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# Phosphorus speciation in agricultural catchment soils and in fresh and dried sediments of five constructed wetlands

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## Abstract

Constructed wetlands and ponds (CWs) are installed to trap suspended material and particulate phosphorus (P) in agricultural runoff. This study investigated whether the P speciation and P sorption capacity of source soils differ from those of CW sediments and whether drying of dredged sediment changes its characteristics. Samples collected from five agricultural CW sites in south-west Finland, two with chemical-aided (aluminium chloride and ferric sulphate) P precipitation and all representing fine-textured mineral soils, were analysed for various P plant availability indices. Clay contents of the CW sediments were much higher than in catchment soils, likely because of selective erosion. All CW sediments were characterised by similar total P content but clearly higher content of anion exchange resin-extractable P in fresh sediments than the source soils. In general, sediment content of $NH_4F$-extractable (aluminium (Al)-associated) P was significantly lower and NaOH-extractable (iron (Fe)-associated) significantly higher than in source soils. Reduced

conditions, conducive to mobilisation of Fe-associated P, were observed in all CWs. Accumulation of sulphur (S) in sediments and a pH decline of up to two units upon drying suggested presence of Fe sulphides. Drying also increased oxalate-extractable Al and Fe (hydr)oxide content by 9-47%, resulting in lower degree of P saturation. These results indicate that dredged CW sediments differ greatly in their P retention characteristics from their parent soils. Returning CW sediments to fields is likely to decrease the amount of readily available P for crop uptake.

## 1. Introduction

In south-west Finland, many catchments are dominated by fine-textured agricultural soils. Nutrient loading over the years from these soils to watercourses is evident as eutrophication of rivers and lakes in the area and of the Baltic Sea. Water quality in the region suffers especially from excess phosphorus (P), derived mainly from intensively cultivated soils rich in P and sensitive to erosion (Ekholm, 1998).

Constructed wetlands and ponds (CWs) have been included in the Finnish agro-environmental support scheme since Finland joined the EU in 1995. In order to qualify for subsidies, a CW must be larger than 0.3 ha, it must comprise more than 0.5% of the upstream catchment area and more than 20% of the catchment area must consist of agricultural land. CWs have become popular tools in attempts to decrease the load of nutrients and eroded soil from agricultural land to watercourses. Since 1995, 1064 subsidised CWs have been established in Finland (Westinen, pers. comm.).

The dissolved P fraction in agricultural runoff is entirely available for biological utilisation (Ekholm and Krogerus, 2003). However, most of the P (73-94%; Uusitalo et al., 2003) carried by surface runoff and field drainage waters from clay soils in SW Finland is in particulate form, denoting P bound to suspended clay and organic matter, and more than half of particulate P is potentially bioavailable (Maynard et al., 2009), which can be utilised by algae, bacteria and plants (see e.g. Sharpley et al., 1991; Ekholm, 1994; Uusitalo et al., 2003). Decreasing the load of suspended particles to freshwaters is important in controlling eutrophication.

The material ending up in CWs is subjected to several processes which affect the P content and other characteristics of the eroded material, during erosion and after sedimentation in CWs. Phosphorus bound to Al (hydr)oxides primarily controls the P concentration in the soil solution of non-calcareous soils (Hartikainen, 1982) and, during water erosion events, adds to dissolved P stock

transported because of dilution of the soil solution. After off-field transport and sedimentation in CWs, mobilisation of redox-sensitive P bound to Fe(III)(hydr)oxides may take place, depending on oxygen ($O_2$) conditions in the sediment. Under anoxic conditions, Fe(III) is reduced to Fe(II) and P bound to this sorption component is released to pore water (Wildung et al., 1977; Olila and Reddy, 1997) and, via diffusion, to overlying water. Dissolution of Fe(III) is conducive to decreased P retention capacity of sediments in coastal marine areas (Jensen et al., 1995), but also in waterlogged soils and sediments (Khalid et al., 1977). In water bodies receiving high amounts of organic carbon (C) in the presence of $SO_4^{2-}$, Fe(III) can be reduced to Fe sulphides, which are not active P sorption associations, decreasing the capacity of the sediment to retain P (Roden and Edmonds, 1997; Lehtoranta et al., 2009, 2015).

Over time, much soil material originating from surrounding fields accumulates in the bottom of CWs and has to be removed regularly. When dredged, anoxic sediment is brought into an oxic environment and Fe(II) is reoxidised to Fe(III)(hydr)oxides. Drying also increases the amount of Al (hydr)oxides by breaking down Al complexed with organic matter. These newly formed metal oxide surfaces are effective in retaining P.

The Ministry of Agriculture and Forestry in Finland recommends that farmers recycle CW sediment back to fields, with the aim of closing the agricultural P cycle. Therefore it is important to identify key factors affecting changes in the P solubility of sedimented material and predict the likely environmental consequences of field application of CW sediments. Our aim was to determine how soil material transport from soil to CW, often with reduced conditions at the bottom, is reflected in its P speciation. The second aim was to test how dredging and oxidation of sediment matter affects the abundance of P pools and the P sorption capacity of the material. This information is essential when assessing the value of the dredged material as a P source to plants, and if the material affects soil P sorption characteristics when returned to the field.

## 2. Materials and methods

### *2.1 Study sites*

The study sites represented five agricultural CWs established on fine-textured mineral soils in SW Finland (Fig. 1, Table 1). In all surrounding catchments, soil type according to the WRB system (IUSS Working Group WRB, 2014) is Stagnosol. The CWs had been constructed 6-17 years before the start of the study. Two of the sites (Kakskerta and Nautela) had chemically assisted P precipitation, with aluminium chloride solution (trade name Kempac 18) at Kakskerta and granular ferric sulphate ($Fe_2(SO_4)_3$, trade name Ferix-3) at Nautela being added into the water entering the CWs. This chemical treatment has been performed for 9 years at Kakskerta (since 2003), with the exception of occasional interruptions, and for 1.5 years at Nautela (since 2011; see Uusitalo et al., 2015).

Arable land comprises 50-100% of the land use in the five catchments (Table 1), mostly for growing cereals. At all sites, the fields have subsurface pipe drainage system. The catchment areas around the CWs at Liedonperä, Hovi and Nautela have conventional crop rotation with autumn ploughing, whereas at Kakskerta site the catchment is agricultural grassland, and at Ojainen a no-till cropping system is applied. Only Hovi and Liedonperä CWs meet the mandatory requirements on size and share of the catchment area, although the Hovi CW is an order of magnitude larger than the recommended size in relation to the small catchment. A more detailed description of that CW can be found in Liikanen et al. (2004).

### *2.2 Soil samples*

The samples studied were collected in August 2012. Composite soil samples were taken from the surrounding fields of each CW on three transects that were visually set to represent the field area

99 from which most of the CW sediments would likely originate. The samples representing each
100 transect consisted of three subsamples taken approximately every 30 m from the CW diagonally to
101 the main slope. Sampling was carried out with a spade from the Ap horizon (0-20 cm depth). Soil
102 samples were allowed to air-dry, crushed and sieved (2 mm).

103

104 *2.3 Sediment samples*

105 The sediment samples were collected with a Limnos (Limnos Ltd, Turku, Finland) sediment
106 sampler (acrylic plastic cylinder, 94 mm in diameter, 600 mm in length) from an open water area,
107 when present, in the deepest parts of the CWs with a water depth of about 1-2 m. The depth of the
108 relatively loosely settled sediment profiles reached with the sampler was 29 cm at Ojainen,
109 Liedonperä and Hovi. However, because the Kakskerta and Nautela CWs were built as a widening
110 of the ditch, there were no deeper open water areas and the sediments were collected with a long-
111 handled dipper at about 0-10 cm depth. During sampling, the temperature of the sediments ranged
112 between +11.5 and +15.5 °C.

113 Redox potential (Eh) and pH of the sediments from 0-10 cm depth were measured immediately in
114 the field with a platinum electrode and pH electrode using a handheld Scientific Instruments IQ170
115 pH/Eh meter. The samples were then stored in plastic buckets fitted with lids and transported to the
116 laboratory within two hours. A subsample of each sediment was allowed to air-dry, crushed in a
117 mortar and sieved (2 mm) for later analyses. The remaining samples were stored wet at +5 °C in
118 darkness until analysed.

