



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



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

Civil Engineering, National University of Ireland, Galway, Co. Galway, Ireland

ARTICLE INFO

Article history:

Received 19 March 2015
Received in revised form 6 October 2015
Accepted 7 October 2015

Keywords:

Phosphorus
Forestry
Peat
Clearfelling
Harvesting
Buffer zones
Adsorption

ABSTRACT

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

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

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

Nutrient enrichment, or eutrophication, of inland waters is recognized as Ireland's most serious environmental pollution problem (Department of the Environment, 2002). As P has been

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

The sustained release of P following forestry harvesting has been highlighted as an issue of particular concern, as much of Ireland's current peatland forestry stock was planted between the 1950s and the 1990s (Renou and Farrell, 2005) and has now reached, or is reaching, harvestable age (Rodgers et al., 2010). Clearfelling is the harvesting technique most prevalent in Ireland, and accounted for

Abbreviation: Al-WTR, aluminum water treatment residual.

* Corresponding author.

E-mail address: raymond.brennan@nuigalway.ie (R.B. Brennan).

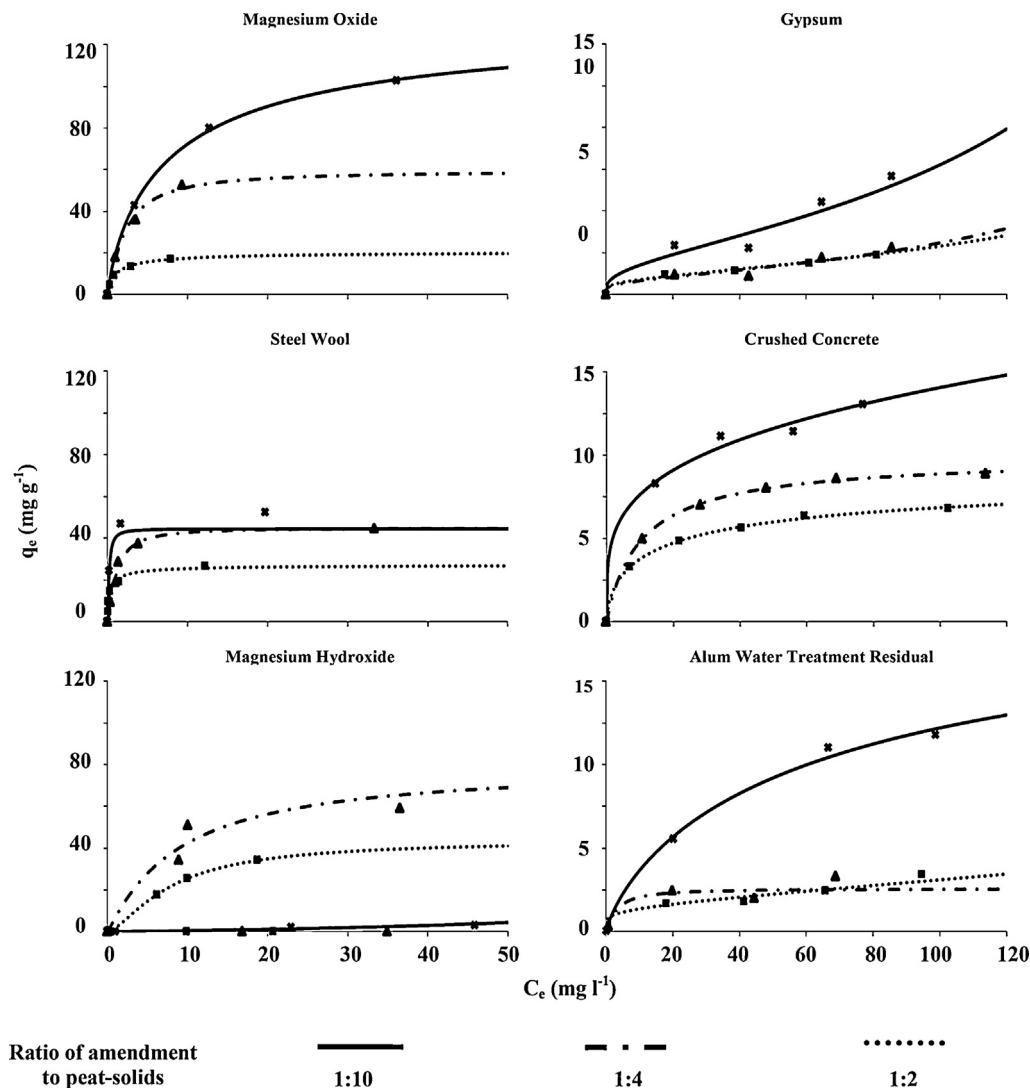


Fig. 1. Best fit Koble–Corrigan adsorption isotherm models derived using non-linear regression methods for (a) magnesium oxide, (b) gypsum, (c) steel wool, (d) crushed concrete, (e) magnesium hydroxide, and (f) Al-WTR, at amendment to peat–solid ratios of 1:10, 1:4, and 1:2.

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

While rates of afforestation on blanket peats have been in decline in recent years (National Forest Inventory, 2012), the harvesting of presently established forest is inevitable, as are the resulting water quality issues, if effective pollution mitigation

measures are not implemented. Current best management practices advocate the use of riparian buffer strips between forestry and adjacent aquatic zones (Forest Service, 2000). Previous research has found the use of suitably large riparian buffer zones on peat soils to be largely successful in protecting surface waters from influxes of suspended sediments and associated particulate nutrients (Nieminen et al., 2005). However, with peat's low P adsorption capacity, the performance of these buffer zones in satisfactorily mitigating the flow of dissolved P off site varies greatly. Moreover, it has been found that these buffer zones' effect can be anywhere from positive, with total retention of released P (Vaananen et al., 2008), to negative, compounding the issue with additional P release (Vasander et al., 2003; Liljaniemi et al., 2003).

