and other fauna in lakes and rivers as well as drinking water quality, especially in states such as New York, where drinking water for a large portion of the population is derived from surface water reservoirs (*4*).

Until the mid 1990s, research largely focused on P losses by erosion (*5*−*7*). Leaching losses of P were generally considered insignificant because of the strong adsorption capacity of clay minerals for inorganic phosphate. Phosphate is able to form binuclear bridges with OH surface groups on minerals, and soil solution concentrations of P are therefore commonly low (*8*). However, the continued application of animal manure to soil over the past decades has created situations whereby P leaching actually occurred (*9*−*15*). Greater P leaching losses may accelerate P exports from agricultural landscapes to surface waters. Leaching of P would then also bypass efforts to reduce surface runoff and surface transport of P (*16*) and is in general more difficult to control when P export from critical watershed areas is targeted (*17*). Several studies have been conducted to determine how much P can be applied with manure before significant P leaching occurs (*18*) and how much P is leached after thresholds are reached (*2*, *19*−*21*). However, there is a lack of studies that address the extent of inorganic and organic P leaching in relationship to the properties of organic and inorganic P pools in soil.

To evaluate the mobility of P in soils with a long-term manure history, a better understanding of the relative contributions of different forms of P is needed. Currently, only a few studies inform about both inorganic and organic P pools in excessively manured soils (*11*, *22*). Most of the data on P levels in soils with excess manure applications have been obtained by soil testing methods designed for predicting plant response to fertilizer P and dilute salt extractions as environmental risk indicators (*14*, *17*, *23*). While this approach is valuable for conducting risk analyses (*24*−*26*), it does not yield mechanistic information about P cycling in soils. Organic P may significantly contribute to leached P under manure additions (*27*, *28*) and agronomic soil tests may not necessarily quantify those organic and inorganic P pools that control P leachate concentrations. Research is needed to determine which forms of P are most readily leached in heavily manured fields and how these P forms in leachate relate to P forms in the soil.

Separate analyses of inorganic and organic P pools in soil and soil solution will allow for an improved understanding of the mechanisms involved in soil controls on P leaching. Some studies report on either soil P fractionation (*29*) or leachate P analyses (*28*). Little information is currently available that relates both inorganic and organic P in soil to inorganic and organic P in leachates for a wide range of soil P contents. Since most of the P in animal manure is in inorganic form (*29*), the dominance of organic P may decrease in excessively manured soils. If on the other hand organic P is an important form of leached P in manured soils, as shown by several studies (*27*, *28*), changes in the amounts of organic P may be also reflected by changes in the composition of organic P in soils (*22*). In soils with large amounts of cattle manure additions, ^{31}P NMR spectroscopy of soil extracts indicated a shift from monoester to diester

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TABLE 1. Site Description and Characteristics of Soils with Different Histories of Manure Applications

sample ID[a]	duration of application[b] (years)	source[b]	cropping systems	BD[c] $(Mg\ m^{-3})$	clay (%)	pH (H_2O)	OM[c] (%)	RP[d] $(mg\ kg^{-1})$	Ca[d] $(mg\ kg^{-1})$	Al[d] $(mg\ kg^{-1})$
FO	0	none	none	nd	19	4.09	8.3	42	188	1555
S1	6	DC	corn	1.36	17	5.96	7.2	21	1223	714
S2	<2	DC	pasture	nd	17	6.83	6.8	78	2438	703
S3	6	PM, PF	corn	nd	16	7.23	6.3	725	3230	709
M1	10−15	DC, PF	corn−alfalfa−hay	nd	24	7.42	7.8	565	2612	572
M2	10−15	PM, DC, PF	corn−alfalfa−hay	nd	16	7.36	6.3	1469	4960	624
M3	10−15	PM, DC, PF	corn−alfalfa−hay	1.18	15	7.06	7.0	1070	4474	729
L1	≈25	PM, PF	corn−alfalfa−hay	nd	15	7.35	5.7	1120	4709	608
L2	>25	PM, DC, PF	corn	1.05	15	7.05	7.5	1834	6165	508
L3	>25	PM, DC, PF	corn	nd	12	7.14	6.7	2330	8576	460

[a] Sample identification; FO, forest; S, short-term; M, medium-term; L, long-term manure applications. [b] Estimated from farm records; PM, poultry manure; DC, dairy cow manure; PF, phosphorus fertilizer. [c] nd, not determined; BD, bulk density; OM, organic matter. [d] Nutrients and Al extracted by the Mehlich-3 method. RP, reactive phosphorus.

orthophosphate with manure additions to soil (*30*). Long-term dynamics of P forms along a gradient of manure additions, however, have not been investigated up to now.

The objectives of this work are to study the long-term dynamics of manure additions to soil with respect to forms and properties of P in soil in relationship to leachate. Samples were taken along a chronosequence of soils differing in number of years of poultry and/or dairy manure applications ranging from a forest soil without a manure history to fields with more than 25 years of manure application showing extremely high accumulation of P. We hypothesized that organic P is an important source of leachable P and that forms of organic P compounds in soil change under long-term manure applications. Small column experiments as well as sequential P fractionation and ^{31}P NMR spectroscopy were used to test these hypotheses.

Experimental Methods

Experimental Site. The experimental site is located in Steuben County in southern New York state. Mean annual temperature is about 7.2 °C and mean annual rainfall is 933 mm (from the North American Climate Center for Alfred, NY). The soils are silt loams, glacial till soils with low pH (5−6 in water) and moderate organic matter contents (40−60 mg g^{-1}). They are classified as coarse-loamy, mixed, mesic Typic Fragiudepts (Wellsboro channery silt loam) to loamy-skeletal, mixed, mesic Dystrudepts (Oquaga channery silt loam) (*31*). Slopes are 2−5% and soils are moderately well drained.

