

Phosphorus Mobility in Soil Columns Treated With Dairy Manures and Commercial Fertilizer

David Dale Tarkalson and April B. Leytem

Abstract: The concentration of animal production in some areas of the United States has led to concern about the environmental fate of manure-derived phosphorus (P) in soils. A column study was conducted to quantify P leaching in a calcareous soil treated with monoammonium phosphate (MAP), two solid dairy manures (D1S and D2S), and two liquid dairy manures (D1L and D2L). A control with no P application was also included. Treatments were applied at 166 kg P ha⁻¹ to columns packed with 20 cm of a Warden fine sandy loam (coarse-loamy, mixed superactive, mesic Xeric Haplocalcids) in a completely randomized design with four replications and housed in a climate-controlled growth chamber. Simulated irrigation water was added to the columns at a rate of 47.4 mm (450 mL) during 13 events during a 9-week period, with leachate collected, volume recorded, and concentrations of total organic carbon (TOC) and total P (TP) determined for each event. At the end of the leaching events, each soil column was divided into eight 2.5-cm segments. Then, soil was air-dried, ground, and analyzed for TP, total carbon, calcium (Ca), iron, and manganese, and water-soluble P. The masses of TP and TOC in leachate were in the order D1L = D2L > MAP = D1S = D2S = Control. There was a positive linear relationship between the cumulative mass of TOC and cumulative mass of TP lost in leachate over all manure treatments ($r^2 = 0.98$). The masses of TP and water-soluble P for treatments in the entire soil columns were in the order MAP > D1L = D2L > D1S = D2S = Control. Masses of P and C in leachate and soil show that P mobility in soil was in the order liquid dairy manures > MAP > solid dairy manures. At the end of the study, the total C was greater in the surface 2.5 cm of the soil columns for the solid manure treatments compared with the other treatments/depth combinations. The greater leaching of P in the liquid manure treatments compared with the solid manure treatments may be caused by a combination of factors including microbial activity, organically complexed metals, coating of P adsorption sites on clay particles by organic C compounds, and P-Ca and P-aluminum reactions.

Key words: Phosphorus, phosphorus leaching, phosphorus mobility, organic carbon, dairy manure, calcareous

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The state of Idaho has recently experienced rapid growth of the dairy industry. The number of milk cows has increased approximately 88% in the past decade, with a 120% increase in milk production (USDA-NASS, 2007). Idaho is the second largest milk producer in the 12 western US states and has become the fourth largest milk-producing state in the United States. This increased concentration of dairy production in the region has led to increased land application of manure from

these operations and sometimes increased concentrations of nutrients in soils.

Of particular concern is phosphorus (P), as most manure application strategies seek to supply the N requirements of crops, and in the process, they supply more P than needed for crop production. The imbalance between the N and P contents of manures and the N and P requirements of crops has led to increased soil test P concentrations in close proximity to confined animal operations, which can accelerate P transfer in runoff to water bodies. This process can contribute to eutrophication in freshwater ecosystems, and numerous examples of water-quality impairment associated with P pollution from animal operations now exist (Borsch et al., 2001; Burkholder and Glasgow, 1997; USGS, 1999).

Despite this concern over increasing soil P concentrations, there is little information on the mobility of P in manure-amended irrigated soils of the semiarid western United States. A few studies have assessed the solubility of P in manure-amended alkaline soils (El-Barony and Olsen, 1979; Robbins, et al. 2000; Leytem and Westermann, 2003 and 2005). Phosphorus reactions in alkaline soils have traditionally been associated with calcium carbonate, whereas in acid soils, reactions are mainly associated with aluminum (Al) and iron (Fe) oxide and hydroxide minerals (Lindsay, 1979). However, recent research suggests that organic carbon (OC) may influence P reactions in calcareous soil, influencing the potential P transport via water in runoff and leaching.

In a laboratory study, Leytem and Westermann (2003) obtained P sorption isotherms on eighteen calcareous soils in the Pacific Northwest and found that organically complexed Fe and manganese (Mn) played a more significant role in P sorption than calcium carbonate concentration. Leytem and Westermann (2005) determined that in soils previously fertilized with different P sources, water-soluble P (WSP) concentrations of the soils were in the order of inorganic P fertilizers > liquid manures > solid and composted manures. The authors theorized that OC was stimulating microbial uptake of P and/or there are chemical interactions between OC and P that influence the solubility of P applied in various sources. Leytem et al. (2005) determined that as the C:P ratio of P sources increased, the bicarbonate-extractable P decreased, and the stimulation of microbial biomass by added OC reduced the solubility of P in amended soils. As added OC has been shown to alter soil P solubility and calcium (Ca) forms precipitates with P, the objective of this study was to quantify the mobility of P in a calcareous soil treated with commercial fertilizer P, solid dairy manure, or liquid dairy manure.

