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2016

Laakso , J M , Uusitalo , R & Yli-Halla , M J 2016 , ' Phosphorus speciation in agricultural catchment soils and in fresh and dried sediments of five constructed wetlands ' , *Geoderma* , vol. 271 , pp. 18-26 . <https://doi.org/10.1016/j.geoderma.2016.02.007>

<http://hdl.handle.net/10138/173465>

<https://doi.org/10.1016/j.geoderma.2016.02.007>

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1 **Phosphorus speciation in agricultural catchment soils and in fresh and dried**
2 **sediments of five constructed wetlands**

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10

11 **Abstract**

12 Constructed wetlands and ponds (CWs) are installed to trap suspended material and particulate
13 phosphorus (P) in agricultural runoff. This study investigated whether the P speciation and P
14 sorption capacity of source soils differ from those of CW sediments and whether drying of dredged
15 sediment changes its characteristics. Samples collected from five agricultural CW sites in south-
16 west Finland, two with chemical-aided (aluminium chloride and ferric sulphate) P precipitation and
17 all representing fine-textured mineral soils, were analysed for various P plant availability indices.
18 Clay contents of the CW sediments were much higher than in catchment soils, likely because of
19 selective erosion. All CW sediments were characterised by similar total P content but clearly higher
20 content of anion exchange resin-extractable P in fresh sediments than the source soils. In general,
21 sediment content of NH₄F-extractable (aluminium (Al)-associated) P was significantly lower and
22 NaOH-extractable (iron (Fe)-associated) significantly higher than in source soils. Reduced

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

29 **1. Introduction**

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

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

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

48 The material ending up in CWs is subjected to several processes which affect the P content and
49 other characteristics of the eroded material, during erosion and after sedimentation in CWs.

50 Phosphorus bound to Al (hydr)oxides primarily controls the P concentration in the soil solution of
51 non-calcareous soils (Hartikainen, 1982) and, during water erosion events, adds to dissolved P stock

52 transported because of dilution of the soil solution. After off-field transport and sedimentation in
53 CWs, mobilisation of redox-sensitive P bound to Fe(III)(hydr)oxides may take place, depending on
54 oxygen (O₂) conditions in the sediment. Under anoxic conditions, Fe(III) is reduced to Fe(II) and P
55 bound to this sorption component is released to pore water (Wildung et al., 1977; Olila and Reddy,
56 1997) and, via diffusion, to overlying water. Dissolution of Fe(III) is conducive to decreased P
57 retention capacity of sediments in coastal marine areas (Jensen et al., 1995), but also in waterlogged
58 soils and sediments (Khalid et al., 1977). In water bodies receiving high amounts of organic carbon
59 (C) in the presence of SO₄²⁻, Fe(III) can be reduced to Fe sulphides, which are not active P sorption
60 associations, decreasing the capacity of the sediment to retain P (Roden and Edmonds, 1997;
61 Lehtoranta et al., 2009, 2015).

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

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

76 **2. Materials and methods**

77 *2.1 Study sites*

78 The study sites represented five agricultural CWs established on fine-textured mineral soils in SW
79 Finland (Fig. 1, Table 1). In all surrounding catchments, soil type according to the WRB system
80 (IUSS Working Group WRB, 2014) is Stagnosol. The CWs had been constructed 6-17 years before
81 the start of the study. Two of the sites (Kakskerta and Nautela) had chemically assisted P
82 precipitation, with aluminium chloride solution (trade name Kempac 18) at Kakskerta and granular
83 ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$, trade name Ferix-3) at Nautela being added into the water entering the
84 CWs. This chemical treatment has been performed for 9 years at Kakskerta (since 2003), with the
85 exception of occasional interruptions, and for 1.5 years at Nautela (since 2011; see Uusitalo et al.,
86 2015).

