



Provided by the author(s) and University of Galway in accordance with publisher policies. Please cite the published version when available.

Title	Use of amendments in a peat soil to reduce phosphorus losses from forestry operations
Author(s)	Callery, Oisin; Brennan, Raymond B.; Healy, Mark G.
Publication Date	2015-10-18
Publication Information	Callery, O., Brennan, R. B., & Healy, M. G. (2015). Use of amendments in a peat soil to reduce phosphorus losses from forestry operations. <i>Ecological Engineering</i> , 85, 193-200. doi: http://dx.doi.org/10.1016/j.ecoleng.2015.10.016
Publisher	Elsevier
Link to publisher's version	https://doi.org/10.1016/j.ecoleng.2015.10.016
Item record	http://hdl.handle.net/10379/6671
DOI	http://dx.doi.org/10.1016/j.ecoleng.2015.10.016

Downloaded 2024-04-09T23:01:32Z

Some rights reserved. For more information, please see the item record link above.



1 *Published as: Callery, O., Brennan, R.B., Healy, M.G. 2015. Use of amendments in a peat*
2 *soil to reduce phosphorus losses from forestry operations. Ecological Engineering 85: 193 –*
3 200. <http://dx.doi.org/10.1016/j.ecoleng.2015.10.016>
4

5 **Use of amendments in a peat soil to reduce phosphorus losses from forestry operations**

6
7 O. Callery, R.B. Brennan*, M.G. Healy

8
9 Civil Engineering, National University of Ireland, Galway, Co. Galway, Rep. of Ireland.

10
11 *Corresponding author. Tel: +353 91 494442; Fax: +353 91 494507. E-mail address:

12 raymond.brennan@nuigalway.ie
13
14

15 **Abbreviations:** Al-WTR, aluminum water treatment residual

16 **Abstract**

17 Forestry harvesting on peats is known to result in significant losses of soil phosphorus (P) to
18 adjacent waters, and the issue is becoming an increasingly serious concern as peatland forest
19 stocks mature and reach harvestable age. One potential solution could be the use of low-cost
20 P recovery techniques based on the chemical precipitation and/or adsorption of the dissolved
21 fraction of soil P, which would otherwise be lost. Such recovery techniques have shown
22 promise in similar applications on mineral soils. However, the interaction of peat with P
23 adsorbing materials can significantly alter their adsorptive characteristics, and it is
24 consequentially not known what materials might be suitable for this application. This study
25 compared the performance of six potential soil amendments (aluminum water treatment
26 residual (Al-WTR), crushed concrete, gypsum, magnesium hydroxide, magnesium oxide, and
27 steel wool) in removing P from aqueous solution in the presence of a typical forest peat soil.
28 Comparison of adsorption isotherms plotted from these batch adsorption studies showed that
29 the observed P adsorption maxima of Al-WTR and steel wool were increased by the presence
30 of peat, from 10.6 mg g⁻¹ and 20.4 mg g⁻¹, to 11.8 mg g⁻¹ and 52.5 mg g⁻¹, respectively. In
31 contrast, the observed P adsorption maxima of crushed concrete, gypsum, and magnesium
32 oxide were reduced in the presence of peat, by 44%, 87%, and 37%, respectively. The
33 maximum P adsorption achieved by magnesium hydroxide was increased from 29.8 mg g⁻¹ to
34 59 mg g⁻¹ at an amendment to peat-solid ratio of 1:4, but decreased from 73.9 mg g⁻¹ to 23.6
35 mg g⁻¹ at an amendment to peat-solid ratio of 1:10. It was concluded that Al-WTR, in
36 particular, shows considerable promise for use as a soil amendment for P immobilization in a
37 peat environment.

38
39 **Keywords:** Phosphorus; forestry; peat; clearfelling; harvesting; buffer zones; adsorption

40 **Introduction**

41 Ireland's forestry stock of 731,000 ha covers about 10.5% of the country, of which 44% is
42 planted on peats (National Forest Inventory, 2012). Peats, especially ombrotrophic upland
43 blanket peats, are generally lacking in minerals like aluminum (Al) and iron (Fe), and
44 consequently have extremely low soil phosphorus (P) sorption capacities (Renou et al.,
45 2000). As a result, any P released by the forestry operations, such as clearfelling and
46 afforestation, is liable to leach unimpeded into adjacent receiving waters, even with the
47 application of current best management practices targeted at preventing such pollution
48 (Finnegan et al., 2014).

49 Nutrient enrichment, or eutrophication, of inland waters is recognized as Ireland's most
50 serious environmental pollution problem (Department of the Environment, 2002). As P has
51 been identified as the primary nutrient limiting eutrophication in freshwaters (Carpenter et al.,
52 1998; Boesch et al., 2001), preventing its migration from soil to aquatic environments is
53 paramount. The oligotrophic nature of Ireland's upland catchments, and the unique flora and
54 fauna present in these waters, make them particularly sensitive to eutrophication (Mainstone
55 and Parr, 2002; Hutton et al., 2008). These forested peat catchments are headwaters for many
56 of Ireland's river systems, a great number of which contain important salmonid populations
57 (Giller and O'Halloran, 2004), as well as other species protected under European Union (EU)
58 legislation (O'Driscoll et al., 2012; Reid et al., 2013). Consequentially, pollution from
59 diffuse, low concentration sources of P, such as forestry, is capable of causing considerable
60 environmental damage to an area much larger than that which is forested.

61 The sustained release of P following forestry harvesting has been highlighted as an issue of
62 particular concern, as much of Ireland's current peatland forestry stock was planted between
63 the 1950s and the 1990s (Renou and Farrell, 2005) and has now reached, or is reaching,

64 harvestable age (Rodgers et al., 2010). Clearfelling is the harvesting technique most prevalent
65 in Ireland, and accounted for 76.6% of timber felled between 2006 and 2012 (National Forest
66 Inventory, 2012). Clearfelling involves the removal from site of the commercially-viable
67 portions of the forestry crop (i.e. tree trunks), leaving large amounts of P to remain onsite,
68 present both in the soil and in the non-commercial logging residues, or 'brash'. This brash
69 accounts for a considerable percentage of the above ground nutrients contained in a typical
70 coniferous tree (Moffat et al., 2006), and it has been shown to release these nutrients for
71 many years following its deposition (Titus and Malcolm, 1999; Hyvönen et al., 2000). To
72 compound the issue, the use of brash mats to form temporary driving surfaces for heavy
73 felling machinery is an essential management practice, as it prevents serious damage to the
74 underlying soil (Moffat et al., 2006). Clearfelling completely disrupts natural P cycling in a
75 forest ecosystem, with the deposition of brash mats resulting in increased P availability, while
76 the concurrent removal of trees from site results in decreased P uptake and sequestration - a
77 situation which greatly increases the threat of P leaching to aquatic ecosystems (Schaller et
78 al., 2015).

