



Metal speciation in rivers affected by enhanced soil erosion and acidity

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ABSTRACT

Dissolved (<1 kDa), colloidal (1 kDa–0.45 μm) and particulate (>0.45 μm) size fractions of 30 elements were determined for four rivers (Sirppujoki, Laajoki, Mynäjoki and Paimionjoki), including 12 low-order inflow streams, largely affected by soil erosion and acidity in SW Finland. In addition, geochemical modelling was used to predict the formation of free ions and complexes in these rivers. Total metal concentrations were relatively high but most of the elements occurred mainly in a colloidal or particulate form and even elements expected to be very soluble occurred to a large extent in colloidal form. According to geochemical modelling these patterns could be explained by in-stream metal complexation/adsorption only to a limited extent. 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 acid sulphate (AS) soils, known to exist in the catchment, could be clearly distinguished in Sirppujoki river as it had very high concentrations of dissolved metals, while in the two nearby rivers (Laajoki and Mynäjoki) the influence of AS soils was largely masked by eroded phyllosilicates. In Paimionjoki river the colloidal and particulate fractions dominated very strongly, indicating that total metal concentrations are almost solely controlled by erosion of phyllosilicates. Consequently, rivers draining clay plains sensitive to erosion, like those in SW Finland, have generally high “background” metal concentrations due to erosion of relatively non-toxic colloidal/particulate phyllosilicates. Thus, relying on only semi-dissolved (<0.45 μm) concentrations obtained in routine monitoring and/or speciation modelling can lead to a great overestimation of the water toxicity in this environment.

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1. Introduction

Distribution, mobility and toxicity of metals in natural waters are strongly related to their aqueous speciation. Thus, the bioavailability of metals and their potential for environmental pollution depends not simply on total concentrations but on their chemical form. Consequently, knowledge of aqueous metal speciation is essential in investigating potential metal toxicity and mobility (Ure and Davidson, 2002; Gaillardet et al., 2003; Guéguen et al., 2004; Forsberg et al., 2006).

In conventional water analyses metals have commonly been subdivided into two fractions, “dissolved” and “particulate” fractions, according to an operationally defined limit (usually 0.45 μm ; Guéguen and Dominik, 2003). In reality the “dissolved” fraction (in this study referred to as semi-dissolved) also includes a significant amount of colloids 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. Colloids play a significant role due to their

dual properties, behaving in some respects as soluble matter and thus having a high toxic effect on the living organism and in others as less soluble and, therefore, not being directly viewed as available for microorganisms (Campbell, 1995; Koukal et al., 2003). Moreover, colloids are efficient in binding trace metals and can thus decrease toxicity of many chemicals for some aquatic organisms by decreasing the free concentration of the molecules (Kördel et al., 1997; Weltens et al., 2000), but at the same time they can increase the bioavailability for 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. However, metals associated with larger particles (>0.7 μm ; Filella and Buffle, 1993; Vignati et al., 2006) are usually progressively concentrated in the sediments and are generally not available for the biota, but if circumstances change (usually low pH and/or low O_2 content) such metals can again dissolve in the water column (Sigg et al., 2000; Eggleton and Thomas, 2004; Butler et al., 2008).

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

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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).

In Finland, coastal acid sulphate (AS) soils constitute a massive supplier of metals and acidic compounds to the aquatic environment. 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; Boman et al., 2010). 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 sulphides 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; Åström and Åström, 1997; Fältmarsch et al., 2008).

Although there is now quite a lot of information on overall metal concentrations in rivers in Finland (e.g. Lahermo et al., 1996), including the rivers and streams severely affected by AS soils (e.g. Roos and Åström, 2005a), little is known about the actual chemical form and size distribution of these metals. Such information is of importance when estimating ecotoxicological effects in metal-enriched waters. The overall aim of this study was to give an overview of the behaviour, i.e. chemical form and size distribution, and origin of major and trace elements in 4 selected boreal rivers that are ecologically important and carry elevated concentrations of several metals.

2. Description of the study area

The study area with the selected rivers (i.e. Sirppujoki, Laajoki, Mynäjoki and Paimionjoki) is located in SW Finland (Fig. 1) and the bedrock of the area consists mainly of 1.83 Ga microcline

Table 1

Drainage area and proportion of cultivated land, forest and peat in the catchments of the monitored rivers. 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

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 ($1\text{--}7\text{ L s}^{-1}\text{ km}^{-2}$; HERTTA database, Finnish Environmental Centre) but during snow melt and heavy rains in spring and autumn, the water flow increases up to $20\text{ L s}^{-1}\text{ km}^{-2}$ (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 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 sulphides and development of acid sulphate soils. These soils are in SW Finland mainly located at 0–45 m above the current sea-level due to post-glacial isostatic land uplift (5 mm/a ; Palko, 1994) and are known to be relatively common in the catchment of Sirppujoki (Triipponen, 1997), but there are also indications of AS soils in Laajoki and Mynäjoki (Lemmettyinen and Virtanen, 1980; Nyberg et al., 2011).