There has been increasing interest in the use of soil amendments to control P losses from diffuse sources, such as land spreading of manure from dairy cattle (Brennan et al., 2011a,b) and pigs (O'Flynn et al., 2012), land spreading of dairy waste water from washing of milking parlors (Serrenho et al., 2012), and construction of wetlands on sites previously used for agriculture (Ann et al., 1999). The use of chemical amendments has shown much promise in these instances, though there has been little to no investigation into the practice's potential in abating the loss of P from peatland forestry.

Table 1
Peat and amendment characteristics.

Material	Total exchange capacity (meq 100 g ⁻¹)	pH	Organic matter (%)	P ^a (mg kg ⁻¹)	Bray II P (mg kg ⁻¹)	Ca ^a (mg kg ⁻¹)	Mg ^a (mg kg ⁻¹)	Fe ^a (mg kg ⁻¹)	Al ^a (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	11,858	296	111	66
Crushed concrete	145.15	11.7	0.82	<1	<1	27,593	622	405	441
MgO	267.55	10	1.04	<1	<1	2734	29,760	77	<1
Mg(OH) ₂	247.78	9.8	23.53	<1	<1	739	28,660	57	<1

^a Mehlich-3 extractable.

The performance of chemical amendments in this context has the potential to be quite different, as the interaction of amendments with the complex chemistry of peat can significantly alter their P removal performance (James et al., 1992).

This study tested the hypothesis that chemical amendments could immobilize P in a forest peat soil. To address this hypothesis, the aim of this study was to identify and compare potential soil amendments which function well in a peat chemistry environment and, when mixed with peat onsite, could increase the adsorptive capacity of the soil to the point where P losses from a forestry site would no longer pose a risk to receiving surface waters. Specifically, the objectives of this study were to: (1) identify chemical amendments capable of removing P from an aqueous solution which mimics the chemistry of runoff/ground water on a forested peat site; (2) compare the performance of each amendment and identify the amendment most ideally suited to application in a forested peat site; (3) analyze the effect of peat on the performance of each amendment in terms of its adsorptive capacity.

2. Materials and methods

2.1. Collection and characterization of peat samples

Samples of blanket peat were collected from a recently clear-felled riparian buffer zone, located near the town of Oughterard, County Galway, Ireland (approx. coordinates 53.375 N, -9.419 E). The peat was collected from a stratum of homogeneous composition, at a depth of 5–25 cm 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).

2.2. 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).

2.3. 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 PL⁻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.

