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R. B. Brennan[abc], D. P. Wall[b], O. Fenton[b], J. Grant[d], A. N. Sharpley[c] & M. G. Healy[a]

[a] Civil Engineering, National University of Ireland, Galway, County Galway, Republic of Ireland

[b] Teagasc, Environmental Research Centre, Johnstown Castle, County Wexford, Republic of Ireland

[c] Department of Crop, Soil, and Environmental Sciences, Division of Agriculture, University of Arkansas, Fayetteville, Arkansas, USA

[d] Teagasc Research Centre, Ashtown, County Dublin, Republic of Ireland

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Impact of Chemical Amendment of Dairy Cattle Slurry on Soil Phosphorus Dynamics Following Application to Five Soils

R. B. BRENNAN,[1,2,3] D. P. WALL,[2] O. FENTON,[2] J. GRANT,[4] A. N. SHARPLEY,[3] AND M. G. HEALY[1]

[1]Civil Engineering, National University of Ireland, Galway, County Galway, Republic of Ireland
[2]Teagasc, Environmental Research Centre, Johnstown Castle, County Wexford, Republic of Ireland
[3]Department of Crop, Soil, and Environmental Sciences, Division of Agriculture, University of Arkansas, Fayetteville, Arkansas, USA
[4]Teagasc Research Centre, Ashtown, County Dublin, Republic of Ireland

A 9-month incubation study was conducted to investigate the effectiveness of amending dairy cattle slurry with either alum, lime, poly-aluminum chloride (PAC), or ferric chloride ($FeCl_3$) in reducing water-extractable P (WEP) levels in five soils (four mineral and one organic). Alum, lime, and PAC were the most effective amendments in decreasing WEP (compared to a slurry-control) for the four mineral soils (by an average of 47% at the end the 9-month incubation period). In comparison, $FeCl_3$ increased WEP (compared to the slurry-control) by an average of 35% at the end the study. None of the amendments examined effectively reduced WEP of the organic soil. No amendment reduced soil-test P [(Morgan's P (P_m) and Mehlich 3 P (M3P)] compared to the soil-only treatment. Alum maintained the greatest levels of M3P across the four mineral soils with the least risk of P loss to overlying water.

Keywords Alum, lime, management practices, poly-aluminum chloride, soil-test phosphorus, water-extractable phosphorus

Introduction

Land application of dairy cattle slurry can result in incidental and chronic phosphorus (P) losses to a water body (Buda et al. 2009), which may lead to eutrophication (Carpenter et al. 1998). Incidental P losses occur when a rainfall event occurs shortly after slurry application and runoff is generated before the slurry has infiltrated the soil, whereas chronic P losses are long-term losses of P from soil as a result of a buildup in soil test P (STP) caused by the repeated or overapplication of inorganic fertilizers and manure (Preedy et al. 2001; Buda et al. 2009). The current study focuses on P loss from soils receiving chemically amended dairy cattle slurry. When dairy cattle slurry is applied to soil, it results in an increase in STP (Sharpley, McDowell, and Kleinman 2004). Once STP levels increase above agronomic optima, there is a greater risk of P loss to water bodies than from soils with lower STP

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Address correspondence to R. B. Brennan, Civil Engineering, National University of Ireland, Galway, Ireland. E-mail: raymond.brennan@nuigalway.ie

levels (Sharpley et al. 1996; Sharpley, McDowell, and Kleinman 2004). Water bodies near farms with a limited land base to distribute slurry are at particular risk, as slurry may be applied or is more likely to be applied to high STP soils (Doody et al. 2012; Wall et al. 2013). In these situations, both long- and short-term P-management measures, such as implementing P-drawdown strategies, transporting P off-farm, and soil, slurry and manure amendments that sequester P, may need to be utilized.

Chemical amendments have been shown to be effective in decreasing P solubility in dairy cattle and swine slurries (Dao and Daniel 2002; Dou et al. 2003; Brennan et al. 2011a) and in mitigating incidental P losses in runoff (Smith et al. 2001; Elliott et al. 2005; Torbert, King, and Harmel 2005; Brennan et al. 2011b; O'Flynn et al. 2012; Brennan et al. 2012). There has been limited research on the effect of chemical amendments used to lower soil P solubility on long-term P dynamics (Ann, Reddy, and Delfino 1999; Callahan et al. 2002; Kalbasi and Karthikeyan 2004; Moore and Edwards 2007). Kalbasi and Karthikeyan (2004) examined a silt loam soil with three different STP levels (12, 66, and 94 mg kg^{-1} Bray 1 P, respectively) in an incubation experiment conducted over 24 months. An untreated slurry control and slurry amended with alum, ferric chloride ($FeCl_3$), or lime were added to the three different STP soils. Kalbasi and Karthikeyan (2004) found that the effect of chemical amendment depended on treatment type, P application rate, and background STP level and recommended that more work was needed to investigate the effectiveness of amendments in soils varying in physical and chemical characteristics. Callahan et al. (2002) amended four loam soils with seven P sorbing amendments and found that gypsum and water treatment residual (WTR) effectively decreased soil water-extractable phosphorus (WEP) without any adverse agronomic effects. Moore and Edwards (2007) examined the effects of chemical amendment of poultry litter on a silt loam over a 20-year study. They found that long-term land application of alum-amended poultry litter decreased P runoff and that aluminum (Al) availability was lower from plots receiving alum-treated poultry manure than plots receiving ammonium (NH_4-N) fertilizer. Therefore, there is a need to examine how amendments perform across different soil types in order to identify situations (soil types, STP levels, climate, etc.) where they may be most effective.

Soil type plays a significant role in soil P solubility and it is critical that soil type is considered when examining the potential of amendments to reduce chronic P losses. Tunney (2000) found a strong association between STP (measured using Morgan's extracting solution) and dissolved reactive P (DRP) concentrations in overland flow in Irish grassland soils. This relationship can vary between different hydrological conditions (Kurz et al. 2005) and soil types (Daly, Jeffrey, and Tunney 2001; Regan et al. 2010). Daly, Jeffrey, and Tunney (2001) examined 11 soils chosen to best represent important agricultural grassland soils in Ireland varying in parent material, drainage, soil type, and chemical properties and found that although STP was an important factor controlling P desorption, soil type also affected levels of sorption and desorption. Of particular interest is the effectiveness of amendments in organic soils, which are commonly found in parts of Ireland, mainland Europe, and the United States. Such soils are often intensively farmed and require P applications annually, as they have poor P-retention capacity. Amendments may also offer the potential to apply slurry to peat soils with reduced risk of P losses and improved plant availability.