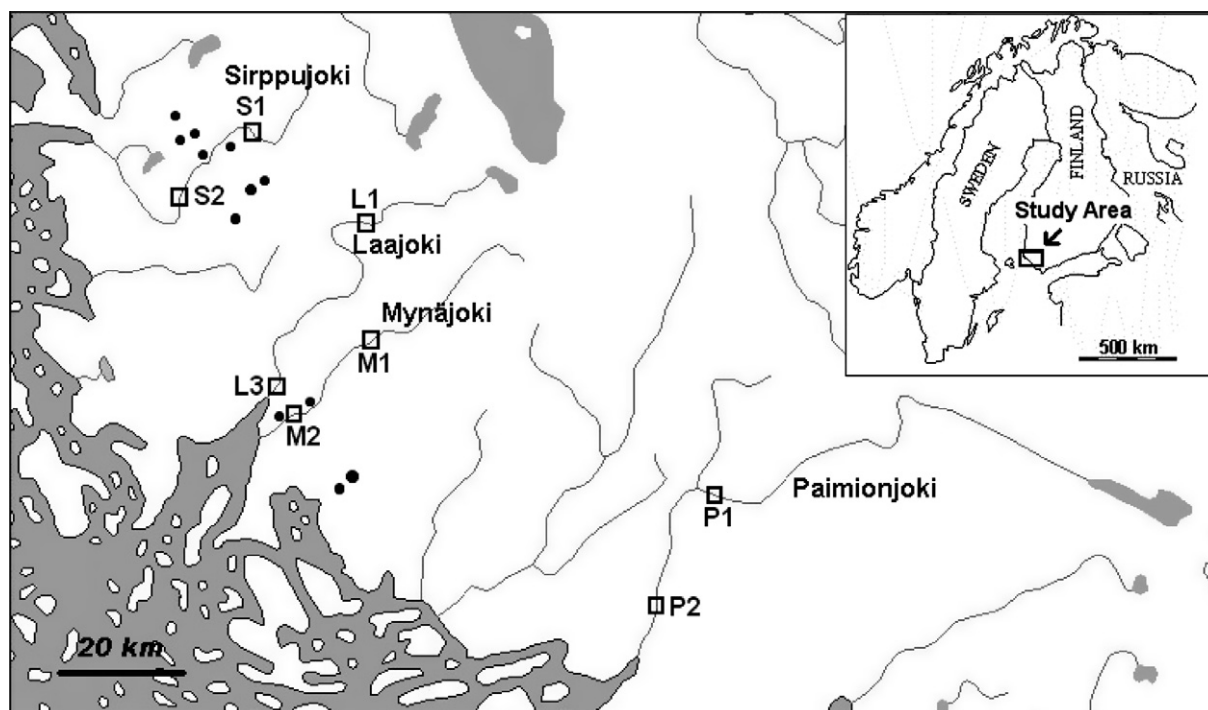


Fig. 1. Location of the study area and sampling sites in the Sirppujoki- (S), Laajoki- (L), Mynäjoki- (M) and Paimionjoki (P) rivers in SW Finland, including 12 low-order streams (filled dots) to Sirppujoki and Mynäjoki.

Paimionjoki, on the contrary, is not known to be affected by AS soils (Nyberg et al., 2011). No major sources of pollution are known to exist in the area.

3. Methodology

3.1. Sampling and analyses

Sampling was carried out in May 2006 in the rivers Sirppujoki, Mynäjoki, Laajoki and Paimionjoki (upper and lower reaches; Fig. 1) and from 12 first and second order stream sites (Fig. 1) in the drainage area 2 weeks after the spring high-water flow peak. As the water sampling was performed in late spring, the water temperature had risen to about 10 °C. 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 prioritised, i.e. streams with low pH and high electrical conductivity (EC) draining low-relief farmlands.

The 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. After filtration and ultrafiltration the samples, including 12 duplicates and four method blank samples, were immediately acidified with 2% ultrapure HNO₃ and analysed in randomised order for 30 elements with the inductively-coupled-plasma mass-spectrometry (As, Ba, Br, Ca, Cd, Co, Cs, Cu, Fe, Hf, K, La, Mg, Mn, Na, Ni, Pb, Rb, Si, Sr, Th, Ti, Tl, U, V, Y and Zr) and inductively-coupled-plasma atomic-emission-spectrometry (Al and S). The samples were spiked with internal standards to correct for instrumental drift and matrix suppression. Blanks and system blanks were run to verify clean and uncontaminated conditions, and certified reference materials (such as SLRS-4 and NIST 1640) were used to control accuracy. 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.

Water temperature, pH and specific electric conductivity were measured in the field. Alkalinity and acidity were measured on filtered (0.45 µm) water samples by potentiometric titration with H₂SO₄ (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. Samples for analyses of 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 collected in pre-cleaned 15 mL polyethylene test tubes. Fifteen duplicates and four method blank samples were included, and all samples were stored in darkness at +5 °C for 4 weeks prior to analyses in randomised order with a Shimadzu Organic Carbon 5050 analyzer. 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 stations along the rivers the particulate fraction was determined according to Björkvald et al. (2008) and Åström et al. (2010); from the differences between total concentrations (non-filtered samples treated with HNO₃ 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).

3.2. Ultrafiltration

Isolation of colloidal matter by ultrafiltration can be conducted either using cross-flow or frontal ultrafiltration (Buffle and Leppard, 1995). Since cross-flow requires large-volume samples (10–1000 L, Guéguen et al., 2002), frontal filtration was selected for easy handling. Frontal ultrafiltrations were performed using a 400 mL polycarbonate cell (Amicon 8400) equipped with a suspended magnet stirring bar located above the filter in order to prevent clogging during ultrafiltration. Its major advantage over the more frequently used tangential filtration in hydrochemistry is the very small size of the filter and low amount of pore space, which minimises adsorption inside the filter during filtration (Pokrovsky and Schott, 2002). Chen and Buffle (1996) also recommended stirring to minimise surface coagulation, but at the same time recommended minimising 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). Nitrogen pressure (2.5 bars) was used as the driving force, and a 1 kDa regenerated cellulose acetate membrane (Millipore) was selected. 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. There is no consensus on the optimal cf for ultrafiltration, but for this specific technique (i.e. frontal ultrafiltration with Amicon 8400) a low cf is recommended (3–13; Waeles et al., 2008).

Frontal ultrafiltration is subject to a variety of potential artifacts (i.e. concentration polarisation and clogging; Buffle and Leppard, 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 HNO₃) 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. For Zn the ultrafiltered blank was four 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, but the concentrations for these elements in the water samples were generally so high that the potential contamination could be ignored, although some caution might be necessary for samples that have low concentrations.

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.

The recovery was for most of the elements 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 (Åström et al., 2010). Only for Cr was the recovery (median) over 130% and, therefore, Cr is excluded from further discussion.

