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Element speciation and behaviour in metal-rich Boreal river and estuarine systems using ultrafiltration and chemical modelling

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Abstract

The bioavailability of metals and their potential for environmental pollution depends not simply on total concentrations, but is to a great extent determined by their chemical form. Consequently, knowledge of aqueous metal species is essential in investigating potential metal toxicity and mobility. The overall aim of this thesis is, thus, to determine the species of major and trace elements and the size distribution among the different forms (e.g. ions, molecules and mineral particles) in selected metal-enriched Boreal river and estuarine systems by utilising filtration techniques and geochemical modelling. On the basis of the spatial physicochemical patterns found, the fractionation and complexation processes of elements (mainly related to input of humic matter and pH-change) were examined. Dissolved (<1 kDa), colloidal (1 kDa-0.45 µm) and particulate (>0.45 µm) size fractions of sulfate, organic carbon (OC) and 44 metals/metalloids were investigated in the extremely acidic Vörå River system and its estuary in W Finland, and in four river systems in SW Finland (Sirppujoki, Laajoki, Mynäjoki and Paimionjoki), largely affected by soil erosion and acid sulfate (AS) soils. In addition, geochemical modelling was used to predict the formation of free ions and complexes in these investigated waters.

One of the most important findings of this study is that the very large amounts of metals known to be released from AS soils (including Al, Ca, Cd, Co, Cu, Mg, Mn, Na, Ni, Si, U and the lanthanoids) occur and can prevail mainly in toxic forms throughout acidic river systems; as free ions and/or sulfate-complexes. This has serious effects on the biota and especially dissolved Al is expected to have acute effects on fish and other organisms, but also other potentially toxic dissolved elements (e.g. Cd, Cu, Mn and Ni) can have fatal effects on the biota in these environments. In upstream areas that are generally relatively forested (higher pH and contents of OC) fewer bioavailable elements (including Al, Cu, Ni and U) may be found due to complexation with the more abundantly occurring colloidal OC. In the rivers in SW Finland total metal concentrations were relatively high, but most of the elements occurred largely in a colloidal or particulate form and even elements expected to be very soluble (Ca, K, Mg, Na and Sr) occurred to a large extent in colloidal form. According to geochemical modelling, these patterns may only to a limited extent be explained by in-stream metal complexation/adsorption. Instead there were strong indications that the high metal concentrations and dominant solid fractions were largely caused by erosion of metal bearing phyllosilicates. A strong influence of AS soils, known to exist in the catchment, could be clearly distinguished in the Sirppujoki River as it had very high concentrations of a metal sequence typical of AS soils in a dissolved form (Ba, Br, Ca, Cd, Co, K, Mg, Mn, Na, Ni, Rb and Sr). In the Paimionjoki River, metal concentrations (including Ba, Cs, Fe, Hf, Pb, Rb, Si, Th, Ti, Tl and V; not typical of AS soils in the area) were high, but it was found that the main cause of this was erosion of metal bearing phyllosilicates and thus

these metals occurred dominantly in less toxic colloidal and particulate fractions. In the two nearby rivers (Laajoki and Mynäjoki) there was influence of AS soils, but it was largely masked by eroded phyllosilicates. Consequently, rivers draining clay plains sensitive to erosion, like those in SW Finland, have generally high background metal concentrations due to erosion. Thus, relying on only semi-dissolved (<0.45 μm) concentrations obtained in routine monitoring, or geochemical modelling based on such data, can lead to a great overestimation of the water toxicity in this environment.

The potentially toxic elements that are of concern in AS soil areas will ultimately be precipitated in the recipient estuary or sea, where the acidic metal-rich river water will gradually be diluted/neutralised with brackish seawater. Along such a rising pH gradient Al, Cu and U will precipitate first 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 together with elements such as Ba, Cd, Co, Cu and Ni. Iron oxides, on the contrary, are not important scavengers of metals in the estuary, they are predicted to be associated only with As and PO_4.

Sammanfattning

Biotillgängligheten av metaller och deras potentiella risker för föroreningar i jord och vatten beror inte endast på deras totala metallkoncentrationer, utan styrs till hög grad av den kemiska förekomstformen (metallspecies). Därför är kunskapen om metallspecies i miljön viktig vid en riskbedömning av metallernas toxicitet och mobilitet. Den huvudsakliga målsättningen med denna avhandling är att öka förståelsen för species av huvud- och spårelement och deras fördelning i olika storleksfraktioner i utvalda metallrika boreala å- och estuariesystem, som i hög grad är påverkade av sura sulfatjordar och/eller erosion. Detta har gjorts genom att undersöka upplösta (<1 kDa), kolloidala (1 kDa-0.45 µm) och partikulära (>0.45 µm) fraktioner för sulfat, organiskt material (OC) och 44 metaller/metalloider i 4 åar i sydvästra Finland (Sirppujoki, Laajoki, Mynäjoki och Pemar å), och i det extremt sura Vörå åsystemet och dess estuarie i västra Finland. På basis av identifierade spatiala fysikalisk-kemiska mönster och geokemisk modellering (Visual MINTEQ), har fraktionerings- och komplexeringsprocesser (främst relaterade till humusmaterial och pH-förändringar) undersökts.

Resultaten visar att de enorma mängder metaller som frigörs från sura sulfatjordar (inklusive Al, Ca, Cd, Co, Cu, Mg, Mn, Na, Ni, Si, U och lantanoiderna) huvudsakligen förekommer i toxisk form; som fria joner och/eller sulfatkomplex. I synnerhet upplöst Al, men även andra toxiska upplösta element (t.ex. Cd, Cu, Mn och Ni), kan anses vara särskilt toxiska för fiskar och andra levande organismer i dessa miljöer. I övre delar av åsystemet, som vanligen har större andel skogsmark med högre pH och organiskt material, kan dock en betydande andel av metallerna (inkluderat Al, Cu, Ni och U) förekomma i en mindre biotillgänglig form genom att bilda komplex med organiskt material (OC). I åarna i SV Finland var de totala metallkoncentrationerna relativt höga. De flesta elementen förekom emellertid i en kolloidal eller partikulär form och även element som förväntades förekomma i en upplöst form (Ca, K, Mg, Na och Sr) upphittades till en stor del i en kolloidal form. Enligt den geokemiska modelleringen kan detta endast delvis förklaras genom metallkomplexerings- och/eller adsorptionsprocesser som sker i vattnet. Istället fanns det starka indikationer på att de höga metallkoncentrationerna och dominerande fasta fraktionerna i hög grad beror på erosion av metallbärande fyllosilikater. I Pemar å var de flesta metallkoncentrationerna (inklusive Ba, Cs, Fe, Hf, Pb, Rb, Si, Th, Ti, Tl och V som inte är typiska för sura sulfatjordarna i området) höga och kontrol-lerades huvudsakligen av erosion av metallbärande fyllosilikater, medan metallhalterna i de två närliggande åarna (Laajoki och Mynäjoki) kontrollerades av både sulfatjordar och erosion. Följaktligen, har erosionskänsliga åar likt de i SV Finland höga bakgrundskoncentrationer av metaller, som förekommer som relativt icke-toxiska kolloidala/partikulära fyllosilikater som kan dölja eventuellt inflytande av sura sulfatjordar eller andra utsläppskällor. Således kan analys

efter konventionell filtrering (0.45 µm) och geokemisk modellering baserat på semi-upplösta (0.45 µm) koncentrationer leda till en överskattning av vattentoxiciteten.

De potentiella toxiska elementen som urlakas ur sura sulfatjordar fälls ut i estuariet eller havet, där de sura metallrika åvattnen gradvis utspäds/neutraliseras med bräckt havsvatten. Längs en sådan stigande pH gradient fälls först Al, Cu, U och lantanoiderna ut tillsammans med organiskt material närmast åmynningen. Mangan är relativt lösligt och fälls ut som Mn-oxider längre ut i estuariet tillsammans med element såsom Ba, Cd, Co, Cu och Ni. Järnoxider är däremot viktiga endast för utfällning av As och PO_4.

List of publications

This thesis is composed of six studies, of which four have been published in scientific journals (I-III and V) and one has been submitted to the scientific journal "Applied Geochemistry" (IV). The final study is presented in the form of an as yet unsubmitted manuscript (VI). The scientific papers, listed below, are referred to in the text by their corresponding Roman numerals I-VI. Papers I-III and V are reproduced by permission of the journals concerned.

I. Åström, M. E., Nystrand, M., Gustafsson, J. P., Österholm, P., Nordmyr, L., Reynolds, J. K., Peltola, P., 2010. Lanthanoid behaviour in an acidic landscape. Geochimica et Cosmochimica Acta 74, 829-845.

II. Nystrand, M. I., Österholm, P., Nyberg, M. E., Gustafsson, J. P., 2012. Metal speciation in rivers affected by enhanced soil erosion and acidity. Applied Geochemistry 27, 906-16.

III. Nyberg, M. E., Österholm, P., Nystrand, M. I., 2012. Impact of acid sulfate soils on the geochemistry of rivers in south-western Finland. Environmental Earth Sciences 66, 157-168.

IV. Nystrand, M. I., Österholm, P. Metal species in a Boreal river system affected by acid sulfate soils. Submitted to Applied Geochemistry.

V. Åström, M. E., Österholm, P., Gustafsson, J. P., Nystrand, M., Peltola, P., Nordmyr, L., Boman, A., 2012. Attenuation of rare earth elements in a boreal estuary. Geochimica et Cosmochimica Acta 96, 105-119.

VI. Nystrand, M. I, Österholm, P., Åström, M. E. Metal species in a Boreal estuary affected by acid sulfate soils. Manuscript.

Miriam Nystrand was chiefly responsible for paper II, IV, and VI, and chiefly responsible for water sampling, water filtrations/ultrafiltrations and partly responsible for the analyses and interpretations in paper I and V. In paper III Miriam Nystrand was partly responsible for water sampling and analyses.

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1. Introduction

Distribution, mobility and toxicity of elements in waters are strongly related to their aqueous chemical species (i.e. specific forms of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structures; Templeton et al., 2000). Thus, the bioavailability of elements and their potential for environmental pollution depends not simply on total concentrations, but is to a great extent determined by their chemical form. Consequently, knowledge of aqueous element species is essential in investigating potential metal toxicity and mobility (Benoit et al., 1994; Campell, 1995; Ure and Davidson, 2002; Gaillardet et al., 2003; Guéguen et al., 2004; Forsberg et al., 2006). In natural water systems, elements can be partitioned between different physical states such as free or complexed, associated with colloids or with particles (Buffle and Leewen, 1992; Guéguen et al., 2004). In this sense, size fractionation of bulk water samples is one of the most widely practiced approaches to study element speciation (i.e. the distribution of an element among its chemical species including combinations of the element with complexing sites on suspended particles and dissolved or colloidal ligands; Buffle, 1988; Templeton et al., 2000; Vignati et al., 2005).

Historically, after Goldberg et al. (1952), elements in a bulk water sample have been subdivided into two fractions, "dissolved" and "particulate" fractions, on the basis of their ability to pass or not through the pores of a 0.45 μm membrane filter. However, the "dissolved" fraction (in this study referred to as semi-dissolved) clearly does not represent the truly dissolved metal ions, which is composed of free metals, complex ions, metals bound to a variety of ligands and metals forming molecules of various dimensions and chemical characteristics. These may further be bound to larger entities of colloidal size. Association of metals with carriers of different dimensions determines their transport and their bioavailability. As colloidal fractions also can be very important in natural water, the determination of particulate and dissolved fractions is not sufficient to predict the mobility and availability of metals in the aquatic environment (Buffle and van Leewen, 1992; Honeyman and Santschi, 1992; Buesseler, 1996; Wen et al., 1999; Ross and Sherrell, 1999; Ran et al., 2000; Guéguen, et al, 2002), and thus it is more appropriate to divide metals mainly into three groups: dissolved forms (<1 kDa), colloids (1 kDa–0.45 μm) and particles (>0.45 μm). The dissolved form is the most mobile and bioavailable and is generally the most toxic fraction (Benoit et al., 1994; Campell, 1995). Colloids are increasingly recognised for their high specific surface area and strong adsorption capacity (Puls and Powell, 1992; Dai et al., 1995; Gustafsson and Gschwend, 1997; Lead et al., 1997). It is shown by Perret et al. (1994) for the Rhine River that the colloids contribute less than 2% of the total particle volume and mass, but represent a dominant proportion of the available surface area for adsorption of pollutants. Consequently, the abundance of colloids, their fate

through coagulation and sedimentation processes in natural waters therefore control the abundance of a number of elements, and can thus play a major role in regulating the concentrations of many potentially toxic elements (McCarthy and Zachara, 1989; Stumm and Morgan, 1996; Gaillardet et al., 2003; Doucet et al., 2007; Pédrot et al., 2008). Their efficiency in binding trace metals can thus decrease toxicity of many chemicals for some aquatic organisms by decreasing the free concentration of the molecules (Körder et al., 1997; Weltens et al., 2000), but can also increase the bioavailability for other specific organisms, i.e. filter feeding organisms (Farag et al., 1994; Weltens et al., 2000). According to Allen et al. (1995) and Weltens et al. (2000), contaminated food colloids and even particles can affect food uptake occasionally even more than dissolved contaminants. Moreover, metals bound to colloids have a relative long residence time in water and may be transported over long distances before aggregating into settling particles (Sigg et al., 2000; Guéguen and Dominic, 2003). Organic matters, metallic oxyhydroxides (e.g. mainly Fe-, Al- and Mn-oxyhydroxides), clays and siliceous phases are the most common colloids (Tessier et al., 1996; Küchler et al., 1994; Gaillardet et al., 2003; Lyvén et al., 2003; Baalousha et al., 2006). Organic colloids are mainly humic and fulvic acids (humic substances) and derive from an incomplete degradation of soil organic matter (Gaillardet et al., 2003). Inorganic and organic colloids are often intimately associated: i.e. associations of organic colloids with clays and with iron hydroxides are commonly described in natural waters (Tipping, 1981; Koskinen and Harper, 1990; Herrera Ramos and McBride, 1996). Metals associated with larger particles (>0.7 um; Filella and Buffle, 1993; Vignati et al., 2006) are, on the other hand, usually progressively concentrated in the sediments and are generally not available for the biota, but if circumstances change (usually low pH and/or low oxygen content) such metals can again dissolve in to the water column (Sigg et al., 2000; Eggleton and Thomas, 2004; Butler et al., 2008).

Due to the importance of the size distribution among the different element forms in investigating metal behaviour in waters, different filtration techniques have been applied (e.g. ultrafiltration, dialysis, centrifugation, gel techniques; Hoffman et al., 1981; Davlson and Zhang, 1994; Perret et al., 1994; Holm et al., 1995; Gimpel et al., 2003; Pokrovsky et al., 2006). Among them, ultrafiltration techniques (used in this work) are increasingly used to characterise the proportion of dissolved and colloidal forms in surficial aquatic environments such as seawater, rivers and lakes (Sholkovitz, 1995; Ingri et al., 2004; Pokrovsky et al., 2006; Waeles et al., 2008; Ren et al., 2010; Vasyukova et al., 2010). This low-cost technique is easy to implement and is one of the few separation methods functioning without auxiliary reagents. However, some potential artefacts might occur under the ultrafiltration process, but these can be reduced by using appropriate filters and filtration conditions (Lead et al., 1997; Suzumura et al., 1998; Burba et al., 1998; Waeles et al., 2008). Over the past decades, the understanding of sorption processes has also been improved true

geochemical modelling programmes as PHREEQE, MINTEQA2 and Visual MINTEQ performing specialized calculations and predicting changes in solution chemistry caused by different processes (i.e. dissolution/precipitation, ion exchange/adsorption; Gaillardet et al., 2003). Although these methods (i.e. geochemical modelling programmes) have been applied in several studies (Rönnback et at., 2008; Butler et al., 2009; Sjöstedt et al., 2010; Wällstedt et al., 2010; Meck et al., 2011), there is still not enough information on element species to understand all processes linked to the potential metal toxicity and mobility, and especially in Finland these methods have not been commonly used.

Metals are a natural part of the environment, i.e. occurring in bedrock and soils, and they enter natural waters from a variety of sources, mostly by the weathering of soils in the catchments. Besides the natural processes, anthropogenic factors such as agricultural activities, present and former mining activities and local point source effluents, also lead to an increased input of metals in soils and waters. The observed metal distribution in natural waters is, thus, a complex result of natural and human-induced inputs (Krishna and Govil, 2007; Lepane et al., 2007).

Acid sulfate (AS) soils, which occupy an area of over 17 million ha worldwide (in Africa, Australia, Asia and Latin America; Ritsemaa et al., 2000; Andriesse and van Mensvoort, 2002), are regarded as the nastiest soils in the world (Dent and Pons, 1995). Independent of the geographical locality of these soils, they pose a great threat to their surrounding environment if disturbed (Hamming and van den Eelaart, 1993; Lin and Melville, 1994; Tin and Wilander, 1995; Sammut et al., 1996; Portnoy, 1999; Powell and Martens, 2005; White et al., 2007). In Finland such soils cover in total at least 43,000-130,000 ha of the Finnish coastal plains (Yli-Halla et al., 1999) and they constitute a massive supplier of metals and acidic compounds to the aquatic environment, even higher than that from the entire Finnish industry (Sundström et al., 2002). These environmentally unfriendly soils (e.g. causing frequent fish kills in streams and estuaries) are developed upon oxidation of former sulfidic marine sediments (Sundström et al., 2002; Österholm and Åström, 2004; Le et al., 2008; Boman et al., 2010; Santos and Eyre, 2011). The oxidation causing the formation of these acidic soils is generally an effect of anthropogenic lowering of the groundwater table associated with ditching, which enables atmospheric O_2 to penetrate the soil and react with the sulfides producing H_2SO_4. This gives rise to very acidic conditions (pH < 4), which in turn mobilises enormous quantities of metals from these soils into the aquatic environments (Palko and Yli-Halla, 1988, 1990; Åström and Björklund, 1995, 1996; White et al., 1997; Åström and Åström, 1997; Smith et al., 2003; Macdonald et al., 2007; Fältmarsch et al., 2008).

Although there is now fairly much knowledge about overall metal concentrations in rivers (Lahermo et al., 1996; Minh et al., 1997; Gaillardet et al., 2003; Salminen et al., 2005), including the rivers and streams severely affected by AS soils (e.g. Roos and Åström, 2005a; Macdonald et al., 2007; White et al., 2007), little is known about the actual element size distribution and element species. Moreover, no international scientific study is published on element speciation (including size distribution) in waters affected by AS soils, although such information is of importance when estimating ecotoxicological effects in metal-enriched waters.

2. Aim of the research

The overall aim of this thesis was to determine the species of major and trace elements and the size distribution among the different forms (e.g. ions, molecules and mineral particles) in selected metal-enriched Boreal river and estuarine systems by utilising filtration techniques and geochemical modelling. The aim was in particular to: (1) determine speciation, including size distribution, of elements in Boreal river and estuarine systems, (2) assess element species from AS soils and to distinguish them from other potential element sources, (3) assess fractionation and complexation processes of elements during their transport through river and estuarine systems, and (4) assess ecotoxicological implications of these physicochemical patterns.

3. Study areas

3.1 River systems in SW Finland

The selected rivers in SW Finland were the Sirppujoki -, Laajoki -, Mynäjoki - and Paimionjoki Rivers (Fig. 1 and Photo 1). The bedrock of the area consists mainly of 1.83 Ga microcline granite, 1.58 Ga rapakivi granite and 1.89 Ga mica schist and mica gneiss, with smaller contributions of 1.89 Ga mafic metavolcanic rocks and 1.88 Ga granodiorite, tonalite and quartz diorite. The bedrock is mainly covered by Quaternary deposits, including till and glaciofluvial material, marine and lacustrine clays, silts, peat and littoral sediments (Perttunen et al., 1984). Only a small percentage (0.3-2.0%) of the drainage areas consist of lakes and thus flow variations are relatively great. During dryer periods in summer and winter, the runoff is generally low (1-7 $Ls^{-1}km^{-2}$; HERTTA database, Finnish Environmental Centre) but during snow melt and heavy rains in spring and autumn, the water flow increases up to 20 $Ls^{-1}km^{-2}$ (HERTTA database, Finnish Environmental Centre). Forest is the dominant land type in the catchments for all rivers (Table 1) and dominates in the upstream areas of the rivers, but the proportion of cultivated land (i.e. main
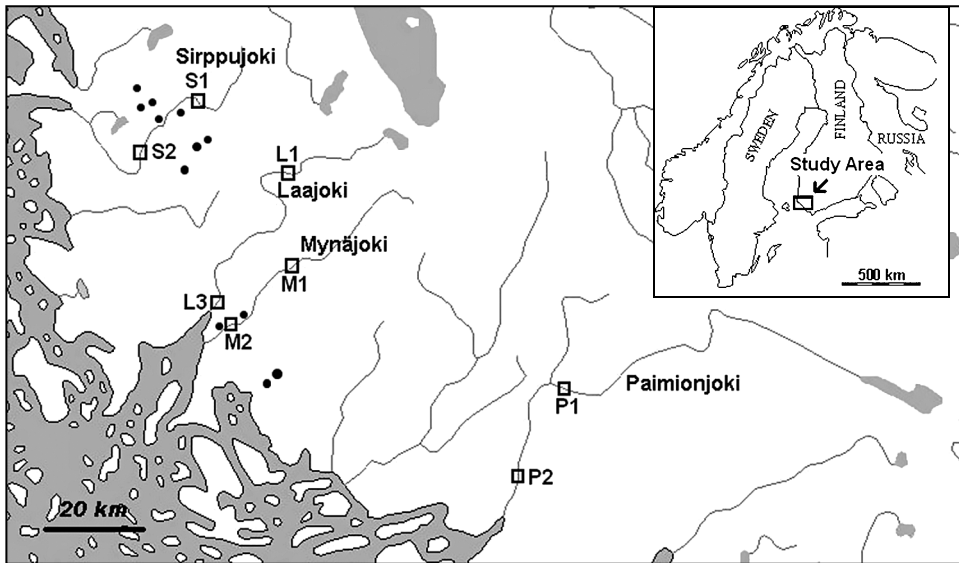
Fig. 1. Location of the study area and sampling sites in the Sirppujoki - (S), Laajoki - (L), Mynäjoki - (M) and Paimionjoki (P) Rivers in SW Finland, including 12 low-order streams (filled dots) to the Sirppujoki and Mynäjoki Rivers.