The objectives of this study were to investigate (1) the effectiveness of chemical amendments to reduce the solubility of P in dairy cattle slurry across five different Irish soils with different physical and chemical characteristics, (2) changes and relationships between soil WEP and STP following incorporation of amended slurry into soil under controlled laboratory conditions, and (3) using the results to make recommendations on which soils, or soil properties, can be used to select locations within catchments most suitable for strategic use of chemical amendments.

Materials and Methods

Soil Collection and Analysis

Soils with different texture, organic matter (OM), and pH were selected to test the effectiveness of the amendments in a variety of conditions and to represent some common soil types used in dairy farming in Ireland. The five soils collected were in the agronomic optimum STP range (Morgan's P levels of 5.1 to 8 mg L^{-1}) for productive grasslands with the exception of soil C (Table 1), which was in the P-deficient range (<5.0 mg L^{-1}) and the peaty soil (soil E; 24.6 mg L^{-1}), which had an excessive STP level (>8.0 mg L^{-1}). The STP index system used in Ireland ranges from 1 to 4, where a soil with P index 1 (very low) and 2 (low) has a likely response to P fertilizers; a P index 3 (agronomic optimum) and P index 4 (excessive) has no response to additional P fertilizer application and has a high risk of P loss. A peat soil was included, as there is a particular risk of P loss in runoff from peat soils due to their limited capacity to absorb P (Iyamuremye and Dick 1996; Cummins and Farrell 2003).

The soils were collected from five grassland sites, air dried, and crushed to pass a 2-mm sieve. Plant-available soil P was determined by Morgan's P extract, the standard agronomic soil P testing method in Ireland (Morgan 1941) and by Mehlich 3 extractant (M3P) (Mehlich 1984). Mehlich 3 Al and iron (Fe) (M3-Al and M3-Fe) were used to estimate degree of P saturation in the soils (Maguire and Sims 2002). Mehlich 3 calcium (Ca), cobalt (Co), copper (Cu), potassium (K), magnesium (Mg), manganese (Mn) and zinc (Zn) were also analyzed. Soil WEP was determined after McDowell and Sharpley (2001) using a 100:1 deionized water-to-soil ratio.

Soil pH (n = 3) was determined using a pH probe (WTW, Oberayern, Germany) and a 2:1 ratio of deionized water to soil. Particle-size distribution (PSD) was determined using hydrometer method (B.S.1377-2:1990; British Standards 1990a) and the OM concentration of soil determined using loss of ignition (LOI) test (B.S.1377 3; British Standards 1990b). The results are presented in Table 1.

The approximate field capacity for each soil was determined after Bond, Maguire, and Havlin (2006). The approximate bulk density of each soil used in this study was determined based on the container volume occupied by 100 g of sieved soil after field capacity was achieved (Table 1).

Slurry Collection and Analysis

Slurry from dairy replacement heifers was taken from a farm (53° 18′ N, 8° 47′ W) in County Galway, Republic of Ireland, in June 2010. The slurry in the storage tanks was fully agitated (mixed) prior to sampling and the slurry samples were transported to the laboratory in 10-L drums. Slurry samples were stored for 48 h at 4 °C prior to the incubation study and analysis was completed within 24 h of slurry being added to soil. Slurry pH was determined using a pH probe (WTW, Oberbayern, Germany). The total P (TP), total nitrogen (N) (TN), and total K (TK) of the dairy cattle slurry were determined following digestion of 3 g of well-mixed slurry in a 100-mL Kjedahl digestion flask with 10 mL of concentrated sulfuric acid (H_2SO_4) and 6 mL of 100 volumes hydrogen peroxide (H_2O_2) with selenium lithium sulfate tablets as a catalyst for 2 h before diluting the cooled digestate to 100 mL

Table 1
Soil location, texture, and physical and chemical properties

Parameter	Unit	Soil A Cork	Soil B Wexford	Soil C Wexford	Soil D Galway	Soil E Sligo
Coordinates		52° 07′ N, 8° 16′ W	52° 17′ N, 6° 31′ W	52° 17′ N, 6° 31′ W	53° 21′ N, 8° 34′ W	54° 04′ N, 8° 52′ W
Soil texture		Sandy loam	Clay loam	Loam	Silty loam	—
Sand content	%	56.2 (1.1)	51.8 (4.2)	37.8 (1.1)	15.0 (1.4)	—
Silt content	%	25.8 (1.3)	28.1 (4.9)	31.1 (1.0)	72.0 (1.1)	—
Clay content	%	18.0 (2.4)	20.1 (2.2)	31.1 (2.1)	13.0 (1.2)	—
Organic matter	%	7.9 (0.6)	7.8 (0.3)	6.7 (0.5)	13.3 (0.2)	77.4 (0.4)
Soil pH		6.1 (0.9)	5.7 (0.1)	6.50 (0.02)	5.10 (0.04)	5.6 (0.1)
P index[a]		3	3	1	3	4
Water-extractable phosphorus (WEP)	mg kg^{-1}	7.2 (1.2)	6.2 (2.1)	2.7 (0.9)	3.2 (1.5)	42.5 (4.5)
Morgan's extractable phosphorus (P_m)	mg L^{-1}	5.8 (0.3)	5.7 (0.1)	2.6 (0.2)	5.1 (0.4)	24.6 (0.2)
Degree of phosphorus saturation (DPS)	%	3.94 (0.39)	5.62 (0.09)	1.52 (0.07)	3.34 (0.13)	17.3 (0.2)
Mehlich 3–extractable phosphorus (M3P)	mg kg^{-1}	47.3 (2.4)	68.7 (1.2)	16.2 (0.9)	34.7 (1.1)	121.0 (5.4)
Mehlich 3–extractable aluminum (M3-Al)	mg kg^{-1}	765 (60)	871 (9)	969 (4)	620 (17)	304 (24)
Mehlich 3–extractable copper (M3-Ca)	mg kg^{-1}	1780 (57)	1320 (37)	1340 (9)	258 (19)	657 (117)
Mehlich 3–extractable cobalt (M3-Co)	mg kg^{-1}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Mehlich 3–extractable copper (M3-Cu)	mg kg^{-1}	2.7 (0.7)	3.1 (0.2)	3.4 (0.0)	4.5 (0.1)	1.8 (0.1)
Mehlich 3–extractable iron (M3-Fe)	mg kg^{-1}	516 (2)	447 (10)	213 (2)	479 (6)	444 (6)
Mehlich 3–extractable potassium (M3-K)	mg kg^{-1}	168 (4)	133 (4)	270 (5)	153 (7)	336 (3)
Mehlich 3–extractable magnesium (M3-Mg)	mg kg^{-1}	199 (5)	203 (6)	305 (5)	122 (3)	1110 (7)
Mehlich 3–extractable molybdenum (M3-Mn)	mg kg^{-1}	93 (5)	102 (1)	127 (13)	75.3 (0.6)	14.9 (1.1)
Mehlich 3–extractable zinc (M3-Zn)	mg kg^{-1}	2.3 (0.1)	4.8 (0.0)	3.5 (0.9)	3.7 (0.1)	17.1 (3.6)
Container capacity (CC)	kg water kg soil^{-1}	675 (32)	634 (12)	539 (8)	825 (43)	2110 (59)
Soil bulk density	kg m^{-3}	1.29	1.15	1.08	0.93	0.27