MATERIALS AND METHODS

Soil Collection and Analysis

A Warden fine sandy loam (coarse-loamy, mixed superactive, mesic Xeric Haplocalcids) was collected from a depth of 0 to 20 cm in an agricultural field in South-Central Idaho, air-dried, and sieved through a 5-mm sieve before analysis. Organic

USDA-ARS NWISRL, Kimberly, ID 83301. Dr. Tarkalson is corresponding author. E-mail: david.tarkalson@usda.ars.gov
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C was determined using the method of Walkley and Black (1934). The pH was determined in a saturated paste with a combination electrode (Robbins and Wiegand, 1990). Cation exchange capacity was determined by saturating the soil with 1 M sodium acetate at pH 7, and analysis of Na using atomic absorption spectrometry (United States Salinity Laboratory Staff, 1969). Calcium carbonate equivalent (CCE) was determined using a titrimetric method by Allison and Moodie (1965). Sodium bicarbonate-extractable P was determined using a method by Olsen et al. (1954). Oxalate-extractable Fe, Al, Mn, and P were determined by extraction with 0.2 M ammonium oxalate at pH 3 (Jackson et al., 1986). Measured properties of the soil are presented in Table 1.

Solid Manure Collection and Analysis

Deposited manure was collected from dry lots of two local dairies (Dairy 1 and Dairy 2). The manure was transported to the laboratory and immediately frozen (-80°C), lyophilized, and ground (2 mm) for analysis. Total elements (Al, Ca, Fe, and P) were determined using inductively coupled plasma optical emission spectroscopy after microwave-assisted digestion of a 0.5-g sample with 8 mL of concentrated HNO_3 and 2 mL of 30% (vol/vol) hydrogen peroxide. Water-soluble P was determined in a 1:100 manure-to-deionized water ratio, shaken for 1 h, filtered through a 0.45- μm membrane, and analyzed using the ascorbic acid-molybdate blue method (Murphy and Riley, 1962). Total C (TC) and N were determined by combusting a 25-mg sample using a FlashEA1112 CNH analyzer (Elantech, Lakewood, NJ). Measured properties of the solid manures are presented in Table 2.

Liquid Manure Collection and Analysis

Liquid manures were collected from settling ponds of the same dairies where the solid manures were collected (Dairy 1 and Dairy 2). The samples were transported to the laboratory and immediately stored in a cooler (4°C) and analyzed as received for total elements (Al, Ca, Fe, and P) and WSP. Total elements were determined using inductively coupled plasma optical emission spectroscopy after microwave-assisted digestion of a 10-mL sample aliquot with 4 mL of concentrated HNO_3 , 2 mL of concentrated HCl, and 2 mL of 30% (vol/vol) hydrogen peroxide. Water-soluble P was determined in a 1:50 manure-to-deionized water ratio, shaken for 1 h, filtered through a 0.45- μm membrane, and analyzed using the ascorbic acid-molybdate blue method (Murphy and Riley, 1962). Total C and

TABLE 1. Selected Warden fine sandy loam soil properties

Soil property	
Clay, g kg^{-1}	62.0
OC, g kg^{-1}	4.3
pH	7.1
CEC, $\text{cmol}_c \text{ kg}^{-1}$	13.0
CCE, g kg^{-1}	13.7
Olsen P, mg kg^{-1}	9.3
$\text{Al}_{\text{ox}}^{\dagger}$, g kg^{-1}	0.62
$\text{Fe}_{\text{ox}}^{\dagger}$, g kg^{-1}	1.64
$\text{Mn}_{\text{ox}}^{\dagger}$, g kg^{-1}	0.26
$\text{P}_{\text{ox}}^{\dagger}$, g kg^{-1}	0.26

CEC: cation exchange capacity.

† Ammonium oxalate extractable.

TABLE 2. Selected manure properties

Manure property	DIS ¹	D2S ²	D1L ¹⁸	D2L ¹⁹
	mg kg^{-1} ¹¹		mg L^{-1}	
Total P	7144.0	3957.4	49.1	89.7
Total Ca	30,050.7	28,211.2	142.4	325.5
Total Al	7119.8	6297.5	5.3	27.9
Total Fe	5297.3	6104.9	4.2	22.6
Total Mn	313.8	247.2	1.59	3.3
WSP	2288.1	1704.7	34.4	51.4
Solids	—	—	0.016	0.0327
			%	
WSP of TP	32.0	43.1	70.1	57.3
			g kg^{-1}	
Total N	19.5	12.8	48.2	32.8
Total C	242.6	202.1	374.1	343.1
C/N	12.4	15.8	7.8	10.5
C/P	34.0	51.1	125.0	125.1

¹DIS: Dairy 1 solid manure; D2S: Dairy 2 solid manure.