Photo 1. The Mynäjoki River in SW Finland. In all investigated rivers erosion of clay was clearly seen as a greyish colour (Photo by Miriam Nystrand).

Table 1. Drainage area and proportion of cultivated land, forest and peat in the catchments of the monitored rivers in SW Finland. The area of cultivated land is roughly equivalent to that of clay soils (HERTTA database, Finnish Environmental Centre).

River	Drainage area (km^2)	Cultivated (%)	Forest (%)	Peat (%)
Sirppujoki	438	29	63	8
Laajoki	393	15	67	19
Mynäjoki	288	25	63	12
Paimionjoki	1088	43	47	10

parts of the fine-grained sediments) is also relatively large (Table 1) and dominates in the downstream areas. The drainage areas are largely well-drained as a result of extensive and deep ditching. The groundwater table has, therefore, dropped, which in areas with former sulfidic marine sediments has resulted in oxidation of metal sulfides and development of acid sulfate soils. These soils are in SW Finland mainly located at 0-45 m above the current sea-level due to postglacial isostatic land uplift (5 mm/a; Palko, 1994) and are known to be relatively common in the catchment of the Sirppujoki River (Triipponen, 1997), but there are also indications of AS soils in the Laajoki - and Mynäjoki Rivers (Lemmetyinen and Virtanen, 1980; Paper III). The Paimionjoki River, on the contrary, is not known to be affected by AS soils (Paper III). No major sources of pollution are known to exist in the area.

3.2 Vörå River system and its estuary

In W Finland, the Vörå River (35 km long; Nordmyr et al., 2008) and its estuary were investigated (Fig. 2 and 3). The catchment area (223 km^2) 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) and the mean annual specific runoff is c. 7 $Ls^{-1}km^{-2}$ (HERTTA database, Finnish Environmental Centre). Forest is the dominant land type in the catchment (54%) and dominates in the upstream area of the river, but the proportion of cultivated land (i.e. main parts of the fine-grained sediments) is also extensive (31%) and dominates in the downstream areas. Also mires (15%) are found in the area (Rautio and Ilvessalo, 1998). In valleys and depressions up to 50 m above the
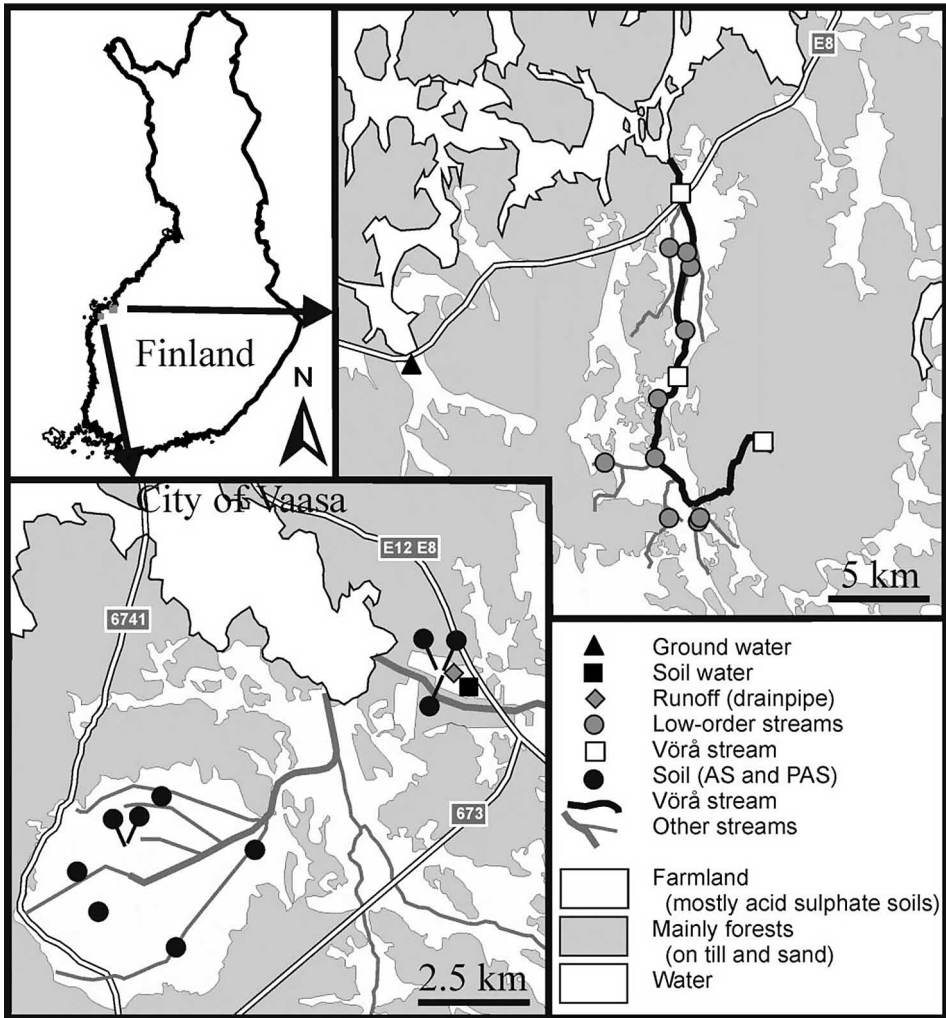
Fig. 2. Location of the study area and sampling sites in the Vörå River (including 3 ditches and 7 low-order streams to the Vörå River) and soil sampling sites in W Finland.

present sea level, Holocene brackish-water (Baltic Sea) sediments are abundant as a result of post glacial isostatic land uplift (9 mm/year; Palko, 1994). Since the early 19th century these fine-grained sediments have to ever greater extent been turned into farmland, initially by manual drainage and over the last few decades with more sophisticated drainpipe techniques. These land-use activities have increased the rate by which these sediments are oxidised, and thus turned into AS soils. As a consequence, the Vörå River is one of the most heavily AS soil-impacted rivers in Europe (Photo 2; Roos and Åström, 2005a; Nordmyr et al., 2008). The Vörå River discharges into a shallow and biologically sensitive

brackish water estuary (into the Gulf of Bothnia) and therefore the existence of fish and other organisms are very limited in these waters. The inner estuary 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., 2008). The estuary is unaffected by tide and during a large part of the year (December-April/May) covered by ice (up to 70 cm thick).
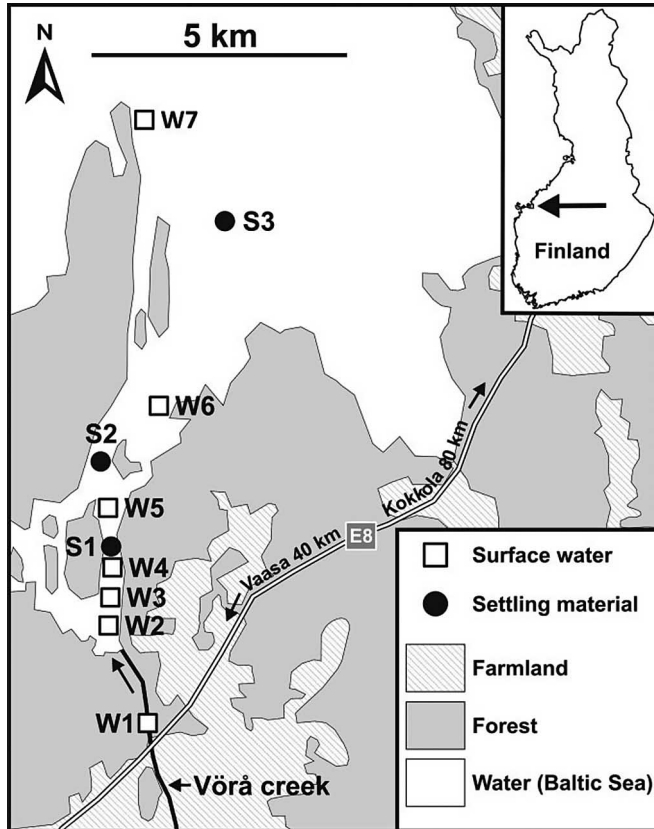
Fig. 3. Location of the study area and sampling sites in the Vörå River and the estuary of the Vörå River in W Finland.

Photo 2. A low-order stream to the Vörå River in W Finland. The clear water is typical for waters affected by acid sulfate soils (Photo by Miriam Nystrand).

4. Methodology

4.1 Water sampling and analyses

Water samples for paper III were collected during different hydrological conditions and seasons, in total on seven occasions during two years (2004-2005), from the Sirppujoki -, Laajoki -, Mynäjoki - and Paimionjoki Rivers (upper, middle and/or lower reaches; Fig. 1), and from three low-order streams. These samples were filtered through a 0.45 μm filter, but not ultrafiltered.

For paper I, II and IV, sampling was carried out in May 2006 in the Sirppujoki, Mynäjoki -, Laajoki -, Paimionjoki - and Vörå Rivers (upper, middle and/or lower reaches; Fig. 1 and 2) and from 22 first and second order stream sites (Fig. 1 and 2) in the drainage area 2 weeks after the spring high-water flow peak. For paper I, additionally non-filtered and acidified (HNO_3 to a volume of 0.2%) water samples were collected 12 times at the Vörå River outlet during the course of 2.5 years. In SW Finland it is notable that the low-order streams are not representative for the area as a whole. As AS soils were expected to be the

major source of metals, streams expected to drain such areas were prioritized, i.e. streams with low pH and high electrical conductivity (EC) draining low-relief farmlands. All samples were collected in 500 mL polyethylene bottles and within 9 h they were first pre-filtered with a 0.45 μm filter (the first 5-10 mL of the filtrate was always discarded) and then ultrafiltered (Photo 3). The acidified samples (HNO_3 to a volume of 2%), including duplicates and method blank samples, were analysed in randomised order for 42 elements by the ICP-MS (As, Ba, Br, Ca, Cd, Co, Cs, Cu, Fe, Hf, K, Mg, Mn, Na, Ni, Pb, Rb, Si, Sr, Th,

Photo 3. Fontal ultrafiltration was performed with a 400 mL polycarbonate cell (Amicon 8400) with a suspended magnet stirring bar located above the filter in order to prevent clogging during ultrafiltration. Nitrogen pressure (around 2.5 bars) was used as the driving force, and a concentration factor of 6 was applied (For more details see in Cheryan, 1998).

Ti, Tl, U, V, Y, Zr and the lanthanoids) and ICP-OES (Al and S) at Activation Laboratories Ltd. in Canada. The analytical precision, based on random analytical duplicates (Gill, 1997), was <10% for all elements except for Th (15%) and Ce (14%). The filtered and ultrafiltered samples were analysed for all water samples and for the river samples the non-filtered water was also analysed. Fluoride was analysed in random order on filtered (0.45 µm) water samples with a Hach DR/2010 spectrophotometer (Spadns method). For paper III, also Tot-N (FIA; EN ISO-11905) was determined on untreated samples. Nitrate analysis (Cadmium Reduction Method, middle range, with a Hach DR/2010 spectrophotometer) on unfiltered samples showed that most of the Tot-N in the samples occurred as nitrate.

For paper V and VI, water samples were collected twice during high flow seasons when the dispersion of river water in the estuary is greatest: after rains in autumn (December 1st 2009) and after snow melting in spring (May 5th 2010) from the lower reach of the Vörå River (W1; Fig. 3) and from the estuary of the Vörå River (Fig. 3) in a transect from close to the river mouth (i.e. inner estuary: W2-W4) to the outer estuary (W5-W7). These samples were all filtered and ultrafiltered and then acidified with 2% HNO_3 (including duplicates and method blank samples) and analysed in randomised order for 26 elements by ICP-SFMS (As, Ba, Ca, Cd, Co, Cu, Mg, Na, Ni, Si, Sr, U and the lanthanoids) at ALS Laboratory Group in Luleå, Sweden. Iron, Mn and Al were determined by ICP-AES (Optima 4300 DV, Perkin Elmer). The analytical precision was <11% for most of the elements. Only for Ca, Na and U the analytical precision was poorer, 15%, 18% and 21%, respectively. The concentrations of Cl^-, F^- and SO_4^{2-} were analysed by ion 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 were within 5%.

For all studies water temperature, pH and specific electric conductivity were measured in the field (YSI Model 63). Alkalinity and acidity were measured on filtered (0.45 µm) water samples by potentiometric titration with H_2SO_4 (pH end point of 4.5) and NaOH (pH end point of 8.3), respectively, on the day of sampling. Alkalinity and acidity were not, however, measured on samples with a pH under 5.5 and above 7, respectively, and not on the water samples in the estuary of the Vörå River. Samples for TOC (total organic C), semi-dissolved OC (water filtered with a 0.45 µm filter), COC (colloidal organic C) and DOC (dissolved organic C) were analysed in randomised order with a Shimadzu Organic Carbon 5050 analyser (for paper I, II, III and IV) and a Shimadzu Organic Carbon TOC-V$_{CSN}$ analyser (for paper V and VI). Scanning electron microscopy (SEM; Leo Gemini 1530 with a Thermo Scientific Ultra Dry Silicon Drift Detector) with attached energy dispersive X-ray analysis (EDX; with the ThermoNORAN Vantage X-ray detector) was used to study particles

on the 0.45 µm filter and to check if the ultrafilters are susceptible to fouling (i.e. unwanted adsorption of colloids on the ultrafilter).

At the sampling sites along the rivers the particulate fraction was determined according to Björkvald et al. (2008); from the differences between total concentrations (non-filtered samples treated with HNO_3 to a volume of 2%) and concentrations in the filtered (0.45 µm) sample. The terms "total concentration" and "particulate fraction" are used for simplicity, although metals strongly bound to particle surfaces or within lattices may not have been included due to particle sedimentation in the sample bottles (Gundersen and Steinnes, 2003).

4.2 Ultrafiltration

Ultrafiltration has proven to be one of the most useful techniques to obtain separation and concentration of colloids from bulk natural samples (Belzile and Guo, 2006), and latest applications of ultrafiltration have advanced our understanding of the abundance, distribution, chemical composition and environmental behaviours of colloids in aquatic systems (including freshwater, seawater and ground water; Guo and Santschi, 2007). Isolation of colloidal matter by ultrafiltration can be conducted either using cross-flow (i.e. tangential) or frontal (i.e. dead-end) ultrafiltration (Buffle and Leppard, 1995). In cross-flow ultrafiltration the water is recirculated parallel to the filter membrane at a high flow rate, where a hydrostatic pressure drives components smaller than the membrane pore size through the filter. In contrast, constituents larger than the membrane pore size will be recycled in the process and retained in the retentate reservoir (Lead et al., 1997; Forsberg, 2005). In frontal ultrafiltration the water is directly pumped from the concentration side to the permeate side without circulation. In the ultrafiltration process different prefilter pore sizes and different ultrafiltration membranes with different molecular weight cut off (MWCO) have been employed and, thus, concentrations of the dissolved and colloidal fraction in the literature are not always directly comparable. Membranes are also available in different materials with different sorptive capacities and may interact with certain chemical species. Thus, membranes need to be selected accordingly to the purpose of the study (Guo and Santchi, 2007).

Since cross-flow requires large-volume samples (10–1000 L, Guéguen et al., 2002), frontal filtration was selected for easy handling. Moreover, membranes with small surface area, a low amount of pore space (i.e. minimises adsorption inside the filter during filtration) and a small dead volume may be more suitable for trace metal work and for processing small volumes of sample (Pokrovsky and Scott, 2002; Guo and Santschi, 2007). Therefore, a 1 kDa (around 2 nm) regenerated cellulose acetate membrane (Millipore) was selected. Noticeable is

that the pores of a filter with a cut-off of 1 kDa generally range between around 0.7 and 1.3 kDa, as the real cut-off depends on the structure and chemical composition of the present metal species (Larsson et al., 2002; Forsberg et al., 2006). Consequently, the < 1 kDa fraction might contain some colloids and larger complexes, especially in the seawater samples as a major part of seawater colloids are just above 1 kDa in size (Guo and Santschi, 1997).

Frontal ultrafiltrations were performed using a 400 mL polycarbonate cell (Amicon 8400; Photo 3) equipped with a suspended magnet stirring bar located above the filter in order to prevent clogging during ultrafiltration. Chen and Buffle (1996) recommended stirring to minimise surface coagulation, but also to minimise stirring as much as possible as it may favour coagulation in the bulk solution, inside the filtration cell. Coagulation can, however, be minimised if the water samples are filtered/ultrafiltered within 2–3 days of sample collection (Chen and Buffle, 1996) and, thus, ultrafiltrations were performed within 24 h of collection. Moreover, the time elapsed between sample collection and filtration/ultrafiltration may change the speciation, and should therefore be as brief as possible (at most two days; Lead et al., 1997). Nitrogen pressure (around 2.5 bars) was used as the driving force, and a concentration factor (cf; ratio of volume of the initial sample to the retentate volume) of 6 was applied, and calculated according to Dupré et al. (1999): $cf = V_{tot}/V_{retentate}$, where V_{tot} is the total volume and $V_{retentate}$ the retentate volume. It is important to find the optimal CF, as concentrations of especially Ca, Mg and SO_4 in the permeate might increase with increasing CF during ultrafiltration (Guo et al., 2001). For this specific technique (i.e. frontal ultrafiltration with Amicon 8400) a low cf is recommended (3–13; Waeles et al., 2008).

In principle ultrafiltration is based simply on size separations, but in practice there are a number of potential artefacts that might appear under the ultrafiltration. Typical observations of permeate flux over time reveal a rapid initial decline followed by a more gradual long-term decline. Mostly, the initial decline is attributed to concentration polarisation, but also a formation of a gel layer might occur (Buffle and Leppard, 1995; Lead et al., 1997; Chen et al., 2004). Concentration polarisation is a rapid build-up of solute particle concentration near the membrane surface, while a long-term decline is attributed to various modes of membrane fouling (i.e. gel layer). A formation of a gel layer might occur if an increase of the colloidal concentration occurs directly above the membrane surface due to a slow back diffusion of colloids compared to their movement, under pressure, towards the membrane. These may result in fractionation occurring in a different size range to that expected from the nominal pore size of the membrane (Lead et al., 1997; Chen et al., 2004). These artefacts can, though, be minimised by using a magnet stirring bar (Buffle, 1992). During the ultrafiltration procedures it is assumed that no potential artefact occurred, as no traces of membrane fouling/clogging was

found on a 1 kDa filter used on water from the Paimionjoki River, when the filter was analysed with SEM.

Additional problems of filtration are related to contaminations (Buffle, 1995) and care was taken to avoid these to the greatest extent possible. The membrane was, as recommended by the manufacturer, washed in ultrapure water for 1 h before ultrafiltration and used only once. This should, according to Pokrovsky and Schott (2002), greatly decrease the probability of cross-contamination during sample filtration, improve the OC blank, provide unique conditions of filtration for all samples and allow high recovery of colloidal particles. The ultrafiltration system and all material associated with metal sampling were acid-cleaned (0.1 M HNO_3) and flushed with ultrapure water before use and finally precontaminated (i.e. flushed) by the collected water samples. System blank tests were performed to control the level of pollution induced by sampling, filtration and ultrafiltration. For organic C and most elements the concentrations in the blanks were below analytical detection limits or just above the detection limits. However, for the study done on the rivers in SW Finland (i.e. paper II) there were some elements enhanced in the blanks. For Zn the ultrafiltered blank was 4 times higher than the mean dissolved Zn concentration in the river samples and was, therefore, excluded. Traces of Ce, Gd, La, Pb and Y were also detected in the blank samples, but the concentrations for these elements in the river water samples were generally so high that the potential contamination could be ignored, although some caution might be necessary for samples that have low concentration.

Recovery (R) was calculated for all ultrafiltered runs as follows (Ren et al., 2010): $R = ((C_{permeate}V_{permeate}+C_{retentate}V_{retentate})/(C_{filt}V_{filt}))*100$, where C is concentration, V volume, permeate water ultrafiltered with a 1 kDa membrane, retentate water retained during ultrafiltration and "filt" water filtered with a 0.45 µm filter. For the element analyses done on the river and low-order stream samples in SW Finland, the recovery for most of the elements was between 90 and 110% which can be considered as very good (Vasyukova et al., 2010) and for Cd and Pb between 110 and 120% which still is satisfactory. Only for Cr was the recovery (median) over 130% and, therefore, Cr is excluded from further discussion. For the element analyses done on the samples taken from the Vörå River and its low-order streams, recovery was in 11 samples very good (generally 90-100%) and in two samples approximately 125%. In the samples taken from the estuary of the Vörå River, the recovery was for most of the elements generally between 85-115% (i.e. good) and occasionally 75-80%.