3.3. Speciation modelling

The geochemical modelling program Visual MINTEQ (vers. 3.0; Gustafsson, 2010) was used to predict metal speciation in the investigated rivers. The following variables were used: pH, temperature, alkalinity, and total concentrations (i.e. concentrations of non-filtered samples) for Al, Ba, Br, Ca, Co, Cs, Cu, Fe, K, La, Mg, Mn, Na, Ni, Pb, Si, SO₄, Ti, Zn and OC. The lanthanides generally have similar chemical patterns and therefore La is considered to represent all the lanthanides. The Stockholm humic model (SHM) was used to describe the formation of metal-DOM (dissolved organic matter) complexes. It was assumed that the ratio of active DOM to DOC (dissolved organic C) was 1.65 (Sjöstedt et al., 2010) and that 100% of the active DOM was fulvic acid (FA; Sjöstedt et al., 2010). In addition, Al was allowed to precipitate and the solubility constant selected was Al(OH)₃ with a log *K_s* of 8.28 at 25 °C and a reaction enthalpy of –105 kJ/mol. The Diffuse Layer Model of Dzombak and Morel (1990) was used to determine the adsorption of metals by colloidal hydrous ferric oxide. The concentration of Fe³⁺ was estimated by calculating precipitation of ferrihydrite with a log *K_s* of 3.2 at 25 °C and a reaction enthalpy of –100.4 kJ/mol. Colloidal ferrihydrite was assumed to have a specific surface area of 600 m²/g and a site density of 2.31 n/m² (Dzombak and Morel, 1990).

4. Results

4.1. General hydrochemistry

The low-order streams had a low pH (3.3–5.7), high electric conductivity (545–1368 µS/cm) and high acidity (18–188 mg/L CaCO₃; Supplementary Table S1). In the rivers Sirppujoki, Laajoki and Mynäjoki acidity was considerably lower (8–17 mg/L CaCO₃) and pH higher (5.6–6.3; Supplementary Table S1). In Paimionjoki the water was circumneutral (between 7.0 and 7.3) and the alkalinity relatively high (29.5–41.2 mg/L CaCO₃; Supplementary Table S1). The electric conductivity (EC) of the rivers varied between 56 and 214 µS/cm (highest EC in Sirppujoki; Supplementary Table S1) and was thus lower than in the low-order streams, but still high when compared to the median of Finnish headwater streams (44 µS/cm; Lahermo et al., 1996).

All rivers exhibited a high concentration of semi-dissolved organic C (11–20 mg/L), with the highest and lowest concentrations in Mynäjoki and Paimionjoki, respectively. The semi-dissolved OC concentrations decreased downstream, except in Paimionjoki, where fine sediments are abundantly distributed in the catchment throughout the whole river. As found by other studies in boreal regions (Pokrovsky et al., 2010), the dissolved concentrations of OC were remarkably stable in all rivers and low-order stream sites (usually 2–5 mg/L; Supplementary Table S1), although the semi-dissolved concentrations varied. The particulate OC was negligible except in M1, where it accounted for around 10% of the total OC (Fig. 2).

In Sirppujoki the dissolved concentrations of SO₄ and many elements (Ba, Br, Ca, Cd, Co, K, Mg, Mn, Na, Ni, Rb and Sr) were relatively high 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; Supplementary Table S1). Downstream Cd exceeded the proposed standards for priority pollutants under EU regulations (0.08 µg/L; 2008/105/EU). In Laajoki and Mynäjoki dissolved concentrations of these metals and SO₄ were generally also elevated, and commonly increased by a factor of 2 downstream (Supplementary Table S1). In Paimionjoki, in contrast, dissolved concentrations of several elements (i.e. Al, Ba, Cs, Fe, Hf, Pb, Rb, Th, Ti, Tl and V) were usually lower compared to concentrations in the other investigated rivers (Supplementary

Table S1), although total concentrations of these elements were higher. In the low-order stream sites the dissolved concentrations for SO₄ and almost all the elements were considerably higher than in the rivers, with the exception of V and Zr (Supplementary Table S1). Consequently, Cd and Ni concentrations were far over the acceptable limits of current EU regulations for priority pollutants (0.08 µg/L and 20 µg/L, respectively; 2008/105/EU).

4.2. Fractionation of organic carbon, sulphate and metals in rivers

Differences in size fractionation of the investigated elements, ions and organic compounds were observed and, therefore, they have been grouped according to the following rationale; (1) Most soluble elements and ions, (2) Organic C and elements mainly in the colloidal fraction, (3) Elements mainly in particulate fraction, and (4) Elements exhibiting large variation.

4.2.1. Most soluble elements and ions: Ca, Cd, K, Mg, Mn, Na, SO₄, Si and Sr

Most of the alkali and alkaline earth metals (Ca, K, Mg, Na and Sr) and Cd, Mn, SO₄ and Si in the rivers were generally found in dissolved form (Fig. 2; as the fractionation for these elements were approximately the same, only the most relevant elements for this study were shown). However, in Paimionjoki the dissolved fraction for Ca, Mg, Na, SO₄ and Si were markedly lower (10–68%; Fig. 2) than in the other rivers (39–92%; Fig. 2). Although the dissolved concentrations of these elements and SO₄ in Sirppujoki increased downstream, the dissolved relative abundance (i.e. percentage of the dissolved fraction) decreased. In the other rivers both the dissolved concentrations and relative abundance of these elements and SO₄ rose downstream.

The speciation modelling with Visual MINTEQ indicated that K, Na and Si should be almost entirely in the form of free ions (>97%; Table 2). Calcium, Mg, Mn and SO₄ were also predicted to be present mostly as free ions (>80%; Table 2), while small fractions of Ca, Mg and Mn would also be expected to be associated with organic C, SO₄, Fe oxide and/or carbonate (Table 2). Some of these predicted associations may, however, be <1 kDa in size and thus the “soluble” fraction passing through the 1 kDa filter for all elements is most likely somewhat higher.

4.2.2. Organic carbon and elements mainly in colloidal fraction: OC, lanthanides, Th, U, Y and Zr

Organic C in all four rivers was mainly found in the colloidal fraction (68–85%), with slightly lower colloidal fractions in Paimionjoki (Fig. 2). The remaining OC (14–32%) was in the dissolved phase. In Sirppujoki, Laajoki and Mynäjoki the actinides, lanthanides and Zr occurred mainly as colloids (42–90%; Fig. 2) but also substantially as particles (2–53%; Fig. 2), while generally relative little (<25%) was found in the dissolved form. In Paimionjoki the fractionation pattern of actinides, lanthanides and Y was considerable different, with a very high fraction in the particulate phase (47–80%; Fig. 2) and less than 3% in the dissolved fraction. The fractionation patterns of these elements up- and downstream in each river were similar (within around ±10%), except for Th and Zr in Sirppujoki and Laajoki (Fig. 2).

