



Distribution and speciation of metals, phosphorus, sulfate and organic material in brackish estuary water affected by acid sulfate soils



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ABSTRACT

Dissolved (<1 kDa) and colloidal (1 kDa–0.45 μm) size fractions of sulfate, organic carbon (OC), phosphate and 17 metals/metalloids were investigated in the acidic Vörå River and its estuary in Western Finland. In addition, geochemical modelling was used to predict the formation of free ions and complexes in these waters. The sampling was carried out during high-water flow in autumn and in spring when the abundantly occurring acid sulfate (AS) soils in the catchment area are extensively flushed. Based on the high concentrations of sulfate, acidity and several metals, it is clear that the Vörå River and its estuary is strongly affected by AS soils. The high dissolved form of metals limits also the existence of fish and other organisms in this estuary, and certainly also in other similar shallow brackish estuaries elsewhere in the Gulf of Bothnia. However, generally already <20% saline sea water reduces the concentration for OC and several elements (Al, Cu, Cr, Fe, Pb, PO₄ and U) by half and c. 20–30% saline sea water is needed to halve concentrations of Cd, Co, Mn, Ni and Zn. Consequently, these elements as well as organic matters were rapidly precipitated in the estuary, even after mixing with fairly small amounts of the alkaline brackish sea water. Aluminium, Cu, Fe and U most likely precipitate together with organic matter closest to the river mouth. Manganese is relatively persistent in solution and, thus, precipitates further down the estuary as Mn oxides, which concomitantly capture Ba, Cd, Co, Cu, Ni and Zn. In the inner estuary, the high contents of Al is as important than Fe in removing PO₄ and, thus, also reducing the risk of algae blooms in near coastal areas influenced by AS soils in the Gulf of Bothnia. Moreover, the dispersion of metals far out in the estuary is dependent on hydrological conditions, i.e. with high flows the plume of metal-rich water will spread further out in the estuary. Furthermore, the extensive drainage of the catchment and subsequent artificial enlargement of the river channel during recent decades has not only enabled oxidation of sulfidic sediments, but strongly increased flow peaks that reach further out in the estuary.

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1. Introduction

In aquatic environments, the bioavailability and toxicity of metals are closely related to different physical states such as free or complexed, associated with colloids or with particles (Morel and Hering, 1993; Guéguen et al., 2004; Balisterieri et al., 2007). The dissolved forms (<1 kDa), including free hydrated ions and inorganic complexes, are generally considered to be the most toxic fractions, because of their high mobility and bioavailability. Colloids (1 kDa–0.45 μm), consisting notably of Fe, Mn and Al hydroxides,

phyllosilicates and organic matters, have high adsorption capacities and play, thus, a vital role in regulating the speciation, transport, bioavailability, toxicity and environmental fate of many trace metals (Wang et al., 2003; Pédrot et al., 2008). However, metals associated with colloids are, though, not soluble and generally not accessible to the biota, but this metal fraction is prone to remobilization (i.e. dissociation from mineral surfaces) in response to changes in physico-chemical conditions (e.g. pH, ionic strength and complexing ligands). In contrast, metals associated with larger particles (>0.7 μm; Filella and Buffle, 1993; Vignati et al., 2006) are usually rapidly settled and buried in the sediments, and are generally not available for the biota (Sigg et al., 2000; Eggleton and Thomas, 2004; Butler et al., 2008).

Estuaries, as one of the most important reservoirs for contaminants carried by rivers and streams, are of great importance in

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biogeochemical cycling of metals and other elements, and also possible future sources of heavy metals in estuary systems due to possible remobilization of elements (Li et al., 2000; Tessier and Campbell, 1988; Yang et al., 2012). Conditions in the estuaries are affected not only by seasonal and hydrological changes, but also by tides, multiple inputs, diurnal changes and fluctuating river flows (Callahan et al., 2004). In the estuarine mixing zone, “river-transported compounds are subjected to a variety of physical, chemical, and biological transformation processes”, including transfer reactions between the dissolved, colloidal and particulate phase (Beck et al., 2012). All of these processes vary with pH, salinity, turbidity, ionic strengths and redox conditions (Sholkovitz and Copland, 1981; Gustafsson et al., 2000; Andersson et al., 2001; Lyven et al., 2003; Jiann et al., 2005; Beck et al., 2012).

On the coastal plains of western Finland, acid sulfate (AS) soils widely occur and export large amounts of potentially toxic metals (such as Al, Mn, Cd, Cu, Ni, Zn) and acidity to receiving watercourses (Edén et al., 1999; Roos and Åström, 2005; Österholm and Åström, 2004; Nordmyr et al., 2008a,b). Particularly during high water flow conditions in spring and in autumn, acidic pore water rich in metals is flushed to recipient streams (Palko et al., 1985; Hudd and Kjellman, 2002; Nyberg et al., 2012). These metal loads are ultimately transported to and deposited in recipient estuaries along the coast, causing a number of adverse effects on the estuarine ecosystems and aquatic organisms, e.g. an acid and metal plume coinciding with the hatching period can occasionally exterminate whole populations of many fish species using coastal areas as a hatching ground (Hudd and Kjellman, 2002). Several widespread mass kills of adult fish have been documented (e.g. Hudd and Leskelä, 1998) and the latest mass kills occurred in autumn/winter 2006 (Nordmyr et al., 2008a; Toivonen and Österholm, 2011). Despite the massive export of metals from AS soils and associated environmental problems, relatively little is known about chemical form and size distribution of these metals in the recipient estuaries, although this information is of great importance when estimating ecotoxicological effects in metal-enriched waters and in management of the biologically-sensitive estuarine ecosystems (Åström and Corin, 2000; Mosley et al., 2014; Wallin et al., 2015).

This study focuses on the estuary of Vörå River (hereafter “the estuary”) in western Finland. The river runs through a landscape with an abundance of AS soils, and is thus periodically severely acidified and loaded with high levels of toxic metals occurring mainly in toxic forms of free ions and sulfate-complexes (Åström et al., 2010; Nystrand and Österholm, 2013). This has serious effects on the biota and particularly dissolved Al is expected to have acute effects on fish and other organisms (Sammut et al., 1996; Earle and Callaghan, 1998). In the estuary elevated metal concentrations have been detected in both suspended material and sediments (Nordmyr et al., 2008a; Wallin et al., 2015). Although the attenuation mechanisms for rare earth elements (REEs) in the estuary water have been investigated (Åström et al., 2012), the behaviour of major elements and other trace element species (particularly potentially toxic ones) have not been studied. In this study we, therefore, present the results for these elements and also new interpretations and modelling results for some metals briefly presented earlier (Åström et al., 2012). The overall aim is to examine the concentration, size distribution and species of major and trace elements in the estuary of a Boreal acidic river (i.e. Vörå River) in order to assess the speciation changes of these metals and the possible associated ecological risk therein. On the basis of the spatial physicochemical patterns found we examine the fractionation, complexation and precipitation processes of elements mainly related to the input of humic matter and changes in pH and salinity.