Ultrafiltration was used successfully in these studies, but there are some disadvantages associated with the ultrafiltration procedure. It is a rather expensive and time-consuming procedure (i.e. the ultrafiltration procedure takes up to 8 h) and it is notable that potential artefacts might occur during the

ultrafiltration procedure (Buffle and Leppard, 1995; Lead et al., 1997; Forsberg et al., 2006). In the future, cheaper in situ techniques, e.g. utilisation of dialysis techniques may become more advantageous.

4.3 Geochemical modelling

The geochemical modelling program Visual MINTEQ (vers, 2.53; Gustafsson, 2007, and vers. 3.0; Gustafsson, 2010) was used to predict metal speciation in the rivers, stream sites of the Vörå River and the estuary of the Vörå River. In each paper a different amount of variables were used and, thus, an overview of the used variables is presented in Table 2. It was noticed that a higher amount of elements used for modelling predicts a more accurate element speciation; i.e. more alike the ultrafiltration results, and thus in general more elements were used for the calculations than were discussed in the papers. The Stockholm humic model (SHM) was used to describe the formation of metal-DOM (dissolved organic matter) complexes. It was in most papers 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. In addition, Al was generally 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 Fe^{3+} was estimated by calculating 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 m^2/g and a site density of 2.31 n/m^2 (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 Mn^{2+} was estimated by calculating precipitation of birnessite ($\log*K_s=18.091$ at 25 °C) with a specific surface area of 746 m^2/g.

For paper I, different modelling programmes were used (for more details see paper I):

1. One set of simulations were made with Visual MINTEQ (vers. 2.53; Gustafsson, 2007) using recently detailed inorganic and organic complexation constants (Rönnback et al., 2008) and the database of Milne et al. (2003).
2. Similar simulations were carried out with WHAM-Model V (Tipping, 1994), using the model parameterisation of Sonke (2006).
3. Also, simulations with Model VI (Tipping, 1998) were made, using the recently proposed binding constants of Pourret et al. (2007a), which

	Paper I	Paper II	Paper IV	Paper V	Paper VI
modelling program	1. Visual MINTEQ vers. 2.53 (Gustafsson, 2007) 2. WHAM-Model V (Tipping, 1994) 3. Model VI (Tipping, 1998)	Visual MINTEQ vers. 3.0 (Gustafsson, 2010)	Visual MINTEQ vers. 3.0 (Gustafsson, 2010)	Visual MINTEQ vers. 3.0 (Gustafsson, 2010)	Visual MINTEQ vers. 3.0 (Gustafsson, 2010)
DOM (The Stockholm humic model, SHM)					
aqueous OM consisted of : ratio of active DOM to DOC:	50% C by weight (Bryan et al., 2003) 70% fulvic acid (Bryan et al., 2003) 30% inactive (Bryan et al., 2003)	1.65 (Sjöstdt et al., 2010) 100% fulvic acid (Sjstedt et al., 2010)	1.65 (Sjöstdt et al., 2010) 70% fulvic acid (Bryan et al., 2003) 30% inactive (Bryan et al., 2003)	50% C by weight (Sjöstdt et al., 2010) 82.5% fulvic acid (Sjöstdt et al., 2010) 27.5% inactive (Sjöstdt et al., 2010)	1.65 (Sjöstdt et al., 2010) 70% fulvic acid (Bryan et al., 2003) 30% inactive (Bryan et al., 2003)
Al	allowed to precipitate as ferrihydrite	allowed to precipitate as ferrihydrite allowed to precipitate as birnessite	allowed to precipitate as ferrihydrite allowed to precipitate as birnessite allowed to precipitate as $Al(OH)_3$	allowed to precipitate as ferrihydrite	allowed to precipitate as ferrihydrite allowed to precipitate as birnessite allowed to precipitate as $Al(OH)_3$
Fe (DLM of Dzombak and Morel, 1990) Mn (DLM of Tonkien et al., 2004) Al	X X	X	X	X X	X
size fraction modelled <0.45 um: <1 kDa: unfiltered samples:					
Variables	pH, T, acidity La, Ce, Pr, Nd, Sm Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ca, F, Fe, K, Mg, Mn, Na, Ni, Si, SO$_4$	pH, T, acidity or alkalinity, Al, Ba, Br, Ca, Co, Cs, Cu, Fe, K, La, Mg, Mn, Na, Ni, Pb, Si, SO$_4$, Ti, Zn	pH, T, acidity, Al, As, Ba, Br, Ca, Cd, Co, Co, Cs, Cu Cu, F, Fe, K, La, Mg, Mn, Na, Ni, PO$_4$, Pb, Rb, Si, SO4, Sr, Th, Ti, Tl, U, Zn	pH, T, La, Ce, Pr, Nd, Sm Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ca, F, Fe, K, Mg, Mn, Na, Ni, Si, SO$_4$	pH, T, Al, As, Ba, Ca, Cd, Co, Cu, F, Fe, K, La, Mg, Mn, Na, Ni, PO$_4$, Pb, Rb, Si, SO$_4$, U, Yb, Zn

Table 2. The geochemical modelling program Visual MINTEQ (Gustafsson, 2007; Gustafsson, 2010) was used to predict metal speciation in the investigated waters. As the inputs in the modelling program varied in the different papers, an overview of adjustments and variables used are shown. DOM = Dissolved organic matters; OC = Organic matters; DOC = Dissolved organic carbon; DLM = The Diffuse Layer Model; C = Carbon.

they parameterized using their own ultrafiltration data.

As the geochemical models applied in paper I, were not successful in predicting the measured fractionation patterns, some new corrections and assumptions were applied for paper V. A more detailed description about the assumptions used can be found in paper V.

4.4 Sediment - and sediment-trap material and chemical analyses

Only an overview of the media sampled and parameters determined are presented here. A more detailed description about the analyses and precision of the analyses can be found in paper I and V.

The soil sampling in paper I was carried out on farmland fields which are known to carry AS soils in W Finland. Ten sites were selected for the soil sampling (Fig. 2) and at each of these, a bulk sample was collected of, first, the entire AS soil and, second, the underlying potential acid sulfate (PAS) soil material. The median pH of the AS soil was 3.9 and of the PAS soil material 7.4, which is typical for the AS soils throughout the region. At one of the soil sampling sites filtered (0.45 μm) and acidified water samples were collected from the drainpipe outlet 26 times during the ice-free period (April-December) in a single year, and from two lysimeters located in the acidic soil a total of four times. Ground water, i.e. the water residing in the saturated PAS soil material (Fig. 2), was collected by a polycarbonate dialysis membrane (0.45 μm) equilibration pore water sampler (Carignan et al., 1994; Van Oploo et al., 2008). Lanthanoids and other chemical elements (Mg, Ca, Na, K, Fe, Mn, Al and Si) in the dried soil materials were extracted by four chemical solutions and analysed in randomised order by ICP-MS and ICP-OES at Activation Laboratories Ltd (ISO/IEC 17025). The concentrations of lanthanoids, Al, Fe and Mn in the extracted solutions were determined in a similar manner.

For paper V, sediment traps (Limnos) were moored two m:s above the bottom at distances of 1.7 km, 4 km and 9 km from the Vörå River mouth (sites S1-S3, respectively) and additionally at 7 m:s above the bottom at the 4 km distance site (Fig 3). The water depth at these three sites was 10 m, 17 m and 10 m, respectively. The material deposited in the traps was collected a total of 8 times during three consecutive years (2004-2006; Nordmyr et al., 2008). In the laboratory, the material in the traps was allowed to settle before draining off the water, where after the material was oven dried and finally homogenised and split into sub-portions. In a commercial laboratory with accreditation (ISO 9001 accredited) four solutions were used to extract REE from the solid material (for a more detailed description see in Nordmyr et al., 2008), and the concentrations of REE in the extracted solutions were determined by ICP-MS (Perkin Elmer

ELAN 9000). Ancillary variables such as major metals (Fe, Mn, Al) and organic matter (loss on ignition) have been determined previously and are reported elsewhere (Nordmyr et al., 2008).

5. Results and discussion

5.1 Metal species in rivers affected by acid sulfate soils

River chemistry is very sensitive to alteration by many human activities, especially mining and the chemistry industries, but also agricultural and other anthropogenic activities may increase the input of metals in aquatic environments. In Finland acid sulfate soils are common in coastal areas (largest AS soil occurrence in Europe; Andriesse and van Mensvoort, 2006), and especially on the coastal plains of central-western Finland these soils are contributing strongly to high acid, SO_4 and metal (Al, Ca, Co, Cu, the lanthanoids, Mn, Ni, SO_4 and Zn; Åström and Björklund, 1995, 1996; Österholm and Åström, 2004; Roos and Åström, 2005a) loadings on adjacent surface waters and coastal waterways. For several heavy metals the amounts even exceed the total metal discharge in effluents from the entire Finnish industry (Sundström et al., 2002), and most likely also those of the Finnish mining industry. Also in other parts of Finland (i.e. SW Finland) AS soils do occur and although they might be smaller and less widespread in these areas (Palko 1994; Paper II), they may still have a considerable impact on the water quality causing significant harm to the aquatic ecology (Cook, 2000; Österholm and Åström, 2002). This happens especially in periods of flood following drought or periods of low rainfall, where large volumes of acidity can be flushed/leached into sensitive aquatic/marine habitats. Impacts may include low dissolved oxygen, fish kills and damage to oysters (Cook, 2000). In most of the investigated rivers concentrations of SO_4 (i.e. the conservative variable that best describe the extent and degree of sulfide oxidation) and several elements were highly enriched. Thus, AS soils need to be considered when investigating metals in the streams, rivers and estuaries of the study areas, especially as even smaller AS soil occurrences have been shown to have a considerable impact on water quality in W Finland (i.e. frequent and extensive episodes of fish kills; Hudd et al., 1986; Urho et al., 1990; Roos and Åström, 2005b; Fältmarsch et al., 2008; Paper III). Typical for watercourses with small AS soil occurrences is that the water quality deteriorates significantly for shorter periods of time and they are, thus, more difficult to characterise (Nordmyr et al., 2008; Paper III).

5.1.1 Vörå River and its low-order streams

In this chapter, the general results of paper I and IV are presented.

The low-order stream sites in the catchment area of the Vörå River had a very low pH (3.3-3.8), relatively low OC (4.96-7.71 mg/L), high electric conductivity (968-2146 μS/cm) and acidity (92-324 mg/L CaCO$_3$; Table 3). In these acidic waters most of the semi-dissolved (<0.45 μm) sulfate and metal concentrations were highly enriched, as compared to corresponding concentrations in the nearby Lapväärtinjoki River with minor AS soil impact (Table 3; Roos and Åström, 2005a). A substantial amount of all elements occurred also in a dissolved form (D/filt. ratio >0.65; Table 4), including those elements that typically occur in a non-dissolved (i.e. Al, As, Fe; Table 4) form, and due to only small pH changes in these waters the element fractionation was rather similar. Moreover, these strongly acid streams are remarkably similar in terms of sulfate concentrations, which indicate that the AS soils are relatively similar in the investigated area and that these streams drain AS soils almost exclusively.

The electric conductivity, SO$_4$ and element concentrations in the brooks of the Vörå River were lower than in the streams, but still high when compared to corresponding concentrations in the nearby Lapväärtinjoki River (Table 3; Roos and Åström, 2005a). The lower SO$_4$ and element concentrations combined with the somewhat higher OC concentrations (Table 3) indicate, however, that these brooks are not drained by AS soils exclusively, but also diluted by forest areas, typically underlain with till and peat. Another possible explanation is that the moderately acidic brooks drain AS soils with a lower intensity of sulfide oxidation or a lower pool of sulfide, but this would not explain the higher OC concentration. Although the water in the brooks was slightly less acidic (pH around 4.6; Table 3), the elements still occurred mainly in a dissolved form (Table 4). Only for Al, Cu and U the colloidal fraction was considerably higher in the brooks compared to the more acidic streams (Table 4). This is explained by an association to the more abundantly occurring colloidal organic matters in the brooks, as Al, Cu and U were predicted to occur partly as OC complexes in the brooks, but not in the more acidic streams (Fig. 4). Moreover, due to high sulfate concentrations in the streams and brooks, sulfate complexes were very important (Fig. 4); the higher the sulfate concentrations, the more abundant were the predicted sulfate complexes (Table 3 and Fig. 4). Consequently, several metals in AS soil discharge (high sulfate concentrations) occur mainly as sulfate complexes.

The water along the Vörå River was acidic, but the acidity was though considerably lower when compared to the streams (Table 3). pH was relatively similar (4.3-4.6; Table 3), while the electric conductivity increased markedly and continuously from 175 to 406 μS/cm (Table 3). Compared to the nearby Lapväärtinjoki River (Roos and Åström, 2005a) semi-dissolved concentrations of several elements (Al, Ca, Cd, Co, Cu, Mg, Mn, Na, Ni, SO$_4$, the lanthanoids, Si and U) were in the Vörå River highly elevated (Table 3) and, moreover,

Table 3. pH, electric conductivity (EC), acidity and semi-dissolved (<0.45 μm) concentrations for organic carbon, sulfate and metals in low-order streams (VF) and brooks (VFB) of the Vörå River and the Vörå River (V). na = not analysed; LR = mean concentrations in the Lapväärtinjoki River, a nearby river with no influence of AS soils (Roos and Åström, 2005a).

Sample	pH	EC μS/cm	T	Acidity (CaCO₃) mg/L	OC mg/L	Al mg/L	As μg/L	Ba μg/L	Ca mg/L	Cd μg/L	Co μg/L	Cs μg/L	Cu μg/L	Fe μg/L	Hf μg/L
VF22	3.3	2146	7.3	324	7.71	49.0	3.45	6.7	93.3	2.59	199	0.148	43.3	1790	0.463
VF19	3.6	1193	14.4	92	4.96	12.1	1.04	19.1	60.5	0.97	98.7	0.054	19.9	1000	0.149
VF24	3.6	1171	10.4	212	7.03	28.9	1.30	13.2	59.8	1.34	119	0.072	34.7	2500	0.240
VF25	3.6	1077	2.8	228	5.97	34.3	1.84	6.7	65.5	1.53	134	0.066	58.7	270	0.451
VF28	3.7	968	7.8	156	5.33	18.2	1.30	22.0	62.1	1.93	194	0.033	26.0	2080	0.263
VF21	3.8	1975	8.0	252	7.06	26.7	1.06	8.8	62.9	1.59	142	0.075	24.0	1160	0.299
VF27	3.8	1216	5.3	116	5.96	16.2	1.12	17.2	73.4	1.53	146	0.037	20.3	380	0.174
VFB26	4.3	366	5.1	52	19.64	7.8	0.74	18.2	19.6	0.48	32.6	0.023	12.2	910	0.098
VFB23	4.3	273	5.3	36	9.67	3.7	0.45	14.5	14.0	0.31	22.7	0.022	11.9	790	0.040
VFB20	4.4	322	8.0	44	8.34	3.9	0.41	14.1	19.1	0.36	21.3	0.028	9.0	390	0.043
V1 upper	4.6	175	8.5	28	22.24	1.2	0.39	9.7	7.2	0.10	7.1	0.019	2.6	930	0.020
V2 middle	4.6	296	10.3	25	13.72	2.0	0.46	14.0	14.4	0.26	19.3	0.023	5.0	310	0.032
V3 lower	4.3	406	11.0	32	10.67	4.3	0.31	15.6	17.6	0.39	27.3	0.031	6.5	360	0.051
LR mean	6.71	67.6	na	na	13.8	0.311	0.54	9.4	5.1	0.12	0.52	na	2.5	770	na

Sample	K mg/L	La μg/L	Mg mg/L	Mn μg/L	Na mg/L	Ni μg/L	Pb μg/L	PO₄ μg/L	SO₄ mg/L	Si mg/L	Sr μg/L	Ti μg/L	U μg/L	V μg/L
VF22	15.5	318	85.9	7870	115	433	0.68	276	963	45.1	580	6.3	3.620	1.1
VF19	20.3	139	47.2	6120	77	207	0.41	153	516	37.6	600	4.6	1.850	0.5
VF24	17.0	197	50.1	4720	36	247	1.01	245	591	40.8	480	6.6	2.110	0.5
VF25	12.0	188	47.4	4680	25	293	0.25	245	534	37.1	240	5.6	2.450	0.0
VF28	18.5	198	42.9	8960	22	310	1.52	215	471	46.3	610	7.9	1.450	0.0
VF21	15.6	180	53.9	5160	87	284	0.6	215	579	28.0	450	3.9	1.660	0.0
VF27	20.4	162	62.0	9180	57	295	1.53	184	573	41.3	730	4.5	0.905	0.4
VFB26	4.1	43	14.8	1340	9	71.8	0.28	184	165	11.9	97.6	5.5	0.579	1.2
VFB23	3.9	23	8.8	837	7	46.6	0.29	184	102	13.6	108	3.0	0.340	0.3
VFB20	8.2	25	12.8	905	14	55.7	0.12	184	126	16.0	109	2.3	0.423	0.2
V1 upper	1.3	6	4.0	288	5	14.5	0.12	215	45	5.0	50.4	4.7	0.137	0.7
V2 middle	3.6	17	8.5	773	10	40.8	0.15	153	96	9.7	96.8	1.9	0.175	0.3
V3 lower	4.6	32	11.9	1020	14	59.7	0.23	215	141	11.9	128	1.9	0.338	0.0
LR mean	1.56	na	2.5	44.2	4.62	2.01	0.6	32	7.65	3.77	na	na	0.1	0.84

Table 4. Ratios between dissolved (<1 kDa) and semi-dissolved (<0.45 μm) concentrations, and the proportion of free ions (%) and element complexes (%) modelled with Visual MINTEQ in low-order streams (VF) and brooks (VFB) of the Vörå River and in the Vörå River (V) . The results <1% are not shown in the table. D = <1 kDa; filt = <0.45 μm.

Component	Species name	VF22	VF19	VF24	VF25	VF28	VF21	VF27	VFB26	VFB23	VFB20	V1	V2	V3
Al	D/filt ratio	0.58	0.61	0.71	0.62	0.68	0.85	0.64	0.55	0.57	0.62	0.69	0.54	0.56
	Al^{+3}	16	14	15	23	18	18	19	24	28	22	4	13	19
	Al-oxyhydroxide								1	1	1		1	1
	F-complexes	2	8	4	3	5	5	5	8	11	17	50	27	16
	SO_4^{-2}-complexes	81	77	80	74	76	77	75	55	49	49	5	29	54
	PO_4-complexes										1		1	1
	organic complexes						1	1	12	11	9	39	29	10
As	D/filt ratio	0.48	0.89	0.87	0.82	0.83	0.42	1.00	0.68	0.56	1.00	0.92	0.65	0.81
	H_3AsO_4	6	3	1	3	1	2	2	1		1			1
	H_2AsO_4-	93	65	39	97	42	66	98	77	60	84	95	99	95
	Fe-oxides		32	59		57	32		22	39	16	4		4
Ba	D/filt ratio	0.91	0.87	0.98	0.81	0.85	1.00	0.88	0.85	0.76	0.77	0.94	0.86	0.71
	Ba^{+2}	80	83	82	84	84	83	83	90	93	92	93	92	91
	SO_4^{-2}-complexes	20	16	17	16	16	17	17	9	7	8	4	7	9
	organic complexes											3	1	
Ca	D/filt ratio	0.84	0.86	1.00	0.87	0.94	1.00	0.87	0.94	0.82	0.62	1.00	0.85	0.81
	Ca^{+2}	73	77	76	80	79	78	77	87	90	89	91	89	87
	SO_4^{-2}-complexes	26	23	24	20	21	22	22	12	9	11	5	10	12
	organic complexes								1			4	1	
Cd	D/filt ratio	0.88	0.85	1.00	0.83	0.88	1.00	0.93	0.83	0.77	0.69	1.00	0.85	0.77
	Cd^{+2}	64	69	74	74	75	69	71	86	89	85	86	87	86
	Cl-complexes	10	8	2	7	4	10	7		1	3			
	SO_4^{-2}-complexes	25	22	24	19	21	21	21	12	9	10	5	9	12
	organic complexes								2	1	1	9	3	1
Co	D/filt ratio	0.89	0.83	1.00	0.81	0.86	1.00	0.88	0.96	0.76	0.78	0.97	0.77	0.74
	Co^{+2}	76	79	78	81	81	80	79	88	91	90	88	89	88
	SO_4^{-2}-complexes	24	21	22	18	19	20	20	11	8	10	5	9	11
	organic complexes								1	1	1	7	2	1
Cs	D/filt ratio	0.95	0.96	1.00	0.85	0.79	1.00	0.95	0.91	0.95	0.96	1.00	1.00	0.87
	Cs^{+1}	96	97	97	97	98	97	97	99	99	99	99	99	99
	SO_4^{-2}-complexes	4	3	3	2	2	3	3	1	1	1		1	1
Cu	D/filt ratio	0.84	0.90	0.97	0.82	0.91	1.00	0.91	0.59	0.35	0.62	0.65	0.58	0.58
	Cu^{+2}	74	76	76	79	78	77	77	74	82	80	47	66	77
	SO_4^{-2}-complexes	25	22	23	19	20	21	21	10	8	9	3	7	10
	organic complexes	1	1	2	2	2	2	2	15	10	10	50	27	12
Fe	D/filt ratio	0.80	0.77	0.96	0.63	0.78	0.89	0.79	0.73	0.61	0.56	0.53	0.48	0.56
	Fe^{+3}	4	1	2	1	1	1	1						
	$FeOH^{+2}$	20	19	18	11	18	13	11	1	2	1			1
	$Fe(OH)^{2+}$	3	8	7	4	9	7	6	2	4	4	1	1	3
	SO_4^{-2}-complexes	43	15	16	8	11	7	6						
	PO_4-complexes	2	1	1	2	1	1	1						
	organic complexes	27	55	57	74	59	71	76	96	94	95	99	98	96
K	D/filt ratio	1.00	0.91	0.86	1.00	1.00	0.88	1.00	0.97	1.00	0.70	1.00	1.00	0.89
	K^{+1}	98	98	99	99	99	99	99	99	100	100	100	100	99
	SO_4^{-2}-complexes			1	1	1	1	1	1					1
	organic complexes	2	1											
Mg	D/filt ratio	0.80	0.82	0.83	0.97	0.91	0.81	1.00	0.81	0.87	0.57	1.00	0.88	0.72
	Mg^{+2}	77	80	80	82	82	81	81	89	92	91	92	91	89
	SO_4^{-2}-complexes	23	20	20	17	18	19	19	10	8	9	5	8	10
	organic complexes								1			4	1	
Mn	D/filt ratio	0.96	0.81	0.79	0.92	0.87	0.88	1.00	0.76	0.90	0.67	0.97	0.89	0.80
	Mn^{+2}	79	81	81	84	83	82	82	90	92	91	92	92	90
	SO_4^{-2}-complexes	21	19	19	16	17	17	18	9	7	8	4	7	9
	organic complexes								1			4	1	
Na	D/filt ratio	0.95	0.91	0.83	1.00	0.89	0.93	1.00	0.91	1.00	0.67	1.00	0.94	0.87
	Na^{+1}	98	99	99	99	99	99	99	99	100	100	100	100	99
	SO_4^{-2}-complexes	2	1	1	1	1	1	1	1					
Ni	D/filt ratio	0.89	0.83	0.82	0.99	0.83	0.85	1.00	0.76	0.93	0.73	0.98	0.78	0.72
	Ni^{+2}	75	79	78	81	80	79	79	85	89	88	77	85	86
	SO_4^{-2}-complexes	24	21	22	19	19	20	20	11	8	9	4	8	11
	organic complexes			1			1	1	4	3	3	19	7	3

Table 4. Continued.