Note. Values in parentheses are standard deviations.
[a]P index: soils in Ireland ranked based on risk of P loss (soil P availability for plant uptake).

and filtering through No. 2 Whatman filter paper. Analyses for TP and TN were carried out colorimetrically using an automatic multichannel segmented flow analyzer (Burkard, United Kingdom) after Basson, Stanton, and Böhmer (1968). Total K was analyzed using a Varian Spectra 400 Atomic Absorption (Varian, Cham, Switzerland). The WEP of slurry and amended slurry was measured at the time of soil application after Kleinman et al. (2007).

The slurry application was based on an application rate of 33 m^3 ha^{-1}, which is common practice on grassland in Ireland (Coulter and Lalor 2008). This was equivalent to an application of 37.4 kg TP ha^{-1} and approximately 0.94 kg WEP ha^{-1}. The same slurry application rate was selected for all soils to allow convenient randomization. Amendments were applied at a stoichiometric ratio based on the TP of the slurry to the metal in the amendment. Alum was applied at 1.5:1 (Al/TP), lime at 16:1 (Ca/TP), poly-aluminium chloride (PAC) at 1.4:1 (Al/TP), and $FeCl_3$ at 1.5:1 (Fe/TP).

Incubation Experiment

This 9-month incubation study comprised six treatments, conducted in triplicate, at a fixed temperature of 11 °C on (1) soil only (to take account of the effects of incubation on soil P), (2) soil mixed with dairy cattle slurry (slurry-control), and soil mixed with dairy cattle slurry, which was amended with either (3) alum, (4) lime, (5) PAC, or (6) $FeCl_3$.

First, 100-g samples of air-dried soil, passed through a 2-mm sieve, were placed in 0.5-L square containers (70 × 70 mm base). Then, slurry, or amended slurry, was added to soil and mixed before adding the volume of deionized water required to achieve 50% approximate field capacity (after Bond, Maguire, and Havlin 2006). The mineral soils had a mean bulk density of 1.12 ± 0.15 g cm^{-3} (Table 1). For the purpose of selecting slurry application rate, it was assumed that surface-applied slurry only interacts with the upper 20 mm of soil (Andraski, Bundy, and Kilian 2003; Sharpley 2003). Although the peat (soil E) had a significantly different bulk density, slurry was applied at the same rate to the peat for consistency. Following this, the soil, slurry, and water mixture was compacted using a custom packer to an appropriate bulk density similar to that in the field situation (Table 1). The containers were covered with parafilm and perforated for air circulation. Throughout this study, the containers were weighed and water was added intermittently to ensure that approximately 50% field capacity was maintained during the incubation.

After 1, 3, 6, and 9 months, the containers of soil were destructively sampled and the dry matter (DM) and WEP of wet soil was determined. The remaining soil sample was air dried and crushed to pass a 2-mm sieve. Subsamples were taken, dried at 40 °C for 72 h, and analyzed for soil pH and P_m using Morgan's extracting solution. In addition, the 9-month soil samples were analyzed for M3-P and M3-Al, Ca, Co, Cu, Fe, K, Mg, Mn, and Zn to determine the effects of amendments on metal and nutrient availability.

Statistical Analysis

Data from the four sampling events were analyzed as a factorial design with soil type, time, and treatment as factors. All interactions were examined. Soil type was a blocking effect in this structure, but its interactions with the randomized factors were of interest. The interactions were interpreted in the first instance by testing simple effects and then making comparisons of means, with adjustment for multiplicity of testing. The GLIMMIX procedure of SAS 9.2 was used to fit the analysis model (SAS 2004; SAS Institute, Cary, N.C., USA). This procedure allowed the addition of heterogeneous variance structures and a number of options for comparing large numbers of means. Residual checks were made to check the assumptions of the analysis method.

Results and Discussion

Slurry and Amended Slurry Analysis

The results of the slurry analysis are shown in Table 2. At the rates used in this study, all of amendments examined reduced the WEP concentration of dairy cattle slurry by approximately 99% compared to the slurry-control ($P < 0.001$). Alum addition reduced slurry pH from approximately 7.2 (slurry-control) to 5.1, PAC reduced pH to 5.7 and $FeCl_3$ to 5.4 ($P < 0.001$), whereas lime addition increased slurry pH to 12 ($P < 0.001$). The effectiveness of amendments in reducing P solubility in slurry was in agreement with previous studies (Dao 1999; Lefcourt and Meisinger 2001; Dou et al. 2003; Brennan et al. 2011a). Lefcourt and Meisinger (2001) reported a 97% reduction in WEP of dairy cattle slurry when 2.5% (by weight) of alum was added in a laboratory batch experiment. Dao and Daniel (2002) added alum (810 mg Al L^{-1}) and $FeCl_3$ (810 mg Fe L^{-1}) (compared to 1,710 mg Al L^{-1} and 4,560 mg Fe L^{-1} in the current study) to dairy slurry and observed that slurry WEP was reduced by 66 and 18%, respectively.

Phosphorus in Soil and Slurry Treatments

There was a significant interaction among soil type, month, and treatment for WEP ($P < 0.001$). The WEP levels from each soil before the start of the incubation period and at each sampling event during the incubation period are shown in Table 3. There was an initial decline in WEP levels for the mineral soils at the 1-month sampling interval (although there was an increase in WEP from soil E) for the soil-only treatment, followed by an increase at 3- and 6-month sampling intervals and a trend toward pseudosteady state by the end of the study. The WEP levels from the soil-only treatment did not vary significantly during the study. As expected, the addition of dairy cattle slurry to soils resulted in observed increases in soil WEP compared to

Table 2
Slurry and amended slurry properties (standard deviation in parentheses)

Treatment	DM (%)	pH	TN (mg L^{-1})	TP (mg L^{-1})	WEP (mg kg^{-1})	TK (mg L^{-1})
Slurry-control	10.45 (0.78)	7.2 (0.3)	4860 (425)	1140 (93)	2.86 (0.42)	3110 (254)
Alum	10.1 (0.4)	5.1 (0.4)	4660 (201)	1120 (19)	0.003 (0.001)	2840 (167)
Lime	13.8 (0.2)	12.0 (0.3)	3590 (459)	944 (79)	0.025 (0.001)	2620 (430)
PAC	9.9 (0.4)	5.7 (0.4)	5320 (379)	1280 (154)	0.003 (0.001)	3060 (617)
$FeCl_3$	11.4 (0.7)	5.4 (0.1)	5020 (283)	1180 (84)	0.020 (0.005)	3100 (153)

Notes. DM, dry matter; TN, total nitrogen; TP, total phosphorus; WEP, water-extractable phosphorus; TK, total potassium; PAC, poly-aluminium chloride.