Field sites were selected based on estimated history of manure applications [short-term (S), <6 years; medium-term (M), 10−15 years; and long-term (L), >25 years of manure application] in comparison to an unmanured forest (Table 1). Three fields were chosen in each category of manured fields. The sites are located within an area of 4 km^2 and are 2−4 ha in size. The spatial proximity, similar slope and landscape position, and similar soil texture (Table 1) confirm that soil parent material is comparable between fields and that observed differences in soil properties can be attributed to different manure management and not to differences in preexisting soil properties. Fields varied in P accumulation as a function of years of application but also due to varying application rates and manure sources (poultry versus dairy) (Table 1). Fields dominated by a dairy manure history received an estimated 30−140 kg total P $ha^{-1}\ yr^{-1}$ while the highest P fields had received poultry manure only (Table 1) at estimated rates of 120−310 kg total P $ha^{-1}\ yr^{-1}$. The history of Mehlich 3-extractable P concentrations for each of the fields since 1985 is shown in Figure 1 (sampling and analysis methods described below). The methods of manure application and other operations were similar for all fields as they were all located on the same farm.

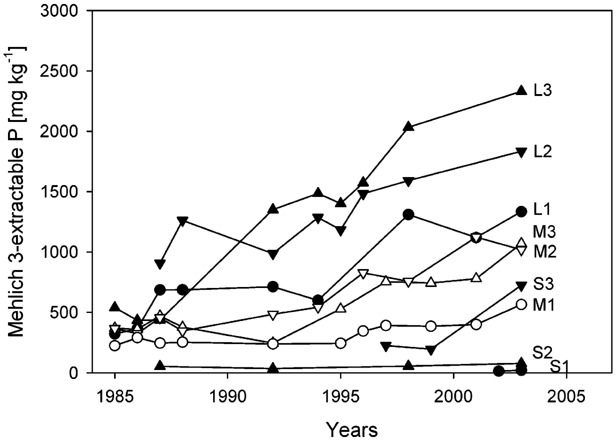

FIGURE 1. Mehlich 3-extractable total P for soils with historically different duration of manure applications in southern New York state (Table 1).

For at least the past 20 years for which records were available, fields in corn crops were chisel-ploughed to a depth of no more than 0.175 m (7 in.) prior to planting but no other tillage took place (i.e., surface application of manure without incorporation). Cropping systems differed for the different sites (Table 1). For fields S1, S3, L2, and L3, the cropping system was continuous corn (*Zea mays* L.), S2 was a permanent pasture, and M1−3 and L1 were in a corn−alfalfa (*Medicago sativa* L.)−hay rotation. Corn is generally planted in May and harvested in September. The annual fertilizer application for continuous and rotational corn (in addition to manure) was 20−25 kg of N ha^{-1} (as diammonium phosphate, DAP) or 0−15 kg of P ha^{-1} (as triple super phosphate, TSP) in the 1990s, but none of the fields had received inorganic fertilizers since 1996−1999. Alfalfa was not fertilized.

Soil Sampling and Wet-Chemical Analysis. Samples (one composite sample from 15 subsamples per field) were taken from 0 to 0.175 cm (0−7 in.) in irregular intervals always in spring since 1985, air-dried at room temperature (about 20 °C), and sieved to pass 2 mm prior to chemical analyses. Mehlich 3-extractable reactive P (RP) (*32*) was determined by the molybdate ascorbic acid method (*33*) immediately following sample preparation. All air-dried samples were stored in a dry and cool storage facility for no longer than a few weeks before processing. Calcium and aluminum (for the data in Figure 1 also P) were measured in the same extract by inductively coupled plasma atomic emission spectrometry, ICP-AES [Ciros (CCD), Spectro, Germany]. The pH was measured with a glass electrode (SP20, Thermo Orion), and organic matter was determined by loss on ignition (*34*). Adsorption isotherms were obtained by equilibrating 3 g of soil, from a subset of the samples (S2, M1−3, L2−3) obtained in April 2003, in a 50-mL centrifuge tube with 30 mL of a 0.01 M KCl solution containing either 1, 5, 10, 20, 40, 80, 160, or 320 mg of P L^{-1} from KH_2PO_4. One drop of chloroform was added to each tube to suppress microbial activity. The tubes were agitated on a reciprocal shaker at room temperature (about 20 °C) for 3 days. Preceding experiments showed that equilibrium was reached after 3 days. Samples were centrifuged at 5000 rpm (relative centrifugal force of 2988*g*) for 10 min and the supernatant was analyzed for RP by the molybdate ascorbic acid method (*33*). For quantification of desorption, 30 mL of 0.01 M KCl without P was added to remaining soils in centrifuge tubes from fields S2, M3, and L2 that were used for the adsorption. Desorption was determined with the same procedure as the adsorption (3-day extraction time).

Soil samples from 2003 were also analyzed for inorganic and organic P pools by sequential fractionation (*35*). Inorganic P was measured by the molybdate ascorbic acid method and given as reactive P (RP) and total P by ICP-AES (not by persulfate digestion). Organic P was calculated as the difference between total and RP. All values of organic P may be slightly underestimated, because they were computed by difference with reactive P that can contain some organic P and are therefore given as unreactive P (UP). Each sample for adsorption and sequential extraction was analyzed in duplicate.