Component	Species name	VF22	VF19	VF24	VF25	VF28	VF21	VF27	VFB26	VFB23	VFB20	V1	V2	V3
Pb	D/filt ratio	0.88	0.88	0.94	0.68	0.97	1.00	1.00	0.68	0.45	0.92	0.75	1	0.57
	Pb^{+2}	31	9	18	9	6	53	7	6	4	2	2	2	3
	$PbCl^{+}$	2				4	3							
	SO_4^{-2}-complexes	30	6	15	6		40	5	2	1	1			1
	Mn-oxides	36	84	65	84	88	0	87	88	94	97	90	97	95
	organic complexes	1	1	1			4	1	3	1	1	7	1	1
PO_4	D/filt ratio	0.67	1.00	0.88	0.88	0.57	1.00	0.83	0.67	1.00	1.00	0.86	0.80	0.86
	HPO_4^{-2}				52									
	$H_2PO_4^{-}$	39	38	31	3	25	20	54	21	60	20	29	48	44
	H_3PO_4	1		1			1	1		1				
	$CaH_2PO_4^{+}$				1			1		1				
	$AlHPO_4^{+}$	6	27	18	13	17	8	31	23	21	9	1	18	26
	$Al_2PO_4^{+3}$		2	2	1	1		3	3	1	1		1	1
	Fe-oxides	53	32	48	31	57	72	10	53	16	69	70	33	29
SO_4	D/filt ratio	0.74	0.81	0.75	0.91	0.90	0.82	1.00	0.68	0.76	0.74	0.87	0.84	0.66
	SO_4^{-2}	67	77	71	69	74	72	75	83	87	86	96	91	86
	HSO_4^{-}	1	1	1	1	1								
	Al-complexes	16	7	15	18	11	14	8	10	6	6		2	6
	$MnSO_4$ (aq)					1								
	$MgSO_4$ (aq)	8	7	7	6	6	7	8	4	3	4	2	3	3
	$CaSO_4$ (aq)	6	6	6	6	7	6	7	4	3	4	2	3	4
	$NaSO_4^{-}$	1	1				1	1						
Si	D/filt ratio	1.00	0.98	0.88	1.00	0.89	0.88	1.00	0.97	1.00	0.74	1.00	1.00	0.95
	H_4SiO_4	100	100	100	100	100	100	100	100	100	100	100	100	100
Ti	D/filt ratio	1.00	0.96	0.91	0.88	0.65	0.93	1.00	0.83	0.38	0.74	0.57	1.00	0.89
	$Ti(OH)_4$	81	95	93	84	92	94	92	97	97	98	99	99	99
	$Ti(OH)_3^{+}$	19	5	7	16	8	6	8	3	3	2	1	1	1
U	D/filt ratio	0.80	0.78	0.80	0.93	0.87	0.84	1.00	0.43	0.33	0.52	0.55	0.39	0.43
	UO_2^{+2}	29	26	25	27	28	24	24	6	10	9	1	3	7
	UO_2OH^{+}					1	1	1	1	1	1		1	1
	SO_4^{-2}-complexes	49	41	38	29	35	32	31	4	4	5		2	5
	$UO_2H_3SiO_4^{+}$	1	1	1	1	2	1	2	1	1	1			1
	organic complexes	20	31	35	41	34	43	43	89	84	84	97	94	86

increased markedly downstream (commonly 2-4 times higher; Table 3 and Fig. 5). This is explained by a corresponding downstream increase in the proportional cover of AS soil, delivering more acid runoff from these soils strongly enriched in sulfate and metal ions. In contrast, semi-dissolved concentrations of OC were highest upstream the river (Table 3 and Fig. 5), which is explained by a higher proportion of forest and peat in the upstream area. Waters rich in humic acids may also be relatively acidic (pH <5), but the slightly higher pH upstream indicate that the humic substances are not major contributors to the acidity in the Vörå River. On the contrary, upstream of the Vörå River these humic waters from the forested areas may be considered as dilutants, as they are less acidic and do not contain high metal contents. This has also been observed by Toivonen and Österholm (2011) in other streams affected by acid sulfate soils in W Finland.

Metals are more mobile under low pH conditions and thus pH is one of the most important key factors controlling the element solubility and associations (Gundersen and Steinnes, 2003). Most of the alkali and alkaline earth metals, Cd, Co, Mn, Ni, SO_4 and Si, were in the Vörå River generally found in a dissolved form (61-86%; Fig. 5). Aluminium, As, Cu, OC and U were found in a dissolved and colloidal form (Fig. 5). Caesium, Fe and Ti were, in contrast,
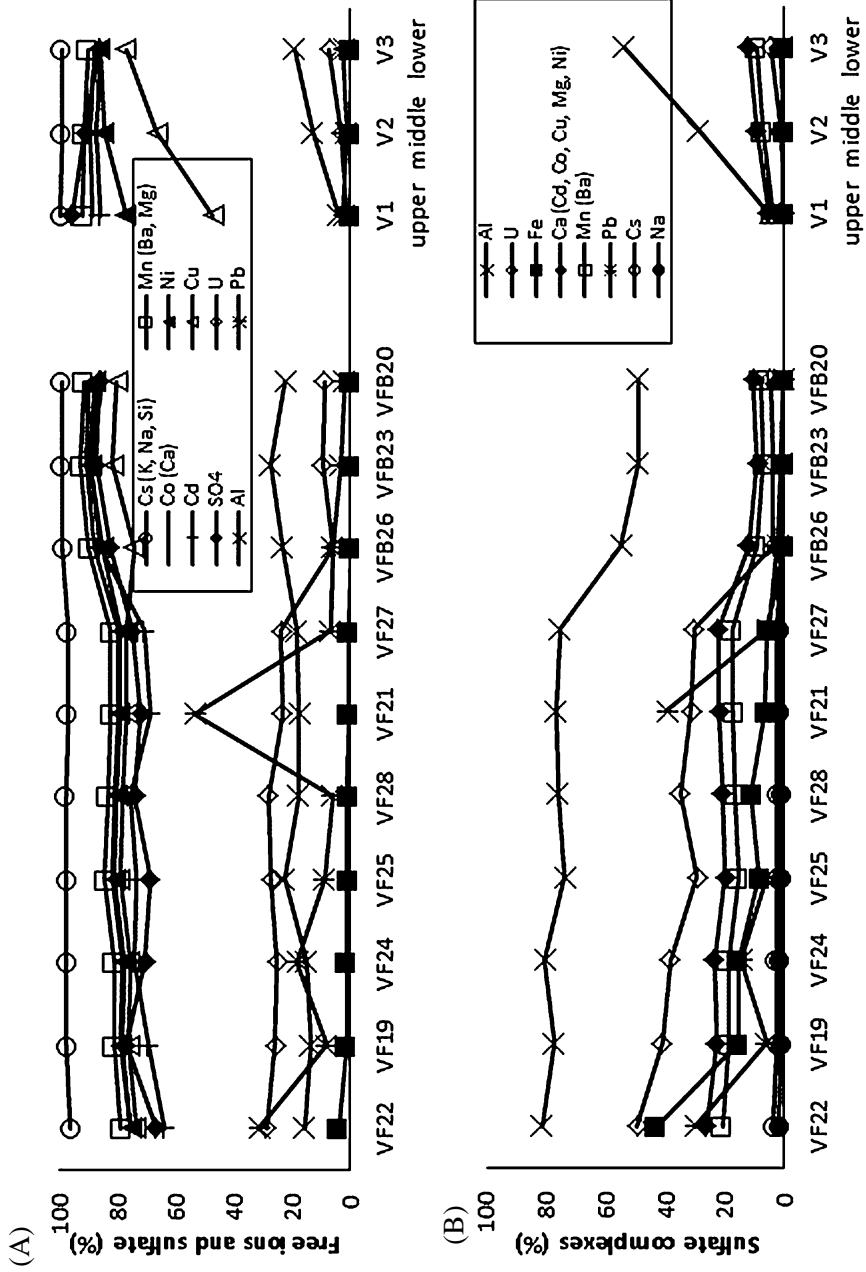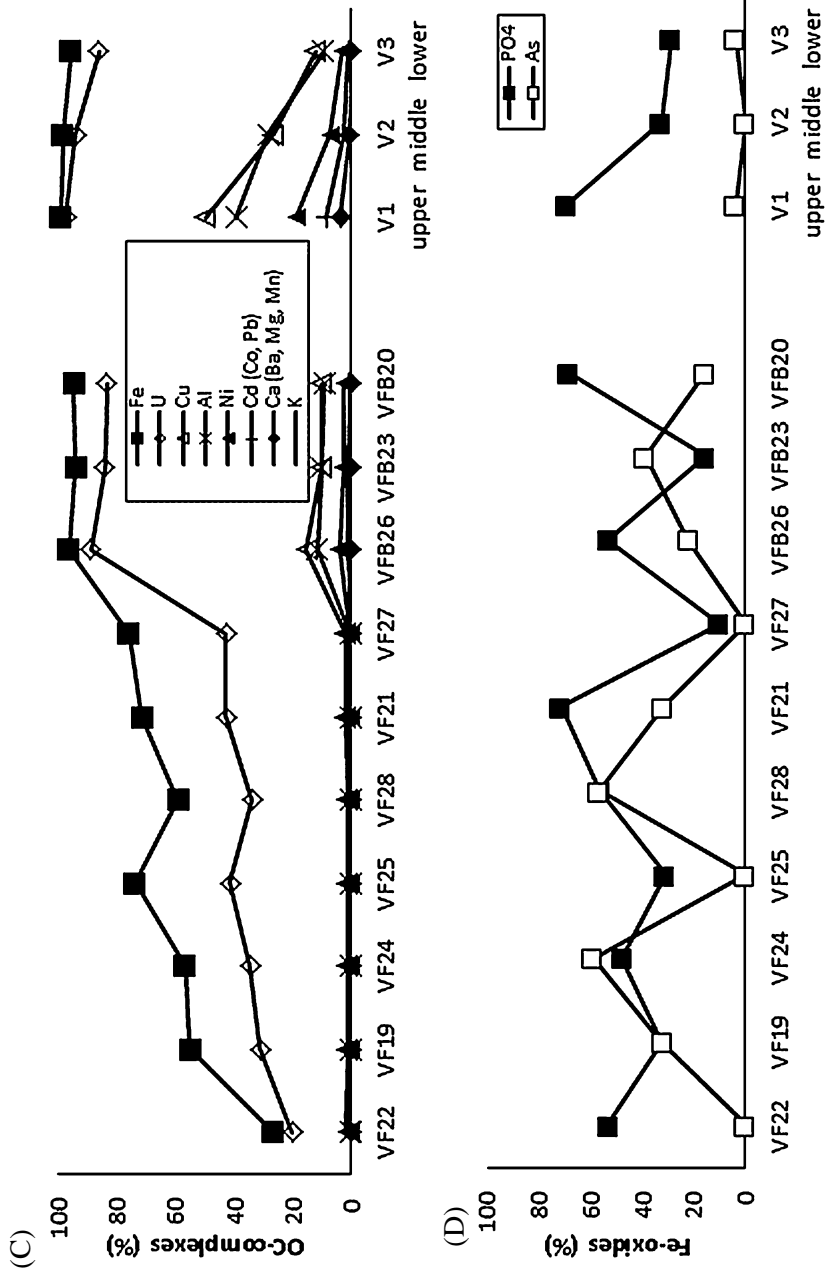
Fig. 4. Free ions (A), and element complexes with sulfate (B), organic carbon (C) and Fe (D) modelled with Visual MINTEQ for the low-order streams (VF) and brooks (VFB) of the Vörå River, and for the Vörå River (V). The streams and brooks are arranged from the lowest (left) to the highest (right) pH (pH 3.3-4.4). 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).
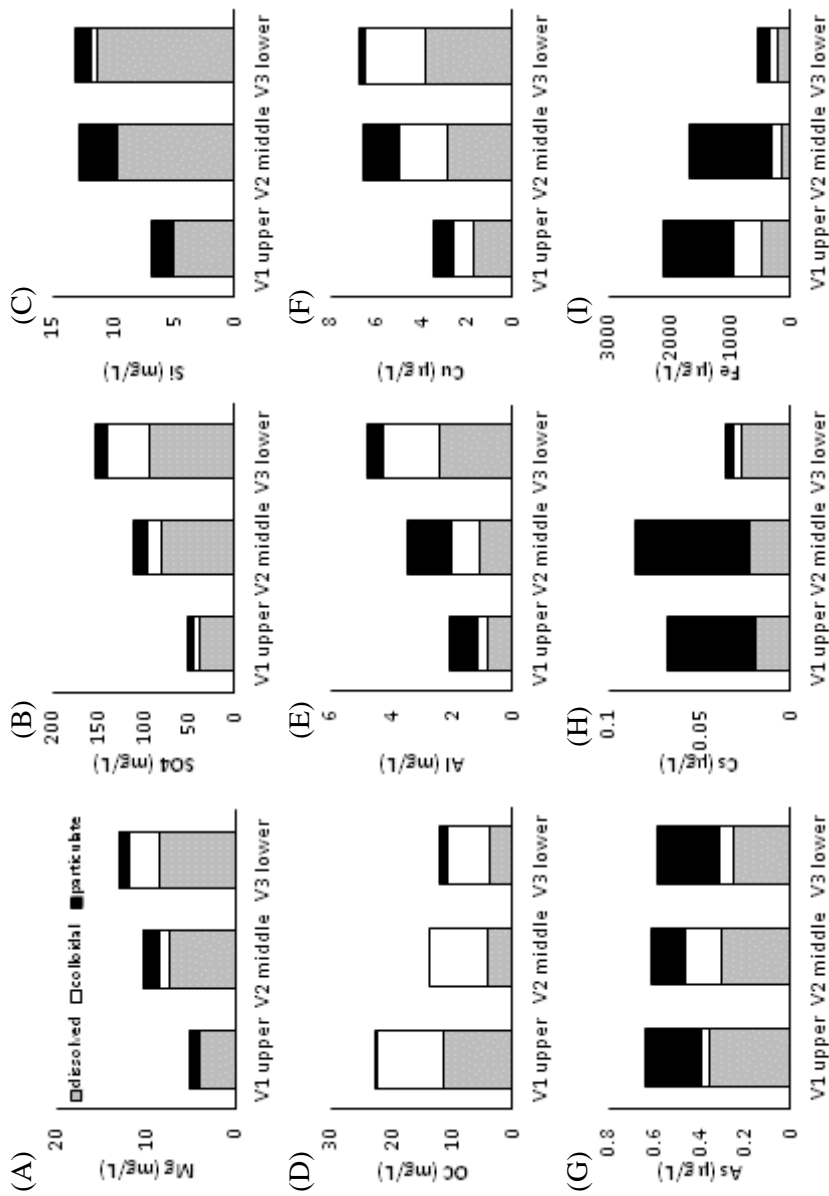
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Fig. 5. Dissolved - (<1 kDa), colloidal - (1 kDa-0.45 μm) and particulate (>0.45 μm) fractions in the Vörå River (V).
(A-C)   Most soluble elements and ions: Ba, Ca, Cd, Co, K, Mg, Mn, Na, Ni, SO₄, Si and Sr
(D)   Elements mainly in dissolved and colloidal fraction: OC
(E-F)   Elements in dissolved, colloidal and particulate fraction: Al, Cu, Hf, the lanthanoids and U
(G-H)   Elements mainly in dissolved and particulate fraction: As, Cs, Pb and PO₄
(I)   Elements mainly in particulate fraction: Fe, Ti and V

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substantially associated with particles (Fig. 5). For most of the elements (except for Fe and Ti) the dissolved and colloidal concentrations markedly increased downstream (Fig. 5), which is explained by the corresponding downstream increase of AS soils. A rather peculiar pattern, though, is the small downstream decrease of the relative abundance (i.e. the ratios between dissolved and semi-dissolved concentrations; Table 4) for sulfate and elements (Al, Ba, Ca, Cd, Co, Cu, Mg, Mn and Ni) predicted to form complexes with sulfate in the Vörå River (Table 4 and Fig. 4), although the relative abundance would rather be expected to increase downstream due to the increase of acidity. Thus, it seems that a significant portion of the formed metal-sulfate complexes do not penetrate the 1 kDa filter and can, with the operational definition used in this work, be considered to be colloids (Lottermoser, 2007). Consequently, this phenomenon is most likely explained by an increase of element complexation with sulfate downstream (Fig. 4), but not by co-precipitation (i.e. associations) of elements with Al, Fe and Mn as these element complexations were predicted to be rather unimportant in the Vörå River. In contrast, OC complexes were predicted to be important for several elements (Al, Cd, Cu, Fe, Ni and U; Fig 4) in the Vörå River, especially in the forested area upstream the river, where the river water had a slightly higher pH and carried a higher load of OC concentrations. This was likely as it is commonly known that the exchangeable capacity of OC increases with an increase of pH (Gundersen and Steinnes, 2003). Also, the higher concentrations probably contributed to higher element associations with OC, but only in a dissolved and colloidal form as OC did not occur in a particulate form (Fig. 5).

5.1.2 Rivers and their low-order streams in SW Finland

This chapter is based on the results from paper II and III and on original unpublished results of element species modelled with the modelling programVisual MINTEQ.

Also the streams in SW Finland (low-order streams of the Sirppujoki - and Mynäjoki Rivers) were acidic (18-188 mg/L $CaCO_3$), had a low pH (3.3-5.7), relatively low semi-dissolved OC (with some exceptions; 4.44-24.53 mg/L), high electric conductivity (545-1368 µS/cm) and high semi-dissolved sulfate (48-555 mg/L) and metal concentrations (Table 5). Moreover, most of the elements in the streams were substantially found in a dissolved phase (Table 6), as in the low-order streams of the Vörå River, and also sulfate complexes were predicted to be important (Fig. 6). Consequently, these results show that these streams are strongly affected by AS soils. There were, though, some variations in terms of sulfate and OC concentrations (lower and higher concentrations, respectively; Table 5), showing that some streams (especially SYV18) were diluted by forest areas.

Table 5. pH, electric conductivity (EC), acidity ($CaCO_3$) and semi-dissolved (< 0.45 µm) concentrations for organic carbon, sulfate and metals in the investigated rivers and stream sites in SW Finland. S = Sirppujoki River; L = Laajoki River; M = Mynäjoki River; P = Paimionjoki River; S-SYV = low-order stream sites to the Sirppujoki River; M-SYV = low-order stream sites to the Mynäjoki River; na = not analysed.