Table 3
Water-extractable phosphorus concentration (WEP) and percentage decrease for each treatment at each sampling event

Soil	Month	Soil-only (mg kg^{-1})	Slurry-control (mg kg^{-1})	Alum (mg kg^{-1})	(%)	Lime (mg kg^{-1})	(%)	PAC (mg kg^{-1})	(%)	$FeCl_3$ (mg kg^{-1})	(%)
A	0	7.2 (0.9)									
	1	2.3 (0.3)	4.1 (1.5)	2.4 (0.1)	38	1.6 (1.0)	59	4 (2)	2	5.0 (3.1)	−26
	3	4.6 (1.0)	19.9 (3.4)*[a]	4.8 (0.5)*[b]	75	7.5 (1.5)	61	8.9 (1.1)	55	2.2 (1.6)*[b]	88
	6	3.4 (0.3)	8.4 (0.3)	4.0 (0.2)	51	4.1 (0.3)	51	6.2 (0.7)	25	8.2 (4.2)	2
	9	3.3 (1.1)	6.1 (1.0)	3.3 (0.2)	44	4.0 (0.5)	33	5.2 (0.4)	13	10.2 (0.3)	−71
B	0	6.2 (1.3)									
	1	4.7 (0.7)	9.1 (2.7)	1.0 (1.4)*[b]	88	0.5 (0.3)*[b]	93	2.8 (1.6)*[b]	68	4.5 (1.9)	50
	3	5.8 (1.4)	13.0 (2.4)	8.4 (2.0)	38	10.2 (2.6)	24	9.8 (1.3)	27	15.2 (2.4)	−12
	6	6.3 (4.1)	8.7 (0.1)	4.8 (0.4)	43	4.9 (0.3)	42	11.0 (0.2)	−28	1.3 (0.0)	84
	9	3.0 (0.3)	7.9 (1.3)	3.4 (0.9)	56	4.9 (1.1)	38	5.8 (0.4)	26	13.4 (0.2)	−70
C	0	2.6 (0.7)									
	1	0.1 (0.0)	7.3 (1.2)*[a]	0.10 (0.04)*[b]	97	0.1 (0.0)*[b]	97	0.10 (0.01)*[b]	97	1.4 (2.2)*[b]	80
	3	0.6 (0.1)	5.4 (1.3)*[a]	3.1 (0.6)	42	0.6 (0.2)*[b]	88	2.6 (1.9)	52	10.3 (0.9)	−92
	6	5.5 (0.5)	8.8 (1.8)	1.4 (0.2)	83	2.3 (0.4)	73	5.7 (1.4)	35	2.5 (0.2)	71
	9	1.3 (0.1)	5.7 (0.3)*[a]	2.2 (0.6)	61	1.6 (0.5)	72	1.7 (0.5)	69	5.9 (0.3)	−5
D	0	3.2 (1.3)									
	1	0.2 (0.1)	6.0 (2.2)*[a]	0.3 (0.2)*[b]	94	0.2 (0.1)*[b]	96	0.5 (0.4)*[b]	91	2.8 (1.9)	53
	3	4.8 (0.3)	10.0 (0.7)	0.60 (0.03)*[b]	94	2.3 (3.1)*[b]	77	0.50 (0.02)	94	8.2 (2.8)	21
	6	2.9 (0.2)	10.4 (0.9)	5.2 (3.2)	50	4.3 (1.1)	58	7.5 (1.0)	27	7.4 (1.4)	28
	9	2.3 (0.2)	6.2 (0.6)	2.8 (1.2)	53	3.4 (0.2)	45	3.1 (0.7)	50	5.9 (0.5)	4

(*Continued*)

Table 3
(Continued)

Soil	Month	Soil-only (mg kg^{-1})	Slurry-control (mg kg^{-1})	Alum (mg kg^{-1})	(%)	Lime (mg kg^{-1})	(%)	PAC (mg kg^{-1})	(%)	$FeCl_3$ (mg kg^{-1})	(%)
E	0	43.0 (4.4)									
	1	46.9 (8.5)	63.8 (9.0)	51 (12)	19	56.9 (7.3)	10	44.8 (1.12)	29	67.5 (3.5)	−7
	3	61.8 (8.5)	104 (7)	92 (16)	10	74.5 (12.6)	27	69.0 (13.9)	33	90.4 (17.4)	12
	6	63.1 (4.2)	88.6 (8.9)	78.6 (9.4)	10	97.1 (13)	−11	64.3 (1.7)	26	109 (13)	−24
	9	48.0 (3.4)	64.9 (0.3)	53 (8)	17	64.2 (3.3)	0	55.0 (12.6)	14	85.1 (6.1)	−32

*Statistical significance of 0.05.
[a]Compared with soil-only treatment.
[b]Compared to slurry-control. *Note.* PAC, poly-aluminium chloride.

the soil-only treatment for all soils, but these increases in WEP for the slurry treatment were not always statistically significant. There was significantly greater WEP levels following the application of slurry to soils A, C, and D compared to the soil-only treatment at the 1-month sampling ($P < 0.05$). The WEP levels from the slurry treatment remained significantly greater than the soil-only treatment at the 3-month sampling for soil C ($P < 0.05$). There were no significant differences between WEP levels for the soil-only and all slurry treatments at the 6- and 9-month sampling events for all four mineral soil types.

The initial reduction in WEP observed in the current study was in agreement with similar incubation studies (Maguire et al. 2001; Griffin, Honeycutt, and He 2003; Leytem et al. 2004; Kalbasi and Karthikeyan, 2004; Penn and Bryant, 2006; Dail et al. 2007). Penn and Bryant (2006) examined the effect of rewetting air-dried sieved soil (2 mm) on WEP and M3P concentration and concluded that decreases in WEP following incubation were likely due to increased microbial activity during initial incubation, resulting in P immobilization into microbial biomass. The WEP decrease may also have been a result of changes in soil pH, where there was a shift from labile inorganic P to forms that were mineral-associated and less soluble. Changes in pH may have been due to increases in the amount of exchangeable Ca and Mg caused by the breaking down of soil by grinding and sieving. Dail et al. (2007) also found that drying of soil had a significant effect on soil P solubility and concluded that variations due to drying effects should be considered when comparing manures and studies where different drying procedures have been used.