2. Methodology

2.1. Study area

The sampling sites are situated at the lower reach of Vörå River and its estuary, in western Finland (Fig. 1). The catchment area (223 km²) is underlain by Proterozoic granitoids and gneisses (Laitakari, 1942), which is mainly covered by Quaternary deposits, including till and glaciofluvial material, sulfide-bearing marine and lacustrine clays and silts, littoral sediments, and peat. No lakes exist in the drainage area and the influence of industrial and urban effluents is minor. Runoff is generally highest after snow melt in spring (April–May; Korhonen, 2007) and the mean annual specific runoff is c. 7 Ls⁻¹km⁻² (HERTTA database, Finnish Environmental Centre). Forest is the dominant land cover type in the catchment (54%) and dominates in the upstream area of the river, but the proportion of cultivated land, largely underlain by fine grained sulfide-bearing marine and lacustrine sediments, is also extensive (31%) and dominates in the downstream areas. Also mires (15%) are found in the area (Rautio and Ilvessalo, 1998) that may be underlain by sulphide-bearing sediments. The catchment (i.e. mostly the cultivated land areas) is well-drained as a result of extensive and deep ditching (Åström et al., 2010). Therefore, the groundwater table has dropped, which in areas with sulfidic marine sediments has resulted in extensive metal-sulfide oxidation and development of acid sulfate soils. As a consequence, Vörå River is one of the most heavily AS soil-impacted rivers in Europe (Roos and Åström, 2005; Nordmyr et al., 2008a), and moreover discharges into a shallow and biologically sensitive brackish water estuary; i.e. into the Gulf of Bothnia. The estuary is relatively well confined with Vörå River

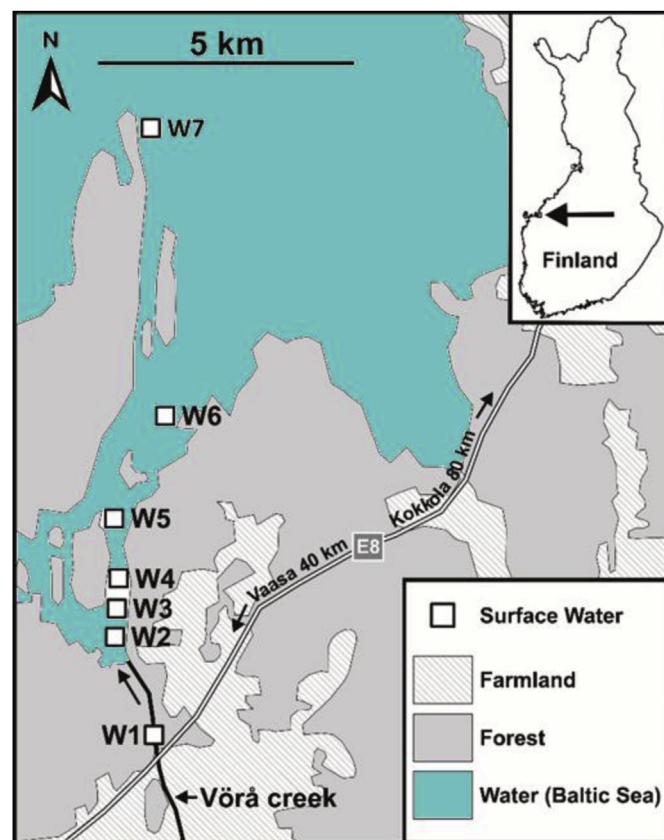


Fig. 1. Location of the study area and sampling sites in the Vörå River (W1) and the inner (W2–W4) and outer (W5–W7) estuary of Vörå River in W Finland.

being the main source of fresh water. The inner estuary (0–1.7 km from the river mouth) is shallow (2–10 m deep) and sheltered from wave action by surrounding land areas and islands, while further out the water depths are commonly between 10 and 17 m (Nordmyr et al., 2008a). The salinity is low (1–3‰; Nordmyr et al., 2008b) and during a large part of the year (December–April/May) the estuary is covered by ice (up to 70 cm thick).

2.2. Sampling and analyses

Water samples at a depth of 1 m from the water surface were collected twice during high flow seasons, when the dispersion of acidic river water is greatest, from the lower reach of Vörå River (W1; Fig. 1) and from the estuary of Vörå River (W2–W7; Fig. 1) in a transect from close to the creek mouth (i.e. inner estuary, W2–W4) to the outer estuary (W5–W7). The sampling locations were spiked with a GPS. Kyrö River (Oiva database) was used to assess the hydrological conditions during sampling. The first sampling event was conducted during a rising limb in late autumn (December 1st 2009) two weeks after prolonged rains had increased the specific runoff from c. 3 to 16 $\text{L s}^{-1}\text{km}^{-2}$ and the 14 day average prior to sampling was 11 $\text{L s}^{-1}\text{km}^{-2}$ (Fig. 2). The second sampling event occurred in spring (May 5th 2010) three weeks after the spring flow peak (85 $\text{L s}^{-1}\text{km}^{-2}$) caused by snow smelting. The runoff at the day of sampling was 14 $\text{L s}^{-1}\text{km}^{-2}$ and the 14 day average prior to sampling was 14 $\text{L s}^{-1}\text{km}^{-2}$ (Fig. 2). The water temperature at the sampling days was around 4° C in autumn and around 6° C in spring.

The samples were collected in 500 ml polyethylene bottles and filtrated with a 0.45 μm Millipore filter (the first 5–10 ml of the filtrate was always discarded) and then ultrafiltrated. Frontal ultrafiltration was performed following the procedure by (Nystrand et al. 2012; Nystrand 2012) using a 400-ml polycarbonate cell (Amicon 8400) and a 1 kDa regenerated cellulose acetate membrane (Millipore). Nitrogen pressure (2.5 bars) was used as the driving force and a concentration factor (cf) of 6 was applied. The cf was calculated according to Dupré et al. (1999): $cf = V_{\text{tot}}/V_{\text{retentate}}$, where V_{tot} is the total volume and $V_{\text{retentate}}$ the retentate volume. There is still no consensus about the optimal cf for the ultrafiltration process, but for this specific technique (i.e. frontal ultrafiltration with Amicon 8400) a low cf is recommended (3–13; Waelles et al., 2008). System blank tests were performed to control the

level of pollution induced by sampling, filtration and ultrafiltration.