The speciation modelling results for the lanthanides were in line with the results obtained by ultrafiltration; only a small amount of the lanthanides were predicted to appear as free ions (<6%; Table 2). In most river samples the lanthanides were predicted to have elevated presence as organic complexes (>93%; Table 2), but downstream in Sirppujoki, with lower pH and high SO₄ concentrations, there was a slightly smaller predicted proportion of OC-lanthanide complexes and a corresponding slightly larger predicted proportion of free metal (6%) and SO₄ complexes (6%).

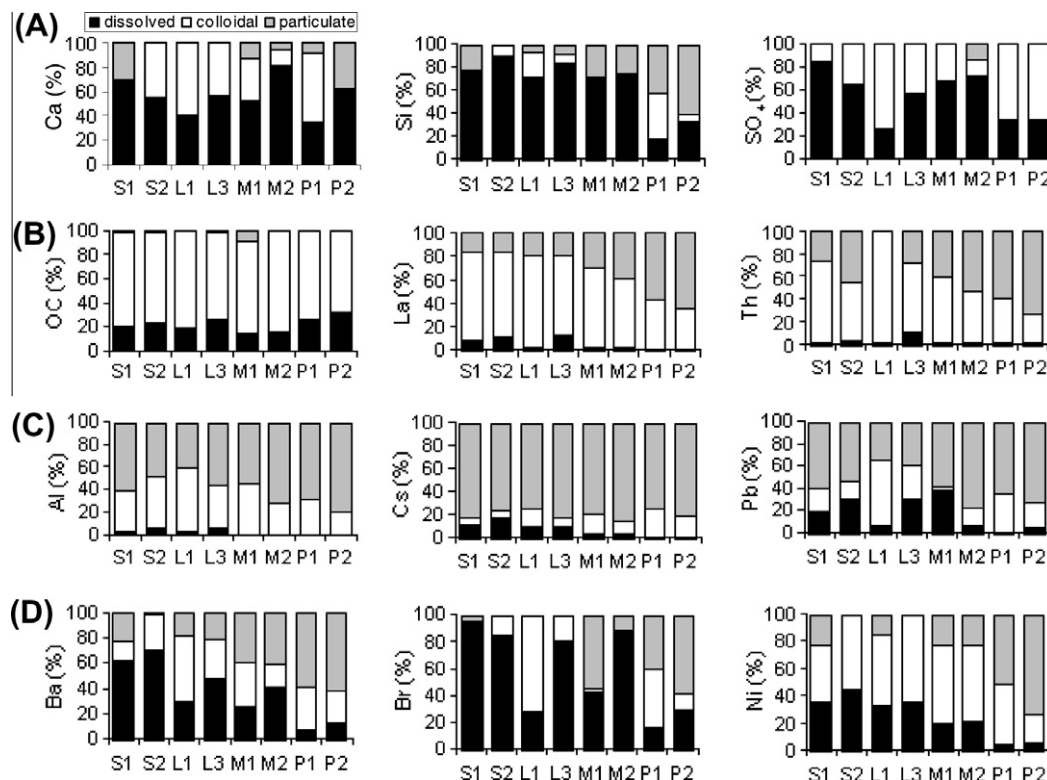


Fig. 2. Dissolved- (<1 kDa), colloidal- (1 kDa–0.45 μ m) and particulate (>0.45 μ m) fractions (%) in Sirppujoki (S), Laajoki (L), Mynäjoki (M) and Paimionjoki (P). (A) Most soluble elements and ions: Ca, Cd, K, Mg, Mn, Na, SO_4 , Si and Sr. (B) Organic C and elements mainly in colloidal fraction: OC, Th, U, Y, Zr and the lanthanides. (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.

4.2.3. Elements mainly in particulate fraction: Al, Cs, Fe, Hf, Pb, Ti and V

In general Al, Cs, Fe, Hf, Pb, Ti and V occurred as particles (27–86%; Fig. 2). Between 17% and 57% of Al and Fe was colloidal, whereas the dissolved fraction in most cases was <5% (Fig. 2). It is notable that colloidal and/or particulate Al correlated significantly (Spearman $r_s = 0.72$ – 0.92) with the corresponding fractions of Fe, Mg and Si, all constituents of clay minerals. Lead exhibited similar fractionation patterns to Al and Fe, but with larger fractions in the dissolved phase in Sirppujoki, Laajoki and Mynäjoki (6–39%; Fig. 2). For Hf the colloidal fraction was between 36% and 65% in the rivers, with usually less than 14% in the dissolved phase. Cesium, Ti and V in all rivers were almost exclusively associated with particles (>60%), with only between 6% and 25% in the colloidal phase and less than 17% in the dissolved phase. The fractionation patterns for Cs, Fe, Ti and V were relatively similar up- and downstream in each river, but for Al, Hf and Pb there were some differences (Fig. 2).

Iron and Al were predicted to precipitate in all rivers (Fe $\geq 99\%$ and Al $\geq 17\%$). The remaining non-precipitated Al fraction was in S1 33%, S2 20%, L1 83%, L3 22%, M1 25%, P1 1% and P2 1%. Nearly all of the non-precipitated Al and Fe fractions were predicted to be present as organic complexes (Table 2). Lead was strongly predicted to be adsorbed to the precipitated Fe oxides; above 61% at all sites, except in upper Laajoki (40%) were organic complexes were very important (55%). Speciation modelling is, thus, quite in line with results obtained by ultrafiltration. However, as free ions of Fe and Al were predicted to be nearly nonexistent and free ions of Pb < 4%, it seems that some of the organic complexes and even some nano-scale Fe-oxides may pass through the 1 kDa filter. The predicted results for Cs were, in contrast, completely different to the observed results, as Cs was predicted to occur as free ions (>99%; Table 2) in all rivers.

