

Evaluation of Amendments to Control Phosphorus Losses in Runoff from Dairy-Soiled Water

Owen Fenton · Ana Serrenho ·
Mark Gerard Healy

Received: 15 December 2010 / Accepted: 4 April 2011 / Published online: 15 April 2011
© Springer Science+Business Media B.V. 2011

Abstract Amendments with the potential to reduce phosphorus (P) losses from agricultural grassland arising from the land application of dairy-soiled water (DSW) were investigated. Optimal application rates were studied, and associated costs and feasibility were estimated. First, batch tests were carried out to identify appropriate chemicals or phosphorus sorbing materials to control P in runoff from DSW. Then, the best four treatments were examined in an agitator test. In this test, soil—placed in a beaker—was loaded with DSW or amended DSW at a rate equivalent to 5 mm ha⁻¹ (the maximum permissible application rate of DSW allowable in a 42-day period in Ireland). The soil was overlain with continuously stirred water to simulate runoff on land-applied DSW. Optimum application rates were selected based on percentage removal of dissolved reactive phosphorus in overlying water and the estimated cost of amendment. The costs of the amendments, per cubic metre of DSW, increased in the order: bottom ash (1.55 €), alum (1.67 to 1.92 €), FeCl₂·4H₂O (3.55 to 8.15 €), and lime (20.31 to 88.65 €). The feasibility of the amendments, taking into account their cost, potential

adverse effects, public perception, and their performance, decreased in the order: alum > FeCl₂·4H₂O > bottom ash > lime. Amendments to DSW could be introduced in critical source areas—areas where high soil test P and direct migration pathways to a receptor overlap.

Keywords Dairy-soiled water · Iron (II) chloride tetrahydride · Lime · Alum · Bottom ash

1 Introduction

Nutrient transfer from agriculture to a waterbody can lead to eutrophication and occurs in three different ways: (a) point source losses from farmyards and excessive rates of water application through the use of rotational irrigators; (b) diffuse losses from soil, which is related to soil phosphorus (P) and nitrogen (N) concentrations in excess of crop requirements; and (c) incidental losses (the focus of this study) from direct losses of dairy-soiled water (DSW) during land application, or where a rainfall event occurs immediately after application (Preedy et al. 2001).

Dairy-soiled water is water from concreted areas, hard stand areas, and holding areas for livestock that has become contaminated by livestock faeces or urine, chemical fertilisers, and parlour washings (Statutory Instrument 610 of 2010; Martínez-Suller et al. 2010). The water volumes generated may vary according to the practices applied by the farmers.

O. Fenton
Teagasc, Johnstown Castle Environmental Research Centre,
Wexford, Co. Wexford, Republic of Ireland

A. Serrenho · M. G. Healy (✉)
Civil Engineering, National University of Ireland,
Galway, Co. Galway, Republic of Ireland
e-mail: mark.healy@nuigalway.ie

Factors such as frequency of milking and the number of cows present at the same time affect the volumes generated. Dairy-soiled water has been estimated at 50 L per cow per day (Department of the Environment and Department of Agriculture, Food and Forestry 1996), but this value can be frequently exceeded especially where there is indifferent management of water usage. In Ireland, DSW is defined as wastewater with a 5-day biological oxygen demand (BOD₅) of less than 2,500 mg L⁻¹ and a dry matter (DM) content of less than 1%. More concentrated effluent is considered to be slurry and is stored separately. Dairy-soiled water contains high and variable amounts of nutrients, as well as other constituents such as spilt milk and cleaning agents (Fenton et al. 2008). Its composition is inherently variable due to the different facilities and management practices that exist on farms, seasonal changes in weather, and management practices (Ryan 1990). Dairy-soiled water contains nutrients that are potentially available to plants, but also pose a potential threat to water quality if not managed correctly. However, these nutrients are present in far lower concentrations than in slurry and, in Ireland, DSW is not subject to closed periods for landspreading, although it is subject to other limitations protecting water quality, such as application rates, which must not exceed 50 mm year⁻¹ (Statutory Instrument 610 of 2010) soil and weather conditions, slope and proximity to water sources. A number of studies in the UK and Ireland show the nutrient variability in the chemical composition of DSW due to geographical location or seasonal sampling times (ADAS 1994; Cumby et al. 1999; Ryan et al. 2006; Fenton et al. 2009; Minogue et al. 2010; Martínez-Suller et al. 2010).