119

120

121 *2.4 Laboratory analyses*

122 The soil and sediment samples were analysed for the indices of P bioavailability, P sorption
123 properties and some other characteristics listed below. For most analyses, both fresh and dried
124 sediment samples were used to illustrate the changes upon dredging and drying of the sediment.

125

126 *2.4.1 Anion exchange resin (AER) extraction*

127 To estimate the amount of potentially desorbable P from soil and sediment material, soil samples
128 and fresh and dried sediment samples were extracted by anion exchange resin (AER) (Sibbesen,
129 1977; Uusitalo and Ekholm, 2003) 4 weeks after sampling. In the method used, 1 g strong basic
130 AER (Dowex 1×8, Fluka Chemika, Neu-Ulm, Germany), with about 2 mmol anion exchange
131 capacity, was enclosed in small nylon netting (Sefar Nitex, Sefar Inc., Heiden, Switzerland) bags
132 with mesh size 0.25 mm. Before extraction, AER was converted into $HCO_3^-$ form by washing the
133 bags for 4 h with two portions of 0.5 M $NaHCO_3$ solution (Sibbesen, 1978).

134 The extraction was performed with 1 g sample dry matter and 40 ml deionised water in a 50-ml
135 extraction tube with one AER bag. The tubes were shaken overnight (20 h) on an orbital shaker at
136 100 rpm. The AER bag was then removed, washed with deionised water and shaken in 40 ml 0.5 M
137 NaCl for 4 h to displace P from the AER into the solution. The bag was removed from the
138 extraction vessel and the NaCl solution was acidified with 1 ml 6 M HCl and allowed to stand
139 overnight to remove $CO_2$. The P concentration of the NaCl solution was measured with a Lachat
140 (Milwaukee, WI) QC Autoanalyzer using the method of Murphy and Riley (1962) with ascorbic
141 acid as the reducing agent. The AER extraction was performed in triplicate.

142

143 *2.4.2 Extraction of redox-sensitive P*

144 Both fresh and dried sediment samples (but not soil samples) were extracted with bicarbonate-
145 buffered sodium dithionite (BD) solution to analyse redox-sensitive P, as described by Uusitalo and
146 Turtola (2003). In brief, 0.2 g sediment samples were weighed into 250-ml plastic bottles and 100
147 ml deionised water were added. Aliquots of 2.5 ml of both solutions were added to the samples,
148 bicarbonate (0.298 M $NaHCO_3$) being prepared for daily use and the dithionite solution (0.574 M
149 $Na_2S_2O_4$) just before extraction. The sample bottles were capped and shaken on an orbital shaker for
150 15 min at 120 rpm. After extraction, the samples were immediately filtered through a 0.2 µm
151 Nuclepore polycarbonate filter (Whatman, Maidstone, UK). Then 10 ml filtrate were digested with
152 4 ml persulphate (50 g $K_2S_2O_8$ in 1 l of 0.4 M $H_2SO_4$) in an autoclave (+120 °C, 100 kPa, 30 min)
153 in order to oxidise the excess dithionite. The P concentration was measured as in AER-P analysis.
154 The BD extraction was performed with quadruplicate samples.

155

156 *2.4.3 Total P and organic P*

157 Total P in the soil and dried sediment samples was determined in duplicate with the $H_2SO_4$-$H_2O_2$-
158 HF extraction method (Bowman, 1988). Organic P was determined by the ignition method of Olsen
159 and Sommers (1982) using 0.5 M $H_2SO_4$ extraction (1:50 w:v; 16 hours) on triplicate samples. The
160 P concentration was determined using the method of Murphy and Riley (1962) with ascorbic acid as
161 the reducing agent. A Lachat (Milwaukee, WI) QC Autoanalyzer and a spectrophotometer
162 (Shimadzu UV-120-02, Kyoto, Japan) were employed for total and organic P measurements,
163 respectively.

164

165

166 *2.4.4 Inorganic P fractions*

167 The inorganic P reserves in the soil and (fresh and dried) sediment samples were determined by the
168 method of Chang and Jackson (1957) as modified by Hartikainen (1979). Triplicate samples were
169 sequentially extracted, using a soil-to-solution ratio 1:50, with: i) 1 M $NH_4Cl$ (30 min), assumed to
170 extract the most easily soluble P and exchangeable Ca; ii) 0.5 M $NH_4F$ (pH 8.5) (1 h), Al-bound P;
171 iii) 0.1 M NaOH (16 h), Fe-bound P; and iv) 0.25 M $H_2SO_4$ (1 h), Ca-bound apatitic P. The
172 suspensions were centrifuged (15 min, 3846×*g*) and $NH_4Cl$ extracts were filtered through Munktell
173 OOR paper filters (Munktell Filter AB, Grycksbo, Sweden). For $NH_4F$ and NaOH extracts,
174 dissolved humus was removed by precipitation with 0.5 M $H_2SO_4$ (Hartikainen, 1979). The soil
175 matter pellet remaining after the $NH_4F$ and NaOH extractions was washed with saturated NaCl
176 solution to prevent carryover of P to the following step. The P concentration was analysed with the
177 molybdenum blue method of Murphy and Riley (1962) using a spectrophotometer (Shimadzu UV-
178 120-02, Kyoto, Japan).

179

180 *2.4.5 Oxalate-extractable Al and Fe, degree of P saturation*

181 The short-range ordered (hydr)oxides of Al and Fe ($Al_{ox}$ and $Fe_{ox}$) were analysed in dry soil and
182 (fresh and dried) sediment samples using the ammonium oxalate extraction method by
183 Schwertmann (1964) followed by ICP determination. Duplicate 0.5 g samples were extracted with
184 25 ml acidic (pH 3.0) ammonium oxalate solution (57% 0.2 M $(NH_4)_2C_2O_4 \times H_2O$, 43% 0.2 M
185 $C_2H_2O_4 \times 2\ H_2O$) for 4 h in the dark. After centrifuging (15 min, 3846×*g*), the aliquots were filtered
186 through a blue ribbon paper filter (Schleicher & Schuell, Dassel, Germany).

187 The P sorption capacity (PSC; Lookman et al., 1995) was calculated as:

188 $$PSC\ (mmol\ kg^{-1}) = 0.5 \times (Al_{ox} + Fe_{ox}) \quad (1)$$

The degree of P saturation (DPS) was then calculated according to Peltovuori et al. (2002) using the results of the Chang and Jackson fractionation as:

$$DPS_{\Sigma}\ (\%) = 100 \times P_{\Sigma} / PSC \quad (2)$$

where $P_{\Sigma}$ is the sum of $NH_4Cl$-, $NH_4F$- and NaOH-extractable P in mmol $kg^{-1}$. We also calculated the DPS separately for $Al_{ox}$ and $Fe_{ox}$ on molar basis (Lookman et al., 1995; Hartikainen et al., 2010) as:

$$DPS_{Alox}\ (\%) = 100 \times Al\text{-}P / 0.5 \times Al_{ox} \quad (3)$$

$$DPS_{Feox}\ (\%) = 100 \times Fe\text{-}P / 0.5 \times Fe_{ox} \quad (4)$$

where Al-P is $NH_4F$-extractable P and Fe-P is NaOH-extractable P by Chang and Jackson fractionation.

*2.4.6 Other soil and sediment characteristics*

Total contents of C and nitrogen (N) were determined with a LECO CN-analyzer (TruSpec, Leco Corporation, St. Joseph, MI, USA). Total sulphur (S) content was determined by the aqua regia extraction method according to ISO 11466:1995. The concentration of sulphate-sulphur ($SO_4^{2-}$-S) was measured by ICP-OES (Thermo Scientific iCAP 6300 Duo MFC, Waltham, USA) in acidic ammonium acetate extracts (0.5 M acetic acid, 0.5 M ammonium acetate, pH 4.65, AAAc) according to the Finnish agronomic soil testing protocol (Vuorinen and Mäkitie, 1955). The AAAc solution is used to determine readily plant-available macronutrients, including S, in soil. Extraction is performed at a 1:10 soil-to-solution ratio for one hour. Particle size distribution of soils and sediments was analysed with a pipette method (Elonen, 1971).