2.4. 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 Eq. (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

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

Amendment	Mass of amendment (g)	Mass of peat (g)	Koble–Corrigan parameters			Hybrid error	$q_{e,calc}$ vs $q_{e,exp}$	
			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

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 Eq. (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 (Eq. (2)), $q_{e,i,meas}$ is the value of q_e obtained from Eq. (1), and $q_{e,i,calc}$ is the value of q_e obtained from Eq. (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 C_o . Substituting Eq. (1) into Eq. (2) gives:

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

An iterative approach, using Microsoft Excel's Solver™, was then used to determine values of C_e for any given value of C_o . The

impact of peat on the amendments' performance was evaluated using:

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

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

3. 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.

3.1. Equilibrium adsorption isotherms

Fig. 1 shows the adsorption isotherms obtained by fitting the Koble–Corrigan model to each of the peat amendment-mixtures.

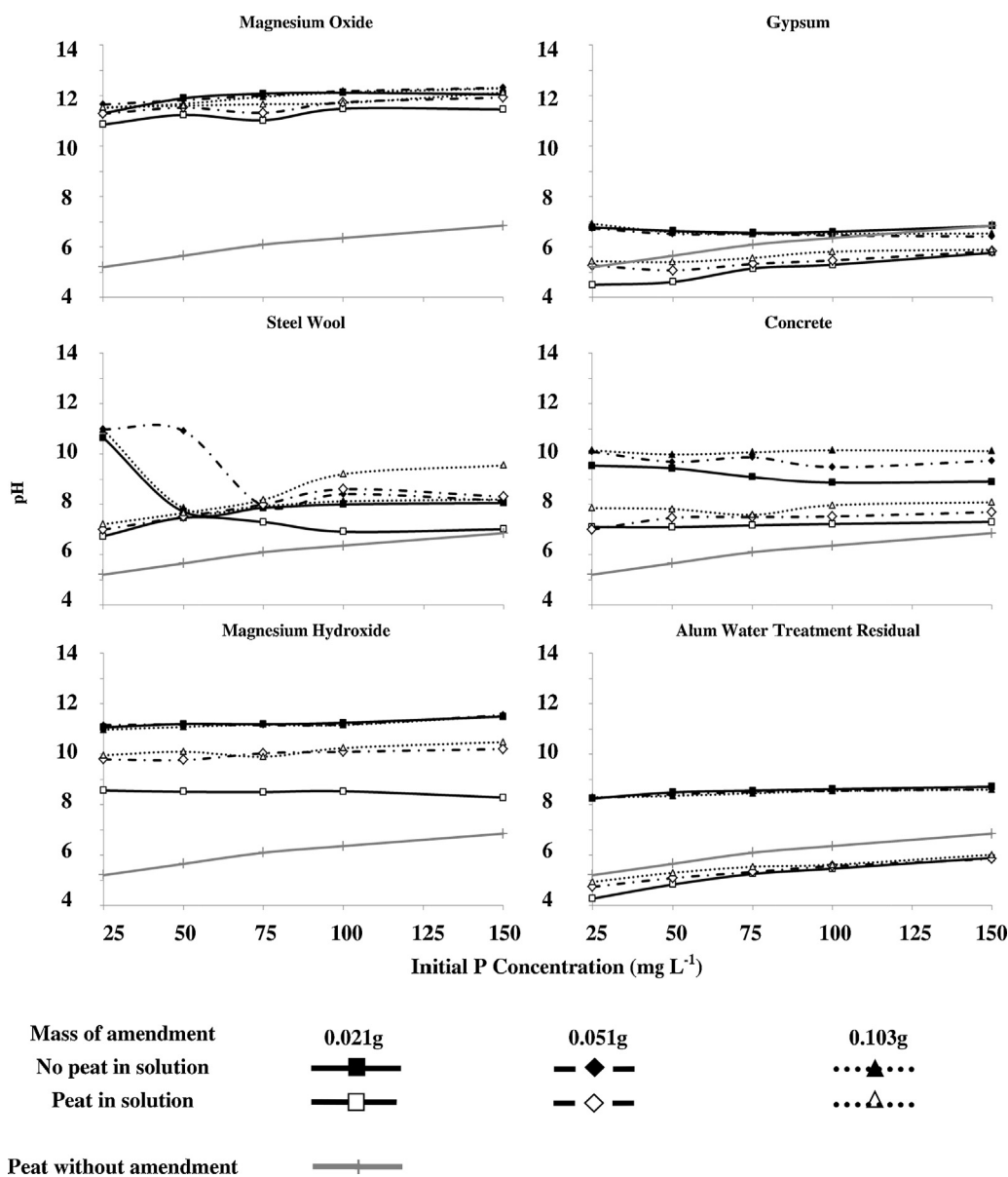


Fig. 2. Effect of peat on pH at equilibrium.