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

95

96 *2.2 Soil samples*

97 The samples studied were collected in August 2012. Composite soil samples were taken from the
98 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 NaHCO₃) being prepared for daily use and the dithionite solution (0.574 M
149 Na₂S₂O₄) 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 K₂S₂O₈ in 1 l of 0.4 M H₂SO₄) 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 H₂SO₄-H₂O₂-
158 HF extraction method (Bowman, 1988). Organic P was determined by the ignition method of Olsen
159 and Sommers (1982) using 0.5 M H₂SO₄ 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 NH₄Cl (30 min), assumed to
170 extract the most easily soluble P and exchangeable Ca; ii) 0.5 M NH₄F (pH 8.5) (1 h), Al-bound P;
171 iii) 0.1 M NaOH (16 h), Fe-bound P; and iv) 0.25 M H₂SO₄ (1 h), Ca-bound apatitic P. The
172 suspensions were centrifuged (15 min, 3846×g) and NH₄Cl extracts were filtered through Munktell
173 OOR paper filters (Munktell Filter AB, Grycksbo, Sweden). For NH₄F and NaOH extracts,
174 dissolved humus was removed by precipitation with 0.5 M H₂SO₄ (Hartikainen, 1979). The soil
175 matter pellet remaining after the NH₄F 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 (NH₄)₂C₂O₄×H₂O, 43% 0.2 M
185 C₂H₂O₄×2 H₂O) 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
$$\text{PSC (mmol kg}^{-1}\text{)} = 0.5 \times (\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}}) \quad (1)$$

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

$$191 \text{ DPS}_{\Sigma} (\%) = 100 \times P_{\Sigma} / PSC \quad (2)$$

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

$$195 \text{ DPS}_{\text{Al}_{\text{ox}}} (\%) = 100 \times \text{Al-P} / 0.5 \times \text{Al}_{\text{ox}} \quad (3)$$

$$196 \text{ DPS}_{\text{Fe}_{\text{ox}}} (\%) = 100 \times \text{Fe-P} / 0.5 \times \text{Fe}_{\text{ox}} \quad (4)$$

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

199

200 *2.4.6 Other soil and sediment characteristics*

201 Total contents of C and nitrogen (N) were determined with a LECO CN-analyzer (TruSpec, Leco
202 Corporation, St. Joseph, MI, USA). Total sulphur (S) content was determined by the aqua regia
203 extraction method according to ISO 11466:1995. The concentration of sulphate-sulphur ($\text{SO}_4^{2-}\text{-S}$)
204 was measured by ICP-OES (Thermo Scientific iCAP 6300 Duo MFC, Waltham, USA) in acidic
205 ammonium acetate extracts (0.5 M acetic acid, 0.5 M ammonium acetate, pH 4.65, AAAC)
206 according to the Finnish agronomic soil testing protocol (Vuorinen and Mäkitie, 1955). The AAAC
207 solution is used to determine readily plant-available macronutrients, including S, in soil. Extraction
208 is performed at a 1:10 soil-to-solution ratio for one hour. Particle size distribution of soils and
209 sediments was analysed with a pipette method (Elonen, 1971).

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

214

215 *2.5 Statistical analyses*

216 For the parameters analysed, differences in means between soils, fresh sediment and dried sediment
217 within each site were tested with one-way analysis of variance followed by post-hoc separation of
218 means using the Tukey's test. In cases of non-normality (total P, NH₄Cl-P, NH₄F-P, NaOH-P,
219 AER-P, Al_{ox}, Fe_{ox}), logarithmic transformation was performed prior to the analysis. For analysis of
220 the general trends in the material over all sites, paired tests were performed between soil and fresh
221 sediment, and fresh sediment and dry sediment, using the nonparametric Wilcoxon signed rank test.
222 Significance was taken as $p < 0.05$. Statistical analyses were conducted with IBM SPSS Statistics 22.

223 **3. Results**

224 *3.1 General properties of the soils and sediments*

225 With 50-100% arable land in the catchments and the clayey topsoil texture (Table 2), the soils were
226 prone to erosion. Clear signs of erosion were not present in August 2012 during sampling, but most
227 of the annual erosion in this area takes place during winter rains and spring snowmelt (see Turtola
228 et al., 2007). Subsurface drainflow and surface runoff are both important transport pathways for soil
229 particles and particulate P in the clay soils of SW Finland (Turtola et al., 2007; Uusitalo et al.,
230 2003).

231 At Ojainen and Hovi, ^{137}Cs activities in sediments were 64 and 59 Bq kg^{-1} , respectively, whereas
232 the contents in the field soils of these sites were lower, 53 and 55 Bq kg^{-1} . The enrichment ratios for
233 ^{137}Cs (ER, the ratio of ^{137}Cs activity in sediment to that in topsoil samples) were 1.22 and 1.08 at
234 Ojainen and Hovi, respectively. The ^{137}Cs activities in the sediments of Liedonperä, Kakskerta and
235 Nautela were 69, 46 and 74 Bq kg^{-1} , respectively. Because ^{137}Cs is only found in topsoil (to the
236 maximum depth of tillage of about 20 cm), activity in subsoil being less than 10 Bq kg^{-1} in southern
237 Finland (Uusitalo et al., 2001), these results suggest that the sediment matter originates mainly from
238 the topsoil of catchment fields.

