Use of soil amendments to reduce soluble phosphorus in dairy soils [*]

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Abstract

The objective of this research was to determine the effectiveness of soil amendments on reducing soluble P in Spodosols under dairy animal land-use. Dairy animal manure is a P source contaminating surface waters of the northern watersheds of Lake Okeechobee in south Florida. Phosphorus contamination has originated from manure-loaded soils found adjacent to milking barns, holding pens, feed lots under intensive animal use, and also developed pastures. In various batch-incubation studies, manure-loaded soils (7.0 to 120.9 g kg^{-1} as total organic C) were treated alone or in combination with varying rates of calcium carbonate (to pH 7.5), gypsum (0 to 100 g kg^{-1} soil), ferrous sulfate (0 to 1000 mg kg^{-1} as Fe), and alum (0 to 1000 mg kg^{-1} as Al). The influence of aerobic and anaerobic conditions on soluble P were also studied. Soluble phosphate concentrations were reduced 40 to 63% from gypsum application up to 100 mg kg^{-1} soil; nitrate and soluble organic carbon concentrations were similarily reduced by 45% and 49%, respectively. Increasing water-soluble Ca and the soil pH to 7.5 decreased soluble phosphate concentrations in manure-loaded soils. Gypsum amendments were effective under a broad range of manure loading, pH, and redox conditions. Bacterial activities were also affected by gypsum-amended soils. Calcium carbonate effectiveness was limited to lower pH soils (< pH 7.0). Although Fe and Al soil amendments increased P retention to over 400% from unamended soils, source costs and questionable biological toxicities may limit their usefulness. Evidence indicated that both precipitation and microbial mechanisms are involved in P retention/desorption in soils loaded with animal manures.

Keywords: Geochemistry; Gypsum; Lake Okeechobee; Soil management; Spodosols

1. Introduction

Phosphorus (P) is often recognized as the limiting nutrient in lake surface waters responsible for eutrophication (Syers et al., 1973). Phosphorus in surface waters has also been implicated as the causal nutrient responsible for accelerating eutrophic conditions in Lake Okeechobee, Florida (Federico et al., 1981; LOTAC, 1986; Little, 1988; LOTACII, 1988). In the northern watersheds of the Lake Okeechobee Watershed (LOW), significant quantities of P originating from soils under dairy and beef land use are leached into surface waters (Federico et al., 1981; Allen, 1988). Much attention has focused on studying the mechanisms of P transport and management practices that will prevent P release (Little, 1988; LOTACII, 1988).

Although highly variable, the native surface soils in the northern LOW region are sandy-textured haplohumods or haploaquods, with mean bulk density ranging from 1.2 to 1.5 g cc^{-1}, low pH (mean pH < 5.5), low clay contents (mean 1.3 dg g^{-1}), low cation exchange capacity (CEC; 1.4–13.2 me 100 g^{-1}), low contents of aluminum (Al), iron (Fe), and calcium (Ca), and low P retention (Yuan, 1966, 1980; Carlisle et al., 1988). Soils containing high amounts of manure are located adjacent to milking barns, holding pens, and feeding lots under intensive animal use. Soils under this land use generally have a high pH (> 7.0) due to the presence of calcium carbonate marl used in the elevation of barn and feedlot foundations and due to the high concentrations of manure (Ward et al., 1978). Under the above conditions, P retention is more related to domination of Ca in soil solution rather than to Fe and Al (Cogger and Duxbury, 1984). Under low pH (< 5.5) conditions found in outlying pastures, soluble Al and Fe probably will be more important than Ca.

The soils in this region are typically acid, coarse-textured, low in Ca, and with none to only a few percentages of clay (Graetz and Nair, 1995). As a result of intensive leaching, surface horizons are depleted of reactive Al and Fe, as well as Ca and Mg. A vast majority (74%) of soils in the LOW region are Spodosols with a leached E horizon and spodic horizon 51 to 89 cm in depth (McCollum and Pendleton, 1971). The spodic horizon is commonly adjacent or below the water table most of the year, and subsoil seepage and drainage of these soils are poor (aquod suborder). Under extensive drainage, significant lateral movement of organic C occurs (humod suborder). The physical and chemical properties in surface soils are not conducive to long-term P retention, however, the spodic subsurface horizon accumulates high amounts of P.

Three studies were conducted to determine the effectiveness of soil amendments in reducing soluble P in selected dairy soils. The principal working hypotheses of these studies are that Al, Fe, pH, and Ca interactions control P release in Spodosols; that under high P loading, high levels of Ca may be the predominant cation necessary to reduce P release; that high pH alone will not account for the reduction in P release; and that microbial activities are responsible for P mineralization and release. The soils selected for these studies were Spodosols of the nature described containing varying amounts of manure measured as organic C.

Table 1
Selected sites and soils for Study I and II

Site	Dairy use	Code	Series	Family/subgroup	TOC (mg kg^{-1})
1.	Intensive	C & MI2	Myakka fs	Sandy, siliceous hyperthermic Aeric Haplaquod	86
2.	Holding	C & MH1	Myakka fs	Sandy, siliceous hyperthermic Aeric Haplaquod	121
3.	Intensive	DL1I1	Immokalee fs	Sandy, siliceous hyperthermic Arenic Haplaquod	77
4.	Holding	DL1H1	Immokalee fs	Sandy, siliceous hyperthermic Arenic Haplaquod	35
5.	Pasture	DL133	Immokalee fs	Sandy, siliceous hyperthermic Arenic Haplaquod	25
6.	Pasture	DL189	Immokalee fs	Sandy, siliceous hyperthermic Arenic Haplaquod	21
7.	Pasture	L6CP1	Pomello fs	Sandy, siliceous hyperthermic Typic Haplohumod	23
8.	Intensive	WFRI1	Immokalee fs	Sandy, siliceous hyperthermic Arenic Haplaquod	23
9.	Holding	WFRH2	Immokalee fs	Sandy, siliceous hyperthermic Arenic Haplaquod	7
10.	Pasture	WFRCP2	Myakka fs	Sandy, siliceous hyperthermic Aeric Haplaquod	14

The objective of the first study was to determine the soil amendment or amendment combination most effective in reducing soluble P under a broad range of manure-loading and soil conditions. The objective of the second study was to verify the effectiveness of this amendment treatment under high manure-loading conditions. The objective of the third study was to determine whether biological activities are influenced by an imposed soil amendment practice.

