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 NH₄F-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
from which most of the CW sediments would likely originate. The samples representing each
transect consisted of three subsamples taken approximately every 30 m from the CW diagonally to
the main slope. Sampling was carried out with a spade from the Ap horizon (0-20 cm depth). Soil
samples were allowed to air-dry, crushed and sieved (2 mm).

2.3 Sediment samples

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

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

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

2.4.1 Anion exchange resin (AER) extraction

To estimate the amount of potentially desorbable P from soil and sediment material, soil samples and fresh and dried sediment samples were extracted by anion exchange resin (AER) (Sibbesen, 1977; Uusitalo and Ekholm, 2003) 4 weeks after sampling. In the method used, 1 g strong basic AER (Dowex 1×8, Fluka Chemika, Neu-Ulm, Germany), with about 2 mmol anion exchange capacity, was enclosed in small nylon netting (Sefar Nitex, Sefar Inc., Heiden, Switzerland) bags with mesh size 0.25 mm. Before extraction, AER was converted into HCO$_3^-$ form by washing the bags for 4 h with two portions of 0.5 M NaHCO$_3$ solution (Sibbesen, 1978).

The extraction was performed with 1 g sample dry matter and 40 ml deionised water in a 50-ml extraction tube with one AER bag. The tubes were shaken overnight (20 h) on an orbital shaker at 100 rpm. The AER bag was then removed, washed with deionised water and shaken in 40 ml 0.5 M NaCl for 4 h to displace P from the AER into the solution. The bag was removed from the extraction vessel and the NaCl solution was acidified with 1 ml 6 M HCl and allowed to stand overnight to remove CO$_2$. The P concentration of the NaCl solution was measured with a Lachat (Milwaukee, WI) QC Autoanalyzer using the method of Murphy and Riley (1962) with ascorbic acid as the reducing agent. The AER extraction was performed in triplicate.
2.4.2 Extraction of redox-sensitive P

Both fresh and dried sediment samples (but not soil samples) were extracted with bicarbonate-buffered sodium dithionite (BD) solution to analyse redox-sensitive P, as described by Uusitalo and Turtola (2003). In brief, 0.2 g sediment samples were weighed into 250-ml plastic bottles and 100 ml deionised water were added. Aliquots of 2.5 ml of both solutions were added to the samples, bicarbonate (0.298 M NaHCO$_3$) being prepared for daily use and the dithionite solution (0.574 M Na$_2$S$_2$O$_4$) just before extraction. The sample bottles were capped and shaken on an orbital shaker for 15 min at 120 rpm. After extraction, the samples were immediately filtered through a 0.2 µm Nuclepore polycarbonate filter (Whatman, Maidstone, UK). Then 10 ml filtrate were digested with 4 ml persulphate (50 g K$_2$S$_2$O$_8$ in 1 l of 0.4 M H$_2$SO$_4$) in an autoclave (+120 °C, 100 kPa, 30 min) in order to oxidise the excess dithionite. The P concentration was measured as in AER-P analysis. The BD extraction was performed with quadruplicate samples.

2.4.3 Total P and organic P

Total P in the soil and dried sediment samples was determined in duplicate with the H$_2$SO$_4$-H$_2$O$_2$-HF extraction method (Bowman, 1988). Organic P was determined by the ignition method of Olsen and Sommers (1982) using 0.5 M H$_2$SO$_4$ extraction (1:50 w:v; 16 hours) on triplicate samples. The P concentration was determined using the method of Murphy and Riley (1962) with ascorbic acid as the reducing agent. A Lachat (Milwaukee, WI) QC Autoanalyzer and a spectrophotometer (Shimadzu UV-120-02, Kyoto, Japan) were employed for total and organic P measurements, respectively.
2.4.4 Inorganic P fractions

The inorganic P reserves in the soil and (fresh and dried) sediment samples were determined by the method of Chang and Jackson (1957) as modified by Hartikainen (1979). Triplicate samples were sequentially extracted, using a soil-to-solution ratio 1:50, with: i) 1 M NH₄Cl (30 min), assumed to extract the most easily soluble P and exchangeable Ca; ii) 0.5 M NH₄F (pH 8.5) (1 h), Al-bound P; iii) 0.1 M NaOH (16 h), Fe-bound P; and iv) 0.25 M H₂SO₄ (1 h), Ca-bound apatitic P. The suspensions were centrifuged (15 min, 3846×g) and NH₄Cl extracts were filtered through Munktell OOR paper filters (Munktell Filter AB, Grycksbo, Sweden). For NH₄F and NaOH extracts, dissolved humus was removed by precipitation with 0.5 M H₂SO₄ (Hartikainen, 1979). The soil matter pellet remaining after the NH₄F and NaOH extractions was washed with saturated NaCl solution to prevent carryover of P to the following step. The P concentration was analysed with the molybdenum blue method of Murphy and Riley (1962) using a spectrophotometer (Shimadzu UV-120-02, Kyoto, Japan).

