



# Long-term accumulation and retention of Al, Fe and P in peat soils of northern treatment wetlands



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## ABSTRACT

In a study on northern treatment wetlands, we examined whether P adsorption capacity remained high, with maintained P retention, after almost 20 years of loading. We also examined the most important processes for the treatment wetlands as a long-term P sink and analysed peat and water quality in the peat soils of the wetland. We tested P adsorption capacity by comparing batch test results with peat P and pore water PO<sub>4</sub>-P concentrations. The results showed that P adsorption capacity in the treatment wetland did not change in a 12-year period according to batch testing but the maximum sorption capacity may have been reached, although P retention level remained high after almost 20 years of wetland use. Phosphorus accumulation through peat accretion as a long-term sink was only of minor importance for P retention (0.5–7%). The main retention mechanisms for P in runoff in the wetlands were found to be filtration, sedimentation and precipitation with metals. Iron (Fe) accumulation in the surface peat indicated that its origin was peat extraction runoff. Thus long-term P retention depends on the hydrogeological setting and the quality of the water, which depends on the source. Calculations based on inlet/outlet loads from treatment wetlands may not always provide a reliable estimate of long-term P retention due to occasional P release from Fe under anaerobic conditions. Therefore new sites or sites experiencing problems with P retention should be sampled to determine the balance between peat P content and pore water PO<sub>4</sub>-P concentration and the availability of metals for precipitation.

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## 1. Introduction

Phosphorus (P) is one of the key nutrients causing eutrophication and algae bloom in surface water bodies (Hilton et al., 2006; Rahm and Danielsson, 2007; Råike et al., 2003; Withers and Jarvie, 2008). Despite increased attention to water pollution control in Europe in recent decades, poor chemical and ecological status still persists in many surface water bodies in European countries, including Finland. As a result, the regulatory pressure to further lower P concentrations in wastewaters and runoff has intensified (Council of the European Union, 2000). The use of constructed wetlands for treating different types of wastewater and runoff is seen as a cost-efficient measure to reduce diffuse and point loads (Kadlec and Knight, 1996; Koskiaho and Puustinen, 2005; Wittgren and Maehlum, 1996). Constructed wetlands include various types of

systems, ranging from natural wetlands receiving wastewater to filter systems where wastewater flows either horizontally or vertically depending on structural configuration. For all such systems designed for P retention, P adsorption and retention capacity is a major concern and an important design criterion to achieve long-term removal capacity.

Different filter materials can be used in P removal in constructed wetlands (Vohla et al., 2011; Johansson Westholm, 2006). These should be low-cost materials with high P retention capacity (Babatunde et al., 2009). The P processes involved have been widely studied, but less attention has been paid to peat as a filter material (Couillard, 1992, 1994; Kõiv et al., 2009; Todt et al., 2014; Xiong and Mahmood, 2010). Peat is abundant in regions with high moisture (boreal zone and the tropics), where it has potential for use in wastewater treatment. Peat can provide an effective medium for retention of nitrogen (N), P and suspended solids (SS) (Bulc et al., 1997; Heikkinen et al., 1995a,b; Kieckbusch and Schrautzer, 2007) and also of dissolved metals (aluminium, iron, nickel) (Brown et al., 2000; Räsänen et al., 2001) and metalloids such as arsenic (Palmer et al., 2015), which are toxic to many organisms.

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In wetlands, P can be present in dissolved form or suspended in water, sorbed to the surface of peat and metal particles, or organic form, within the structure of humic substances, biomass and soil particles (Broberg and Persson, 1988; Ekholm and Krogerus, 2003; Kadlec and Knight, 1996; Vymazal, 2007). The retention of P is mediated by biological uptake by vegetation, microbiological assimilation, (ad)sorption and precipitation. Adsorption and precipitation within the wetland are regarded as the major process whereby P is trapped in the porous medium, as P reacts with minerals such as hydrous oxides of iron (Fe) and aluminium (Al) in acid soils, and with calcium (Ca) and magnesium (Mg) in alkaline soils (Yuan and Lavkulich, 1994; Heikkinen et al., 1995b; Kadlec and Knight, 1996; Richardson, 1985; Seo et al., 2005; Søvik and Kløve, 2005). Biological uptake by vegetation and microbes has been found to be a minor sink of P in treatment wetlands (Huttunen et al., 1996; Stottmeister et al., 2003; Vymazal, 2007).

In this study, P sorption experiments by Heikkinen et al. (1995b) were repeated, taking peat samples from the same treatment wetlands and using the same method (batch test with artificial  $\text{KH}_2\text{PO}_4$  solution). The aim was to determine possible changes in P adsorption capacity after nearly 20 years of use of the wetlands. In addition, a new approach was applied to study the P sorption capacity of the treatment wetlands. In this approach, metals (Al and Fe) and P concentrations in peat and pore water were studied in order to find the equilibrium state in field conditions. The ultimate objective of the study was to estimate long-term accumulation and peat adsorption in the treatment wetlands. Long-term studies on P removal in constructed wetlands are currently scarce (Craft and Richardson, 1993; Reddy et al., 1993; Mitsch et al., 2012; Vymazal, 2011; Vymazal and Březinová, 2014). The hypotheses tested in this study were that: (1) P adsorption capacity in the wetlands is still high, after almost 20 years of use, due to accumulation of Fe and Al, which maintain peat sorption properties; and (2) precipitation, sorption and peat accretion are the most important processes for P retention in the treatment wetlands studied.