79 While rates of afforestation on blanket peats have been in decline in recent years (National
80 Forest Inventory, 2012), the harvesting of presently established forest is inevitable, as are the
81 resulting water quality issues, if effective pollution mitigation measures are not implemented.
82 Current best management practices advocate the use of riparian buffer strips between forestry
83 and adjacent aquatic zones (Forest Service, 2000). Previous research has found the use of
84 suitably large riparian buffer zones on peat soils to be largely successful in protecting surface
85 waters from influxes of suspended sediments and associated particulate nutrients (Nieminen
86 et al., 2005). However, with peat's low P adsorption capacity, the performance of these buffer
87 zones in satisfactorily mitigating the flow of dissolved P off site varies greatly. Moreover, it
88 has been found that these buffer zones' effect can be anywhere from positive, with total

89 retention of released P (Vaananen et al., 2008), to negative, compounding the issue with
90 additional P release (Vasander et al., 2003; Liljaniemi et al., 2003).

91 There has been increasing interest in the use of soil amendments to control P losses from
92 diffuse sources, such as land spreading of manure from dairy cattle (Brennan et al., 2011a,b)
93 and pigs (O' Flynn et al., 2012), land spreading of dairy waste water from washing of milking
94 parlors (Serrenho et al., 2012), and construction of wetlands on sites previously used for
95 agriculture (Ann et al., 1999). The use of chemical amendments has shown much promise in
96 these instances, though there has been little to no investigation into the practice's potential in
97 abating the loss of P from peatland forestry. The performance of chemical amendments in
98 this context has the potential to be quite different, as the interaction of amendments with the
99 complex chemistry of peat can significantly alter their P removal performance (James et al.,
100 1992).

101 This study tested the hypothesis that chemical amendments could immobilize P in a forest
102 peat soil. To address this hypothesis, the aim of this study was to identify and compare
103 potential soil amendments which function well in a peat chemistry environment and, when
104 mixed with peat onsite, could increase the adsorptive capacity of the soil to the point where P
105 losses from a forestry site would no longer pose a risk to receiving surface waters.

106 Specifically, the objectives of this study were to: (1) identify chemical amendments capable
107 of removing P from an aqueous solution which mimics the chemistry of runoff/ground water
108 on a forested peat site (2) compare the performance of each amendment and identify the
109 amendment most ideally suited to application in a forested peat site (3) analyze the effect of
110 peat on the performance of each amendment in terms of its adsorptive capacity.

Materials and Methods

Collection and characterization of peat samples

Samples of blanket peat were collected from a recently clearfelled riparian buffer zone, located near the town of Oughterard, County Galway, Ireland (approx. coordinates 53.375N, -9.419E). The peat was collected from a stratum of homogeneous composition, at a depth of 5-25cm from the surface (the surface layer of vegetation and semi-decayed sphagnum moss was discarded, along with any larger roots and plant fibers). Before testing, the samples were homogenized by repeatedly folding and kneading the peat until its texture and water content were entirely uniform. Once homogenized, peat samples were sealed in airtight Ziploc® bags and stored in a temperature-controlled room at 11°C until testing commenced. The water content of the homogenized peat was determined to be 89.7%±0.08% by oven drying the peat for 24 h at 105°C (BSI, 1990).

Sourcing and characterization of amendments

The following amendments were used in this study (Table 1): dewatered aluminum sulphate water treatment residual (Al-WTR; oven dried for 24 h at 105°C and ground to pass a 0.5 mm sieve), crushed concrete cubes (pulverized with a mortar and pestle and ground to pass a 0.5 mm sieve), gypsum (sourced from recycled plasterboard, supplied as a powder, and passed through a 0.5 mm sieve to ensure uniformity), magnesium oxide (MgO; sourced from seawater, supplied as a powder, and passed through a 0.5 mm sieve to ensure uniformity), magnesium hydroxide (Mg(OH)₂; sourced from seawater, supplied as a paste, and passed through a 0.5 mm sieve to ensure uniformity) and steel wool (grade 00, fiber diameter approx. 0.04 mm).

Batch test procedure

Samples were prepared comprising two grams (wet weight) of the homogenized peat, mixed with each of the six amendments, at amendment to peat-solid ratios of 1:10, 1:4 and 1:2. These masses provided a material to solution ratio that was small enough to ensure non-zero equilibrium concentrations, thus allowing the determination of the entire isotherm curve. The material to solution ratio used in the current study was comparable to ratios used in similar studies (Li et al., 2006; Chardon et al., 2012). The samples were placed in separate 50 ml conical flasks and overlain by 25 ml of deionized water, with ortho-phosphorus (PO₄-P) concentrations (prepared by adding various amounts of K₂HPO₄ to deionized water) of 0, 25, 50, 75, 100, and 150 mg P L⁻¹. This range of P concentrations was determined to be sufficiently wide to account for the variation in the amendments' adsorptive capacities, and the dependence of adsorption capacity on the initial concentration (Seo et al., 2005). The flasks were sealed with Parafilm and shaken in a reciprocal shaker (250 rpm) at room temperature (25°C) for 24 h. After 24 h had elapsed, the samples were centrifuged at 14,500 rpm for 5 min, and the supernatant water was passed through a 0.45 µm filter. Dissolved P concentrations of the supernatant water were determined using a nutrient analyzer (Konelab 20, Thermo Clinical Lab systems, Finland) after APHA (1998). Experiments were conducted at neutral pH to ensure that all observed changes in pH could be attributed to the addition of peat to the solution. The same procedure was also carried out using identical masses of amendment but without the addition of peat.

Analysis of experimental data

The mass of P adsorbed per gram of adsorbent, q_e , at equilibrium was calculated by:

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

where C_o and C_e are the initial and final PO₄-P concentrations of the solution (mg L⁻¹), V is the volume of solution (L), and m is the dry weight of adsorbent (g). For the purpose of these

calculations, the PO₄-P adsorbency of the peat was considered to be negligible, and for solutions containing peat and amendment, only the dry weight of the amendment was considered in Eqn 1.