Cesium-137, originating from the fallout of the Chernobyl accident in 1986, was analysed on air-dried sediments of all CWs and on soil samples of Ojainen and Hovi without replicates. The $^{137}Cs$ activity was measured with a gamma counter (Ultro gamma 1280, 3" x 3" NaI(Tl), Wallac Oy, Turku, Finland). The counting efficiency of the gamma counter was 47%.

### *2.5 Statistical analyses*

For the parameters analysed, differences in means between soils, fresh sediment and dried sediment within each site were tested with one-way analysis of variance followed by post-hoc separation of means using the Tukey´s test. In cases of non-normality (total P, $NH_4Cl$-P, $NH_4F$-P, NaOH-P, AER-P, $Al_{ox}$, $Fe_{ox}$), logarithmic transformation was performed prior to the analysis. For analysis of the general trends in the material over all sites, paired tests were performed between soil and fresh sediment, and fresh sediment and dry sediment, using the nonparametric Wilcoxon signed rank test. Significance was taken as $p<0.05$. Statistical analyses were conducted with IBM SPSS Statistics 22.

## 3. Results

### *3.1 General properties of the soils and sediments*

With 50-100% arable land in the catchments and the clayey topsoil texture (Table 2), the soils were prone to erosion. Clear signs of erosion were not present in August 2012 during sampling, but most of the annual erosion in this area takes place during winter rains and spring snowmelt (see Turtola et al., 2007). Subsurface drainflow and surface runoff are both important transport pathways for soil particles and particulate P in the clay soils of SW Finland (Turtola et al., 2007; Uusitalo et al., 2003).

At Ojainen and Hovi, $^{137}$Cs activities in sediments were 64 and 59 Bq kg$^{-1}$, respectively, whereas the contents in the field soils of these sites were lower, 53 and 55 Bq kg$^{-1}$. The enrichment ratios for $^{137}$Cs (ER, the ratio of $^{137}$Cs activity in sediment to that in topsoil samples) were 1.22 and 1.08 at Ojainen and Hovi, respectively. The $^{137}$Cs activities in the sediments of Liedonperä, Kakskerta and Nautela were 69, 46 and 74 Bq kg$^{-1}$, respectively. Because $^{137}$Cs is only found in topsoil (to the maximum depth of tillage of about 20 cm), activity in subsoil being less than 10 Bq kg$^{-1}$ in southern Finland (Uusitalo et al., 2001), these results suggest that the sediment matter originates mainly from the topsoil of catchment fields.

At all sites, the sediment had a brown and slightly fluffy surface layer (0.5-2.0 cm). Below the surface, the relatively loosely settled matter sampled was light or dark grey and there were regular black spots, presumably indicative of the presence of sulphides. The Eh values (meter readings in situ) varied from -21 mV at Ojainen to 105 mV at Nautela (Table 2). The bottom of all CWs thus seemed to be in anoxic conditions. The sediments in the CWs were very fine-textured, consisting 54-82% of clay-sized particles (<0.002 mm). Compared with the catchment soils, the sediments contained 10-80% more clay-sized particles.

246 Some accumulation of Tot-C and Tot-N in the sediments was observed, particularly in the CWs
247 where sedimentation was chemically assisted (Table 3). The addition of Fe and Al salts most likely
248 resulted in flocculation of fine particles and dissolved humus in low flow periods, resulting in
249 higher C and N concentrations than in parent soils. The sediments contained 2.5- to 7-fold more
250 Tot-S than the corresponding soils. Furthermore, considerably more $SO_4^{2-}$-S was extracted from the
251 dried sediments than from the soils (Table 3). The low ratio of $SO_4^{2-}$-S/Tot-S in the agricultural
252 soils (Table 3) indicated that S was mainly organic, but more inorganic S was found in the
253 sediments in the Ojainen, Hovi and Nautela CWs. This, together with the low redox potential in the
254 fresh sediments in these CWs, might be associated with formation of sulphide minerals, which were
255 subsequently oxidised to $SO_4^{2-}$ upon drying of the sediments.

256 The pH in the soils was in the range 6.0-6.9 and in four of the five fresh sediments it was in the
257 range 6.3-7.3. At Nautela, the pH was lower (5.2) in fresh sediment, most probably as a result of
258 application of acidic ferric sulphate into the incoming water (Table 2). After drying of the
259 sediments, the pH value decreased most (by 2.2 pH units) at Ojainen, whereas for other sediments
260 the pH decrease was 1.6 for Liedonperä and 0.6 for Hovi and Kakskerta. The pH decrease was
261 probably due to the acidity produced in the oxidation reaction of Fe sulphides.

262

263 *3.2 Total P in soils and sediments*

264 The amount of total P (TP) in the sediments was similar to the amount in the parent soils, the
265 difference being within ±10%. The highest TP contents in the soil (1450 mg P $kg^{-1}$) and sediment
266 (1467 mg P $kg^{-1}$) were found at Ojainen (Fig. 2), a clay soil known to have received much dairy
267 cow manure in the past (P class good to high, AAAc-extractable P at 24 mg $l^{-1}$). Organic P
268 accounted for 19-38% (mean 27%) of TP in soils and 9-27% (mean 19%) in four of the sediments.

In the Kakskerta sediment, however, 45% of the TP was in organic form (Fig. 2) and this sediment also had by far the highest Tot-C content.

### *3.2.1 Chang and Jackson P fractions*

The Chang and Jackson fractionation extracted 29-55% (mean 44%) and 37-53% (mean 47%) of TP from the soils and sediments, respectively. The largest Chang and Jackson P fraction in the studied soils and sediments was either NaOH-P or $H_2SO_4$-P (Fig. 2). Loosely bound P, the $NH_4Cl$-extractable pool, was negligible (<1 mg $kg^{-1}$) in all samples. The average share of residual P, not accounted for in the different fractions, was 29% (range 19-46%).

At three of the sites, the $NH_4F$-P fraction (Al-associated P) was clearly lower in sediments than in soils, comprising 39-54% of the parent soil content. The exceptions were Kakskerta and Hovi CWs. The Kakskerta sediment was affected by Al chemical feed to incoming water, an obvious reason for the increase in Al-associated P. At Hovi, Al-P was also clearly higher in the sediment than in soil, but without any known inputs of reactive Al. The most striking difference from the other sites was the very large size of the Hovi CW, 5% of the catchment area (Table 1). Pairwise statistical testing over all sites suggested that $NH_4F$-P concentrations were lower in fresh sediments than in soils when the Kakskerta CW was excluded from the testing.

The sediment NaOH-P pool, representing P bound by Fe (hydr)oxides, was substantially greater than in the parent soils at three of the sites, while at Liedonperä it was about equal to the parent soil content. At Kakskerta, Fe-P was lower in sediment than in soil. Because Al feed at the CW inlet has added an unknown Al oxide mass to the Kakskerta sediment over the years, comparisons between the soil and the sediment P fractions may not be meaningful at this site. A comparison of NaOH-P

291 concentrations over all sites showed that fresh sediments had significantly higher concentrations
292 than the parent soils (even when Kakskerta was included in the test).

293 As for the $H_2SO_4$-P, there were no statistically significant differences between soils and sediments
294 and no consistent trends were found in the material. The sum of the P fractions also behaved
295 inconsistently, but it was noted that at Hovi, the sum of P fractions was higher for the sediment than
296 for the soil (Fig. 2).

297 The comparisons between fresh and dried sediments revealed that drying had some influence on P
298 fractions (Fig. 2). The $NH_4F$-P pool decreased in the sediments from Kakskerta, Liedonperä and
299 Hovi after drying, but was unaffected in the Ojainen and Nautela sediments. Over all sites, $NH_4F$-P
300 was found not to differ between fresh and dried sediments. Drying of the sediments also
301 significantly ($p$=0.012) decreased the NaOH-P pool in all cases except at Hovi, where it was
302 unaffected. Some increases in the $H_2SO_4$-P pool upon drying were recorded at all sites, but these
303 increases were not statistically significant.