Samples	pH	EC uS/cm	Acidity mg/L	OC mg/L	Al µg/L	As µg/L	Ba µg/L	Br µg/L	Ca mg/L	Cd µg/L	Co µg/L	Cs µg/L	Cu µg/L	Fe µg/L	Hf µg/L	K mg/L	La µg/L
S 1 upper	6.1	120	8.8	15.29	355	0.29	7.3	80	4.8	0.06	1.64	0.011	1.4	390	0.012	1.28	2.70
S 2 lower	5.8	214	9.2	14.81	803	0.38	14.8	264	15.9	0.15	7.82	0.019	2.9	500	0.018	3.22	8.94
L 1 upper	5.6	56	9.2	19.87	473	0.49	9.2	39	4.0	0.08	1.36	0.019	2.7	710	0.016	0.97	2.16
L 3 lower	6.0	110	8.0	17.63	610	0.45	13.3	83	7.4	0.15	2.66	0.019	2.6	640	0.021	1.68	3.81
M 1 upper	6.2	67	9.6	19.06	654	0.52	11.9	29	4.2	0.03	0.856	0.032	2.2	720	0.025	0.92	2.62
M 2 lower	6.3	139	16.8	16.86	430	0.40	11.7	74	6.5	0.04	1.25	0.022	2.0	500	0.016	1.49	2.72
P 1 upper	7.3	101	na	11.88	1890	0.71	19.5	15	6.5	0.02	0.613	0.167	5.7	1460	0.052	2.40	2.64
P 2 lower	7.0	103	na	13.12	1090	0.53	16.1	21	6.1	0.04	0.507	0.112	3.9	900	0.045	1.99	2.10
S-SYV 1	3.3	1159	188	10.28	26700	1.24	15.8	2210	69.8	1.55	96.7	0.191	22.1	2590	0.178	10.60	166.0
S-SYV 2	5.0	893	168	6.54	2400	0.64	22.7	1340	62.7	0.77	52.9	0.06	2.3	35500	0.035	9.88	39.5
S-SYV 3	4.6	804	116	4.71	10100	0.82	18.8	2210	54.5	1.09	59.3	0.039	10.1	450	0.113	9.31	93.1
S-SYV 4	4.7	603	64	4.46	7600	0.68	21.0	974	43.2	0.59	29.4	0.041	7.4	280	0.077	8.82	61.6
S-SYV 5	4.1	867	140	6.04	17700	0.93	17.8	2370	57.2	1.07	60.1	0.048	13.6	450	0.2	9.49	132.0
S-SYV 10	5.3	562	33.2	5.30	632	0.56	17.3	1060	32.3	0.36	14.5	0.006	4.2	120	0.03	6.65	23.6
S-SYV 12	5.1	545	43.2	4.44	2300	0.82	24.2	1690	33.6	0.48	26.4	0.009	8.5	160	0.054	9.62	55.3
S-SYV 16	5.3	611	48	4.81	1520	0.46	20.6	1360	46.0	0.63	32.2	0.038	3.9	390	0.054	7.56	47.2
S-SYV 17	5.0	583	32	24.53	1710	0.77	29.6	444	47.1	0.73	36.8	0.063	4.5	630	0.035	8.94	11.3
S-SYV 18	6.1	169	88	19.37	933	0.51	14.8	101	10.9	0.10	4.4	0.022	2.5	760	0.031	2.26	6.8
M-SYV 8	4.9	791	40	4.63	2000	0.40	20.2	1540	46.6	0.76	36.1	0.009	5.2	70	0.089	9.67	57.7
M-SYV 9	5.7	576	17.6	4.61	347	0.56	23.8	793	32.2	0.40	19.3	0.008	5.5	110	0.027	6.49	33.4

Samples	Mg mg/L	Mn µg/L	Na mg/L	Ni µg/L	Pb µg/L	PO_4 mg/L	Rb µg/L	SO4 mg/L	Si mg/L	Sr µg/L	Th µg/L	Ti µg/L	Tl µg/L	U µg/L	V µg/L	Y µg/L	Zr µg/L
S 1 upper	2.07	77	4.64	5.0	0.16	0.215	2.57	18	4.7	27.1	0.076	4.7	0.02	0.12	0.4	1.97	0.30
S 2 lower	6.19	372	8.36	20.5	0.24	0.215	4.98	66	6.9	85.7	0.094	3.9	0.03	0.23	0.3	6.85	0.39
L 1 upper	1.48	124	1.84	2.8	0.43	0.215	2.45	12	2.6	20.6	0.134	6.6	0.02	0.14	0.7	1.81	0.53
L 3 lower	2.99	156	3.91	7.5	0.40	0.245	3.40	27	5.1	39.9	0.127	7.4	0.02	0.21	0.5	3.07	0.61
M 1 upper	2.06	49	2.71	2.7	0.33	0.153	2.33	9	4.3	24.8	0.205	15.7	0.02	0.26	1.0	1.78	0.67
M 2 lower	3.20	82	5.66	5.4	0.18	0.245	2.37	18	5.3	37.2	0.114	12.0	0.02	0.26	0.8	2.00	0.51
P 1 upper	4.38	26	5.34	3.3	0.87	0.337	4.52	9	8.4	41.9	0.302	68.7	0.03	0.49	3.4	1.24	1.68
P 2 lower	3.65	33	5.65	1.9	0.58	0.337	3.30	9	5.3	33.5	0.188	42.1	0.02	0.45	2.3	0.952	1.29
S-SYV 1	42.3	3820	35.5	205.0	1.23	0.184	26.30	555	47.5	470	0.182	7.0	0.14	2.14	0.9	123.0	0.22
S-SYV 2	23.8	1860	28.5	96.0	0.15	0.153	13.90	339	20.5	300	0.014	4.6	0.05	0.28	0.2	26.7	0.06
S-SYV 3	27.9	2920	27.0	144.0	0.53	0.153	15.00	339	30.4	280	0.010	3.9	0.05	0.63	0.2	64.3	0.14
S-SYV 4	17.7	1330	14.3	67.5	0.37	0.215	12.00	219	20.7	220	0.019	3.5	0.05	0.66	0.3	41.1	0.11
S-SYV 5	30.0	3420	16.1	155.0	2.04	0.245	15.00	381	33.9	330	0.153	4.6	0.06	1.32	0.2	96.1	0.17
S-SYV 10	14.0	711	34.2	44.2	0.10	0.215	6.98	126	18.9	168	0.004	3.1	0.02	0.27	0.4	14.8	0.09
S-SYV 12	22.0	1150	28.5	87.5	0.36	0.184	9.04	180	24.8	210	0.008	3.8	0.03	0.44	0.5	34.2	0.09
S-SYV 16	19.6	1570	22.4	76.3	0.14	0.215	9.61	240	11.9	240	0.004	1.5	0.04	0.30	0.0	31.5	0.04
S-SYV 17	25.9	2070	10.6	75.3	0.09	0.215	10.20	237	7.7	240	0.044	1.8	0.08	0.15	0.4	10.5	0.55
S-SYV 18	4.6	275	5.7	11.0	0.24	0.215	3.45	48	5.8	58.1	0.229	7.6	0.028	0.30	0.6	4.7	0.66
M-SYV 8	19.5	1290	48.7	99.9	0.16	0.184	8.72	204	19.7	188	0.003	3.1	0.03	0.37	0.0	43.3	0.05
M-SYV 9	16.5	797	30.7	56.0	0.25	0.215	7.09	147	14.5	170	0.003	2.5	0.03	0.16	0.3	16.2	0.05

Table 6. The ratios between dissolved (<1 kDa) and semi-dissolved (<0.45 μm) concentrations for organic carbon, sulfate and metals in the investigated rivers and stream sites in SW Finland. S = Sirppujoki River; L = Laajoki River; M = Mynäjoki River; P = Paimionjoki River; S-SYV = low-order stream sites to the Sirppujoki River; M-SYV = low-order stream sites to the Mynäjoki River.

Samples	OC	Al	As	Ba	Br	Ca	Cd	Co	Cs	Cu	Fe	Hf	K	La	Mg
S 1 upper	0.20	0.08	0.76	0.79	1.00	1.00	0.50	0.71	0.64	1.00	0.03	0.08	1.00	0.08	1.00
S 2 lower	0.23	0.11	0.50	0.71	0.85	0.55	0.73	0.57	0.74	0.41	0.10	0.11	0.72	0.12	0.62
L 1 upper	0.18	0.05	0.41	0.36	0.28	0.40	1.00	0.29	0.37	0.19	0.03	0.19	0.65	0.02	0.43
L 3 lower	0.27	0.16	0.62	0.60	0.81	0.57	0.47	0.50	0.58	0.42	0.17	0.19	0.79	0.15	0.63
M 1 upper	0.16	0.04	0.56	0.41	0.93	0.60	0.33	0.31	0.19	0.27	0.04	0.04	0.86	0.03	0.67
M 2 lower	0.15	0.05	0.55	0.67	1.00	0.86	0.50	0.54	0.23	0.25	0.02	0.13	1.00	0.02	0.91
P 1 upper	0.25	0.01	0.17	0.17	0.27	0.38	0.50	0.04	0.01	0.09	0.01	0.06	0.44	0.01	0.43
P 2 lower	0.32	0.02	0.40	0.32	0.71	1.00	0.50	0.23	0.03	0.31	0.01	0.04	1.00	0.01	1.00
S-SYV 1	0.55	0.63	0.96	0.89	0.98	0.85	0.87	0.82	0.93	0.86	0.80	0.80	0.85	0.80	0.84
S-SYV 2	0.64	0.73	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.94	1.00	1.00	1.00
S-SYV 3	0.69	0.86	0.73	0.99	1.00	1.00	0.98	0.92	1.00	0.87	0.87	0.77	1.00	0.91	0.99
S-SYV 4	0.66	0.62	0.79	0.78	0.79	0.78	0.75	0.81	0.83	0.76	0.75	0.86	0.80	0.69	0.68
S-SYV 5	0.66	0.69	0.76	0.76	0.83	0.77	0.78	0.73	0.79	0.76	0.89	0.63	0.74	0.80	0.78
S-SYV 10	0.74	0.19	0.54	1.00	1.00	1.00	1.00	1.00	1.00	0.62	0.17	0.50	1.00	0.85	1.00
S-SYV 12	0.73	0.35	0.33	0.89	0.89	0.88	1.00	0.86	0.89	0.62	0.31	0.81	0.82	0.77	0.76
S-SYV 16	0.57	0.59	1.00	0.71	0.93	0.71	0.75	0.68	0.79	0.64	0.87	0.54	0.83	0.67	0.80
S-SYV 17	0.30	0.43	0.55	0.66	0.67	0.66	0.62	0.62	0.73	0.33	0.29	0.09	0.62	0.35	0.58
S-SYV 18	0.15	0.07	0.49	0.59	0.85	0.65	0.50	0.56	0.41	0.40	0.04	0.03	0.86	0.03	0.67
M-SYV 8	0.60	0.50	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.81	1.00	1.00	1.00	1.00	0.97
M-SYV 9	0.52	0.19	1.00	0.89	1.00	0.97	0.95	1.00	1.00	0.45	1.00	0.33	1.00	0.71	1.00

| Samples	Mn	Na	Ni	Pb	Rb	SO$_4$	Si	Sr	Th	Ti	Tl	U	V	Y	Zr
S 1 upper	1.00	1.00	0.46	0.50	1.00	0.83	0.07	1.00	0.01	0.32	1.00	0.07	0.25	0.09	0.03
S 2 lower	0.60	0.69	0.44	0.67	0.80	0.64	0.11	0.64	0.05	0.28	0.85	0.14	0.33	0.10	0.10
L 1 upper	0.39	0.61	0.39	0.12	0.61	0.25	0.03	0.42	0.01	0.27	0.65	0.03	0.43	0.03	0.26
L 3 lower	0.56	0.79	0.36	0.50	0.76	0.56	0.15	0.62	0.16	0.31	0.81	0.16	0.40	0.14	0.33
M 1 upper	0.55	0.92	0.26	0.94	0.71	0.67	0.03	0.60	0.02	0.04	0.70	0.04	0.40	0.05	0.03
M 2 lower	0.82	1.00	0.28	0.28	0.91	0.83	0.02	0.85	0.02	0.06	0.87	0.05	0.38	0.02	0.02
P 1 upper	0.27	0.48	0.09	0.01	0.15	0.33	0.01	0.49	0.01	0.01	0.12	0.03	0.15	0.02	0.10
P 2 lower	0.82	1.00	0.21	0.17	0.37	0.33	0.01	0.96	0.02	0.02	0.30	0.07	0.26	0.03	0.21
S-SYV 1	0.84	0.89	0.80	0.94	0.93	0.78	0.79	0.85	0.58	0.96	0.96	0.81	0.89	0.77	0.27
S-SYV 2	1.00	1.00	1.00	1.00	1.00	1.00	0.98	1.00	0.29	1.00	1.00	0.89	1.00	0.99	0.67
S-SYV 3	1.00	1.00	0.92	0.96	0.94	0.99	0.94	1.00	0.60	0.82	0.98	0.85	1.00	0.84	0.64
S-SYV 4	0.71	0.75	0.81	0.92	0.87	0.73	0.69	0.79	0.42	0.74	0.81	0.66	0.67	0.70	0.36
S-SYV 5	0.77	0.80	0.72	0.78	0.77	0.77	0.75	0.76	0.56	0.87	0.79	0.70	1.00	0.68	0.41
S-SYV 10	1.00	1.00	1.00	0.50	1.00	1.00	0.56	1.00	0.50	0.74	1.00	0.66	0.00	0.74	0.22
S-SYV 12	0.71	0.77	0.84	1.00	0.96	0.83	0.76	0.86	0.38	1.00	0.80	0.65	0.20	0.78	0.33
S-SYV 16	0.78	0.89	0.70	0.86	0.79	0.70	0.65	0.74	0.25	0.80	0.82	0.45	1.00	0.63	0.25
S-SYV 17	0.59	0.69	0.61	0.67	0.71	0.67	0.24	0.69	0.05	0.50	0.71	0.22	0.50	0.27	0.05
S-SYV 18	0.61	0.84	0.36	0.29	0.82	0.56	0.03	0.71	0.01	0.12	0.75	0.06	0.33	0.03	0.03
M-SYV 8	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.67	1.00	1.00	0.84	0.00	0.96	0.40
M-SYV 9	1.00	1.00	0.87	0.48	1.00	0.92	0.45	1.00	0.33	1.00	1.00	0.65	1.00	0.55	0.40
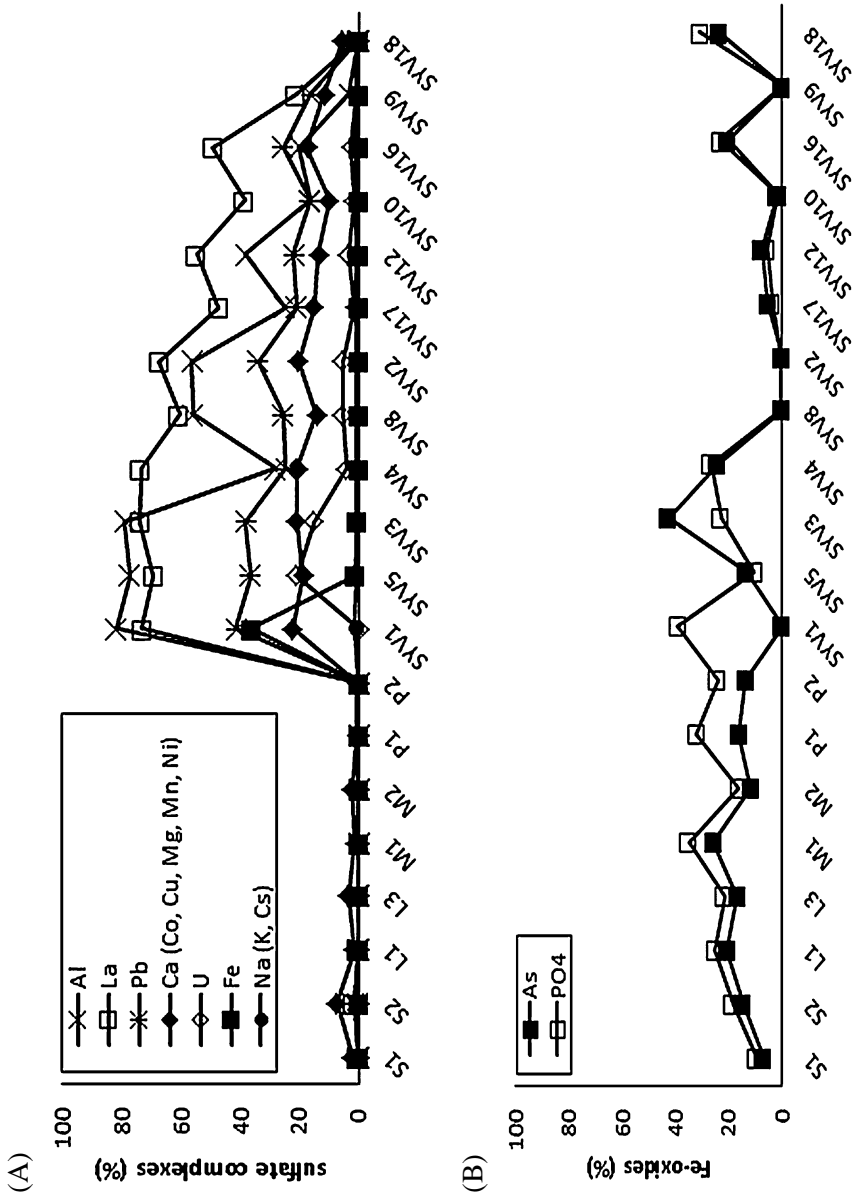
Fig. 6. Element complexes with sulfate (A) and Fe (B) modelled with Visual MINTEQ in the Sirppujoki - (S), Laajoki - (L), Mynäjoki - (M) and Paimionjoki (P) Rivers, including 12 low-order streams. The streams are arranged from the lowest (left) to the highest (right) pH (pH 3.3-6.1). As the predicted results for some elements were very similar, only one representative element is shown for these element groups (elements not shown are in brackets).

During several sampling occasions in the Sirppujoki River, pH was close to or below 5.5 (Fig. 7). pH also decreased remarkably with increasing flow, and the low pH values were associated with high acidity and EC (Fig. 7), showing that they were not caused by dilution effects (Hem, 1985) or the increased input of OC (i.e. humic acids) due to the higher flow path during the higher flow (Laudon, 2000). Also the semi-dissolved concentrations of SO_4, acidity and many elements (Ba, Br, Ca, Cd, Co, K, Mg, Mn, Na, Ni, Rb and Sr; Table 5) were high in the Sirppujoki River compared to semi-dissolved median metal concentrations of 1161 Finnish stream waters (Lahermo et al., 1996), and increased markedly downstream (commonly 2–4 times higher; Table 5). Consequently, it is obvious that the middle and lower Sirppujoki River is strongly affected by AS soils. This is in line with previous soil profile studies (Palko et al., 1985; Triipponen, 1997; Beucher et al., in press), which also showed the presence of AS soils in the midstream section of the Sirppujoki River.

In the Mynäjoki River, pH was only on one occasion <5.5, and on the other occasions between 6 and 7 (Fig. 7). Conductivity and concentrations of SO_4 and metals were, however, elevated, and commonly increased by a factor of 2 downstream (Table 5). These results in combination of the low pH and high SO_4 and metal concentrations in the low-order streams of the Mynäjoki River showed that the lower Mynäjoki River is affected by AS soils.

On several sampling occasion in the Laajoki River, pH was below or close to 5.5 (Fig. 7). pH were generally lowest upstream and decreased with flow only in L3 (Fig. 7). Also acidity was relatively high and generally somewhat higher in the upper part of the Laajoki River (Fig. 7), and although EC and concentrations of SO_4 and elements were lower than in the Sirppujoki River, they still were considerably higher (Table 5) compared to background values of Finland in general (Lahermo et al., 2006), and increased furthermore downstream (generally by a factor of 2; Table 5). Also the temporal patterns of these elements (especially SO_4) in the Laajoki River have close resemblance to patterns in the Sirppujoki River, and thus it is likely that even the Laajoki River is affected by AS soil.