The C_e and q_e data obtained from the batch tests were fitted to the Koble-Corrigan equation, which was chosen for its ability to model adsorption over a wide range of data, as well as for its being more universally applicable than the commonly used Langmuir and Freundlich equations (Koble and Corrigan, 1952). The Koble-Corrigan equation is as follows:

$$q_e = \frac{A_{KC}C_e^p}{1+B_{KC}C_e^p} \quad (2)$$

where A_{KC}, B_{KC} and p are the Koble-Corrigan isotherm constants determined by using an iterative approach to minimize the value returned by the hybrid fractional error function (HYBRID), an error function used to fit Eqn. 2 to the observed data (Porter et al., 1999):

$$\frac{100}{n-p} \sum_{i=1}^n \frac{(q_{e,i,meas} - q_{e,i,calc})^2}{q_{e,i,meas}} \quad (3)$$

where n is the number of experimental data points, p is the number of isotherm constants in the Koble-Corrigan equation (Eqn. 2), q_{e,i,meas} is the value of q_e obtained from Eqn. (1), and q_{e,i,calc} is the value of q_e obtained from Eqn. (2). By fitting the experimental data for each adsorbent to the Koble-Corrigan equation, it was possible to make predictions for values of C_e and q_e for any given C₀. Substituting Eqn. 1 into Eqn. 2 gives:

$$\frac{V(C_0 - C_e)}{m} = \frac{A_{KC}C_e^p}{1+B_{KC}C_e^p} \quad (4)$$

An iterative approach, using Microsoft Excel's SolverTM, was then used to determine values of C_e for any given value of C₀. The impact of peat on the amendments' performance was evaluated using:

$$\phi = \frac{q_{e,a}^{calc}}{q_{e,b}^{calc}} \quad (5)$$

179 where $q_{e,a}^{calc}$ is the modelled mass of P adsorbed by the amendment in a solution containing
 180 peat, and $q_{e,b}^{calc}$ is the modelled mass of P adsorbed by the amendment in a solution containing
 181 no peat. Calculated values of $\Phi > 1$ indicate a synergistic effect was obtained by exposing an
 182 amendment to peat, i.e. the influence of peat chemistry was favorable for P adsorption, while
 183 values of $\Phi < 1$ suggest the opposite, i.e. that the effect was antagonistic. In this way, ϕ could
 184 be considered to be a coefficient of synergy.
 185

Results and Discussion

All of the amendments were effective at removing P from aqueous solution, both with and without the presence of peat in solution. The addition of peat did, however, influence the behavior of all amendments, leading to either improved or diminished adsorptive performance.

Equilibrium adsorption isotherms

Figure 1 shows the adsorption isotherms obtained by fitting the Koble-Corrigan model to each of the peat amendment-mixtures. The Koble-Corrigan fitting coefficients (A_{kc} , B_{kc} , and p) as well as slope, and R^2 values obtained from plots of $q_{e\text{ calc}}$ (calculated using the Koble-Corrigan equation) vs $q_{e\text{ exp}}$, are shown in Table 2. The Koble-Corrigan model fitted the experimental data well, and there was a very good correlation (average $R^2 = 0.94 \pm 0.1$) between predicted and experimental values. In general, higher values of q_e were observed when the ratio of adsorbent to solution was smaller. This is in agreement with a review conducted by Cucarella and Renman (2009), who reported that smaller adsorbent-to-solution ratios may lead to higher concentrations of P sorbed to the adsorbent material. Al-WTR, in particular, showed a much larger increase in P adsorption capacity (maximum observed $q_e = 11.8\text{ mg g}^{-1}$) when added to peat-containing solutions at an amendment to peat-solid ratio of 1:10, compared to amendment to peat-solid ratios of 1:4 and 1:2 (maximum observed $q_e = 3.3\text{ mg g}^{-1}$ and 3.6 mg g^{-1} , respectively).

Maximum q_e values observed for concrete were 15 mg g^{-1} , 8.9 mg g^{-1} , and 6.8 mg g^{-1} at amendment to peat-solid ratios of 1:10, 1:4, and 1:2, which were similar to q_e values of 26.8 mg g^{-1} , 15.1 mg g^{-1} , and 6.6 mg g^{-1} observed for the same masses of concrete, but without the addition of peat. These values are all comparable to the q_e range of $5.1\text{--}19.6\text{ mg g}^{-1}$ observed by Egemose et al. (2012). With respect to gypsum, the presence of peat in solution resulted in

210 greatly reduced maximum observed q_e values of 10.8 mg g^{-1} , 4.4 mg g^{-1} , and 3.6 mg g^{-1} at
211 amendment to peat-solid ratios of 1:10, 1:4, and 1:2, compared to values of 84.8 mg g^{-1} , 58.4
212 mg g^{-1} , and 34 mg g^{-1} observed for the same masses without the addition of peat.

213 Magnesium oxide and Mg(OH)_2 displayed the highest P adsorption capacities, with MgO
214 having the greatest of the two, with a maximum q_e of 102.7 mg g^{-1} observed at an amendment
215 to peat-solid ratio of 1:10. Liu et al. (2011) found that removal of As(III) from aqueous
216 solution by MgO was due to the *in situ* formation of Mg(OH)_2 by reaction of the MgO with
217 water, followed by subsequent adsorption/reaction of the newly formed Mg(OH)_2 with the
218 As(III) anion. Liu et al. (2011) also reported that the adsorptive performance of Mg(OH)_2
219 formed *in situ* was greater than that of pre-formed Mg(OH)_2 , at least partially as a result of
220 the former's larger specific surface area, which was almost 5.5 times greater than that of the
221 latter ($58.4 \text{ m}^2 \text{ g}^{-1}$ vs. $10.7 \text{ m}^2 \text{ g}^{-1}$, respectively). The results of our study indicate that Mg(OH)_2
222 formed *in situ* also had a greater adsorptive capacity for $\text{PO}_4\text{-P}$ compared to that of pre-
223 formed Mg(OH)_2 . Stoichiometrically, MgO contains approximately 45% more Mg per unit
224 weight than Mg(OH)_2 ; however, its P adsorption capacity was observed to be up to 120%
225 greater than that of preformed Mg(OH)_2 in solutions where peat was absent (data not shown).

