



Can limestone, steel slag or man-made sorption materials be used to enhance phosphate-phosphorus retention in treatment wetland for peat extraction runoff with low phosphorous concentration?



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ABSTRACT

This study examined possibilities to enhance phosphorus (P) retention in wetlands using different materials that could enhance removal of phosphate P ($\text{PO}_4\text{-P}$) from runoff waters with fairly low P concentrations (P_{tot} average $80\text{--}90\ \mu\text{g L}^{-1}$ and $\text{PO}_4\text{-P}$ $25\text{--}30\ \mu\text{g L}^{-1}$) typical for peat extraction runoff. The retention potential of sorption materials, that had previously shown good retention capacity was first studied in laboratory batch tests using steel slag (basic oxygen furnace slag (BOF)), Filtralite[®]P (high Ca and Mg clay), CFH 12 (ferrihydroxide), limestone, Phoslock[®] (95% bentonite clay material + 5% lanthanum) and iron gypsum in year 2010. Based on batch test results and material properties (column tests not suitable for fine clay materials such as Phoslock[®]), steel slag, CFH 12 and iron gypsum products were selected for column tests. The column experiments were run for almost three months during spring 2011. Steel slag and Phoslock[®] were selected for further testing *in situ* in a treatment wetland. In the laboratory set-ups, all materials tested retained $\text{PO}_4\text{-P}$ (70–90% in batch tests and approximately 10–80% in column experiments). However, in the field scale set-up, neither steel slag nor Phoslock[®] successfully retained $\text{PO}_4\text{-P}$. The reasons may be e.g. for steel slag, too low pH, too large grain size, and too short retention time. Also, for some set-up, the given instruction were not followed during construction works. Further studies are needed to test different particle sizes and new potential materials for retaining P in treatment wetlands with high hydraulic loading rate, low P concentration and low pH.

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1. Introduction

Treatment wetlands (TWs) are globally used for wastewater purification purposes, and their ability to retain suspended solids (SS) is usually high (70–90%), but the ability to retain phosphorus (P) is lower (30–60%) (Vymazal, 2010). In Finland, TWs have mainly been constructed on intact peatlands, where they can retain on average 40–55% of phosphorus (P) from peat extraction runoff (Heikkinen et al., 2002; Kløve et al., 2012). In addition, TWs are used for polishing municipal wastewater, and TWs constructed on pristine peatlands show P retention of 12–83% when the hydraulic load range from of $21\text{--}44\ \text{mm d}^{-1}$ (Ronkanen and Kløve, 2009). According to the recent Finnish national peatland use strategy, peat extraction areas should be established on previously drained

peatlands with little ecological value. Thus treatment wetlands are also often constructed on drained peatlands. According to Postila et al. (2014), some of the TWs constructed on drained areas retain phosphate phosphorus ($\text{PO}_4\text{-P}$) nearly as well as wetlands constructed on intact areas. However, in the same study some of the TWs released $\text{PO}_4\text{-P}$, especially during the first years after their establishment. Phosphorus release after rewetting of drained peatlands in wetland restoration has also been observed in other studies (Kieckbusch and Schrautzer, 2007; Koskinen et al., 2011; Nieminen et al., 2005). P leaching may partly occur due to reduction of iron (Fe) under anaerobic conditions, resulting in PO_4^{3-} releases (Reddy and DeLaune, 2008). Also high P concentration in surface peat layer (Postila et al., 2014) and the death of forest species (Jauhainen et al., 2002) can lead to P leaching after rewetting.

Possibilities to enhance P retention in TWs have been studied with different materials mainly at laboratory scale (Vohla et al., 2011). The factors found to affect P retention in sorption materials are e.g. material grain size (e.g. Xu et al., 2006), P inflow

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concentration (e.g. Lyngsie et al., 2015), pH (e.g. Oliveira et al., 2015), hydraulic loading rate (Vohla et al., 2011), retention time (e.g. Lyngsie et al., 2015; Penn et al., 2012), water velocity (Claveau-Mallet et al., 2012), and organic matter content (e.g. Xu et al., 2006). Sorption materials can be divided into: (1) natural materials, such as the siliceous sedimentary rock opoka (Johansson and Gustafsson, 2000), shell sand (Ådåm et al., 2007) and peat (e.g. Kõiv et al., 2009); (2) industrial by-products, such as slags (e.g. Johansson 1999; Vohla et al., 2011) and ash (e.g. Xu et al., 2006); and (3) man-made products, such as Filtralite P® (Ådåm et al., 2005; Vohla et al., 2011). The materials can also be divided according to their chemical composition into: (a) materials which contain metals (such as aluminium (Al) and Fe); (b) materials which contain soluble divalent earth metals (calcium (Ca) and magnesium (Mg)); and (c) mixtures of these (Klimeski et al., 2012). By-product materials such as slags have been frequently tested, because they are widely available and cheap materials. However, based on Klimeski et al. (2012) review, P sorption tests are usually conducted using water with a high P concentration, whereas the average P concentrations in peat extraction runoff are 80–90 µg P_{tot} L⁻¹ and 25–30 µg PO₄-P L⁻¹ (Postila et al., 2014; Tuukkanen et al., 2012).

Addition of Fe, Al and Ca can increase PO₄-P retention due to their sorption capacity (Richardson, 1985; Seo et al., 2005). However, Fe and Al sorb P in acidic conditions, whereas Ca sorbs P under near-neutral conditions (Reddy and DeLaune, 2008). The aim of this study was to determine whether addition of sorption materials can enhance PO₄-P retention in TWs constructed for purification of peat extraction runoff. Batch and column tests were first carried out in the laboratory and then promising candidate materials were tested *in situ* in a TW. Our starting hypothesis was that sorption materials can retain P in laboratory and field conditions.