All rivers exhibited a high concentration of semi-dissolved organic C (14–20 mg/L; Table 5), with the highest and lowest concentrations in the Mynäjoki River and the Sirppujoki River, respectively. The semi-dissolved OC concentrations decreased downstream due to the corresponding increase of AS soils downstream the rivers (Fig. 8). It is also notable that in both the Laajoki - and Mynäjoki Rivers, pH is controlled more by OC (i.e. humic acids) from the peatlands in the upstream areas (indicated by high OC and lower element concentrations; Fig. 8) and the relatively well buffered waters in downstream areas, than by AS soil discharge.   One peculiar pattern was that the dissolved
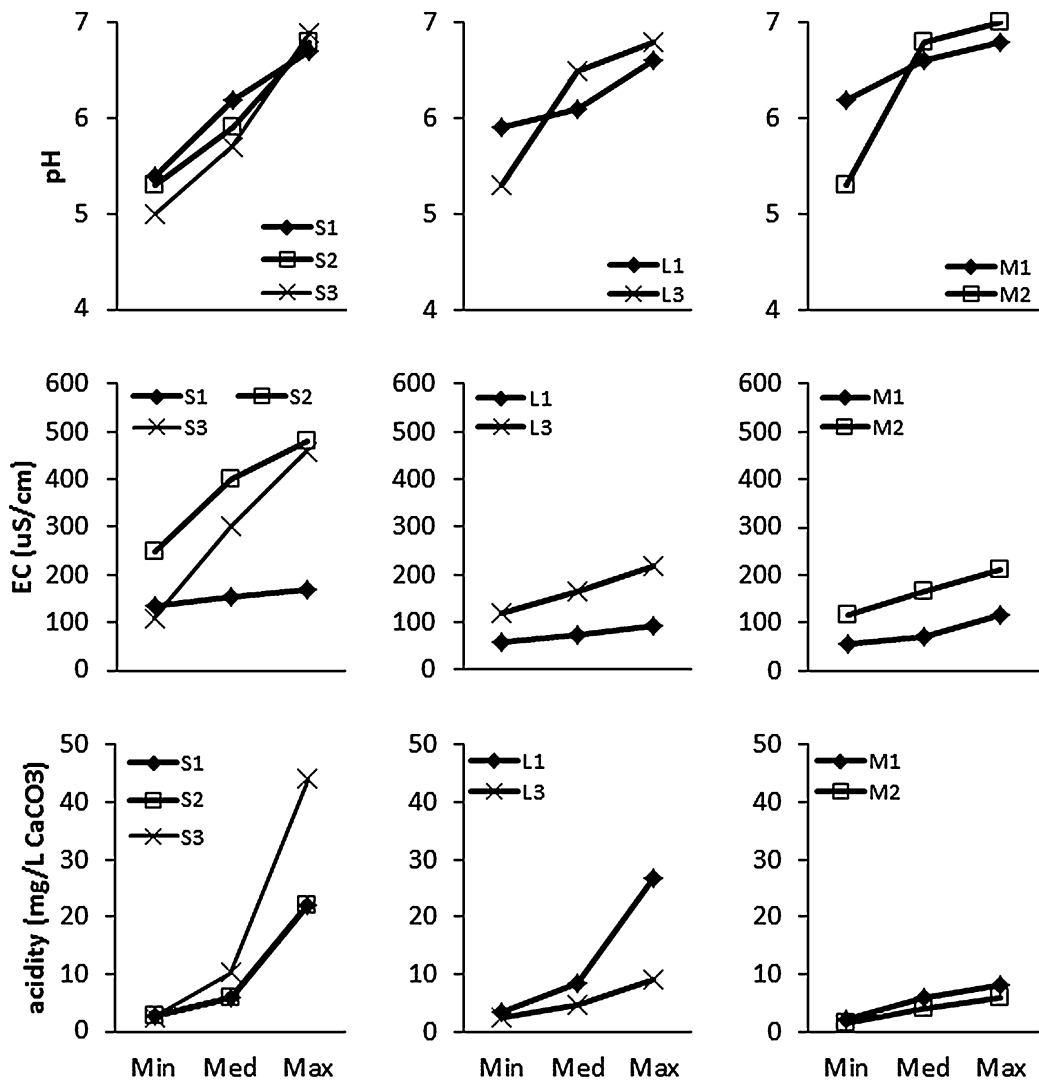
Fig. 7. Minimum, median and maximum (n = 7) concentrations of pH, electric conductivity (EC) and acidity in the Sirppujoki - (S), Laajoki - (L) and Mynäjoki - (M) Rivers. Min = Minimum; Med = Median; Max = Maximum.
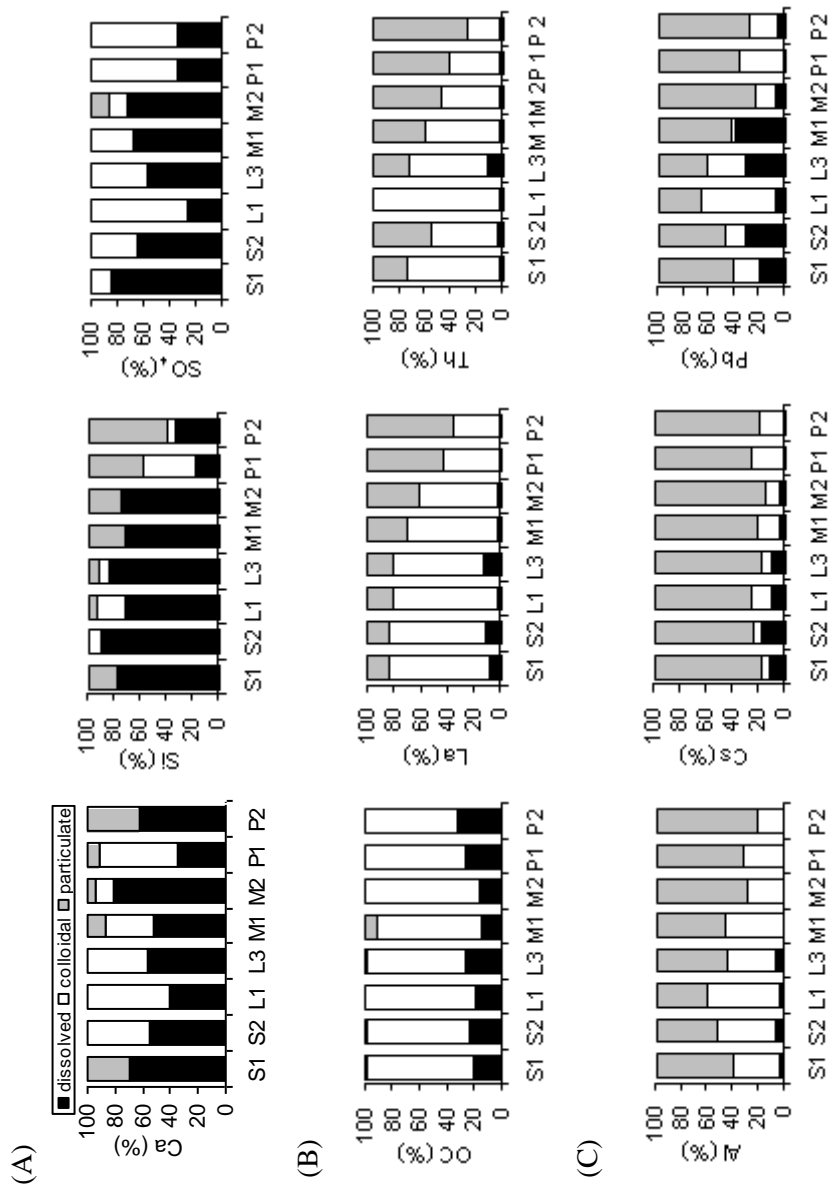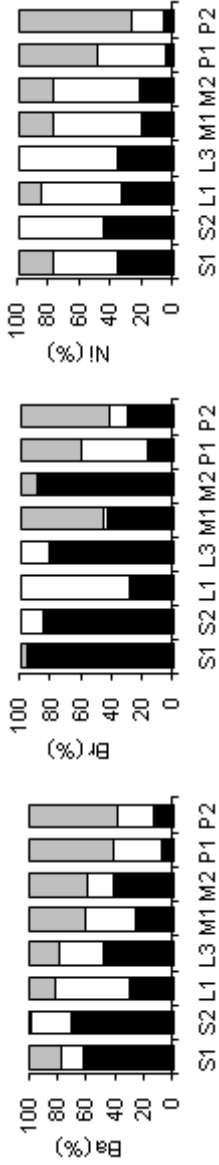
Fig. 8. Dissolved- (<1 kDa), colloidal- (1 kDa-0.45 µm) and particulate (>0.45 µm) fractions (%) in the Sirppujoki - (S), Laajoki - (L), Mynäjoki - (M) and Paimionjoki (P) Rivers.

(A) Most soluble elements and ions: Ca, Cd, K, Mg, Mn, Na, PO₄, SO₄, Si and Sr

(B) Organic C and elements mainly in colloidal fraction: OC, Th, U, Y, Zr and the lanthanoids

(C) Elements mainly in particulate fraction: Al, Cs, Fe, Hf, Pb, Ti and V

(D) Elements exhibiting large variations: As, Ba, Br, Co, Cu, Ni, Rb and Tl

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concentrations of OC were remarkable stable in all rivers and low-order stream sites (generally 2-5 mg/L), although the semi-dissolved concentrations varied. This was also observed in the Vörå River and in other studies in boreal regions (Pokrovsky et al., 2010). The particulate OC was negligible in all sites, except in the upper part of the Mynäjoki River (Fig. 8).

There were significant differences between the fractionation patterns for the elements, SO_4 and OC in the investigated rivers in SW Finland. Calcium, Cd, K, Mg, Mn, Na, SO_4, Si and Sr were as expected the most soluble elements in the rivers (Fig. 8), as several of these elements (i.e. alkali and alkaline earth metals) are generally very soluble and favour the free ionic form or small complexes in freshwater (Stumm and Morgan, 1996; Guéguen and Dominik, 2003). The lanthanoids, Y and OC were mostly found as colloids (Fig. 8), similar to previous studies from smaller boreal rivers in NW Russia (Pokrovsky and Schott, 2002; Pokrovsky et al., 2006; Vasyukova et al., 2010). Similar to fractionation patterns reported for boreal organic-rich rivers in Sweden and NW Russia (Ingri et al., 2000; Pokrovsky and Schott, 2002; Pokrovsky et al., 2006; Vasyukova et al., 2010), Al, Fe and Pb were almost entirely colloidal- and particle-sized in the rivers (Fig. 8) partly due to the relatively high pH (5.6-6.3; in the samples ultrafiltered), causing in-stream precipitation. Moreover, the elements As, Ba, Br, Co, Cu, Ni, Rb and Tl exhibited very large variation in fractionation in the rivers (Fig. 8), which indicates that these elements are sensitive to variations in hydrochemistry and catchment-soil geochemistry. The solubilities of several of these elements (especially As, Ba, Cu, Ni, Rb and Tl) were found to be largely controlled by pH within a pH range between 5.6 and 7.3 (here included the Paimionjoki River, see section 5.2). Thus, the dissolved (most toxic) fraction of most of these elements was highest in the Sirppujoki River (northernmost and most acidic river), and decreased southwards being lowest in the Paimionjoki River (southernmost and circumneutral river; Fig. 8). These phenomenon was also observed for the other elements (also the most soluble ones; Fig. 8), although in smaller variations. Consequently, given the trend of increasing pH and decreasing dissolved metals southwards, there appears to be a trend of decreasing AS soil occurrences from north to south.

5.1.3 Elements not elevated in the acidic waters

In this chapter, results of paper II and IV are presented, as well as original unpublished results of element species not discussed in these papers.

In contrast to most of the investigated elements, As, Cs, Fe, Hf, Pb, Ti, V and PO_4 were not enriched or only moderately enriched in the Sirppujoki -, Laajoki -, Mynäjoki - and Vörå Rivers (Table 3 and 5), indicating that these elements are rather immobile during oxidation and weathering of the soils. According to

Brookins (1988), Ti has a very low mobility under almost all environmental conditions, but the most acid conditions (below pH 2), and also Hf is known to be only slightly mobile in soils (Kabata-Pendias, 2001). Also Nordmyr et al. (2006), investigating the amount of element leakage from Finnish AS soils, found that Ti and V were mostly associated with more resistant fractions in the soils, which explains why these metals are not abundantly leached from the soils. Moreover, this most likely explains the occurrence of mainly particulate Ti and V in the rivers (Fig. 5 and 8), and the predicted existence of Ti in a fully hydrated form (Table 4 and 7). Although increased amounts (up to 100 mg/L) of Fe have been observed in some especially Finnish acidic soil waters (pH 2.5-3.0; Åström and Corin, 2000), it is more likely that Fe is not especially abundant and has a relatively low mobility and transport capacity in Finnish AS soils (e.g. Österholm and Åström, 2002; Nordmyr et al., 2008), due to precipitation of Fe-oxides in soil cracks after oxidation of sulfides, thus inhibiting release of Fe from these soils. This can also explain the relative low concentrations of As in these acidic waters as As generally adsorb on Fe oxides under acidic to neutral conditions (pH <7; Lavergren et al. 2009; Wällstedt et al., 2010) and thus most likely co-precipitate with Fe oxides in the soil cracks. Arsenic is, thus, also predicted to be associated to ferrihydrite in most of the investigated streams, ditches and rivers (Fig. 4 and 6) and can, thus, make As less bioavailable when occurring in a colloidal and/or particulate form (Sjöstedt et al., 2009). The adsorption of As on Fe-oxides is generally pH dependent (Wang and Mulligan, 2006), but this was not as clearly seen as probably would have been expected. In SW Finland the predicted associations between As and Fe were higher in the rivers (pH ~ 5.8-7.3) compared to the more acidic streams (Fig. 6). On the contrary, in the Vörå River (pH 4.3-4.6) the element associations to SO_4 were generally lower compared to the more acidic streams (Fig. 4). Indeed, the Vörå River water was more acidic compared to the waters of the investigated rivers in SW Finland, which can explain the different aqueous arsenic speciation. However, in some of the inflow-streams to the Vörå River (VF22, VF25 and VF27) no associations between As and Fe were predicted (Fig. 4), which might depend on the high SO_4 concentrations in these waters as high SO_4 concentrations might reduce the adsorption capacity of As(III) in acidic waters (Jain and Loeppert, 2000). This might also explain the lower As-Fe associations in the more acidic streams in SW Finland. Moreover, PO_4 does also have similar properties as As in waters and soils (Manning and Goldberg, 1996; Hongshao and Stanforth, 2001), and thus PO_4 was expected to be closely tied to the iron cycle in the more acidic waters. This is shown by the predicted associations between PO_4 and Fe in the acidic waters (Fig. 4 and 6). Lead is also generally associated with Fe- and/or Mn-oxides in waters and soils (Taillefert et al., 2000; Dong et al., 2003), and Pb was predicted to be partially associated with Fe-oxides in several of the investigated rivers in SW Finland (Table 7), and with Mn-oxides in the Vörå River and its inflow streams (Table 4).

Table 7. Free ions and element associations modelled with Visual MINTEQ and the dissolved fraction (%) obtained by ultrafiltration in the rivers and stream sites in SW Finland. The results <1% are not shown in the table. <1 kDa = dissolved fraction obtained by ultrafiltration.

Element	Species name	S1 %	S2 %	L1 %	L3 %	M1 %	M2 %	P1 %	P2 %
Al	Al <1kDa	3	6	3	7	2	1		
	Al-oxyhydroxide							1	
	organic complexes	100	99	100	100	100	100	99	100
Ba	Ba <1kDa	62	70	29	48	25	40	7	12
	Ba^2	92	92	88	91	87	91	94	95
	SO_4^{2-}-complexes	2	5	1	2	1	2	1	1
	Fe-oxides							1	
	organic complexes	6	3	10	7	12	7	4	3
Br	Br <1kDa	95	85	28	81	42	89	16	29
	Br	100	100	100	100	100	100	100	100
Ca	Ca <1kDa	70	55	40	57	52	81	35	62
	Ca^2	87	88	84	85	80	85	90	91
	SO_4^{2-}-complexes	2	7	2	3	1	3	1	1
	CO_3-complexes							1	
	organic complexes	10	5	14	11	19	12	8	7
Co	Co <1kDa	56	57	26	50	21	34	1	5
	Co^2	67	77	69	65	53	59	56	64
	SO_4^{2-}-complexes	2	6	1	2	1	2	1	1
	CO_3^{2-}-complexes	1	1	1	1		1	2	2
	Fe-oxides							6	3
	organic complexes	30	16	29	32	46	38	34	30
Cs	Cs <1kDa	11	17	9	10	4	3		1
	Cs	100	99	100	100	100	100	100	100
	SO_4^{2-}-complexes		1						
Cu	Cu <1kDa	23	36	19	42	19	14	6	15
	Cu^2	1	4	5	1	1			
	Fe-oxides	1	1	1	1	2	1	5	5
	organic complexes	97	94	93	97	97	98	95	95
Fe	Fe <1kDa	1	4	1	8	1	1		
	$FeOH^{+2}$						3		2
	$Fe(OH)^{2+}$	5	8	7	4	3		2	
	organic complexes	95	92	93	96	97	97	98	98
K	K <1kDa	77	72	61	79	61	83	31	50
	K	100	100	100	100	100	100	100	100
La	La <1kDa	7	10	2	12	2	1	1	
	La^3	2	6	5	1	1			
	SO_4^{2-}-complexes	1	6	1	1				
	organic complexes	97	86	93	98	99	99	100	100
Mg	Mg <1kDa	76	62	43	63	57	77	35	53
	Mg^2	88	90	85	87	82	87	91	92
	SO_4^{2-}-complexes	2	6	1	3	1	2	1	1
	CO_3^{2-}-complexes							1	
	organic complexes	10	4	13	10	17	11	7	6
Mn	Mn <1kDa	80	60	39	56	40	73	10	31
	Mn^2	87	89	85	86	80	85	81	87
	SO_4^{2-}-complexes	2	5	1	3	1	2	1	1
	CO_3^{2-}-complexes							3	1
	Fe-oxides							7	3
	organic complexes	11	5	14	11	19	12	8	7
Na	Na <1kDa	82	69	61	79	92	89	48	68
	Na	100	100	100	100	100	100	100	100
Ni	Ni <1kDa	35	44	33	36	20	21	4	6
	Ni^2	33	49	38	30	20	24	22	28
	SO_4^{2-}-complexes	1	4	1	1		1		
	CO_3^{2-}-complexes		1		1		1	1	1
	Fe-oxides							13	7
	organic complexes	66	46	61	68	79	74	63	63

Table 7. Continued.

Element	Species name	S1 %	S2 %	L1 %	L3 %	M1 %	M2 %	P1 %	P2 %
Pb	Pb <1kDa	20	31	8	31	39	6		5
	Pb^2	1	4	4	1				
	SO$_4^{2-}$-complexes		1						
	Fe-oxides	72	61	40	71	82	84	97	97
	organic complexes	26	33	55	28	17	15	3	2
SO$_4$	SO$_4$<1kDa	83	64	25	56	67	71	33	33
	SO$_4$	97	93	98	96	97	96	96	94
	MgSO$_4$ (aq)	1	2	1	1	1	2	2	3
	CaSO$_4$ (aq)	2	4	1	2	1	2	2	3
H$_4$SiO$_4$	Si <1kDa	78	90	71	84	72	75	17	34
	H$_4$SiO$_4$	99	99	99	99	98	99	97	97
	Fe-oxides	1	1	1	1	2	1	3	3
Ti(OH)$_4$	Ti <1kDa	6	4	7	5	1	1		
	Ti(OH)$_4$	100	100	100	100	100	100	100	100

5.2 Impact of soil erosion on metal species

This chapter is mostly based on the results from paper II, III and IV.

In the Paimionjoki River pH was circumneutral (between 7.0 and 7.3) and the alkalinity and EC relatively high (29.5-41.2 mg/L CaCO$_3$ and 101-103 μS/cm, respectively; Table 5). Semi-dissolved organic C were lower in the Paimionjoki River (11-13 mg/L; Table 5) compared to the other investigated rivers, due to the higher proportion of fine grained sediments in the catchment area. The semi-dissolved concentrations increased downstream (Table 5), which is explained by the abundantly distributed fine sediments in the catchment throughout the whole river. In the Paimionjoki River, the SO$_4$ and metal patterns are not typical for AS soils, e.g. total concentrations of Ba, Cs, Fe, Hf, Pb, Rb, Si, Th, Ti, Tl and V are high, while Br, Mn and SO$_4$ are relatively low. Also the spatial variations for these elements were relatively small, probably as a result of the homogeneous nature of the Paimionjoki Rivers drainage area and abundance of cultivated land. Moreover, the fractionation pattern was quite different to those of the other rivers (Fig. 8), i.e. most of the elements occurred mainly in a colloidal and particulate fraction probably due to the high pH in the river. Also those elements generally occurring in a dissolved form (Ca, K, Mg, Na and Sr; Stumm and Morgan, 1996; Guéguen and Dominik, 2003) were relatively insoluble in the Paimionjoki River (Fig. 8). These results all indicate that there are no or only minor influences of AS soils in the Paimionjoki River, and thus it has to be considered that other metal binding material or elements could influence the element concentration and speciation.

In comparison to the observed results, the predicted results (Visual MINTEQ) generally showed a lower proportion metals >1 kDa in size in several of the investigated rivers (Table 7). In the Vörå - and Sirppujoki Rivers the observed and predicted proportion of metal colloids and particles matched relatively well

(except for Cs, Cu and Pb in the Sirppujoki River), but the difference between predicted and observed results increased successively from the Laajoki River to the Paimionjoki river (especially for Ba, Br, Ca, Co, K, Mg, Mn and Si; Fig. 8 and Table 7). Although there are some inherent uncertainties when using "model predictions", e.g. lack of adjustment possibilities (Weber et al., 2006; Pourret et al., 2007b; Rönnback et al., 2008), these differences cannot be explained by this alone. Nor can they be explained by potential artefacts during frontal ultrafiltration, as no traces of membrane fouling was found on a 1 kDa filter used on water from the Paimionjoki River, when the filter surface was analysed with SEM. Even the possibility of electrostatic interaction between major ions (mainly Ca, Mg, SO_4) and the charged ultrafiltration membrane during ultrafiltration, generally causing a higher colloidal fraction of major ions than the models would predict (Buffle, 1990; Viers et al. 1997; Dupré et al. 1999; Guo et al., 2001; Guo and Santschi, 2007), is unlikely to cause such noticeable differences as the recovery for Ca, Mg and SO_4 was approximately 107%, 108% and 98%, respectively. Also the median recovery was satisfactory for most of the elements (see section 4.2). A more likely explanation is that other metal binding material (e.g. clay colloids) or elements not used in the simulations with Visual MINTEQ could influence the element speciation if these concentrations are high (Unsworth et al., 2006; Rönnback et al., 2008; Paper II).