304

305 *3.2.2 Desorbable and redox-sensitive P*

306 Over all CWs studied, the concentrations of desorbable P, estimated by AER extraction, in fresh
307 sediments were significantly ($p$=0.017) higher than in the parent soils (Fig. 3a). Thus P would be
308 released by desorption more easily from a unit mass of fresh CW sediment than from the
309 agricultural soil in its catchment area. The difference in AER-P concentrations between parent soils
310 and fresh sediments was especially large at Ojainen and Hovi, with a 10-fold higher concentration
311 in Hovi CW fresh sediment, but distinct (1.6- to 3.6-fold) differences were also recorded for the
312 other sites.

313 Upon drying of the sediments, AER-P declined to about the level in the parent soil except for Hovi
314 CW, where drying did not greatly decrease P extractability by AER. Over all sites, a pairwise
315 comparison between the fresh and dried sediments showed a decline that was close to marginally
316 statistically significant ($p$=0.047).

317 High concentrations of redox-sensitive (BD-extractable) P were found in fresh and dried sediments
318 (Fig. 3b). The fresh sediments released as much as 8-48% of TP during the BD extraction, with the
319 highest values in Ojainen sediment and the lowest in Kakskerta sediment. Drying decreased BD-
320 extractable P in all sediments, but within-site differences were significant only at Ojainen.

321

322 *3.3 Degree of P saturation*

323 Among the catchment soils, the highest PSC value (Eq. 1) was found at Kakskerta (Table 4), which
324 had the highest clay content (72%) and the highest C concentration (4.6%) of the fields studied.
325 Fresh sediments had mostly similar, or at Liedonperä somewhat higher, PSC than their parent soils.
326 However, as a result of the Al chemical treatment at Kakskerta, sediment PSC was twice that in the
327 parent soil. The sediment in the other chemical-assisted CW, Nautela, did not bear any notable
328 traces of the $Fe_2(SO_4)_3$ feeding to the inflow, with only slightly higher Fe (hydr)oxide content in
329 sediment than in the parent soil (Table 4). Drying of the sediments, on the other hand, increased
330 their PSC values in all cases.

331 The DPS indices showed the same trend as the Chang and Jackson P fractions, in that $DPS_{Feox}$ was
332 larger than $DPS_{Alox}$ in all sediments and soils (Table 4). $DPS_{Alox}$ was smaller in the dried than the
333 fresh sediments, because drying substantially increased the $Al_{ox}$ concentration, and consequently the
334 PSC. When the DPS of $Al_{ox}$ and $Fe_{ox}$ was combined in the same index ($DPS_{\Sigma}$), the dried sediments
335 were less saturated with P than the fresh sediments.

## 4. Discussion

### *4.1 Parent soils and CW sediments*

Our first objective was to compare the content, pools and potential bioavailability of P in the parent soils with those in their sediment counterparts in actual CWs, i.e. without drying. The differences observed between the parent soils and fresh sediments are probably partly a result of selective mobilisation and transport of soil matter and the changes that occur during transport from field. They are also partly affected by resuspension and settling cycles in CWs and the chemical and biological factors operating during sediment consolidation.

Accumulation of clay-sized material in CWs was substantial, and likely a result of selective erosion and transport of fine-sized soil material. The sediment organic C and N contents were typically also higher than in the parent soils, especially when Al or Fe chemicals had been added to the CW inflow. Considerable amount of S was accumulated in CWs at all sites and all sediments appeared anoxic during sampling that occurred in August.

In all cases studied, the amount of TP in CW sediments was practically the same as in the parent soils. Concentrations in soils (975-1450 mg $kg^{-1}$) were typical of fertilised clay soils in Finland (e.g. Hartikainen, 1979; Uusitalo et al., 2003; Soinne et al., 2011). The average proportion of organic P in the soils studied (at 27%) was somewhat lower than reported in other studies of plough layers of Finnish cultivated mineral soils (35%) (Kaila, 1963a; Peltovuori, 2006). Organic P in CW sediments was on average only slightly lower (24%) than in the parent soils. The similarity in TP and organic P between the soils and sediments studied suggests that the sediment sampled from the bottom of CWs was soil material originating from the surrounding fields, and not the subsoil of the CW. This was also supported by the relatively high $^{137}Cs$ activity of the sediment samples. Because

of low mobility of fallout $^{137}Cs$ in soil, its elevated concentration in sediments suggests that topsoil is the source of the CW sediments (see Mahara, 1993; Walling and Woodward, 1995).

Even though the TP content was not changed during the erosion process and the residence of soil material in the CWs, there were differences in the P fractions between the soil and sediment. In Finnish non-calcareous soils, P originating from fertiliser is generally retained to Al (hydr)oxides ($NH_4F$-P) and Fe (hydr)oxides (NaOH-P) (e.g. Kaila, 1963b; Hartikainen, 1989; Peltovuori, 2006). In our material the sum of Al- and Fe-bound P was the largest pool found in soils of the catchments, but these fractions proved to be clearly affected by transport and the processes in CWs, anoxic sediment conditions presumably being one driver for these changes. The fresh sediments were typically lower in Al-associated P (except Hovi and Kakskerta), but higher in Fe-associated P (except Kakskerta) than their parent soils (Fig. 2). During the transport and residence in CWs, the ambient solution (i.e. runoff water or water in CW) surrounding eroded soil becomes lower in dissolved P concentration than was present in soil solution, and a considerable fraction of Al-bound P may be depleted (Hartikainen, 1982).

Changes in P saturation of one sorption component (Al or Fe (hydr)oxide surface) likely affects the P saturation of the other component (see Hartikainen, 1982; Hartikainen et al., 2010). In particular, Fe (hydr)oxides can be assumed to be partly dissolved and re-precipitated as redox conditions shift periodically in the bottom of the CWs. Once the sediment turns anoxic, P saturation of Al (hydr)oxides most likely increases as a result of solubilisation of Fe-P associations. Subsequently, when oxic conditions are re-established, Fe (hydr)oxide precipitation produces fresh, P-depleted surfaces that are effective sinks for P and compete with Al (hydr)oxides that seek to buffer the changes in P concentration of the ambient solution.

At the time of sampling, redox state was low in all CW sediments studied and much higher concentrations of AER-extractable P were present in sediments than their parent soils. Chemical

384 reduction by BD extraction also showed that there were large reserves of redox-sensitive P,
385 representing 23-48% of TP in the sediments (excluding Kakskerta, where Al-chemical treatment
386 had diminished the BD-P fraction). Thus, the redox state during sampling, even if anoxic, had not
387 depleted redox-labile P pool in sediments. Some part of the reductant-soluble P most likely
388 originates from organic complexes, e.g. Farmer et al. (1994) estimated that 16% of reductant-
389 soluble P was derived from organic P in lake sediments having 7-10% organic C. Suzumura and
390 Kamatani (1995) found that the extent and rate of organic P mineralisation is strongly regulated by
391 the redox conditions in marine environments. Inositol hexaphosphate is a significant carrier of
392 organic P in suspended matter, and under anoxia it may be rapidly and extensively mineralised as a
393 result of the release of inositol hexaphosphate molecule from the Fe-associated sediment particles
394 upon their dissolution at low redox conditions (Suzumura and Kamatani, 1995).

395 The two special cases in our material were Hovi, with its very large surface area in relation to
396 catchment size, and Kakskerta, with its long history of Al addition. Hovi CW had the highest
397 amount of Al-bound P in fresh sediment of all CWs examined (excluding the chemically treated
398 Kakskerta) and the highest $DPS_{Feox}$ in the dried sediment. In a previous study, Hovi CW was
399 identified as very efficient in retaining P (Liikanen et al., 2004). This high efficiency was suggested
400 by Liikanen et al. (2004) to result from the CW being established on subsoil of former arable land
401 that is poor in P and rich in reactive oxides. As in the present study, Liikanen et al. (2004)
402 demonstrated the important role of Al (hydr)oxides in retaining P, since the wetland retained P even
403 in anoxic conditions. However, relatively high amounts of AER-P were extracted from both fresh
404 and dried sediment samples, suggesting that substantial amounts of the P retained in the Hovi CW
405 sediment could be mobilized if water becomes depleted in dissolved P.