226

227 When steel wool was examined, P adsorption was observed to be inhibited at high initial
228 $\text{PO}_4\text{-P}$ concentrations (C_o), both with and without the addition of peat. This appeared to be
229 the result of high $\text{PO}_4\text{-P}$ concentrations inhibiting the formation of the iron oxides/hydroxides
230 responsible for P removal, and it was observed that much less of the steel wool had rusted in
231 these comparatively high concentration solutions. Similar observations were made by Pryor
232 and Cohen (1953), who found that solutions of orthophosphate passivate iron; i.e. iron
233 became less reactive due to presence of a micro coating in the presence of dissolved air, and

Harahuc et al. (2000), who found that phosphate at or above concentrations of 25 mmol inhibited the solubilization of iron.

pH effects

Figure 2 summarizes the effect the addition of peat had on the pH of the solution at equilibrium (after 24 h). The peat displayed a strong buffering capacity, and its addition altered the final pH of the solution at equilibrium in all cases. In real-world applications, an amendment that has a strong effect on pH may not be desirable, as large fluctuations in pH may have a deleterious impact on the environment. For example, the addition of an amendment which increases the soil's pH may increase soil nitrate (NO_3) concentrations, and the risk of NO_3 leaching could be particularly great during the clearfelling of forestry (Wickström, 2002). After shaking for 24h, the pH of samples containing peat mixed with Al-WTR was found to be closest to those of a solution containing peat only. The performances of P adsorbent materials are known to be strongly affected by pH, and in acidic soils such as peats, Al and Fe are known to be responsible for the sorption of P (Sato et al., 2005), while binding by calcium (Ca) and magnesium (Mg) is responsible for P immobilization in alkaline soils (Faulkner and Richardson, 1989; Reddy et al., 1999).

Synergistic Effects

The results indicate that, at certain initial $\text{PO}_4\text{-P}$ concentrations, a degree of synergy exists between the peat and certain amendments; i.e. their adsorption performance was better in an environment whose chemistry was influenced by peat (Figure 3). Al-WTR and steel wool, in particular, showed improved performance across a large range of concentrations, while concrete, gypsum, and MgO showed largely diminished efficacy. The effect of peat on P adsorption by $\text{Mg}(\text{OH})_2$ varied from beneficial to detrimental, depending on the ratio of peat to amendment in solution.

One mechanism by which an amendment's P sorption performance may improve when in a peat environment is as a result of the interaction of humic substances with soluble metal ions. Humic substances facilitate the removal of P through reactions with Al and Fe ions, which results in the formation of insoluble phosphate complexes (Bloom, 1981; Renou et al., 2000). Conversely, humic materials inhibit the removal of P by precipitation with Ca by competing with the phosphate anion for Ca, with this effect being more exaggerated at lower pH (Alvarez et al., 2004; Song et al., 2006; Cao et al., 2007). The formation of humic complexes may therefore contribute both to the observed improvement in Al-WTR and steel wool's adsorptive performance, as well as the diminished performance of concrete and gypsum. Phosphorus sorption by gypsum, for example, is directly related to its solubility, as its P removal is largely due to precipitation reactions (Penn et al., 2007) and thus the availability of Ca for the formation of calcium phosphates (Kordlaghari and Rowell, 2006).

The concrete used in this study had significantly higher levels of Al and Fe present than the gypsum (Table 1), which may explain why its P removal performance was not as adversely affected as gypsum's. Oğuz et al. (2003) found that P removal by concrete was by precipitation of metallic PO_4 salts, which were adsorbed onto the surface of the concrete, and AlPO_4 appeared to be the main product adsorbed onto the surface of the gas concrete examined in their study. This result suggests that the Al and Fe content of the concrete examined in this study, perhaps more so than its Ca content, plays a crucial role in P adsorption. Berg et al. (2005) reported that P removal by crushed gas concrete was not affected by the presence of organic matter in the form of dissolved organic carbon. However, as concrete's adsorption of P is strongly related to pH, and improves with increasing pH (Oğuz et al., 2003), it appears that the acidification of the solution by the peat is at least partially responsible for the observed reduction in performance.

282 The pH buffering action of the peat is also likely to have contributed to the observed
283 synergistic effects by lowering the solution pH, which can improve Al-WTR's P adsorption,
284 as observed by Yang et al. (2006), and promote corrosion of the steel wool to form P
285 adsorbing iron oxide/hydroxides. Consequently, the peat had a stronger effect on pH at this
286 rate, with the final solution pH ranging from 8.3-8.6, compared to 9.8-10.2 and 9.9-10.5 at
287 amendment to peat-solid ratios of 1:4 and 1:2, respectively. It was also observed that when
288 $\text{Mg}(\text{OH})_2$ was added at an amendment to peat-solid ratio of 1:10, recorded q_e values were
289 much lower than solutions containing $\text{Mg}(\text{OH})_2$ at amendment to peat-solid ratios of 1:4 and
290 1:2. While the reason for this is not entirely clear, the marked difference in pH accompanied
291 by the significant drop in P adsorption strongly suggests that the pH buffering effect of the
292 peat may also be responsible for reducing the P adsorbency of $\text{Mg}(\text{OH})_2$ at this lowest rate of
293 amendment. Xie et al. (2013) reported that fulvic and humic acids had a slight negative effect
294 on PO_4 adsorption by a magnesium oxide nanoflake-modified diatomite adsorbent, and
295 attributed this observation to the effects of competitive adsorption. It is quite possible that at
296 low $\text{Mg}(\text{OH})_2$ to peat ratios this effect is more exaggerated.

Conclusions

This study found that the presence of peat in solution increased the P adsorption capacities of Al-WTR and steel wool, while the adsorptive capacities of crushed concrete, gypsum, and magnesium oxide were decreased. Magnesium hydroxide showed both increased and decreased adsorptive capacity, depending on the ratio of peat to amendment in solution. Throughout the study, peat displayed considerable ability to buffer the peat-amendment mixture pH. However, the equilibrium pH of solutions containing Al-WTR and gypsum were observed to be closest to the peat's natural pH, indicating that these amendments were best suited to the peat environment. Taking these factors into consideration, the results of this study indicate that Al-WTR, in particular, holds great promise for utilization in the mitigation of P runoff caused by forestry operations on blanket peat sites. Previous research into the use of Al-WTR has shown it to be effective in preventing P runoff when used as a soil amendment in an agricultural context, and this study's findings demonstrate that the chemistry of a peat forest environment is likely to interact with Al-WTR in such a manner as to improve its P removal performance at low P concentrations. As a waste material, an additional benefit lies in the fact that it does not have the production costs associated with other high performing amendments studied, i.e. steel wool and $Mg(OH)_2$.

Acknowledgements

The first author would like to acknowledge the Irish Research Council for funding.

