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1 Estuarine behaviour of metal loads leached from coastal lowland Acid Sulphate soils

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ABSTRACT

The estuarine behaviour of the metal load leaching from acid sulphate (AS) soils was studied in a selected river system (the Vörå River), in western Finland. Large amounts of metals were transported with the river and deposited within the estuary, causing highly elevated metal concentrations in both the sediment traps and in the underlying bottom sediments. Among the metals, there was a diverging deposition pattern where Al, Cu, La and U demonstrated a strong association with organic matter and were deposited within approximately 4 km from the river mouth. In contrast, the deposition of Co, Mn, Ni and Zn occurred when pH reached circumneutral conditions further out in the estuary. Yet other metals were not abundantly leached from the AS soils and thus not elevated in the river and estuary (Fe, Ti, Cr, V). Five separate chemical extractions indicated the geochemical speciation of the metals.

Keyword: metal load; estuarine sediments; sediment-trap material; acid sulphate soils; Vörå River; Baltic Sea

1. INTRODUCTION

Acid sulphate soils (AS soils) occupy worldwide an area of at least 17 million ha (Andriesse and Van Mensvoort, 2005), and are formed on sulphide-rich marine sediments. Disturbance of such sediments by anthropogenic operations like draining for agricultural purposes, and to a smaller extent river dredging and excavation for road- and house building, enables oxidation of the sulphides therein. As a consequence sulphuric acid is produced and an AS soil is developed (Dent and Pons, 1995; van Breemen, 1973). The subsequent low pH in these soils (pH <4) results in release of chemical elements from the sulphides and accelerates the mineral weathering, i.e. alteration of silicates and dissolution of associated metals (e.g. Joukainen and Yli-Halla, 2003; Sohlenius and Öborn, 2004; Åström and Björklund, 1997; Österholm and Åström, 2002).

The environmental problems related to AS soils are continuously increasing, since these soils are mainly located in coastal areas where there is an increasing pressure from population and industry, including regions such as eastern and western Australia, the Mekong Delta, western Africa, Sweden and Finland (Andriesse and Van Mensvoort, 2005; Dent and Pons, 1995). The extensive export of acidity from these soils and the often associated biological damage, have been highlighted in many studies on several continents over the last two to three decades (e.g. Cook et al., 2000; Dent and Pons, 1995; Hudd and Leskelä, 1998; Macdonald et al., 2007; Minh et al., 1997; Ritsema et al., 2000; Sammut et al., 1996; van Beers, 1962).

In Finland, which have the largest AS soil occurrences in Europe, discharge from AS soils exports hundreds of tons of metals and acidity into coastal rivers (Edén et al., 1999; Roos and Åström 2005; Österholm and Åström, 2004), with serious effects on many fish species that use coastal areas as a hatching ground. An acid and metal flush coinciding with the hatching period can occasionally exterminate whole fish populations (Hudd and Kjellman, 2002). In Finland several widespread mass kills of adult fish have been documented (e.g. Hudd and Leskelä, 1998) and a recent large one occurred in autumn 2006.

The estuarine behaviour of the metal loads leached from AS soils is poorly known. Part of the discharged metals can be lost by processes such as acid and/or humus related precipitation/sorption followed by sedimentation and also to some extent by uptake by aquatic plants in streams and rivers before entering the estuary. However, when the acid metal-rich river water enters the estuary with higher pH and salinity, the metals are likely to be removed from solution through precipitation (Braungardt et al., 2003; Johnson, 1986; Lopez-Gonzalez et al., 2006; Sholkovitz, 1976) and consequently deposited within the estuary. Despite the massive export of metals from AS soils only a few studies have so far examined the fate of the metal load in the recipient estuaries (Heikkilä, 1999; Nordmyr et al., 2007; Macdonald et al., 2004).

The objective of this study, which focuses on the boreal AS soil landscape, was to: (1) identify the transport patterns of metals from the river out to the estuary, (2) determine in which forms the metals are bound in the sediment-trap material and in the bottom sediments, (3) assess the depositional mechanisms, and (4) elucidate the extent of spatial metal contamination in the estuary.

2. DESCRIPTION OF THE STUDY AREA

The Vörå River situated in western Finland, discharging into the Gulf of Bothnia (Fig. 1), is 35 km long and has a drainage area of 223 km² of which 31% is agricultural fields, 54% forest and 15% mires. No lakes exist in the drainage area and the influence of industrial and urban effluents is minor. In the river valleys the dominating Quaternary deposits are the sulphide-bearing clays and silts, which are largely used as agricultural land and wherein AS soils are developed. The precise extent of AS soils in the area is unknown, but results by Roos (2005) indicate that the proportion of these soils is very large and most likely they exist under the main part of the agricultural land. Elsewhere, in the forested areas, glacial till (podzols) dominates. The bedrock in the area consists mainly of acidic Precambrian granites, granodiorites and gneisses (Laitakari, 1942) and therefore the area has an overall low buffering capacity.

[Figure 1 here]

Vörå River is one of the most heavily AS soil-impacted rivers in Finland (Roos and Åström 2005) and Europe, and discharges into a shallow and biologically sensitive brackish water estuary. The existence of fish and other organisms is therefore very limited in these waters. Vörå River was seriously flooded in summer of 2004, causing large damages to the land areas close to the river. As a consequence the

river was cleared and widened in late autumn/early winter of 2005/6 and 2006/7, without consideration of chemical effects on the environment.

The inner estuary is shallow (2-10 m deep) and sheltered from wave action by surrounding land areas and islands, while further out (at Oravaisfjärden, Monåfjärden and Kalotfjärden) the water depths are commonly between 10 and 17 m (Fig. 1). The water level in the area is unaffected by tide, but affected by wind and air pressure which commonly results in ± 20 cm sea level variations and occasionally more than ± 50 cm (Fig. 2; data obtained from the Finnish Institute of Marine Research). The mean temperature in the area is 3°C and the mean annual precipitation approximately 500 mm. During a significant part of the year (December- April/May) the river and estuary are ice covered thus limiting the runoff and transport of material to the estuary.