Spectroscopic Analyses. Organic P forms were determined by liquid-state ^{31}P nuclear magnetic resonance (NMR) spectroscopy. Air-dried bulk soil samples obtained in April 2003 were extracted with a 0.1 M NaOH and 0.4 M NaF mixture at a soil to extraction solution ratio of 1:5 (w/v) under N_2 environment. The extraction procedure followed the outline of Schnitzer (*36*), as modified by Solomon et al. (*37*). Subsequently, the 0.1 M NaOH/0.4 M NaF extracts were filtered through a 0.2-μm membrane filter (Gelman Supor; Pall Gelman Laboratory) under pressure. This procedure was repeated once more with the same membrane filter, where the partial plugging of the filter helped to remove fine clay. The extracts were transferred into dialysis tubes [Spectra/Por Membrane, molecular weight cutoff (MWCO) 12 000−14 000 Da; Spectrum Laboratories] and dialyzed against distilled−deionized water in order to eliminate soluble salts (*37*, *38*). Finally the extracts were freeze-dried. Fifty milligrams of freeze-dried materials were dissolved in 1.5 mL of 0.5 M NaOD in NMR tubes and analyzed within 12 h by ^{31}P NMR spectroscopy. Liquid-state ^{31}P NMR spectra were acquired on a Bruker DRX 400 NMR spectrometer (Bruker Instruments) at 162 MHz without ^1H decoupling and at a temperature of 300 K. An accusation time of 0.1 s, a 90° pulse, and a relaxation delay of 2 s were used. Spectra were recorded with a line broadening of 20 MHz after 13 000 scans were collected. Preliminary measurements with different relaxation times of 0.311−3.1 s showed that such a delay would give better resolution of spectra. Chemical shifts were determined relative to 85% orthophosphoric acid before the measurement of each sample. Intensities of signals were quantified by electronic integration of peaks. The resonances around δ = 15.5 ppm were assigned to phosphonates. Intense signals between δ = 1.7 and 1.3 ppm represent orthophosphate monoesters, a diverse P form comprising inositol phosphate, sugar phosphate, and mononucleotides (*39*). The signals around δ = 0.4 ppm may originate from teichoic acids, an orthophosphate diester that consists of glycerol or sugar molecules linked by phosphate groups (*40*). Resonances around δ = −2.0 and−5.0 ppm have not yet been identified (*38*, *41*); thus they were assigned as unknown A and B, respectively. Orthophosphate diesters (phospholipids and DNA) resonate at δ = −3.0 to −3.6 ppm. Signals accounting for inorganic orthophosphate P appeared around δ = 2.5 ppm, while the peaks around δ = −7.6 ppm were assigned as pyrophosphates. Polyphosphates usually appear around δ = −20.0 ppm.

Equilibrium Solution Concentrations. In April 2003, undisturbed samples were taken in steel cylinders with a diameter of 0.1 m and a length of 0.15 m; they therefore represent approximately the depth of the plough layer of not more than 0.175 m. Samples were stored field-moist at 4 °C before leaching started in order to avoid artifacts by drying and rewetting (*42*). Three replicate cylinders per field were slowly saturated with deionized water from below and mounted by use of steel fittings, Teflon seals, and Tygon tubing (MH 2075) to avoid contamination with soluble organics. The solution was pumped (peristaltic pump, BVK-MS/CA8-6, Ismatec) through the columns by saturated hydraulic conductivity (50 mm day^{-1}) at room temperature (20 °C) and added to the top of the column in a closed loop. Saturated conductivity was determined by measuring the falling head using the same columns (N = 6; minimizing water level differences and changes in flow characteristics). Solution samples were taken after each full displacement of one pore volume and samples were analyzed for dissolved reactive P (DRP) as described above. This was repeated until a steady state of DRP concentrations was achieved. Final equilibrium solution samples were filtered at 0.45 μm, DRP was analyzed by the ascorbic acid method, and organic P was determined by difference between DRP and total P and given as dissolved unreactive P (DUP). Total dissolved P (TDP) was measured by the ascorbic acid method after digestion of organic P with ammonium persulfate (*35*). It is important to note that the conditions under which these equilibrium P concentrations were obtained do not represent natural conditions. First, P flow paths under saturated conditions include both matric and preferential flow and this may not be the case throughout the entire year. Second, the closed loop experiment may result in an overestimation of P concentrations since contact times are longer. However, leachate TDP concentrations obtained with open cylinders were strongly related to those obtained in a closed loop (r = 0.89; N = 9) with about half the concentration (regression slope of 0.4). Solution concentrations were less variable between replicate cylinders for closed (CV = 2−45%) than open cylinders (CV = 6−90%). The 0.15-m core length was chosen to be at or slightly shorter than the depth of the plough layer in order to enable a comparison between DRP or TDP in leachate and soil P contents as well as properties, assuming that the plough layer is well mixed and no significant vertical gradient exists within the core.

Data Analyses. The amount of additionally sorbed P was calculated as the difference between the initial solution concentration and the equilibrium concentration after shaking with soil. Langmuir sorption maximum X_a (milligrams of P per kilogram of soil) and the affinity constant k (liters per milligram) for added inorganic phosphate to the studied soils were calculated from the linear form of the Langmuir equation:

$$X = X_a - \left(\frac{1}{k}\right)\left(\frac{X}{C}\right)$$

with X as the amount of added P sorbed to soil (grams of P per kilogram of soil) and C as the equilibrium concentration (illigrams of P per liter) after adsorption. Linear regressions of adsorption isotherms were tested by the general linear models procedure in the Statistical Analysis System framework (SAS Institute Inc., Cary, NC).