318 **References**

- 319 Alvarez, R., L.A. Evans, P.J. Milham and M.A. Wilson. 2004. Effects of humic material on
320 the precipitation of calcium phosphate. *Geoderma* 118: 245–260.
- 321 Ann, Y., K.R. Reddy, and J.J. Delfino. 1999. Influence of chemical amendments on
322 phosphorus immobilization in soils from a constructed wetland. *Ecol. Eng.* 14: 157–
323 167.
- 324 American Public Health Association. (APHA), American Water Works Association., and
325 Water Environment Federation. 1998. Standard methods for the examination of water
326 and wastewater. American Public Health Association, Washington, DC.
- 327 Berg, U., D. Donnert, A. Ehbrecht, W. Bumiller, I. Kusche, P.G. Weidler, and R. Nüesch.
328 2005. “Active filtration” for the elimination and recovery of phosphorus from waste
329 water. *Colloid. Surface. A* 265: 141–148.
- 330 Bloom, P.R. 1981. Phosphorus Adsorption by an Aluminum-Peat Complex1. *Soil Sci. Soc.*
331 *Am. J.* 45: 267.
- 332 Boesch, D.F., R.B. Brinsfield, and R.E. Magnien. 2001. Chesapeake Bay Eutrophication. *J.*
333 *Environ. Qual.* 30: 303–320.
- 334 Brennan, R.B., O. Fenton, J. Grant, and M.G. Healy. 2011a. Impact of chemical amendment
335 of dairy cattle slurry on phosphorus, suspended sediment and metal loss to runoff
336 from a grassland soil. *Sci. Tot. Environ.* 409: 5111–5118.
- 337 Brennan, R.B., O. Fenton, M. Rodgers, and M.G. Healy. 2011b. Evaluation of chemical
338 amendments to control phosphorus losses from dairy slurry. *Soil Use Manage.* 27:
339 238–246.
- 340 British Standards Institution (BSI). 1990. British Standard methods of test for soils for civil
341 engineering purposes. British Standards Institution, Milton Keynes [England].
- 342 Cao, X., W.G. Harris, M.S. Josan, and V.D. Nair. 2007. Inhibition of calcium phosphate
343 precipitation under environmentally-relevant conditions. *Sci. Tot. Environ.* 383: 205–
344 215.
- 345 Carpenter, S.R., N.F. Caraco, D.L. Correll, R.W. Howarth, A.N. Sharpley, and V.H. Smith.
346 1998. Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen. *Ecol.*
347 *Appl.* 8: 559–568.
- 348 Chardon, W.J., J.E. Groenenberg, E.J. Temminghoff, and G.F. Koopmans. 2012. Use of
349 reactive materials to bind phosphorus. *J. Environ. Qual.* 41: 636–646.
- 350 Cucarella, V., and G. Renman. 2009. Phosphorus Sorption Capacity of Filter Materials Used
351 for On-site Wastewater Treatment Determined in Batch Experiments-A Comparative
352 Study. *J. Environ. Qual.* 38: 381–392.
- 353 Department of the Environment, C. and L.G. 2002 Making Ireland’s Development
354 Sustainable Review, Assessment and Future Action
355 Available at [http://www.environ.ie/en/Environment/SustainableDevelopment/](http://www.environ.ie/en/Environment/SustainableDevelopment/PublicationsDocuments/FileDownload,1847,en.pdf)
356 [PublicationsDocuments/FileDownload,1847,en.pdf](http://www.environ.ie/en/Environment/SustainableDevelopment/PublicationsDocuments/FileDownload,1847,en.pdf) (verified 9 Nov 2014).
- 357 Egemose, S., M.J. Sønderup, M.V. Beinthin, K. Reitzel, C.C. Hoffmann, and M.R. Flindt.
358 2012. Crushed concrete as a phosphate binding material: A potential new
359 management tool. *J. Environ. Qual.* 41: 647–653.
- 360 Faulkner, S.P., and C.J. Richardson. 1989. Physical and chemical characteristics of
361 freshwater wetland soils. p. 41 – 72. *In* D.A. Hammer (ed.) *Constructed wetlands for*
362 *wastewater treatment.* CRC Press, Boca Raton, FL.
- 363 Finnegan, J., J.T. Regan, M. O’Connor, P. Wilson, and M.G. Healy. 2014. Implications of
364 applied best management practice for peatland forest harvesting. *Ecol. Eng.* 63: 12–
365 26.

- Forest Service. 2000. Code of Best Forest Practice. Available at <http://www.agriculture.gov.ie/forests-service/publications/code-of-best-forest-practice/> (verified 10 Nov 2014).
- Giller, P.S., and J. O'Halloran. 2004. Forestry and the aquatic environment: studies in an Irish context. *Hydrol. Earth Syst. Sc.* 8: 314–326.
- Harahuc, L., H.M. Lizama, and I. Suzuki. 2000. Selective Inhibition of the Oxidation of Ferrous Iron or Sulfur in *Thiobacillus ferrooxidans*. *Appl. Environ. Microbiol.* 66: 1031–1037.
- Hutton, S., S. Harrison, and J. O'Halloran. 2008. An evaluation of the role of forests and forest practices in the eutrophication and sedimentation of receiving waters. Available at http://www.wfdireland.net/docs/22_ForestAndWater/Forest%20and%20Water_UCC_Draft%20Final%20Report.pdf (verified 9 May 2014).
- Hyvönen, R., B.A. Olsson, H. Lundkvist, and H. Staaf. 2000. Decomposition and nutrient release from *Picea abies* (L.) Karst. and *Pinus sylvestris* L. logging residues. *For. Ecol. Manag.* 126: 97–112.
- James, B.R., M.C. Rabenhorst, and G.A. Frigon. 1992. Phosphorus Sorption by Peat and Sand Amended with Iron Oxides or Steel Wool. *Wat. Environ. Res.* 64: 699–705.
- Koble, R.A., and T.E. Corrigan. 1952. Adsorption Isotherms for Pure Hydrocarbons. *Ind. Eng. Chem.* 44: 383–387.
- Kordlaghari, M.P., and D.L. Rowell. 2006. The role of gypsum in the reactions of phosphate with soils. *Geoderma* 132: 105–115.
- Li, Y., C. Liu, Z. Luan, X. Peng, C. Zhu, Z. Chen, Z. Zhang, J. Fan, and Z. Jia. 2006. Phosphate removal from aqueous solutions using raw and activated red mud and fly ash. *J. Haz. Mat.* 137: 374–383.
- Liljaniemi, P., K.-M. Vuori, T. Tossavainen, J. Kotanen, M. Haapanen, A. Lepistö, and K. Kenttämies. 2003. Effectiveness of Constructed Overland Flow Areas in Decreasing Diffuse Pollution from Forest Drainages. *Environ. Manage.* 32: 602–613.
- Liu, Y., Q. Li, S. Gao, and J.K. Shang. 2011. Exceptional As (III) sorption capacity by highly porous magnesium oxide nanoflakes made from hydrothermal synthesis. *J. Am. Ceram. Soc.* 94: 217–223.
- Mainstone, C.P., and W. Parr. 2002. Phosphorus in rivers — ecology and management. *Sci. Tot. Environ.* 282–283: 25–47.
- Moffat, A.J., B.M. Jones, W.L. Mason, and G. Britain. 2006. Managing brash on conifer clearfell sites. Forestry Commission. [http://www.forestry.gov.uk/pdf/FCPN013.pdf/\\$FILE/FCPN013.pdf](http://www.forestry.gov.uk/pdf/FCPN013.pdf/$FILE/FCPN013.pdf) (verified 26 Nov. 14)
- National Forest Inventory. 2012. National Forest Inventory. Available at <https://www.agriculture.gov.ie/nfi/nfisecondcycle2012/nationalforestinventorypublications2012/> (verified 9 May 2014).
- Nieminen, M., E. Ahti, H. Nousiainen, S. Joensuu, and M. Vuollekoski. 2005. Capacity of riparian buffer zones to reduce sediment concentrations in discharge from peatlands drained for forestry. *Silva Fennica* 39: 331–339.
- O'Driscoll, C., E. de Eyto, M. Rodgers, M. O'Connor, Z.-Z. Asam, and L. Xiao. 2012. Diatom assemblages and their associated environmental factors in upland peat forest rivers. *Ecol. Indic.* 18: 443–451.
- O'Flynn, C.J., O. Fenton, and M.G. Healy. 2012. Evaluation of amendments to control phosphorus losses in runoff from pig slurry applications to land. *CLEAN—Soil Air Water* 40: 164–170.
- Oğuz, E., A. Gürses, and N. Canpolat. 2003. Removal of phosphate from wastewaters. *Cement Concrete Res.* 33: 1109–1112.

