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# 1 Evaluation of Amendments to Control 2 Phosphorus Losses in Runoff from Dairy Soiled 3 Water

4 Owen Fenton<sup>1</sup>, Ana Serrenho<sup>2</sup>, Mark Gerard Healy<sup>2\*</sup>

6  
7 <sup>1</sup>*Teagasc, Johnstown Castle, Environmental Research Centre, Co Wexford, Rep. of*  
8 *Ireland*

9 <sup>2</sup>*Civil Engineering, National University of Ireland, Galway, Co. Galway, Rep. of Ireland.*

10

11 Corresponding author. Tel: +353 91 495364; fax: +353 91 494507. E-mail address:

12 [mark.healy@nuigalway.ie](mailto:mark.healy@nuigalway.ie)

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15 **control phosphorus losses in runoff from dairy soiled water. *Water, Air and Soil Pollution***  
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17

18 **Abstract** Amendments with the potential to reduce phosphorus (P) losses from agricultural grassland  
19 arising from the land application of dairy soiled water (DSW) were investigated. Optimal application rates  
20 were studied, and associated costs and feasibility estimated. First, batch tests were carried out to identify  
21 appropriate chemicals or phosphorus sorbing materials (P SM) to control P in runoff from DSW. Then, the  
22 best 4 treatments were examined in an agitator test. In this test, soil – placed in a beaker – was loaded with  
23 DSW or amended DSW at a rate equivalent to 5 mm ha<sup>-1</sup> (the maximum permissible application rate of  
24 DSW allowable in a 42-d period in Ireland). The soil was overlain with continuously stirred water to  
25 simulate runoff on land-applied DSW. Optimum application rates were selected based on percentage  
26 removal of dissolved reactive phosphorus (DRP) in overlying water and the estimated cost of amendment.  
27 The costs of the amendments, per m<sup>3</sup> of DSW, increased in the order: bottom ash (€1.55), alum (€1.67 to  
28 €1.92), FeCl<sub>2</sub>.4H<sub>2</sub>O (€3.55 to €8.15), and lime (€20.31 to €88.65). The feasibility of the amendments,  
29 taking into account their cost, potential adverse effects, public perception, and their performance, decreased  
30 in the order: alum > FeCl<sub>2</sub>.4H<sub>2</sub>O > bottom ash > lime. Amendments to DSW could be introduced in critical  
31 source areas – areas where high soil test P and direct migration pathways to a receptor overlap.

32

33 **Keywords:** *Dairy soiled water; iron (II) chloride tetrahydride; lime; alum; bottom ash.*

34

## 35 **1 Introduction**

36

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

44

45 Dairy soiled water is water from concreted areas, hard stand areas, and holding areas for  
46 livestock that has become contaminated by livestock faeces or urine, chemical fertilisers  
47 and parlour washings (SI No. 610 of 2010; Martínez-Suller et al. 2010). The water  
48 volumes generated may vary according to the practices applied by the farmers. Factors  
49 such as frequency of milking and the number of cows present at the same time affect the  
50 volumes generated. Dairy soiled water has been estimated at 50 litres per cow per day  
51 (Department of the Environment and Department of Agriculture, Food and Forestry  
52 1996), but this value can be frequently exceeded especially where there is indifferent  
53 management of water usage. In Ireland, DSW is defined as wastewater with a 5-day  
54 biological oxygen demand (BOD<sub>5</sub>) of less than 2,500 mg L<sup>-1</sup> and a dry matter (DM)  
55 content of less than 1 %. More concentrated effluent is considered to be slurry and is  
56 stored separately. Dairy soiled water contains high and variable amounts of nutrients, as  
57 well as other constituents such as spilt milk and cleaning agents (Fenton et al. 2008). Its  
58 composition is inherently variable due to the different facilities and management  
59 practices that exist on farms, seasonal changes in weather, and management practices  
60 (Ryan 1990). Dairy soiled water contains nutrients that are potentially available to plants,  
61 but also pose a potential threat to water quality if not managed correctly. However, these  
62 nutrients are present in far lower concentrations than in slurry and, in Ireland, DSW is not  
63 subject to closed periods for land-spreading, although it is subject to other limitations  
64 protecting water quality, such as application rates, which must not exceed 50 mm yr<sup>-1</sup> (SI  
65 610 of 2010) soil and weather conditions, slope and proximity to water sources. A

66 number of studies in the UK and Ireland show the nutrient variability in the chemical  
67 composition of DSW due to geographical location or seasonal sampling times (ADAS  
68 1994; Cumby et al. 1999; Ryan et al. 2006; Fenton et al. 2009; Minogue et al. 2010;  
69 Martínez-Suller et al. 2010).