4.2.4. Elements exhibiting large variation: As, Ba, Br, Co, Cu, Ni, Rb and Tl

The elements As, Ba, Br, Co, Cu, Ni, Rb and Tl exhibited the largest variation in fractionation between the rivers (Fig. 2). Similar to the other elements, the particulate and colloidal fraction of these elements were highest in Paimionjoki (35–78% and 12–59%, respectively), with only a small fraction in the dissolved phase (1–29%). In Mynäjoki the elements were relatively evenly distributed between all three fractions, while the dissolved phase was high (26–81%) in Laajoki and highest (23–95%) in Sirppujoki.

The predicted results for Ni were in line with those obtained by ultrafiltration (Table 2); with the highest proportion of free ion species in Sirppujoki and lower proportions in Mynäjoki and Paimionjoki. The predicted results for Co and Cu were somewhat different to the observed results in that >53% and <5%, respectively, were predicted to occur as free ions. Moreover, these elements were predicted to be associated with organic C and in Paimionjoki, to a small extent, also with Fe oxide (Table 2). Barium and Br were, in contrast to the results obtained by ultrafiltration, predicted to occur mostly as free ions in all river samples (>87%; Table 2).

4.2.5. Element associations with organic carbon and iron

Although modelling with Visual MINTEQ predicted a close association with organic C and several elements, generally no correlation (Spearman correlation, $p = 0.05$) occurred between organic C and the other elements in the rivers (Table 3). On the other hand, within all fractions Fe correlated positively with a large number of elements (Table 3). Moreover, it is notable that in the particulate phase, Fe even correlated with Ca, Cd, K, Mg, Mn and Si; i.e. with elements mostly appearing in a dissolved form (Table 3). Thus it seems that Fe is closely related to the origin of and/or to association/adsorption of the other elements. The negative correlation of particulate Fe with the relative abundance of the majority of

Table 2

Free ions and element associations modelled with Visual MINTEQ and the dissolved fraction (%) obtained by ultrafiltration. 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 < 1 kDa	3	6	3	7	2	1		
	Al-oxyhydroxide organic complexes	100	99	100	100	100	100	1 99	100
Ba	Ba < 1 kDa	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 organic complexes	6	3	10	7	12	7	1 4	3
Br	Br < 1 kDa	95	85	28	81	42	89	16	29
	Br ⁻¹	100	100	100	100	100	100	100	100
Ca	Ca < 1 kDa	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 ²⁻ -complexes organic complexes	10	5	14	11	19	12	1 8	7
Co	Co < 1 kDa	56	57	26	50	21	34	1	5
	Co ²⁺	68	78	69	65	53	59	56	65
	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 organic complexes	30	16	29	32	46	38	6 34	3 30
Cs	Cs < 1 kDa	11	17	9	10	4	3		1
	Cs ¹⁺	100	99	100	100	100	100	100	100
	SO ₄ ²⁻ complexes		1						
Cu	Cu < 1 kDa	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 < 1 kDa	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 < 1 kDa	77	72	61	79	61	83	31	50
	K ¹⁺	100	100	100	100	100	100	100	100
La	La < 1 kDa	7	10	2	12	2	1	1	
	La ³⁺	2	6	5	1	1			
	SO ₄ ²⁻ -complexes	1	6	1	1				
	organic complexes	98	87	93	98	99	99	100	100
Mg	Mg < 1 kDa	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 < 1 kDa	80	60	39	56	40	73	10	31
	Mn ²⁺	87	89	85	86	80	85	82	87
	SO ₄ ²⁻ complexes	2	5	1	3	1	2	1	1
	CO ₃ ²⁻ -complexes							3	1
	Fe-oxides organic complexes	11	5	14	11	19	12	7 8	3 7
Na	Na < 1 kDa	82	69	61	79	92	89	48	68
	Na ¹⁺	100	100	100	100	100	100	100	100
Ni	Ni < 1 kDa	35	44	33	36	20	21	4	6
	Ni ²⁺	33	50	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 organic complexes	66	46	61	68	79	74	13 63	7 63
Pb	Pb < 1 kDa	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

(continued on next page)

Table 2 (continued)

Element	Species name	S1 (%)	S2 (%)	L1 (%)	L3 (%)	M1 (%)	M2 (%)	P1 (%)	P2 (%)
SO ₄	SO ₄ ²⁻ < 1 kDa	83	64	25	56	67	71	33	33
	SO ₄ ²⁻	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 < 1 kDa	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 < 1 kDa	6	4	7	5	1	1		
	Ti(OH) ₄	100	100	100	100	100	100	100	100

Table 3

Correlations ($p = 0.05$) between Fe and metals in various fractions, as well as OC and metals in various fractions. Bold font = correlations occur for both concentrations and the relative abundances; normal font = correlations occur for concentrations only; () = correlations occur for relative abundances only; italics font = negative correlations; D = dissolved fraction (<1 kDa); C = colloidal fraction (1 kDa–0.45 μ m); P = particulate fraction (>0.45 μ m).