- Penn, C.J., R.B. Bryant, P.J.A. Kleinman, and A.L. Allen. 2007. Removing dissolved phosphorus from drainage ditch water with phosphorus sorbing materials. *J. Soil Water Conserv.* 62: 269–276.
- Porter, J.F., G. McKay, and K.H. Choy. 1999. The prediction of sorption from a binary mixture of acidic dyes using single- and mixed-isotherm variants of the ideal adsorbed solute theory. *Chem. Eng. Sci.* 54: 5863–5885.
- Pryor, M.J., and M. Cohen. 1953. The Inhibition of the Corrosion of Iron by Some Anodic Inhibitors. *J. Electrochem. Soc.* 100: 203–215.
- Reddy, K.R., R.H. Kadlec, E. Flaig, and P.M. Gale. 1999. Phosphorus Retention in Streams and Wetlands: A Review. *Crit. Rev. Env. Sci. Tec.* 29: 83–146.
- Reid, N., A. Keys, J.S. Preston, E. Moorkens, D. Roberts, and C.D. Wilson. 2013. Conservation status and reproduction of the critically endangered freshwater pearl mussel (*Margaritifera margaritifera*) in Northern Ireland. *Aquatic Conserv: Mar. Freshw. Ecosyst.* 23: 571–581.
- Renou, F., and E.P. Farrell. 2005. Reclaiming peatlands for forestry: the Irish experience. Restoration of boreal and temperate forests. CRC Press, Boca Raton: 541–557.
- Renou, F., S. Jones, and E.P. Farrell. 2000. Leaching of phosphorus fertilizer applied on cutaway peatland forests recently established in central Ireland. *Sustaining our peatlands 2*: 984–990.
- Rodgers, M., M. O'Connor, M.G. Healy, C. O'Driscoll, Z.-Z. Asam, M. Nieminen, R. Poole, M. Müller, and L. Xiao. 2010. Phosphorus release from forest harvesting on an upland blanket peat catchment. *Forest Ecology and Management* 260(12): 2241–2248.
- Sato, S., D. Solomon, C. Hyland, Q.M. Ketterings, and J. Lehmann. 2005. Phosphorus Speciation in Manure and Manure-Amended Soils Using XANES Spectroscopy. *Environ. Sci. Technol.* 39: 7485–7491.
- Seo, D.C., Cho, J.S., Lee, H.J., Heo, J.S., 2005. Phosphorus retention capacity of filter media for estimating the longevity of constructed wetland. *Water Res.* 39, 2445–2457.
- Serrenho, A., O. Fenton, P.N.C. Murphy, J. Grant, and M.G. Healy. 2012. Effect of chemical amendments to dairy soiled water and time between application and rainfall on phosphorus and sediment losses in runoff. *Sci. Tot. Environ.* 430: 1–7.
- Schaller, J., Tischer, A., Struyf, E., Bremer, M., Belmonte, D.U., Potthast, K., 2015. Fire enhances phosphorus availability in topsoils depending on binding properties. *Ecology* 96, 1598–1606.
- Song, Y., H.H. Hahn, E. Hoffmann, and P.G. Weidler. 2006. Effect of humic substances on the precipitation of calcium phosphate. *J. Environ. Sci.* 18: 852–857.
- Titus, B.D., and D.C. Malcolm. 1999. The long-term decomposition of Sitka spruce needles in brash. *Forestry* 72(3): 207–221.
- Vaananen, R., M. Nieminen, M. Vuollekoski, H. Nousiainen, T. Sallantausta, E. Tuittila, and H. Ilvesniemi. 2008. Retention of phosphorus in peatland buffer zones at six forested catchments in southern Finland. *Silva Fennica* 42(2): 211.
- Vasander, H., E.-S. Tuittila, E. Lode, L. Lundin, M. Ilomets, T. Sallantausta, R. Heikkilä, M.-L. Pitkänen, and J. Laine. 2003. Status and restoration of peatlands in northern Europe. *Wetland. Ecol. Manage.* 11: 51–63.
- Wickström, H. 2002. Action plan to counteract soil acidification and to promote sustainable use of forestland. National Board of Forestry, Jönköping. Available at <http://shop.skogsstyrelsen.se/shop/9098/art63/4645963-efc63c-1546.pdf> (verified 26 Nov. 14)
- Xie, F., F. Wu, G. Liu, Y. Mu, C. Feng, H. Wang, and J.P. Giesy. 2013. Removal of Phosphate from Eutrophic Lakes through Adsorption by in Situ Formation of Magnesium Hydroxide from Diatomite. *Env. Sci. Tech.* 48: 582–590.