[Figure 2 here]

3. MATERIAL AND METHODS

3.1. Sampling and sample treatment

Depositing particulate matter was collected in LIMNOS sediment traps (polycarbonate plastic cylinders with $d = 6.2$ cm and $h = 40$ cm). The traps were placed at three sites along the expected river plume path in the Vörå estuary (Fig. 1; Table 1): Hellnäs (H) (water depth 10 m/distance from river mouth 1.7 km), Bentasholm (B) (17 m/4 km) and Stora Granskär (SG) (10 m/9 km). The traps were moored approximately 2 m from the bottom, and at site B an additional upper trap was placed 5 m above the bottom-trap (7 m from the bottom). The collection of particulate matter started every year shortly after the ice broke up. The traps were emptied with one-two month intervals and removed in autumns before the build up of ice. The study period thereby comprised spring, summer and autumn, and are presented in Figure 2. During the flooding year 2004, no sampling of sediment-trap material was done during the maximum flooding. However, during the dredging activity of the Vörå River in early spring (March) and in autumn (September-November) 2006, sampling of sediment-trap material was carried out.

[Table 1 here]

The material collected in the sediment traps was mostly a brown fluffy material with contributions of black and grey layers. Such layers indicate that there might exist relatively rapid variations in the sedimentation patterns within the sampling periods. After sampling, the material was immediately transported to the laboratory, where excess water was removed after the particulate matter had settled. The remaining material was dried at 40°C and weighed. Before metal analysis, the dried material was comminuted by hand in an agate mortar. The reported metal concentrations per weight of dried samples were corrected for the weight of salt in the evaporated water, according to Blomqvist and Larsson (1994).

At every sampling occasion (2004-2006) the specific electric conductivity (EC), pH and temperature were measured (*in situ*) at the same locations as the sediment traps with a multiparametric probe (YSI model 63), in a water profile extending from the water surface down to the bottom (Fig. 1; Table 1). Water samples ($n=12$) were at the same time collected from the lower part of Vörå River. The water samples were collected in polyethylene bottles and acidified with 0.2% ultrapure HNO₃. The runoff is not monitored in the Vörå River, therefore we used the runoff from the nearby (c. 20 km away) Kyrö River (Skatila) which has similar meteorology and catchment characteristics as Vörå River. The mean specific runoff for Kyrö River (Skatila) was 8.8 l s⁻¹ km⁻² for year 2004-2006 (Fig. 2).

In September 2004 three bottom sediment profiles were sampled with a Niemistö gravity corer (Niemistö, 1974) at the same locations as the sediment traps. In the field, sediment cores were divided into 2-cm thick sub samples and immediately placed in airtight plastic bags. In order to minimise oxidation, the samples were kept cool until placed in a freezer. Before metal analysis, the sub samples were dried at 40°C and comminuted by hand in an agate mortar. At site H an erosion layer (coarse material) was reached at 6 cm. Consequently, only a 6-cm long core is presented from this site. All three sediment cores had a c. 4-cm brown oxidised surface layer. At site B the 22-cm long core was black at 4-14 cm and at 14-22 cm brown-grey spots were observed in the material. At site SG the 22-cm long core was black at 6-22cm. The black colour in the sediment is most likely caused by monosulphides and the grey colour indicates absence of such mineral (Georgala, 1980; Wiklander

and Hallgren, 1949). As it only takes small concentrations of monosulphides to produce the characteristically black colour (Smith and Melville, 2004), other sulphide species are likely to co-exist.

3.2. Chemical analysis

Dried and pulverized sub samples of both the sediment-trap material and bottom sediments were sent to Acme Analytical laboratories Ltd. (ISO 9001 accredited) for multi elemental analysis. In addition to conventional quality assurance/control by the lab (including calibration against standards, blanks and reruns), the analytical precision was controlled and determined from 7-20 replicates analysed in random order (see below). The concentrations of 12 metals were determined after five separate selective extractions (not sequentially), which are described below.

(1) Strong 4-acid (total) extraction: A 0.25 g portion of dried and pulverised sample was heated in a solution of HClO_4 , HNO_3 and HF to fuming and taken to dryness. The residue is dissolved in HCl and the solution is analysed with an inductively coupled plasma mass spectrometer (ICP-MS). A total of 90 samples, including blind replicates ($n=20$), were analysed in random order for Al (analytical precision: 1.5%), Co (2.7%), Cr (4.4%), Cu (3.2%), Fe (2.8%), La (4.8%), Mn (2.0%), Ni (3.2%), Ti (1.6%), U (5.9%), V (4.3%) and Zn (3.5%). The analytical precision was calculated based on the random replicate pairs according to the method proposed by Gill (1997). Standards and blanks were repeatedly run to control the analytical quality and the samples were analysed in random order to exclude potential artefacts due to instrumental drift. This leach dissolves the most resistant fractions and thus represents the total concentrations of the samples (Hall et al., 1996a).

(2) *Aqua regia* extraction: A 0.5 g portion of the dried and pulverised sample was partially digested in 3 ml 2:2:2 HCl:HNO₃:H₂O (*aqua regia*) for one hour at 95°C, diluted to 10 ml and thereafter analysed with an ICP-MS. A total of 90 samples, including blind replicates ($n=18$), were analysed in random order for Al (analytical precision: 2.9%), Co (2.8%), Cr (5.3%), Cu (2.3%), Fe (2.2%), La (3.3%), Mn (4.7%), Ni (1.9%), Ti (5.6%), U (4.8%), V (4.3%) and Zn (2.5%). *Aqua regia* efficiently dissolves organic matter, metal-sulphides, phyllosilicates such as clay minerals, and some micas (mainly trioctahedral), while quartz, feldspars, amphiboles and dioctahedral micas (sericite or muscovite) are dissolved to a limited extent or not at all (Chao, 1984; Koljonen and Malisa, 1991; Räsänen et al., 1992). The reference data used in this study, referred to as background concentrations and representing *aqua regia* extractable concentrations, were received from a study by Åström and Björklund (1997), where 317 samples of reduced mother sediments (deposited a long time before the industrialisation) were collected throughout mid-western Finland.