In the investigated rivers in SW Finland, but also in the Vörå River, erosion of clay was clearly seen as a greyish colour (Photo 1) and thus also eroded suspended solids (probably to a large extent phyllosilicates) most likely contribute to high metal concentrations in the rivers and is partly even masking the effects of AS soils in these rivers. Clay colloids and small size particles (e.g. clay material) have a high specific surface area, strong adsorption capacity and very low settling velocity, and can thus carry and transport various metals a long way from its source (Parker and Rae, 1998). This would explain why Cs, generally present as free cations in freshwater (Eyrolle and Charmasson, 2001) and in most rivers predicted to occur as free cations (Table 7), is partly also found as particles (Fig. 8) in the rivers. Also the discrepancy between predicted and observed results in the rivers in SW Finland (mostly in the Paimionjoki River) and the unpredicted lack of associations for Fe indicated the influence of clay minerals. Other arguments were SEM images and EDX analyses of suspended colloidal size clay matter (i.e. flakes) on the 0.45 µm filter surfaces (Fig. 9) showing that these flakes mainly consist of O, Si and Al, and previous gravimetric analysis of suspended matter from nearby rivers also indicating a phyllosilicate composition (i.e. the Aurajoki River; Nystrand et al., unpublished). Moreover, during the time of sampling the turbidity in the rivers in SW Finland was between 17 (in the Sirppujoki River) and 140 FNU (in the Paimionjoki River; HERTTA database, Finnish Environmental Centre), indicating an increasing content of suspended matters from north to south. Also
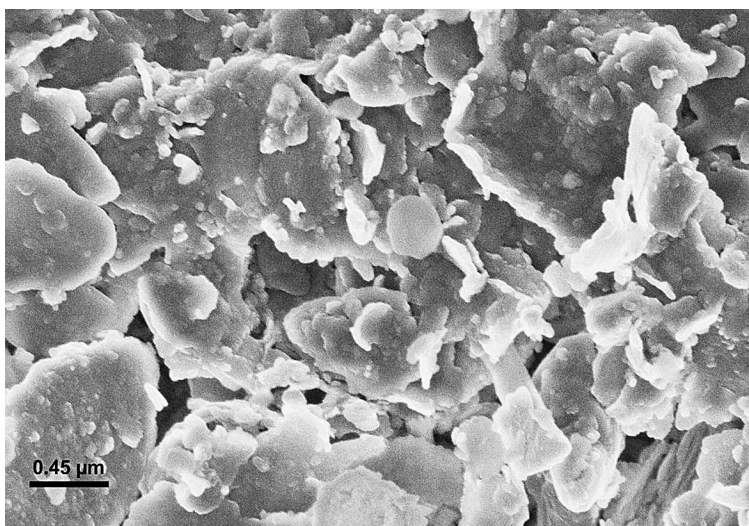
Fig. 9. SEM image of suspended matter seen as flakes (several also <0.45 µm) on a 0.45 µm filter surface used on water from the Paimionjoki River (P2). Analysis with EDX showed that the flakes consist mainly of O, Si and Al and also substantially of Fe, K, Na and Mg, i.e. they are most likely phyllosilicates that were removed from the water column by the filter.

the proportion of clay soils in the catchments is relatively large (15-43%; Table 1) and the catchment with the highest proportion of clays (i.e. the Paimionjoki River) has the highest concentration of colloidal/particulate matter (Fig. 8). Moreover, elements that are normally highly soluble in stream water and which are at the same time major elements in minerals (Ca, K, Mg, Mn and Si) also occurred to a considerable extent in a solid phase (Fig. 8), especially in the Paimionjoki River. For instance Si occurred substantially as colloids (up to 5.9 mg/L) and particles (up to 8.1 mg/L) and correlated significantly (Spearman r_s=0.83) with the abundantly occurring Al (0.8-6 mg/L) that is the second most abundant component of clay minerals after Si. Moreover, in colloidal and/or particulate phases Si and Al also correlated significantly (r_s=0.72-0.92) with Fe, K and Mg, all constitutes of clay minerals (illite is presumably the most common clay mineral in the studied area; Uusinoka, 1975). Consequently, the high total metal concentrations in the rivers in SW Finland and in the Vörå River are not entirely explained by the influence of AS soils only, but also by erosion of metal bearing colloidal and/or particulate phyllosilicates from clay lands. Thus, relying on only semi-dissolved concentrations obtained in routine analysis will frequently lead to an overestimation of the water toxicity as the eroded colloidally-bound metals of clay lands are generally in a relatively non-

toxic form compared to, for example, the discharge of dissolved toxic metals from AS soils.

5.3 Estuary of the Vörå River

In this chapter, the general results of paper V and VI are presented, as well as original unpublished results of element species not discussed in the papers.

Estuaries are gigantic mixing vessels where water with very different characteristics mix (i.e. fresh water and sea water mix) and where large physical-chemical gradients are created, larger than anywhere else in the fresh water or in the sea water realm (Benoit et al., 1994; SCOPE 42, 1991). During mixing chemical reactions may or may not occur, i.e. certain components mix conservatively from fresh to salt water, while others undergo chemical scavenging, coagulation, flocculation, sedimentation, desorption, or are consumed by biological activity (SCOPE 35, 1988; Santos-Echeandía et al., 2012). In particular, the salinity and pH increase plays an essential role in controlling the flocculation of the dissolved load and the composition of the sediment (Dorval et al., 2005; Olías et al., 2006; Hannigan et al., 2010; Delgado et al., in press). However, an acidic fluvial water discharge in an estuarine system confers special hydrochemical characteristics to the mixed water by the existence of two processes: the acidic neutralization and then salt-induced mixing (typical of marine estuaries; Carro et al., 2011; Delgado et al., in press). The acidic neutralisation with sea water involves generally the flocculation of colloids and particles formed by organic compounds and Fe-, Mn- and/or Al-oxides (Olías et al., 2006; Delgado et al., in press). Consequently, many biogeochemical characteristics created naturally or anthropogenically in rivers upstream develop their full environmental impact in estuaries. Vice versa, the study of estuaries teaches much about the geochemistry of specific river basins, their water discharge, their sediment load and their nutrient concentrations as well as about the physical structure of mixing waters (SCOPE 42, 1991).

In the estuary of the Vörå River the electric conductivity and pH successively increased in the transect extending from the river mouth to the outer estuary (Table 8). This was expected as the river water was successively mixed with the alkaline brackish Baltic Sea water (i.e. higher salinity). The pH gradient was more or less the same on both sampling occasions, but the electric conductivity values were in spring 2010 much lower compared to those from autumn 2009 (Table 8). This was due to higher flow rates in spring 2010, causing dilution of the saline sea water. Several element concentrations (Al, Cd, Co, Cu, Mn and Ni; Fig. 10) were exceptional high in the inner estuary (i.e. near the river mouth) and in spring 2010 these concentrations were remarkably high even far out in the estuary. Consequently, the proportion of acidic river water in the

estuary was in autumn lower than in spring. This clearly demonstrates that the dispersion of metals far out in the estuary is not only dependent on high concentrations in the river but on hydrological conditions, i.e. with high flows the plume of metal rich water will spread further out in the estuary. Thus, potential hydrological changes caused by climate change causing higher flow in autumn-winter and less extreme spring floods have significant effects on the extent of the dispersion at different seasons. More importantly, 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. Worst events occur in situations such as that in the late autumn of 2006 when a severely dry summer (maximising oxidation of sulfides) coincide with a subsequent severe wet spell (Österholm and Åström, 2008; Saarinen et al., 2010) causing widespread fish kills in rivers and estuaries in Midwestern and Northwestern Finland.

Based on the concentrations of semi-dissolved concentrations of organic carbon, sulfate and the investigated elements in the estuary, two main groups of elements were identified. Concentrations of Ca, Cl, K, Mg, Na and SO_4 (Group 1; Fig. 10a), i.e. conservative elements typically strongly enriched in freshwater AS soil environments, increased with an increasing proportion of seawater towards the outer estuary as concentrations of these element are naturally higher in the sea. As expected for OC and the rest of the metals (except Ba and U), occurring in higher concentrations in the river (Group 2; Fig. 10b), concentrations decreased towards the outer estuary due to dilution, flocculation and/or scavenging processes. For several of these elements (Al, Cd, Co, Cu, Fe, Mn and Ni) there was an indication of non-conservative behaviour, as these elements in a dissolved and colloidal phase decreased at a rate much faster (i.e. precipitation) than dilution with brackish sea-water alone would produce (Fig. 11). This phenomenon was observed for Al and Fe at both sampling occasions and for Cd, Co, Cu, Mn and Ni also in spring 2010 (Fig. 11). This shows that when the load of these elements transported by the acidic river is dispersed in the estuary, there are processes acting to rapidly relocate the metal from the dissolved phase to the particulate phase; i.e. scavenging and/or flocculation processes.

Organic matters, but also solid phases of Al, Fe and Mn, are known of adsorbing other elements, and thus it is likely that those will adsorb metals and different chemicals in the estuary, and settle to the bottom. Consequently, this will accumulate toxic metals onto the fine grained bottom sediments of the estuary, and act as an important reservoir for contaminant by reducing the potential toxicity to some aquatic organisms (i.e. for non-bottom-feeding organisms). Several elements (Al, Cu, Fe and Ni) were predicted to be associated to OC in the inner estuary and, furthermore, these associations

Table 8. pH, electric conductivity (EC) and semi-dissolved (<0.45 μm) concentrations for organic carbon, sulfate and metals in the Vörå River (W1) and in the estuary of the Vörå River (W2-W7).

Sample	date	pH	EC μS/cm	T	OC mg/L	Al mg/L	Na mg/L	Ni μg/L	As μg/L	Ba μg/L	Ca mg/L	Cd μg/L	Cl mg/L	Co μg/L	Cu μg/L	F mg/L
W1	1.12.2009	4.4	526	6.9	13.00	8.400	18	82.0	0.135	15.58	27.60	0.546	23	35.80	9.60	0.87
W2	1.12.2009	5.0	1959	3.3	5.67	1.040	503	46.2	0.400	16.00	42.20	0.294	900	20.40	3.97	0.50
W3	1.12.2009	5.6	3209	3.6	5.23	0.134	566	25.4	0.500	12.70	35.70	0.182	1200	11.40	2.04	0.17
W4	1.12.2009	6.3	4400	3.4	5.66	0.075	920	25.4	0.500	18.26	56.40	0.162	1400	11.02	2.38	0.31
W5	1.12.2009	6.5	5290	3.0	5.87	0.040	929	15.1	0.695	14.90	52.20	0.098	1600	6.21	1.97	0.25
W6	1.12.2009	6.8	5550	2.8	4.94	0.050	980	10.5	0.520	14.60	52.90	0.066	1600	3.71	1.99	0.14
W7	1.12.2009	7.0	6210	2.5	5.21	0.033	999	3.9	1.167	13.48	50.82	0.055	1700	0.88	1.04	0.17
W1	5.5.2010	4.6	422	4.2	9.77	6.433	15	65.9	0.252	14.08	22.47	0.531	17	28.55	9.92	0.76
W2	5.5.2010	5.0	730	6.6	8.18	5.325	44	58.7	0.386	14.63	22.70	0.437	72	26.50	8.43	0.68
W3	5.5.2010	5.8	1450	6.5	6.71	2.257	126	39.9	0.700	14.47	21.58	0.365	220	18.90	5.26	0.40
W4	5.5.2010	6.3	1623	6.8	6.83	2.327	125	40.5	0.667	18.53	21.53	0.324	210	18.95	5.42	0.41
W5	5.5.2010	6.2	1643	7.6	6.65	0.237	227	25.2	0.917	14.33	22.98	0.220	410	12.68	3.17	0.29
W6	5.5.2010	7.0	2452	7.7	5.98	0.119	366	17.6	0.917	13.73	26.53	0.132	680	7.37	2.07	0.21
W7	5.5.2010	7.4	4294	5.0	5.55	0.129	685	3.6	1.167	12.12	36.18	0.070	1200	1.12	1.31	0.16

Sample	date	Fe μg/L	La μg/L	Mg mg/L	Mn μg/L	Na mg/L	Ni μg/L	Pb μg/L	PO₄ μg/L	SO₄ mg/L	Si mg/L	Sr μg/L	U μg/L
W1	1.12.2009	568	43.80	18.5	1578	18	82.0	0.226	31.14	220	21.40	165	0.55
W2	1.12.2009	69	20.80	70.4	954	503	46.2	0.064	6.86	240	13.50	464	0.160
W3	1.12.2009	29	8.05	68.7	544	566	25.4	0.017	4.84	240	7.53	440	0.085
W4	1.12.2009	19	5.56	118.8	546	920	25.4	0.041	9.81	250	7.62	744	0.159
W5	1.12.2009	10	2.90	114.0	322	929	15.1	0.053	6.86	260	5.02	708	0.199
W6	1.12.2009	9	1.40	119.0	207	980	10.5	0.032	7.39	250	3.53	736	0.256
W7	1.12.2009	14	0.23	117.3	45	999	3.9	0.021	9.41	260	1.50	743	0.317
W1	5.5.2010	369	38.72	14.0	1215	15	65.9	0.254	21.27	150	18.62	138	0.460
W2	5.5.2010	542	34.38	16.4	1155	44	58.7	0.231	21.43	150	17.35	151	0.381
W3	5.5.2010	252	19.62	23.5	891	126	39.9	0.168	14.84	120	12.48	183	0.219
W4	5.5.2010	207	20.27	23.5	885	125	40.5	0.146	13.69	130	12.45	181	0.219
W5	5.5.2010	58	8.23	33.4	692	227	25.2	0.069	10.32	120	9.14	238	0.092
W6	5.5.2010	35	2.61	47.6	485	366	17.6	0.055	13.20	140	6.41	323	0.093
W7	5.5.2010	83	0.45	80.8	77	685	3.6	0.080	17.60	180	2.16	517	0.234
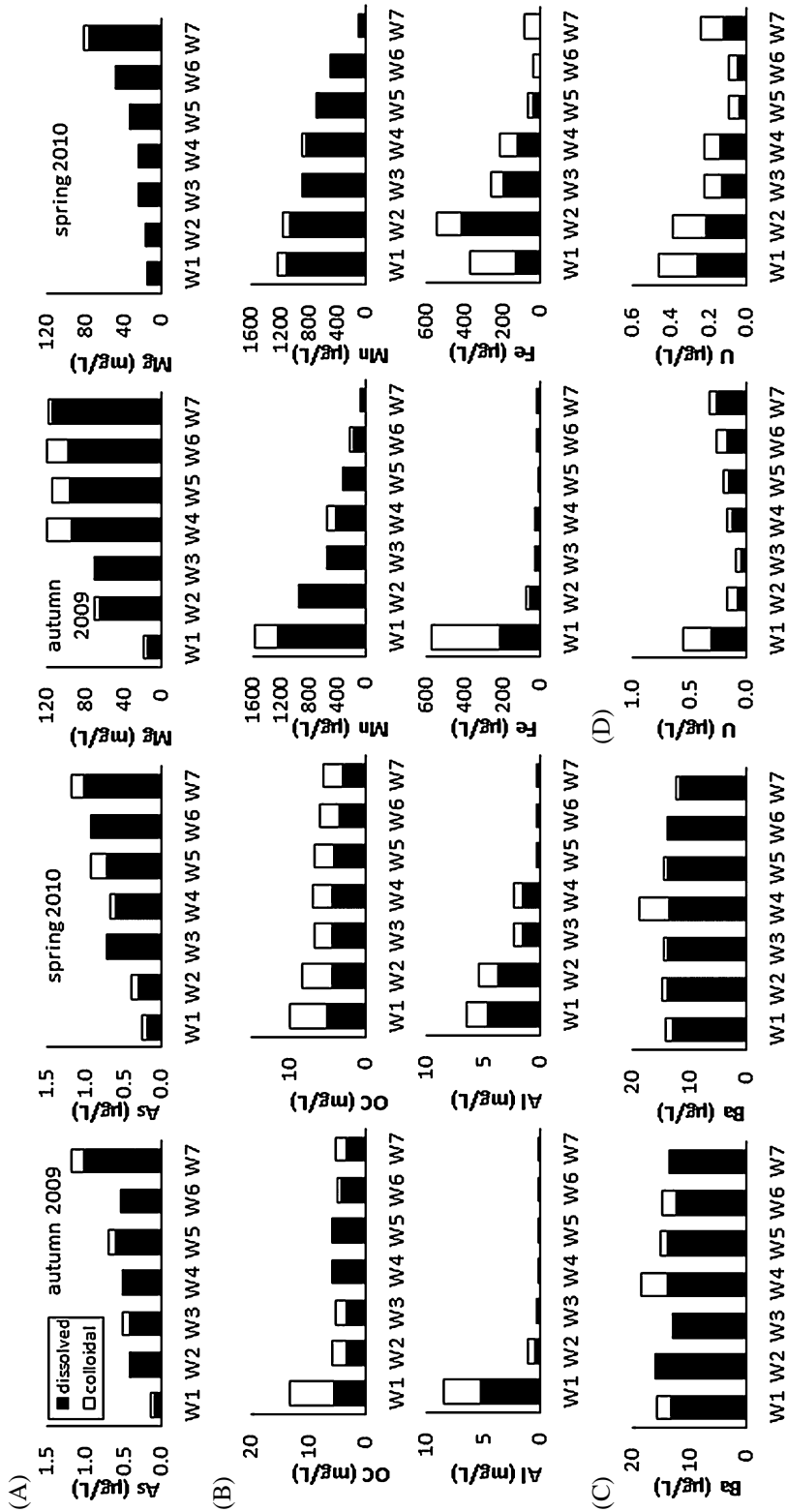
Fig. 10. Dissolved- (<1 kDa) and colloidal (1 kDa–0.45 μm) fractions in the Vörå River (W1) and in the estuary of the Vörå River (W2-W7).

(A) Elements with an increasing concentration from the Vörå River to the outer estuary: As, Ca, Cl, K, Mg, Na, SO₄ and Sr
(B) Elements with a decreasing concentration towards the sea: OC, Al, Cd, Co, Cu, Fe, Mn, Ni and Si
(C) Elements with relatively constant concentrations at all sampling points: Ba
(D) Elements with variable concentrations: U

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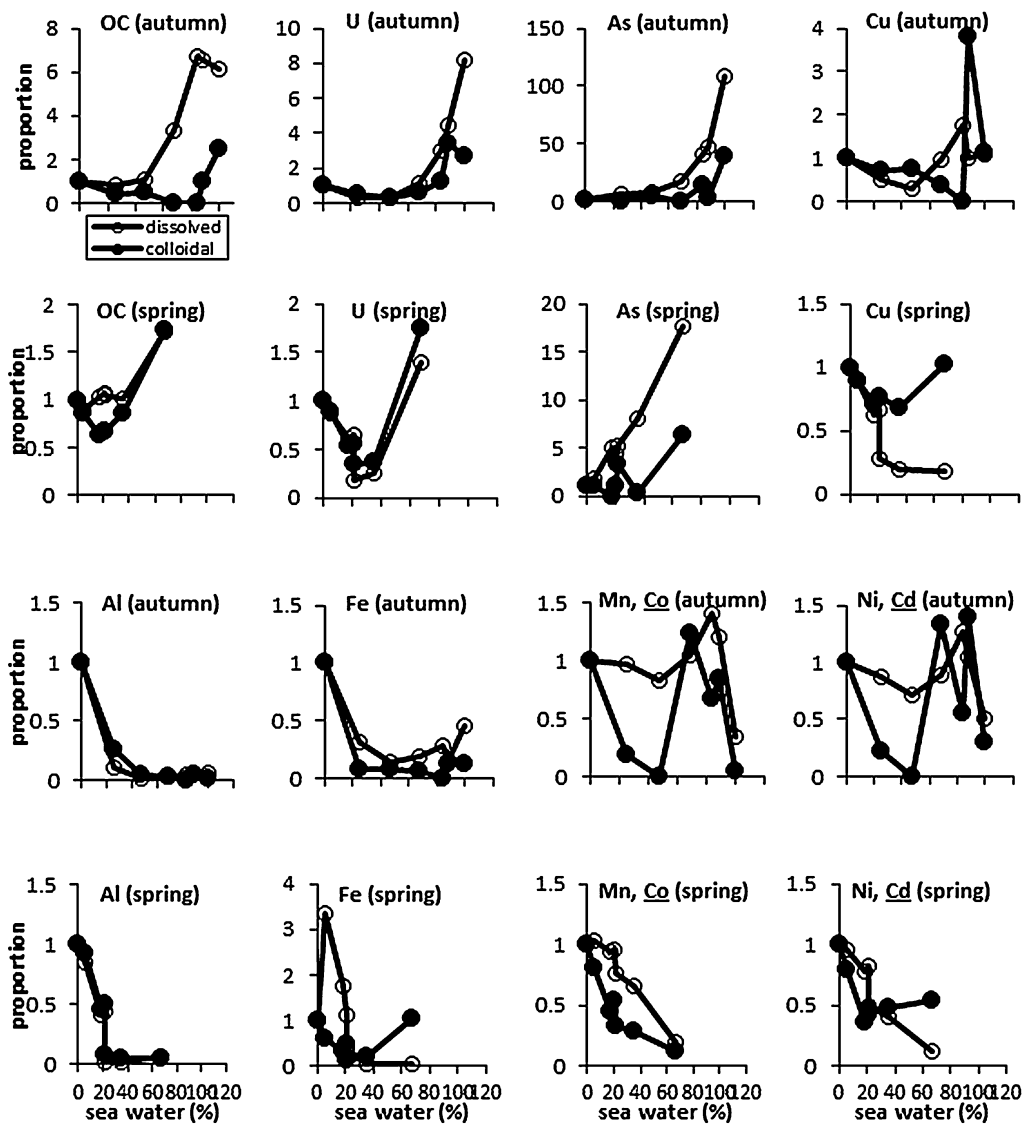
Fig. 11. Proportion of river water (based on electrical conductivity) and metal concentration (dissolved and colloidal) down the estuary of the Vörå River as compared to the lower part of the Vörå River. As the results for some elements were very similar, only one representative element is shown for these element groups (elements not shown are underline). Proportion = based on the ratios of dissolved, respectively colloidal, concentrations and the proportion of river water.