	Fe(D)	Fe(C)	Fe(P)
D	Al, Ce, Cs, Dy, Er, Eu, Gd, Ho, La, Nd, Pb, Pr, Sm, Tb, Th, Y, Yb (Cu, Ni, Lu, Rb, Si, Ti, Tm)	<i>Ba, Br, Co, Dy, Er, Gd, La, Mn, Nd, Ni, Pr, Rb, SO 4, Si, Sm, Ti, V, Y</i> (Al, Cd, Cs, Eu, Hf, Ho, Lu, Th, Ti, Tm, Yb)	Cd, Co, Cs, Dy, Er, Gd, Ho, Mn, Nd, Ni, Pr, Sm, Tb, Ti, V, Y (Al, As, Ce, Eu, Hf, Rb, Ta, Th, Ti, Tm, Yb)
C	Ce, Co, Dy, Er, Gd, Lu, Mn, Nd, Pr, Sm, Tb, Tm, Yb (Al, Fe, U, Y)	Al, As, Ba, Cs, Cu, Ho, Hf, Rb, Th, Ti, U, Y, V, Zr (Ce, Co, Dy, Er, Eu, Gd, La, Lu, Mn, Nd, Pr, Sm, Tm, Yb)	Cs, Hf, Ho, Th, Ti, U, V, Y, Zr (Al, Ce, Co, Dy, Er, Eu, Gd, La, Lu, Mn, Nd, Pr, Sm, Tb, Tm, Yb)
P	Ca, Co, Cu, K, Mg, Mn, Ni, Rb, Si (Al, Ba, Br, Ce, Cd, Dy, Er, Eu, Fe, Gd, Ho, Lu, Pb, Pr, Sm, Sr, Tb, Ti, Tm, U, Y, Yb)	Ba, Cs, Hf, Ti, V, Y (Al, Br, Ca, Ce, Cd, Co, Dy, Er, Eu, Gd, Ho, K, La, Lu, Mn, Nd, Ni, Pb, Pr, Rb, Si, Sm, Sr, Tb, Th, Tm, U, Yb)	Al, Br, Co, Cs, Eu, Hf, Gd, Ho, K, Mg, Mn, Nd, Ni, Pb, Pr, Rb, Si, Sm, Th, Ti, Tl, Tm, U, V, Y, Zr (Ba, Ca, Cd, Cu)
	OC(D)	OC(C)	OC(P)
D	Zr (Na)		
C	SO ₄		
P	(Ta, V)	(V)	

elements in dissolved form (indicating depletion) and the corresponding positive correlation to the relative abundance of more than half of these elements in the particulate fraction (Table 3) would support the latter processes (i.e. adsorption). However, this hypothesis is not supported by correlation patterns for colloidal Fe or by modelling that only predicts strong binding of Fe to Pb (in all rivers) and Co, Cu, Mn and Ni (in Paimionjoki; Table 3).

4.3. Sulphate, OC and element solubility in the low-order streams and influence of pH

The solubility for several elements increased with decreasing pH (Fig. 3) and consequently all elements were generally more soluble in the low-order streams than in the rivers (Supplementary Table S2). The most visible influence of pH could be seen for the elements generally appearing in a particulate form (Al, Cs, Fe, Hf, Th, Ti and V); the ratios between dissolved and semi-dissolved concentrations in the rivers and the streams were commonly <0.4 and >0.4 (Supplementary Table S2), respectively, but also those elements exhibiting the largest fractionation variation were found to be significantly controlled by pH (Fig. 3). The elements generally appearing in a colloidal form (REE, U and Y) in rivers were most likely to be controlled to some extent by pH (Supplementary Table S2), but according to the pH versus elements solubility (Fig. 3) the influence of pH was somewhat uncertain. As expected, there were no significant differences between the solubilities for Br and most of the elements appearing as dissolved in the low-order streams and in the rivers, except at the upper sites of Paimionjoki and Laajoki, where the solubility was lower (Supplementary Table S2).

5. Discussion

Industrial, agricultural and other anthropogenic activities commonly lead to an increased input of metals in soils and natural waters (Cundy et al., 2003). In the investigated rivers concentrations of SO₄ and several elements were highly enriched and as acid sulphate soils are abundant on the littoral clay plains in Finland, particular consideration needs to be given to them when investigating metals in the rivers of the study area, especially as smaller and less frequent 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; Fältmarsch et al., 2008; Nyberg et al., 2011). This is highlighted by Roos and Åström (2005b), who found that a river in W Finland with only 2% of AS soils in its catchment was substantially loaded with several potentially toxic metals (i.e. Al, Cd, Co, Cu, La, Mn and Y) leached from this soil type. Because this river did not experience severe drops in pH, a typical indicator of AS soils, Roos and Åström (2005b) concluded that this river carried a hidden load of AS soil related hazardous elements, i.e. the water quality in rivers draining moderate to small amounts of AS soils can be fairly good for most of the year, but under certain meteorological/hydrological conditions the water in affected rivers and estuaries may become very acid and mobile metal concentrations critically high. Such phenomena may be explained by severe dry spells in the summer (enabling oxidation of sulphides) and subsequent severe wet spells in late autumn that enables flushing of large amounts of acidity and metals from the AS soils (Österholm and Åström, 2008; Saarinen et al., 2010; Nyberg et al., 2011). An example of this