(3) Hydroxylamin (Ha) extraction: A 1 g portion of dried and pulverised sample was digested with 10 ml 0.25M hydroxylamine (0.25M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.25M HCl) in 90°C for two hours (pH c. 1-2) and thereafter analysed by ICP-MS. A total of 90 samples, including replicates ($n=19$) were analysed in random order for Al (5.3%), Co (4.6%), Cu (7.2%), Fe (3.6%), La (5.3%), Mn (7.3%), Ni (5.1%), Ti (0.0%), U (3.9%), V (2.9%) and Zn (3.4%). The reason for the value of 0.0% for Ti is that for many replicate pairs the two values were identical and close to the detection limit (low resolution). For such data, the precision calculated according to Gill (1997) is misleadingly low. According to e.g. Chao (1984) and Hall (1998), the Ha leach dissolves elements held in amorphous Fe-hydroxides and crystalline Mn-hydroxides. Since the samples were dried before analysis, it is likely that oxidation of monosulphides into ferric oxides and elemental S has occurred, while pyrite should have remained largely unaffected (van Breemen, 1973). Since drying of sediments promotes oxidation of Fe and Mn, the amount of Fe- and Mn-oxyhydroxides might be somewhat overestimated (Bordas and Bourg, 1998; Zhang et al., 2001).

Based on the results of the extractions above (1-3), 17 samples from sediment traps were selected and separately extracted with sodium pyrophosphate and ammonium acetate-EDTA, according to the methods below:

(4) Sodium pyrophosphate (Na-pr) extraction: A 1.0 g portion of dried and pulverised sample was digested with 10 ml 0.1 M $\text{Na}_3\text{P}_2\text{O}_7$ (sodium pyrophosphate) and rolled for one hour, and thereafter analysed by ICP-MS. A total of 36 samples including blind replicates ($n=7$) were analysed in random order for Al (8.6%), Co (3.6%), Cu (33%), Fe (5.8%), La (1.8%), Mn (4.4%), Ni (8.0%), U (3.2%), V (0.7%) and Zn (2.9%). Ti was under the analytical detection limit. Sodium pyrophosphate is an alkaline complexing agent, whose effectiveness in removing the easily extractable organic matter has been attributed to its availability to chelate with Ca and trivalent metal ions (Hall et al., 1996b). Sodium pyrophosphate extracts elements adsorbed by organic matter and does not attack sulphides nor does it dissolve significant amounts of amorphous iron oxides (Chao, 1984; Hall et al., 1996b).

(5) Ammonium acetate-EDTA (Am-ac) extraction: A 1.0 g portion of dried and pulverised sample was digested with 20 ml ammonium acetate-EDTA (pH=4.65), rolled for 1 hour followed by analysis with ICP-MS. A total of 36 samples including blind replicates ($n=7$) were analysed in random order for Al (5.3%), Co (3.4%), Cu (1.4%), Fe (4.3%), La (3.8%), Mn (3.7%), Ni (1.1%), U (1.8%) and Zn (3.9%). Titan and V were under the analytical detection limit. Ammonium acetate extracts exchangeable cations adsorbed by clay and elements co-precipitated with carbonates (Figueiras et al., 2002).

It is notable that the methods are operationally defined and that the different digestions overlap each other to some extent.

Loss on ignition (LOI) was determined on both the sediment-trap material and the bottom sediments by combustion of 1.0 g of dried sample (105 °C) in a muffle oven at 500 °C for 4 hours (Radojević and Bashkin 1999). In addition, in cases where we had enough material, organic carbon (OrgC) was determined by IR detection of vapour after pyrolysis at 850 °C (LECO). According to Ball (1964), Radojević and Bashkin (1999), Heiri et al. (2001) and Boyle (2004), LOI is proportional to the concentration of OrgC and is a rapid and reasonably accurate method for estimating the organic matter concentration and can thus be used to estimate the organic matter concentration. This was also checked and verified for the bottom sediment samples of this study, in which LOI and OrgC were strongly correlated ($r=1.00$ with both Pearson and Spearman correlations) and LOI was higher than OrgC by a factor of 2.7. Consequently, only LOI is discussed below.

The unfiltered and acidified water samples from Vörå River were analysed for chemical elements at Activation Laboratories Ltd. with an inductively coupled plasma mass spectrometer/optical emission spectroscope (ICP-MS/OES). In addition to conventional quality assurance/control by the lab (including calibration against standards, blanks and reruns), the analytical precision was controlled and determined from 10 replicates analysed in random order. A total of 22 samples including blind replicates ($n=10$) were analysed in random order for Al (0.9%), Co (3.6%), Cu (13%), Fe (2.0%), La (4.6%), Mn (1.4%), Ni (17%), Ti (5.3%), U (1.8%), V (7.4%) and Zn (7.8%). Earlier studies (e.g. Åström and Björklund, 1995; Åström and Corin, 2000) have concluded that metals in acid rivers like Vörå River are mostly in dissolved form. Therefore, the results in this study can be considered quite comparable to analysis of filtered samples in other studies.

3.3. Mixing experiment

An experiment with sea water mixed with 0%, 25%, 50%, 75% and 100% river water (Vörå River) was performed in order to determine the relation between EC and pH to the proportion of sea water mixed with river water. The specific EC was measured after c. 30 minutes of mixing and the results showed that EC was strongly linearly proportional to the mixing ratio. Consequently, it was possible to reliably determine the proportion of river water in the water profiles from EC measurements. The mixing ratios were also fairly consistent with pH (linear to H_2O concentration) and therefore pH in the various part of the estuary is to a large extent a function of the mixing ratio and pH in the river.

3.4. Contaminant load

The approximate metal load transported by the Vörå River was calculated as follows:

$$\text{tonne a}^{-1} = C_i \cdot q \cdot A$$

where C_i is the runoff weighted average concentration ($g l^{-1}$) of element i in the Vörå River during 2004-2006, q is the mean specific runoff from Skatila for the period 1.1.2004 - 31.12.2006 ($8.8 l s^{-1} km^{-2}$) and A is the drainage area ($223 km^2$).

4. RESULTS

4.1. Hydrochemistry of Vörå River

The pH in the Vörå River was low (median 4.5) (Table 1) and uncorrelated with runoff, while the specific electric conductivity (EC) and the concentrations of Al, Co, Cu, La, Mn, Ni, U and Zn increased with the high water flows in spring and autumn (Fig. 3). Compared to the nearby Lappfjärd River with no (or minor) AS soil impact (Roos and Åström, 2005), these metals were 5-72 times enriched in the Vörå River (Table 2). The concentrations of Cr, Fe, Ti and V were only marginally

elevated or even depleted as compared to Lappfjärd River (Table 2) and uncorrelated with flow (Fig. 3). The mean annual load from the Vörå River drainage area was in decreasing order 590 tonne (t) Al > 110 t Mn > 100 t Fe > 13 t Zn > 6.4 t Ni > 3.8 t La > 3.0 t Co > 1.9 Cr > 0.85 t Cu > 0.79 Ti > 0.75 t U > 0.60 t V.