While addition of slurry resulted in an observed increase in WEP for the organic soil E, the increase was not significant (Table 3). Soil E behaved differently than the mineral soils, and WEP and STP values were typically an order of magnitude greater than for mineral soils. For clarity, the mineral soils and Soil E will be considered separately for the remainder of this article.

Water-Extractable Phosphorus-Amended Slurry Treatments

Alum addition decreased WEP of the four mineral soils compared to the slurry-control by between 38 and 97% after 1 month (Table 3) and, on average, by between 52 and 73% for the four sampling events. Lime addition decreased WEP by between an average of 59 and 97% after 1 month (50 and 83% for the four sampling events). Poly-aluminium chloride decreased WEP by between 2 and 55% after 1 month. However, PAC increased WEP of soil B at the 6-month sampling (Table 3). While this increase was not significant, PAC did not perform as well as alum and lime. Ferric chloride was the least effective at decreasing WEP compared with the other amendments and, in the cases of soils A, B, and C, increased WEP compared to the slurry-control. Inherent variability in the consistency of concentrations of TP and WEP within any sample of slurry, combined with different rates in the uptake of slurry P by soil sorption, may complicate interpretation of percentage reductions. These results indicate a difference in effectiveness across soil types and future work must examine the most effective amendments over a much wider range of soil chemical and physical properties.

Water-extractable P released (as a percentage of total applied P) was used to give a relative comparison of each treatment and soil type after 9 months (Figure 1). The overall treatment trends observed were consistent for the different sampling events of the study and therefore the 9-month values were used as best representing the long-term effect of the amendments on these soils. The treatments with the greatest WEP release compared to the soil-only treatment (in order of decreasing WEP release) were slurry = $FeCl_3$ > PAC > lime = alum for soils A and B. For soils C and D, slurry = $FeCl_3$ > PAC = alum = lime

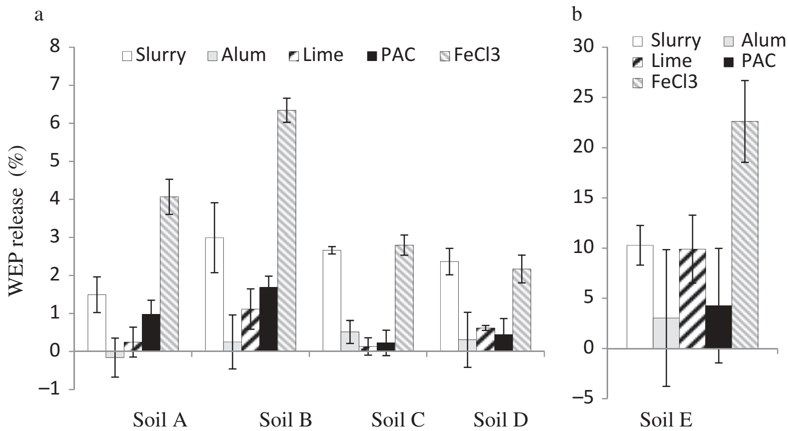

Figure 1. Water-extractable phosphorus release (WEP) expressed as a percentage of total phosphorus applied for 9 months compared to soil-only treatment: (a) the four mineral soils and (b) peat soil (PAC, poly-aluminum chloride).

in terms of WEP release. This shows that alum, lime, and PAC were the most effective amendments at decreasing WEP with slurry-amended soils, while $FeCl_3$ increased WEP compared to the slurry-control treatment.

In a study that examined the effect of soil P level in a silt loam soil (samples incubated at 25 °C), Kalbasi and Karthikeyan (2004) reported that applications of alum and $FeCl_3$-amended slurry to soil decreased P solubility, whereas lime amendments increased WEP. In the present study, alum and $FeCl_3$ were applied to slurry at lower rates (ratio of 1.5:1 Al/TP and Fe/TP compared to a ratios of 4:1 and 3.6:1, respectively) than Kalbasi and Karthikeyan (2004). The lower amendment rates used in the present study may somewhat explain the poorer performance of $FeCl_3$ in reducing WEP levels compared with results from Kalbasi and Karthikeyan (2004), who found $FeCl_3$ to be the most effective amendment. In addition, the present study used calcium hydroxide [$Ca(OH)_2$] as the liming product, whereas Kalbasi and Karthikeyan (2004) used calcium oxide (CaO). There were also procedural differences between these two studies: The slurry used by Kalbasi and Karthikeyan (2004) had a much lower DM (2%) than that of the present study (10%), and the slurry application rate used was much lower than in the present study.

In addition to chemical amendment of manure, studies have examined the addition of amendments to high STP soils to reduce P losses (McFarland, Hauck, and Kruzic 2003; Novak and Watts 2005; Brauer et al. 2005). Brauer et al. (2005) incorporated alum (127 kg Al ha^{-1}) and gypsum at two rates (349 and 1163 kg Ca ha^{-1}) into the upper 10 cm of a high STP soil on an annual basis for 3 yr. Only the high gypsum treatment was observed to reduce WEP and STP values significantly during the study. A limited number of runoff studies have been carried out with chemical amendment of dairy cattle slurry (Elliott, Brandt, and O'Connor 2005; Torbert, King, and Harmel 2005) and swine slurry (Smith et al. 2001), but little work has focused on the long-term effects of chemical amendments to slurry on the nutrient content of soil.

Soil pH

Within each treatment and soil type, soil pH did not vary significantly with incubation time, with the exception of the $FeCl_3$ treatment in which soil pH increased with time compared with the other amendments (Table 4). The change in pH may explain the poor performance of $FeCl_3$, which effectively reduced the WEP of slurry prior to application, but was ineffective when the amended slurry was incubated with soil. There was a strong correlation between soil pH and M3-Al, M3-Ca, M3-Fe, WEP, and P_m ($P < 0.001$) for the four mineral soils across all treatments.

The pH of a soil has a significant influence on nutrient availability (Tunney et al. 2010), and changes in pH can alter community composition and activity of microbes in soil (Sylvia et al. 2005). In addition, if the amendments adversely affect microbial activity, the microbes could potentially change the pH by their activity.