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 calc (calculated using the Koble–Corrigan equation) vs q_e 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 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 amendment to peat-solid ratios of 1:10, 1:4, and 1:2, compared to values of 84.8 mg g^{-1} , 58.4 mg g^{-1} , and 34 mg g^{-1} observed for the same masses without the addition of peat.

Magnesium oxide and $\text{Mg}(\text{OH})_2$ displayed the highest P adsorption capacities, with MgO having the greatest of the two, with a maximum q_e of 102.7 mg g^{-1} observed at an amendment to peat-solid ratio of 1:10. Liu et al. (2011) found that removal of As(III) from aqueous solution by MgO was due to the in situ formation of $\text{Mg}(\text{OH})_2$ by reaction of the MgO with water, followed by subsequent adsorption/reaction of the newly formed $\text{Mg}(\text{OH})_2$ with the As(III) anion. Liu et al. (2011) also reported that the adsorptive performance of $\text{Mg}(\text{OH})_2$ formed in situ was greater than that of pre-formed $\text{Mg}(\text{OH})_2$, at least partially as a result of the former's larger specific surface area, which was almost 5.5 times greater than that of the latter ($58.4 \text{ m}^2 \text{ g}^{-1}$ vs. $10.7 \text{ m}^2 \text{ g}^{-1}$, respectively).