[Figure 3 and table 2 here]

4.2. Hydrochemistry of the estuary

Based on EC the layer of lighter fresh river water was as expected thickest in the vicinity of the river mouth and attenuated towards the sea. At site H (c. 2 km from the river mouth) the uppermost 2-3 m of the water column was composed of 30-80% river water and from 3 m down to the bottom (10 m) the proportion of river water was 5-30%. At site B (c. 4 km from the river mouth) the proportion of river water was somewhat lower. The uppermost 2-3 m was for the most part composed of 20-50% river water (80% due to high runoff and/or low sea level in spring 2005 (Fig. 2)) and from 3 m to the bottom, the proportion of river water was consistent (5-10%). Even at site SG, which is 9 km from the river mouth, river water was detected. However the proportion of river water was well below 10% in the uppermost 3-5 m and insignificant below 5 m.

Surface waters have the lowest pH, which increases downwards due to the lower proportion of river water at depth. Consequently, pH at the surface represents the minimum pH of the water profiles. The surface water pH at site H and B was occasionally low but was for the most part above 7 (Fig. 4) and were consistent with the pH of the river (Fig. 3). However, the runoff and pH at the different sites were also very consistent i.e. the lowest pH at these sites is found at high runoff (Fig. 4; Fig. 2). At site SG, the pH was considerably lowered in autumn 2006 at the highest runoff, but otherwise variations in pH and runoff did not affect pH much at this site (Fig. 4).

[Figure 4 here]

4.3. Sediment-trap material

4.3.1. Physics

The amount of settling material was as expected highest closest to the river mouth at site H and lowest in the outermost estuary at site SG (Fig. 5). At site B the lower trap collected somewhat more material than the upper trap (Fig. 5). The variations in deposition were relatively constant at site B and SG, while significant fluctuations occurred at site H (Fig. 5). There were only weak indications (not statistically significant) that runoff increased the overall amounts of deposited material and metals (Fig. 5). Since the deposition under ice was only determined once in March-May 2006 at site H, the amount of material deposited during the winter period is poorly known. However, the data indicates minimal deposition in the drainage area during winter (Fig. 5). The sedimentation rate based on trap measurements (Fig. 5) is in reasonable good agreement with corresponding sedimentation rates obtained by ¹³⁷Cs dating on sediment cores in a previous study by Nordmyr et al (2007).

[Figure 5 here]

4.3.2. Chemistry

Based on the temporal and spatial variations in the *aqua regia* extractable elemental concentrations in the trap material, the metals can be organized in three groups: (1) those that occurred below background concentrations (Fe, Cr, Ti and V) (Fig. 6a), (2) those that were enriched at site H and B (1.7 km and 4 km from the river mouth, respectively) and occurred close to background concentrations (Al, Cu, La and U) at site SG (c. 9 km from the river mouth) (Fig. 6b) and (3) those that were particularly strongly enriched in both the upper and lower trap at site B (Co, Mn, Ni and Zn) (Fig. 6c). These results are thus in line with the hydrochemical data for the inflowing river, with low relative concentration of Cr, Fe, Ti and V and elevated relative concentrations of Al, Co, Cu, La, Mn, Ni and Zn (Fig. 3; Table 2). The organic matter (LOI) concentration in the trap material had a pattern similar to the metals of the second group (Fig. 6b). In terms of *aqua regia* concentrations of trap material, the metals of group 2 tended to increase with decreasing pH in the estuary, while concentration of metals in group 3 tended to increase with increasing pH (Fig. 4; Fig. 6b-c). There was no clear connection

between the overall metal discharge from the river and corresponding metal deposition in the sediment traps.

[Figure 6a-c here]

The concentrations of metals extracted by the weaker reagents showed only small variations over time (Fig. 7a-c). Since extractions by Am-ac and Na-pr were only done on selected samples we preferred to illustrate these results with median, minimum and maximum values only (Table 3).

The Ha leach efficiently extracted (medians in decreasing order) Mn (c. 85% of the *aqua regia* concentrations) > Zn (75%) > Co (51%) > La (48%) > Ni (48%) > Fe (43%) > Al (40%) > U (32%). This indicates that these metals are abundantly associated with Al-, Fe- and Mn-oxyhydroxides and/or possibly to some degree to monosulphides and carbonates. Copper, Ti and V were on the other hand weakly extracted with Ha (Table 3).

The Na-pr leach efficiently extracted U (c. 53% of the *aqua regia* concentrations) and moderately to weakly (in decreasing order) Zn (23%) > Cu (19%) > La (18%) > Al (14%) > Mn (13%) > Ni (8%) > Fe (8%) > V (7%) > Co (6%).

The Am-ac leach efficiently extracted U (c. 46% of the *aqua regia* concentrations) and Mn (30%), and moderately to weakly (in decreasing order) Zn (21%) > La (14%) > Al, Co, Ni (9%) > Cu (8%) > Fe (2%).

[Table 3 here]

[Figure 7a-c here]

4.4. Bottom sediments

The concentrations and spatial patterns of the *aqua regia* extractable metal concentrations and LOI in the bottom sediments were very similar to those in the corresponding sediment-trap materials (Fig. 6a-c). In addition, the different chemical extractions delivered approximately similar results for the bottom sediments as for the sediment-trap material, i.e. the metals are associated to the same fractions in both the sediment-trap material and in the bottom sediments (Fig. 7a-c).

At site SG (furthest out in the estuary) the *aqua regia* extractable concentrations of Co, Mn, Ni and Zn were higher in the trap material than in the underlying bottom sediments (Fig. 6a-c). In addition, Mn and associated metals (Co, Ni and Zn) were to a large part associated with the Ha fraction in the uppermost oxidized layer in the bottom sediment at this site (Fig. 7c). At site B, an opposite pattern was seen, i.e. only small amounts of Mn and the associated metals (Co, Ni and Zn) were extracted with Ha in the surface sediment, while the Ha fraction increased with depth (Fig. 7c).