2. Methods

2.1. Soil collection and analyses

Dairy soils under holding, intensive, and low-intensity use were selected and bulk sampled (0–15 cm) on January 18–21, 1988 from 10 sites (Table 1) located north of Lake Okeechobee, FL. Field bulk density was determined by the core method (Blake, 1965; Method 30.2). Soils were screened (2-mm mesh), air-dried, blended, and stored in sealed plastic barrels. The soils were analyzed for pH, water-soluble P_w, and acetic acid soluble P_a, K_a, Ca_a, and Mg_a (Anderson and Beverly, 1985; Sanchez, 1990). The pH buffer capacity, i.e. soil lime requirement, was determined to establish amounts of $CaCO_3$ needed to adjust soil pH to 7.0 (Jackson, 1958, 1973). Total organic carbon (TOC) in soil was determined by a Leco Gasometric Carbon Analyzer (Leco Corp., St. Joseph, MI).

Total soil nutrients were determined by ashing 0.25 g of oven-dry soil for 2 h at 400°C and 2 h at 500°C in a muffle furnace, dissolving the ash with 5 ml M HCl, heating the contents to dryness on a hot plate (80°C), and redissolving the contents with 50 m M HCl. The decant solution was filtered (0.45 μm) and the filtrate was analyzed for total P_t, K_t, Ca_t, Mg_t, Al_t, and Fe_t using inductively-coupled argon plasma (ICAP). Soluble P (measured as PO_4-P, P_s) was determined by weighing 0.4 g soil into 50 ml Oakridge-type glass centrifuge tubes, adding 40 ml distilled water, mixing with a rotary shaker (15 rpm) at 20°C for 1 h, and analyzing for PO_4-P in the filtrate (0.45 μm) using anion chromatography (ALPHA, 1985). The total soluble P_{ts} and Ca_{ts} determined by ICAP. Ammonium oxalate extractable Al_{ox} and Fe_{ox} (total) were determined after McKeague and Day (1966) and Schwertmann (1973).

2.2. Soil amendment evaluation study

The soil amendments chosen for evaluation were: Al as alum (Al; $Al_2(SO_4)_3 \cdot 18H_2O$, 98.0–102.0% assay), iron as ferrous sulfate (Fe; $FeSO_4 \cdot 7H_2O$, 99.0% assay), combinations of Al and Fe (AlFe), calcium carbonate (CC; $CaCO_3$, 99% assay), combinations of Al, Fe, and CC (AlCCFe), gypsum (G; $CaSO_4 \cdot 2H_2O$, 98% assay), combinations of CC and G (CCG), and combinations of Al, Fe, CC, and G (AlCCFeG). Because the soils used in this study varied in manure loading and chemistry, amendment treatment addition varied with each soil (Table 2). The soils from each site were separated into two groups using the following criteria: *Group 1*: pH > 7.0 and high levels of P_w, P_a and K_a (i.e. high loading); *Group 2*: pH < 7.0 and low-to-medium levels of P_w, P_a and K_a (low-to-medium loading).

Calcium carbonate was only applied to the lower pH Group 2 soils. Gypsum (Ca addition) was applied to all soils. Iron was applied to two soils in Group 1 and to all soils in Group 2. Aluminum was applied to only 4 of the 10 soils from Group 1 and 2. Subsamples (100 g) from each of the 10 soils were treated and incubated under aerobic (60% moisture capacity) and anaerobic (100% water saturated) conditions at 20°C $\pm$ 2°C for 12 weeks. Moisture contents were maintained by addition of deionized/distilled water every 2 days. A factorial design was utilized using three replications for each treatment combination (amendments and redox condition). The uncorrected redox potential was determined potentiometrically on the flooded anaerobic treated soils (Hesse, 1971, Method 17:4:2). Data were statistically analyzed using SAS (1985).

The P buffer power b_p was measured on selected amendment treatments (CC, CCG, CCFEG) under aerobic conditions using the procedures and mathematical functions described by Pagel et al., 1981, 1982 and Hartikainen, 1982. Absorption characteristics from the relationship, $dQ = b_o + b_p$ Sqrt(I), were determined (SAS, 1985) when the model was signficant ($p < 0.1$) for the selected soil × amendment combinations.

2.3. Gypsum amendment study

The objective of this study was to verify the effectiveness of gypsum amendment under high manure-loading conditions. The four Group 1 soils containing high

levels of total organic carbon as a result of dairy animal land use (Table 1) were selected for additional gypsum amendment studies. To 100 g of each soil, four rates of $CaSO_4$ were added (0, 4, 8, and 16 g kg^{-1}) using four replications. The soils were brought to WHC and allowed to incubate at 20°C for 7 weeks. After incubation, the soils were air-dried, screened (60-mesh), and final moisture contents (g g^{-1}) determined. Total soil P_t and Ca_t, P_s, P_{ts}, and pH were determined as previously described. Statistical analyses were performed using SAS (1985).

