HOW CAN WE ENHANCE PHOSPHORUS REMOVAL IN CONSTRUCTED FARM WETLANDS?

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Abstract

Constructed and restored wetlands have significant potential to reduce nutrient losses in drainage waters from New Zealand farms. While both types of wetland show reasonably good nitrogen removal efficiencies, they are not always so effective at phosphorus (P) removal and their flooded topsoils can be net sources of P. Wetland P removal efficiency could be enhanced, either by adding a P-retentive amendment to the soil in the bottom of the wetland, or installing a porous filter with a high P adsorbency and retention capacity at the end of the wetland.

A review was carried out to evaluate a range of natural, processed, modified and waste materials reported in the scientific literature as having the ability to remove P from water (Ballantine and Tanner, 2010), on which this contribution is based. The reported performance of the materials reviewed varied widely. A simple scoring system based on P removal characteristics, availability, likely cost and potential reuse and ease of disposal on saturation was used to identify the materials with most promise as soil amendments for constructed wetlands. Allophane, Papakai tephra, limestone and alum were judged as materials with the most potential as soil amendments. Field and lab tests are now underway to determine which of the above materials might be most suitable to enhance P removal in constructed farm wetlands. Another possible approach is to use subsoil or a mix of subsoil and topsoil as the growth media in the base of the wetland to avoid P release on flooding of P-rich agricultural topsoils.

Introduction

In an attempt to reduce nutrient losses from farm drainage systems, constructed wetlands have been trialled to evaluate their ability to remove nutrients and other pollutants from drainage water (Tanner et al. 2005). While constructed wetlands are effective in removing N (entering in the form of nitrate through microbial denitrification), their capacity to remove P tends to be much lower and more variable, and they can be either sources or sinks of P (Reddy et al. 1999). In studies of natural and constructed wetlands treating diffuse agricultural run-off, retention of sediment-associated P deriving from cultivated cropland can be significant (Braskerud 2002; Mitsch et al. 1995), but removal of dissolved forms of P tends to require large wetland areas, long residence times and is more variable. In studies of constructed wetlands treating tile drainage from grazed pastures carried out in New Zealand (Sukias et al. 2006; Tanner et al. 2005), the P loads measured at the outlets of farm drainage wetlands at Toenepi and Bog Burn have remained higher than at the inflow over periods of 3-5 years, meaning that these wetlands have actually been net sources of P.

P retention in constructed wetlands occurs through substratum adsorption, chemical precipitation, bacterial immobilisation, plant and algal uptake, incorporation into organic matter and sediment accretion (Kadlec & Knight 1996). One possible way to enhance P

retention in constructed wetlands is to add a substrate material to the wetland to enhance P removal. Another option is through the addition of a separate porous filter unit that contains a readily changeable filter material with a high P sorption capacity. Only substrate materials are considered in this article. For a wider and more comprehensive review of both potential substrate and filter materials, please refer to Ballantine and Tanner, 2010.

When considering a suitable substrate for P retention, various aspects must be considered as follows:

P adsorption and retention capacity
The P sorption capacity of the substrate material will have an important influence on its useful lifetime. The material should have a high P adsorption and retention capacity and should be able to retain P over the long term. It is essential to remember that any potential substrate material will have a finite capacity to adsorb P, and once saturated, it will stop adsorbing P and may become a P source if physico-chemical conditions change (Braskerud et al. 2005; Novak et al. 2004; Reddy et al. 1999).

Texture of the material
A suitable substrate material should be fine textured with a high surface area. Substrate materials need to be sufficiently permeable to allow water to flow through them without rapid clogging (Drizo et al. 1999).

Geochemical composition
Investigations of several different substrate materials have shown that Al, Fe, and Ca ions are particularly important properties for P sorption (Cui et al. 2008). The pH of the environment is also important.

Reuse potential
Ideally the P sorbing material should be reusable once saturated with P (Leader et al. 2008). It could be used directly as a P-rich soil amendment. If saturated materials are to be reused as soil amendments, materials should be non-toxic, to avoid contaminating the soil. Alternatively, the P may be reclaimed from the media and used as fertiliser, an option which will perhaps increase in the future as worldwide P reserves are consumed and costs of P fertiliser rise.

On a practical level, the P-sorbing materials chosen should ideally be low-cost (e.g. industrial by-products), generated locally (to reduce transport costs), widely available in large quantities, non-toxic and, if not reusable, able to be readily and safely disposed of.