406 At the Kakskerta site, the chemically assisted sedimentation was reflected in an obvious manner: a
407 high share of Al-associated P and twice as high PSC value of the sediment compared with the

parent soil. The higher AER-P of the sediment than the soil at this site suggested that here too, the sediment may periodically act as a source of soluble P.

*4.2 Reoxidation of CW sediments*

Our second objective was to investigate how dredging and drying (reoxidation) affected the P solubility and P sorption capacity of CW sediments. The clay-enriched sediment material was rich in oxides after drying. In particular, the content of Al (hydr)oxides increased after drying of the sediments. The origin of the newly formed oxides can be assumed to be the drying-induced breakdown of Al and Fe complexes of organic matter (Bartlett and James, 1980; Haynes and Swift, 1985). For example, Peltovuori and Soinne (2005) observed an increase in Al and Fe contents assumed to originate from soil organic matter, after air-drying of soils. The modest, statistically non-significant increase in Fe (hydr)oxides after drying of sediments in the present study may also be a result of dissolved Fe(II) ions being oxidised to Fe(III). Newly formed Fe (hydr)oxides have a high specific surface area and a high amount of reactive sites for P adsorption, and thus good efficiency at removing soluble P (e.g. Mayer and Jarrel, 2000). The lower $DPS_{\Sigma}$ of the dried sediments compared with the fresh sediments and parent soils, except at Hovi, indicate that applying dredged sediments to soils would add to soil stocks of reactive Al and Fe (hydr)oxides, which in turn might diminish the plant availability of P.

The $H_2SO_4$-P fraction, which can be assumed to be primary apatitic P, represents a relatively large P fraction in Finnish soils and is very resistant to weathering and P transformations during runoff. The increase in the $H_2SO_4$-P fraction in dried sediments in this study was most likely a result of non-recovered NaOH-P fraction. Drying of the sediment allows formation of a more ordered crystalline structure, which could be resistant to NaOH-extraction.

A high accumulation of S in all CW sediments was observed, despite the relatively S-poor agricultural topsoils in their parent catchments. During sampling, we observed black spots, presumably indicative of sulphides, and in some cases a distinct drop in pH upon drying of the sediments. The high $SO_4^{2-}$-S concentrations found in dried sediments may thereby be due to sulphide oxidation. At Kakskerta, the content of Tot-S was more than double than at the other sites, probably as a result of the geological history of the soil. Considerably high Tot-S concentration and a coastal location indicate acid sulphate soil features and a soil originating from the Littorina period (Kivinen, 1950). At other sites, the use of S-containing fertilisers was the most likely cause of the increased $SO_4^{2-}$ input to CWs. Accumulation of $SO_4^{2-}$-S and Tot-S in sediments adjacent to agricultural areas in the Florida Everglades has been observed by Bates et al. (2002), who also identified the importance of fertilisers as a source of S in studies using stable isotope signatures.

## 5. Conclusions

Soil material is subjected to depletion of easily soluble P during the erosional runoff process. Simultaneously, selective erosion concentrates clay particles and some Al and Fe (hydr)oxides, increasing the potential P sorption capacity of the sediment. However, high concentrations of reversibly bound P in fresh sediments were indicated by AER extraction. Anoxic conditions and reducing reactions in CW bottom sediments might result in mobilisation of Fe-bound P from the redox-sensitive reserves into the water phase and some of this P is most likely transported onwards as dissolved P out of the CW. The measured large reserves of redox-sensitive P bound to Fe (hydr)oxides indicate a risk of P release from the sediments during prolonged anoxia. Among the five Finnish CWs studied here, Hovi stands out as regards the high Al-bound P content of the sediment, indicating sorption of P even in anoxic conditions. Although the agricultural topsoils were low in S, high S accumulation into the CW sediments was observed. If associated with Fe sulphide formation, this might decrease the P sorption capacity of the CW sediments. Drying of dredged sediment probably increases the P adsorption capacity of eroded soil material by forming new Al and Fe (hydr)oxide surface via drying-induced breakdown of metal complexes with organic matter, and perhaps also via oxidation of Fe sulphides and dissolved Fe.

In summary, returning dredged sediment material back to fields surrounding CWs established on fine-textured mineral soils might decrease P supply to plants. Reoxidation of the sediments markedly increases the P sorption capacity of eroded soil material, in which the accumulated Al and Fe compounds form new, P-depleted oxide surfaces.

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467 **References**


468 Bartlett, R., James, B., 1980. Studying dried, stored soil samples – some pitfalls. Soil Sci. Soc. Am.
469 J. 44, 721-724.

470 Bates, A. L., Orem, W.H., Harvey, J.W., Spiker, E.C., 2002. Tracing sources of sulfur in the Florida
471 Everglades. J. Environ. Qual. 31, 287-299.

472 Bowman, R.A., 1988. A rapid method to determine total phosphorus in soils. Soil Sci. Soc. Am. J.
473 52, 1301-1304.

474 Chang, S.C., Jackson, M.L., 1957. Fractionation of soil phosphorus. Soil Sci. 84, 133-144.

475 Ekholm, P., 1994. Bioavailability of phosphorus in agriculturally loaded rivers in southern Finland.
476 Hydrobiologia 287, 179-194.

477 Ekholm, P., 1998. Algal-available phosphorus originating from agriculture and municipalities.
478 Monog. Bor. Environ. Res. 11. Finnish Environ. Instit., Helsinki.

479 Ekholm, P., Krogerus, K., 2003. Determining algal-available phosphorus of differing origin:
480 Routine phosphorus analyses versus algal assays. Hydrobiologia 492, 29-42.

481 Elonen, P., 1971. Particle size analysis of soil. Acta Agral. Fenn. 122, 1-122.

482 Farmer, J.G., Bailey-Watts, A.E., Kirika, A., Scott, C., 1994. Phosphorus fractionation and mobility
483 in Loch Leven sediments. Aquat. Conserv. Mar. Freshw. Ecosys. 4, 45-56.

484 Hartikainen, H., 1979. Phosphorus and its reactions in terrestial soils and lake sediments. J. Scient.
485 Agric. Soc. Finland 51, 537–624.

486 Hartikainen, H., 1982. Water soluble phosphorus in Finnish mineral soils and its dependence on soil
487 properties. J. Scient. Agric. Soc. Finland 54, 89-98.

Hartikainen, H., 1989. Effect of cumulative fertilizer dressing on the phosphorus status of mineral soils. I. Changes in inorganic phosphorus fractions. J. Agric. Sci. Finland 61, 55-59.

Hartikainen, H., Rasa, K., Withers, P., 2010. Phosphorus exchange properties of European soils and sediments derived from them. Eur. J. Soil Sci. 61, 1033-1042.

Haynes, R.J., Swift, R.S., 1985. Effects of air-drying on the adsorption and desorption of phosphate and levels of extractable phosphate in a group of acid soils, New Zealand. Geoderma 35, 145–157.

IUSS Working Group WRB, 2014. World Reference Base for Soil Resources 2014.International soil classification system for naming soils and creating legends for soil maps. World Soil Res. Rep. 106. FAO, Rome.

Jensen, H.S., Mortensen, P.B., Andersen, F.Ø., Rasmussen, E., Jensen, A., 1995. Phosphorus cycling in a coastal marine sediment, Aarhus Bay, Denmark. Limnol. Oceanogr. 40, 908-917.

Kaila, A., 1963a. Organic phosphorus in Finnish soils. Soil Sci. 95, 38-44.

Kaila, A., 1963b. Fertilizer phosphorus in various fractions of soil phosphorus. J. Agric. Sci. Finland 35, 36-46.

Khalid, R.A., Patrick, W.H., DeLaune, R.D., 1977. Phosphorus sorption characteristics of flooded soils. Soil Sci. Soc. Am. J. 41, 305-310.

Kivinen, E., 1950. Sulphate soils and their management in Finland. 4th Int. Congr. Soil Sci., Amsterdam II, pp. 259-262.