2.4. Microbial activity study

The objective of this study was to determine whether biological activities are influenced by an imposed soil amendment practice. During April of 1991, an Immokalee soil (*sandy, siliceous, hyperthermic Arenic Haplaquod*) was sampled (0 to 15 cm) within a dairy feedlot located in Okeechobee County, FL. The soil was screened (60 mesh) field moist and refrigerated (5°C) until study initiation. Treatments consisted of four rates of gypsum applied to the soil (90 g dry-weight equivalent) with one control: 0, 0.1, 1.0, 10, and 100 g kg^{-1} dry weight equivalent of soil. Soils were placed in 250 ml filtration flasks for incubation (Fig. 1). A continuous flow of CO_2-free air was maintained through each soil (0.1 ml air min^{-1}) for the duration of incubation (5 months). Treatments were replicated 6 times. Carbon dioxide evolution was estimated using 1 M NaOH CO_2-traps measuring bicarbonate accumulation at 15-day intervals for the duration of the study, but the data were highly variable and could not be used to evaluate microbial respiration.

Incubated soils were leached monthly with two aliquots of 35 ml 0.01 M KCl under suction (500–650 mm Hg). As previously described, the leachates were filtered (0.45 μm) for analyses of PO_4-P, NO_3-N, SO_4-S, and Cl using anion chromatography (APHA, 1985), total soluble K_{ts}, Ca_{ts}, and Mg_{ts} using ICAP, total dissolved C (TDC) and total dissolved organic C (DOC) using a Dohrmann Carbon Analyzer (DC-90, Xertex Corp., Santa Clara, CA), and solution pH and electrical conductivity (EC). Total soil N was determined using a Nitrogen-Carbon Analyzer NA-1500 (Carlo Erba Instrumentazione, Milan, Italy). The incubated soils with filter apparatus were weighed after each leaching period, and 0.01 M KCl was added as necessary to maintain constant soil moisture (w:w) for the duration of the study. At the termination of the study, soil water-extractable PO_4-P, NO_3-N, SO_4-S, Cl, Ca_{ts}, K_{ts}, and Mg_{ts} were determined (1:100 soil:H_2O wt vol^{-1} for 1 h, filtered at 0.45 μm) as previously described. Soil bacterial populations were determined after the final leaching. The b_p was measured as described previously on all soils before and after the final incubation period. Statistical analyses were performed using SAS (1985).

2.4.1. Bacterial enumeration

Soil samples (1 g) were aseptically diluted 10-fold in sterile 0.1% (wt vol^{-1}) sodium pyrophosphate solution and placed on a shaker for 30 min. Ten-fold serial dilutions were prepared in 0.85% (wt vol^{-1}) sodium chloride for inoculation of

Table 2
Initial soil data and treatments used in Study 1 [a]

Site	pH	P_w	P_a	K_a	Al_{ox}	Fe_{ox}	Ca_t	P_s	P_{ts}	P_i	P_s/P_i %[b]	P_{ts}/P_i %[c]	Treatments[d]	Uncorrected Redox Potential[e]
		mg kg^{-1}					g kg^{-1}	mg kg^{-1}						
1	7.96	17.2	62.9	560	106	588	76	419	539	2550	6.4	21.1	G,	−427 Group 1
2	7.41	14.1	182.3	371	103	385	213	584	796	9733	6.0	8.2	G, FeG, ALG	−431
3	7.38	15.8	87.1	350	90	578	68	416	597	2433	17.1	24.5	G,	−401
4	7.20	13.5	22.9	379	77	577	61	322	341	1077	29.9	31.7	G, AlFeG, FeG, ALG	−416
5	6.14	3.2	4.9	52	80	565	78	28	37	300	9.2	12.5	CCG, CCFeG, G, FeG, ALG	−340 Group 2
6	5.78	1.1	4.9	34	110	583	52	25	34	380	6.5	8.9	CCG, CCFeG	−304
7	5.80	1.6	2.8	18	114	552	71	16	32	210	7.6	15.0	CCG, CCFeG	−301
8	5.77	2.8	8.9	13	88	512	71	21	32	430	4.9	7.4	CCG, CCFeG	−329
9	6.12	0.7	0.9	11	82	338	29	4	5	293	1.3	1.6	CCG, CCFeG, G, FEG, ALG	−351
10	6.62	1.2	1.4	16	74	561	17	10	18	153	6.3	12.0	CCG, CCFeG	−309

[a] Complete factorial design using three replications for each treatment/treatment combination. Treatments were done under aerobic (60% moisture) and anaerobic (100% moisture) conditions.

[b] % P_s/P_i, index of the relative availability of ortho-P (PO_4-P fraction) in soil.

[c] % P_{ts}/P_i, index of the relative availability of total soluble P (PO_4-P plus organic P fraction) in soil.

[d] Gypsum (G) added at 0, 4, 8, and 16 g kg^{-1} soil; calcium carbonate (CC) rates taken individual soil lime buffer curves to achieve pH 7; iron (Fe) as $FeSO_4 \cdot 7H_2O$ added at 0, 50, 100, 250, 1000 mg Fe kg^{-1} soil; aluminum (Al) as $Al_2(SO_4)_3$ added at 0, 50, 100, 250, 1000 mg Al kg^{-1} soil.