¹⁸D1L: Dairy 1 liquid manure; D2L: Dairy 2 liquid manure. Total C and N, and solid concentrations determined from lyophilized samples. Remainder of analysis determined on liquid manure samples.

¹⁹WSP, TP converted to g kg^{-1} ; $(\text{kg solids L}^{-1}/\text{mg total P L}^{-1})/1000$.

¹¹Analysis reported on a dry weight basis.

N were determined by combusting a 25-mg lyophilized sample using a FlashEA1112 CNH analyzer. Measured properties of the liquid manures are presented in Table 2.

¹³C-NMR Analysis of Manures

To qualitatively determine the C characteristics of the four manures, ¹³C-nuclear magnetic resonance spectrometry (¹³C NMR) was used for both the liquid (solution) and solid (solid state) manure samples (Fig. 1). Both solution and solid-state ¹³C-NMR spectra were obtained with a Bruker Avance 500 MHz spectrometer operating at 125.758 MHz for ¹³C. Solution ¹³C-NMR samples were analyzed using a 3- μsec pulse (40 degrees), a delay time of 1.0 sec, an acquisition time of 0.4 and 0.9 sec for the Dairy 1 and Dairy 2 samples, respectively, and with broadband proton decoupling (WALTZ16). The number of scans was 54,753 and 34,928 for the Dairy 1 and Dairy 2 samples, respectively, and was plotted with a line broadening of 20 and 15 Hz for the Dairy 1 and Dairy 2 samples, respectively. Solid-state ¹³C-NMR samples were spun at the magic angle at 12-kHz in a solid-state probe. Spectra were obtained by using a 4- μsec pulse (40 degrees), a delay time of 1.0 sec, and an acquisition time of 0.04 sec. The number of scans was 75,256 and 78,235 for the Dairy 1 and Dairy 2 samples, respectively, and was plotted with a line broadening of 20 Hz. Tetrakis(trimethylsilyl)silane was added to the samples as an internal standard, and chemical shift values are relative to the tetrakis(trimethylsilyl)silane carbon at 0 ppm.

Column Study

This study was conducted using 24 soil columns constructed from polyvinyl chloride with a diameter of 11 cm and a height of 31 cm and housed in a climate-controlled growth chamber. Each column had nylon mesh glued to the bottom, and a 2.5-cm layer of acid (1 M HCl)-washed sand (475 g) was

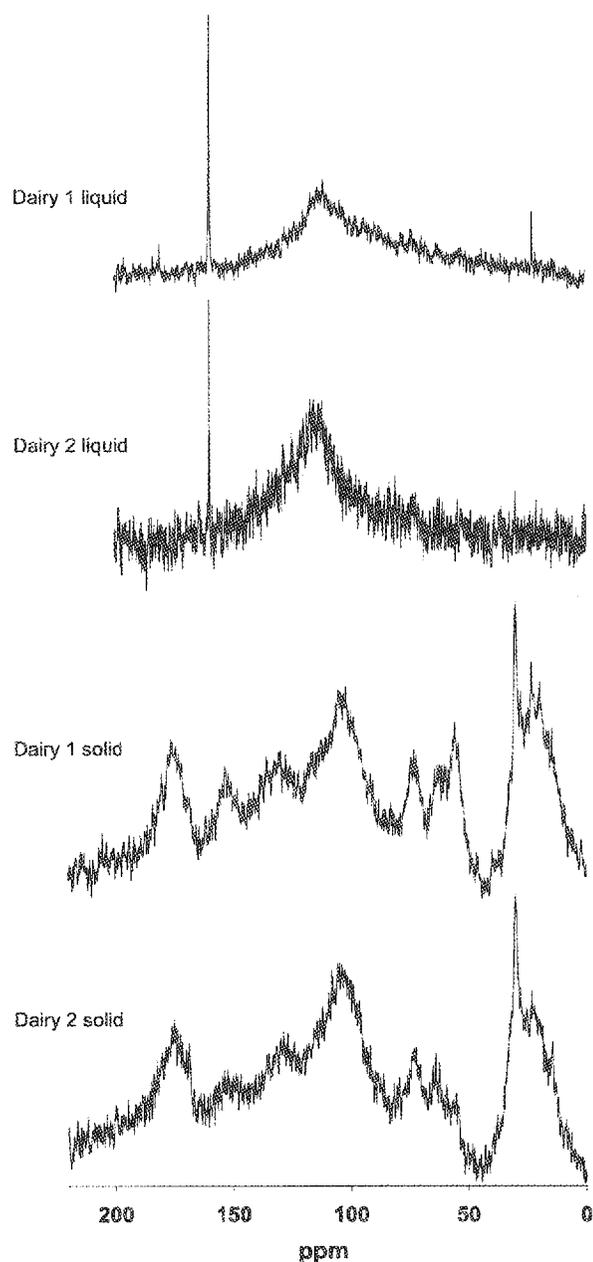


FIG. 1. ^{13}C -NMR spectra of manure samples.

added above the nylon mesh to retain soil in columns and filter soil particles from leachate. Each column received 3000 g of the air-dried and sieved (5 mm) Warden soil and then saturated with simulated irrigation water ([SIW] 1:1, tap water-reverse-osmosis water) and allowed to drain to field capacity and naturally settle. The soil columns were placed in a rack with a funnel placed below each column to direct leachate into 500-mL glass bottles.