Table 4
Soil pH for each treatment at each sampling event

Soil	Month	Soil only (mg kg^{-1})	Slurry-control (mg kg^{-1})	Alum (mg kg^{-1})	Lime (mg kg^{-1})	PAC (mg kg^{-1})	$FeCl_3$ (mg kg^{-1})
A	0	6.1 (0.9)					
	1	5.40 (0.02)	5.5 (0.1)	5.10 (0.01)	5.8 (0.7)	5.50 (0.01)	6.3 (0.8)
	3	5.5 (0.0)	6.2 (0.7)	5.6 (0.1)	6.4 (0.8)	5.7 (0.4)	6.2 (1.1)
	6	5.20 (0.03)	5.10 (0.02)	4.70 (0.02)	5.00 (0.01)	4.98 (0.01)	6.1 (1.1)
	9	5.30 (0.06)	5.20 (0.05)	4.70 (0.06)	5.00 (0.04)	5.00 (0.02)	6.9 (0.1)*[a,b]
B	0	5.70 (0.08)					
	1	5.00 (0.01)	5.20 (0.03)	5.00 (0.02)	5.40 (0.02)	5.6 (0.1)	6.2 (0.2)
	3	5.9 (0.7)	6.0 (1.2)	5.9 (0.7)	5.8 (0.9)	5.5 (0.3)	5.5 (0.2)
	6	5.4 (0.1)	4.8 (0.1)	4.50 (0.03)	4.80 (0.02)	5.3 (0.8)	6.3 (0.0)
	9	5.0 (0.1)	4.80 (0.02)	4.50 (0.06)	4.80 (0.02)	4.80 (0.02)	6.6 (0.2)
C	0	6.50 (0.02)					
	1	6.30 (0.03)	6.20 (0.04)	5.60 (0.01)	6.1 (1.1)	6.30 (0.04)	7.3 (0.1)
	3	6.1 (0.4)	5.7 (0.2)	5.6 (0.5)	6.8 (1.1)	5.8 (0.5)	6.1 (0.9)
	6	5.5 (0.5)	5.9 (0.4)	5.6 (0.1)	5.7 (0.1)	6.3 (0.9)	6.6 (1.4)
	9	6.30 (0.03)	6.10 (0.03)	5.40 (0.03)	5.60 (0.03)	5.70 (0.03)	7.3 (0.1)
D	0	5.10 (0.04)					
	1	5.30 (0.02)	5.60 (0.05)	5.50 (0.06)	6.10 (0.03)	6.3 (0.0)	6.7 (0.1)*[a]
	3	5.60 (0.05)	6.5 (1.1)	5.50 (0.01)	6.1 (0.7)	5.9 (0.3)	5.9 (0.6)
	6	5.1 (0.1)	5.0 (0.3)	5.0 (0.2)	5.2 (0.1)	5.5 (0.5)	6.0 (0.7)
	9	5.00 (0.05)	5.0 (0.1)	4.8 (0.1)	5.0 (0.1)	5.1 (0.1)	6.4 (0.1)
E	0	5.60 (0.05)					
	1	5.8 (0.2)	5.70 (0.06)	5.60 (0.02)	5.70 (0.01)	6.00 (0.04)	5.50 (0.02)
	3	5.3 (0.2)	5.3 (0.1)	5.3 (0.2)	5.4 (0.2)	5.4 (0.3)	5.70 (0.01)
	6	5.20 (0.04)	5.1 (0.1)	5.09 (0.05)	5.3 (0.3)	5.5 (0.2)	5.20 (0.01)
	9	5.3 (0.1)	5.10 (0.01)	5.1 (0.1)	5.10 (0.05)	5.7 (0.2)	5.20 (0.04)

*Statistical significance of 0.05.
[a]Compared with soil-only treatment.
[b]Compared to slurry-control.
Note. PAC, poly-aluminium chloride.

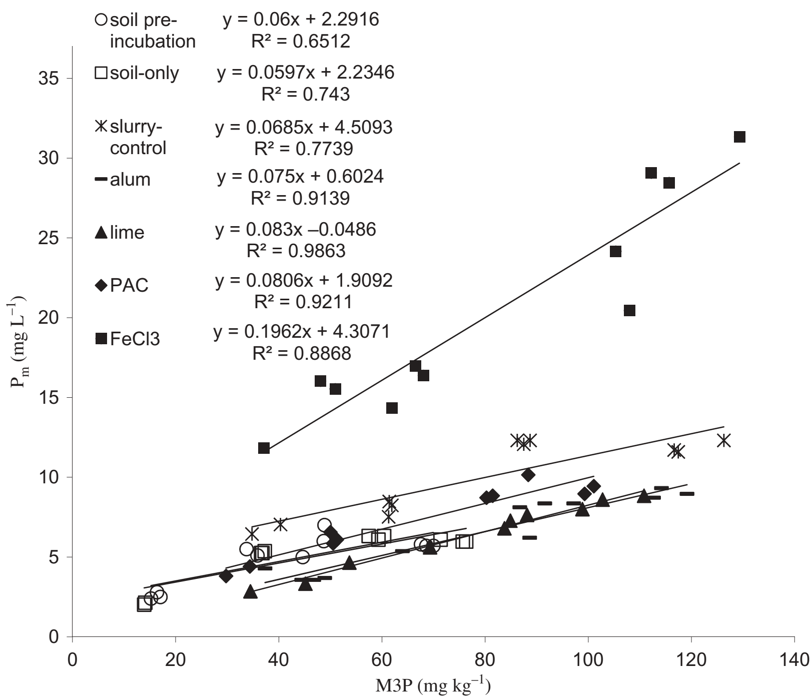

Figure 2. Morgan's P (P_m) against Mehlich 3–extractable phosphorus (M3P) for the four mineral soils by treatment (9 months of data).

Morgan's and Mehlich 3 Phosphorus

Figure 2 shows the relationship between P_m and M3P for each treatment at the 9-month sampling event for the mineral soils. There were positive linear relationships between P_m and M3P across all treatments for the mineral soils ($P < 0.01$). The Morgan's P test extracted P from $FeCl_3$-amended slurry treatment more readily than the M3P test. This was most likely due the difference in pH between Morgan's (4.8) and Mehlich extractants (2.5). These results highlight the importance of selecting the most appropriate extraction methods to assess subsequent soil P availability.

Table 5 shows the temporal variability of P_m over the incubation period for each treatment by soil type combination. There was a significant interaction among soil type, sampling month, and treatment for the P_m of the soil ($P < 0.001$). The P_m of the soil-only treatment did not vary significantly during the course of the experiment. The P_m of the slurry-control remained relatively constant throughout the course of the experiment after the initial increase at 1 month. The P_m of the slurry-control was significantly different to the soil-only treatment for soil D (3 month, $P < 0.05$) and soil C (9 month, $P < 0.15$). These results show that use of chemical amendments did not significantly affect plant availability of soil P. The P_m of the $FeCl_3$-amended slurry was significantly greater than the slurry-control for soil A (9 month, $P < 0.05$) and soil B (6 and 9 months, $P < 0.05$). This was consistent with the results of McFarland, Hauck, and Kruzic (2003) and Kalbasi and Karthikeyan (2004). With the exception of these studies, the authors are not aware of any other studies examining the effect chemical amendment of dairy cattle slurry with alum, $FeCl_3$, and lime on plant availability of P in soils following land application of the slurry.