239 At all sites, the sediment had a brown and slightly fluffy surface layer (0.5-2.0 cm). Below the
240 surface, the relatively loosely settled matter sampled was light or dark grey and there were regular
241 black spots, presumably indicative of the presence of sulphides. The Eh values (meter readings in
242 situ) varied from -21 mV at Ojainen to 105 mV at Nautela (Table 2). The bottom of all CWs thus
243 seemed to be in anoxic conditions. The sediments in the CWs were very fine-textured, consisting
244 54-82% of clay-sized particles (<0.002 mm). Compared with the catchment soils, the sediments
245 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 $\pm 10\%$. The highest TP contents in the soil ($1450 \text{ mg P kg}^{-1}$) and sediment
266 ($1467 \text{ mg P kg}^{-1}$) 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.

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

271

272 *3.2.1 Chang and Jackson P fractions*

273 The Chang and Jackson fractionation extracted 29-55% (mean 44%) and 37-53% (mean 47%) of TP
274 from the soils and sediments, respectively. The largest Chang and Jackson P fraction in the studied
275 soils and sediments was either NaOH-P or H₂SO₄-P (Fig. 2). Loosely bound P, the NH₄Cl-
276 extractable pool, was negligible (<1 mg kg⁻¹) in all samples. The average share of residual P, not
277 accounted for in the different fractions, was 29% (range 19-46%).

278 At three of the sites, the NH₄F-P fraction (Al-associated P) was clearly lower in sediments than in
279 soils, comprising 39-54% of the parent soil content. The exceptions were Kakskerta and Hovi CWs.
280 The Kakskerta sediment was affected by Al chemical feed to incoming water, an obvious reason for
281 the increase in Al-associated P. At Hovi, Al-P was also clearly higher in the sediment than in soil,
282 but without any known inputs of reactive Al. The most striking difference from the other sites was
283 the very large size of the Hovi CW, 5% of the catchment area (Table 1). Pairwise statistical testing
284 over all sites suggested that NH₄F-P concentrations were lower in fresh sediments than in soils
285 when the Kakskerta CW was excluded from the testing.

286 The sediment NaOH-P pool, representing P bound by Fe (hydr)oxides, was substantially greater
287 than in the parent soils at three of the sites, while at Liedonperä it was about equal to the parent soil
288 content. At Kakskerta, Fe-P was lower in sediment than in soil. Because Al feed at the CW inlet has
289 added an unknown Al oxide mass to the Kakskerta sediment over the years, comparisons between
290 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 $\text{H}_2\text{SO}_4\text{-P}$, 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 $\text{NH}_4\text{F-P}$ 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, $\text{NH}_4\text{F-P}$
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 $\text{H}_2\text{SO}_4\text{-P}$ 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 $\text{Fe}_2(\text{SO}_4)_3$ 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_{Σ}), the dried sediments
335 were less saturated with P than the fresh sediments.

336 **4. Discussion**

337

338 *4.1 Parent soils and CW sediments*

339

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

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

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

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

362 Even though the TP content was not changed during the erosion process and the residence of soil
363 material in the CWs, there were differences in the P fractions between the soil and sediment. In
364 Finnish non-calcareous soils, P originating from fertiliser is generally retained to Al (hydr)oxides
365 ($\text{NH}_4\text{F-P}$) and Fe (hydr)oxides (NaOH-P) (e.g. Kaila, 1963b; Hartikainen, 1989; Peltovuori, 2006).
366 In our material the sum of Al- and Fe-bound P was the largest pool found in soils of the catchments,
367 but these fractions proved to be clearly affected by transport and the processes in CWs, anoxic
368 sediment conditions presumably being one driver for these changes. The fresh sediments were
369 typically lower in Al-associated P (except Hovi and Kakskerta), but higher in Fe-associated P
370 (except Kakskerta) than their parent soils (Fig. 2). During the transport and residence in CWs, the
371 ambient solution (i.e. runoff water or water in CW) surrounding eroded soil becomes lower in
372 dissolved P concentration than was present in soil solution, and a considerable fraction of Al-bound
373 P may be depleted (Hartikainen, 1982).