This contribution provides details on a selection of materials which, based on scientific literature, have potential to enhance P retention in constructed farm wetlands. Details of a wider range of materials is available in Ballantine and Tanner (2010). Materials discussed include naturally occurring, processed and waste materials.

Naturally occurring materials

Allophane
Allophane is the name given to a group of clay-size minerals which contain silica, alumina and water (Parfitt 1990). While allophanes form from volcanic ash materials and are major components of volcanically derived soils, they may also be found in the clay fraction of non-volcanically derived soils (Sparks 1995). They occur over much of the North Island, for

example, they make up the major portion of the clay fraction in the yellow-brown loams derived from old volcanic ash beds, such as the Tongariro and Taranaki deposits, but in many places have been buried under later volcanic deposits (During 1984). Allophane has a large specific surface area, and its soils are highly porous, have a low bulk density and are excellent filters for effluent and heavy metals (Parfitt 2009). Allophanic soils used for agriculture are well known to require larger amounts of fertiliser P than non-allophanic soils to overcome their inherent P-retention properties and provide sufficient labile P to meet the needs of crops (Edmeades et al. 2006).

When phosphate solutions are added to allophane at pH 5-6 with $CaCl_2$ present, P is strongly and rapidly adsorbed initially, while as surface coverage increases, later increments of phosphate are more weakly adsorbed (Parfitt 1989), and it is thought that aluminium phosphate precipitates are formed.

In recent tests by Gibbs et al. (2008) on materials for "capping" lake sediments, allophane showed higher P removal than alum, Phoslock™ and modified zeolite, and had a P binding capacity of 16 g P kg^{-1} allophane at pH 7, the optimal pH for P sorption by allophane (Gibbs et al. 2008). Yuan and Wu (2007) also observed that allophane had a higher P removal capacity than Phoslock™.

Allophane is cheap and abundant in New Zealand, and can be obtained in large quantities from deposits which are close to main roads. It is also likely to be safe to use because it is a natural material and does not require extensive chemical modification before usage. It is recoverable after use because it occurs as granules which do not disperse in aqueous media, and the P saturated allophane can be recycled to farmland (Yuan & Wu 2007). While allophane has been tested in anoxic conditions and was found to be able to effectively retain sorbed P, it has not been tested in a wetland setting; however its properties and the findings noted above suggest that it could be useful for P removal in farm drainage wetlands.

Tephra
Tephra is a general term for all the fragmental material erupted explosively from a volcano. The fragments are classified according to size with ash particles being less than 2 mm in diameter, lapilli between 2 and 64 mm and volcanic bombs or blocks greater than 64 mm. Tephra, at various stages of development, occurs over extensive areas of the North Island of New Zealand, and it often contains varying, and frequently large, amounts of allophane, which suggests that it has potential for P removal from farm drainage wastewater.

In laboratory and field trials, Hanly et al. (2008) tested the P removal capacity of a New Zealand tephra from drainage waters. The Papakai tephra material used was collected from the Mangatoetoenui Quarry in the Tongariro Volcanic Zone, North Island. It had an average P retention value of 83%, with the finest fraction (< 2mm) having the highest P retention. Column experiments using the 1-4 mm size fraction showed that when the influent DRP concentration was 0.25 mg P l^{-1}, P removal efficiency was 96%, while when the DRP concentration was 12 mg P l^{-1}, the P removal efficiency was reduced to 51%, suggesting that P removal efficiencies were higher at lower P influent concentrations. The tephra also reduced the P concentrations in drainage water in a field trial, but P removal was lower than was attained in the column experiments, possibly attributable to the shorter residence times encountered in the field trial. Hanly et al. (2008) concluded that the Papakai tephra was an effective P adsorbent, with P removal comparable to that observed by other researchers for

industrial furnace ashes and slags. In the context of a farm drainage wetland, the finer fractions of the Papakai tephra may have potential as a soil amendment.

In an earlier study of the potential for different tephras to remove P from sewage effluent, Ryden et al. (1975) found that a moderately weathered andesitic tephra (Okato tephra, Taranaki) was most effective at P removal from the variety of andesitic and rhyolitic tephras examined. Their study demonstrated that the properties of different tephras were highly variable and that not all shared the same high P retention capacities. Different tephras therefore merit further testing.

While various types of tephra are abundant in the Central North Island and Taranaki regions of New Zealand, precise details about available reserves are unknown. There may be issues around resource consent for mining tephra, however, in some cases, tephra may be a waste product from deeper mining and quarrying activities, and therefore more readily available.