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

The short-range ordered (hydr)oxides of Al and Fe (Al_{ox} and Fe_{ox}) were analysed in dry soil and (fresh and dried) sediment samples using the ammonium oxalate extraction method by Schwertmann (1964) followed by ICP determination. Duplicate 0.5 g samples were extracted with 25 ml acidic (pH 3.0) ammonium oxalate solution (57% 0.2 M (NH₄)₂C₂O₄×H₂O, 43% 0.2 M C₂H₂O₄×2 H₂O) for 4 h in the dark. After centrifuging (15 min, 3846×g), the aliquots were filtered through a blue ribbon paper filter (Schleicher & Schuell, Dassel, Germany).

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

\[ \text{PSC (mmol kg}^{-1}\text{)} = 0.5 \times (\text{Al}_{ox} + \text{Fe}_{ox}) \]  

(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:

\[
\text{DPS}_\Sigma(\%) = 100 \times \frac{P_\Sigma}{P_{\text{SC}}} \quad \text{(2)}
\]

where \(P_\Sigma\) is the sum of NH\(_4\)Cl-, NH\(_4\)F- and NaOH-extractable P in mmol kg\(^{-1}\). We also calculated the DPS separately for Al\(_{\text{ox}}\) and Fe\(_{\text{ox}}\) on molar basis (Lookman et al., 1995; Hartikainen et al., 2010) as:

\[
\text{DPS}_{\text{Al}_{\text{ox}}}(\%) = 100 \times \frac{\text{Al-P}}{0.5 \times \text{Al}_{\text{ox}}} \quad \text{(3)}
\]

\[
\text{DPS}_{\text{Fe}_{\text{ox}}}(\%) = 100 \times \frac{\text{Fe-P}}{0.5 \times \text{Fe}_{\text{ox}}} \quad \text{(4)}
\]

where Al-P is NH\(_4\)F-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$_4$Cl-P, NH$_4$F-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.
Some accumulation of Tot-C and Tot-N in the sediments was observed, particularly in the CWs where sedimentation was chemically assisted (Table 3). The addition of Fe and Al salts most likely resulted in flocculation of fine particles and dissolved humus in low flow periods, resulting in higher C and N concentrations than in parent soils. The sediments contained 2.5- to 7-fold more Tot-S than the corresponding soils. Furthermore, considerably more SO$_4^{2-}$-S was extracted from the dried sediments than from the soils (Table 3). The low ratio of SO$_4^{2-}$-S/Tot-S in the agricultural soils (Table 3) indicated that S was mainly organic, but more inorganic S was found in the sediments in the Ojainen, Hovi and Nautela CWs. This, together with the low redox potential in the fresh sediments in these CWs, might be associated with formation of sulphide minerals, which were subsequently oxidised to SO$_4^{2-}$ upon drying of the sediments.

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

### 3.2 Total P in soils and sediments

The amount of total P (TP) in the sediments was similar to the amount in the parent soils, the difference being within ±10%. The highest TP contents in the soil (1450 mg P kg$^{-1}$) and sediment (1467 mg P kg$^{-1}$) were found at Ojainen (Fig. 2), a clay soil known to have received much dairy cow manure in the past (P class good to high, AAAC-extractable P at 24 mg l$^{-1}$). Organic P 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$_2$SO$_4$-P (Fig. 2). Loosely bound P, the NH$_4$Cl-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$_4$F-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$_4$F-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
concentrations over all sites showed that fresh sediments had significantly higher concentrations than the parent soils (even when Kakskerta was included in the test).

As for the H$_2$SO$_4$-P, there were no statistically significant differences between soils and sediments and no consistent trends were found in the material. The sum of the P fractions also behaved inconsistently, but it was noted that at Hovi, the sum of P fractions was higher for the sediment than for the soil (Fig. 2).