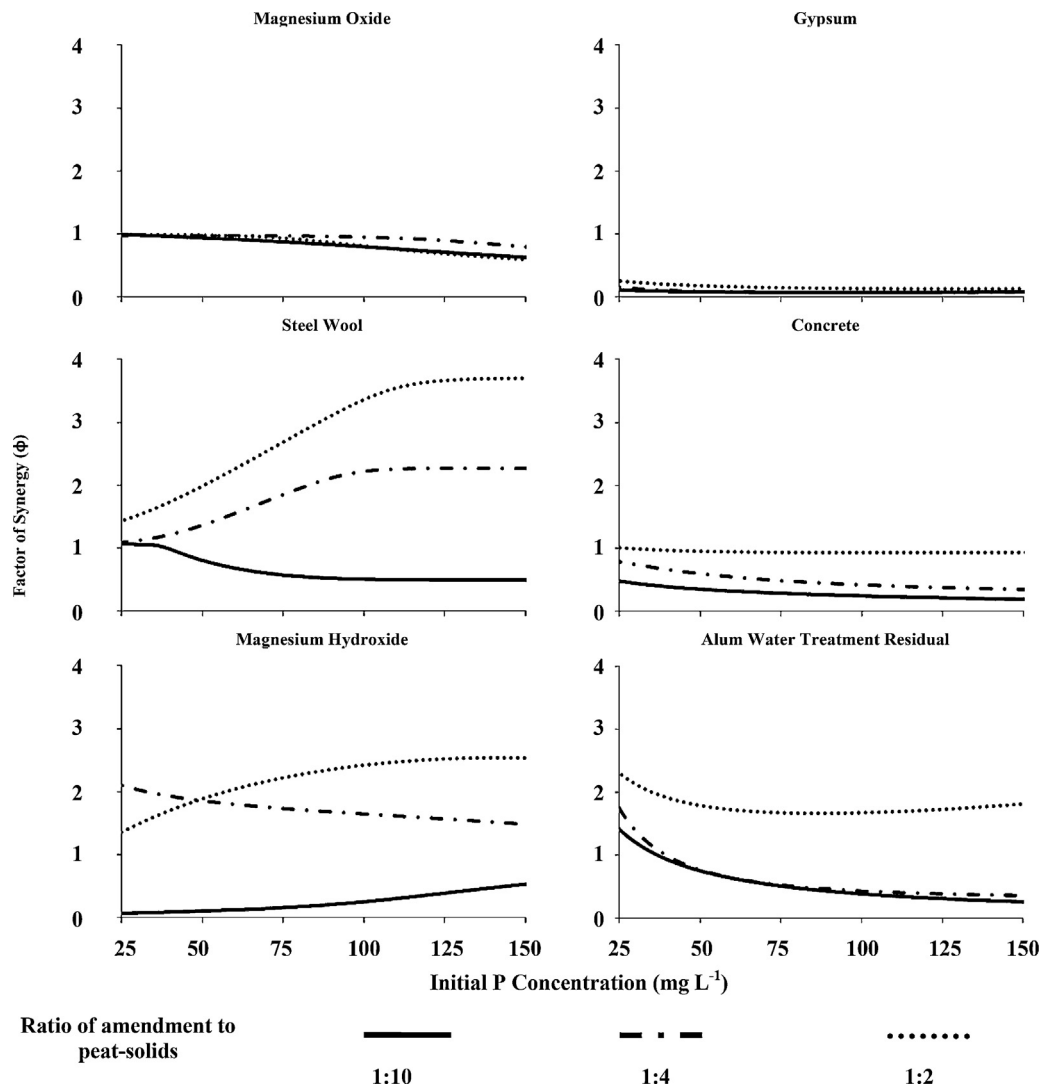


Fig. 3. Synergistic effect of peat on P adsorption (refer to Eq. (5)).

The results of our study indicate that $\text{Mg}(\text{OH})_2$ formed in situ also had a greater adsorptive capacity for $\text{PO}_4\text{-P}$ compared to that of preformed $\text{Mg}(\text{OH})_2$. Stoichiometrically, MgO contains approximately 45% more Mg per unit weight than $\text{Mg}(\text{OH})_2$; however, its P adsorption capacity was observed to be up to 120% greater than that of preformed $\text{Mg}(\text{OH})_2$ in solutions where peat was absent (data not shown).

When steel wool was examined, P adsorption was observed to be inhibited at high initial $\text{PO}_4\text{-P}$ concentrations (C_0), both with and without the addition of peat. This appeared to be the result of high $\text{PO}_4\text{-P}$ concentrations inhibiting the formation of the iron oxides/hydroxides responsible for P removal, and it was observed that much less of the steel wool had rusted in these comparatively high concentration solutions. Similar observations were made by Pryor and Cohen (1953), who found that solutions of orthophosphate passivate iron; i.e. iron 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.

3.2. pH effects

Fig. 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 24 h, 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).

3.3. 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 (Fig. 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.

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

4. 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 $\text{Mg}(\text{OH})_2$.

Acknowledgement

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

References

- Alvarez, R., Evans, L.A., Milham, P.J., Wilson, M.A., 2004. Effects of humic material on the precipitation of calcium phosphate. *Geoderma* 118, 245–260.
- Ann, Y., Reddy, K.R., Delfino, J.J., 1999. Influence of chemical amendments on phosphorus immobilization in soils from a constructed wetland. *Ecol. Eng.* 14, 157–167.
- American Public Health Association (APHA), American Water Works Association, and Water Environment Federation, 1998. *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, Washington, DC.
- Berg, U., Donnert, D., Ehbrecht, A., Bumiller, W., Kusche, I., Weidler, P.G., Nüesch, R., 2005. "Active filtration" for the elimination and recovery of phosphorus from waste water. *Colloids Surf. A* 265, 141–148.