After both filtration and ultrafiltration the samples (including duplicates and method blank samples) were immediately acidified with 2% ultrapure HNO_3 and analysed in randomised order for 14 elements (Ba, Ca, Cd, Co, Cr, Cu, K, Mg, Na, Ni, Si, Sr, U and Zn) by ICP-SFMS (ELEMENT2, Thermo-Scientific) at ALS Laboratory Group in Luleå, Sweden. Iron, Mn and Al were determined by ICP-AES (Optima 4300 DV, Perkin Elmer) and when the detection limit was insufficient, by ICP-SFMS as above. The results for Al, Fe and Mn have also partly been presented elsewhere (Åström et al., 2012). The filtered and ultrafiltered samples were analysed for all water samples. The samples were spiked with internal standards to correct for instrumental drift and matrix suppression. Blanks and system blanks were run to verify clean and uncontaminated conditions, and certified reference materials were used to control accuracy. A more detailed description of the measurement conditions and operation parameters is given elsewhere (Olofsson et al., 2000; Rodushkin et al., 2005). For all investigated elements the concentrations in the blanks were below or just above the analytical detection limits, and the analytical precision, based on random analytical duplicates (Gill, 1997), was <11% for all elements, except for Ca, Na and U of which the analytical precision was 15%, 18% and 21%, respectively. The reliability of the analyses was additionally evaluated by calculating the recovery factors for all ultrafiltered runs as follows (Ren et al., 2010): $R = ((C_{\text{permeate}}V_{\text{permeate}} + C_{\text{retentate}}V_{\text{retentate}})/(C_{\text{filt}}V_{\text{filt}})) * 100$, where C is concentration, V volume, permeate water ultrafiltrated with a 1 kDa membrane, retentate water retained during ultrafiltration and “filt” water filtered with a 0.45 μm filter. The recovery was generally within the range of 85–115%, which can be considered as good (Vasyukova et al., 2010) and occasionally down to 75–80% and up to 120–125%, which still are satisfactory (Åström et al., 2010).

Water temperature, pH and specific electric conductivity (EC) were measured with a field electrode (YSI Model 63) precalibrated using buffer solutions of citrate (pH = 4.00) and phosphate (pH = 7.00) for pH measurements and 50 mS/cm conductivity standards for EC calibrations. Samples for analyses of OC were analysed in randomised order with a Shimadzu Organic Carbon TOC-V_{CSN} analyser (see for more details in Åström et al., 2012; and Nystrand, 2012). Twelve duplicates and 4 method blank samples were included. Analytical precision for the OC analyses was <10%. The concentrations of Cl^- , F^- and SO_4^{2-} were analysed by ion

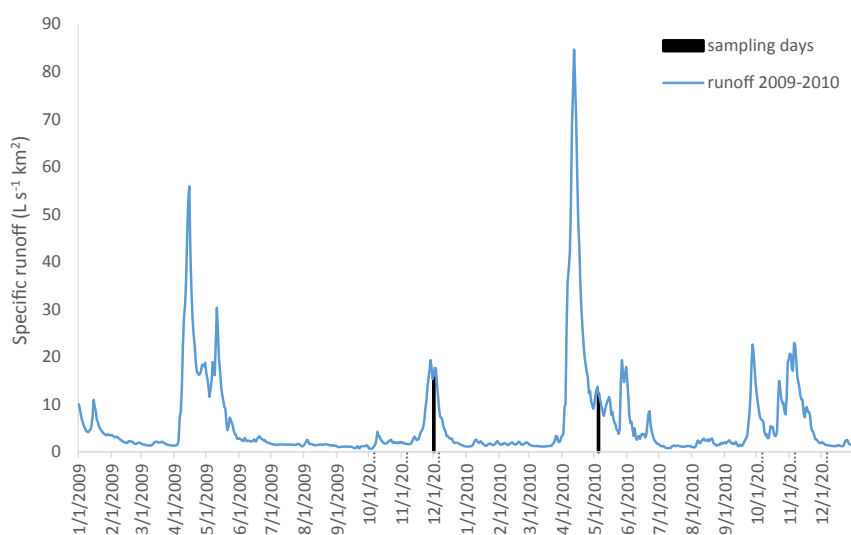


Fig. 2. The specific runoff in the Kyrö River during year 2009–2010 and for the specific sampling days (1.12.2009 and 5.5.2010).

chromatography (Dionex DX-120) and total reactive phosphorus was determined with the acidic molybdenum-blue method (spectrophotometer: Lachat QuickChem FIA+ 800). The analytical precision for these measurements was within 5%.

2.3. Speciation modelling

The geochemical modelling program Visual MINTEQ (vers. 3.0; Gustafsson, 2011) was used to predict metal speciation in Vörå River and its estuary. For the calculations, the following variables were used: pH, temperature, and filtrated concentrations (i.e. concentrations of 0.45 μm filtered water samples) for Al, As, Ba, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, K, La, Mg, Mn, Na, Ni, PO₄, Pb, Rb, Si, SO₄, U, Yb, Zn and OC. It was noticed that a higher number of elements used for modelling predicts a more accurate element speciation; i.e. more alike the ultrafiltration results, and thus more elements (As, La, Pb, Rb, Yb) were used for the calculations than were discussed in this paper. The Stockholm humic model (SHM) was used to describe the formation of metal-DOM (dissolved organic matter) complexes. It was assumed that the ratio of active DOM to DOC (dissolved organic carbon) was 1.65 (Sjöstedt et al., 2010) and that 70% of the active DOM was fulvic acid (FA) and the remaining 30% inactive with respect to proton and metal binding (Åström et al., 2010). In addition, Al was allowed to precipitate and the solubility constant selected was Al(OH)₃ with a log K_s of 8.28 at 25 °C and a reaction enthalpy of –105 kJ/mol. The Diffuse Layer Model of Dzombak and Morel (1990) was used to determine the adsorption of metals by colloidal hydrous ferric oxide. The concentration of colloidal ferrihydrite was estimated by allowing precipitation of ferrihydrite (aged) with a log K_s = 2.69 at 25 °C and a reaction enthalpy of –100.4 kJ/mol. Ferrihydrite was assumed to have a specific surface area of 600 m²/g and a site density of 2.31 n/m² (Dzombak and Morel, 1990). Similarly, the double-layer HMO surface complexation sub-model (Tonkin et al., 2004) was used to determine metal binding to colloidal Mn oxide. The concentration of colloidal Mn oxide was calculated by allowing precipitation of birnessite (log K_s = 18.091 at 25 °C) with a specific surface area of 746 m²/g.

3. Results

The water in Vörå River (W1) was acidic (pH 4.4–4.6) and had high electric conductivity (422–526 $\mu\text{S}/\text{cm}$; Table 1). Compared to nearby Lapväärtinjoki river with minor AS soil impact (Roos and Åström, 2005), concentrations of SO₄ and filtrated (<0.45 μm) concentrations of several elements (Al, Ca, Cd, Co, Cr, Cu, Mg, Mn, Na, Ni, Si, U and Zn) were in Vörå River highly elevated (Table 1 and Fig. 3). The filtrated concentrations for Cd, Cu and Zn were in Vörå River (W1) relatively similar on both sampling occasions, but for most of the elements the concentrations were, though, slightly (10–20%) lower, and more than 30% lower for Fe, PO₄ and SO₄ in spring 2010 (Table 1).

From the transect extending from the river mouth to the outer estuary the electric conductivity and pH successively increased (Table 1) as the river water was successively mixed with the alkaline brackish Baltic Seawater. The pH gradient was more or less the same on both sampling occasions, but the electric conductivity, sulfate and other elements abundant in sea water (Ca, Cl, K, Mg, Na and Sr) were much lower in spring 2010 than in autumn 2009 (Table 1 and Fig. 3). On the contrary, in spring when the water flow was high, filtrated concentrations for elements associated with AS soils in the catchment (Al, Cd, Co, Cu, Mn, Ni, U and Zn; Åström et al., 2010; Nystrand and Österholm, 2013) as well as Fe, were remarkably higher (Table 1 and Fig. 3).