Lehtoranta, J., Ekholm, P., Pitkänen, H., 2009. Coastal eutrophication thresholds: A matter of sediment microbial processes. Ambio 38, 303–308.

508 Lehtoranta, J., Ekholm, P., Wahlström, S., Tallberg, P., Uusitalo, R., 2015. Labile organic carbon
509 regulates phosphorus release from eroded soil transported into anaerobic coastal systems. Ambio
510 44, 263–273.

511 Liikanen, A., Puustinen, M., Koskiaho, J., Väisänen, T., Martikainen, P., Hartikainen, H., 2004.
512 Phosphorus removal in a wetland constructed on former arable land. J. Environ. Qual. 33, 1124-
513 1132.

514 Lookman, R., Vandeweert, N., Merckx, R., Vlassak, K., 1995. Geostatistical assessment of the
515 regional distribution of phosphate sorption capacity parameters (Feox and Alox) in northern
516 Belgium. Geoderma 66, 285– 296.

517 Mahara, Y., 1993. Storage and migration of fallout strontium-90 and cesium-137 for over 40 years
518 in the surface soil of Nagasaki. J. Environ. Qual. 22:722–730.

519 Mayer, T.D., Jarrell, W.M., 2000. Phosphorus sorption during iron(II) oxidation in the presence of
520 dissolved silica. Water Res. 34, 3949–3956.

521 Maynard, J.J., O'Geen, A.T., Dahlgren, R.A., 2009. Bioavailability and fate of phosphorus in
522 constructed wetlands receiving agricultural runoff in the San Joaquin Valley, California. J. Environ.
523 Qual. 38, 360−372.

524 Murphy, J., Riley, J.P., 1962. A modified single solution method for determination of phosphate in
525 natural waters. Anal. Chim. Acta 27, 31-36.

526 Olila, O.G., Reddy, K.R., 1997. Influence of redox potential on phosphate-uptake by sediments in
527 two sub-tropical eutrophic lakes. Hydrobiologia 345, 45-57.

528 Olsen, S.R., Sommers, L.E., 1982. Organic phosphorus – Ignition Method, in: Page et al. (Eds.),
529 Methods of Soil Analysis, part 2 – Chemical and Microbiological Properties, second ed. Agronomy
530 Book Series No. 9. Am. Soc. Agron. and Soil Sci. Soc. Am. Madison, WI, USA, pp. 411-413.

531 Peltovuori, T., 2006. Phosphorus in agricultural soils of Finland – characterization of reserves and
532 retention in mineral profiles. Doc. diss., Univ. Helsinki. URL:
533 https://helda.helsinki.fi/handle/10138/20819

534 Peltovuori, T., Soinne, H., 2005. Phosphorus solubility and sorption in frozen, air-dried and field-
535 moist soil. Eur. J. Soil Sci. 56, 821–826.

536 Peltovuori, T., Uusitalo, R., Kauppila, T., 2002. Phosphorus reserves and apparent phosphorus
537 saturation in four weakly developed cultivated pedons. Geoderma 110, 35–47.

538 Roden, E.E., Edmonds, J.W., 1997. Phosphate mobilization in iron-rich anaerobic sediments:
539 Microbial Fe(III) oxide reduction versus iron-sulfide formation. Arch. Hydrobiol. 139, 347–378.

540 Schwertmann, U., 1964. The differentiation of iron oxides in soil by extraction with ammonium-
541 oxalate solution. Z. Pflanzenernahr. Dungung Bodenk. 105, 194-202.

542 Sharpley, A.N., Troeger, W.W., Smith, S.J., 1991. The measurement of bioavailable phosphorus in
543 agricultural runoff. J. Environ. Qual. 20, 235-238.

544 Sibbesen, E., 1977. A simple ion exchange resin procedure for extracting plant-available elements
545 from soil. Plant Soil 46, 665-669.

546 Sibbesen, E., 1978. An investigation of the anion exchange resin method for soil phosphate
547 extraction. Plant Soil 50, 305-321.

548 Soinne, H., Uusitalo, R., Sarvi, M., Turtola, E., Hartikainen, H., 2011. Characterization of soil
549 phosphorus in differently managed clay soil by chemical extraction methods and $^{31}$P NMR
550 spectroscopy. Commun. Soil Sci. Plant Anal. 42, 1995-2011.

551 Suzumura, M., Kamatani, A., 1995. Mineralization of inositol hexaphosphate in aerobic and
552 anaerobic marine sediments: implications for the phosphorus cycle. Geochim. Cosmochim. Acta 59,
553 1021-1026.

554 Turtola, E., Alakukku, L., Uusitalo, R., Kaseva, A., 2007. Surface runoff, subsurface drainflow and
555 soil erosion as affected by tillage in a clayey Finnish soil. Agric. Food Sci. 16, 332-351.

556 Uusitalo, R., Ekholm, P., 2003. Phosphorus in runoff assessed by anion exchange resin extraction
557 and an algal assay. J. Environ. Qual. 32, 633-641.

558 Uusitalo, R., Närvänen, A., Kaseva, A., Launto-Tiuttu, A., Heikkinen, J., Joki-Heiskala, P., Rasa,
559 K., Salo, T., 2015. Conversion of dissolved phosphorus in runoff by ferric sulfate to a form less
560 available to algae: Field performance and cost assessment. Ambio 44, 286-296.

561 Uusitalo, R., Turtola, E., 2003. Determination of Redox-Sensitive Phosphorus in Field Runoff
562 without Sediment Preconcentration. J. Environ. Qual. 32, 70-77.

563 Uusitalo, R., Turtola, E., Kauppila, T., Lilja, T., 2001. Particulate phosphorus and sediment in
564 surface runoff and drainflow from clayey soils. J. Environ. Qual. 30, 589-595.

565 Uusitalo, R., Turtola, E., Puustinen, M., Paasonen-Kivekäs, M., Uusi-Kämppä, J., 2003.
566 Contribution of particulate phosphorus to runoff phosphorus bioavailability. J. Environ. Qual. 32,
567 2007-2016.

568 Vuorinen J., Mäkitie O., 1955. The method of soil testing in use in Finland. Agrogeol. Publ. 63, 1-
569 44.

570 Walling, D.E., Woodward, J.C., 1995. Tracing sources of suspended sediment in river basins: A
571 case study of the river Culm, Devon, UK. Mar. Freshwater Res. 46:327–336.

572 Westinen, H., personal communication. Agency for Rural Affairs, P.O. Box 405, FI-60101
573 Seinäjoki, Finland.

574 Wildung, R.E., Schmidt, R.L., Routson, R.C., 1977. The phosphorus status of eutrophic lake
575 sediments as related to changes in limnological conditions – Phosphorus mineral components. J.
576 Environ. Qual. 6, 100-104.

Table 1. Size and characteristics of the Ojainen, Liedonperä, Hovi, Kakskerta and Nautela constructed wetlands (CW) and their catchments.

| Site (Municipality) | Year established | Size, $m^2$ | Catchment area, $km^2$ | CW as % of catchment area | Arable land in catchment, % | Dominant soil texture in catchment[a] | Chemical, dosing for P precipitation, kg:$m^3$ water |
|---|---|---|---|---|---|---|---|
| Ojainen (Jokioinen) | 2000 | 370 | 0.16 | 0.23 | 100 | silty clay | - |
| Liedonperä (Tarvasjoki) | 1995 | 4850 | 0.99 | 0.49 | 50 | silty clay loam | - |
| Hovi (Vihti) | 1998 | 6000 | 0.12 | 5.0 | 100 | clay | - |
| Kakskerta (Turku) | 2006 | 850 | 0.73 | 0.12 | 64 | clay | aluminium chloride, 1:30 |
| Nautela (Lieto) | 2005 | < 100 | 0.61 | < 0.02 | 63 | silty clay | ferric sulphate, 1:50 |

[a]According to USDA texture classes.