[e] The uncorrected redox potential measured for treatments under flooded conditions after 3 months.
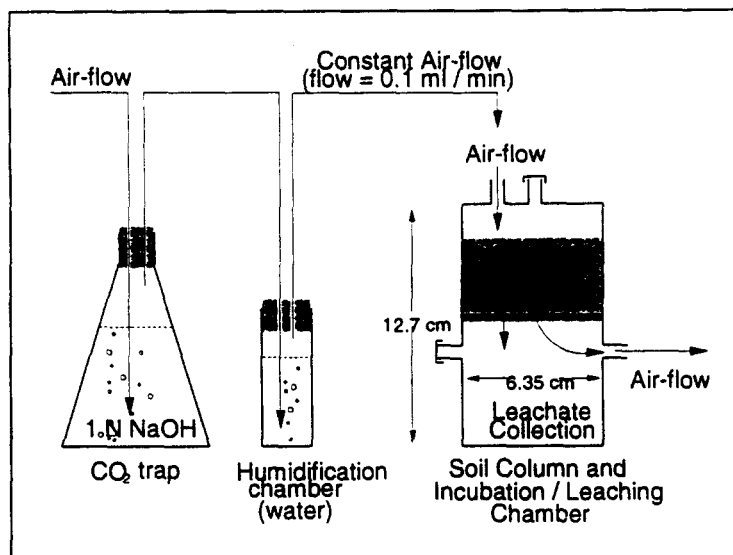
Fig. 1. Closed system apparatus setup for soil column leaching study.

various solid and liquid medium. For enumeration of aerobic heterotrophic microorganisms, diluted samples were spread-plated in duplicate on (i) peptone-tryptone-yeast-glucose (PTYG) agar (Balkwill, 1990) and (ii) 10% trypticase soy agar (TSA). The PTYG medium contained (per liter) 0.05 g peptone; 0.1 g yeast extract; 0.1 g D-glucose; 0.6 g $MgSO_4 \cdot 7H_2O$; 0.07 g $CaCl_2 \cdot 2H_2O$; and 15 g Bacto Agar. The TSA medium contained (per liter) 3 g trypticase soy broth and 15 g Bacto Agar. Plates were incubated at 25°C in the dark for 7 days. Both media are a non-selective, general-purpose media designed to recover heterotrophic bacteria from environmental samples.

Sulfur-oxidizing microorganisms were enumerated on thiosulfate agar which contained (per liter) 4.0 g K_2HPO_4; 1.5 g KH_2PO_4; 0.3 g $(NH_4)_2SO_4$; 0.5 g $MgSO_4 \cdot 7H_2O$; 10 g $Na_2S_2O_3 \cdot 5H_2O$; and 10 ml of trace metals solution. The trace metal stock solution contained (per liter) 2.2 g $ZnSO_4 \cdot 7H_2O$; 7.34 g $CaCl_2 \cdot 2H_2O$; 2.5 g $MnCl_2 \cdot 4H_2O$; 0.5 g $CoCl_2 \cdot 6H_2O$; 0.5 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$; 5.0 g $FeSO_4 \cdot 7H_2O$; 0.2 g $CuSO_4 \cdot 5H_2O$. The trace metal stock solution was adjusted to pH 6.0 with 1 M NaOH. Yeast extract (0.1 g l^{-1}) was added to provide additional trace nutrients. The medium was solidified with 1% (wt vol^{-1}) Bacto Agar. The plates were incubated at 25°C in the dark for 21 days.

Denitrifying bacteria were enumerated by a most-probable-number (MPN) method using a liquid medium which contained (per liter) 8.0 g nutrient broth and 0.5 g KNO_3. Decimal dilutions of each sample were inoculated (1%) in five replicates of autoclaved screw-cap test tubes partially filled with medium. After inoculation, each tube was filled to capacity with medium. After a 2-week incubation at 25°C in the dark, samples were withdrawn from each tube and tested for NO_3^- or NO_2^- by adding drop-wise up to six drops of diphenylamine reagent. The

reagent was prepared by dissolving 0.2 g of diphenylamine $(C_6H_5)_2NH$ in 100-ml of concentrated sulfuric acid (Tiedje, 1982). In this test, a blue color indicates the presence of NO_3^- or NO_2^- and the result is thus recorded as negative. A colorless response is considered presumptive evidence of denitrification, recorded as a positive result (i.e. denitrification).

Sulfate-reducing bacteria were enumerated by MPN in a liquid medium which contained (per liter) 0.5 g K_2HPO_4; 1.0 g NH_4Cl; 1.0 g Na_2SO_4; 0.1 g $CaCl_2 \cdot 2H_2O$; 2.0 g $MgSO_4 \cdot 7H_2O$; 3.5 g Na-lactate (70%); 1.0 g yeast extract; 0.5 g $FeSO_4 \cdot 7H_2O$; 0.1 g ascorbic acid; and 0.1 g Na-thioglycolate; adjusted to pH 7.4 with HCl. The medium was dispensed in test tubes and autoclaved. The tubes were inoculated in the same manner as described for denitrification, with five replicate tubes for each sample dilution and medium-filled headspace. Inoculated tubes were incubated for four weeks at 25°C in the dark. The samples were assessed for growth by the presence (positive results) or absence (negative results) of a black precipitate (FeS). Statistical analyses were performed using SAS (1985).

3. Results and discussion

3.1. Soil amendment evaluation study

Determining the conditions under which P release is minimized under manure loading soil conditions is necessary for selection of amendments that can be used to manipulate soil parameters such as soil pH, Ca, Al, and Fe.

3.1.1. Relationship of P release to soil pH, Ca, Fe, and Al

An index of the relative release of soluble P (PO_4-P and organic fractions) from each soil is measurable using the percentage ratios of the ortho-P (P_s) or total soluble P (P_{ts}) to the total soil P (P_t) content (Table 2). An increasing percentage ratio indicates that a greater percentage of the total soil P is released in a soluble fraction. Relative P releases were greater from three Group 1 soils with high C and P_t (Table 1 and 2) than the other soils. Despite the high C and P content at site 2 (Group 1), this soil demonstrated higher P retention, as indicated by the relative release indices, than other soils with a lesser C and P content.