Based on filtrated concentrations, two main groups of elements

were identified; (1) Ca, Cl, F, K, Mg, Na, SO₄ and Sr (Fig. 3a) with lower concentrations in Vörå River than in sea water, and, thus, increasing concentrations with an increasing proportion of seawater towards the outer estuary, and (2) organic carbon, Al, Cd, Co, Cr, Cu, F, Fe, Mn, Ni, PO₄, Si and Zn (Fig. 3b) with higher concentrations in Vörå River and, thus, decreasing concentrations towards the sea. In contrast, the behaviour for U and Ba differed as the concentrations for Ba was relatively constant (i.e. the same concentrations in the river and estuary; Fig. 3c), and the concentration for U varied incoherently as it first decreased in the inner estuary and later increased in the outer estuary (Fig. 3d). Nevertheless, U did not increase above the concentrations in the river.

Several elements (Ba, Ca, Cd, Co, K, Mg, Mn, Na, Ni, Si, Sr and Zn) were in the estuary mostly found as dissolved (D/filt ratio generally over 0.9; Supplementary data Table S1 and Fig. 3), although the proportion of colloidal Ni was slightly higher at some sites (Supplementary data Table S1). On the contrary, OC, Al, Cr, Cu, Fe and U were found both in a dissolved and colloidal phase (Fig. 3). The median D/filt ratio for these elements was 0.63–0.92 in autumn 2009 and 0.45–0.72 in spring 2010 (Supplementary data Table S1 and Fig. 3).

The filtrated (<0.45 μm) fraction of several studied elements decreased down the estuary considerably faster (i.e. precipitation) than would occur at conservative behaviour (dilution only; Fig. 4). Already <20% saline water reduces the concentration for OC, Al, Cu, Cr, Fe, Pb, PO₄ and U by half, and only 20–30% saline sea water is needed to halve concentrations of Cd, Co, Mn, Ni and Zn (Fig. 4). As the proportion of sea water is increased to c. 50% the concentrations for OC, Cd, Co, Mn, Ni and Zn are reduced to c. 20% relative to the concentration in the river, and Cu, Cr, Pb, PO₄ and U to c. 10% (Fig. 4). The concentrations for Al and Fe dropped extremely fast in the inner estuary, but also for OC, Cu, Cr, PO₄ and U the concentrations decreased almost as fast in the estuary (Fig. 4). Several other elements (Ba, Cd, Co, Mn, Ni and Zn) behaved also non-conservative, but those concentrations decreased, though, slower in the estuary (Fig. 4). Moreover, the concentrations of all elements in the dissolved (<1 kDa) fraction closely followed the trend of the filtrated fraction.

The speciation modelling with Visual MINTEQ predicted that Al as Al(OH)₃(s) was precipitated in most of the sites (21–97%; the precipitation increased out to the sea, but mostly in the inner estuary). Also Mn as birnessite was predicted to precipitate (c. 95%) further out in the estuary (W6 and W7) and Fe as ferrihydrite (35–75%) in the inner estuary (W1–W3). The remaining concentrations of Al, Mn and Fe were predicted to occur as free ions and/or complexes in the water (Fig. 5, Fig. 6 and Supplementary Data Table S1). In all filtrated waters Ca, K, Mg and Na were predicted to almost entirely occur in the form of free ions (Fig. 5). Also Ba, Cd, Co, Mn, Ni and Zn were predicted to occur as free ions in the inner estuary (W2–W5), but further out in the estuary (W6 and W7) these elements were predicted to be largely associated with Mn oxides (Fig. 5). Another group of elements (Al, Cu, Fe, Ni and U) were predicted to form complexes with organic matters (Fig. 5) and these predictions correspond with the rapid decrease of several of these element concentrations in the inner estuary (Fig. 4). Iron and U were predicted to be adsorbed almost entirely to OC (Fig. 5). Aluminium, though, was in Vörå River predicted to occur mostly as sulfate complexes and as free ions, and in the inner estuary also as Al–F-complexes. Moreover, associations to OC was predicted to become significant in the inner estuary with the increasing pH (Fig. 5). A similar increasing association to OC could also be seen for Cu in the inner estuary (Fig. 5), but in the outer estuary the associations to OC decreased and instead the association to Mn increased considerably (Fig. 5). Moreover, PO₄ was predicted to form complexes with Al and Fe in the Vörå River and in the inner

Table 1
pH, electric conductivity (EC) and concentrations for sulfate, phosphate and filtrated (<0.45 µm) metals in the Vörå River (W1) and in the estuary of Vörå River (W2–W7). Some of the variables (pH, EC, T, Cl, F, PO₄, SO₄, OC, Al, Fe, Mn) were also presented in [Åström et al., 2012](#).

Sample	Date	pH	Ec µS/cm	T	OC	Al mg/L	As mg/L	Ba µg/L	Ca µg/L	Cd mg/L	Cl µg/L	Co mg/L	Cu µg/L
W1	1.12.2009	4.4	526.6	9	12.83	7.533	0.138	15.1	25.6	0.612	23.33	0.72	9.46
W2	1.12.2009	5.0	1959	3.3	5.98	0.833	0.443	17.0	42.0	0.344	900	21.45	4.03
W3	1.12.2009	5.6	3209	3.6	6.00	0.067	0.448	13.6	38.6	0.188	1200	12.33	2.00
W4	1.12.2009	6.3	4400	3.4	6.59	0.043	0.513	14.3	46.3	0.157	1400	8.48	2.31
W5	1.12.2009	6.5	5290	3.0	6.79	0.041	0.589	13.8	45.0	0.098	1600	5.83	2.32
W6	1.12.2009	6.8	5550	2.8	5.52	0.037	0.537	12.7	46.0	0.056	1600	3.37	1.00
W7	1.12.2009	7.0	6210	2.5	5.21	0.033	1.167	13.5	50.8	0.055	1700	0.88	1.04
W1	5.5.2010	4.6	422	4.2	9.77	6.433	0.252	14.1	22.5	0.531	17	28.55	9.92
W2	5.5.2010	5.0	730	6.6	8.18	5.325	0.386	14.6	22.7	0.437	72	26.50	8.43
W3	5.5.2010	5.8	1450	6.5	6.71	2.257	0.700	14.5	21.6	0.365	220	18.90	5.26
W4	5.5.2010	6.3	1623	6.8	6.83	2.327	0.667	14.6	21.5	0.324	210	18.95	5.42
W5	5.5.2010	6.2	1643	7.6	6.65	0.237	0.917	14.3	23.0	0.220	410	12.68	3.17
W6	5.5.2010	7.0	2452	7.7	5.98	0.119	0.917	13.7	26.5	0.132	680	7.37	2.07
W7	5.5.2010	7.4	4294	5.0	5.55	0.129	1.167	12.1	36.2	0.070	1200	1.12	1.31
Sample	Date	F mg/L	Fe µg/L	Mg mg/L	Mn µg/L	Na mg/L	Ni µg/L	PO ₄ µg/L	-P SO ₄ mg/L	Si mg/L	Sr µg/L	U µg/L	Zn µg/L
W1	1.12.2009	0.87	477	16.7	1332	17	77.4	28	220	20.45	152.0	0.511	172
W2	1.12.2009	0.50	72	70.3	981	506	48.4	6	240	13.40	465	0.131	103
W3	1.12.2009	0.17	21	74.6	595	581	28.1	4	240	7.80	476	0.076	55
W4	1.12.2009	0.31	14	97.3	433	735	20.2	3	250	5.92	605	0.127	39
W5	1.12.2009	0.25	10	98.5	291	771	14.2	<2	260	1.79	605	0.168	28
W6	1.12.2009	0.14	6	103.2	184	838	8.9	<2	250	3.07	635	0.205	17
W7	1.12.2009	0.17	14	117.3	45	999	3.9	<2	260	1.50	743	0.317	6
W1	5.5.2010	0.76	439	14.0	1215	15	65.9	12	150	18.62	138	0.460	175
W2	5.5.2010	0.68	542	16.4	1155	44	58.7	7	150	17.35	151	0.381	137
W3	5.5.2010	0.40	252	23.5	891	126	39.9	8	120	12.48	183	0.219	90
W4	5.5.2010	0.41	207	23.5	885	125	40.5	8	130	12.45	181	0.219	103
W5	5.5.2010	0.29	58	33.4	692	227	25.2	7	120	9.14	238	0.092	56
W6	5.5.2010	0.21	35	47.6	485	366	17.6	5	140	6.41	323	0.093	29
W7	5.5.2010	0.16	83	80.8	77	685	3.6	5	180	2.16	517	0.234	10