5. DISCUSSION

5.1. Cr, Fe, Ti & V

Chromium, Fe, Ti and V were not enriched in any of the media examined in this study and are consequently not particularly mobile in AS soil landscapes (Table 2; Fig. 6a). The background concentrations of Cr, Ti and V in the river water and estuarine sediments are explained by their participation in chemically resistant fractions in the AS soils (Sohlenius and Öborn, 2004; Åström, 1998). The low relative mobility and transport of Fe are typical for Finnish (boreal) AS soils (Nordmyr et al., 2006; Sohlenius and Öborn, 2004; Åström, 1998; Österholm and Åström, 2002) and a possible explanation is precipitation of Fe-oxyhydroxides in soil cracks after oxidation of sulphides, thus inhibiting release of Fe from these soils (Ritsema et al., 1992; Sohlenius and Öborn, 2004).

In a study by Åström and Corin (2000) in a nearby similar river (Petalax River), Fe was mostly transported in the particulate phase as a result of co-flocculation with humic substances (>50%) and only to a minor extent as Fe-oxyhydroxides coated with negatively charged humic substances (the anionic fraction) and as Fe²⁺ and/or uncoated positively charged Fe-oxyhydroxides (cationic fraction). In the trap material and in the bottom sediments Fe was to a large extent extracted with Ha (c. 40 % of the *aqua regia* concentration), which shows that Fe abundantly occurs as hydroxides and/or monosulphides (Table 3). Because none of the metals enriched in the studied materials had a

distribution pattern similar to Fe, it is assumed that Fe-oxyhydroxides are of minor importance in controlling the geochemical patterns and dynamics in the studied environment.

5.2. Al, Cu, La & U

The high concentrations and loads of Al, Cu, La and U (the Al-group metals) in the river water (Table 2; Fig. 3) are a result of leakage from the AS soils in the area (Åström and Björklund, 1995), since the low pH in these soils cause phyllosilicates to release large amounts of metals like Al (Ritsema et al., 1992; van Breemen, 1973) and La into the drainage water. Copper on the other hand is most likely released from the sulphides (Huerta-Diaz and Morse, 1992) and U from oxidation of U (IV) minerals in the AS soils (Åström et al., accepted). In the nearby AS soil affected Petalax River, sampled on one occasion by Åström and Corin (2000), Al was mostly transported in cationic form (Al^{3+} , inorganic phase) but also to some extent in the humus-associated phase (anionic form) and on particles. On the other hand, 50% of Cu was transported as particles and in humus-associated phases (anionic form) and 50% in the inorganic phase (cationic form) (Åström and Corin, 2000). La and U were not included in that study.

The similar spatial and temporal concentration patterns of LOI and the Al-group metals (*aqua regia* extractable) in both the sediment-trap material and the underlying bottom sediments (Fig. 6b) indicate that these metals are strongly associated with organic matter. This is supported by the association of Al and Cu with humic substances in the river (see above), and in line with results of other studies (Boyle et al., 1977; Elbaz-Poulichet et al., 1999; Forsberg et al., 2006; Hoyle et al., 1984; Sholkovitz, 1976; Widerlund, 1996). In addition, the Al-group metals were moderately to extensively extracted with Na-pr (removes easily extractable organic matter), i.e. 14-53% of the *aqua regia* extractable concentration (Table 3). The relatively low extractability of Cu with both Na-pr and Ha is noteworthy (Table 3), and suggests that Cu is preferentially associated with an organic-matter phase not dissolved by the Na-pr extraction (Hall et al., 1996b).

Aluminium and La were, however, more abundantly leached with Ha than with Na-pr (Table 3). This is interpreted as association preferentially with a hydroxide phase, which is in line with our field observations of lighter coloured water (even whitish) in the inner estuary compared to the river mouth and with flocs clearly visible approximately within 200 m from the river mouth. In Australia the same phenomenon with white flocs has occasionally been observed and has been interpreted as Al-hydroxides or Al-hydroxysulfate (Sammut et al., 1996). The importance of precipitation/adsorption processes in the estuarine zone, where a sharp increase in pH and salinity occurs, is well documented (e.g. Boyle et al., 1977; Crerar et al., 1981; Johnson, 1986). Since the Al-group metals have background concentrations at site SG, these metals are normally not transported to such far distances in the estuary. Moreover, as the highest concentrations of the Al-group metals in the sediment trap material were found during low pH conditions at site H and B (Fig. 4; Fig 6b) it is also possible that at high pH conditions a significant part of the Al is deposited (depleted from the water column) before reaching site H and B.

The similar distribution pattern of Al and LOI is thus caused by either: (1) direct binding of Al by organic matter ultimately depositing in the estuary, (2) a common spatial settling pattern for Al-oxyhydroxides and organic matter or (3) formation of mixed particles composed of Al-oxyhydroxides and organic compounds. Accordingly, the metals Cu, La and U, which were closely associated with LOI and Al, might either be bound to the organic matter, to the fresh Al-hydroxide precipitates or to the mixed particles.

Copper is to a lesser extent transported to site B compared to Al, La and U (Fig. 6b). This indicates that Cu is more readily precipitated close to the river mouth than the other metals. Lanthanum on the other hand occurred in relatively high concentrations at site B, as compared to those at site H (Fig. 6b). This may be pH dependent patterns, as it can be expected that pH always increase, more or less, when going from the river mouth into the estuary.

In autumn 2006, after a extremely dry summer followed by abundant rain, the Vörå River and its estuary were strongly affected by acid and metal rich waters discharging from the AS soils (river water sampling was done in November; Fig. 3), resulting in serious and significant fish kills and turquoise coloured water as far out as 7-8 km from the river mouth. At this time at site H, thick layers of Al-flocks were observed at the bottom and significant amounts of dead fish. However, at site SG no Al-hydroxide precipitates were observed, which is in line with the chemical data (Fig. 7b). The fish probably died as a result of low pH and Al-precipitates clogging the gills (Bjerknes et al., 2003; Peuranen et al., 1993; Björkqvist and Wepppling, 1987). While there is no question that the huge

amounts of metals in the river in autumn 2006 (Fig. 3) were caused by the flushing of farmland AS soils in the catchment, sulphidic dredge materials excavated in autumn/winter 2005 and 2006 and placed along the banks of the lower reaches of the river, may have contributed to the metal load of the river.

5.3. Co, Mn, Ni & Zn

The high concentrations and loads of Co, Mn, Ni and Zn (the Mn-group metals) in the river water (Table 2; Fig. 3) are most likely partly released from silicates in AS soils due to the low pH in the soil (Sohlenius and Öborn, 2004) and from sulphides due to oxidation (e.g. Huerta-Diaz and Morse, 1992; Huerta-Diaz et al., 1998; Morse and Luther III, 1999; Sohlenius and Öborn, 2004). These metals are presumably carried as cations in the river water, as in the nearby AS soil affected Petalax River (Åström and Corin, 2000).