Five P source treatments, monoammonium phosphate (MAP), Dairy 1 solid manure (D1S), Dairy 2 solid manure (D2S), Dairy 1 liquid manure (D1L), and Dairy 2 liquid manure (D2L) were applied at a P application rate of 167 kg ha^{-1} . This application rate was selected to simulate an overapplication of P, which has been common under N-based application strategies.

A control treatment was also included that received no P application. Each treatment was replicated four times and placed in a completely randomized design. The total application rates of selected elements are presented in Table 3.

The MAP and solid manures were ground to pass through a 2-mm sieve for even distribution in the soil, and mixed into the soil during a one-time application to a depth of 2.5 cm (Table 4). The liquid manures were applied to columns over six separate applications during a period of 3 weeks (Table 4). Simulated irrigation water was applied to the MAP, solid manures, and D2L treatments during the liquid manure applications to equalize water volume with the D1L treatment. After all liquid manure treatments were applied, SIW was applied to all treatments at an equal rate (Table 4). The liquid manure treatments and SIW were applied to the columns using a drip apparatus. The drip apparatus controlled the application rates to match infiltration rates. Total water applied to each column was approximately 620 mm. The growth chamber was programmed to deliver 12 h of light and 12 h of night, with mean daytime and night time temperature of 30°C and 14°C , respectively. These temperatures represent 30-year average daytime and night time temperatures from July 16 to August 7 in Twin Falls, Idaho.

Leachate Analysis

Leachate was collected in 500-mL glass bottles from each column during each application date. Total volume of leachate was determined, and a subsample from each column was analyzed for total elements (Al, Ca, Fe, and P), and total OC (TOC). Procedures for the total element analysis were the same as those used for analysis of the liquid manures. Total organic carbon was determined from a mixture of 1 mL of filtered sample ($0.45 \mu\text{m}$), 9 mL of reverse-osmosis water, and 0.1 mL of 2 M HCl using a TOC-5050A Total Organic Carbon Analyzer (Shimadzu Scientific Instruments Inc, Columbia, MD).

Soil Analysis (Poststudy)

After the leaching portion of the study, soils were collected from each column in 2.5-cm increments from 0 to 20.3 cm. Soils were air-dried, sieved through a 5-mm screen, and analyzed. Total elements (Ca, Fe, Mn, and P) and WSP were determined using the same procedure described for analysis of the solid manures. Total C and N were determined by combusting a 50-mg sample using a FlashEA1112 CNH analyzer (Elantech, Lakewood, NJ).

Statistical Analysis

Bartlett test was conducted to test for the hypothesis of homogeneity of error variances for the data of independent variables (Snedecor and Cochran, 1989). Variables with nonhomogeneity of error variances were log transformed before analysis. Analysis of variance was conducted using the Completely Randomized Model from Statistix 8 (Analytical and Software, 2003). The least significant difference (LSD) method was used for mean separations. Significance was determined at the $\alpha = 0.05$ probability level for all statistical analyses. Where statistical analysis was conducted on transformed data, nontransformed values are shown in tables and figures.

RESULTS

Initial Soil Properties

Analysis indicates that the Warden soil had a high potential to adsorb P. The soil was low in bicarbonate-extractable P (Olsen-P, 9.3 mg kg^{-1}) with respect to agronomic P

TABLE 3. Application rates of elements in dairy manures to columns

Element	MAP	DIS	D2S	D1L	D2L
	kg ha ⁻¹ (mg column ⁻¹)				
P	166.8 (135.2)	166.8 (135.2)	166.8 (135.2)	166.8 (135.2)	166.8 (135.2)
N	80.8 (65.5)	455.0 (368.7)	537.6 (435.6)	2681.4 (2172.7)	1997.4 (1618.5)
C	—	5663.4 (4589.1)	8519.3 (6903.2)	20,816.8 (16,867.9)	20,892.1 (16,928.9)
Al	—	166.2 (134.7)	265.4 (215.1)	18.0 (14.6)	52.0 (42.1)
Ca	—	701.6 (568.5)	1189.0 (963.4)	483.9 (392.1)	605.3 (490.5)
Fe	—	123.7 (100.2)	257.3 (208.5)	14.3 (11.6)	42.0 (34.0)
Mn	—	7.3 (5.9)	10.4 (8.4)	5.4 (4.4)	6.2 (5.0)

recommendations for most crops (Table 1). For example, in Idaho, the fertilizer guidelines for irrigated field corn from the University of Idaho would suggest an application of 39 kg P ha⁻¹ to this soil to optimize yield (Brown and Westermann, 1988). The degree of P saturation (DPS = $\{[P_{ox}/(Al_{ox} + Fe_{ox})]*100\}$; Pote et al., 1996), which is defined as the percent of total soil P adsorption capacity that is already saturated, was 11.5%. The soil was slightly alkaline (pH = 7.1, CCE = 13.7) and was low in clay and OC content (Table 1).