- Bloom, P.R., 1981. Phosphorus adsorption by an aluminum-peat complex. *Soil Sci. Soc. Am. J.* 45, 267.
- Boesch, D.F., Brinsfield, R.B., Magnien, R.E., 2001. Chesapeake bay eutrophication. *J. Environ. Qual.* 30, 303–320.
- Brennan, R.B., Fenton, O., Grant, J., Healy, M.G., 2011a. Impact of chemical amendment of dairy cattle slurry on phosphorus, suspended sediment and metal loss to runoff from a grassland soil. *Sci. Total Environ.* 409, 5111–5118.
- Brennan, R.B., Fenton, O., Rodgers, M., Healy, M.G., 2011b. Evaluation of chemical amendments to control phosphorus losses from dairy slurry. *Soil Use Manage.* 27, 238–246.
- British Standards Institution (BSI), 1990. *British Standard Methods of Test for Soils for Civil Engineering Purposes*. British Standards Institution, Milton Keynes, England.
- Cao, X., Harris, W.G., Josan, M.S., Nair, V.D., 2007. Inhibition of calcium phosphate precipitation under environmentally-relevant conditions. *Sci. Total Environ.* 383, 205–215.
- Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol. Appl.* 8, 559–568.
- Chardon, W.J., Groeneweg, J.E., Temminghoff, E.J., Koopmans, G.F., 2012. Use of reactive materials to bind phosphorus. *J. Environ. Qual.* 41, 636–646.
- Cucarella, V., Renman, G., 2009. Phosphorus sorption capacity of filter materials used for on-site wastewater treatment determined in batch experiments—a comparative study. *J. Environ. Qual.* 38, 381–392.
- Department of the Environment, Community and Local Government, 2002. Making Ireland's Development Sustainable Review, Assessment and Future Action, Available at: <http://www.environment.ie/en/Environment/SustainableDevelopment/PublicationsDocuments/FileDownload,1847.en.pdf> (verified 09.11.14).
- Egemose, S., Sønderup, M.J., Beintin, M.V., Reitzel, K., Hoffmann, C.C., Flindt, M.R., 2012. Crushed concrete as a phosphate binding material: a potential new management tool. *J. Environ. Qual.* 41, 647–653.
- Faulkner, S.P., Richardson, C.J., 1989. Physical and chemical characteristics of freshwater wetland soils. In: Hammer, D.A. (Ed.), *Constructed Wetlands for Wastewater Treatment*. CRC Press, Boca Raton, FL, pp. 41–72.
- Finnegan, J., Regan, J.T., O'Connor, M., Wilson, P., Healy, M.G., 2014. Implications of applied best management practice for peatland forest harvesting. *Ecol. Eng.* 63, 12–26.