The Mn-group metals behave in a different manner than the Al-group metals in the estuary. This is seen by the much higher concentrations (*aqua regia* extraction) in the sediment-trap material and underlying bottom sediments at site B compared to site H (Fig. 6c). In addition, these metals are only marginally extracted by Na-pr (Table 3), which suggests that the precipitation and deposition mechanisms are different as compared to that of the Al-group metals. This is in line with the deposition patterns of Mn in an adjacent AS soil affected estuary (Heikkilä (1999), and with other studies suggesting low association of Mn and Zn with organic complexes (Burton et al., 2006; Forsberg et al., 2006; Tribovillard et al., 2006).

Manganese was nearly quantitatively extracted with the Ha leach (Fig. 7c) and moderately extracted with the Am-ac leach (Table 3). This strongly indicates that the high Mn concentrations are predominantly the result of precipitation and deposition of Mn-oxyhydroxides with additional contribution by Mn-carbonates (the acid Am-Ac leach). However, it cannot be excluded that a small amount of Mn-sulphides and/or Mn adsorbed to FeS was converted into hydroxides during sample handling. Since Co, Ni and Zn had similar spatial patterns and response to chemical reagents as Mn, it is reasonable to suggest that these metals are adsorbed and controlled by Mn-oxyhydroxides and possibly Mn-carbonates (Drever, 1982; Tribovillard et al., 2006).

The most likely explanation for the relatively low concentrations of the Mn-group metals at site H is that above circumneutral (alkaline) pH conditions are needed for significant amounts of Mn to precipitate (Braungardt et al., 2003; Ponter et al., 1992). Thus, the plume of strongly to slightly acidic surface water acts as an efficient carrier of the Mn-group metals far out in the estuary. The variable concentrations of Mn (and partly for Co, Ni and Zn) in the sediment-trap material and in the bottom sediments, particularly at site B (Fig. 6c), can consequently be ascribed to pH variations caused by the relative contribution by, and quality of, the inflowing river water. This spatial and temporal variability is supported by the geochemistry of the underlying sediments and other deep sediment cores from the same area (Nordmyr et al., 2007).

At site SG, the metal concentrations (*aqua regia* extractable) were higher in the trap material than in the underlying bottom sediments (Fig. 6c). This indicates relatively little deposition at this site and/or resuspension due to strong flows at this relatively open and unsheltered site. In the surface layer of the bottom sediment at site SG, the Mn-group metals were, however, above background concentrations and quantitatively extracted with Ha, while down core they approached background concentrations and were only marginally extracted by this reagent (Fig. 6c; Fig. 7c). This suggests reduction of Mn-oxyhydroxides at depth and associated release of Mn^{2+} into the pore water with subsequent migration up to the oxidised brownish surface layer, where re-precipitation as oxyhydroxides occurs. This mechanism is supported by other studies (Morford et al., 2005; van den Berg et al., 2000; Widerlund and Ingri, 1996).

In contrast, at site B where the Mn-group metals were particularly abundant in both the sediment-trap material and in underlying bottom sediments (Fig. 6c), the Ha-extractable fraction in the uppermost sediment layer was lower than down the core and also lower than in the upper layers at site SG (Fig. 7c). This might be explained by a decline in bottom-water (and thus sediment) redox potential during the last few years (or during the winter before the sediment sampling), causing the release of Mn^{2+} and associated metals in the surface sediments and thus leaching into the overlying water (Morford et al., 2005; van den Berg et al., 2000). Re-precipitation of Mn-oxyhydroxides is likely to occur at oxidising conditions in the water column (Ingri et al., 1991) and thus there is potential for re-deposition of Mn-oxyhydroxides in the sediment traps.

6. CONCLUSION

This study shows that AS soils, formed as a result of farmland drainage, strongly affect both the chemistry of the downstream waters and the downstream estuarine sediments.

In the estuary, a strong fractionation in depositional patterns of a suite of metals abundantly leached from AS soils was detected: (1) precipitation and deposition of Al, Cu, La and U occurred in the inner estuary either together with organic matter and/or Al-hydroxides, and (2) deposition of Co, Mn, Ni and Zn occurred in the central/outer estuary mainly in the form of Mn-oxyhydroxides with co-precipitated Co, Ni and Zn. Yet other metals (Fe, V, Cr and Ti) were not, in relative terms, abundantly leached from AS soils and thus not enriched in the river and its estuary. These patterns are largely the result of pH and salinity gradients, the behaviour of organic matter, redox variations and different precipitation and settling mechanisms

The on-going sedimentation and isostatic land uplift continuously decrease the water depth in the estuary of the Vörå River. This will ultimately lead to more pronounced pH surges, and also to extending dredging activities in order to maintain water depths required for the boat traffic. There is thus a risk of both chemical and physical mobilisation of the high metal concentrations found in the bottom sediments throughout the estuary. It is therefore strongly recommended that detailed risk assessments are carried out in the Vörå River estuary, as well as in other similar estuaries in Finland and elsewhere, where an abundance of acid sulphate soils in the catchments are delivering large amounts of acidity and metals to downstream waters.

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FIGURE CAPTIONS

Fig. 1. The sampling locations in the estuary of Vörå River. The shaded areas in Finland represent the land area covered by water since the retreat of the Pleistocene ice sheet. In depressions and valleys within this area, sulphur-rich brackish-water sediments are abundant on which AS soils are developed.

Fig. 2. The specific runoff in Kyrö River during year 2004-2006 and for the specific sampling periods and the sea level in the nearby city of Vasa during 2004-2006. Sea level data was obtained from the Finnish Institute of Marine Research.

Fig. 3. Hydrochemistry and specific runoff for the Vörå River during 2004-2006.

Fig. 4. The pH in the surface water at respective sites during the beginning and end of the sampling periods. The pH in the surface water represent the minimum pH in the water profiles.

Fig. 5. The amount of material deposited in the sediment traps and the mean specific runoff (Vörå River) during the sampling periods. Note that winter/spring sampling (17.03-24.04.2006) only occurred at site H.

Fig. 6a. *Aqua regia* extractable concentrations of Fe, Cr, Ti and V in the sediment-trap material over time (to the left) and in the underlying bottom sediments (to the right). The background concentration is the median concentration of 317 samples of similar sediments deposited before industrialisation (Åström and Björklund 1997).