The present approach of a chronosequence has been frequently used to study the effect of time on soil processes where no long-term experiments are available (*43*), as in our case. The challenge typically is that field histories are not identical within the margins of information gathered from farm management histories. The strength is that any observed trends are very robust as such trends are observed despite the variability in field treatments. Comparison of means between fields with different duration of manure applications (long L, medium M, short S) was performed by analyses of variance with a completely randomized design with three replicates (SAS Institute Inc., Cary, NC). In addition, linear and nonlinear regressions between total P in soil and different P forms in soil were computed with SigmaPlot 8.0 (Systat Software Inc., Richmond, CA).

Results and Discussion

Phosphorus Availability and Retention. All fields with the exception of the forest soil (FO), S1, and S2 were classified as very high in P with respect to crop P needs and environmental risk (*44*), but Mehlich 3 RP concentrations were significantly ($p < 0.05$; $N = 3$) higher in the soils that received manure applications for long periods of time (L1–3) containing mainly poultry litter compared to those with short-term manure applications (S1–3) (Table 1). Those soils with high available P concentrations in 2003 also showed high P concentrations in previous years, and P concentrations increased progressively since 1985, when the monitoring of Mehlich 3 soil test levels started (Figure 1). The history of Mehlich 3-extractable P also points out the challenges identifying duration and rates of manure applications from farm management plans. On the fields with long-term manure additions (L1–3), the levels of Mehlich 3-extractable P were extremely high compared to soils investigated in previous studies. Ketterings et al. (*45*) reported Mehlich 3 values between 17 and 575 mg of P kg^{-1} among 235 soils from eight major agricultural areas in New York state. Soils in Texas and Oklahoma with estimated additions of 90–1880 kg of P ha^{-1} yr^{-1} by animal manures for 9–35 years (the maximum annual values of applied P may have been overestimated) reached Mehlich 3 P levels of 85–419 mg of P kg^{-1} (*46*), while Novak et al. (*12*) reported 376-435 mg of P kg^{-1} in a coastal plain soil amended with swine manure for 10 years. Sharpley et al. (*5*) noted that hotspots in Inceptisols and Ultisols in an agricultural watershed of Mahantango Creek, PA, reached Mehlich 3 levels as high as 788 mg of P kg^{-1} as a result of pig slurry applications. Thus, the values obtained in our study on the highest P fields are at a minimum a factor of 2 greater than those obtained in studies from other sites. This provides us with the opportunity to investigate relationships between concentrations and forms of leachable P also for other soils, if current practices of excessive application of P are continued.

The capacity of the soils to adsorb additional fertilizer P decreased with increasing duration of manure additions (Table 2). Soils lost their ability to adsorb significant amounts of P once total P levels reached 1000–2000 mg kg^{-1}. A capacity to adsorb additional P (X_a) below 100 mg kg^{-1} and affinity constants below 0.1 L mg^{-1} are very low compared to maximum adsorption capacities generally found in soils of temperate climates (*47*). In five different glacial till soils of New York State, adsorption capacities determined with batch experiments were found to be 526–1430 mg of P kg^{-1} (*48*). In manured soils, lowest maximum adsorption capacities were reported from 654 mg kg^{-1} in several soils from the northeastern United States and 120 mg kg^{-1} in the United Kingdom ((*19*) adding desorption C_0), to 143 mg kg^{-1} in Reading, U.K. (*49*). The 95% difference in P sorption capacity as a response to long-term manure application in our study (from S2 to L3, Table 2) was significantly greater than the 7–66% reduction found by Siddique and Robinson (*50*). The latter was an incubation study of five different agricultural soils from the United Kingdom, each amended with 100 mg of P kg^{-1} as cattle slurry. Desorption in relationship to adsorption was higher in L2 (208% of adsorption) than S2 (56%) in our study (Table 2). Therefore, adsorption sites for phosphate were largely occupied in our soils following medium- and long-term manure additions, and less inorganic P could be retained than in comparative studies.

TABLE 2. Phosphorus Adsorption,[a] Desorption, and Equilibrium Leachate Concentrations

sample ID[b]	X_a (mg kg^{-1})	k (L mg^{-1})	R	desorption[c] (mg kg^{-1})	leachable TDP (mg L^{-1})
S2[c]	1118.9	0.161	0.74[e]	200.0 (56)	0.11 (90)[d]
M1	604.5	0.119	0.28[f]	nd	0.19 (53)
M2	145.1	0.116	0.34[f]	nd	0.58 (22)
M3	129.3	0.085	0.41[g]	241.5 (83)	0.14 (42)
L2	51.3	0.048	0.90[e]	333.1 (208)	7.64 (2)
L3	58.6	0.039	0.89[e]	nd	5.45 (15)

[a] Maximum Langmuir adsorption capacity (X_a) and affinity constants (k) were obtained from adsorption isotherms by use of the linear form of the Langmuir equation ($X = X_a - (1/k)(X/C)$; with X as additionally adsorbed P and C as equilibrium P concentration in solution [coefficient of variation (CV) < 10%]. [b] Soils with short- (S), medium- (M), and long-term (L) manure histories (Table 1). [c] Desorption from soil with 80 mg L^{-1} phosphate added (values in parentheses are % of adsorption; $N = 2$; CV < 3%). nd, not determined. [d] Values in parentheses are % DUP of TDP ($N = 3$ lysimeters; CV = 2–45%). [e] Significant at 0.001. [f] Not significant. [g] Significant at 0.1.