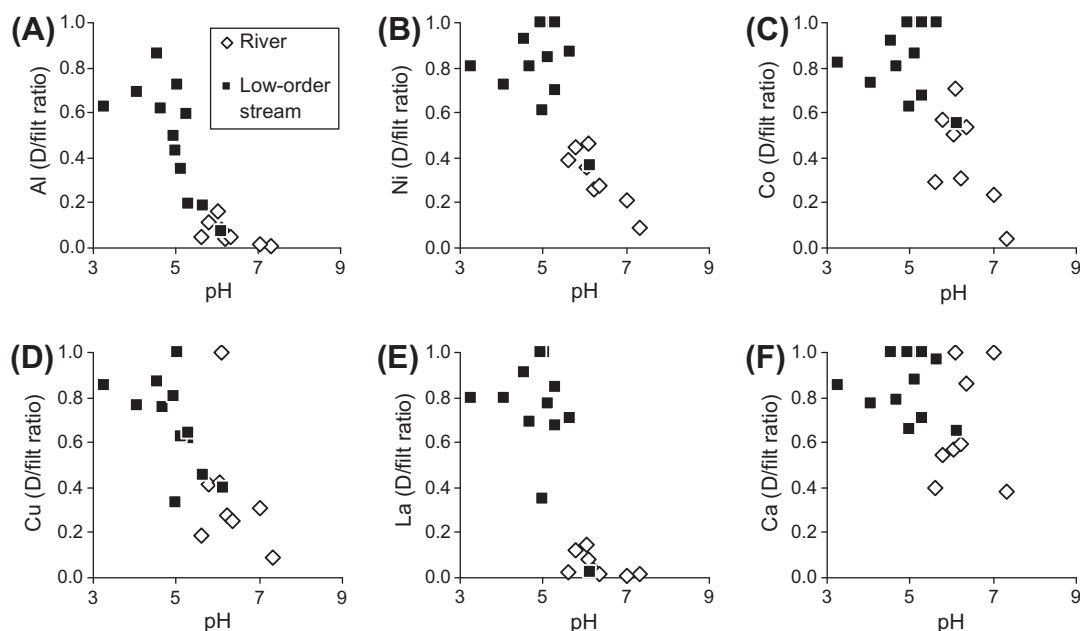


Fig. 3. pH versus element solubility. The element solubility is shown as the ratios between dissolved ($D < 1$ kDa) and semi-dissolved ($\text{filt} = < 0.45 \mu\text{m}$) concentrations. (A) Influence of pH in the low-order streams: Al, Si and Th. (B and C) Influence of pH in the rivers: As, Ba, Co, Cs, Ni, Rb, Tl and V. (D) Minor influence of pH: Cu, Fe, Hf, Pb and Zr. (E) The influence of pH is uncertain: lanthanides, U and Y. (F) No influence of pH: OC, Br, Ca, Cd, K, Mg, Mn, Na, SO_4 and Sr.

was widespread fish kills in a significantly high portion of rivers in midwestern and northwestern Finland in autumn 2006 (Nordmyr et al., 2008; Nyberg et al., 2011).

In the current study area, it was obvious from SO_4 , metal and pH patterns in the river and low-order streams, that the middle and lower Sirppujoki is strongly affected by AS soils. The presence of AS soils in the midstream section of Sirppujoki has also been shown by soil profile studies in the catchment (Palko et al., 1985; Triipponen, 1997). Low pH in association with high dissolved SO_4 and metal concentrations in the low-order streams of Mynäjoki showed that the lower Mynäjoki is also affected by AS soils. Moreover, Nyberg et al. (2011) studying the same rivers under different hydrological conditions found that although the concentrations of AS soil related elements in Laajoki are significantly lower than in Sirppujoki, the temporal patterns of these elements (in particular SO_4) in Laajoki have a close resemblance to patterns in Sirppujoki, and thus it is likely that even Laajoki is affected by AS soils. In accordance with this study, Nyberg et al. (2011) also found that in Laajoki and Mynäjoki, pH is controlled more by humic acids from the peatlands in the upstream areas (indicated by high filterable OC) and the relatively well buffered waters in downstream areas, than by AS soil discharge. In Paimionjoki, in contrast, the SO_4 and metal patterns are not typical for AS soils, e.g. total concentrations of Ba, Cs, Fe, Pb, Si, Th, Ti and V are high, while Br, Mn and SO_4 are relatively low.

There were significant differences between the fractionation patterns for the elements, SO_4 and OC in the investigated rivers and, therefore, four groups of elements were distinguished (see Section 4.2). Aluminium, Fe and Pb were almost entirely colloidal- and particle-sized in the rivers, similar to previous studies from small boreal rivers in NW Russia (Pokrovsky and Schott, 2002; Pokrovsky et al., 2006; Vasyukova et al., 2010). In the low-order streams, however, these elements were mainly dissolved due to the low pH (generally < 5.3 ; Supplementary Table S1). Furthermore, 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), the lanthanides and Y in the rivers were mostly found as colloids. Moreover, in Paimionjoki these elements occurred substantially as

particles (Fig. 2). In the low-order streams, however, the lanthanides and Y occurred mainly in dissolved form. It is though somewhat uncertain if pH influences the fractionation patterns for these elements (Fig. 3), but according to Gaillardet et al. (2003) the lanthanides in boreal regions are generally controlled by pH. 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). It was, therefore, expected that several of these elements (Ca, K, Mg, Na and Sr) would be soluble in the investigated rivers although even these elements were relatively insoluble in Paimionjoki. Sulphate occurred mainly in the dissolved fraction, but was unexpectedly also, to a substantial degree, associated with colloids, probably adsorbed to some of the abundantly occurring colloidal cations.

The elements As, Ba, Br, Co, Cu, Ni, Rb and Tl exhibited very large variation in fractionation in the rivers, which indicates that these elements are sensitive to variations in hydrochemistry and catchment-soil geochemistry. The solubilities of several of these elements (in particular 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 (Fig. 3). Thus, the dissolved fraction of most of these elements was highest in Sirppujoki (northernmost and most acidic river), and decreased southwards being lowest in Paimionjoki (southernmost and circumneutral river; Fig. 2). Apart from affecting element solubility, pH is probably the most important chemical parameter influencing metal sorption (Gundersen and Steinnes, 2003). This is also supported by a modelling experiment (where the pH value in the model was varied between 3 and 8) which showed that a gradual increase in pH predicted a markedly and continuously increase of element complexation. 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.

While in general the dissolved form is the most toxic fraction (i.e. As and Cu; Fritzsche et al., 2011; Masson et al., 2011), it is notable that not all dissolved metals are toxic, or occur in toxic concentrations (such as Ca, K and Mg; Löhr et al., 2007). In contrast, some element complexes in a colloidal or particulate form might be toxic. In the low-order streams the dissolved concentrations of Cd and Ni were well over the acceptable limits of current EU

regulations for priority pollutants (2008/105/EU), while in the rivers the dissolved concentrations of Cd and Ni were mostly under these limits. The EU regulations are, however, based on semi-dissolved fractions operationally defined by 0.45 µm filtered water samples (Meland et al., 2010). Consequently, if taking into account the semi-dissolved (dissolved + colloidal) fraction, Ni in Sirppujoki and Cd in Sirppujoki and Laajoki exceeded these regulations.

In comparison to the observed results, the predicted results (Visual MINTEQ) generally showed a lower proportion of colloidal and particulate metals in the rivers. In Sirppujoki the observed and predicted proportion of metal colloids and particles matched relatively well (except for Cs, Cu and Pb), but the difference between predicted and observed results increased successively from Laajoki to Paimionjoki (especially for Ba, Br, Ca, Co, K, Mg, Mn and Si; Fig. 2 and Table 2). Although there are some inherent uncertainties when using “model predictions”, e.g. lack of adjustment possibilities (Weber et al., 2006; Pourret et al., 2007; 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 Paimionjoki, when the filter surface was analysed with SEM. Even the possibility of interaction between major ions (mainly Ca and Mg) 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), is unlikely to cause such noticeable differences as the recovery for Ca and Mg was 107% and 108%, respectively. Moreover, in addition the median recovery for the other elements was satisfactory (see Section 3.2), indicating that the frontal ultrafiltrations were performed accurately.