estuary (Fig. 6 and Supplementary Data Table S1). Cadmium was in larger amounts predicted to form complexes with Cl (Supplementary data Table S1). Sulfate complexes were generally predicted to occur in Vörå River, but they decreased to the outer estuary due to the increasing pH (Fig. 5).

4. Discussion

4.1. Element dispersion in the estuary

The water in the estuary of Vörå River, and especially the water in the inner estuary, is strongly affected by AS soils, because: (1) as indicated by the electric conductivity, the river water was clearly detectable even at the outermost sampling site, especially in spring 2010 with higher water flows (Figs. 2 and 4), (2) sulfate and metals known to be abundantly leached from AS soils and thus occurred in high concentrations in the river (e.g. Al, Cd, Co, Cu, Mn, Ni and Zn) were moderately to strongly elevated in several (W2–W4) of the estuarine sampling sites, especially in spring 2010 with higher water flows (Figs. 2 and 3), and (3) no other major sources of pollution (i.e. industries) are known to exist in the area. This is in line with the study by [Roos and Åström \(2005\)](#), which compared 21 rivers in mid-western Finland and concluded that Vörå River was one of the rivers receiving the highest sulfate and metal loads and therefore is one of the most heavily AS soil impacted rivers in Finland and Europe.

In the transect extending from the river mouth to the outer estuary there was a successive in-mixing of brackish sea water (Fig. 4) and therefore an increase in pH and salinity (Table 1). It was, thus, demonstrated that the rate of discharge plays a more

important role for the dispersion of metal-rich river water to the outer estuary than temporal variations in the water quality. This phenomenon is strengthened by the fact that the concentrations of AS soils related elements tend to be highest during high flow conditions ([Nyberg et al., 2012](#)). Thus, potential hydrological changes triggered by climate change (e.g. global warming) causing higher flow in autumn–winter and less extreme spring floods have significant effects on the extent of the dispersion dynamics at different seasons. Moreover, the extensive drainage of the catchment and artificial enlargement of the river channel during recent decades has not only enabled oxidation of sulfidic sediments, but strongly increased flow peaks that enable large temporary plumes of acidic river water to reach further out in the estuary ([Nordmyr et al., 2008a](#)). Worst events occur in situations such as that in the late autumn of 2006 when a severely dry summer (maximising oxidation of sulfides in the AS soils) coincide with a subsequent severe wet spell ([Österholm and Åström, 2008](#); [Saarinen et al., 2010](#)) causing widespread fish kills in rivers and estuaries in Mid-western and Northwestern Finland.

Concentrations of Ca, Cl, K, Mg, Na and SO₄, i.e. typically strongly enriched in freshwater AS soil environments, increased with an increasing proportion of seawater towards the outer estuary as concentrations of these elements are naturally higher in the sea. These elements behave, thus, conservatively and the increase of concentration is mainly due to the dilution (i.e. mixing) with sea water. As expected, for OC and the rest of the elements (except Ba and U), occurring in higher concentrations in the rivers (Group 2; Fig. 3), concentrations decreased towards the outer estuary, not only due to dilution, but even more importantly, due to flocculation and/or scavenging processes as indicated by their non-conservative