Fig. 6b. *Aqua regia* extractable concentrations of LOI, Al, Cu, La and U in the sediment-trap material over time (to the left) and in the underlying bottom sediments (to the right). The background concentration for Al, Cu and La is from 317 sampled reduced mother sediments from western Finland published in Åström and Björklund (1997). Since LOI and U were not determined by Åström and Björklund (1997) the background values for these are from a similar study by Nordmyr et al. (2006).

Fig. 6c. *Aqua regia* extractable concentrations of Co, Mn, Ni and Zn in the sediment-trap material over time (to the left) and in the underlying bottom sediments (to the right). The background concentration is the median concentration of 317 samples of similar sediments deposited before industrialisation (Åström and Björklund 1997).

Fig. 7a-c. The vertical distribution of different fractions of metals in the sediment cores (to the left) and the temporal and spatial distribution of the same fractions in the sediment-trap material (to the right) at site H, B and SG. Ha = Hydroxylamine extractable concentration, AR = the *aqua regia* extractable concentrations minus the Ha extractable concentrations, and residual = total concentrations minus the *aqua regia* extractable concentrations.

TABLES

Table 1. General characteristics of the sampling sites.

	Vörå River	Site H	Site B	Site SG
Lat. N	63°14.364'	63°16.224'	63°17.287'	63°19.589'
Long. E	22°15.593'	22°14.428'	22°14.18'	22°16.621'
Distance from the river mouth (km)		c.1.7	c. 4	c. 9
Water depth (m)	—	c. 10	c.17	c. 10
Surface water: pH	Min	4.3	4.7	6.1
	Median	4.5	6.6	6.9
	Max	6.9	7.6	7.6
Surface water: specific EC (mS cm ⁻¹)	Min	0.3	1.4	1.5
	Median	0.6	3.1	4.0
	Max	1.59	5.7	5.1

Table 2. Hydrochemistry of Vörå River (VR) and Lappfjärd River (LR). The latter is used as a reference for a river not affected by AS soils.

		VR		LR [*]	VR/LR
		Median	Mean	Mean	Mean
Al	mg l ⁻¹	5.9	6.8	0.31	22
Cu	µg l ⁻¹	11	11	2.5	4.5
La	µg l ⁻¹	39	48	—	—
U	µg l ⁻¹	0.75	0.69	0.10	7.0
Co	µg l ⁻¹	34	38	0.52	72
Mn	µg l ⁻¹	1400	1500	44	34
Ni	µg l ⁻¹	77	85	2.0	42
Zn	µg l ⁻¹	170	180	15	12
Cr	µg l ⁻¹	1.9	2.1	1.1	1.8
Fe	µg l ⁻¹	1100	2100	770	2.8
Ti	µg l ⁻¹	3.7	13	—	—
V	µg l ⁻¹	0.60	1.3	0.84	1.5

— = not determined

^{*} Data published in Roos and Åström (2005).

752 Table 3. The elemental concentrations (median, min and max) in the sediment-trap material measured
753 with five different separately performed chemical extractions.