The low maximum adsorption capacity and high desorption led to high equilibrium TDP concentrations in leachate obtained from saturated columns of long-term manured soils, with highest values being 5.5–7.6 mg L^{-1} (5.1–7.5 mg of DRP L^{-1} for L3 and L2, respectively; Table 2). These values from the equilibrium leaching experiment in a closed loop correlated well with a related experiment where 0.01 M $MgCl_2$ was leached through the columns in an open system ($r = 0.89$; $N = 9$; $p < 0.05$), albeit with lower concentration (slope of 0.4). Even those soils with medium-term manure applications (M1–3) showed comparatively high concentrations of leachable TDP in saturated soil (0.2–0.6 mg of TDP L^{-1}; 0.1–0.5 mg of DRP L^{-1}). Average baseline concentrations of DRP in leachate from undisturbed soil columns of glacial till soils obtained from New York state were 0.03 mg P L^{-1} (*48*), and those of soils from the Appalachian Valley were 0.005–0.009 mg P L^{-1} (*51*). In the first leachate collections after poultry manure applications to 30- and 50-cm intact columns of a Typic Hapludult and an Aquic Fragiudult, DRP immediately peaked with maximum values of 1.1–11.2 mg L^{-1} but decreased rapidly thereafter to values of less than 10% of peak concentrations (*51*). Long-term manured soils from the United Kingdom (described as being “many years” or “longer than 50 years”) showed highest DRP values of 3.7 mg L^{-1} in soil solution obtained from ceramic cups, while lysimeter leachates from NE United States did not exceed 1.5 mg L^{-1} (*19*). Highest DRP concentrations in leachate from 0.2-m deep lysimeters obtained from Delmarva Peninsula, U.S., were found to be 15.3 mg L^{-1} (*21*), compared to a maximum of 32.2 mg L^{-1} found in one of our lysimeters at initial stages of the leaching before equilibrium was reached. Dissolved reactive P values from tiles draining various manure-amended soils from Flanders, Belgium, ranged from <0.1 to 1.5 mg of P L^{-1} (*52*). Therefore, soils that received animal manures for long periods of time such as in our study represent conditions of comparatively high P mobility in soil. The TDP and DRP concentrations obtained in this experiment can only with caution be applied to leachate concentrations under field conditions, as they were obtained under saturated conditions that may not be typical transport conditions and

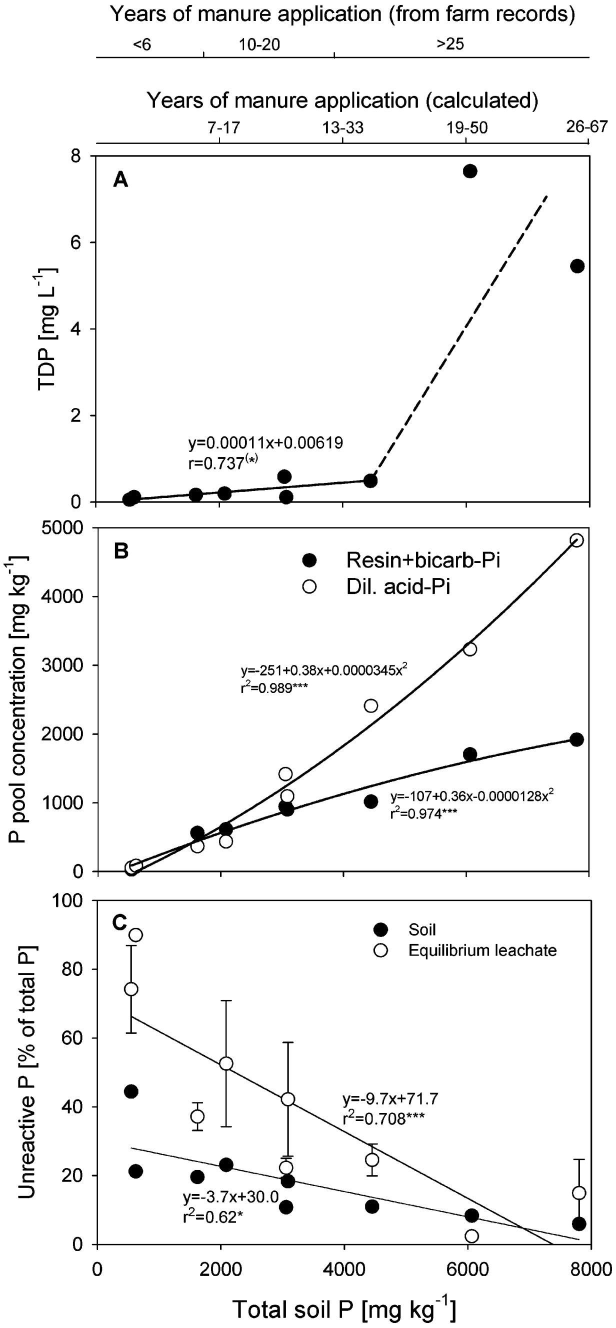

FIGURE 2. Relationship between total P concentrations in soil and (A) concentration of TDP in equilibrium leachate solution under saturated conditions ($N = 3$ replicate cylinders; solid line is regression excluding the values above 5000 mg kg^{-1}, and dashed line is a visual trend), (B) available reactive P (resin + bicarbonate-extractable reactive soil P), and dilute-acid extractable reactive P, and (C) proportion of DUP in equilibrium leachate solution ($N = 3$) and of UP in soil with different duration of manure additions. Years of manure application are estimates from farm planning records and from calculations based on the range of estimated annual applications (see text); $^{(*)}$Significance at $p < 0.1$; *significance at $p < 0.05$; * significance at $p < 0.001$.**

in small columns that may not adequately capture preferential flow (*52*, *53*).