1.1 Amendments to Sequester P

Application to land is the most common method for disposal of DSW. However, when it is applied at rates exceeding a maximum application rate of 50,000 L ha⁻¹ in any 48-day period (Statutory Instrument 610 of 2010), it can give rise to surface runoff of P, N, and suspended sediment (SS; Regan et al. 2010); subsurface leaching of N and—depending on the soil type—P (Knudsen et al. 2006); and greenhouse gas (GHG) and ammonia (NH₃) emissions (Hyde et al. 2003). Alternatively DSW can be applied through centre

pivot or low irrigation systems. In addition, repeated application to agricultural land causes soil test phosphorus (STP) to build up in soils (Hao et al. 2008). Schulte et al. (2010) showed that it may take many years for elevated soil P concentrations to be reduced to agronomically and environmentally optimum levels. Reductions in excessive STP may be observed within 5 years, but may take years-to-decades to be completed.

Chemical amendments can be used to sequester P from DSW and prevent accidental losses in runoff. Targeted land application of amended DSW in critical source areas—areas where ground or surface water pollution is likely to occur due to farming activities—may be an option. Studies examining the use of amendments have traditionally focused on dairy slurry (Lefcourt and Meisinger 2001; Dou et al. 2003) and swine slurry (Smith et al. 2001), but, at the time of writing, no study could be found that examines the addition of amendments to DSW with the aim of reducing surface runoff of nutrients. Penn et al. (2011) examined the sorption and retention mechanisms of several amendments, including acid mine drainage treatment residuals, water treatment residuals (WTR), fly ash, bauxite mining residual, and flue gas desulphurisation by-product (FGD), in laboratory experiments and found the degree of sorption of P to be strongly influenced by the solution pH, buffer capacity of manure, and ionic strength of amendments.

Laboratory-scale batch experiments, although allowing quick determination of adsorption capacities of amendments, are unrealistic when considering nutrient losses in runoff following DSW application. These small-scale tests do not account for the interaction between applied wastewater and soil, and the effect of infiltration and skin formation on the release of P to surface runoff. An agitator test, wherein an intact soil core, placed in a beaker, is overlain with continuously stirred water (Mulqueen et al. 2004), enables achievement of batch experiment results, but also simulates runoff on land-applied DSW.

The objectives of this study were to: (1) use a laboratory agitator test to identify the most effective amendment to reduce P loss from the soil surface after land application of DSW; (2) to identify optimum amendment application rates for a similar P reduction in different amendments; (3) to estimate the cost of

each treatment; and (4) to evaluate the feasibility of using treatments in a real on-farm scenario.

2 Materials and Methods

2.1 Soil Preparation and Analysis

To collect undisturbed soil core samples ($n=72$) from a local dry stock farm in Athenry, Co. Galway, 120-mm-high and 100-mm-diameter aluminium coring rings were used. Soil samples ($n=3$)—taken from upper 100 mm from the same location—were air dried at 40°C for 72 h, crushed to pass a 2-mm sieve, and analysed for P using Mehlich 3 (MP3) extracting solution (Mehlich, 1984) and Morgan's P using Morgan's extracting solution (Byrne 1979). Soil pH ($n=3$) was determined using a pH probe and a 2:1 ratio of deionised water to soil. Shoemaker-McLean-Pratt (SMP) buffer pH was determined, and the lime requirement (LR) of the soil was calculated after Pratt and Blair (1963). The particle size distribution (PSD) was determined using B.S.1377-2:1990 (BSI, 1990a) and the organic matter content of the soil was determined using the loss of ignition test (B.S.1377-3; BSI 1990b).

The soil used had a MP3 of 107 ± 2.8 mg P kg⁻¹, a soil pH of 5.6 ± 0.1 and a P index of 3 ($5.1\text{--}8$ mg L⁻¹ Morgan's P). The phosphorus index system is used in Ireland to describe soils. A P index of 3 means that only maintenance rates of P are required to maintain soil fertility. The soil SMP buffer pH was 6.1 ± 0.2 and the LR was 9.9 ± 1 t ha⁻¹. The soil used was loamy sand which comprised 15% gravel (2–60 mm), 72% sand (0.06–2 mm), and 13% fines (<0.06 mm), with an organic matter content of $16.2\pm 0.2\%$.

2.2 DSW Sampling and Analysis

DSW produced from 137 spring calving dairy cows at the Environmental Research Centre (Teagasc, Wexford) was collected in November, 2009. This is the same facility as used by Martínez-Suller et al. (2010). The tanks were agitated for 20 min until the DSW was homogenized, and DSW samples were collected in 10-L drums and transported to the laboratory. The DSW was stored at 4°C until immediately prior to the start of the agitator test. It was fully characterized for the following water-quality parameters: ammonium-N,

nitrite-N, nitrate-N, total ammonical N, dissolved reactive P (DRP), and total P (TP) in accordance with the standard methods (APHA 1995). pH was measured using a pH probe (WTW, Germany) and the dry matter was determined by drying at 40°C for 72 h.