Table 2. Clay content, pH and redox potential (Eh) of the catchment soils and of fresh and dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments.

| Site | | Clay % | pH | Eh[4] mV |
|---|---|---|---|---|
| Ojainen | Soil | 45 | 6.7[3] | NA |
| | Fresh sediment | NA | 7.3[4] | -21 |
| | Dry sediment | 82 | 5.1[3] | NA |
| Liedonperä | Soil | 35 | 6.7[3] | NA |
| | Fresh sediment | NA | 6.8[4] | 5 |
| | Dry sediment | 62 | 5.2[3] | NA |
| Hovi | Soil | 58 | 6.9[3] | NA |
| | Fresh sediment | NA | 6.3[4] | 25 |
| | Dry sediment | 82 | 5.7[3] | NA |
| Kakskerta | Soil | 72 | 6.0[3] | NA |
| | Fresh sediment[1] | NA | 6.5[4] | 21 |
| | Dry sediment[1] | 79 | 5.9[3] | NA |
| Nautela | Soil | 45 | 6.8[3] | NA |
| | Fresh sediment[2] | NA | 5.2[4] | 105 |
| | Dry sediment[2] | 54 | 5.2[3] | NA |

NA not analysed.

[1]Aluminium chloride solution assisted sedimentation.

[2]Granular ferric sulphate ($Fe_2(SO_4)_3$) assisted sedimentation.

[3]pH measured 1:5 $H_2O$.

[4]Meter reading, pH/Eh measured in situ.

Table 3. Total carbon (Tot-C), total nitrogen (Tot-N), total sulphur (Tot-S), sulphate-sulphur ($SO_4^{2-}$-S) and sulphate-sulphur ($SO_4^{2-}$-S) to Tot-S ratio of the catchment soils and the dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments. $SO_4^{2-}$-S results are given as mean ± SE.

| Site | | Tot-C | Tot-N | Tot-S | $SO_4^{2-}$-S | $SO_4^{2-}$-S/Tot S |
|---|---|---|---|---|---|---|
| | | % | % | % | mg kg$^{-1}$ | % |
| Ojainen | Soil | 2.8 | 0.19 | 0.03 | 17±0 a | 7 |
| | Sediment | 3.6 | 0.34 | 0.13 | 877±4 b | 67 |
| Liedonperä | Soil | 1.7 | 0.12 | 0.02 | 20±0 e | 10 |
| | Sediment | 1.3 | 0.12 | 0.14 | 98±1 f | 7 |
| Hovi | Soil | 1.8 | 0.14 | 0.02 | 20±0 h | 8 |
| | Sediment | 2.2 | 0.19 | 0.05 | 227±1 i | 44 |
| Kakskerta | Soil | 4.6 | 0.37 | 0.12 | 136±9 c | 11 |
| | Sediment[1] | 15.0 | 0.95 | 0.64 | 449±2 d | 7 |
| Nautela | Soil | 1.8 | 0.15 | 0.02 | 20±0 j | 9 |
| | Sediment[2] | 5.2 | 0.42 | 0.10 | 284±2 k | 28 |

[1]Aluminium chloride solution assisted sedimentation.

[2]Granular ferric sulphate ($Fe_2(SO_4)_3$) assisted sedimentation.

Different letters for samples from each site represent significant differences ($p$<0.05, Tukey's test). Each site was tested separately.

Table 4. Acid ammonium oxalate-extractable aluminium ($Al_{ox}$) and iron ($Fe_{ox}$), phosphorus sorption capacity (PSC), degree of P saturation of oxides ($DPS_{Alox}$, $DPS_{Feox}$), the sum of $NH_4Cl$-, $NH_4F$- and NaOH-extractable Chang and Jackson P fractions ($P_\Sigma$) and P saturation calculated as $P_\Sigma$/PSC ($DPS_\Sigma$) in the catchment soils and fresh and dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments. Values are mean ± SE.

| Site | | $Al_{ox}$ | $Fe_{ox}$ | PSC | $DPS_{Alox}$ | $DPS_{Feox}$ | $P\Sigma(NH_4Cl, NH_4F, NaOH)$ | $DPS_\Sigma$ |
|---|---|---|---|---|---|---|---|---|
| | | mmol $kg^{-1}$ | mmol $kg^{-1}$ | mmol $kg^{-1}$ | % | % | mmol $kg^{-1}$ | % |
| Ojainen | Soil | 112±9 a | 223±18 a | 168 | 7.6 | 10.6 | 16 | 9.6 |
| | fresh sediment | 181±28 a | 253±31 a | 217 | 2.5 | 13.9 | 20 | 9.2 |
| | air-dry sediment | 292±5 b | 261±3 a | 277 | 1.7 | 11.1 | 17 | 6.1 |
| Liedonperä | Soil | 93±3 f | 191±13 c | 142 | 3.5 | 6.2 | 8 | 5.4 |
| | fresh sediment | 124±11 g | 315±48 d | 220 | 1.0 | 3.9 | 7 | 3.1 |
| | air-dry sediment | 186±2 g | 351±4 d | 269 | 0.3 | 3.2 | 6 | 2.2 |
| Hovi | Soil | 158±4 h | 203±14 e | 181 | 1.1 | 3.9 | 5 | 2.7 |
| | fresh sediment | 145±1 h | 189±3 e | 167 | 3.9 | 10.7 | 13 | 7.8 |
| | air-dry sediment | 191±3 h | 172±3 e | 182 | 1.2 | 12.1 | 12 | 6.4 |
| Kakskerta | Soil | 159±19 c | 257±16 b | 208 | 1.2 | 7.0 | 10 | 4.8 |
| | fresh sediment[1] | 611±75 d | 204±12 b | 408 | 1.9 | 5.4 | 11 | 2.8 |
| | air-dry sediment[1] | 728±4 e | 249±2 b | 489 | 1.2 | 4.0 | 9 | 1.9 |
| Nautela | Soil | 81±3 i | 195±14 f | 138 | 5.4 | 10.6 | 12 | 9.1 |
| | fresh sediment[2] | 73±3 i | 206±5 f | 140 | 3.2 | 13.8 | 15 | 11.0 |
| | air-dry sediment[2] | 117±2 i | 225±2 f | 171 | 2.0 | 8.0 | 10 | 6.0 |

[1]Aluminium chloride solution assisted sedimentation.

[2]Granular ferric sulphate ($Fe_2(SO_4)_3$) assisted sedimentation.

Different letters for samples from each site represent significant differences ($p$<0.05, Tukey's test). Each site was tested separately.