The comparisons between fresh and dried sediments revealed that drying had some influence on P fractions (Fig. 2). The NH$_4$F-P pool decreased in the sediments from Kakskerta, Liedonperä and Hovi after drying, but was unaffected in the Ojainen and Nautela sediments. Over all sites, NH$_4$F-P was found not to differ between fresh and dried sediments. Drying of the sediments also significantly ($p=0.012$) decreased the NaOH-P pool in all cases except at Hovi, where it was unaffected. Some increases in the H$_2$SO$_4$-P pool upon drying were recorded at all sites, but these increases were not statistically significant.

3.2.2 Desorbable and redox-sensitive P

Over all CWs studied, the concentrations of desorbable P, estimated by AER extraction, in fresh sediments were significantly ($p=0.017$) higher than in the parent soils (Fig. 3a). Thus P would be released by desorption more easily from a unit mass of fresh CW sediment than from the agricultural soil in its catchment area. The difference in AER-P concentrations between parent soils and fresh sediments was especially large at Ojainen and Hovi, with a 10-fold higher concentration in Hovi CW fresh sediment, but distinct (1.6- to 3.6-fold) differences were also recorded for the other sites.
Upon drying of the sediments, AER-P declined to about the level in the parent soil except for Hovi CW, where drying did not greatly decrease P extractability by AER. Over all sites, a pairwise comparison between the fresh and dried sediments showed a decline that was close to marginally statistically significant ($p=0.047$).

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

3.3 Degree of P saturation

Among the catchment soils, the highest PSC value (Eq. 1) was found at Kakskerta (Table 4), which had the highest clay content (72%) and the highest C concentration (4.6%) of the fields studied. Fresh sediments had mostly similar, or at Liedonperä somewhat higher, PSC than their parent soils. However, as a result of the Al chemical treatment at Kakskerta, sediment PSC was twice that in the parent soil. The sediment in the other chemical-assisted CW, Nautela, did not bear any notable traces of the Fe$_2$(SO$_4$)$_3$ feeding to the inflow, with only slightly higher Fe (hydr)oxide content in sediment than in the parent soil (Table 4). Drying of the sediments, on the other hand, increased their PSC values in all cases.

The DPS indices showed the same trend as the Chang and Jackson P fractions, in that DPS$_{Feox}$ was larger than DPS$_{Alox}$ in all sediments and soils (Table 4). DPS$_{Alox}$ was smaller in the dried than the fresh sediments, because drying substantially increased the Al$_{ox}$ concentration, and consequently the PSC. When the DPS of Al$_{ox}$ and Fe$_{ox}$ was combined in the same index (DPS$_{Σ}$), the dried sediments 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$_4$F-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
reduction by BD extraction also showed that there were large reserves of redox-sensitive P,
representing 23-48% of TP in the sediments (excluding Kakskerta, where Al-chemical treatment
had diminished the BD-P fraction). Thus, the redox state during sampling, even if anoxic, had not
depleted redox-labile P pool in sediments. Some part of the reductant-soluble P most likely
originates from organic complexes, e.g. Farmer et al. (1994) estimated that 16% of reductant-
soluble P was derived from organic P in lake sediments having 7-10% organic C. Suzumura and
Kamatani (1995) found that the extent and rate of organic P mineralisation is strongly regulated by
the redox conditions in marine environments. Inositol hexaphosphate is a significant carrier of
organic P in suspended matter, and under anoxia it may be rapidly and extensively mineralised as a
result of the release of inositol hexaphosphate molecule from the Fe-associated sediment particles
upon their dissolution at low redox conditions (Suzumura and Kamatani, 1995).

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

At the Kakskerta site, the chemically assisted sedimentation was reflected in an obvious manner: a
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$_2$SO$_4$-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$_2$SO$_4$-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.

Acknowledgements

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


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

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

<table>
<thead>
<tr>
<th>Site (Municipality)</th>
<th>Year established</th>
<th>Size, m²</th>
<th>Catchment area, km²</th>
<th>CW as % of catchment area</th>
<th>Arable land in catchment, %</th>
<th>Dominant soil texture in catchment</th>
<th>Chemical, dosing for P precipitation, kg:m³ water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ojainen (Jokioinen)</td>
<td>2000</td>
<td>370</td>
<td>0.16</td>
<td>0.23</td>
<td>100</td>
<td>silty clay</td>
<td>-</td>
</tr>
<tr>
<td>Liedonperä (Tarvasjoki)</td>
<td>1995</td>
<td>4850</td>
<td>0.99</td>
<td>0.49</td>
<td>50</td>
<td>silty clay loam</td>
<td>-</td>
</tr>
<tr>
<td>Hovi (Vihti)</td>
<td>1998</td>
<td>6000</td>
<td>0.12</td>
<td>5.0</td>
<td>100</td>
<td>clay</td>
<td>-</td>
</tr>
<tr>
<td>Kakskerta (Turku)</td>
<td>2006</td>
<td>850</td>
<td>0.73</td>
<td>0.12</td>
<td>64</td>
<td>clay</td>
<td>aluminium chloride, 1:30</td>
</tr>
<tr>
<td>Nautela (Lieto)</td>
<td>2005</td>
<td>&lt; 100</td>
<td>0.61</td>
<td>&lt; 0.02</td>
<td>63</td>
<td>silty clay</td>
<td>ferric sulphate, 1:50</td>
</tr>
</tbody>
</table>

*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.