2.3 Classification and Determination of Suitable Amendments for Use in the Agitator Test

Before the agitator test commenced, a preliminary batch test was conducted to determine the suitability of various amendments for the removal of P from DSW. Chemicals examined were: aluminium sulfate (alum; Al₂(SO₄)₃·18H₂O), calcium hydroxide (lime; Ca(OH)₂), iron (II) chloride tetrahydrate (FeCl₂·4H₂O), aluminium chloride (AlCl₃·6H₂O). Phosphorus sorbing materials (PSM) examined were: coal combustion by-products (fly ash and bottom ash) and WTR sludge. Coal combustion by-products were provided by the Electricity Supply Board (ESB) and the WTR was provided by a water treatment plant in Galway City. The pH of the amendments was measured using 2:1 deionised water/dry amendment ratio. In the case of the WTR sludge, it was possible to measure pH of the sludge with a pH probe. DM content was determined by drying at 40°C for 72 h. Total metal and P of the amendments were measured after 'aqua regia' digestion using a Gerhard Block digestion system (Cottenie and Kiekens 1984), which is described by Fenton et al. (2009). The water extractable phosphorus content of the amendments was determined after Dayton and Basta (2001).

In a preliminary batch test, different quantities of each amendment were added to 15 ml of DSW ($n=3$). Chemicals were applied based on metal: TP stoichiometric rate (for alum, FeCl₂·4H₂O, or lime) or, in the case of PSM, based on kg of PSM L⁻¹ of DSW (for fly ash, bottom ash, and WTR). Stoichiometric rate refers to the ratio of the metal to phosphorus expressed on a per gramme basis. Each container was mixed thoroughly and incubated in a temperature-controlled room at 11°C. After 24 h, supernatant water samples were collected, centrifuged for 5 min at 14,000 rpm, and the DRP was measured using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). The performance of each chemical and PSM—along with an optimal rate of amendment addition to the DSW—was determined (results not shown). On the basis of this test, four

different amendments were used in the agitator test: (1) lime; (2) alum; (3) $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; and (4) bottom ash.

2.4 Agitator Test

The agitator test has been used to investigate the release of P from soil (Mulqueen et al. 2004) and soil amended with slurry (Brennan et al. 2011). This experiment replicates the way used by Brennan et al. (2011) in which DSW is applied to soil, allowed to dry, and then subjected to runoff. This experiment does not provide a uniform means of assessing release of P from land-applied DSW; however, it does allow us to compare the effectiveness of amendments in a realistic way.

The agitator test comprised three different treatments ($n=3$): grassed soil only; grassed soil receiving DSW at a rate equivalent to 5 mm ha^{-1} (the study control); and DSW with four amendments applied at the same hydraulic rate. Each of the amendments was applied at two to three different rates (the optimal rate determined in the batch test and up to two other rates) in triplicate. Prior to the start of the agitator test, the intact-soil samples were transferred from the sampling cores into beakers. The depth of soil in the beakers ranged from 40 to 50 mm; this was considered sufficient to include the full depth of influence (Mulqueen et al. 2004). Untreated DSW or amended DSW was applied to the soil ($t=0 \text{ h}$), and was then allowed to interact for 24 h prior to saturation of the sample. After 24 h ($t=24 \text{ h}$), the sample was submerged with 500 ml of water and the paddle of the agitator device was immersed half way in the supernatant water (Fig. 1). Runoff was simulated by gentle agitation of the supernatant water by the paddle rotating at a speed of 20 rpm for 24 h. Over a 1-day study duration, supernatant water samples were tested

for DRP and pH. For each treatment, DSW samples ($n=3$)—with the same volume as applied to the grass sample in the agitator test—were spread at the bottom of a beaker to allow pH to be measured at 24 h without disturbing the sample used in the agitator test.

2.5 Water Sampling and Analysis

Water samples (4 ml) were taken from mid-depth of the water overlying the soil at 0.25, 0.5, 1, 2, 4, 8, 12, and 24 h after the start of each test. All samples were filtered immediately after sample collection using $0.45\text{-}\mu\text{m}$ filters and placed in a freezer (after APHA, 1995) prior to being analysed colorimetrically for DRP using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). The DRP concentrations were used to calculate the mass of DRP in the water overlying the soil samples in the beaker, taking into account the water-volume reduction as the test progressed.