The amounts of total soluble P (P_{ts}) released from untreated manure-loaded soils are potentially high. The relative release rates of P_{ts} were measured by the $P_{ts}:P_t$ ratio, which was modelled as to its relationship to the soil pH, Al_{ox}, Fe_{ox}, and Ca_t contents. From the data collected, extractable Al_{ox} and Fe_{ox} were not significantly ($p < 0.01$) related to the P release index, however, soil pH and Ca_t content were:

$$P_{ts}:P_t = 1411 - 444\,pH + 35\,pH^2 - 0.00011\,Ca_t^2\,pH \quad R^2 = 0.934 \qquad (1)$$

This relationship (1) decribes the combined influence of soil pH and soil Ca_t on P release. Phosphorus release increased under two soil conditions: increasingly acidic soils (pH < 6.3) typically found under native conditions, and soils increasingly

alkaline (pH > 6.3), due to increase in manure content. The relationship expressed by equation 1 also indicates an interaction between Ca and pH. Soil Ca and pH appear to be the most important factors to influence P retention. When soil pH and Ca were increased by the CCG amendment combination (Table 3), P_{ts} was significantly reduced as well or better than the other amendments and combinations.

3.1.2. Amendment treatments and redox conditions

Soils from the Okeechobee area are subject to periodic flooding. The influence of anaerobic and aerobic conditions on P release and the effectiveness of soil amendments to manipulate P release under redox conditions are important to understand. There were significant differences in the amount of extractable P_{ts} among all soils, between aerobic and anaerobic redox conditions, and among the amendment treatments or combinations (Table 3). Group 1 soils (sites 1–4) were significantly different from Group 2 soils (sites 5–10). Across all soils and redox conditions, soil pH adjustment (CC) together with gypsum application was the

Table 3
ANOVA and simple statistics [a] for total soluble P (P_{ts}, mg kg^{-1}) ($R^2 = 0.835$ [b]; Study 1)

Source	df	Mean square	F
Model	43	147 708	94.96 **
Error	808		
Soil sites (1–10)	9	461 083	296.4 **
Redox (aerobic, anaerobic)	1	334 223	214.8 **
Treatment (amendments)	5	25 584	16.4 **
Soil × Redox	9	137 947	88.7 **
Soil × Treatment	12	41 388	26.6 **
Redox × Treatment	2	537	0.3 ns
Soil × Redox × Treatment	5	61	0.04 ns

Sites	P_{ts}	Redox conditions	P_{ts}	Amendment treatment	P_{ts}
4	298 a	Aerobic	69 a	G	180 a
3	181 b	Anaerobic	13.6 b	AlG	115 b
1	164 c	LSD$_{0.05}$ = 5.3		FeG	110 b
8	93 d		AlFeG	100 b	
2	53 e			CCG	16 c
7	23 f			CCFeG	12 c
5	15 fg			LSD$_{0.05}$ = 15.2	
6	8 fg				
9	6 g	Mean ($n = 853$) = 45 mg kg^{-1}			
10	2 g	min. = <1 mg kg^{-1}			
LSD$_{0.05}$ = 15.4		max. = 582 mg kg^{-1}			
		STD = 95 mg kg^{-1}			

[a] Duncan Multiple Range Groupings, means with the same letter are not significantly different ($p < 0.05$).
**, significant at $p < 0.01$; ns, not significant at $p > 0.10$.

simplest and most effective amendment combination (CCG) for reducing P desorption.

Across all soils and soil grouping ($n = 368$), the relationship of P_{ts} with pH and Ca_{ts} under aerobic conditions was determined (model $R^2 = 0.78$, $p < 0.001$; all terms significant at $p < 0.001$):

$$P_{ts} = -2659 + (1.56\,Ca_{ts}) + (901.0\,pH) - (0.518\,Ca_{ts}\,pH) - (73.1\,pH^2)$$
$$+ (0.0413\,Ca_{ts}\,pH^2). \tag{2}$$

Under aerobic soil conditions in the pH range 5.8 and 6.4 and Ca_{ts} was less than 60 mg kg^{-1}, P_{ts} release was the highest. In the same pH range, soil amended with gypsum (G) and calcium carbonate (CC) reduced amounts of P_{ts}. As the soil pH increased, pH had more influence in reducing P_{ts} than Ca_{ts}. At a soil pH of 7.4, the P_{ts} was minimized and unaffected by further Ca_{ts} additions (G). These results suggest that at soil pHs exceeding 7.4 and increasing Ca_{ts}, amendment strategies for further reduction of P_{ts} are not evident under aerobic conditions.

Across all soils and soil groupings ($n = 362$), the relationship of P_{ts} with pH and Ca_{ts} under anaerobic conditions was also determined ($p < 0.001$; $R^2 = 0.81$):

$$P_{ts} = 12.16 - (0.022\,Ca_{ts}) - (0.00000267\,pH^2) + (0.176\,pH). \tag{3}$$

Under anaerobic conditions, soil pH has little control over P release. However, increases of soluble Ca_{ts} applied as gypsum or lime increased P_{ts} retention. The importance of these results is that under flooded and non-flooded conditions, direct soil amendment application of gypsum and/or limestone should be effective in controlling P release in manure-loaded soil systems. More than 5 times more soluble P was released from soils under aerobic conditions than from anaerobic conditions. This indicates two possible mechanisms: increase of Fe^{+2} under low Eh conditions (flooding) and precipitation with P, and that aerobic biological processes (biological oxidation) are contributing to P release.

3.1.3. P buffer power

Phosphorus release/desorption is a characteristic of the Spodosols used in these studies. Typical P isotherms used for adsorption characterization (i.e. Langmuir, van Bemmelen-Freundlich, etc.) are not applicable for soils with desorption characteristics. Consequently, the P quantity/intensity isotherms described by Pagel et al. (1981, 1982) and Hartikainen (1982) were used to examine P desorption and retention. The amount of phosphorus in solid phase (Q, mg P kg^{-1} of soil) is derived as a function of the amount of phosphorus found in liquid phase (I; mg P l^{-1} solution). The isotherm becomes a function of the following equation: $dQ = b_o b_p$ (Sqrt I). The square root of I (Sqrt I) is used for linear transformation of the curvilinear relationship between dQ and I. The intercept (b_o) represents P desorption (d_p). The slope represents the P buffer power (b_p). Positive slopes indicate that the soil retains P; likewise, negative slopes indicate P desorption.