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

382 At the time of sampling, redox state was low in all CW sediments studied and much higher
383 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

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

410

411 *4.2 Reoxidation of CW sediments*

412 Our second objective was to investigate how dredging and drying (reoxidation) affected the P
413 solubility and P sorption capacity of CW sediments. The clay-enriched sediment material was rich
414 in oxides after drying. In particular, the content of Al (hydr)oxides increased after drying of the
415 sediments. The origin of the newly formed oxides can be assumed to be the drying-induced
416 breakdown of Al and Fe complexes of organic matter (Bartlett and James, 1980; Haynes and Swift,
417 1985). For example, Peltovuori and Soinne (2005) observed an increase in Al and Fe contents
418 assumed to originate from soil organic matter, after air-drying of soils. The modest, statistically
419 non-significant increase in Fe (hydr)oxides after drying of sediments in the present study may also
420 be a result of dissolved Fe(II) ions being oxidised to Fe(III). Newly formed Fe (hydr)oxides have a
421 high specific surface area and a high amount of reactive sites for P adsorption, and thus good
422 efficiency at removing soluble P (e.g. Mayer and Jarrel, 2000). The lower DPS_{Σ} of the dried
423 sediments compared with the fresh sediments and parent soils, except at Hovi, indicate that
424 applying dredged sediments to soils would add to soil stocks of reactive Al and Fe (hydr)oxides,
425 which in turn might diminish the plant availability of P.

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

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

442

443

444 **5. Conclusions**

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

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

464

465 **Acknowledgements**

466 The authors are grateful to the Finnish Ministry of Agriculture and Forestry for financial support.

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 Elonon, 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 terrestrial 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.

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

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

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

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

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

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

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

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

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

506 Lehtoranta, J., Ekholm, P., Pitkänen, H., 2009. Coastal eutrophication thresholds: A matter of
507 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., Koskiahho, 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 ³¹P 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-Kämpä, 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

^aAccording 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.

¹Aluminium chloride solution assisted sedimentation.

²Granular ferric sulphate (Fe₂(SO₄)₃) assisted sedimentation.

³pH measured 1:5 H₂O.

⁴Meter reading, pH/Eh measured in situ.

Table 3. Total carbon (Tot-C), total nitrogen (Tot-N), total sulphur (Tot-S), sulphate-sulphur (SO₄²⁻-S) and sulphate-sulphur (SO₄²⁻-S) to Tot-S ratio of the catchment soils and the dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments.

SO₄²⁻-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

¹Aluminium chloride solution assisted sedimentation.

²Granular ferric sulphate (Fe₂(SO₄)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 ($DPS_{Al_{ox}}$, $DPS_{Fe_{ox}}$), the sum of NH_4Cl -, NH_4F - and $NaOH$ -extractable Chang and Jackson P fractions (P_{Σ}) and P saturation calculated as P_{Σ}/PSC (DPS_{Σ}) in the catchment soils and fresh and dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments. Values are mean \pm SE.

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

¹Aluminium chloride solution assisted sedimentation.

²Granular 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.