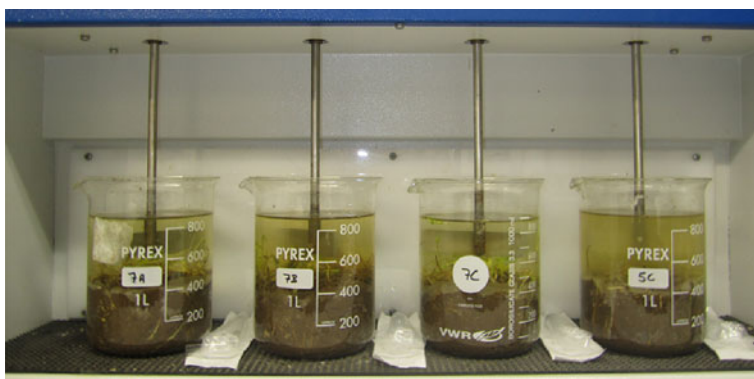
2.6 Statistical Analysis

Proc Mixed (SAS Institute 2004) was used to model the factorial structures (amendment \times application rate; and amendment \times application rate \times time) in the experiment in order to allow for heterogeneous variance across treatments. A group variable was fitted to allow comparisons between the control treatments and the factorial combinations. A multiple comparisons procedure (Tukey) was used to compare means.

2.7 Cost analysis

The cost of amendments was calculated based on the estimated cost of amendment, delivery and DSW

Fig. 1 The agitator test



spreading costs. In contrast to chemical and PSM amendments to slurry, no further cost is needed for addition to DSW as amounts are much smaller, no agitation is required, and there is no volume increase after addition of amendments and therefore no added spreading costs. DSW landspreading costs were estimated based on the equivalent data for slurry application costs from Lalor (2008). It is more likely that DSW will be spread closer to the farmyard than slurry due to the lower nutrient content of the product. The feasibility of amendments was determined based on effectiveness, potential barriers to use, and cost of implementation.

3 Results

3.1 DSW and Amendment Analysis

The DM and nutrient content of the DSW, as presented in Table 1, are within the range outlined by Martínez-Suller et al. (2010). The characteristics of all amendments are presented in Table 2. Analytical grade aluminium chloride (6% Al), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (28% Fe), and lime (53% Ca) were used in the experiments. Further testing would need to be conducted to ensure that the use of PSM, or any other chemical amendment used, would not yield heavy metal concentrations in excess of allowable concentrations in surface waters (75/440/EEC; EEC 1975).

3.2 Agitator Test

Changes in pH in the DSW over a 24-h period and the maximum DRP concentrations and load in the overlying water are given in Table 3. The pH for the DWS water-only treatment (the study control) dropped from 7.1 ± 0.27 ($t=0$ h) to 7.0 ± 0.08 after 24 h. All other amendments—with the exception of

alum (applied at a weight ratio of 8.8:1 Al/TP) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (applied at 200:1 Fe/TP)—caused the pH of the DSW to rise initially.

The maximum DRP load in the water overlying the soil-only was approximately $0.1 \text{ mg DRP m}^{-2}$ compared with 68 mg DRP m^{-2} when the soil was overlain with unamended DSW. The amendments that achieved the best reduction in mass of soluble DRP in the overlying water were: FeCl_2 (89–90%), lime (75–83%), and alum applied at 0.003 kg L^{-1} (72%).

The potential for coal combustion by-products—fly ash and bottom ash—to mitigate P loss was also investigated. Fly ash proved unsuccessful (data not shown), but bottom ash reduced the maximum DRP load in the overlying water by between 42% and 45%. Moneypoint Power Station in County Clare burns approximately two million tonnes of coal per annum of which approximately 9,750 t of bottom ash is currently sent to landfill (ESB 2009). Since this by-product is currently put to landfill, it may be economically and environmentally desirable to find an alternative use for it, but its metal content (Tables 2 and 4) would need to be considered when land application takes place.

The amendments were added slowly to the DSW (after Lefcourt and Meisinger 2001) and effervescence was not noted in any of the experiments. Comparatively, Brennan et al. (2011) noted the occurrence of effervescence when alum was applied to dairy slurry at a rate of 2.44:1 of Al/P. Further trials would need to be conducted before field-scale additions are carried out.

3.3 Statistical Analysis

The overall statistical analysis showed that there was a significant interaction between treatment and application rate, but that the interaction effects were small compared to the main effects.