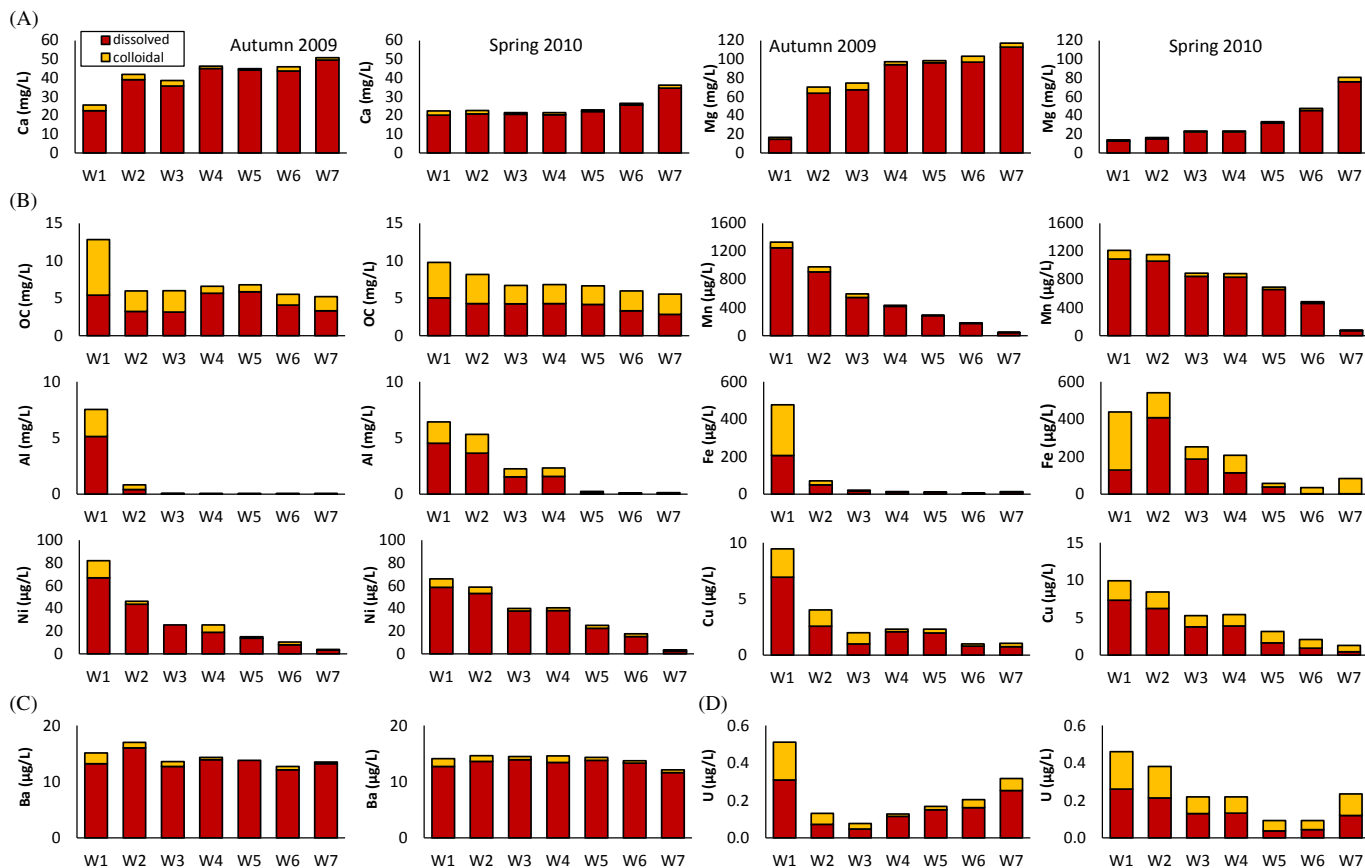


Fig. 3. Dissolved- (<1 kDa) and colloidal (1 kDa–0.45 μm) fractions of selected elements in the Vörå River (W1) and in the estuary of Vörå River (W2–W7). The anomaly in the Fe pattern (W2 in spring) is most likely an analytical error as other Fe concentrations follow a similar pattern. Some of the variables (Cl, F, PO_4 , SO_4 , OC, Al, Fe, Mn) were also presented in [Åström et al., 2012](#). (A) Elements with an increasing concentration from Vörå River to the outer estuary: Ca, Cl, K, Mg, NaSO_4 and Sr (B) Elements with a decreasing concentration towards the sea: OC, Al, Cd, Co, Cr, Cu, F, Fe, Mn, Ni, PO_4 , Si and Zn (C) Elements with relatively constant concentrations at all sampling points: Ba. (D) Elements with variable concentrations: U.

behaviour. As indicated by the correspondence to element patterns in sediments ([Nordmyr et al., 2008a](#)) the dissolved phase is transformed in to the particulate phase and deposited as sediments in the estuary.

4.2. Element associations and the behaviour of phosphorus

Organic matter, but also solid phases of Al, Fe and Mn, are known of adsorbing other elements ([Wang et al., 2003](#); [Pédrot et al., 2008](#)), and thus it is likely that those will adsorb other elements in the estuary. Several elements (Al, Cu, Fe and U) were predicted to be associated to OC in the inner estuary and, furthermore, these associations generally increased rapidly with even small increases of salinity and pH to the outer estuary ([Figs. 4 and 5](#)). This indicates that the first elements to precipitate in the inner estuary are most likely Al, Cu, Fe, and U together with OC. These findings are also in line with those of [Nordmyr et al. \(2008a,b\)](#) studying deposition patterns for several elements in the estuary of Vörå River. They concluded that Al, Cu and U were enriched in sediment traps and bottom sediments close to the river mouth. Also [Åström et al. \(2012\)](#) studying the behaviour of REE in the estuary of Vörå river and its estuary concluded that Al oxyhydroxides and organic substances most likely controls the REE behaviour in the estuary. However, there were some differences between the modelled and measured data for OC, as OC in the inner estuary behaved relatively conservative and the dissolved concentration in some of the places

in the estuary increased ([Fig. 4](#)). This is probably due to another source of OC in the estuary, most likely phytoplankton. Notable is also that OC complexes in the water can be in suspension a long time before flocculating with larger particles and, thus, precipitating. Consequently, some OC complexes will be transported further out in the estuary before settling to the bottom.

It is commonly known that Fe-hydroxides can adsorb PO_4 ([Spiteri et al., 2008](#); [Shao et al., 2014](#)) and, thus, it was expected that PO_4 was predicted to form complexes with Fe in the river and estuary. However, the predicted precipitation of Al and the predicted occurrence of Al- PO_4 complexes in the water indicate also the precipitation of PO_4 with the abundantly occurring Al, especially in the acidic Vörå River, but also in the inner estuary were the proportion of acidic river water is still very high. This is noteworthy, as this association can have a reducing effect on the ongoing eutrophication of surface water, which is a worldwide concern ([Reddy et al., 1999](#); [Smith, 2003](#); [Shao et al., 2014](#)) and occurs also abundantly in the Baltic Sea. Currently, the Baltic Sea has the largest “dead zone” (i.e. low oxygen zone) in the world due to eutrophication ([Diaz and Rosenberg, 2008](#); [Kiedrzyńska et al., 2014](#)) and P is one of the key nutrients that can cause algal blooms and related water quality problems ([Correll, 1998](#); [Smith et al., 1999](#)). However, in near coastal areas of the Gulf of Bothnia algal blooms have been rare, although, further out in the coastal area there have been enormous problems with algal blooms. One of the shown reasons for the lack of algal blooms has been the Fe associations with P