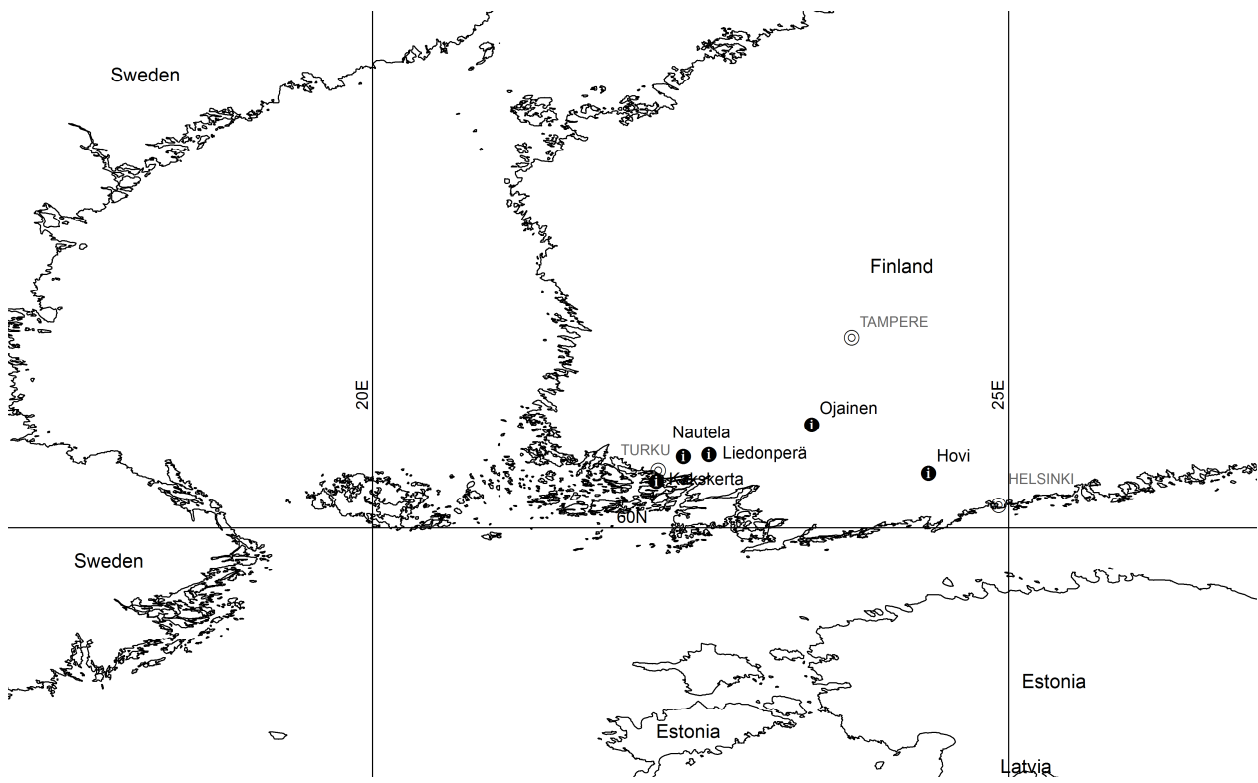


Figure 1. Location of the Ojainen, Liedonperä, Hovi, Kakskerta and Nautela study sites in south-west Finland.