Table 1 Water quality characterisation of dairy-soiled water used in study

<i>n</i> =3	TN	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	TAN	TP	DRP	pH	DM
	mg L ⁻¹							Percent (%)
Concentration	730	110	2.3	256	14.2	7.3	7.9	0.22
±Standard deviation	212	35	0.0	48	0.51	0.36	0.0	0.08

TN total nitrogen, $\text{NH}_4\text{-N}$ ammonium-N, $\text{NO}_3\text{-N}$ nitrate-N, TAN total ammonical N, TP total P, DRP dissolved reactive P, DM dry matter

Table 2 Characterisation of amendments used in the agitator test (mean±standard deviation) tests carried out in triplicate

Amendment	Lime		Alum	Ferrous chloride	Bottom ash
	Ca(OH) ₂		Al ₂ (SO ₄) ₃ ·18H ₂ O	Fe(Cl) ₂	
pH			1.25		
WEP	mg/kg		0		
Al	%		4.2		0.42
Ca		52.6			0.4
Fe			<0.01	13.9	1.6
K					0.04
As	mg/kg		1		
Cd			0.21		0.28
Co					0.43
Cr			2.1		14.3
Cu					8.1
Mg					2120
Mn					92
Mo					0.63
Na					859
Ni			1.4		9.9
P					171
Pb			2.8		3.9
V					13.7
Zn					19.7

WEP water extractable phosphorus

Table 3 Phosphorus removal in the agitator test, pH at $t=0$ h and $t=24$ h, observed peak phosphorus concentration, reduction percentage

PSM	Rate of addition		pH		P max		Time ^a (h)	P reduction (%) ^b
	Weight/volume (kg L ⁻¹)	Molecular	$t=0$ h	$t=24$ h	mg L ⁻¹	mg m ⁻²		
Control–Soil-only			7.51±0.07	7.79±0.02	0.002±0.0003	0.10±0.02	24	
Control–Soil+DSW			7.08±0.27	7.00±0.08	1.10±0.24	68.57±15.16	4	
Lime (Ca(OH) ₂) ^c	0.067	2,500 Ca/P	9.08±0.06	9.33±0.07	0.19±0.06	11.80±3.4	4	83
	0.130	4,884 Ca/P	9.36±0.31	10.07±0.43	0.27±0.05	16.50±3.19	8	75
	0.200	7,514 Ca/P	9.79±0.24	10.37±0.18	0.24±0.01	15.10±0.60	2	78
Alum (Al ₂ (SO ₄) ₃ ·18H ₂ O) ^c	0.001	2.9 Al/P	8.68±1.27	8.03±0.26	0.83±0.18	50.80±11.1	24	25
	0.003	8.8 Al/P	6.91±0.11	7.50±0.00	0.31±0.05	19.03±3.01	24	72
FeCl ₂ ·4H ₂ O ^c	0.010	200 Fe/P	6.90±0.02	7.50±0.00	0.12±0.01	7.52±0.67	0	89
	0.033	660 Fe/P	7.70±1.61	7.85±0.31	0.11±0.03	6.48±1.84	8	90
Bottom ash	0.067		7.54±0.38	7.07±0.02	0.60±0.13	35.84±7.84	24	45
	0.130		7.15±0.24	7.08±0.03	0.61±0.01	36.67±1.77	24	45
	0.200		7.62±0.22	7.49±0.12	0.64±0.08	38.71±4.81	12	42

^a Time of observed peak concentration (hour). Each study had the duration of 24 h in total.

^b P reduction was calculated on the basis of the difference between the phosphorus concentration of water overlying soil onto which unamended and amended DSW was applied.

^c Laboratory chemicals

Table 4 Amendments including cost of supply, delivery and addition of amendments, and cost for 100-cow farm with no DSW irrigation

Amendment	Addition rate (weight ratio)	Cost ^a	Application rate of amendment	Application rate of metal ^b	Spreading ^c	Total	100 cow farm	Max allowable metal spreading rate	
		€ kg ⁻¹	kg m ⁻³	kg m ⁻³	€ m ⁻³	€ m ⁻³	€ farm year ^{-1d} Spreading rate of metal kg ha ^{-1e}		kg ha ⁻¹ yr ⁻¹
Control					1.55		403		
FeCl ₂ ·4H ₂ O (FeCl ₃)	200 Fe/P	0.2	10	2.8	1.55	3.55	923	0.014	No limit
	660 Fe/P		33	9.2	1.55	8.15	2,119	0.046	
Lime	2,500 Ca/P	0.28	67	35.2	1.55	20.31	5281	0.176	No limit
	4,884 Ca/P		130	68.3	1.55	88.65	23,049	0.34	
	7,514 Ca/P		200	105	1.55	57.55	14,963	0.525	
Alum	2.9 Al/P	0.125	1	0.06	1.55	1.67	434	3×10 ⁻⁴	No limit
	8.8 Al/P		3	0.18	1.55	1.92	499	9×10 ⁻⁴	
Bottom ash	0.067 kg L ⁻¹	0	67		1.55	1.55	403		Within limits
	0.130 kg L ⁻¹		130		1.55	1.55	403		Within limits
	0.200 kg L ⁻¹		200		1.55	1.55	403		Within limits