70

71 1.1 Amendments to sequester P

72

73 Application to land is the most common method for disposal of DSW. However, when it  
74 is applied at rates exceeding a maximum application rate of 50,000 L ha<sup>-1</sup> in any 48-day  
75 period (SI 610 of 2010), it can give rise to surface runoff of P, N and suspended sediment  
76 (SS) (Regan et al. 2010); subsurface leaching of N and - depending on the soil type - P  
77 (Knudsen et al. 2006); and greenhouse gas (GHG) and ammonia (NH<sub>3</sub>) emissions (Hyde  
78 et al. 2003). Alternatively DSW can be applied through centre pivot or low irrigation  
79 systems. In addition, repeated application to agricultural land causes soil test phosphorus  
80 (STP) to build up in soils (Hao et al. 2008). Schulte et al. (2010) showed that it may take  
81 many years for elevated soil P concentrations to be reduced to agronomically and  
82 environmentally optimum levels. Reductions in excessive STP may be observed within  
83 five years, but may take years-to-decades to be completed.

84

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

97

98 Laboratory-scale batch experiments, although allowing quick determination of adsorption  
99 capacities of amendments, are unrealistic when considering nutrient losses in runoff  
100 following DSW application. These small-scale tests do not account for the interaction  
101 between applied wastewater and soil, and the effect of infiltration and skin formation on  
102 the release of P to surface runoff. An agitator test, wherein an intact soil core, placed in a  
103 beaker, is overlain with continuously stirred water (Mulqueen et al. 2004), enables  
104 achievement of batch experiment results, but also simulates runoff on land-applied DSW.  
105

106 The objectives of this study were to: (i) use a laboratory agitator test to identify the most  
107 effective amendment to reduce P loss from the soil surface after land application of  
108 DSW; (ii) to identify optimum amendment application rates for a similar P reduction in  
109 different amendments; (iii) to estimate the cost of each treatment; and (iv) to evaluate the  
110 feasibility of using treatments in a real on-farm scenario.

111

## 112 **2 Materials and Methods**

113

### 114 2.1 Soil preparation and analysis

115

116 120 mm-high and 100 mm-diameter aluminium coring rings were used to collect  
117 undisturbed soil core samples (n=72) from a local dry stock farm in Athenry, Co.  
118 Galway. Soil samples (n=3) – taken from upper 100 mm from the same location - were  
119 air dried at 40 °C for 72 hr, crushed to pass a 2 mm sieve, and analysed for P using  
120 Mehlich 3 (MP3) extracting solution (Mehlich, 1984) and Morgan's P using Morgan's  
121 extracting solution (Byrne 1979). Soil pH (n=3) was determined using a pH probe and a  
122 2:1 ratio of deionised water to soil. Shoemaker-McLean-Pratt (SMP) buffer pH was  
123 determined, and the lime requirement (LR) of the soil was calculated after Pratt and Blair  
124 (1963). The particle size distribution (PSD) was determined using B.S.1377-2:1990 (BSI,  
125 1 990a) and the organic matter content of the soil was determined using the loss of  
126 ignition (LOI) test (B.S.1377-3; BSI 1990b).