466 Yang, Y., Y.Q. Zhao, A.O. Babatunde, L. Wang, Y.X. Ren, and Y. Han. 2006.
467 Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge.
468 Sep. Purif. Technol. 51: 193–200.

469 **Legend**

470 **Figure 1.** Best fit Koble-Corrigan adsorption isotherm models derived using non-linear
471 regression methods for (a) magnesium oxide, (b) gypsum, (c) steel wool, (d) crushed
472 concrete, (e) magnesium hydroxide, and (f) Al-WTR, at amendment to peat-solid ratios of
473 1:10, 1:4, and 1:2.

474 **Figure 2.** Effect of peat on pH at equilibrium

475 **Figure 3.** Synergistic effect of peat on P adsorption (Refer to Eqn. 5)

476 **Table 1.** Peat and amendment characteristics

Material	Total exchange capacity (meq 100 g ⁻¹)	pH	Organic matter (%)	P† (mg kg ⁻¹)	Bray II P (mg kg ⁻¹)	Ca† (mg kg ⁻¹)	Mg† (mg kg ⁻¹)	Fe† (mg kg ⁻¹)	Al† (mg kg ⁻¹)
Peat	11.45	3.8	100	5	3	228	142	152	47
Al-WTR	16.78	7	21.62	2	< 1	2983	32	154	2159
Gypsum	64.3	8.8	1.85	6	14	11858	296	111	66
Crushed Concrete	145.15	11.7	0.82	< 1	< 1	27593	622	405	441
MgO	267.55	10	1.04	< 1	< 1	2734	29760	77	< 1
Mg(OH) ₂	247.78	9.8	23.53	< 1	< 1	739	28660	57	< 1

477 †Mehlich -3 extractable

Table 2. Koble-Corrigan fitting coefficients, HYBRID errors, and values of slope and R^2 obtained from plots of $q_{e \text{ calc}}$ vs $q_{e \text{ exp}}$ for all amendments studied.

Amendment	Mass of amendment (g)	Mass of Peat (g)	Koble-Corrigan Parameters			Hybrid Error	$q_{e \text{ calc}}$ vs $q_{e \text{ exp}}$	
			A_{kc}	B_{kc}	P		R^2	Slope
Al-WTR	0.021	-	0.004	0.000	1.748	26.161	0.980	0.994
	0.051	-	0.002	0.001	1.844	21.142	0.870	1.016
	0.103	-	0.029	0.010	1.090	8.652	0.814	0.988
	0.021	2.000	0.710	0.032	0.795	4.725	0.995	1.001
	0.051	2.000	0.669	0.259	1.201	15.625	0.822	1.039
	0.103	2.000	0.001	-0.999	0.000	5.526	0.911	1.041
Crushed Concrete	0.021	-	1.031	-0.072	0.446	0.045	1.000	1.000
	0.051	-	0.510	0.020	0.873	33.659	0.881	1.016
	0.103	-	1.929	0.205	0.514	8.719	0.903	1.003
	0.021	2.000	3.964	-0.099	0.210	3.408	0.969	0.998
	0.051	2.000	1.087	0.109	0.935	0.187	0.997	1.000
	0.103	2.000	1.625	0.169	0.585	0.230	0.996	1.000
Gypsum	0.021	-	0.191	0.002	1.722	1.816	1.000	1.000
	0.051	-	0.004	0.000	2.841	8.108	0.998	0.999
	0.103	-	0.089	-0.950	0.016	72.056	0.963	1.007
	0.021	2.000	0.504	-0.381	0.176	23.740	0.963	0.981
	0.051	2.000	0.000	-0.999	0.000	10.299	0.962	1.011
	0.103	2.000	0.000	-0.999	0.000	0.826	0.994	0.998
Magnesium Oxide	0.021	-	1.686	0.012	2.406	742.198	0.895	1.036
	0.051	-	27.452	0.442	1.438	41.918	0.975	1.008
	0.103	-	17.694	0.252	0.520	17.290	0.986	1.000
	0.021	2.000	23.555	0.177	0.827	4.847	1.000	1.000
	0.051	2.000	24.286	0.407	1.197	34.473	0.994	1.000
	0.103	2.000	18.636	0.895	0.774	3.136	0.996	1.000
Magnesium Hydroxide	0.021	-	1.214	-0.159	0.379	287.793	0.933	0.999
	0.051	-	0.055	0.001	1.474	60.942	0.949	1.007
	0.103	-	0.152	-0.939	0.011	21.583	0.933	1.006
	0.021	2.000	0.047	-0.009	1.011	35.254	0.997	0.992
	0.051	2.000	7.849	0.098	1.065	408.260	0.937	0.932
	0.103	2.000	2.075	0.047	1.473	0.003	1.000	1.000
Steel wool	0.021	-	2.921	0.159	1.484	42.332	0.968	1.009
	0.051	-	4.128	0.411	0.996	0.870	0.999	1.001
	0.103	-	1.181	0.156	1.001	617.693	0.520	1.453
	0.021	2.000	434.832	9.756	1.352	137.919	0.715	1.003
	0.051	2.000	41.715	0.926	1.313	32.093	0.980	0.996
	0.103	2.000	68.370	2.490	0.728	62.409	0.959	0.975

Figure 1.