<table>
<thead>
<tr>
<th>Site</th>
<th>Clay %</th>
<th>pH</th>
<th>Eh mV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ojainen</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>45</td>
<td>6.7$^3$</td>
<td>NA</td>
</tr>
<tr>
<td>Fresh sediment</td>
<td>NA</td>
<td>7.3$^4$</td>
<td>21</td>
</tr>
<tr>
<td>Dry sediment</td>
<td>82</td>
<td>5.1$^3$</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Liedonperä</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>35</td>
<td>6.7$^3$</td>
<td>NA</td>
</tr>
<tr>
<td>Fresh sediment</td>
<td>NA</td>
<td>6.8$^4$</td>
<td>5</td>
</tr>
<tr>
<td>Dry sediment</td>
<td>62</td>
<td>5.2$^3$</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Hovi</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>58</td>
<td>6.9$^3$</td>
<td>NA</td>
</tr>
<tr>
<td>Fresh sediment</td>
<td>NA</td>
<td>6.3$^4$</td>
<td>25</td>
</tr>
<tr>
<td>Dry sediment</td>
<td>82</td>
<td>5.7$^3$</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Kakskerta</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>72</td>
<td>6.0$^3$</td>
<td>NA</td>
</tr>
<tr>
<td>Fresh sediment$^1$</td>
<td>NA</td>
<td>6.5$^4$</td>
<td>21</td>
</tr>
<tr>
<td>Dry sediment$^1$</td>
<td>79</td>
<td>5.9$^3$</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Nautela</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>45</td>
<td>6.8$^3$</td>
<td>NA</td>
</tr>
<tr>
<td>Fresh sediment$^2$</td>
<td>NA</td>
<td>5.2$^4$</td>
<td>105</td>
</tr>
<tr>
<td>Dry sediment$^2$</td>
<td>54</td>
<td>5.2$^3$</td>
<td>NA</td>
</tr>
</tbody>
</table>

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$_2$O.

$^4$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.

<table>
<thead>
<tr>
<th>Site</th>
<th>Tot-C</th>
<th>Tot-N</th>
<th>Tot-S</th>
<th>SO$_4^{2-}$-S</th>
<th>SO$_4^{2-}$-S/Tot S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>mg kg$^{-1}$</td>
<td>%</td>
</tr>
<tr>
<td>Ojainen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>2.8</td>
<td>0.19</td>
<td>0.03</td>
<td>17±0 a</td>
<td>7</td>
</tr>
<tr>
<td>Sediment</td>
<td>3.6</td>
<td>0.34</td>
<td>0.13</td>
<td>877±4 b</td>
<td>67</td>
</tr>
<tr>
<td>Liedonperä</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>1.7</td>
<td>0.12</td>
<td>0.02</td>
<td>20±0 e</td>
<td>10</td>
</tr>
<tr>
<td>Sediment</td>
<td>1.3</td>
<td>0.12</td>
<td>0.14</td>
<td>98±1 f</td>
<td>7</td>
</tr>
<tr>
<td>Hovi</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>1.8</td>
<td>0.14</td>
<td>0.02</td>
<td>20±0 h</td>
<td>8</td>
</tr>
<tr>
<td>Sediment</td>
<td>2.2</td>
<td>0.19</td>
<td>0.05</td>
<td>227±1 i</td>
<td>44</td>
</tr>
<tr>
<td>Kakskerta</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>4.6</td>
<td>0.37</td>
<td>0.12</td>
<td>136±9 c</td>
<td>11</td>
</tr>
<tr>
<td>Sediment$^1$</td>
<td>15.0</td>
<td>0.95</td>
<td>0.64</td>
<td>449±2 d</td>
<td>7</td>
</tr>
<tr>
<td>Nautela</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>1.8</td>
<td>0.15</td>
<td>0.02</td>
<td>20±0 j</td>
<td>9</td>
</tr>
<tr>
<td>Sediment$^2$</td>
<td>5.2</td>
<td>0.42</td>
<td>0.10</td>
<td>284±2 k</td>
<td>28</td>
</tr>
</tbody>
</table>

$^1$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$_4$Cl-, NH$_4$F- 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 ± SE.