^a Where analytical grade products were used, cost was estimated using the most similar commercial product on the market (*in brackets*). Cost includes delivery of material and addition of material to DSW in storage tank

^b Six percent for Al in Al₂(SO₄)₃·18H₂O, 52.5% for Ca in Ca(OH)₂, and 28% for Fe in FeCl₂·4H₂O. Metal analysis for bottom ash is in Table 2

^c Spreading costs from S. Lalor (personal communication). Batch tests showed that no volume increase occurred due to addition of PSM amendment

^d Fifty litres of DSW produced per cow per day for 52 weeks

^e Based on a maximum allowable application rate of 5 mm ha⁻¹ (Statutory Instrument 610 of 2010). Utilising data from Table 2, bottom ash has no metals that are outside spreading limits for the application rates discussed here.

Table 5 Feasibility of amendments

Amendment ^a	Feasibility score	Addition rate	Total	Reduction in DRP	Discussion
		kg m ⁻³	€ m ⁻³	Percentage P	
Alum	1	3	1.92	72	Cheap and widely used in water treatment. Negative public perception about landspreading Al may be problematic. Potential elevated release of greenhouse gases (R.B. Brennan, personal communication)
FeCl ₂ ·4H ₂ O (FeCl ₃)	2	10	3.55	89	Potential elevated release of greenhouse gases (R.B. Brennan, personal communication) Negative public perception about landspreading Fe may be problematic.
Bottom ash	3	67	1.55	45	Contains heavy metals. Settles quickly so thorough mixing may be difficult.
Lime	4	67	20.31	83	Available on farms, no danger of metal losses to the environment, good public perception already, and can help with lime requirement of the soil. Prohibitive cost at application rates required.

^a Where analytical grade products were used, the most similar commercial product on the market (*in brackets*) was used in price calculations to determine feasibility.

3.4 Cost and Feasibility Analysis

The estimated costs of addition of amendments are presented in Table 4. Starting with the cheapest, the amendments were ranked as follows: bottom ash, alum, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and lime. The amendments were also ranked in terms of their feasibility, taking into account their cost, potential adverse effects, and public perception, as well as their performance (Table 5). Based on these parameters, starting with the most desirable, the amendments were ranked as follows: alum, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, bottom ash, and lime.

4 Discussion

Amendment of DSW is attractive since it can be used in strategic areas and implemented quickly without capital expenditure. It allows farmers to utilise the nutrients present in DSW in areas with soils of low STP and, as DSW can be spread throughout the year, it safeguards incidental losses when storm events follow in the days after spreading. In Ireland, DSW is commonly spread using centre pivot irrigation systems. However, there is potential of ponding and leaching of DSW particularly in areas of sand and gravel deposits, or where free draining soils overlay karst limestone with high flow rates and relatively low electrical conductivity (EC) values. The potential of such waterbodies to transfer nutrients to deeper groundwater or surface water is high. The mixing of a chemical or PSM with the DSW in lagoons feeding these centre pivot irrigators may be a viable option to reduce the risk of surface runoff. The impact of the amendments used in this study on leaching of nutrients needs to be investigated.

This experiment examines the effect of amendments on incidental losses. However, the effectiveness of different amendments over longer time spans (months, years) depends on farm management systems, drainage, and soils to which they are applied. For example, Al–P bonds are most stable in acidic soils, while Ca–P bounds are more stable under calcareous conditions (Russell 1988). The present study does not consider the effect of different soil types.

Chemical or PSM amendment of DSW or manure is not presently part of programme of measurements (POM) or supplementary measurements for any country in Europe. It has been included in the COST

869 fact-sheets (Chardon and Doiroz 2008) for possible inclusion by River Basin District Managers, and there is potential that it could be introduced as a supplementary measure in 2015 if POM are found not to be sufficient to meet the requirements of the Water Framework Directive (2000/60/EC: Council of the European Union 2000)

A potential obstacle for chemical amendment is public perception of amendments and this must also be considered in feasibility studies. For this reason, it is important that any amendments used are efficient and that more metals than necessary for P sequestration are not applied. There is no provision for a licence to land spread any of these amendments (with the exception of lime) and, if a suitable amendment were to be used to mitigate P losses, a licencing system would have to be introduced by the Department of Agriculture.