- Forest Service, 2000. Code of Best Forest Practice, Available at: <http://www.agriculture.gov.ie/forests/service/publications/codeofbestforestpractice/> (verified 10.11.14).
- Giller, P.S., O'Halloran, J., 2004. Forestry and the aquatic environment: studies in an Irish context. *Hydro. Earth Syst. Sci.* 8, 314–326.
- Harahuc, L., Lizama, H.M., Suzuki, I., 2000. Selective inhibition of the oxidation of ferrous iron or sulfur in *Thiobacillus ferrooxidans*. *Appl. Environ. Microbiol.* 66, 1031–1037.
- Hutton, S., Harrison, S., O'Halloran, J., 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 09.05.14).
- Hyvönen, R., Olsson, B.A., Lundkvist, H., Staaf, H., 2000. Decomposition and nutrient release from *Picea abies* (L.) Karst. and *Pinus sylvestris* L. logging residues. *For. Ecol. Manage.* 126, 97–112.
- James, B.R., Rabenhorst, M.C., Frigon, G.A., 1992. Phosphorus sorption by peat and sand amended with iron oxides or steel wool. *Water Environ. Res.* 64, 699–705.
- Koble, R.A., Corrigan, T.E., 1952. Adsorption isotherms for pure hydrocarbons. *Ind. Eng. Chem.* 44, 383–387.
- Kordlaghari, M.P., Rowell, D.L., 2006. The role of gypsum in the reactions of phosphate with soils. *Geoderma* 132, 105–115.
- Li, Y., Liu, C., Luan, Z., Peng, X., Zhu, C., Chen, Z., Zhang, Z., Fan, J., Jia, Z., 2006. Phosphate removal from aqueous solutions using raw and activated red mud and fly ash. *J. Hazard. Mater.* 137, 374–383.
- Liljanemi, P., Vuori, K.-M., Tossavainen, T., Kotanen, J., Haapanen, M., Lepistö, A., Kenttämies, K., 2003. Effectiveness of constructed overland flow areas in decreasing diffuse pollution from forest drainages. *Environ. Manage.* 32, 602–613.
- Liu, Y., Li, Q., Gao, S., Shang, J.K., 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., Parr, W., 2002. Phosphorus in rivers – ecology and management. *Sci. Total Environ.* 282–283, 25–47.
- Moffat, A.J., Jones, B.M., Mason, W.L., Britain, G., 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 26.11.14).
- National Forest Inventory, 2012. National Forest Inventory. Available at: [https://www.agriculture.gov.ie/nfi/nfisecondcycle2012/nationalforestinventorypublications2012/\[inventorypublications2012/\]](https://www.agriculture.gov.ie/nfi/nfisecondcycle2012/nationalforestinventorypublications2012/[inventorypublications2012/]) (verified 09.05.14).
- Nieminen, M., Ahti, E., Nousiainen, H., Joensuu, S., Vuollekoski, M., 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., de Eyto, E., Rodgers, M., O'Connor, M., Asam, Z.-Z., Xiao, L., 2012. Diatom assemblages and their associated environmental factors in upland peat forest rivers. *Ecol. Indic.* 18, 443–451.
- O'Flynn, C.J., Fenton, O., Healy, M.G., 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., Gürses, A., Canpolat, N., 2003. Removal of phosphate from wastewaters. *Cement Concrete Res.* 33, 1109–1112.
- Penn, C.J., Bryant, R.B., Kleinman, P.J.A., Allen, A.L., 2007. Removing dissolved phosphorus from drainage ditch water with phosphorus sorbing materials. *J. Soil Water Conserv.* 62, 269–276.
- Porter, J.F., McKay, G., Choy, K.H., 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., Cohen, M., 1953. The inhibition of the corrosion of iron by some anodic inhibitors. *J. Electrochem. Soc.* 100, 203–215.
- Reddy, K.R., Kadlec, R.H., Flaig, E., Gale, P.M., 1999. Phosphorus retention in streams and wetlands: a review. *Crit. Rev. Environ. Sci. Technol.* 29, 83–146.
- Reid, N., Keys, A., Preston, J.S., Moorkens, E., Roberts, D., Wilson, C.D., 2013. Conservation status and reproduction of the critically endangered freshwater pearl mussel (*Margaritifera margaritifera*) in Northern Ireland. *Aquat. Conserv. Mar. Freshw. Ecosyst.* 23, 571–581.
- Renou, F., Farrell, E.P., 2005. Reclaiming Peatlands for Forestry: The Irish Experience. Restoration of Boreal and Temperate Forests. CRC Press, Boca Raton, pp. 541–557.
- Renou, F., Jones, S., Farrell, E.P., 2000. Leaching of phosphorus fertilizer applied on cutaway peatland forests recently established in central Ireland. *Sustain. Peatl.* 2, 984–990.
- Rodgers, M., O'Connor, M., Healy, M.G., O'Driscoll, C., Asam, Z.-Z., Nieminen, M., Poole, R., Müller, M., Xiao, L., 2010. Phosphorus release from forest harvesting on an upland blanket peat catchment. *Forest Ecol. Manage.* 260 (12), 2241–2248.
- Sato, S., Solomon, D., Hyland, C., Ketterings, Q.M., Lehmann, J., 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., Fenton, O., Murphy, P.N.C., Grant, J., Healy, M.G., 2012. Effect of chemical amendments to dairy soiled water and time between application and rainfall on phosphorus and sediment losses in runoff. *Sci. Total 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., Hahn, H.H., Hoffmann, E., Weidler, P.G., 2006. Effect of humic substances on the precipitation of calcium phosphate. *J. Environ. Sci.* 18, 852–857.
- Titus, B.D., Malcolm, D.C., 1999. The long-term decomposition of Sitka spruce needles in brash. *Forestry* 72 (3), 207–221.
- Vaananen, R., Nieminen, M., Vuollekoski, M., Nousiainen, H., Sallantausta, T., Tuittila, E., Ilvesniemi, H., 2008. Retention of phosphorus in peatland buffer zones at six forested catchments in southern Finland. *Silva Fennica* 42 (2), 211.
- Vasander, H., Tuittila, E.-S., Lode, E., Lundin, L., Ilomets, M., Sallantausta, T., Heikkilä, R., Pitkänen, M.-L., Laine, J., 2003. Status and restoration of peatlands in northern Europe. *Wetlands 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 26.11.14).
- Xie, F., Wu, F., Liu, G., Mu, Y., Feng, C., Wang, H., Giesy, J.P., 2013. Removal of phosphate from eutrophic lakes through adsorption by in situ formation of magnesium hydroxide from diatomite. *Environ. Sci. Technol.* 48, 582–590.
- Yang, Y., Zhao, Y.Q., Babatunde, A.O., Wang, L., Ren, Y.X., Han, Y., 2006. Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. *Sep. Purif. Technol.* 51, 193–200.