Manure Properties

Total P was 7144 and 3957 mg kg⁻¹ for D1S and D2S, respectively. The total P in the liquid manures was lower, with 49 and 90 mg kg⁻¹ (liquids had a density of ~1 g cm⁻³) for the D1L and D2L, respectively (Table 2). These values fall within or close to the ranges of total P in dairy manures reported as book

values in the USDA Agricultural Waste Management Handbook. The book values have total P ranges from 4400 to 6900 mg kg⁻¹ for manure excreted directly from the lactating, dry, and heifer cows, and 23 to 99 mg kg⁻¹ from liquid manures flushed from the milking facilities (USDA-NRCS, 1999). The total P book values vary based on manure handling in the milking facilities and the type of cow.

In the solid manures, less than 45% of the total P was in a soluble form, with WSP concentrations of 2288 and 1704 for the DIS and D2S samples, respectively (Table 2). The percentage of total P that was soluble in the liquid manures was much higher and was 70% and 57% for the D1L and D2L samples, respectively. Total N and C in the solid samples averaged 16 and 222 mg kg⁻¹, respectively, whereas total N and C in lyophilized samples of the liquid manures averaged 41 and 359 mg kg⁻¹, respectively. The average C/N ratio was greater in the solid (C/N ratio, 14) than liquid (C/N ratio, 9)

TABLE 4. Phosphorus source and water application strategy

Date	Treatment				
	MAP	DIS [†]	D2S [†]	D1L	D2L
April 24	0.5952 g MAP, 47.7 mm SIW [‡]	18.92 g manure, 47.7 mm SIW	34.15 g manure, 47.7 mm SIW	48.3 mm manure [§]	26.4 mm manure, 21.9 mm SIW
April 26	47.7 mm SIW	47.7 mm SIW	47.7 mm SIW	48.3 mm manure	26.4 mm manure, 21.9 mm SIW
May 1	47.7 mm SIW	47.7 mm SIW	47.7 mm SIW	48.3 mm manure	26.4 mm manure, 21.9 mm SIW
May 3	47.7 mm SIW	47.7 mm SIW	47.7 mm SIW	48.3 mm manure	26.4 mm manure, 21.9 mm SIW
May 8	47.7 mm SIW	47.7 mm SIW	47.7 mm SIW	48.3 mm manure	26.4 mm manure, 21.9 mm SIW
May 10	47.7 mm SIW	47.7 mm SIW	47.7 mm SIW	48.3 mm manure	26.4 mm manure, 21.9 mm SIW
May 17	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW
May 22	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW
May 28	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW
June 5	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW
June 12	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW
June 19	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW
June 25	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW	47.4 mm SIW

[†]Treatments mixed into soil before application of SIW.

[‡]SIW: 1:1, tap water–reverse osmosis water ratio.

[§]48.3 mm of D2L minus solids was equivalent to 47.7 mm of water.

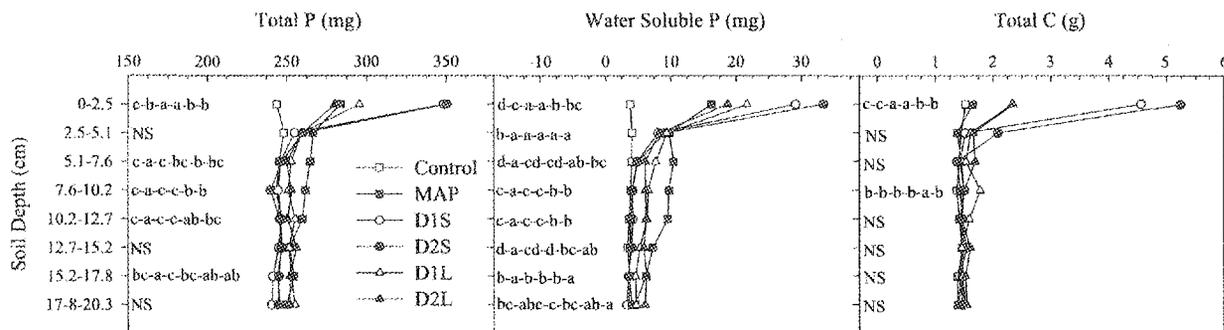


FIG. 2. Total P, WSP, and TC masses with depth for the control, MAP, D1S, D2S, D1L, and D2L treatments. For each depth, treatments with the same letter are not significantly different at the 0.05 probability level based on LSD. Treatment differences represented by letters from left to right correspond to treatments in legend from top to bottom: Control, MAP, D1S, D2S, D1L, D2L, respectively. Error bars represent the SE of the treatment means. NS: not significant.

manures, whereas average C/P ratios were greater in the liquid manures (C/P ratio, 125) than the solid manures (C/P ratio, 43). The influence of N differences between treatments on soil microbial-related influences on P was not measured.