5 Conclusions

This study examined the effectiveness of various chemicals ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, lime and alum) and phosphorus sorbing materials (bottom ash) in reducing phosphorus loss in runoff. The main conclusions from this study were:

1. Starting with the cheapest, the amendments were ranked as follows: bottom ash (1.55 €m^{-3} of DSW), alum (1.67 to 1.92 €m^{-3} of DSW), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (3.55 to 8.15 €m^{-3} of DSW), and lime (20.31 to 88.65 €m^{-3} of DSW).
2. The amendments were ranked in terms of their feasibility (taking into account their cost, potential adverse effects, and public perception, as well as their performance). Starting with the most desirable, the amendments were ranked as follows: alum, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, bottom ash, and lime.
3. The use of amendments to dairy-soiled water should only be used in critical source areas where pollution is likely to occur. The effects of these amendments on groundwater leaching and greenhouse gases should be investigated.

Acknowledgements This study was funded under the Department of Agriculture, Fisheries and Food under the Research Stimulus Programme 2007 (RSF 07 525). The authors acknowledge the help of Ray Brennan, Stan Lalor, and Aidan Lawless.

References

- ADAS, IGER & SSRC (1994). Low rate irrigation of dilute farm wastes. Report for the National Rivers Authority, R and D no. 262, National Rivers Authority, Bristol.
- APHA. (1995). *Standard methods for the examination of water and wastewater*. Washington: American Public Health Association.
- BSI. (1990a). *British standard methods of test for soils for civil engineering purposes. Determination of particle size distribution. BS 1377:1990:2*. London: British Standards Institution.
- BSI. (1990b). *Determination by mass-loss on ignition. British standard methods of test for soils for civil engineering purposes. Chemical and electro-chemical tests. BS 1377:1990:3*. London: British Standards Institution.
- Brennan, R.B., Fenton, O., Rodgers, M., & Healy, M.G. (2011). Evaluation of chemical amendments to control phosphorus losses from dairy slurry. *Soil Use and Management* (in press).
- Byrne, E. (1979). *Chemical analysis of agricultural materials—methods used at Johnstown Castle Research Centre*. Wexford: An Foras Talúntais.
- Chardon, W. J., & Doiroz, J.M. (2008). Fact sheet: Phosphorus immobilizing amendments to soil. COST 869. http://www.cost869.alterra.nl/Fs/FS_immobilization_soil.pdf. Accessed 11 April 2011.
- Cottenie, A., & Kiekens, L. (1984). Report of results of the inter-laboratory comparison: Determination of the mobility of heavy metals in soils. In P. L'Hermite & H. D. Ott (Eds.), *Processing and use of sewage sludge* (pp. 140–149). Dordrecht, The Netherlands: Reidel.
- Council of the European Union (2000) Water Framework Directive 2000/60/EC establishing a framework for community action in the field of water policy. <http://www.wfdireland.ie>. Accessed 15 November 2010.
- Cumby, T. R., Brewer, A. J., & Dimmock, S. J. (1999). Dirty water from dairy farms, I: biochemical characteristics. *Bioresource Technology*, 67, 155–160.
- Dayton, E.A., & Basta, N.T. (2001). Characterisation of drinking water treatment residuals for use as a soil substitute. *Water Environment Research*, 73 (1), 52–57. <http://www.jstor.org/stable/25045460>. Accessed 22 November 2010.
- Department of the Environment & Department of Agriculture, Food and Forestry. (1996). *Code of good agricultural practice to protect waters from pollution by nitrates* (p. 57). Dublin: Department of the Environment and Department of Agriculture, Food and Forestry.
- Dou, Z., Zhang, G. Y., Stout, W. L., Toth, J. D., & Ferguson, J. D. (2003). Efficacy of alum and coal combustion by-products in stabilizing manure phosphorus. *Journal of Environmental Quality*, 32, 1490–1497.
- EEC (1975). Council Directive concerning the quality required of surface water intended for the abstraction of drinking water in the member states. Council of the European Communities, 75/440/EEC.
- ESB (2009). Moneypoint generating station. Annual environmental report for the period 1st of January to 31st December 2008. http://www.epa.ie/licences/lic_eDMS/090151b2802a5f81.pdf. Accessed 11 April 2011.
- Fenton, O., Healy, M. G., & Schulte, R. P. O. (2008). A review of remediation and control systems for the treatment of agricultural wastewater in Ireland to satisfy the requirements of the Water Framework Directive. *Biology and Environment: Proceedings of the Royal Irish Academy*, 108B(2), 69–79.
- Fenton, O., Healy, M. G., & Rodgers, M. (2009). Use of ochre from an abandoned acid mine in the SE of Ireland for phosphorus sequestration from soiled water. *Journal of Environmental Quality*, 38, 1120–1125.
- Hao, X., Godlinski, F., & Chang, C. (2008). Distribution of phosphorus forms in soil following long-term continuous and discontinuous cattle manure applications. *Soil Science Society of America Journal*, 72, 90–97.
- Hyde, B. P., Carton, O. T., O'Toole, P., & Misslebrook, T. H. (2003). A new inventory of ammonia emissions from Irish agriculture. *Atmospheric Environment*, 37, 55–62.
- Knudsen, M. T., Kristensen, I. S., Berntsen, J., Petersen, B. M., & Kristensen, E. S. (2006). Estimated N leaching losses for organic and conventional farming in Denmark. *Journal of Agricultural Science*, 144, 135–149.
- Lalor, S. (2008). Economic costs and benefits of adoption of the trailing shoe slurry application method on grassland farms in Ireland. 13th RAMIRAN International conference Potential for simple technology solutions in organic manure management, Albena, Bulgaria.
- Lefcourt, A. M., & Meisinger, J. J. (2001). Effect of adding alum or zeolite to dairy slurry on ammonia volatilization and chemical composition. *Journal of Dairy Science*, 84, 1814–1821.
- Martinez-Suller, L., Provolo, G., Carton, O. T., Brennan, D., Kirwan, L., & Richards, K. G. (2010). The composition of dirty water on dairy farms in Ireland. *Irish Journal of Agricultural and Food Research*, 49(1), 93–97.
- Mehlich, A. (1984). Mehlich 3 soil test extractant: A modification of the Mehlich 2 extractant. *Communications in Soil Science and Plant Analysis*, 15, 1409–1416.
- Minogue, D., Murphy, P., French, P., Coughlan, F., & Bolger, T. (2010). *Characterisation of soiled water on Irish dairy farms*. Ireland: BSAS & Agricultural Research Forum, Belfast, N.
- Mulqueen, J., Rodgers, M., & Scally, P. (2004). Phosphorus transfer from soil to surface waters. *Agricultural Water Management*, 68, 91–105.
- Penn, C. J., Bryant, R. B., Callahan, M. A., & McGrath, J. M. (2011). Use of industrial byproducts to sorb and retain phosphorus. *Communications in Soil Science and Plant Analysis*, 42, 633–644.
- Preedy, N., McTiernan, K., Matthews, R., Heathwaite, L., & Haygarth, P. (2001). Rapid incidental phosphorus transfers from grassland. *Journal of Environmental Quality*, 30, 2105–2112.
- Pratt, P. F., & Blair, F. L. (1963). Buffer method for estimating lime and sulphur applications for pH control of soils. *Soil Science*, 93, 329.
- Regan, J. T., Rodgers, M., Healy, M. G., Kirwan, L., & Fenton, O. (2010). Determining phosphorus and sediment release rates from five Irish tillage soils. *Journal of Environmental Quality*, 39, 185–192.