127

128 The soil used had a MP3 of  $107 \pm 2.8 \text{ mg P kg}^{-1}$ , a soil pH of  $5.6 \pm 0.1$  and a P index of 3  
129 ( $5.1 - 8 \text{ mg L}^{-1}$  Morgan's P). The phosphorus index system is used in Ireland to describe  
130 soils. A P index of 3 means that only maintenance rates of P are required to maintain soil  
131 fertility. The soil SMP buffer pH was  $6.1 \pm 0.2$  and the LR was  $9.9 \pm 1 \text{ t ha}^{-1}$ . The soil used  
132 was loamy sand which comprised 15% gravel (2 – 60 mm), 72% sand (0.06 – 2mm), and  
133 13% fines ( $< 0.06 \text{ mm}$ ), with an organic matter content of  $16.2 \pm 0.2\%$ .

134

## 135 2.2 DSW sampling and analysis

136

137 DSW produced from 137 spring calving dairy cows at the Environmental Research  
138 Centre (Teagasc, Wexford) was collected in November, 2009. This is the same facility as  
139 used by Martínez-Suller et al. (2010). The tanks were agitated for 20 min until the DSW  
140 was homogenized, and DSW samples were collected in 10-L drums and transported to  
141 the laboratory. The DSW was stored at  $4^\circ\text{C}$  until immediately prior to the start of the  
142 agitator test. It was fully characterized for the following water quality parameters:  
143 ammonium-N ( $\text{NH}_4\text{-N}$ ), nitrite-N ( $\text{NO}_2\text{-N}$ ), nitrate-N ( $\text{NO}_3\text{-N}$ ), total ammonical N  
144 (TAN), dissolved reactive P (DRP) and total P (TP) in accordance with the standard  
145 methods (APHA 1995). pH was measured using a pH probe (WTW, Germany) and the  
146 dry matter was determined by drying at  $40^\circ\text{C}$  for 72 hr.

147

## 148 2.3 Classification and determination of suitable amendments for use in the agitator test

149

150 Before the agitator test commenced, a preliminary batch test was conducted to determine  
151 the suitability of various amendments for the removal of P from DSW. Chemicals  
152 examined were: aluminium sulfate (alum) ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{ H}_2\text{O}$ ), calcium hydroxide (lime)  
153 ( $\text{Ca}(\text{OH})_2$ ), iron (II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), aluminium chloride  
154 ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ). Phosphorus sorbing materials (PSM) examined were: coal combustion by-  
155 products (flyash and bottom ash), and water treatment residual (WTR) sludge. Coal  
156 combustion by-products were provided by the Electricity Supply Board (ESB) and the  
157 WTR was provided by a water treatment plant in Galway City. The pH of the  
158 amendments was measured using 2:1 deionised water: dry amendment ratio. In the case

159 of the WTR sludge, it was possible to measure pH of the sludge with a pH probe. DM  
160 content was determined by drying at 40°C for 72 hr. Total metal and P of the  
161 amendments were measured after ‘aqua regia’ digestion using a Gerhard Block digestion  
162 system (Cottenie and Kiekens 1984), which is described by Fenton et al. (2009). The  
163 water extractable phosphorus (WEP) content of the amendments was determined after  
164 Dayton and Basta (2001).

165

166 In a preliminary batch test, different quantities of each amendment were added to 15 ml  
167 of DSW (n=3). Chemicals were applied based on metal: total P (TP) stoichiometric rate  
168 (for alum,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , or lime) or, in the case of PSM, based on kg of PSM  $\text{L}^{-1}$  of DSW  
169 (for flyash, bottom ash and WTR). Stoichiometric rate refers to the ratio of the metal to  
170 phosphorus expressed on a per gram basis. Each container was mixed thoroughly and  
171 incubated in a temperature-controlled room at 11°C. After 24 hr, supernatant water  
172 samples were collected, centrifuged for 5 min at 14,000 rpm, and the DRP was measured  
173 using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). The  
174 performance of each chemical and PSM – along with an optimal rate of amendment  
175 addition to the DSW – was determined (results not shown). On the basis of this test, four  
176 different amendments were used in the agitator test: (1) lime; (2) alum; (3)  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$   
177 and (4) bottom ash.

178

179 2.4 Agitator test

180

181 The agitator test has been used to investigate the release of P from soil (Mulqueen et al.  
182 2004) and soil amended with slurry (Brennan et al. 2011). This experiment replicates the  
183 way used by Brennan et al. (2011) in which DSW is applied to soil, allowed to dry, and  
184 then subjected to runoff. This experiment does not provide a uniform means of assessing  
185 release of P from land-applied DSW; however, it does allow us to compare the  
186 effectiveness of amendments in a realistic way.