<table>
<thead>
<tr>
<th>Site</th>
<th>Al$_{ox}$ mmol kg$^{-1}$</th>
<th>Fe$_{ox}$ mmol kg$^{-1}$</th>
<th>PSC mmol kg$^{-1}$</th>
<th>DPS$_{Alox}$ %</th>
<th>DPS$_{Feox}$ %</th>
<th>P$_{Σ}$(NH$_4$Cl, NH$_4$F, NaOH) mmol kg$^{-1}$</th>
<th>DPS$_{Σ}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ojainen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>112±9 a</td>
<td>223±18 a</td>
<td>168</td>
<td>7.6</td>
<td>10.6</td>
<td>16</td>
<td>9.6</td>
</tr>
<tr>
<td>fresh sediment</td>
<td>181±28 a</td>
<td>253±31 a</td>
<td>217</td>
<td>2.5</td>
<td>13.9</td>
<td>20</td>
<td>9.2</td>
</tr>
<tr>
<td>air-dry sediment</td>
<td>292±5 b</td>
<td>261±3 a</td>
<td>277</td>
<td>1.7</td>
<td>11.1</td>
<td>17</td>
<td>6.1</td>
</tr>
<tr>
<td>Liedonperä</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>93±3 f</td>
<td>191±13 c</td>
<td>142</td>
<td>3.5</td>
<td>6.2</td>
<td>8</td>
<td>5.4</td>
</tr>
<tr>
<td>fresh sediment</td>
<td>124±11 g</td>
<td>315±48 d</td>
<td>220</td>
<td>1.0</td>
<td>3.9</td>
<td>7</td>
<td>3.1</td>
</tr>
<tr>
<td>air-dry sediment</td>
<td>186±2 g</td>
<td>351±4 d</td>
<td>269</td>
<td>0.3</td>
<td>3.2</td>
<td>6</td>
<td>2.2</td>
</tr>
<tr>
<td>Hovi</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>158±4 h</td>
<td>203±14 e</td>
<td>181</td>
<td>1.1</td>
<td>3.9</td>
<td>5</td>
<td>2.7</td>
</tr>
<tr>
<td>fresh sediment</td>
<td>145±1 h</td>
<td>189±3 e</td>
<td>167</td>
<td>3.9</td>
<td>10.7</td>
<td>13</td>
<td>7.8</td>
</tr>
<tr>
<td>air-dry sediment</td>
<td>191±3 h</td>
<td>172±3 e</td>
<td>182</td>
<td>1.2</td>
<td>12.1</td>
<td>12</td>
<td>6.4</td>
</tr>
<tr>
<td>Kakskerta</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>159±19 c</td>
<td>257±16 b</td>
<td>208</td>
<td>1.2</td>
<td>7.0</td>
<td>10</td>
<td>4.8</td>
</tr>
<tr>
<td>fresh sediment</td>
<td>611±75 d</td>
<td>204±12 b</td>
<td>408</td>
<td>1.9</td>
<td>5.4</td>
<td>11</td>
<td>2.8</td>
</tr>
<tr>
<td>air-dry sediment</td>
<td>728±4 e</td>
<td>249±2 b</td>
<td>489</td>
<td>1.2</td>
<td>4.0</td>
<td>9</td>
<td>1.9</td>
</tr>
<tr>
<td>Nautela</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>81±3 i</td>
<td>195±14 f</td>
<td>138</td>
<td>5.4</td>
<td>10.6</td>
<td>12</td>
<td>9.1</td>
</tr>
<tr>
<td>fresh sediment</td>
<td>73±3 i</td>
<td>206±5 f</td>
<td>140</td>
<td>3.2</td>
<td>13.8</td>
<td>15</td>
<td>11.0</td>
</tr>
<tr>
<td>air-dry sediment</td>
<td>117±2 i</td>
<td>225±2 f</td>
<td>171</td>
<td>2.0</td>
<td>8.0</td>
<td>10</td>
<td>6.0</td>
</tr>
</tbody>
</table>

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 (NH$_4$F-P, NaOH-P, H$_2$SO$_4$-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. ¹Aluminium chloride solution assisted sedimentation. ²Granular 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. ¹Aluminium chloride solution assisted sedimentation. ²Granular ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) assisted sedimentation.