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Extraction	Determinant	Site H	Site B (upper)	Site B (lower)	Site SG
		Median (Min - Max)	Median (Min - Max)	Median (Min - Max)	Median (Min - Max)
Total	Al (%)	8.1 (7.4-10), <i>n</i> =8	7.7 (6.2-8.3), <i>n</i> =8	7.6 (6.9-8.1), <i>n</i> =8	5.4 (1.9-6.6), <i>n</i> =8
<i>Aqua Regia</i>	Al (%)	5.4 (4.1-8.3), <i>n</i> =9	6.0 (4.0-8.8), <i>n</i> =8	6.0 (4.8-8.5), <i>n</i> =8	1.8 (0.85-2.4), <i>n</i> =8
Ha	Al (%)	2.2 (1.3-4.3), <i>n</i> =9	2.8 (1.3-4.9), <i>n</i> =3	2.4 (1.5-4.3), <i>n</i> =8	0.52 (0.29-1.2) <i>n</i> =6
Na-pr	Al (%)	1.5 (0.5-2.1), <i>n</i> =8	0.84 (0.67-2.6), <i>n</i> =3	0.45 (0.18-1.0), <i>n</i> =4	0.11, <i>n</i> =1
Am-ac	Al (%)	0.55 (0.44-0.92), <i>n</i> =8	0.7 (0.24-1.4), <i>n</i> =4	0.57 (0.35-0.92), <i>n</i> =4	0.06, <i>n</i> =1
Total	Cu (µg g ⁻¹)	71 (62-90)	61 (50-74)	60 (56-70)	32 (20-41)
<i>Aqua Regia</i>	Cu (µg g ⁻¹)	64 (56-80)	57 (50-68)	55 (52-66)	31 (19-35)
Ha	Cu (µg g ⁻¹)	4.1 (2.7-5.9)	5.7 (4.0-8.8)	4.0 (2.8-7.2)	7.1 (3.3-13)
Na-pr	Cu (µg g ⁻¹)	17 (10-21)	10 (7.1-18)	8.2 (6.5-12)	4.4
Am-ac	Cu (µg g ⁻¹)	5.5 (4.5-7.5)	5.6 (3.2-6.6)	4.6 (3.2-5.3)	1.9
Total	La (µg g ⁻¹)	184 (130-224)	206 (170-270)	199 (167-295)	91 (51-142)
<i>Aqua Regia</i>	La (µg g ⁻¹)	185 (112-208)	227 (170-313)	219 (172-304)	80 (49-124)
Ha	La (µg g ⁻¹)	87 (31-112)	116 (49-190)	98 (45-172)	40 (20-96)
Na-pr	La (µg g ⁻¹)	62 (17-76)	41 (24-116)	16 (5.4-49)	10
Am-ac	La (µg g ⁻¹)	27 (21-32)	41 (21-45)	36 (27-37)	6.7
Total	U (µg g ⁻¹)	9.8 (6.4-14)	12 (7.5-14)	11 (7.9-15)	4.9 (1.8-6.7)
<i>Aqua Regia</i>	U (µg g ⁻¹)	8.1 (5.7-12)	9.7 (8.0-13)	9.6 (8.0-12)	3.5 (1.5-4.9)
Ha	U (µg g ⁻¹)	2.2 (1.6-2.7)	3.0 (2.2-3.6)	3.0 (2.3-3.3)	1.3 (0.77-1.67)
Na-pr	U (µg g ⁻¹)	4.9 (4.0-5.8)	4.6 (4.1-7.1)	4.3 (3.4-4.5)	2.1
Am-ac	U (µg g ⁻¹)	3.6 (2.6-3.8)	4.1 (2.8-5.0)	4.3 (3.8-4.8)	1.9
Total	Co (µg g ⁻¹)	32 (21-63)	81 (66-143)	95 (76-147)	81 (32-123)
<i>Aqua Regia</i>	Co (µg g ⁻¹)	29 (17-55)	78 (60-138)	85 (70-130)	72 (30-112)
Ha	Co (µg g ⁻¹)	11 (42-31)	40 (19-78)	40 (23-81)	50 (19-97)
Na-pr	Co (µg g ⁻¹)	3.2 (1.8-6.0)	4.2 (2.8-13)	3.2 (2.5-6.3)	2.7
Am-ac	Co (µg g ⁻¹)	4.1 (2.4-6.6)	7.5 (2.5-13)	8.4 (4.1-12)	0.96
Total	Mn (µg g ⁻¹)	817 (607-3464)	6002 (3159-20120)	9300 (5553-21278)	6984 (2300-10229)
<i>Aqua Regia</i>	Mn (µg g ⁻¹)	704 (426-3242)	5585 (3277-23014)	9106 (4950-26673)	6451 (2245-10251)
Ha	Mn (µg g ⁻¹)	497 (248-2834)	5190 (2911-18052)	6578 (3930-20294)	6679 (1750-8933)
Na-pr	Mn (µg g ⁻¹)	169 (63-1030)	683 (369-1797)	750 (246-1888)	611
Am-ac	Mn (µg g ⁻¹)	325 (141-1731)	1349 (1176-2458)	3056 (1233-4293)	955
Total	Ni (µg g ⁻¹)	60 (43-78)	81 (69-109)	83 (73-108)	71 (25-89)
<i>Aqua Regia</i>	Ni (µg g ⁻¹)	58 (37-73)	80 (67-112)	83 (73-106)	63 (26-84)
Ha	Ni (µg g ⁻¹)	24 (9.9-41)	35 (20-67)	34 (21-55)	42 (15-70)
Na-pr	Ni (µg g ⁻¹)	8.4 (3.8-12)	5.0 (4.4-15)	4.1 (3.0-7.4)	3.9
Am-ac	Ni (µg g ⁻¹)	6.0 (4.4-6.8)	6.5 (5.8-6.8)	6.1 (5.7-7.8)	6.8
Total	Zn (µg g ⁻¹)	304 (209-421)	566 (330-676)	544 (368-670)	395 (196-589)
<i>Aqua Regia</i>	Zn (µg g ⁻¹)	278 (159-367)	513 (300-578)	490 (358-615)	325 (157-508)
Ha	Zn (µg g ⁻¹)	199 (95-306)	416 (189-483)	393 (193-525)	222 (108-459)
Na-pr	Zn (µg g ⁻¹)	59 (46-115)	131 (55-219)	76 (71-90)	93
Am-ac	Zn (µg g ⁻¹)	56 (32-95)	94 (65-135)	96 (67-113)	80
Total	Cr (µg g ⁻¹)	48 (45-58)	40 (33-49)	42 (36-50)	48 (11-60)
<i>Aqua Regia</i>	Cr (µg g ⁻¹)	38 (33-41)	33 (29-47)	34 (31-40)	34 (12-48)
Ha	Cr (µg g ⁻¹)	—	—	—	—
Na-pr	Cr (µg g ⁻¹)	—	—	—	—
Am-ac	Cr (µg g ⁻¹)	—	—	—	—
Total	Fe (%)	4.2 (3.7-5.0)	3.8 (3.2-4.5)	4.1 (3.5-4.5)	3.8 (1.4-4.4)
<i>Aqua Regia</i>	Fe (%)	3.4 (2.8-4.2)	3.1 (2.9-3.9)	3.4 (3.0-3.6)	2.6 (1.1-3.3)
Ha	Fe (%)	1.4 (0.83-2.4)	1.5 (0.84-2.1)	1.5 (0.80-1.8)	1.1 (0.53-1.9)
Na-pr	Fe (%)	0.44 (0.17-0.59)	0.26 (0.14-0.63)	0.13 (0.055-0.31)	0.17
Am-ac	Fe (%)	0.081 (0.047-0.14)	0.070 (0.036-0.12)	0.0826 (0.052-0.11)	0.018
Total	Ti (µg g ⁻¹)	2654 (2214-2910)	1950 (1485-2373)	2014 (1749-2560)	3309 (873-3940)
<i>Aqua Regia</i>	Ti (µg g ⁻¹)	874 (805-964)	696 (563-844)	728 (639-812)	873 (305-1118)
Ha	Ti (µg g ⁻¹)	4.7 (2.6-5.4)	4.3 (2.3-6.0)	3.5 (2.7-4.5)	6.0 (3.3-16)
Na-pr	Ti (µg g ⁻¹)	BD	BD	BD	BD
Am-ac	Ti (µg g ⁻¹)	BD	BD	BD	BD
Total	V (µg g ⁻¹)	50 (44-58)	42 (32-51)	45 (34-54)	60 (20-75)
<i>Aqua Regia</i>	V (µg g ⁻¹)	35 (31-36)	34 (24-41)	33 (28-45)	36 (15-47)
Ha	V (µg g ⁻¹)	4.5 (3.0-6.2)	5.0 (3.4-6.7)	4.6 (3.4-7.3)	7.5 (6.7-12)
Na-pr	V (µg g ⁻¹)	3.8 (1.5-4.6)	2.5 (1.5-5.2)	1.6 (1.3-2.3)	1.7
Am-ac	V (µg g ⁻¹)	BD	BD	BD	BD

n = number of samples analysed

— = not analysed

BD = below detection limit

Total extraction (HClO₄-HNO₃-HCl-HF)

Aqua Regia extraction (2:2:2, HCl:HNO₃:H₂O)

Ha = hydroxylamin extraction

Na-pr = Sodium pyrophosphate extraction

Am-ac = ammonium acetate-EDTA extraction

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6(a)

Fig.6(b)

Fig.6(c)

Fig.7(a)

Fig.7(b)

Fig.7(c)