The b_p of selected soil treatments (CC, CCG, CCFeG, AlG, FeG) were determined under aerobic conditions (Table 4). All soils from Group 1 demon-

Table 4
Adsorption characteristics[a] of selected amended soils under aerobic conditions

Sites	Amendment	b_o	b_p	I_{eq}	R^2
		mg kg^{-1}		mg l^{-1}	
1	0	26.2	16.1	2.65	ns
(Group 1)	G	− 17.0	11.1	2.34	0.776 ˙˙
	AlG	− 86.7	68.4	1.61	0.945 ˙˙
	FeG	− 62.0	65.7	0.89	0.924 ˙˙
2	0	− 101.7	33.8	9.04	0.966 ˙˙
(Group 1)	G	− 41.3	57.6	0.51	0.984 ˙˙
3	0	− 62.8	18.9	11.03	0.805 ˙˙
(Group 1)	G	− 12.7	16.3	0.61	0.637 ˙˙
4	0	− 11.6	6.3	3.30	ns
(Group 1)	G	− 15.1	10.2	2.21	0.724 ˙˙
5	0	− 25.0	0.0	1.0	ns
(Group 2)	CC	− 14.0	0.0	1.0	ns
	CCG	− 17.0	0.0	2.9	ns
	CCFeG	− 4.0	5.0	0.63	0.889 ˙˙
6	0	− 12.0	0.0	0.75	ns
(Group 2)	CC	0.5	8.4	0.004	0.717 ˙˙
7	0	− 18.0	0.0	3.20	ns
(Group 2)	CC	2.0	3.6	0.31	0.861 ˙˙
8	0	− 25.0	0.0	3.60	ns
(Group 2)	CC	− 10.0	0.0	1.40	ns
9	0	14.0	− 9.5	2.20	0.914 ˙˙
(Group 2)	CC	− 2.0	0.0	0.25	ns
10	0	− 2.0	0.0	0.25	ns
(Group 2)	CC	− 2.0	0.0	0.01	ns

[a] b_o is the maximum desorption (d_{max}); P buffer power (b_p); I_{eq} = equilibrium P concentration. Absorption characteristics measured across a range of amendment additions.

strated a "positive" b_p (retention), whereas, all soils from Group 2 demonstrated "zero" or "negative" b_p (desorption). Initial equilibrium P concentrations (before P addition) ranged from 11.03 to 0.25 mg l^{-1}. These concentrations were reduced after amendment treatment and incubation.

Group 1 describes soils with a positive P retention capacity. Amendments were generally very effective in increasing retention and reducing P desorption. Gypsum applied at the rate of 4 g kg^{-1} at site 2 increased b_p by 170%, decreased the equilibrium concentration of P (I_{eq}) in solution by 17.7-fold, and decreased the maximum desorption (d_{max}; Hartikainen, 1982) more than 250% from the non-amended soil. Gypsum applied alone did not increase the b_p for every Group 1 soil (at sites 1, 3, and 4), although the equilibrium P concentrations (at b_0) were reduced by 11 to 94%. Greater manipulation of b_p on Group 1 soils appears possible by the addition of Al or Fe with gypsum (soil at site 1); respectively, Al and Fe increased b_p by 420 to 408% from the unamended soil. In combination with gypsum, Al and Fe increased b_p by approximately the same power.

Group 2 describes soils with "zero" P buffer capacity, i.e. P characterized by release rather than by retention. These soils also have low b_{pH} (data not shown)

Table 5
Soluble soil Ca, P, C, and the calculated IAP_{HAP} [a] after gypsum equilibrium (Study 2)

Sites	Gypsum g kg^{-1}	pH	pCa_{ts}	$pHPO_4^{-2}$	pIAP	P_{ts}	TDC	DOC
			moles l^{-1}				mg kg^{-1}	
1	0	7.4	0.972	0.970	58.4	513	1190	976
	4	7.2	0.980	0.977	59.7	328	1088	950
	8	7.1	0.947	0.983	58.0	274	777	671
	16	6.8	0.868	0.985	56.4	308	780	658
2	0	7.7	0.987	0.957	59.2	802	2556	2091
	4	7.4	0.978	0.969	58.9	550	2184	1865
	8	7.2	0.943	0.974	57.1	457	1865	1610
	16	7.1	0.887	0.979	56.0	299	1528	1432
3	0	7.4	0.996	0.970	62.8	563	1355	1132
	4	7.2	0.983	0.978	60.0	335	973	916
	8	7.1	0.957	0.980	58.2	287	946	830
	16	6.9	0.884	0.984	56.5	238	660	576
4	0	7.3	0.996	0.976	63.2	365	1025	820
	4	7.0	0.982	0.987	60.9	311	439	386
	8	7.0	0.952	0.989	58.9	233	493	366
	16	6.9	0.877	0.990	56.9	176	476	387

[a] Ion activity product of HAP after Minzoni and Moroni (1987); $pHPO_4^{-2}$ calculated from P_s.

and required calcium carbonate to raise the soil pH (> 7.0). Calcium carbonate decreased the equilibrium P concentration (I_{eq}) by 0 to 96%, although the b_p increased in only two of the six Group 2 soils. The effectiveness of calcium carbonate and gypsum together was similar to calcium carbonate applied alone. The addition of Fe in combination with calcium carbonate and gypsum, increased b_p and decreased P desorption (b_o) and I_{eq}. Total extractable soil Al_{ox} and Fe_{ox} were not related to P release characteristics, and other soil extraction procedures may prove to be significantly related.