Table 5
Morgan's extractable phosphorus (P_m) for each treatment at each sampling event

Soil	Month	Soil only (mg kg^{-1})	Slurry-control (mg kg^{-1})	Alum (mg kg^{-1})	Lime (mg kg^{-1})	PAC (mg kg^{-1})	$FeCl_3$ (mg kg^{-1})
A	0	6 (1)					
	1	5.9 (0.2)	11.9 (0.9)	6.1 (0.6)	8.2 (2.8)	7.7 (0.6)	10.9 (4.1)
	3	2.6 (0.1)	10.0 (0.6)	4.0 (0.9)	5.7 (2.0)	5.8 (3.0)	10.1 (2.6)*[a]
	6	6.2 (0.3)	12.2 (0.5)	6.8 (0.4)	6.8 (0.2)	8.6 (0.3)	21.4 (4.8)
	9	6.2 (0.1)	12.2 (0.1)	8.3 (0.1)	7.2 (0.4)	9.2 (0.8)	26.8 (2.5)*[a,b]
B	0	5.7 (0.1)					
	1	6.3 (0.2)	10.4 (1.5)	6.8 (0.2)	7.1 (0.1)	7.6 (0.1)	12.1 (2.2)
	3	7.0 (0.4)	15.0 (3.8)	7.9 (1.1)	8.3 (1.0)	8.0 (0.6)	8.9 (3.2)
	6	4.8 (0.1)	11.1 (0.0)	7.6 (0.4)	7.8 (0.1)	8.3 (0.3)	23.2 (3.3)*[a,b]
	9	6.0 (0.1)	11.9 (0.4)	9.0 (0.3)	8.5 (0.4)	9.2 (0.3)	26.8 (5.6)*[a,b]
C	0	2.6 (0.2)					
	1	2.2 (0.2)	6.6 (1.1)	2.7 (0.4)	2.5 (0.3)	3.5 (1.0)	8.6 (4)*[a]
	3	2.4 (0.1)	6.1 (0.8)	7.2 (4.9)	3.9 (1.5)	5.7 (1.5)	14.5 (1.9)*[a]
	6	2.5 (0.5)	6.8 (0.6)	2.7 (0.2)	2.8 (0.6)	6.8 (5.6)	9.1 (4.2)
	9	2.2 (0.2)	6.7 (0.4)	3.6 (0.1)	2.9 (0.4)	4.1 (0.4)	14.4 (2.3)*[a,b]
D	0	5.1 (0.4)					
	1	4.7 (0.4)	9.0 (0.9)	5.4 (0.4)	6.0 (0.3)	7.8 (1.0)	12.7 (2.9)
	3	5.0 (0.1)	9.9 (4.4)*[a]	5.6 (0.0)	6.7 (2.7)	6.7 (0.8)	11.7 (4.0)
	6	4.6 (0.7)	7.5 (1.8)	5.1 (0.2)	6.1 (0.0)	9.6 (5.5)	13.3 (1.0)
	9	5.3 (0.1)	8.1 (0.5)	5.3 (1.0)	5.3 (0.6)	6.2 (0.4)	15.9 (1.4)*[a]
E	0	24.6 (0.2)					
	1	34.6 (4.1)	43.8 (1.4)	38.1 (1.2)	44.1 (1.0)	48.9 (3.6)	49.5 (6.4)
	3	38.3 (1.2)	35.3 (1.3)	40.1 (7.8)	37.8 (0.9)	45.3 (1.9)	39 (7.1)
	6	33.0 (3.4)	37.0 (2.1)	29.9 (1.5)	28.5 (1.3)	31.9 (1.1)	35.3 (0.6)
	9	28.8 (5.4)	40.1 (2.0)	35.9 (1.2)	39.6 (3.5)	40.1 (7.3)	42.3 (3.9)

*Statistical significance of 0.05.
[a]Compared with soil-only treatment.
[b]Compared to slurry-control.
Note. PAC, poly-aluminium chloride.

Mehlich 3 Al, Ca, and Fe Analysis

There were strong correlations between M3-Al and M3-Ca, WEP, pH, and P_m ($P < 0.005$); between M3-Ca and pH, WEP, and P_m ($P < 0.005$), and between M3-Fe and M3-Al, M3P, and pH ($P < 0.005$) for the four mineral soils (data not shown). When these correlations were examined within treatments, there was no strong correlation between WEP and M3-Al or M3-Fe for any of the slurry amendments. However, the alum treatment tended to increase the levels of M3-Al in these mineral soils, which resulted in largest overall decrease in WEP compared to the lime and PAC treatments. The $FeCl_3$ treatment tended to decrease the M3-Al and M3-Fe levels in these soils and resulted in an overall increase in WEP levels compared to the slurry-control treatment. There were no observed trends or differences among treatments for M3- Co, Cu, K, Mg, Mn, and Zn. This shows that none of the treatments examined adversely affected the availability of these metals and nutrients to plants.

Relationship between Soil WEP and M3P

Figure 3a shows soil M3P at t = 0 for preincubation soil and at t = 9 for all treatments versus WEP for each treatment across the four mineral soils. With the exception of the soil-only treatment, there were significant positive relationships between M3P and WEP for each treatment ($P < 0.05$). Slopes for the alum, PAC, and lime treatments are similar, whereas the $FeCl_3$ treatment was steeper, which suggests that for a given rise in M3P, the increase in WEP of the $FeCl_3$ treatment will be greater compared to the other amendments. Alum, lime, and PAC were effective in reducing WEP across the four soil types, which is in agreement with the WEP release results (Table 3).