Equilibrium concentrations of total TDP in soil solution increased linearly ($r = 0.737$) with greater amounts of total P in soil up to about 4500 mg of P kg^{-1} (Figure 2A). Above an estimated threshold of about 4500−5500 mg of P kg^{-1}, TDP concentrations increased more than below this threshold (Figure 2A). For these soils, this change point corresponds to a Mehlich 3 RP value of about 1500 mg kg^{-1} (Table 1), an Olsen RP value of about 500 mg of P kg^{-1}, a Mehlich 1 RP value of about 900 mg of P kg^{-1}, and a Bray 1 RP value of about 1200 mg of P kg^{-1} (data not shown). Other studies report change points of P leachate concentrations that are much lower than found in our experiment; for example, 280 mg kg^{-1} [Mehlich 3 extraction (*19*)], 57 mg kg^{-1} [Olsen extraction (*14*)], 181 mg kg^{-1} [Mehlich 3 extraction (*21*)], 205 mg kg^{-1} [Mehlich 3 extraction (*20*)], or 62 mg kg^{-1} [Olsen extraction (*49*)]. The reason may be that our soil P contents spread over a much wider range than those in previously published experiments with a change point observed at lower leachate P concentrations (DRP of about 0.25 mg L^{-1} in ref *19*, 0.2 mg L^{-1} in ref *14*, 0.2 mg L^{-1} in ref *20*, and 0.14 mg L^{-1} in ref *21*) than in our study (DRP of about 0.4 mg L^{-1}). It may be hypothesized that the cited studies find a change point similar to ours with greater or longer manure applications. In addition, the lack of a change point at about 200 mg kg^{-1} (using Mehlich 3) in our study could be explained by higher soil-solution ratios compared to others, since contact times were long here. Koopmans et al. (*55*) described the disappearance of a threshold in runoff P concentrations with increasing soil-solution ratios.

Factors Controlling P Concentrations. A large proportional increase of the available and most mobile P fractions (resin P and bicarbonate P$_i$) already occurred after short-term manure applications, while it remained at the same level with higher manure loadings (Figure 3). The proportion of the dilute acid P$_i$ pool, however, increased continuously with total number of years and/or loads of application (Figure 3) and amounted to 4815 mg kg^{-1} in the soil with the highest P enrichment (Table 3). The dilute acid P$_i$ may largely contain phosphates that are bound to Ca (*35*). An accumulation of calcium phosphates by manure applications agrees with the large amounts of Mehlich 3-extractable Ca, the high pH, and the low Mehlich 3 Al concentrations (Table 1). This interpretation is also supported by the steadily increasing dilute acid P$_i$ with increasing total P concentrations ($p < 0.05$), while mobile P (resin P and bicarbonate P$_i$) increases appear to approach a maximum (Figure 2B). The calcium phosphate dynamics may control available as well as mobile P in soils with large amounts of added poultry manure, even in the naturally acidic soils studied here. This hypothesis is substantiated by the evidence of calcium phosphates found by near-edge X-ray spectroscopy (XANES) in highly manured soils (*56*). For soils not exceeding 159 mg of P kg^{-1} (Olsen extraction), McDowell and Sharpley (*57*) still found aluminum and iron phosphates to control P release to solution in addition to calcium phosphates, whereas with high Mehlich 3-extractable P water-extractable RP decreased with increasing exchangeable Ca, indicating Ca precipitates (*58*).

The fraction of DUP as TDP was greater in equilibrium leachate (2−90%) than the fraction of UP as TP in soil (6−44%; Figure 2C) (means and regression intercepts significantly different at $p < 0.05$; *t*-test) indicating a greater mobility of organic than inorganic P in our soils. About half of the leachable DRP was DUP at a total soil P of 2000 mg kg^{-1} (Figure 2C, Tables 2 and 3). Similarly, Akhtar et al. (*48*) found high organic P concentrations in leachate of undisturbed columns of various soils from New York state after phytate additions. Chardon et al. (*27*) reported 96% organic P of total leached P after application of 300 kg of P ha^{-1} yr^{-1} as cattle slurry to lysimeters compared to 20% without slurry additions. A greater proportion of dissolved organic P and greater C contents in cow slurry were held responsible for higher concentrations of DRP in the subsoil solution of a long-term experiment in Northern Ireland (*59*). A greater mobility of dissolved organic than inorganic P could explain the deeper movement of manure P than inorganic fertilizer P observed

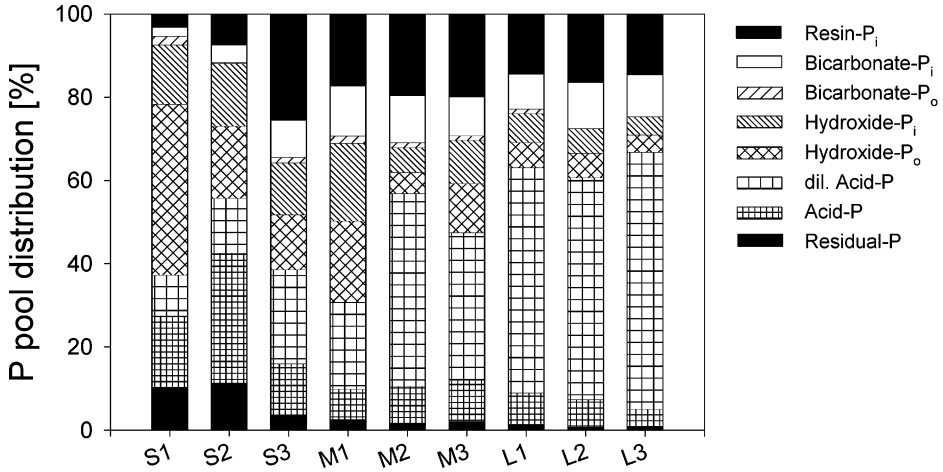

FIGURE 3. Inorganic and organic P pools obtained from sequential fractionation in soil with different duration of manure additions.