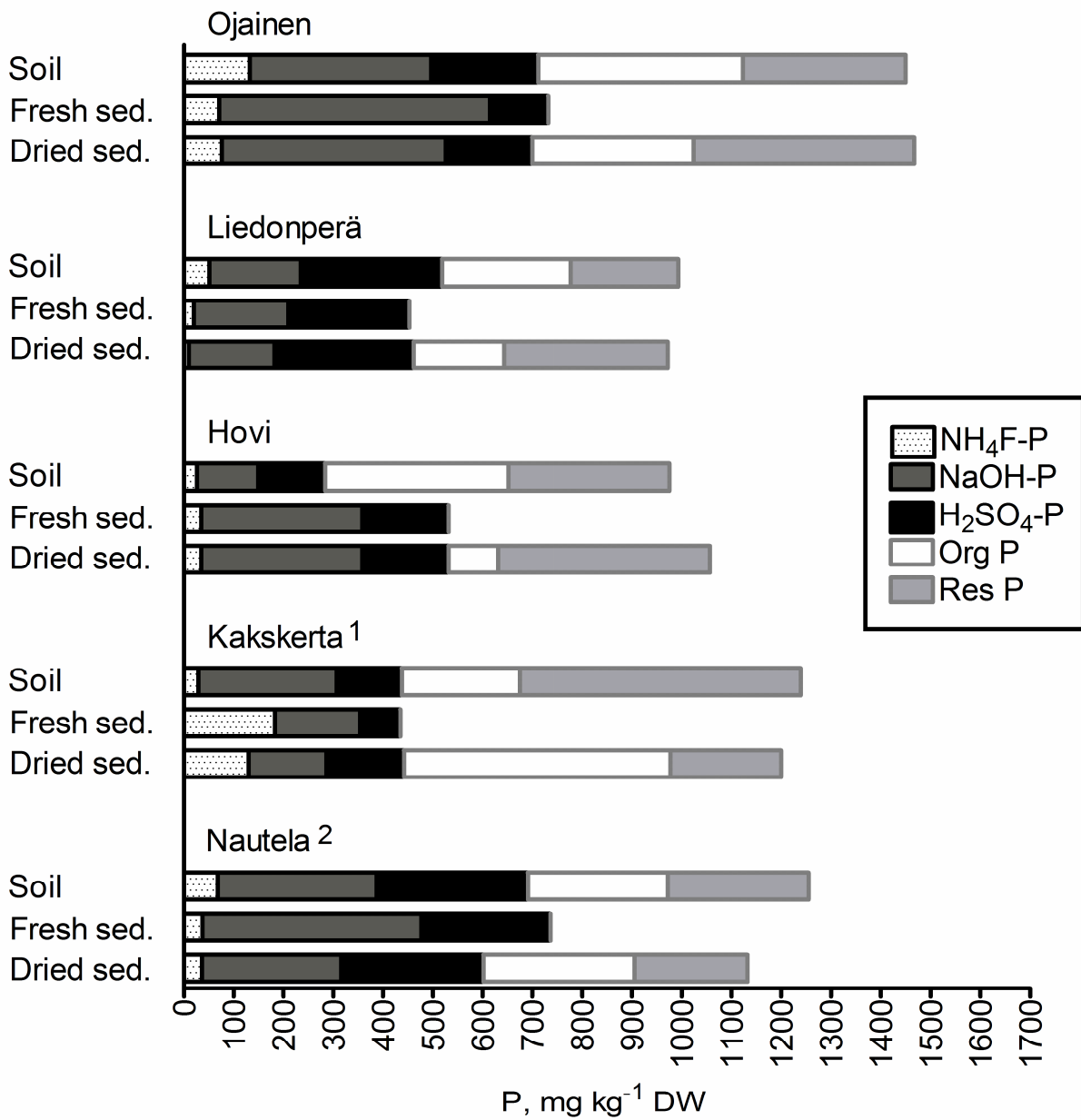


Figure 2. Total phosphorus (TP) concentration, Chang and Jackson P fractions (NH₄F-P, NaOH-P, H₂SO₄-P), organic P (Org P) concentration and calculated residual P (Res P) content of the catchment soils and the dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments. For fresh sediments, the Chang and Jackson P fractions are shown as separate bars. Values shown are mean. ¹Aluminium chloride solution assisted sedimentation. ²Granular ferric sulphate (Fe₂(SO₄)₃) assisted sedimentation.

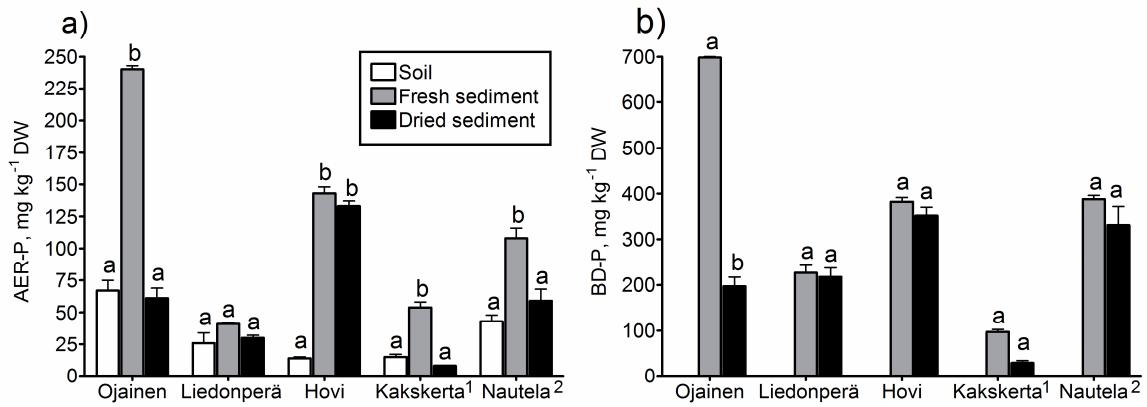


Figure 3. a) Anion exchange resin-extractable phosphorus (AER-P) of the catchment soils and fresh and dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments. b) Bicarbonate-dithionite-extractable P (BD-P) of the fresh and dry sediments. Results are given as mean \pm SE. Different letters for samples from each site represent significant differences ($p < 0.05$, Tukey's test). Each site was tested separately. ¹Aluminium chloride solution assisted sedimentation. ²Granular ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) assisted sedimentation.