According to modelling with Visual MINTEQ, Al, Cu, Ni, and the lanthanides were predicted to exist primarily as organic complexes and Fe should only be an important adsorption agent for Pb in all rivers, and for Co, Cu, Mn and Ni in Paimionjoki. This is somewhat contradictory to element correlations (Table 3) which show strong associations between Fe and the other elements and only few element associations with organic material. According to Unsworth et al. (2006) and Rönnback et al. (2008), there is a possibility that organic complexes (e.g. with Cu, Ni and the lanthanides) are not as abundant as the model predicts if other metal binding concentrations are high. Thus, it has to be considered that other metal binding material (e.g. clay colloids) or elements not used in the simulations (Visual MINTEQ) could influence the element speciation. At least F, not modelled, is known to form complexes with Al (Langmuir, 1997; Sjöstedt et al., 2010) and thereby indirectly influence predicted Al complexation with organic matter. Moreover, Co might have partly oxidised from the Co(II) state to Co(III), which generally has strong associations with OC, clay colloids and/or Fe- and Mn-oxides (Qian et al., 1998; Salminen et al., 2005). For Ti colloidal formation and complexation instability might occur (e.g. for TiO₂), and can thus cause differences between predicted and observed results (Salminen et al., 2005; Neal et al., 2011). The unpredicted associations for Fe, on the other hand, may be largely explained by a common source of metals from the catchment, independent of in stream complexation/adsorption processes.

The most likely metal source in terms of total concentrations, probably also causing the discrepancy between predicted and observed results in the investigated rivers and the unpredicted lack of associations for Fe (modelling with Visual MINTEQ), is thought to be erosion of metal bearing clay minerals because:

- (1) Direct observations of clay material include the greyish colour of the sampled rivers and tributaries, SEM images and EDX analysis of suspended colloidal size clay matter (i.e. flakes) on the 0.45 µm filter surfaces (Fig. 4) showed that these flakes mainly consist of O, Si and Al, and previous

gravimetric analysis of suspended matter from nearby rivers indicated also a phyllosilicate composition (i.e. Aurajoki, Nystrand et al., unpublished). Moreover, during the time of sampling the turbidity in the rivers was between 17 (in Sirppujoki) and 140 FNU (in Paimionjoki; HERTTA database, Finnish Environmental Centre), indicating an increasing content of suspended matters from north to south.

- (2) The proportion of clay soils in catchments is relatively large (15–43%; Table 1) and the catchment with the highest proportion of clays (i.e. Paimionjoki) has the highest concentration of colloidal/particulate matter and the highest discrepancy with modelled results.
- (3) Concentrations of colloidal and particulate metals are very high in the investigated rivers compared to rivers less dominated by clay erosion (Pokrovsky and Schott, 2002; Pourret et al., 2007).
- (4) 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, especially in Paimionjoki. 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 constituents of clay minerals (illite is presumably the most common clay mineral in the studied area; Uusinko, 1975).
- (5) Clay colloids and small size particles 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 their source (Parker and Rae, 1998). This would explain why Cs, generally present as free cations in freshwater (Eyrolle and Charmasson, 2001) and here predicted to occur as free cations, is nearly exclusively found as colloids and particles in the rivers of this study; i.e. Cs most likely occurs in illite substituting for K.

Although the colloidal and particulate concentrations were highest in Paimionjoki, it is notable that the colloidal and particulate concentrations are also relatively high in the rivers affected by AS soils. This indicates that in terms of the total or semi-dissolved (measured by conventional filters) metal load, erosion

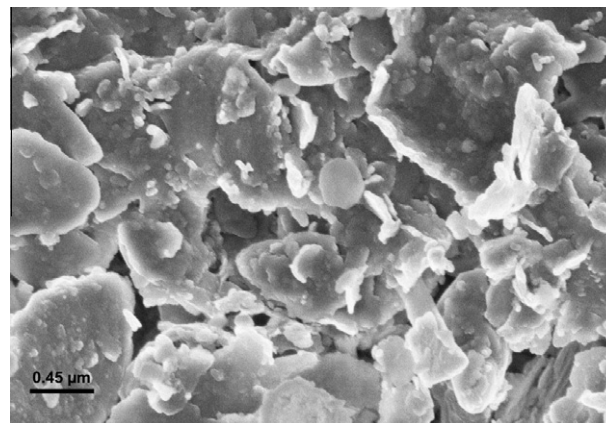


Fig. 4. SEM image of suspended matter seen as flakes (several also <0.45 µm) on a 0.45 µm filter surface used on water from Paimionjoki (P2). Analysis with EDX showed that the flakes consist mainly of O, Si and Al and also substantially of Fe, K, Na and Mg, i.e. they are most likely phyllosilicates that were removed from the water column by the filter.

of phyllosilicates is a significant contributor and is partly masking the effects of AS soils. Thus, relying on only semi-dissolved concentrations obtained in routine analysis will frequently lead to an overestimation of the water toxicity as the eroded colloidal-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. This could be accounted for by speciation modelling for Al, Cu, Fe and Pb, but for other elements it seems that even with modelling the occurrence of bioavailable elements will be significantly overestimated in this environment as could be seen by the difference between predicted and observed results in the investigated rivers.

6. Conclusions

Total concentrations of several elements are highly elevated in the rivers studied but occurred to a large extent in solid colloidal and particulate form due to erosion of clay minerals. The impact of erosion, as indicated by the proportion of solid metals, increases successively from north (Sirppujoki) to south (Paimionjoki). Acid sulphate soils within the northernmost areas were found to increase the concentrations of dissolved toxic metals. This was evident in Sirppujoki river and to some extent in 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 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 and transport of relatively non-toxic colloidal/particulate phyllosilicates into rivers from clay areas (and 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 concentrations obtained in routine monitoring and/or speciation modelling can lead to major overestimation of the water toxicity in this environment.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apgeochem.2012.01.009.

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