The ¹³C-NMR spectra of the four manures are presented in Fig. 1, with peak area assignments based on previous work in cattle and poultry manure (Gómez et al., 2007) and composted organic matter (Chen et al., 1989). The C composition of the two liquid manures was similar, with a broad peak over the range of 100 to 120 ppm, which is a region typically associated with C in aromatic ring structures and a sharp peak at 160 ppm, which is in a range typical of carbonyl carbons in carboxylic acid or phenolic compounds. The C composition of the two solid manures was similar, with peaks in the range of 0 to 50 ppm, which are typically associated with C in aliphatic chain structures; 60 to 112 ppm associated with C in carbohydrates, polysaccharides, and proteins; 112 to 150 ppm associated with aromatic C compounds; and 160 to 185 ppm associated with carbonyl carbons in amide and ester compounds. The C characteristics of the solid manures were similar to that found in cattle manure by Gómez et al. (2007).

Post Leaching Soil Analysis

The distribution of TP, WSP, and TC masses in the soil columns at 2.5-cm depth increments are shown in Fig. 2. In the 0- to 2.5-cm depth, the WSP, TP, and TC masses were greater for the solid manure treatments compared with the liquid manure treatments and MAP, whereas the control was the lowest, except for TC where the MAP and control were not significantly different. In the 2.5- to 5.1-cm depth, there were no differences in WSP between the treatments receiving P, but the treatments were greater than the control. Water-soluble P from the MAP treatment was greater than all other treatments at the 5.1- to 7.6-cm, 7.6- to 10.2-cm, and 10.2- to 12.7-cm depths. In the lower depths, in general, there were less consistent differences

between the treatments. The TP concentrations in the columns followed the pattern of the WSP concentrations (Fig. 2). The P in the solid manures did not leach to the extent P did from MAP and the liquid manure treatments. The Most of the P in the solid manure treatments remained on the surface 5.1 cm, whereas the P in the MAP and liquid manures leached to lower soil depths.

On the surface 2.5 cm, the TC concentrations were in the order of solid manures > liquid manures > MAP and the Control (Fig. 2). This order, referring to solid manures and liquid manures only, was inversely related to the quantity of C added to the columns from the treatments (Table 3). There were no

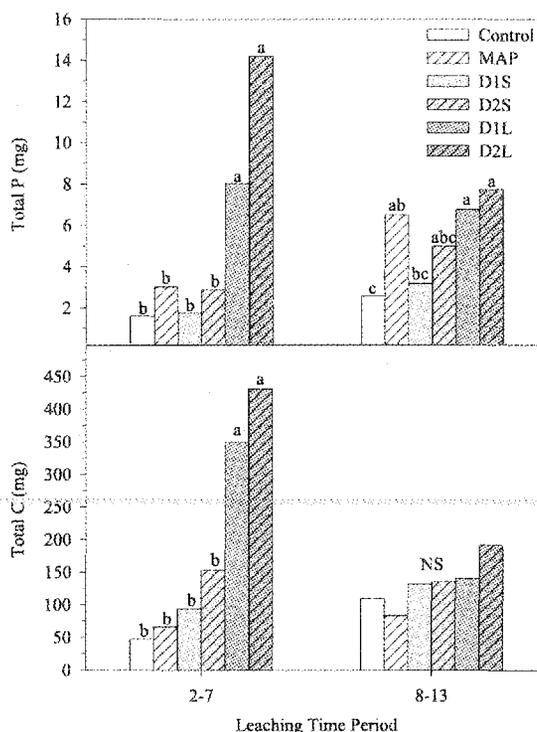


FIG. 3. Total P and TOC masses in leachate for the control, MAP, D1S, D2S, D1L, and D2L treatments summed over Leaching Dates 2 through 7 and 8 through 13. There was no significant treatment effect at Leaching Date 1 for all variables. For each leaching period, treatments with the same letter are not significantly different at the 0.05 probability level based on LSD.