Relationship between Soil WEP and DPS

There was a significant correlation between WEP and DPS for soils A, B, C, and D ($P < 0.05$) (Figure 3b). The WEP-DPS correlation for the soil at t = 0 (pre-incubation) and at t = 9 months show that as the DPS of the soil increases, the WEP increases. Therefore, amendments that reduce the solubility of P in dairy cattle slurry are effectively increasing the sorption capacity of the soil receiving the amended slurry. In the present study, the amendments performed differently across different soil types, which indicated that the amendments would be most effective if used in soils with a high DPS. In high DPS soils, chemical amendments will increase the capacity of the soil to store P. There is already an abundance of P sorption sites in soils with low DPS, and apart from the reduction of WEP immediately after slurry application, the long-term benefits would seem to be limited. This work has identified a need to examine further the effect of soil DPS on the

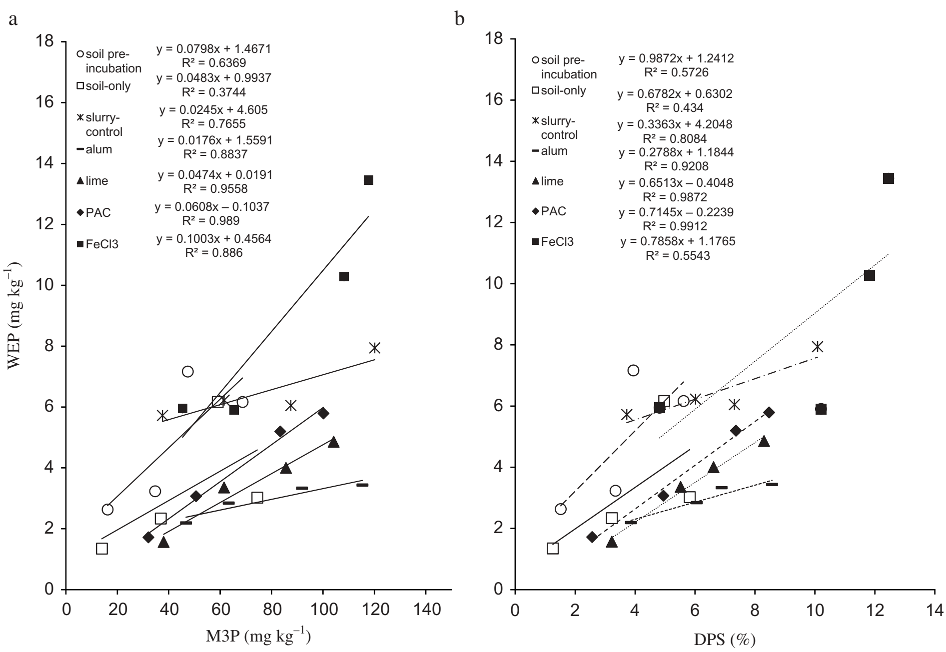

Figure 3. Soil water-extractable phosphorus (WEP) against (a) Mehlich 3–extractable phosphorus (M3P) and (b) degree of phosphorus saturation (DPS) for the four mineral soils (9 months of data).

effectiveness of chemical amendments in reducing chronic P losses. Soil DPS within a catchment, combined with topography and other P-loss risk factors, maybe used to select sites where chemical amendment would be most beneficial.

Organic Soils

The organic soil (soil E) behaved very differently than the mineral soils, as expected (Table 3). None of the amendments effectively reduced the WEP of Soil E (Figure 1). Ann, Reddy, and Delfino (1999) examined use of chemical amendments to immobilize P in highly organic soils from agricultural land that was being converted into wetlands in the United States, with the objective of making the wetlands a sink for nutrients. In laboratory-scale experiments, these researchers (Ann, Reddy, and Delfino 1999) found the order of effectiveness of immobilizing P was $FeCl_3$ > alum > lime when applied at rates of 1–2 g kg^{-1}, 12 g kg^{-1}, and 7–15 g kg^{-1}, respectively, compared to 2.0 g kg^{-1}, 6.6 g kg^{-1}, and 5.6 g kg^{-1}, respectively, in the present study. Ann, Reddy, and Delfino (1999) concluded that high rates of chemical amendments were needed to reduce P levels because of complexation of P-binding cations (Ca, Fe, and Al) with organic matter. Fox and Kamprath (1971) found that addition of $AlCl_2$ to an organic soil reduced P solubility significantly. Litaor et al. (2005) showed that drying and rewetting peat soils resulted in an increased availability of P due to a decrease in P-sorption capacity. Litaor et al. (2005) found that rewetting of previously oxidized organic soils dissolved Fe oxides, resulting in increased P release.

The WEP of soil E initially increased and remained relatively constant for the duration of the study. The levels of WEP release were as follows: slurry > $FeCl_3$ > lime > alum = PAC. The differences and trends were not comparable to the mineral soils. In addition, the WEP of the organic soil was an order of magnitude greater than the WEP of the mineral soils, which further complicated comparisons. There was no correlation between P_m and M3P, Pm and WEP, and WEP and M3-Al or M3-Fe for organic soil (data not shown). These results are in agreement with previous work showing that organic soils have a lower P retention capacity than mineral soils (Iyamuremye and Dick 1996; Daly, Jeffrey, and Tunney 2001).

Outlook for Use of Chemical Amendments

Typically, the use of chemically amended slurry is considered to be most effective within critical source areas (CSAs), where a high STP and a mobilization vector combine to pose a threat to a nearby receptor. However, the findings of the present study suggest that use of chemically amended slurry within a CSA could become more refined based on soil suitability criterion. While incubation experiments similar to the type carried out in this study are an accepted means of comparing treatments under similar environmental conditions, it may not be possible to extrapolate the findings of this study to fully represent the effects under field conditions. This study has shown that the effectiveness of amendments is influenced by soil physical and chemical properties. In addition, amendment reduces P solubility in slurry compared to unamended slurry and offers the opportunity to reduce chronic P losses in addition to their effectiveness in reducing incidental losses.

Future work must examine the long-term effects of amendments at field scale with a range of soil types. The effects of amendments on P leaching, soil microbiology, and structure need to be explored. At present, there is no provision for a license to land spread any of these amendments in Ireland, except lime to optimize soil pH for production. If chemical amendment were to be used to mitigate P losses, a licensing system would have to be introduced by the Department of Agriculture in Ireland and relevant bodies in other countries. This study indicates that use of chemical amendment as a once-off management practice reduced WEP in soil compared to soil amended with slurry but did not decrease STP to levels or have any significant effect on soil physical and chemical properties.

Conclusions

This study found that the WEP of all soils receiving chemically treated dairy cattle slurry was lower than the slurry-control for alum and lime treatments, whereas $FeCl_3$ was ineffective at decreasing P solubility. Alum maintained the greatest levels of plant-available P (M3P) across the four mineral soils with the least risk of P loss to overlying water (i.e., lowest WEP per M3P). This would indicate that alum offers the greatest potential for future research. Further work is needed to examine a much wider range of soil types with a range of DPS with a view to identifying soil parameters that could be used to select sites where amendment would be most effective at reducing chronic P losses. The study found that chemical amendments are not effective in organic soils. Future work must examine how amendments affect nutrient balance and pollution swapping at a field scale under a range of drainage regimes and soil types. While this study has shown that alum is the most effective amendment, further work is required to fully understand the importance of the interactions between the chemistry of amendment and soil and how such interactions might influence the effectiveness of amendments in reducing chronic P losses. These issues must be addressed before recommendations can be made to farmers or catchment managers.

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