TABLE 3. Inorganic and Organic Soil P Pools[a] at 0–0.175 m Depth in Soil with Different Duration of Manure Additions (Table 1)

sample ID	resin P	bicarb P_i	bicarb P_o	hydr P_i	hydr-P_o	dil. acid P_i	acid P_i	acid P_o	res P	sum inorganic[b]	sum organic[c]	total P
S1	17	12	11.3	78	225	54	87	7	57	305	244	548
S2	46	26	0.9	94	108	82	171	23	71	489	132	621
S3	414	145	20.7	203	215	366	121	82	56	1305	317	1622
M1	362	253	35.0	390	407	436	112	41	53	1605	482	2087
M2	599	344	37.5	181	157	1415	134	134	55	2728	329	3056
M3	614	286	32.8	322	364	1094	137	169	69	2521	566	3087
L1	643	372	50.1	309	271	2408	168	166	65	3964	487	4451
L2	1030	673	0.0	360	355	3231	218	184	47	5558	507	6064
L3	1134	783	0.8	346	325	4815	213	134	53	7343	460	7802

[a] All phosphorus values are given in milligrams per kilogram. [b] Sum inorganic = bicarbonate P_i + hydroxide P_i + dil. acid P + acid P_i + residual P. [c] Sum organic = bicarbonate P_o + hydroxide P_o + acid P_o.

in previous studies such as in Nebraska (*9*). A greater proportion of inorganic P than organic P appears to be retained in manured soils, despite the fact that some forms of organic P can adsorb more strongly to soil than inorganic phosphate (*60*).

It was hypothesized that organic P is more important than inorganic P with respect to P leaching under long-term manure applications and that soil organic P is an important driver determining the extent of P leaching. This hypothesis was rejected for those soils with extremely long and high poultry manure loadings, since the proportion of DUP in equilibrium leachate as well as in total soil decreased with increasing total soil P contents and years of manure application (Figures 2C and 3) and since most of the P (up to 98%) in the leachate with the longest manure history was in DRP form (Table 2). A decrease in the proportion of total soil organic P from 64% to 29% was also observed for a Fragiudalf in Tennessee, after 5 years of applications of 280 kg of P ha^{-1} yr^{-1} as dairy manure (*61*). Immediately after an application of poultry manure to a Typic Hapludult and an Aquic Fragiudult in Pennsylvania, the proportion of DRP as total P in leachate increased from 7% to 72% (*51*). In conclusion, the mobile portion of organic P may be less important in soils with a long history of high poultry manure applications than under medium- and short-term manure applications. In addition, DRP was less mobile than DUP in soils with shorter duration of manure additions and low total soil P, but differences disappeared with long-term applications.

The forms of organic P in soil did not show large changes with manure applications as determined by sequential fractionation. The only organic P pool in soil that increased with greater manure loadings was the acid P_o fraction (Table 3 and Figure 3). A combination of a significant proportional increase of the acid P_o fraction and the absence of changes in other soil organic P pools is in agreement with results obtained by Motavalli and Miles (*62*) for a long-term experiment in Missouri (111 years with 13.4 Mg ha^{-1} yr^{-1} manure equivalent to 108 kg of P ha^{-1} yr^{-1}). Increases in the acid P_o fraction are not easily attributed and may indicate an accumulation of either very stable organic P forms or particulate organic P that was not extracted by NaOH (*35*).

Also, ^{31}P NMR results of soil extracts showed very few relevant differences between organic P forms after short- or long-term manure amendments (Figure 4 and Table 4) and the forms of organic P may therefore have limited influence on leachable P. Only the proportion of phosphonates decreased slightly with longer manure applications (Table 4). Representing merely 2.6–5.2% of the total alkali-extractable P, however, the contribution of phosphonates to total P was low and this pool is not expected to play a substantial role in controlling P losses. Orthophosphate monoesters were the dominant forms of P compounds in the NaOH/NaF extracts, which accounted for 51% of alkali-extractable P. Orthophosphate diesters represented 11%, while teichoic acids comprised 3% of the alkali-soluble P. The unknown organic P compounds, identified as unknowns A and B, accounted for 10% and 4% of the alkali-extractable P, respectively. Inorganic orthophosphate represented 17% of the total alkali-extractable P, whereas pyrophosphate accounted only for 1% of the total alkali-extractable P at the two sites and polyphosphates could not be detected.