TABLE 5. Analysis of variance for the concentrations of Ca, Fe, and Mn in soil after the leaching part of the study

	Ca	Fe	Mn
Treatment	<0.001	0.008	<0.001
Depth	<0.001	0.526	0.888
Treatment × depth	<0.001	1.000	0.941

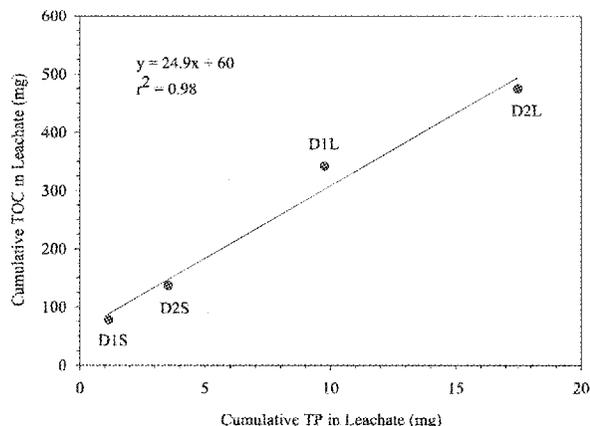


FIG. 4. Relationship between cumulative TP and TOC mass in leachate. Values are the means of the cumulative TP and TOC in the D1L, D2L, D1S, and D2S treatments minus the mean TP and TOC from the control.

treatment differences in masses of TC at the other depths, except at the 7.6- to 10.2-cm depth where the D1L treatment was higher than the other treatments. There were no differences in the masses of TC between the solid manure treatments in the soil, whereas the D2S treatment had approximately 2900 mg more C applied than the DIS treatment.

Analyses of variance for the concentrations of Ca, Fe, and Mn in the soils at the end of the leaching period of the study are shown in Table 5. The significant interaction between treatment and depth for Ca was caused by the Ca concentrations in the soil being in the order of D2S, 0 to 2.5 cm (7656 mg kg^{-1}) > D1S, 0 to 2.5 cm (6727 mg kg^{-1}) > remaining treatment and depth combinations (mean, 4667 mg kg^{-1}). The significant treatment effect for the concentrations of Fe in the soil was in the order of D2S ($41,670 \text{ mg kg}^{-1}$) > MAP ($37,675 \text{ mg kg}^{-1}$) = D2L ($37,173 \text{ mg kg}^{-1}$). The D2L ($40,200 \text{ mg kg}^{-1}$), D1S ($39,664 \text{ mg kg}^{-1}$), and Control ($38,638 \text{ mg kg}^{-1}$) treatments were not significantly different from the D2S, MAP, and D2L treatments. The significant treatment effect for the concentrations of Mn in the soil was caused by the D1S treatment having greater Mn concentrations (516 mg kg^{-1}) than the D2S (501 mg kg^{-1}), Control (500 mg kg^{-1}), D1L (497 mg kg^{-1}), and D2L (495 mg kg^{-1}) treatments. The MAP treatment was not significantly different from the D1S treatment.

Leachate

There were no significant differences in leachate volumes between treatments at each date or totaled over all dates ($P = 0.42$). The average total volume of leachate across all columns and dates was 440 mm (4180 mL), which represents 71.2% of the total water applied.

The masses of TP and TOC were not different between treatments at Leaching Date 1. However, the masses of TP and TOC in leachate summed over events 2 to 7 were in the order D1L = D2L > MAP = D1S = D2S = Control (Fig. 3). The masses of TP summed over Leaching Dates 8 to 13 from the D1L and D2L treatments were not different from the MAP or D2S treatment but were greater than the control and D1S treatments (Fig. 3). There was no significant treatment effect on TOC masses summed over Leaching Dates 8 to 13 (Fig. 3). There was a strong positive linear relationship between cumulative TP and TOC in leachate from the manure-amended soil columns ($r^2 = 0.98$), with the liquid manures having the highest TP and TOC

concentrations, whereas the solid manures had lower concentrations (Fig. 4).

DISCUSSION

As can be seen in Fig. 1, the liquid and solid manures differ greatly in their C composition. The solid manures have a large variety of C compounds including aliphatic C compounds, carbohydrates, polysaccharides, proteins, and carbonyl-containing compounds most likely from undigested feedstuffs. The liquid manures have a more limited variety of C compounds mainly consisting of carboxylic or phenolic compounds and aromatic ring structures, which is most likely a result of the breakdown of larger organic matter in the solid manures into smaller and more stable units via microbial activity. Gómez et al. (2007) reported that the content of aromatic and carbonyl/carbonyl compounds in cattle manures increased because of digestion or composting of manure compared with fresh manure, and that compounds with high aromaticity were more stable. The forms of P in the manures were not determined in this study. However, Hansen et al. (2004) determined the P fractionation of solid and lagoon manures from a commercial dairy in Gooding, Idaho, and found that for both manure types, 70% of the TP was inorganic and 30% of the TP was organic (mostly orthophosphate monoesters). Leytem and Westermann (2005) used phosphorus-31 NMR to characterize the P in solid beef and liquid dairy manures and found that 60% of the P in fresh beef manure and 90% of P in liquid dairy manure were inorganic orthophosphate, with most of the remaining compounds being orthophosphate monoesters. It is likely that this manure had similar P forms.