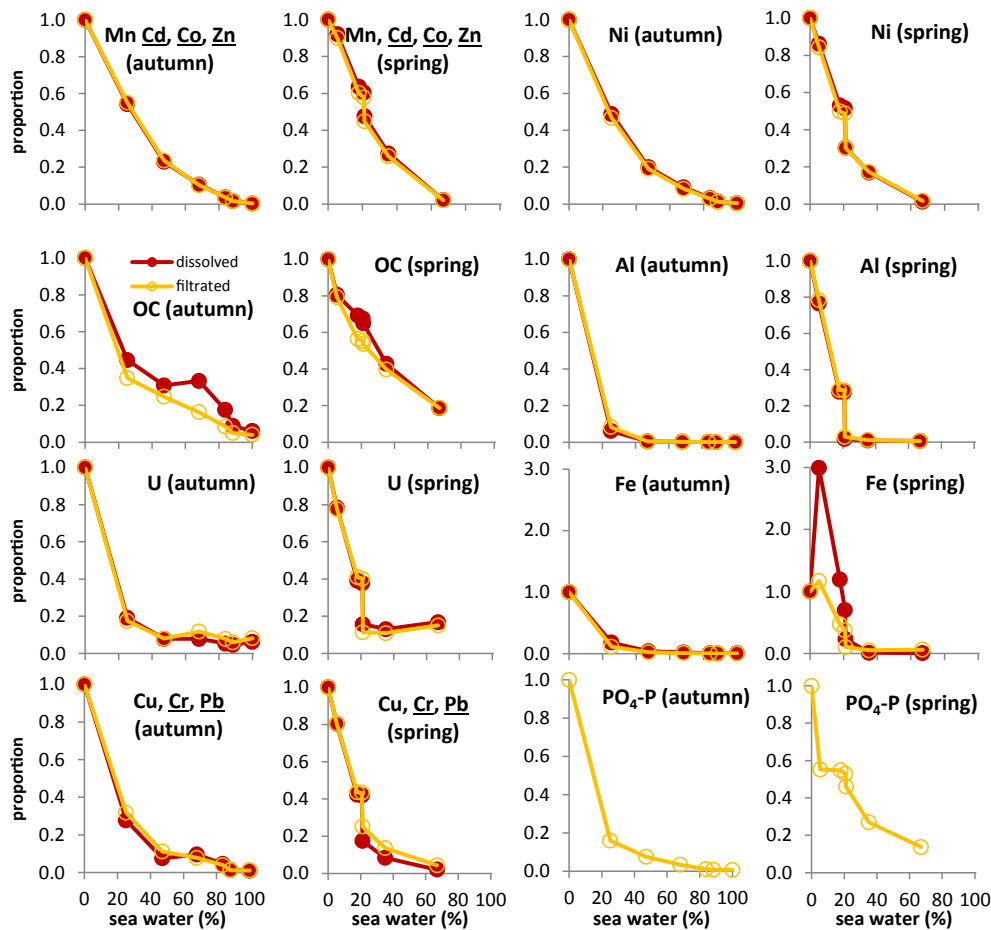


Fig. 4. Relative changes in the proportion of creek water (based on electrical conductivity) and organic material, $\text{PO}_4\text{-P}$ and metal concentration (dissolved, <1 kDa, and filtrated, <0.45 μm , fraction) down the estuary of Vörå River as compared to the lower part of Vörå River. 20–30% saline sea water is needed to halve concentrations of Cd, Co, Mn, Ni and Zn (A), and 20% saline water reduces the concentration for OC, Al, Cu, Cr, Fe, Pb, PO_4 and U by half (B). As the results for some elements were very similar, only one representative element is shown for these element groups (elements not shown are underline). Proportion = the proportion is based on the dissolved, respectively filtrated, concentrations in the end members (W7) and the proportion of river water (W1).

(Niemistö et al., 1978) as Fe can act as a P sink where particulate-bound P settled to the bottom is buried and stored and, thus, not available (Huser and Pilgrim, 2014). Phosphorus in sediments can, though, again be remobilized mainly due to P release from reductant-soluble elements, like Fe, and mineralization of P containing organic compounds (Bydén et al., 2003; Shao et al., 2014). In contrast to Fe, however, Al is not a reductant-soluble element and cycling mobile P from waters and sediments by Al can, thus, reduce P for a long time. Thus, the indicated P association with Al can in these kinds of waters (i.e. in waters with high Al concentrations) be one of the reasons for a reduction of P and, thus, also for a reduction of eutrophication.

In contrast to OC and Al, Mn (as Mn^{2+}) was relatively persistent in solution and travelled a considerable distance through the estuary before oxidizing and transforming to a particulate form in more saline waters and finally precipitating. Moreover, according to modelling, Ba, Cd, Co, Cu and Ni bind to Mn (most likely as Mn-oxhydroxides) at the outermost sites (W6 and W7; Fig. 5), indicating that these elements most likely will co precipitate with Mn oxhydroxides. These findings are in line with those of Nordmyr et al. (2008a,b), showing that Cd, Co, Mn and Ni were enriched in sediment traps and bottom sediments further out in the estuary of Vörå River.

4.3. Uranium pathways

The distribution of U was different from the other elements. Due to the influence of AS soils, the concentration for U was high in the Vörå River. The lower concentrations in the inner estuary most likely depend on a low salinity; modelling predicted U to be complexed with OC in this low-salinity zone, and several previous studies have shown that a substantial fraction of U might be removed at a salinity <1 by Fe- and/or organic-rich colloids during the very initial mixing of river waters with marine waters (Porcelli et al., 1997; Andersson et al., 1998, 2001; Beck et al., 2012). In the outer estuary U concentrations increased, which may be explained by an increase of pH, which enables desorption of uranyl species from colloids and suspended matters and formation of poorly adsorbed uranyl carbonate complexes (Andersson et al., 2001; Beck et al., 2012).

4.4. Toxicity of the estuarine water

A low pH (<5.5) and salinity does generally shift Al and other potentially toxic trace elements towards more reactive toxic species (Kroglund et al., 2008; Nilsen et al., 2010). In the Vörå River and especially in the estuary most of the investigated elements occurred in a dissolved (i.e. most toxic) form, and the