3.2. Gypsum amendment study

Application rates of up to 16 g kg^{-1} gypsum to Group 1 soils resulted in 48 to 57% reduction of P_s (listed as $pHPO_4$) and 40 to 63% of P_{ts} (Table 5). Assuming that all soil characteristics except TOC remain the same, precipitation is a plausible explanation for P retention. Widely acknowledged, the primary factors affecting precipitation mechanisms are pH, Ca_{ts}, P_{ts}, and soluble Al and Fe in soil solution (Stumm and Morgan, 1970; Syers et al., 1973; Berkheiser et al., 1980). At high pH, soluble Al and Fe are insignificant and Ca in soil solution will be the predominate P-reactive cation in soil solution. Therefore, Ca_{ts} applied as gypsum should promote precipitation as calcium phosphate.

Calcium hydroxyapatite (HAP) is likely to be found under the solution conditions listed in Table 5 (Stumm and Morgan, 1970; Lindsay, 1979). The reported ion

activity product of HAP ranges from $pIAP_{HAP} = 50$ to 57 mol^{-1} (Minzoni and Moroni, 1987), where:

$$IAP_{HAP} = (Ca^{2+})^5 \left[(HPO_4^-)/((1 + H^-)/K3) \right.$$

$$\left. + (H^+)^2/(K2\,K3) \right]^3 Kw/(H^-),$$ (4)

Ca^{2+}	= calcium concentration (mol l^{-1}),
HPO_4^-	= orthophosphate concentration (mol l^{-1}),
H^+	= hydrogen concentration (mol l^{-1}),
K2	= ionization constants for mono-basic phosphate (pK2 = 7.165),
K3	= ionization constants for di-basic phosphate (pK3 = 12.18),
Kw	= ionization product of water (pKw = 14).

Under the experimental conditions listed in Table 5, the calculated $pIAP_{HAP}$ ranged from 56.0 to 62.8, which is within the upper range of precipitation for HAP (Bell et al., 1978; Lindsay, 1979; Lofgren and Ryding, 1985). With increasing application of gypsum, the $pIAP_{HAP}$ declined into the range reported for HAP. Although these calculations may indicate that precipitation reactions may be occurring, the corresponding solubility product constants only provide indirect evidence of possible precipitation mechanisms controlling P in soil solution (Sposito, 1984, pp. 122–128).

Precipitation of HAP can be inhibited by organic acids, even though the soil solution is supersaturated with respect to HAP (Inskeep and Silvertooth, 1988). In the presence of animal manures, the extent of interferences of precipitation reactions by fulvic, humic, and tannic acids is unknown (Stevenson, 1981; Tate, 1987). There were significant quantities of TDC and DOC in these soils which also declined with increasing application of gypsum. Gypsum either enhanced precipitation of P, TDC, and DOC or influenced biological immobilization and mineralization releasing them. Regardless of the mechanism, experimental results from this study indicate that Ca_{ts} applied as gypsum increased P and C retention in high manure-loaded dairy soils.

3.3. Microbial activity study

Immokalee soils comprises 26% of the LOW soils (McCollum and Pendleton, 1971) and are indicative of well-drained soils used for milking barns and for high-intensity animal holding areas. Natively, these sandy soils typically contain less than 1% organic matter and contain low quantities of soil N and P. The Immokalee soil selected in Study 3 contained 11.1% organic matter as animal manure and had a C:N:P ratio approximately 100:10:1 (Table 6). Significant quantities of C, N, and P were expected to be mineralized and released from this soil.

Table 6
Soil composition of the Immokalee dairy soil before initiation of Study 3

Characteristic	Value
pH	6.83
Ash	889 g kg^{-1}
C	42.3 g kg^{-1}
N	4.1 g kg^{-1}
P	421 mg kg^{-1}
K	48.2 mg kg^{-1}
Ca	876 mg kg^{-1}
Mg	103 mg kg^{-1}
Al	66.4 mg kg^{-1}
Fe	49.0 mg kg^{-1}

3.3.1. Nutrient leaching and gypsum

Soil treatments were incubated and leached for 5 months. The total accumulated quantities of DOC, NO_3-N, and PO_4-P leached through the amended soil decreased with increasing gypsum application (Table 7: DOC, NO_3-N, and PO_4-P in leachates across all leaching periods were reduced by 49, 45, and 60%, respectively, by comparison to the untreated soil. Sulfate-S, Cl, Ca, Mg, and K in

Table 7
Leachate characteristics across a 5 month incubation period and bacterial enumeration (counts per gram of soil) after incubation (Study 3)

Gypsum applied	pH	EC (mhos cm^{-2})	PO_4-P	NO_3-N	SO_4-S	Cl	Ca	Mg	K	DOC
			mg kg^{-1} soil							
0.00	6.3	2557	274	2172	380	1679	850	288	1598	423
0.01	6.4	2520	243	1928	445	1602	794	284	1597	382
0.10	6.4	2647	227	1859	1115	1649	958	302	1612	364
1.00	6.3	3280	181	1756	4075	1511	2044	410	1664	343
10.00	6.4	2383	110	1190	5805	1672	2577	398	1701	215
LSD$_{0.1}$ [a]	ns [a]	1589	38	612	914	127	323	28	34	58

Gypsum application	Aerobic plate counts		Anaerobic MPN counts	
	TSA	PTYG	SRB [a]	Denitrifiers
0.0	13666	1460	1.3	20502
0.1	806	1770	249	751
1.0	1447	1498	117	455
10.0	940	802	99	265
100.0	763	1130	77	169
LSD$_{0.1}$ [a]	ns [a]	ns	242	17331

[a] LSD$_{0.1}$ determined by PROC ANOVA (SAS, 1985), pairwise t-tests, equivalent to Fisher's least-significant-difference test in the case of equal cell sizes, for all main-effect means; ns, not significant.

leachates increased with gypsum application. The elevated levels of Ca and SO_4-S in leachates were expected from addition and dissolution of $CaSO_4$. Elevated concentrations of Mg and K in leachates could have been a result of Ca exchange on cation exchange sites, although the cation exchange capacity was not determined.