The retention of P in the topsoil and lower TP concentrations found in the leachate of the solid manure treatments indicate that the P in these manures was less mobile compared with the liquid manures and MAP. These data support research findings from Hansen et al. (2004) who reported that P from applied dairy lagoon liquid moved vertically in a calcareous soil to a greater extent than P from solid dairy manure. They found that inorganic P (70% of the TP) was the dominant form of P that moved vertically in the soil, and that organic P (30% of TP) was not mobile and was found predominantly in the soil surface. In their study, they suggest that P movement was much more likely when long-term manure applications have nearly saturated the P adsorption sites. However, our data show significant movement of P in the dairy liquid manure treatments in a soil that was relatively low in adsorbed P (Table 1).

This retention of P in the topsoil of the solid manure treatments could be caused by several factors. The solid manure treatments had higher Ca concentrations in the surface 2.5 cm of the columns than the other treatments, thus increasing the potential for P-Ca reactions and reducing P leaching (Lindsay, 1979). The higher Ca concentrations in the soil were caused by greater application rates of Ca in the solid manure treatments compared with the other treatments (Table 3). The solid manure also likely increased colloidal surfaces, increasing P reactions with Ca. The mobility of P in the treatments was not explained by the concentrations of Fe and Mn in the soil at the end of the leaching period. Although we were not able to analyze for Al in the soils after the leaching period, the Al application rates for the solid manure treatments were greater than the other treatments, thus potentially reducing P mobility in the solid manure treatments (Lindsay, 1979).

There was a strong positive linear relationship between the average cumulative mass of TOC and average cumulative mass of TP lost in leachate from the solid and liquid manure treatments (Fig. 4). Although there was more C added with the

liquid manures compared with the solid manures, the C that was added in the liquid manures had higher aromaticity and therefore was more stable and resistant to aerobic oxidation. Therefore, microbial activity caused by C additions was likely greater in the solid manure treatments than the liquid manure treatments, and therefore, P may have been stabilized in microbial tissue in the solid manure treatments and less available for leaching. This same trend was found in calcareous silt loam soils treated with cattle liquid and solid manure, where the average microbial P was 2-fold greater in soils treated with solid versus liquid manures (A. B. Leytem, Ph.D., oral communication, 2008).

In addition, there could be C and P interactions in the liquid phase, which reduce the ability of P to be sorbed to the soil, and therefore P is moved out of the soil profile in C/P complexes. This theory was supported by Leytem and Westermann (2003) who found that organically complexed Fe and Mn played a significant role in P sorption in some calcareous soils. Chardon et al. (1997) also showed that P associated with organic compounds leached to a greater extent than inorganic P. The strong positive relationship between TOC and TP in the leachate suggests that the formation of these C/P complexes and transport of these out of the soil are likely. As the C in the liquid manure treatments moved to a greater depth in the soil profile, it is possible that these C compounds coated the soil-adsorptive surfaces through metal-C complexes and therefore reduced the ability of P to sorb to these sites, therefore enhancing P leaching.

Alternatively, phosphorus associated with the manures may have leached to a greater extent in the liquid manures because of preferential flow pathways in the soil and soil/column interface. However, this potential experimental error was realized and addressed during the planning of this study. To reduce the potential for significant preferential flow, we selected a soil that had minimal shrink/swell/cracking characteristics, and we eliminated the effect of creating a pressure head on the soil surface during liquid applications by applying all liquid manure and water using a drip apparatus to apply the liquids at a rate equal to the infiltration rate. Leaching of P through soils has been attributed to preferential flow through macropores (Magid et al., 1999; Simard et al., 2000; Hooda et al., 1999; Hansen et al., 2004). The precautions taken in our study ensured that much of the water would flow through the soil matrix. However, regardless of the water and P movement pathways, preferential flow is common in the field and is likely a major conduit for P movement in soils.

CONCLUSIONS

Phosphorus from dairy lagoon liquid manures moved through a calcareous soil to a greater extent than P from dairy solid manures and commercial fertilizer, and P from commercial fertilizer moved to a greater extent than P from dairy solid manures. Several factors likely influenced P mobility in the soil. The greatest masses of P and C moved through the soil during Leaching Events 2 through 7 for the liquid manure treatments. There was a strong relationship between P and C leaching, indicating the potential of C to influence P transport in manure-amended soils. It is possible that the form and quantity of C influences the mobility of P in soils because of several factors including microbial activity, organically complexed metals, and coating of P adsorption sites on clay particles. It is also possible that P reactions with Ca and Al reduced P leaching from the solid manure treatments. More research is needed to further elucidate the various potential factors influencing P leaching in calcareous soils in laboratory and field studies.

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