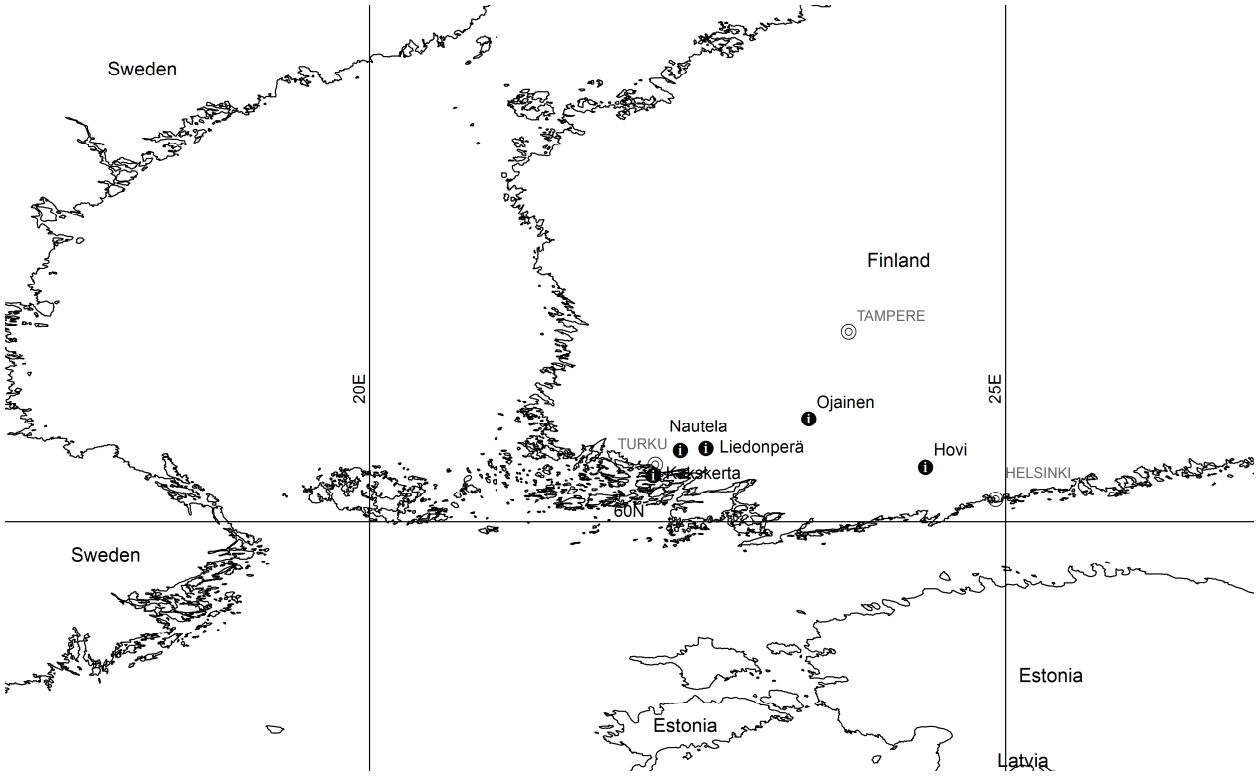



Figure 1. Location of the Ojainen, Liedonperä, Hovi, Kakskerta and Nautela study sites in south-west Finland.

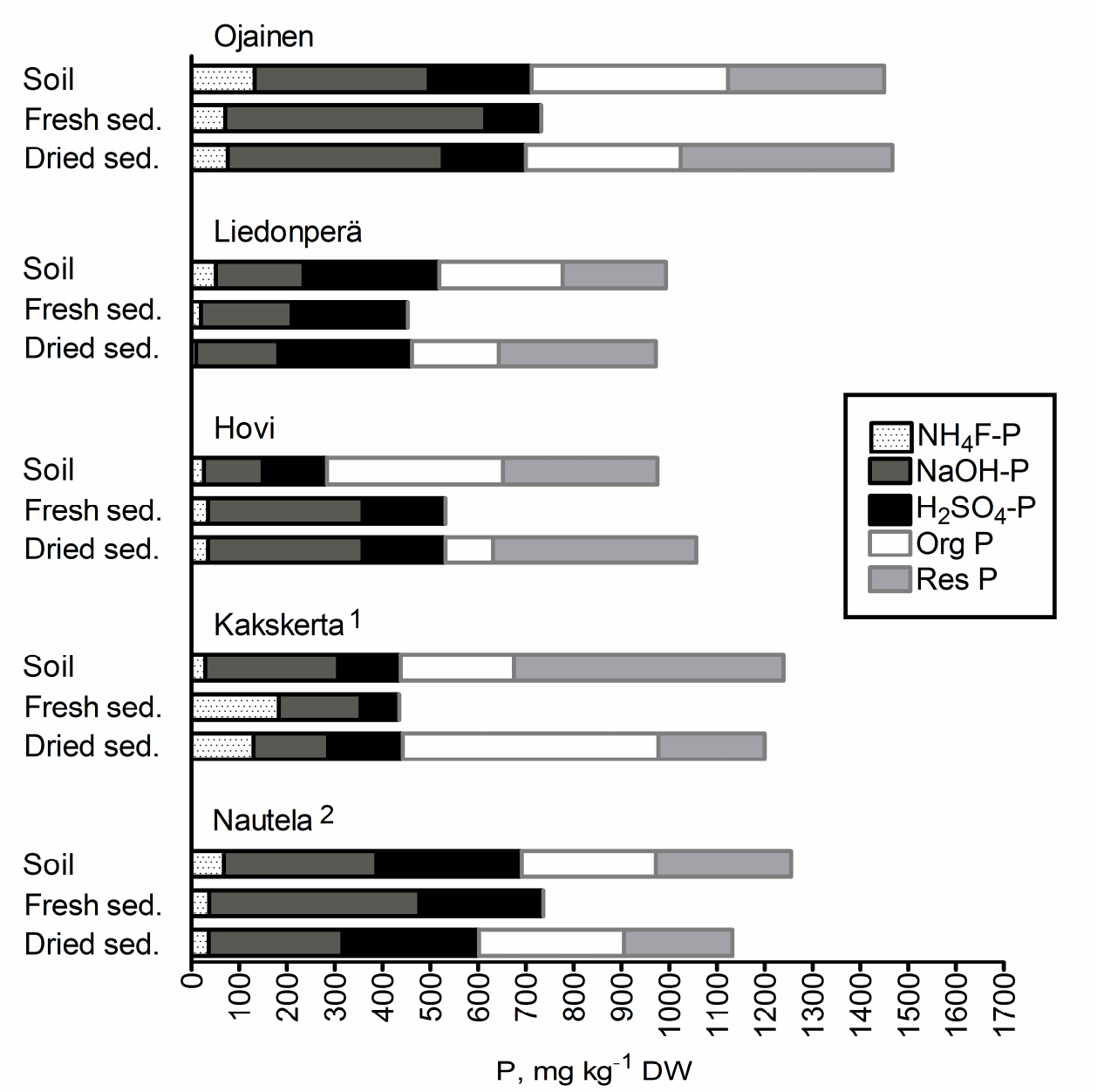



Figure 2. Total phosphorus (TP) concentration, Chang and Jackson P fractions ($NH_4F$-P, NaOH-P, $H_2SO_4$-P), organic P (Org P) concentration and calculated residual P (Res P) content of the catchment soils and the dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments. For fresh sediments, the Chang and Jackson P fractions are shown as separate bars. Values shown are mean. [1]Aluminium chloride solution assisted sedimentation. [2]Granular ferric sulphate ($Fe_2(SO_4)_3$) assisted sedimentation.

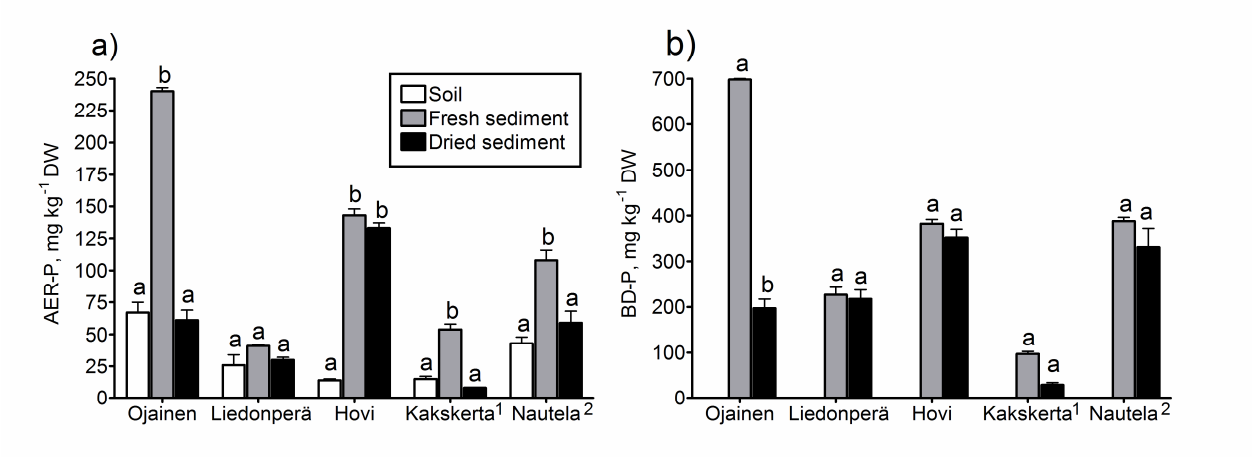



Figure 3. a) Anion exchange resin-extractable phosphorus (AER-P) of the catchment soils and fresh and dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments. b) Bicarbonate-dithionite-extractable P (BD-P) of the fresh and dry sediments. Results are given as mean ± SE. Different letters for samples from each site represent significant differences ($p$<0.05, Tukey's test). Each site was tested separately. [1]Aluminium chloride solution assisted sedimentation. [2] Granular ferric sulphate ($Fe_2(SO_4)_3$) assisted sedimentation.