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increased with increasing pH to the outer estuary (Fig. 12). This indicates that the first elements to precipitate in the inner estuary are most likely Al, Cu, Fe and Ni together with OC. However, there were some differences between the modelled and measured data for OC, as OC in the inner estuary behaved relatively conservatively and the dissolved concentration in the outer estuary did increase (Fig. 11). This is probably due to another source of OC in the estuary, possibly the abundantly occurring phytoplanktons contributing to higher amounts of OC in the outer estuary. In contrast, Mn (as Mn^{2+}) was relatively persistent in solution and thus travelled a considerable distance through the estuary before oxidising and transforming to a particulate form and finally precipitating. This is in accordance with the predicted results, showing an association of Mn with Ba, Cd, Co, Cu and Ni at the most outer sites (W6 and W7; Fig. 12). These elements will, thus, most likely co-precipitate in the form of Mn-oxyhydroxides in the outer estuary. These findings are also in line with those of Nordmyr et al. (2008) studying deposition patterns for several elements in the estuary of the Vörå river; Al, Cu and U were found to be enriched in sediment traps and bottom sediments closest to the river mouth, and Cd, Co, Mn and Ni further out in the estuary. As mentioned earlier, sulfate complexes were important for several elements in the Vörå River. In the estuary, however, the sulfate complexes were not as important (Fig. 12), because SO_4-complexes are only lightly bound complexes and, thus, will desorb easily with even small hydro chemical variations (i.e. increase of pH and salinity in to the sea).

In contrast to most of the element concentrations, the concentrations for U varied incoherently in a peculiar manner as it first decreased in the inner estuary and later increased in the outer estuary (Fig. 10). Due to the influence of AS soils, the concentration for U was highest in the Vörå River. The lower concentrations in the inner estuary most likely depend on a relatively 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 salinity <1 by Fe- and/or organic-rich colloids that aggregate and sink 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 and/or alkalinity, 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).

Arsenic, Fe and PO_4 were not elevated in the estuary of the Vörå River (Table 8). This is in line with the close to normal concentrations of these elements in the source river (i.e. the Vörå River). As in the rivers, also in the estuary a close association between Fe and As could be detected in the more acidic waters (i.e. inner estuary in spring 2010; Fig. 12). However, recovery from acidification in
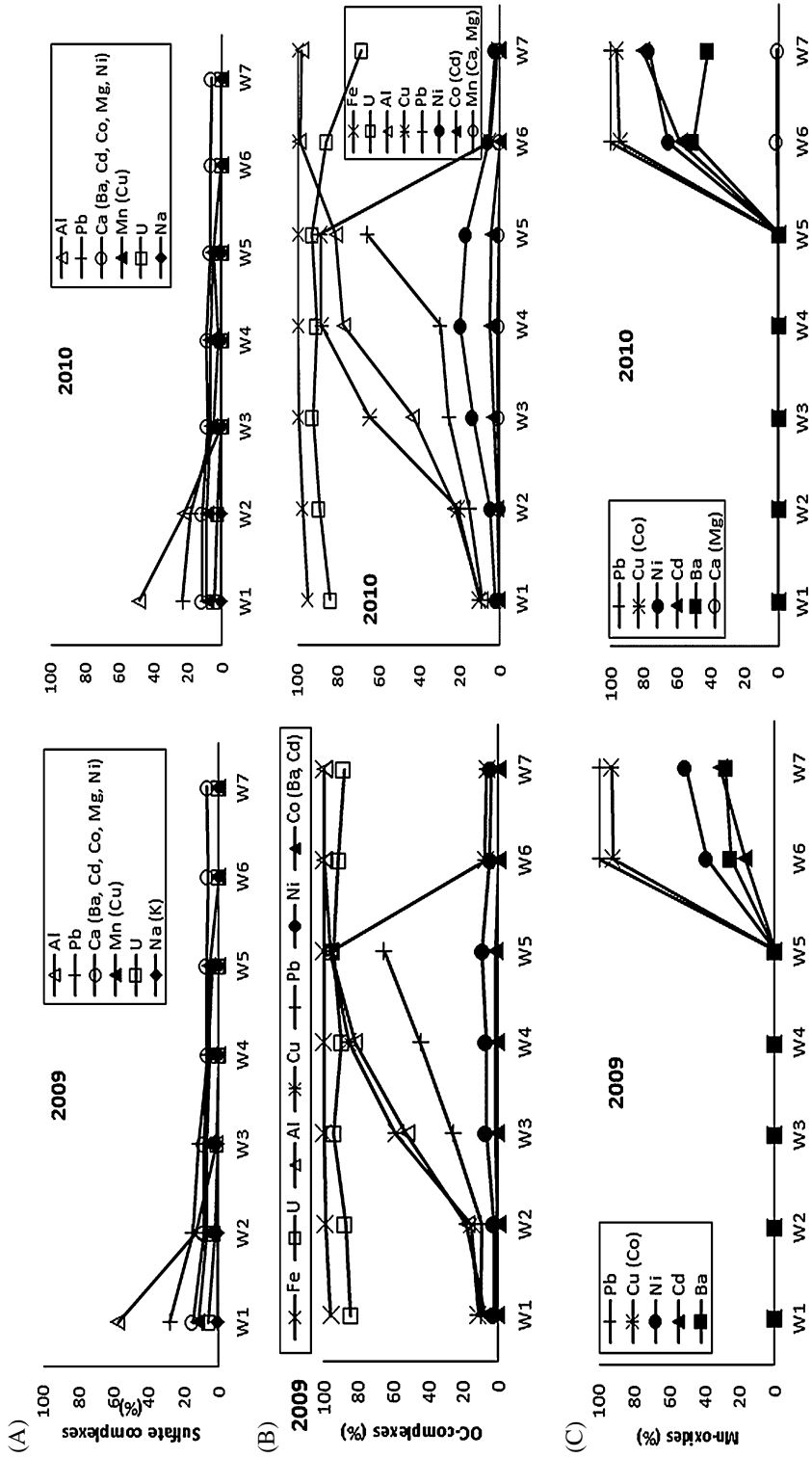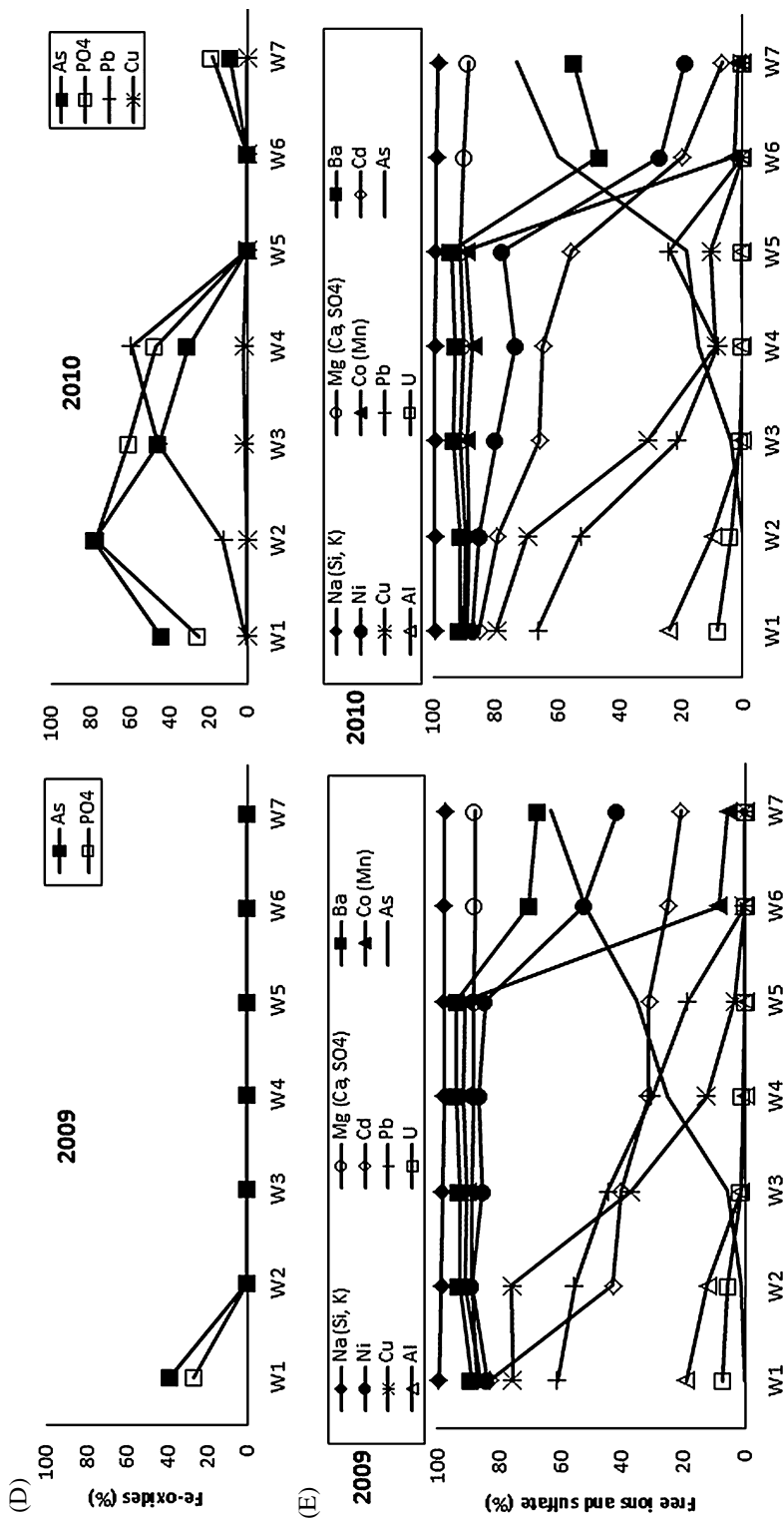
Fig. 12. Element complexes with sulfate (A), organic carbon (B), Mn (C) and Fe (D), and sulfate and free ions (E) modelled with Visual MINTEQ in the Vörå River (W1), and in the estuary of the Vörå River (W2-W7). As the predicted results for some elements were very similar, only one representative element is shown for these element groups (elements not shown are in brackets).

waters with increasing pH may enhance the mobility of As, since a desorption of As from Fe-oxides is favoured as pH values become alkaline (from pH 6 to 9; Dzombak and Morel, 1999; Wang and Mulligan, 2006; Wällstedt et al., 2010). This is due to the change in Fe-oxide net surface charge from positive to negative as pH increase above the point of zero charge (pH at which net surface charge is equal to zero; Stumm and Morgan, 1996). That would explain the increase of dissolved As in the outer estuary of the Vörå River (Fig. 10 and 11), and the lack of predicted associations between As and Fe (Fig. 12); i.e. the increasing pH in the outer estuary will most likely lead to a desorption of As from Fe. Moreover, also PO_4 is associated with Fe-oxides in the estuary, and follows the same speciation behaviour as As, indicating some similar geochemical behaviour of As and PO_4 in the estuarine of the Vörå River. This is in line with other studies done on geochemical behaviour of As, PO_4 and Fe-oxide (Manning and Goldberg, 1996; Hongshao and Stanforth, 2001), where it has been concluded that both also compete for sorption sites.

5.4 Bioavailability of metals

This chapter is mainly based on the results from paper II, IV and V, but also some new information is included.

In recent decades, environmental pollution problems have been a growing interest in the scientific community due to the potentially harmful substances emitted from anthropogenic activity, which can pose a serious hazard to the environment and to the human health (Guillén et al., in press). Aluminium, Mn and heavy metals (such as As, Cd, Co, Cu, Fe, Ni and Pb) are major environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons (Nagajyoti et al., 2010; Delgado et al., 2011). Some of these heavy metals are bioaccumulative, and they neither break down in the environment nor easily metabolizes. Such metals accumulate in ecological food chain through uptake at primary producer level and then through consumption at consumer levels (Nagajyoti et al., 2010). Consequently, as several of these elements occurred in high dissolved (most toxic) concentrations in the investigated waters; a more thoroughly discussion for these elements is needed. Also pH as the most important chemical parameter (Gundersen and Steinnes, 2003) influencing metal sorption/desorption is discussed.

pH in several of the investigated waters was ≤5.3 (Table 3, 5 and 8), which is much lower than the suggested pH tolerance for most aquatic life. While the biota in Finnish water courses is somewhat adapted to lower pH conditions, a pH under 5.5 starts generally to be critical for several organisms (Palko and Myllymaa 1987; Palko et al., 1988; Vuori, 2009), and for some (e.g. roaches

and breams) already a pH of 6 can be lethal (Tuunainen et al., 1991). However, a low pH alone does not necessarily lead to fish kills, indicating that pH acts mainly indirectly through shifting especially Al, but also other elements, towards more reactive toxic species (Kroglund et al., 2008; Nilsen et al., 2010).

Aluminium is one of the most environmentally significant elements associated with AS soils (Photo 4; Poléo et al., 1997; Bjerknes et al., 2003; Fältmarsch et al., 2008; Johnston et al., 2010) and according to Earle and Callaghan (1998), already a "dissolved" Al concentration of around 0.5 mg/L will generally eliminate all fish and many macroinvertebrates in acidic waters. Notably is that most studies (also Early and Callaghan, 1998) have only used a 0.45 µm filter to subdivide metals in to "dissolved" and "particulate" fractions, and so on the "dissolved" (i.e. semi-dissolved) Al concentration of 0.5 mg/L also includes the colloidal fraction. In the investigated streams and in the Vörå River semi-dissolved Al concentrations up to 34 mg/L and 4.3 mg/L, respectively, were observed and substantial amounts occurred in a dissolved fraction (>54%; Table 3 and 4). In the investigated rivers in SW Finland the semi-dissolved concentrations were as well over 0.5 mg/L, and in the streams of the Sirppujoki - and Mynäjoki Rivers even up to 28 mg/L (Table 5). Also in the inner estuary of the Vörå River semi-dissolved concentrations over 0.5 mg/L were measured (Table 8), and especially in spring 2010 due to higher flow rates (see in 5.3). Consequently, the dissolved toxic concentrations of Al were in most investigated sites far over the acceptable limits and are, in combination with the low pH, responsible for the lack of fish and other organisms especially in the Vörå River, in its inner estuary and in the nearby streams. This is most likely also the reason for occasionally fish kills in the Sirppujoki - and Laajoki Rivers and several of the acidic streams in SW Finland. Moreover, the modelling program predicted a high amount of Al to occur as dissolved sulfate complexes in the more acidic waters (i.e. in the Vörå River and in the nearby streams, and also in several of the investigated streams in SW Finland; Fig. 4 and 6), which is toxic to most aquatic organisms (Braungardt et al., 2003). The predicted occurrence of soluble Al-F complexes (8-50%; Table 4) in the brooks and the upper and middle sites of the Vörå River can also partly occur in a toxic form (Ware, 2008). In contrast, the predicted Al-OC complexes (Fig. 4) are probably less toxic/bioavailable, but still tend to keep Al in solution (Gensemer and Playe, 1999). Notable, though, is that Al competes for OC binding sites with other metals (Cu, Pb and Cd; Tipping et al., 2002; Pinheiro et al., 2000), and can, thus, increase the bioavailability of other potentially toxic metals, while reducing its own toxicity by forming complexes with OC. In the Paimionjoki River concentrations of total Al was also highly elevated (up to 6 mg/L), but due to a higher pH (7-7.3) Al was mostly found in a less toxic colloidal/particulate form (Fig. 8): i.e. mostly bound to organic matters (Table 7). These results from the Paimionjoki River show also that relying on only

semi-dissolved concentrations obtained in routine monitoring can occasionally lead to major overestimation of the water toxicity in this environment.

Precipitation of hydrous Fe oxides also releases acids and reduces the dissolved oxygen concentrations, which in combination with the formation of flocs can lead to fish kills (Cook, 2000). This precipitation mechanism was clearly seen in some of the streams as a rusty colour (Photo 4), but as the Fe concentrations were not notably higher in the investigated streams and rivers compared to other Finnish stream waters (Lahermo et al., 1996), Fe most likely only plays a minor role in contributing to toxicity in these waters. Also As is toxic to both plants and animals and generally inorganic As species, e.g. As(III) and As(V), are more toxic than organic forms (Bissen and Frimmel, 2003; Sharma and Sohn, 2009). However, in the investigated waters As was close to background values (Table 3, 5 and 8) and moreover considerably associated with Fe (i.e. reducing the toxicity of As; Sharma and Sohn, 2009), and do therefore not pose overall risks in these investigated waters.

Photo 4. Flocculation of Al with OC (seen as grey flakes; left) and iron oxide precipitation on grass (right) were seen in several of the low-order streams in SW and W Finland (Photos by Miriam Nystrand).

The potentially toxic elements Cd, Cu, Mn and Ni occurred in highly toxic concentrations in most of the streams and in the more acidic Vörå River (2008/105/EU; WHO, 2008). Also in the inner estuary of the Vörå River these elements were still well over the acceptable limits. However, the EU and WHO standards are based on semi-dissolved fractions operationally defined by 0.45 µm filtered water samples (Meland et al., 2010; Kimball et al., 2010), that also include generally less toxic hydrolysed products, complexes, and colloids.

Consequently, if taking into account the semi-dissolved (dissolved + colloidal) fraction, Ni in the Sirppujoki River and Cd in the Sirppujoki - and Laajoki Rivers also exceeded these regulations.

6. Conclusions

Ultrafiltration has frequently and successfully been used to study element species in natural waters, and the use of ultrafiltration in this study was also successful. Some disadvantages are, however, associated with the ultrafiltration procedure. It is a rather expensive and time-consuming procedure and it is notable that potential artefacts might be observed during the ultrafiltration procedure. In the future, cheaper in situ techniques, e.g. utilisation of dialysis sampling may become more advantageous.

Most importantly, it was shown that the very large amounts of metals known to be released from AS soils (including Al, Ca, Cd, Co, Cu, Mg, Mn, Na, Ni, Si, U and the lanthanoids) occur and, moreover, can prevail in toxic forms throughout acidic river systems; as free ions and/or sulfate-complexes. This has obviously serious effects on the biota and especially the high toxic concentration of dissolved Al (also partly complexed with sulfate) is expected to have disastrous effects on fish and other organisms. Only in the less acidic waters in the forested upstream areas, metals (including Al, Cu, Ni, U and the lanthanoids) occurred in significantly fewer bioavailable forms due to complexation with the more abundantly occurring colloidal organic carbon in these waters. Oxides, in contrast, were in the rivers predicted to be rather unimportant as complexing agents: only Fe oxides were predicted to be associated with As, Pb and PO_4, indicating a considerable influence of Fe oxides on the mobilization/immobilization processes of As, Pb and PO_4 in soil and water.

In all studied rivers the total concentrations of several elements are highly elevated, but occurred generally to a large extent in solid colloidal and particulate form (except in the Vörå River) due to erosion of clay minerals. The impact of erosion, as indicated by the proportion of colloidal and particulate metals, increases successively from north (the Vörå River) to south (the Paimionjoki River). Acid sulfate soils within the northernmost areas were found to increase the concentrations of dissolved toxic metals. This was evident in the Vörå River, the Sirppujoki River and to some extent in the Laajoki - and Mynäjoki Rivers, but in these latter rivers the AS soil impact is largely masked by erosion of colloidal and particulate metal-bearing phyllosilicates and/or humic acids from forests and peatlands. Total concentrations of several elements are also very high in the Paimionjoki River, but the element patterns are not typical for AS soils. Consequently, rivers draining clay plains sensitive to erosion, such as those in SW Finland, have high "background" metal

concentrations due to erosion of relatively non-toxic colloidal/particulate phyllosilicates into rivers from clay lands (also from non-AS soils), while elevated metal concentrations due to AS soils occur in a far more toxic dissolved form. Thus, relying on semi-dissolved (<0.45 μm) concentrations obtained in routine monitoring, or geochemical modelling based on such data, can lead to major overestimation of the water toxicity in this environment.

The potentially toxic elements that are of concern in AS soil areas will ultimately be precipitated in the recipient estuary or sea, where the acidic metal-rich river water will gradually be diluted/neutralised with brackish seawater. In the recipient estuary of the Vörå River (that belongs the Gulf of Bothnia) metals occurred in high concentrations and mainly in a dissolved (generally most toxic) form. Also notable is that the dispersion of metals far out in the estuary is not only dependent on high concentrations in the river but on hydrological conditions, i.e. with high flows the surficial plume of metal-rich water will spread further 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 flow peaks that reach further out in the estuary. For several of the elements (Al, Cd, Co, Cu, Fe, Mn, Ni and the lanthanoids) there was also an indication of non-conservative behaviour, especially in spring 2010. This is not explained by a removal of elements by Fe oxides, as Fe was predicted to be rather an unimportant scavenging element in the estuary, but by an association of several of these elements to OC, indicating that the first elements to precipitate in the estuary are most likely Al, Cu, Fe, Ni and the lanthanoids together with OC. Manganese, in contrast, is relatively persistent in solution and, thus, precipitates farther down the estuary as Mn oxides with Ba, Cd, Co, Cu, Ni and Pb. Consequently, this will accumulate toxic metals onto the fine grained bottom sediments of the estuary, and act as an important reservoir for contaminants. Changes in sediment chemistry, though, can result in remobilisation. Subsequently, exposure to a different chemical environment (e.g. the on-going isostatic land uplift in the region combined with the episodic declines in pH) could again result in desorption and transformation of contaminants into more bioavailable (dissolved) or toxic chemical forms.

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