Limestone
Limestone is a sedimentary rock composed largely (more than 50%) of calcium carbonate ($CaCO_3$). Limestone is abundant in New Zealand and is used mainly in a finely crushed form as an agricultural fertiliser, and as an aggregate for roads. Crushed or powdered limestone is widely used as a calcium-rich soil amendment to reduce soil acidity and enhance P retention. It may also be a suitable material for sorbing P in a farm drainage wetland, because of its high Ca content and associated ability to facilitate P precipitation.

There are numerous examples worldwide where limestone has been used to enhance P retention in wetlands and soils. In Lebanon, Zurayk et al. (1997) added crushed lime to a wetland substrate and found that P removal was rapid and positively correlated with the amount of lime added. They found that P fixation was highest in the soil with the highest lime addition (49% $CaCO_3$/ 51% soil) with 99% P removal observed. However, even at the lowest addition (1.5% $CaCO_3$/ 98.5% soil), P retention was higher than for the soil without lime added (93% compared with 88%). Ann et al. (2000a; 2000b) identified lime and slaked lime as preferred amendments to increase P retention in re-flooded P-rich organic soils. This was not only because of their effectiveness in immobilizing P under heavily reduced conditions, but also because of the low solubilities and low desorption potential of Ca-P compounds formed in this soil. The effective amounts of lime and slaked lime required to minimise P release from soil to the overlying floodwater were 7 to 15 g kg^{-1} soil. In laboratory tests comparing the P-sorption capacities of limestone, wollastonite, zeolite, LECA and sand, Yin et al. (2006) found limestone to have the best P sorption characteristics for use in subsurface-flow constructed wetlands. In field studies in Quebec, Canada, Comeau et al. (2001) reported 92% P removal from trout farm effluents in subsurface-flow constructed wetlands with crushed limestone media. Shilton et al. (2005) tested the feasibility of using a New Zealand limestone from the Tararua region in a wetland setting to adsorb P. P removal in a batch experiment with a hydraulic retention time of 12 hours was 64%, but when tested in the field, P removal decreased to an average of 18%. Batch experiments included tests at different temperatures to determine the effect of higher temperatures on P removal. These showed that, as temperature increased, rates of P removal also increased.

Limestone is abundant in New Zealand, with Waikato, in the North Island, and Oamaru, Canterbury, in the South Island, having important quarries. The findings above suggest that lime could provide a low-cost, widely available and effective material for P removal in farm

drainage wetlands, either as a substrate and filter. However caution is required because there are many different limestones available, all of which have unique physical and chemical characteristics, and different P retention properties.

Processed materials

Alum
Alum, the common name for aluminium sulphate $(Al_2(SO_4)_3).16\ H_2O)$, has been used in a variety of settings to reduce the P status of water. Removal of phosphate using alum is through the formation of either aluminium hydroxide, which subsequently adsorbs P, or precipitation of aluminium phosphate.

A number of lake restoration programmes have addressed internal P loading through the addition of alum. For example, in the first full scale use of alum in a New Zealand lake for eutrophication control, alum solution (47% $Al_2 (SO_4)_3.14H_2O$) was added to Lake Okaro in 2003, with results showing an 85% reduction in the P concentrations in the lake (Paul et al. 2008). On fields recently spread with swine manure, Smith et al. (2001) used alum additions to reduce P in runoff and found that P concentrations were up to 84% lower after alum additions of 40.7 kg ha^{-1}. Alum has been tested in a wetland treating municipal wastewater in Florida by Malecki-Brown et al. (2009). Wetland cells treated with alum had significantly lower soluble reactive phosphorus (SRP) than their control counterparts, with removals ranging from 77.3-86.4% depending on the wetland vegetation. On average, alum reduced SRP concentrations to one third of that in the controls.

Ann et al. (2000a; 2000b) investigated the efficacy of alum to increase P retention in soils under flooded conditions. They found that 12 g of alum was needed for each kilogram of soil to minimize P release from soil to overlying water in highly organic Lake Opopka marsh soils that had previously been drained and used for intensive agriculture.

The controlling factor in the effectiveness, and also the toxicity, of alum is the pH of the system (Malecki-Brown et al. 2007). Alum has a pH of 2.4 (Beecroft et al. 1995) and therefore tends to decrease the pH of the system to which it is added. As long as the pH remains between 6 and 8, P inactivation will result, however, if the pH decreases to between 4 and 6, bound P will be released. Below pH 4 and above pH 8 soluble Al^{3+} dominates which may result in aluminium toxicity (Cooke et al. 1993; Ma et al. 2003). An additional concern for alum additions is the effect on biological components of the wetland, for example, Pilgrim and Brezonik (2005) noted that nearly all the invertebrates were eliminated from a settling pond of lake influent which had been treated with alum due to floc accumulation. Due to the success of alum in the above mentioned settings and its wide availability, it could also be useful in a constructed wetland setting.