## 2. Materials and methods

### 2.1. Study sites and sampling

Two water treatment wetlands (Fig. 1) constructed on initially pristine peatland (Kompsasuo:  $65^\circ 44' 43''\text{N}$ ,  $25^\circ 57' 80''\text{E}$  and Puutiosuo:  $65^\circ 42'\text{N}$ ,  $26^\circ 03'\text{E}$ ) were studied after 4–6 and 15–18 years, respectively, of establishment of a peat extraction site. Both treatment wetlands are overland flow area type wetlands and are located in the mid-boreal region, in the southern aapa mire zone of northern Finland (Seppä, 2002). The Finnish guidelines on designing treatment wetlands for construction on pristine peatlands are based on studies conducted in these two peatlands in the early 1990s (Ihme, 1994). The Finnish authorities still consider treatment wetlands to be the best available technology (BAT) for reducing the environmental impact of peat extraction on surrounding waters.

The Kompsasuo treatment wetland (2.2 ha, which is 4.4% of the peat extraction area) was originally an oligo-mesotrophic bog with *Sphagnum* and *Carex* peat and the Puutiosuo treatment wetland (6.0 ha, which is 6.6% of the peat extraction area) was originally a more oligotrophic sedge fen with *Sphagnum* peat. The vegetation in the Kompsasuo wetland has changed during its use for water purification to a more flood meadow type of community comprising plants that tolerate high water level fluctuations (Kaasinen, 2003).

In the frost-free period from May to October (184 d), the typical hydraulic load to the Kompsasuo wetland is about  $15 \text{ mm d}^{-1}$  and to Puutiosuo wetland about  $18 \text{ mm d}^{-1}$ . Annual peak runoff typically occurs during snowmelt in spring. The wetlands are similar

as regards their flow patterns: most of the water flows as near-surface flow in the middle of the wetland (preferential flow area (PFA)), with slow-flow areas located on both sides of the PFA. In the frost-free period, the PFA in Kompsasuo is reported to occupy about 40% of the wetland and in Puutiosuo about 48% of the wetland (Ronkanen and Kløve, 2009). The annual P load to both wetlands in the frost-free period is about  $3.5 \text{ kg ha}^{-1}$ , of which about 52% is removed. The annual P balance for both wetlands was calculated from the inflow and outflow water quality data as loads provided by the peat extraction company Vapo Oy in previous research projects since construction of the treatment wetlands. The water sampling interval varied from once a week to once a month depending on the prevailing monitoring programme.

The depth profiles of peat Al, Fe and P concentrations were studied from the surface layer down to 50 cm depth at intervals of 10 cm in the highly loaded middle line (M1–M4) of the Kompsasuo wetland after 15 years of loading (Fig. 1). At the respective sampling points, the surface peat (0–10 cm) was also sampled two years later. On the same occasion, peat samples were taken by auger (cross-section  $8 \text{ cm} \times 8 \text{ cm}$ , length 70 cm) from 0 to 50 cm depth in both wetlands and in their reference peatlands (50 and 150 m away from the treatment wetlands), which are not affected by peat extraction runoff. The Puutiosuo treatment wetland had been used for 18 years prior to sampling. The data for Kompsasuo from different years proved not to be significantly different (sign test  $p=0.625$ ) and in further analyses the datasets were therefore merged. In order to separate solute concentrations of P and metals from the concentrations in the peat, pore water was also analysed. Peat samples from 0 to 20 cm and 30–40 cm depth in both wetlands (4 sampling points in Kompsasuo and 6 in Puutiosuo) were squeezed to extract water for total P ( $\text{P}_{\text{total}}$ ), total Al ( $\text{Al}_{\text{total}}$ ) and total Fe ( $\text{Fe}_{\text{total}}$ ) analysis. Analysing their concentrations in peat and pore water enabled determination of the fractionation coefficient  $k$ , providing an alternative *in situ* method to traditional batch testing for determining P adsorption isotherms (see Section 4.1). Furthermore, *in situ* measurements of oxygen concentration, redox potential (Eh), pH and pore water temperature were made at 10 cm below the surface, in bore holes.

### 2.2. Peat analyses and sorption capacity

In total, 68 peat samples from Kompsasuo and 50 from Puutiosuo were analysed for  $\text{Al}_{\text{total}}$  and  $\text{Fe}_{\text{total}}$  using the hydrochloric acid (HCl) method (with 6 M HCl digestion) (Andersen, 1976) and for ammonium oxalate-extractable Al ( $\text{Al}_{\text{ox}}$ ) and Fe ( $\text{Fe}_{\text{ox}}$ ) using a method modified from Niskanen (1989). The pore water samples were centrifuged at 4000 rpm for 10 min and the supernatant was filtered (approximately  $1.2 \mu\text{m}$  Whatman GF/C) to separate the liquid phase from the solid phase and analysed for  $\text{Fe}_{\text{total}}$ ,  $\text{Al}_{\text{total}}$ ,  $\text{P}_{\text{total}}$  and  $\text{PO}_4\text{-P}$ . The P concentration was analysed using the standard digestion method for spectrophotometric analysis and Fe and Al were analysed using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

In order to estimate the P adsorption capacity of the Kompsasuo treatment wetland, which had been used in peat extraction runoff treatment for 15 years, adsorption isotherms for peat from the wetland and its reference area were determined by a common batch test procedure. As Nair et al. (1984) noted that many phases in their procedure affect the results, we followed the procedure described by Heikkinen et al. (1995b) to avoid difficulties in comparing the results with those from previous analyses. The measurements were made on samples (4–6 g, 3 replicates) of peat in its natural moisture state. For each isotherm, a set of six 40-mL samples of a standard  $\text{KH}_2\text{PO}_4$ -solution (0, 8, 100, 300, 500, 1000  $\text{mg PL}^{-1}$ ) were processed. The samples were filtered through  $1.2 \mu\text{m}$  (Schleicher & Schuell GF52) and  $0.2 \mu\text{m}$  (Nuclepore) membranes and preserved

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