- Russell, E. J. (1988). *Russell's soil conditions and plant growth* (11th ed.). England: Longman Scientific and Technical, John Wiley and Sons, Burnt Mill, Harlow, Essex.
- Ryan, M. (1990). Properties of different grades of soiled water and strategies for safe disposal. Proceedings of Seminar Environmental Impact of Landspreading of Wastes (May 30–31), Teagasc Research Centre, Johnstown Castle, Co. Wexford, Ireland.
- Ryan, M., Brophy, C., Connolly, J., McNamara, K., & Carton, O. T. (2006). Monitoring of nitrogen leaching on a dairy farm during four drainage seasons. *Irish Journal of Agricultural and Food Research*, 45, 115–134.
- Schulte, R. P. O., Melland, A. R., Fenton, O., Herlihy, M., Richards, K. G., & Jordan, P. (2010). Modelling soil phosphorus decline: Expectations of Water Frame Work Directive policies. *Environmental Science & Policy*, 13, 472–484.
- SAS. (2004). *SAS/STAT® User's Guide*. Cary, NC: SAS Institute Inc.
- Smith, D. R., Moore, P. A., Griffiths, C. L., Daniel, T. C., Edwards, D. R., & Boothe, D. L. (2001). Effects of alum and aluminium chloride on phosphorus runoff from swine manure. *Journal of Environmental Quality*, 30, 992–998.
- Statutory Instrument 610 of 2010. European communities (good agricultural practice for protection of waters) regulations 2010. <http://www.irishstatutebook.ie/2010/en/si/0610.html>. Accessed 11 April 2011.