Waste materials

Drinking water treatment residuals
Drinking water treatment residuals (DWTRs), resulting from alum, calcium oxide, ferric sulphate and polyelectrolyte additions to raw water sources, have been shown to be relatively effective in removing P from solution, with P removal generally due to either aluminium, calcium or iron precipitation.

Tests carried out by Leader et al. (2008) showed that a calcium based DWTR (CaO) had a P sorption capacity of 0.894 +/- 0.020 g kg^{-1}, while an iron based residual (ferric sulphate) had a P sorption capacity of 0.952 +/- 0.016 g kg^{-1}. When equilibrated with P-free solution, they desorbed relatively little P. Dewatered alum sludge cakes, derived from the residual of raw water containing mainly turbidity, colour and humic substances and no toxic substances in most cases, were tested in a reed bed by Zhao et al. (2008) to treat P-rich animal farm wastewater. Results from a long-term trial showed that the P removal of the reed bed was 88.6% ± 7.2% for soluble P, of which 42% was due to P-adsorption by the dewatered alum sludge cakes.

Redding (2007) however, had limited success in his trials using a DWTR (15% alum; initial moisture content 73%) for reducing P loss from pasture in overland flow in New Zealand. While there was high, and rapid, P sorption by the particular DWTR tested when freshly applied, he found that drying degraded its sorption capacity, rendering it unsuitable for reducing P loss in a pasture situation. While DWTRs may not be suitable for use in a pasture setting, they might be useful as a P removal option in wetland soils where they could be maintained moist for the period over which sorption was required.

DWTRs can normally be obtained free-of-charge from drinking water treatment plants, making them a potentially attractive option for P removal. They are typically disposed of in landfill sites, therefore to use them for P retention in wetlands would be an appropriate alternative use. Once saturated, they may be useful as agricultural soil amendments as they contain plant nutrients. They also provide increased cation exchange and water holding capacity, which in turn has benefits for agricultural crops. Land owners should however exercise caution regarding widespread and cumulative applications to land as the build up of aluminium in the soil may cause toxicity problems for plants over time. There may also be potential health risks for those working with DWTRs, as they may contain faecal micro-organisms precipitated out from contaminated water sources, especially (oo) cysts of parasitic pathogens (Cryptosporidium sp. and Giardia sp.). Risks would need to be assessed and suitable safeguards developed before they could be recommended for general on-farm use (e.g. storage periods before use).

Discussion
The above discussion suggests that there is a wide range of materials which could potentially be used in farm drainage wetlands, either as substrates or filters, to enhance P retention. Some of these have been shown from previous experiments to be very effective and others less so. Further, while some have been tested in a wetland setting at the field scale, to date, others remain untested. As suggested by Cui et al. (2008), combinations of materials may also be able to provide enhanced performance and also to satisfy other factors such as cost, availability, disposal and reuse potential.

To meet the initial basic criteria, any material to be used should have the following attributes: (1) moderate to high affinity for P, (2) be relatively abundant, (3) readily available at low cost, (4) non-toxic, (5) suitable for reuse with no risk to soil or water quality in either the short or long term, and (6) ideally a renewable and natural material. A simple additive scoring system was used to summarise the materials reviewed and assist in placing them in rank order (Table 1). Scores ranged between 7 and 9, and are presented in Table 2. Summarised details of the highest scoring materials are given in Table 3.

Materials with most potential as substrates or soil amendments were allophane, Papakai tephra, limestone, alum and DWTRs. Allophane and tephra would be suitable as soil amendments for constructed wetlands in the North Island. Tephras other than Papakai (e.g. andesitic tephras) should also be tested. Alum and limestone are commercially available all over New Zealand, and therefore may be suitable alternatives for the South Island. Drinking water treatment residuals (DWTRs) could also be useful as they would be available from various places throughout the country, but would need further testing to ascertain their specific composition, P adsorbency properties and risk to human health. There may be toxicity and P release issues with these alum-rich materials, both within the wetland, if pH is outside the range 6 – 8, and if applied to land on saturation.