187

188 The agitator test comprised three different treatments (n=3): grassed soil only; grassed  
189 soil receiving DSW at a rate equivalent to  $5\text{mm ha}^{-1}$  (the study control); and DSW with

190 four amendments applied at the same hydraulic rate. Each of the amendments was  
191 applied at 2-3 different rates (the optimal rate determined in the batch test and up to 2  
192 other rates) in triplicate. Prior to the start of the agitator test, the intact soil samples were  
193 transferred from the sampling cores into beakers. The depth of soil in the beakers ranged  
194 from 40 mm to 50 mm; this was considered sufficient to include the full depth of  
195 influence (Mulqueen et al. 2004). Untreated DSW or amended DSW was applied to the  
196 soil (t=0 hr), and was then allowed to interact for 24 hr prior to saturation of the sample.  
197 After 24 hr (t=24 hr), the sample was submerged with 500 ml of water and the paddle of  
198 the agitator device was immersed half way in the supernatant water (Figure 1). Runoff  
199 was simulated by gentle agitation of the supernatant water by the paddle rotating at a  
200 speed of 20 rpm for 24 hr. Over a 1 -d study duration, supernatant water samples were  
201 tested for DRP and pH. For each treatment, DSW samples (n=3) - with the same volume  
202 as applied to the grass sample in the agitator test - were spread at the bottom of a beaker  
203 to allow pH to be measured at 24 hr without disturbing the sample used in the agitator  
204 test.

205

#### 206 2.5 Water sampling and analysis

207

208 Water samples (4 ml) were taken from mid-depth of the water overlying the soil at 0.25,  
209 0.5, 1, 2, 4, 8, 12 and 24 hr after the start of each test. All samples were filtered  
210 immediately after sample collection using 0.45  $\mu\text{m}$  filters and placed in a freezer (after  
211 APHA, 1995) prior to being analysed colorimetrically for DRP using a nutrient analyser  
212 (Konelab 20, Thermo Clinical Labsystems, Finland). The DRP concentrations were used  
213 to calculate the mass of DRP in the water overlying the soil samples in the beaker, taking  
214 into account the water volume reduction as the test progressed.

215

#### 216 2.6 Statistical Analysis

217

218 Proc Mixed (SAS Institute 2004) was used to model the factorial structures (amendment  
219 x application rate; and amendment x application rate x time) in the experiment in order to  
220 allow for heterogeneous variance across treatments. A group variable was fitted to allow



221 comparisons between the control treatments and the factorial combinations. A multiple  
222 comparisons procedure (Tukey) was used to compare means.

223

224 2.7 Cost analysis

225

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

235

### 236 **3 Results**

237

238 3.1 DSW and amendment analysis

239

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

247

248 3.2 Agitator test

249

250 Changes in pH in the DSW over a 24-hr period and the maximum DRP concentrations  
251 and load in the overlying water are given in Table 3. The pH for the DWS water-only

252 treatment (the study control) dropped from  $7.1 \pm 0.27$  (t=0 hr) to  $7.0 \pm 0.08$  after 24 hrs. All  
253 other amendments – with the exception of alum (applied at a weight ratio of 8.8:1 Al:TP)  
254 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.

255

256 The maximum DRP load in the water overlying the soil-only was approximately  $0.1 \text{ mg DRP m}^{-2}$   
257 compared with  $68 \text{ mg DRP m}^{-2}$  when the soil was overlain with unamended  
258 DSW. The amendments that achieved the best reduction in mass of soluble DRP in the  
259 overlying water were:  $\text{FeCl}_2$  (89-90%), lime (75-83%), and alum applied at  $0.003 \text{ kg L}^{-1}$   
260 (72%).