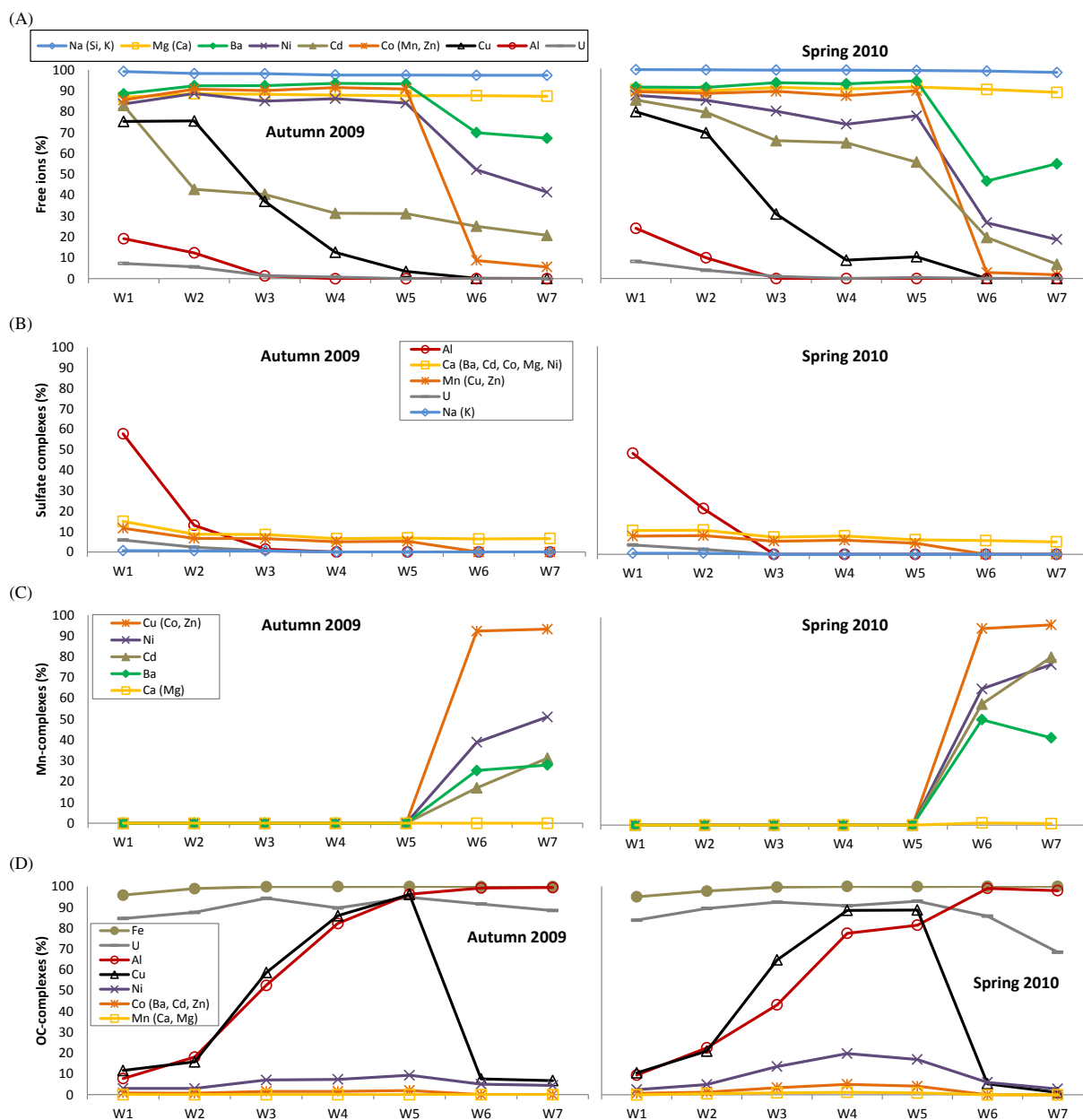


Fig. 5. Free ions (A) and element complexes with sulfate (B), Mn (modelled as birnessite) (C) and organic carbon (D) modelled with Visual MINTEQ for the Vörå River water (W1), and for the estuary water of Vörå River (W2–W7). As the predicted results for some elements were very similar, only one representative element is shown for these element groups (elements not shown are in brackets).

concentrations for Cd, Cu, Mn and Ni were in Vörå River far over the proposed standards by EU (2008/105/EU) and World Health Organisation (WHO, 2008) (Nystrand and Österholm, 2013). In the inner estuary, Ni and Mn concentrations were still higher than 20 µg/L and 400 µg/L, respectively, thus still potentially toxic to the aquatic organisms (2008/105/EU; WHO, 2008). Although cadmium in the estuary is largely present in a dissolved form (Table S1), it was predicted to largely occur as Cd–Cl complexes (Fig. 5; Table S1), which seems to be less toxic/bioavailable (Eggleton and Thomas, 2004). These complexes are, though, presumably only lightly bound complexes and can, thus, easily dissolve. Of the elements abundantly exported from the AS soils, Al is of particular concern (Poléo et al., 1997; Bjerknes et al., 2003; Fältmarsch et al., 2008; Johnston et al., 2010), because it has severe deleterious effects on fish, fish larvae, oysters and a host of other gilled organisms by

clogging the gills of the organisms (Sammut et al., 1996). According to Earle and Callaghan (1998) already a filtrated (<0.45 µm) Al concentration of around 0.5 mg/L will eliminate all fish and many macroinvertebrates in acidic waters. In Vörå River the filtrated concentration was as high as 8.4 mg/L, with a substantial proportion in a dissolved form (69%). In the inner estuary, Al concentrations were still highly elevated and most of the Al occurred in a dissolved form (Fig. 3; Table S1). Moreover, the predicted occurrence of soluble Al–F complexes in Vörå River and its inner estuary can also promote toxicity by hampering organic Al complexation (Berger, 2015; Ware, 2008). Consequently, the dissolved toxic concentrations of Al in Vörå River and also relatively far out in the estuary (especially in spring 2010; Fig. 3) were far over the acceptable limits, and are, in combination with the low pH, most likely the most important reason for the lack of fish and other

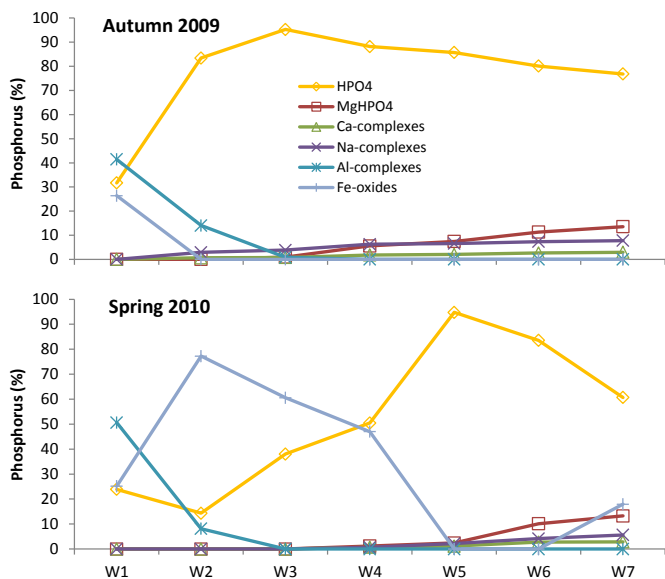


Fig. 6. Phosphorus species/complexes modelled with Visual MINTEQ for the Vörå River water (W1) and for the estuary water of Vörå River (W2–W7).

organisms in the Vörå River and sporadically also in the inner estuary of Vörå River. Notable is, though, that the water quality (i.e. toxicity) in the estuary is highly dependent on the amount of acidic river water flushed out in the estuary (Fig. 3). Consequently, water quality draining AS soils can be good during a long period, but meteorologically/hydrologically driven temporary peaks of poor water quality can be expected, particularly during high flows in autumn and spring (Nyberg et al., 2012). Thus, occasionally the water quality can be good, but the high toxic element concentrations in the near shore sediments can still make it difficult for the biota to survive due to the lack of non-toxic food (Burton and Landrum, 2003). Consequently, although several potentially toxic elements eventually precipitate in the estuary and so on will be in a less toxic form, they still are potentially toxic for several bottom-feeding organisms (Wallin et al., 2015), because geochemical changes (especially episodic declines in pH) in estuarine bottom-water and sediment disturbance can result in a remobilisation of the elements (Eggleton and Thomas, 2004).

5. Conclusion

Filtrated concentrations of several elements are in Vörå River and its recipient estuary highly elevated due to acid sulfate soils and occurs mainly in a dissolved toxic form, having serious effects on fish and other organisms in this and similar shallow estuaries with brackish water in the Gulf of Bothnia. Several elements (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, PO₄ and Zn) as well as organic matter were rapidly precipitated in the estuary, even after mixing with fairly small amounts of the alkaline brackish sea water, and obviously sedimented on the sea bottom. Aluminium, Cu, Fe and U most likely precipitate together with organic matter closest to the river mouth. Manganese is relatively persistent in solution and, thus, precipitates further down the estuary as Mn oxides with elements such as Ba, Cd, Co, Cu, Ni and Zn. In the inner estuary, the high contents of Al is as important than Fe in removing PO₄, thus, also reducing the risk of algae blooms in near coastal areas influenced by AS soils in the Gulf of Bothnia. Due to their non-conservative behaviour, the dispersion of metals far out in the estuary is highly dependent on hydrological conditions; high discharge produce large plumes of river water by which metals can be transported far out in the

estuary. Moreover, the extensive drainage of the catchment and subsequent artificial enlargement of the river channel during recent decades has not only enabled oxidation of sulfidic sediments, but strongly increased temporary flow peaks that enhance large plumes of river water to reach further out in the estuary.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2016.01.003>.

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