Table 1 Scoring system for potential substrate materials

P removal potential	1=Low	2=Medium	3=High
Availability in NZ	1=Low	2=Medium	3=High
Likely cost	1=High	2=Medium	3=Low
Reuse potential	-1=Difficult	0=Neutral	1=Beneficial

Table 2 Scores obtained by potential soil substrate materials

Material	Useful for	P removal	Availability	Likely cost	Reuse	Score
Allophane	Soil amendment	High	Medium	Low	Beneficial	9
Tephra (P)	Soil amendment	High	Medium	Low	Beneficial	9
Limestone	Both	Medium	High	Low	Beneficial	9
Alum	Soil amendment	High	High	Medium	Difficult	7
DWTRs	Soil amendment	High	Medium	Low	Difficult	7
Subsoil	Substrate	Medium	High	Low	Beneficial	9

Using subsoil as a substrate also ranked highly (score of 9). This has been used successfully elsewhere (Liikanen et al. 2004) and involves stripping the topsoil from the wetland site and using the subsoil as the wetland substrate. Without amending or removing the topsoil there is the risk that the wetland would become a source of P due to the equilibrium P concentration of the soil being higher than the mean concentration of the inflowing water. Before adopting this approach, the subsoil should be tested for its P retention and adsorption properties.

Table 3 Advantages and disadvantages of potential soil amendments

Material	Advantages	Disadvantages	Test	P removal	Reference	Availability	Score
Allophane	High P removal, natural product, non toxic, reusable; relatively cheap	Untested in a wetland setting; may be limited supplies	Lab	36 g P kg^{-1} allophane	Yuan and Wu, (2007), Gibbs et al. (2008)	Available in NZ, North Island; localised availability	9
Tephra (Papakai and andesitic)	Papakai and andesitic tephras have high P removal, natural product, non toxic, reusable	Available only in the North Island; variable removal depending on properties; may be limited in supply and difficult to extract; potential issues with extraction	Papakai tephra (lab and field); Andesitic tephra (lab)	1. 80-97% P removal from solution containing 5 mg P/g tephra 2. 0.25-1 mm tephra 2.6 g P kg^{-1}; 1-2 mm tephra 1.6 g P kg^{-1} tephra	1. Ryden et al. (1975) 2. Hanly et al. (2008)	Available in NZ, North Island (Central and Taranaki areas); localised availability	9
Limestone	Moderate P removal in lab tests	Needs tested in field conditions	Lab and field	1. 88-99% removal from 200 ppm P solution (lab) 2. 64% removal from 10mg/l P solution (lab); 18% removal from effluent (field)	1.Zurayk et al. (1997) 2. Shilton et al. (2005)	Available in NZ	9
Alum	High P removal from runoff and effective in reducing P concentrations in lakes	May be expensive; potential negative effects on biological components of the wetland; very sensitive to pH	Field	1. 84% reduction in P in runoff 2. PO$_4$-P concentrations decreased from 40 to 6 mg m^{-3} (85% reduction) 3. 77-86% SRP removal (compared to 58% without alum)	1. Smith et al. (2001) P removal in runoff 2. Paul et al. (2008) P removal in lake 3. Malecki-Brown et al. (2009) P removal in a wetland	Available in NZ to purchase; widespread availability	7
DWTRs	Free of charge; high P removal capacity depending on composition	Potential health risks; material not effective when dry	Field	Soluble P removal from farm waste water was 88.6% ± 7.2%	Zhao et al. (2008)	Available in NZ for free from drinking water treatment plants	7
Subsoil	Potentially high P removal depending on soil type	P removal potential variable depending on soil type – needs tested	Field	49 and 68% for DRP and TP	Liikanen et al. (2004)	Available in NZ; widespread	9

Summary

From a literature review, and supported by the use of a simple scoring system, allophane, limestone, Papakai, and Okato tephras, alum and DWTRs seemed the most suitable materials as soil amendments for P removal. Another possible approach, which ranked highly, is to remove topsoil from the wetland area in the construction phase to avoid P release on flooding the topsoil. The materials listed above should be field tested further to establish their performance in a constructed wetland setting. New Zealand is rich in natural minerals (Christie et al. 2000), some of which may have potential as P removal agents. Also there are many waste products from large and small industries which may be suitable for use. While the availability of the latter is generally localised, it is increasingly easy to locate potentially suitable materials through online resources (e.g. www.nothrow.co.nz). With rising costs associated with the extraction of naturally occurring materials and diminishing availability over time, the reuse of waste materials will become increasingly important and, looking to the future, they may become useful in P removal from wastewater.

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