The average soil pH decreased from 6.8 to 6.4, although gypsum is a neutral salt that should not alter soil pH. Mineralization of manure and other organic matter in the soil will result in soil acidification. Therefore, the importance of factors influencing the formation of solid-phase HAP and the role of biological activity are important. However, the role of manure-derived organic acids in controlling phosphate precipitation is not clear.

Soluble P was reduced after gypsum application which indicates an increase in the apparent P retention of amended soils. Increases in the P buffer power (b_p) should therefore be observed if HAP precipitation occurred. However, no significant ($p < 0.01$) differences in the b_p after soil amendment with gypsum were observed (data not shown). Because soil gypsum application also reduced amounts of soluble C and N lost through leaching, the effect of gypsum on microbial activity must be considered.

3.3.2. Gypsum effect on soil microorganisms

Bacterial enumeration was performed using five culture media. Three were designed for aerobic plate counts; the remaining two were used for anaerobic most-probable-number estimates of denitrifiers and sulfate reducers. Aerobic heterotrophic plate counts were usually higher than the anaerobic counts in these samples. The microbial counts indicated a decrease in populations of about one order of magnitude from the beginning to the end of the experiment.

The two heterotrophic plate count media (TSA and PTYG) yielded comparable bacterial numbers. These heterotrophic plate counts showed relatively little variation in response to gypsum application (Table 7) although, where discernible ($LSD_{0.1}$), the trend indicated a decrease in bacterial numbers with increasing application of gypsum. Enumeration techniques based on cultural recovery yield only comparative information. Therefore, plate counts (and MPN counts) should only be construed to represent relative changes in the recoverable population size in response to the treatment.

The plate counts for thiosulfate-oxidizing microorganisms were $\leq 10^3$ ml^{-1} or g^{-1} (data not shown), but were deemed inaccurate due to high variability of colony counts among replicates. Except for the agar and 0.01% yeast extract, the formulation of the medium was based on inorganic salts, with thiosulfate as the energy source to select for thiobacillus-type bacteria. The variability in colony counts may result from the ability of some heterotrophic organisms to grow with carry-over and agar-derived organic compounds, thereby negating the selectivity of the $S_2O_3^{2-}$ – based medium. In addition, upon prolonged incubation many colonies formed precipitates in the medium, making it difficult to differentiate colonies from the background.

The sulfate-reducing (SRB) and denitrifying bacterial counts were influenced by

gypsum application (Table 7). The SRB counts in untreated samples were orders of magnitude lower than those of denitrifiers. The counts of SRB were relatively steady during incubation, in spite of the presence of sulfate applied as gypsum as a potential anaerobic electron acceptor. Sulfate-reducers are obligate anaerobes and inactivated by dissolved or atmospheric oxygen. Therefore, the lack of increase in sulfate-reducing bacterial counts suggests that anaerobic conditions were negligible throughout the incubation. Denitrifying bacteria, on the other hand, are facultative anaerobes and capable of growing with either oxygen or nitrate as the electron acceptor. Denitrifying bacteria constituted a varying fraction of the recoverable bacterial communities under these experimental conditions. With some samples, the denitrifying bacterial counts were higher than the aerobic plate counts (Table 7). These differences are attributed to a better recovery of bacteria with liquid media vs. solid media from environmental samples. Availability of nitrate (Table 7), the electron acceptor for denitrification, did not appear to be a limiting factor for denitrifiers in untreated and gypsum-amended soils.

4. Conclusions

Manure-loaded soils contain fractions of soluble and insoluble, organic and inorganic P. With time, a portion of the insoluble organic P can be mineralized to a soluble P fraction. Evidence indicates that soil amendments can significantly reduce the amounts of soluble P leached from these soils. These amendments include those investigated in these studies: calcium carbonate, gypsum, Al sulfate, and Fe sulfate. Calcium carbonate was effective when used to raise and maintain the soil pH in the range 7.0 to 7.5. Maintaining this pH is important because solid-phase P will be released should soil acidification occur over time. Gypsum was effective at all pH ranges under anaerobic conditions, but to varying degrees under aerobic conditions. Gypsum was highly effective in Spodosols with high loads of manure. Calcium carbonate and gypsum applied alone or in combination were more effective in reducing soluble P when Al and/or Fe are applied in combination. However, there are recognized limitations. Aluminum can be toxic in acid soils (pH < 5.2), and costs of either Al or Fe may additionally limit the practical use of the Al and Fe sources.

Gypsum as a soil amendment had an impact on bacterial recoveries, but the reason for bacterial suppression was unclear. Bacterial suppression would also occur under anaerobic conditions. Because reagent-grade gypsum was used in this study, the role of toxic trace metals or other impurities can be excluded. Similarly, the data do not indicate that nutrient limitation at increasing gypsum application would have limited bacterial growth with time. The retention of phosphate in soil due to gypsum amendment warrants further investigation in view of the importance of soluble phosphate in the eutrophication process.

The results suggest that land disposal/application of gypsum, as a waste material from the construction industry (gypsum board), coal-burning power plants

(flue-gas desulfurization gypsum), and phosphate production (phosphogypsum) will have an impact on soil microorganisms by cycling and mobilization of nutrients. However, the toxicity of other constituents in these waste materials should also be tested. Further work on the underlying biological and chemical mechanisms involved in land-application of gypsum waste materials under intensive nutrient loading is needed for proper management practices of gypsum disposal.

Acknowledgements

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