261

262 The potential for coal combustion by-products – flyash and bottom ash – to mitigate P  
263 loss was also investigated. Flyash proved unsuccessful (data not shown), but bottom ash  
264 reduced the maximum DRP load in the overlying water by between 42-45%. Moneypoint  
265 Power Station in Co. Clare burns approximately two million t of coal per annum of which  
266 approximately 9750 t of bottom ash is currently sent to landfill (ESB 2009). Since this  
267 by-product is currently put to landfill, it may be economically and environmentally  
268 desirable to find an alternative use for it, but its metal content (Tables 2 and 4) would  
269 need to be considered when land application takes place.

270

271 The amendments were added slowly to the DSW (after Lefcourt and Meisinger 2001) and  
272 effervescence was not noted in any of the experiments. Comparatively, Brennan et al.  
273 (2011) noted the occurrence of effervescence when alum was applied to dairy slurry at a  
274 rate of 2.44:1 of Al:P. Further trials would need to be conducted before field-scale  
275 additions are carried out.

276

277 3.3 Statistical analysis

278

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

282

### 283 3.4 Cost and feasibility analysis

284

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

291

### 292 4 Discussion

293

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

306

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

313

314 Chemical or PSM amendment of DSW or manure is not presently part of programme of  
315 measurements (POM) or supplementary measurements for any country in Europe. It has  
316 been included in the COST 869 fact-sheets (Chardon and Dorioz 2008) for possible  
317 inclusion by River Basin District Managers, and there is potential that it could be  
318 introduced as a supplementary measure in 2015 if POM are found not to be sufficient to  
319 meet the requirements of the Water Framework Directive (WFD) (2000/60/EC: Council  
320 of the European Union 2000)

321

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

329

## 330 **5 Conclusions**

331

332 This study examined the effectiveness of various chemicals ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , lime and alum)  
333 and phosphorus sorbing materials (bottom ash) in reducing phosphorus loss in runoff.

334 The main conclusions from this study were:

335 1. Starting with the cheapest, the amendments were ranked as follows: bottom ash (€1.55  
336  $\text{m}^{-3}$  of DSW), alum (€1.67 to €1.92  $\text{m}^{-3}$  of DSW),  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (€3.55 to €8.15  $\text{m}^{-3}$  of  
337 DSW), and lime (€20.31 to €88.65  $\text{m}^{-3}$  of DSW).

338 2. The amendments were ranked in terms of their feasibility (taking into account their  
339 cost, potential adverse effects and public perception, as well as their performance).

340 Starting with the most desirable, the amendments were ranked as follows: alum,

341  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , bottom ash and lime.

342 3. The use of amendments to dairy soiled water should only be used in critical source  
343 areas where pollution is likely to occur. The effects of these amendments on groundwater  
344 leaching and greenhouse gases should be investigated.

345

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347

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

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n=3	TN	NH <sub>4</sub> -N	NO <sub>3</sub> -N	TAN	TP	DRP	pH	DM
	mg L <sup>-1</sup>							%
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

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

Amendment	Lime (Ca(OH) <sub>2</sub> )	Alum (Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O)	Ferrous chloride Fe(Cl) <sub>2</sub>	Bottom Ash
pH		1.25		
WEP <sup>1</sup>	mg/kg	0		
Al		4.2		0.42
Ca	52.6			0.4
Fe		<0.01	13.9	1.6
K				0.04
As		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

600 <sup>1</sup> WEP, water extractable phosphorus  
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Table 3 Phosphorus removal in the agitator test, pH at t=0 hr and t=24 hr, observed peak phosphorus concentration, reduction percentage.