2. Material and methods

2.1. Laboratory tests

Different sorption materials for retaining PO₄-P were first studied in the laboratory in batch (year 2010) and column (year 2011) tests. The materials studied in batch tests were selected based on a literature review considering material cost-effectiveness, retention efficiency, particle size, availability and costs. Locally available materials and by-products were carefully considered to avoid e.g. high transport costs and steel slag (basic oxygen furnace slag (BOF) including mainly calcium oxide (CaO), Fe and silicon dioxide (SiO₂)) from Raahe Rautaruukki Oyj (nowadays SSAB) was chosen. Filtralite®P (a clay material with high Ca and Mg content), CFH 12 (ferrihydroxide), limestone (mainly CaCO₃), Phoslock® (95% bentonite clay material + 5% lanthanum), and iron gypsum from Kemira Oyj was also selected as promising materials. In these batch tests, runoff from a peat extraction area (8 µg PO₄-P L⁻¹) and pore water from the peat or mineral layer of TWs (40 and 250 µg PO₄-P L⁻¹) were used. The pH in these waters varied from 5.6 to 6.4, with the highest values occurring in runoff water. The batch test on each material was performed with 100 g of sorption material and 200 mL of water in four parallel samples (replicates), because ratio represent more realistically the field conditions. We followed the protocol described by Heikkinen et al. (1995): the mixture of sorption material and water was first shaken mechanically for one hour (shaker speed was selected between 300 and 400 min⁻¹ in order to have all the tested mass be in circulation in the bottle), followed by a 23-h standing time. After this, the samples were shaken for 10 min and centrifuged for 15 min at 4000 revolutions per minute. Finally, the samples were filtered through a Whatman® GF/C filter (pore size 1.2 µm) and a Gelman filter (pore size 0.45 µm). The

samples were analysed for e.g. PO₄-P, pH, Al, Fe, Ca, Mg and sulphur (S) in an accredited laboratory.

Column tests were run with steel slag (grain size 3–10 mm and 10–20 mm, which were used in earlier studies also), CFH 12 and Sachtofer PR (iron gypsum material from Sachtleben Pigments Oy) with peat extraction runoff water with an above-normal PO₄-P concentration (650 µg PO₄-P L⁻¹). In the tests, two different-sized columns were used, so that the diameter was at least 5 time higher than particle size (CEN ISO/TS 17892-11:fi), but the needed water amount was minimized during test. In this way the difficulties in collecting water and storing it were minimized. Columns with inner diameter 10.4 cm and height 20.8 cm were used for steel slag with grain size 10–20 mm and Sachtofer PR, due to their larger particle sizes, while columns with inner diameter 5.2 cm and height 31 cm were used for steel slag with grain size 3–10 mm and for CFH 12. The height of these sorption materials in the columns was about 15 cm. A filter paper (Whatman 114) was installed in smaller columns and a filter mesh (pore size 0.5 mm) in larger columns to prevent sorption material from ending up in the outlet pipe. In smaller columns, a quartz sand layer (grain size 3–5 mm) was also added below (thickness 3 cm) and above (1.5 cm) the sorption material to ensure uniform water flow. Because the grain size of quartz sand was <10–20 mm, this material was not used in larger columns. One column per sorption material was used and the water was fed continuously by pump from the bottom of these columns from 1 m³ containers that were continuously mixed by a small pump. The target outflow for small columns was 2 mL min⁻¹ and for large columns 8 mL min⁻¹. Thus the mean water residence time was calculated to be approximately similar (one h) in all columns. This residence time was used as it was possible to achieve also in field conditions where the water discharge is high. However, the actual mean residence time in columns varied from 1 h to 1.5 h and the flow velocity varied from 1.6 to 1.9 mL min⁻¹ in the small columns and from 5 to 8 mL min⁻¹ in the bigger columns. When the flow velocity was noticed to be clearly under the target outflow (2 or 8 mL min⁻¹), the pumping speed was increased. These experiments were done in hydraulically saturated conditions and run for almost three months (83 days).

The hydraulic conductivity (K) during the column testes was checked regularly to determine clogging effects. First the K was first determined using empty columns where was only filter mesh (large column) or filter paper and a quartz sand layer (small column). The aim of that was to check how the column system restricted water flow (affected hydraulic conductivity). After that, the hydraulic conductivity was determined for the filled columns first one day after the beginning of the test, then approximately every week for two first months, and finally at the end of the test. The hydraulic conductivity (K-value) was calculated as (Tie- ja vesirakennushallitus, 1974):

$$K = \frac{Q \times L}{t \times A \times H} \quad (1)$$

where Q is the amount of water (cm³) flowing through the column sample at certain time t (s), L is the height of sample (cm), A is the surface area of sample (cm²) and H is the pressure height (cm). Q was measured in the space without sorption materials on the top of the column. On the occasions when hydraulic conductivity was measured i.e. approximately every week for two first months, and finally at the end of the test, inflow and outflow samples were also taken and analysed for PO₄-P, total P, pH, Ca, Al, Fe, S, Mg, manganese (Mn), potassium (K), sodium (Na), barium (Ba), strontium (Sr), titanium (Ti) and zinc (Zn) in an accredited laboratory. At the beginning of the test, samples were taken from the water containers supplying inflow water for analyses of total nitrogen (N) (2300 µg L⁻¹), total P (670 µg L⁻¹), chemical oxygen

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