Leinweber et al. (*63*) reported greater proportions of orthophosphate diesters than monoesters in chicken manure with 0.1 M NaOH extractions, and Solomon and Lehmann (*30*) found higher ratios of orthophosphate diester-to-monoester in manured soils. The present study, however, did not show any increases in orthophosphate diesters with increasing duration of manure applications. A greater

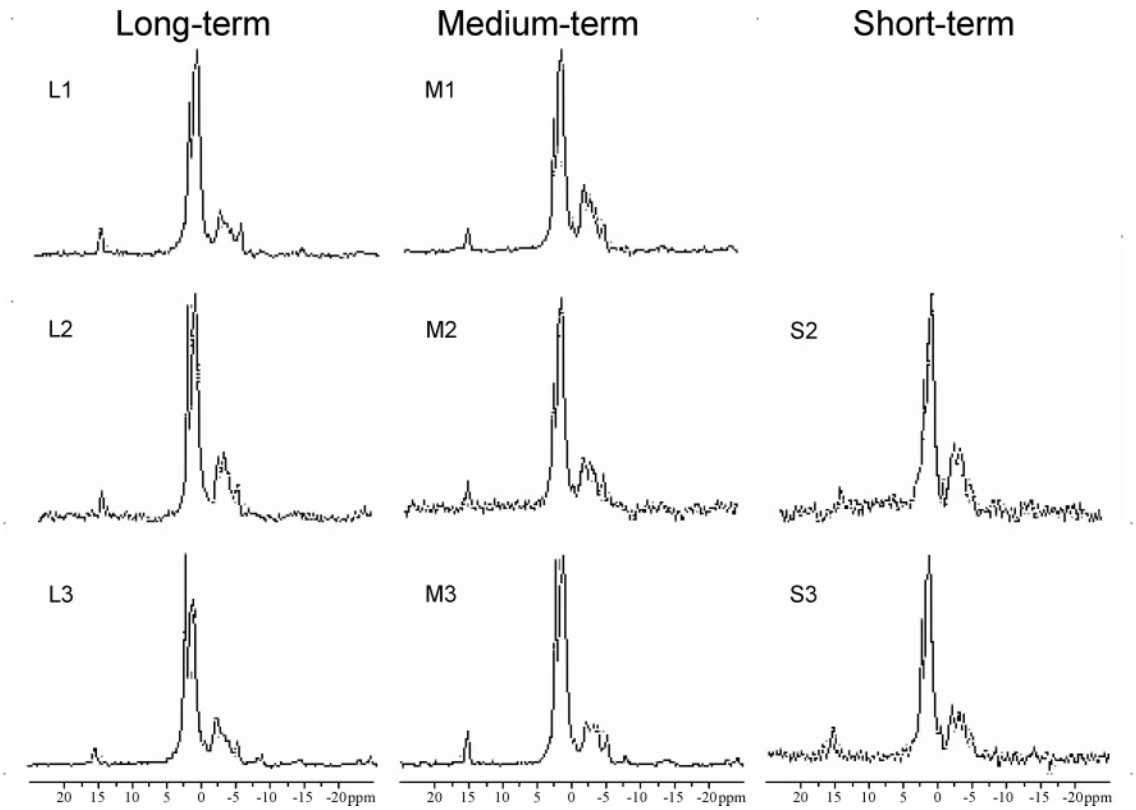

FIGURE 4. Liquid-state ^{31}P NMR spectra of NaOH/NaF extracts from soil with different duration of manure additions.

TABLE 4. Forms of Organic P Obtained from ^{31}P NMR of Extracts from Soil with Different Duration of Manure Additions (Table 1)[a]

ID	diester	monoester	inorganic P	phosphonates	unknown A	unknown B	diester/monoester
FO	nd	nd	nd	nd	nd	nd	nd
S1	nd	nd	nd	nd	nd	nd	nd
S2	11.6	53.8	13.9	4.1	9.7	3.9	0.22
S3	13.7	45.1	13.8	4.3	13.0	5.1	0.30
M1	13.1	47.5	12.3	4.1	12.9	5.1	0.28
M2	12.1	48.2	12.6	5.2	10.9	6.3	0.25
M3	10.5	51.9	17.5	3.8	8.3	4.3	0.20
L1	8.9	53.9	16.8	3.4	9.3	4.8	0.17
L2	13.7	51.0	14.9	2.7	10.3	4.7	0.27
L3	9.4	48.2	19.9	2.6	11.3	4.0	0.20

[a] nd, not determined.

proportion of diesters may have been mineralized to inorganic P, leading to an accumulation of monoesters in our soils, since orthophosphate monoesters are typically more stable than diesters (*64*). This result may have been a reflection of the quality of the manure applied or the long time available for P mineralization.

The solubility and affinity of different organic P forms to minerals was found to differ in previous studies of manure-applied soils with important implications for leaching of organic P (*22, 28*). Highly recalcitrant and adsorptive P forms such as phytic acid were identified in different types of manures (*29*) and may likely be precursors of orthophosphate monoesters observed in extracts from our soils. Specific inositol structures (*22*, *65*) could not be identified in our NaOH/NaF extracts from soils after long-term manure applications. On the basis of the results of our investigation with ^{31}P NMR, organic P forms in soils did not significantly change with long-term manure additions. Further investigations are warranted to determine whether this result is a reflection of potential shortcomings of our NMR experiments.

In summary, long-term manure applications with a dominance of poultry litter at our site resulted in a significant reduction of P retention and in an increase of leachable DRP in saturated soil. The importance of DUP in equilibrium leachate decreased with increasing duration of application. However, the proportion of organic P was greater in leachate than in total soil with short- and medium-term manure applications, indicating a greater mobility of organic than inorganic P except in soils after long-term poultry manure applications. The form of organic P in NaOH/NaF extracts from soils determined by ^{31}P NMR spectroscopy was not significantly affected by manure history. The most distinct changes in P forms with longer manure applications were the increasing proportions of dilute acid P_i, suggesting formation of calcium phosphates in these naturally acidic soils. This may be a specific effect of poultry manure applied to the fields in our study and further research is needed to investigate the effects of different types of manure. A discontinuation of manure application with resulting decreases in soil pH may mobilize these pedogenic calcium phosphates depending on their crystallinity. Spectroscopic studies should be conducted to investigate the types of calcium phosphates formed under long-term manure additions.

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