PSM	Rate of addition		pH		mg L <sup>-1</sup>	P max <sub>2</sub> mg m <sup>-2</sup>	Time (hr) <sup>2</sup>	P reduction <sup>3</sup> %
	Weight/Volume	Molecular	t = 0 hr	t = 24 h				
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) <sub>2</sub> ) <sup>1</sup>	0.067 kg L <sup>-1</sup>	2500 Ca:P	9.08 ± 0.06	9.33 ± 0.07	0.19 ± 0.06	11.80 ± 3.4	4	83
	0.130 kg L <sup>-1</sup>	4884 Ca:P	9.36 ± 0.31	10.07 ± 0.43	0.27 ± 0.05	16.50 ± 3.19	8	75
	0.200 kg L <sup>-1</sup>	7514 Ca:P	9.79 ± 0.24	10.37 ± 0.18	0.24 ± 0.01	15.10 ± 0.60	2	78
Alum (Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 18 H <sub>2</sub> O) <sup>1</sup>	0.001 kg L <sup>-1</sup>	2.9 Al:P	8.68 ± 1.27	8.03 ± 0.26	0.83 ± 0.18	50.80 ± 11.1	24	25
	0.003 kg L <sup>-1</sup>	8.8 Al:P	6.91 ± 0.11	7.50 ± 0.00	0.31 ± 0.05	19.03 ± 3.01	24	72
FeCl <sub>2</sub> .4H <sub>2</sub> O <sup>1</sup>	0.010 kg L <sup>-1</sup>	200 Fe:P	6.90 ± 0.02	7.50 ± 0.00	0.12 ± 0.01	7.52 ± 0.67	0	89
	0.033 kg L <sup>-1</sup>	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 kg L <sup>-1</sup>		7.54 ± 0.38	7.07 ± 0.02	0.60 ± 0.13	35.84 ± 7.84	24	45
	0.130 kg L <sup>-1</sup>		7.15 ± 0.24	7.08 ± 0.03	0.61 ± 0.01	36.67 ± 1.77	24	45
	0.200 kg L <sup>-1</sup>		7.62 ± 0.22	7.49 ± 0.12	0.64 ± 0.08	38.71 ± 4.81	12	42

<sup>1</sup> laboratory chemicals

<sup>2</sup> Time of observed peak concentration (hr). Each study had the duration of 24 hours in total.

<sup>3</sup> 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.

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 <sup>a</sup> € kg <sup>-1</sup>	Application rate of amendment kg m <sup>-3</sup>	Application rate of metal <sup>b</sup> kg m <sup>-3</sup>	Spreading <sup>c</sup> spreading rate € m <sup>3</sup>	Total € m <sup>3</sup>	100 cow farm		Max allowable metal kg ha <sup>-1</sup> yr <sup>-1</sup>
							€ fam yr <sup>-1d</sup>	Spreading rate of metal kg ha <sup>-1e</sup>	
Control					1.55		403		
FeCl <sub>2</sub> .4H <sub>2</sub> O (FeCl <sub>3</sub> )	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	2500 Ca:P	0.28	67	35.2	1.55	20.31	5281	0.176	No limit
	4884 Ca:P		130	68.3	1.55	88.65	23,049	0.34	
	7514 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	3x10 <sup>-4</sup>	No limit
	8.8 Al:P		3	0.18	1.55	1.92	499	9x10 <sup>-4</sup>	
Bottom Ash	0.067 kg L <sup>-1</sup>	0	67		1.55	1.55	403		Within limits
	0.130 kg L <sup>-1</sup>		130		1.55	1.55	403		Within limits
	0.200 kg L <sup>-1</sup>		200		1.55	1.55	403		Within limits

<sup>a</sup>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; <sup>b</sup> 6% for Al in Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.18H<sub>2</sub>O; 52.5% for Ca in Ca(OH)<sub>2</sub>; 28% for Fe in FeCl<sub>2</sub>.4H<sub>2</sub>O. Metal analysis for bottom ash is in Table 2 <sup>c</sup> Spreading costs from S. Lalor (pers. comm.) Batch tests showed that no volume increase occurred due to addition of PSM amendment <sup>d</sup> 50 L of DSW produced per cow per day for 52 weeks. <sup>e</sup> Based on a maximum allowable application rate of 5 mm ha<sup>-1</sup> (SI 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 <sup>a</sup>	Feasibility score	Addition rate kg m <sup>-3</sup>	Total € m <sup>-3</sup>	Reduction in DRP % P	Discussion
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, pers. comm.)
FeCl <sub>2</sub> ·4H <sub>2</sub> O (FeCl <sub>3</sub> )	2	10	3.55	89	Potential elevated release of greenhouse gases (R.B. Brennan, pers. comm.) 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.

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

Figure 1. The agitator test.