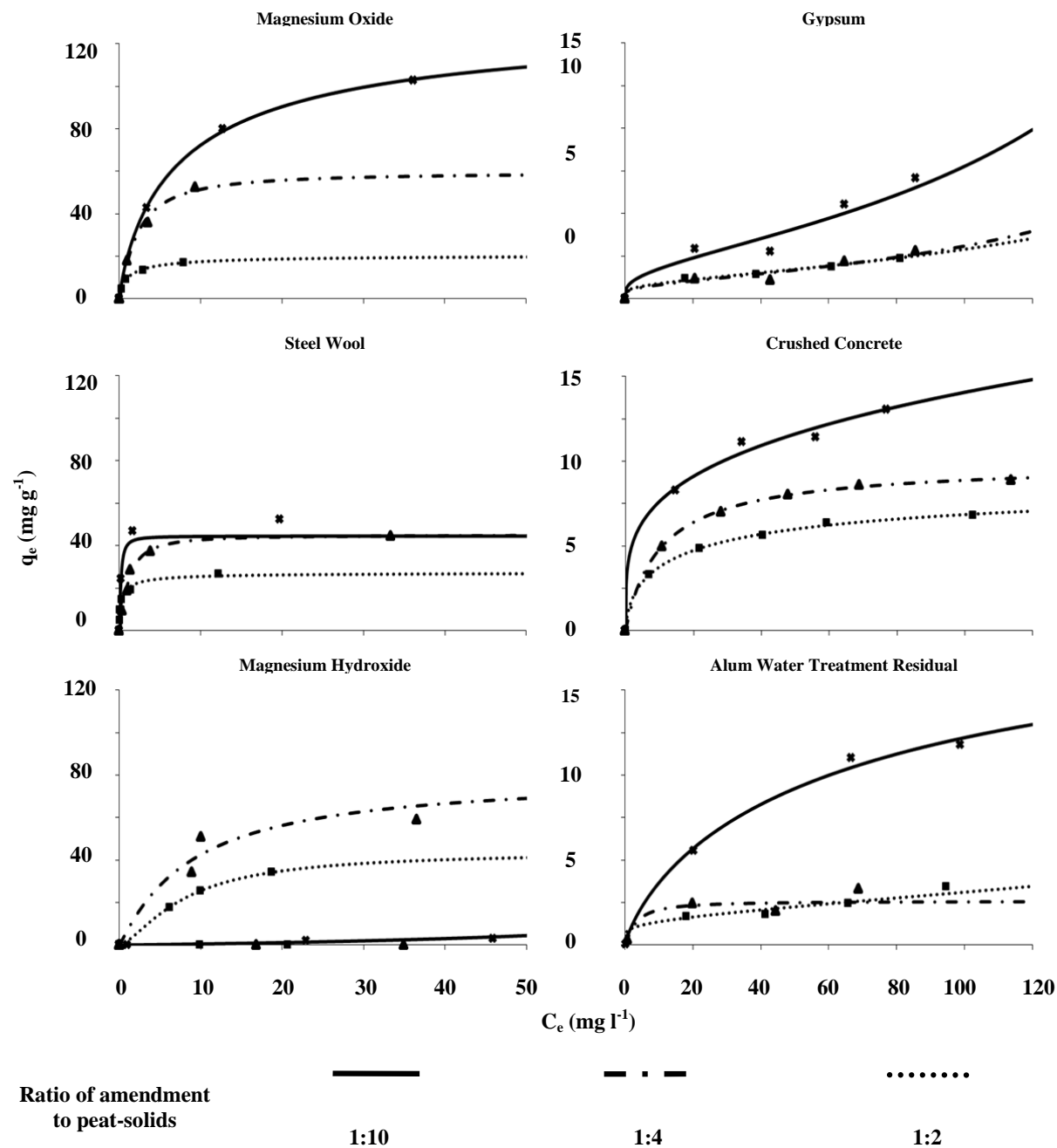


Figure 2.

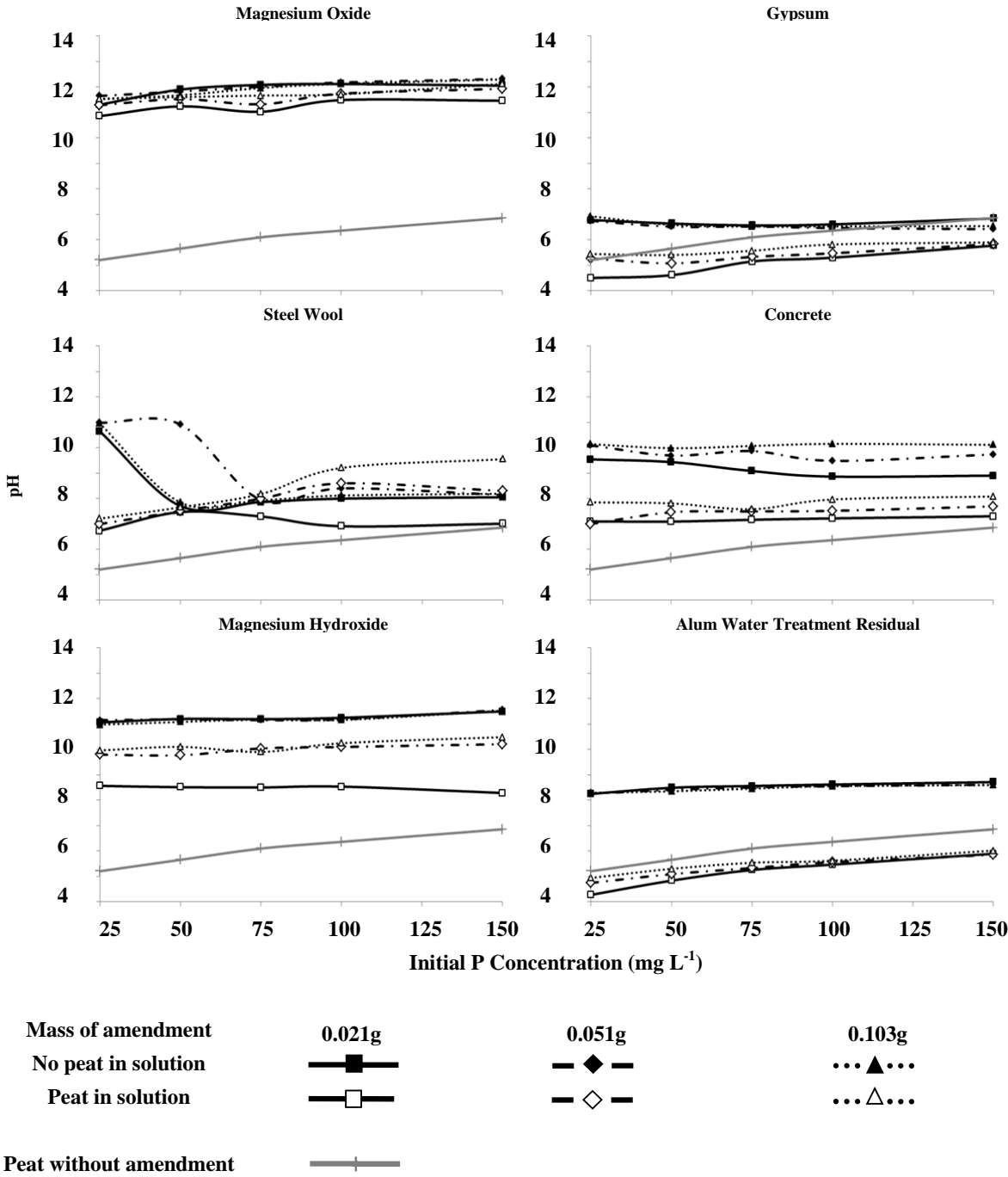


Figure 3.

