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Long-term lake sediment records and factors affecting the evolution of metal(loid) drainage from two mine sites (SW Finland)

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ABSTRACT

Geochemical profiles were analyzed from ^{137}Cs-dated lake sediment cores near two sulfide mines (Ylöjärvi and Haveri) in SW Finland to obtain long-term records of elemental discharge to surface waters from the mine sites before, during and after mining. The results showed that both the intensity and chemical composition of mine water loading changed over time, and that pre-mining land uses (e.g. agriculture) also mobilized mining-associated elements in an area with mine potential. At Ylöjärvi the sulfide-derived metal concentrations peaked during mining, but the lack of post-closure peaks probably resulted from the diffuse nature of the loading from the tailings facility. Major post-mining acid mine drainage (AMD) impact was detected at Haveri, where the relative amounts of metals accumulated in sediments corresponded to the amounts of metals leached from the oxidized layer of the tailings. However, the temporal sequence of metal loading (Ni > Cu, S > Ag, As, Cd, Fe, Zn, V > Co, Mo) did not follow the classical sequence of sulfide weathering due to geochemical processes acting along the pathway to the receiving lake. The metal concentrations gradually decreased in recent sediments because of the progressive depletion of sulfides in the oxidized surface tailings, attenuating mechanisms such as adsorption by secondary Fe(III) minerals and increasing percolation of the contaminant plume into the groundwater. Nevertheless, the recent recorded values remain above the pre-anthropogenic levels, especially for copper. The examination of lake sediment cores allows assessment of the long-term evolution of metal and metalloid drainage from mining areas including pre-mining conditions.

1. Introduction

Sulfide mining and ore processing may have a long-term adverse effect on surface waters and groundwater both during and after mining operations, and natural acid rock drainage may also occur prior to any mining activity (Nordstrom, 2011). Acid mine drainage (AMD), caused by the oxidation of sulfide minerals in waste rock piles and tailings, carries trace metals, metalloids and sulfate, and may deteriorate the surrounding water quality for decades or centuries after mine closure. Many factors affect the quality of mine drainage waters, including the geology of the ore deposit, the climate, mining and mineral processing methods, waste management, and the particle size of mill tailings (Plumlee, 1999).

While the geochemical and mineralogical processes causing contaminated drainage from mine sites have been extensively investigated, long-term studies on the evolution of mine drainage have been less common due to the potentially long time periods involved. Such temporal studies on the evolution of mine drainage would not only elucidate the sequences of events in the breakdown of metal-bearing minerals in mine wastes, but also shed light on the activation of mechanisms that attenuate the metal-laden drainage, such as decreased oxygen diffusion to the oxidation front and the formation of secondary precipitates along flow paths. These data could then be used to estimate the likely course of events at mine sites in various stages of their life cycles. However, the uniqueness of each mine site prevents the compilation of such a scheme by combining data from separate mine sites in different stages of development. Instead, complete histories from mine sites of differing characteristics may provide a more attractive alternative for studying the long-term evolution of mine drainage.

Lake and river sediments are a sink for pollutants transported by surface waters. Undisturbed and dated sediment cores from aquatic environments provide temporal profiles of selected elements, species and radionuclides, allowing estimates of the anthropogenic impact on the load of pollutants over time. Many recent studies have focused on historic metal and metalloid contamination by examining undisturbed lake sediment cores (Couillard et al., 2004, 2008; Salonen

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et al., 2006; Wennrich et al., 2004), and on modern contamination by sampling the recent top sediments of rivers (Gale et al., 2004; Hygelund et al., 2001; Lord and Morgan, 2003; Osán et al., 2007; Pinto et al., 2004).

In 1986, the Chernobyl nuclear fallout formed a prominent peak in environmental ^{137}Cs, especially in Europe. This peak can be analyzed by a gamma-ray counting technique and employed to study sedimentation in any lacustrine depositional environment that was active during that time. With the help of ^{137}Cs dating, the samples collected for this study have been divided in to three sections representing sediments deposited before, during and after the operation of two metal mines. The mining impact can be compared with the background values of deeper pre-mining sediments. The background values additionally indicate the contamination potential due to other land uses in areas with ore potential where, for instance, arsenic (As) concentrations in the bedrock and topsoil may be higher than average.

This study combined mineralogical–geochemical investigations of the processes that affect the generation and dispersion of drainage from two mine sites, the Ylöjärvi Cu–W–As mine and Haveri Au–Cu mine in SW Finland, with long-term spatial and temporal records of metal accumulation in the sediments of the recipient surface water bodies. The aim was to compare the impact of mining on lake sediment records affected by pollution from these contrasting yet low-grade sulfide mines, which have been abandoned for approximately 50 years.

2. Background information

2.1. Site description

The Ylöjärvi Cu–W–As and Haveri Au–Cu mines are situated at the western end of the Tampere Schist Belt in SW Finland (Fig. 1). The belt is mainly composed of felsic-intermediate and mafic metavolcanic rocks, turbiditic metasedimentary rocks and plutonic intrusions cutting the supracrustal rocks (Kähkönen, 1989; Kähkönen and Leveinen, 1994; Ojakangas, 1986). Higher than average As concentrations are characteristic of this belt (median 10 mg/kg in the bedrock vs. 0.9 mg/kg in the whole country; Lahtinen et al., 2005). Even though both mines are located within the Tampere Schist Belt, the ore deposits are very different. The mines are located in the same climatic and vegetation zone. Annual mean temperature is +4 °C and rainfall is 600 mm (Finnish Meteorological Institute). The snow cover typically lasts from mid-December to mid-April.

2.1.1. Ylöjärvi

The Ylöjärvi deposit is hosted by a tourmaline breccia, and the surrounding rocks are mainly tuffites with porphyrite intercalations (Himmi et al., 1979). The main ore minerals in the breccia matrix are pyrrhotite ($Fe_{(1-x)}S$), chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS), and scheelite ($CaWO_4$). They are associated with minor sulfides, oxides, and minute concentrations of uraninite (UO_2), native bismuth, silver, and gold (Himmi et al., 1979) (Table 1). The gangue minerals consist of tourmaline, quartz, chlorite, epidote, plagioclase, and hornblende. Calcite is merely a minor constituent of the mineralization.

The Ylöjärvi Cu–W–As mine was operated from 1943 to 1966 and produced 4 million tons of tailings and sludge deposited in the two tailings areas of 4 and 17 ha (Fig. 1). Copper concentrate was the main product while WO_3 concentrate was recovered from 1948 to 1961, and As concentrate merely from 1949 to 1953 (Kukkonen et al., 1967) (Table 1). Hence, large quantities of arsenopyrite-bearing tailings were deposited in the larger of the two tailings areas, which was inaugurated in 1952. Mining activities left behind two open pits and underground galleries, where tailings (approx. 1.1 Mt) were also deposited in the late stages of the operation. Water from the adjacent Lake Parosjärvi, which has an outlet leading to Lake Vähävahantajärvi, was used in processing the ore in a closed cycle, and the first open pit as a clarification pool. As the mining works proceeded under the lake, it was dewatered, and water from the adjacent Lake Saarijärvi was used for processing. After the mine was closed, Lake Parosjärvi again filled up with water, and part of the smaller tailings area, the open pits and the underground galleries with tailings were consequently inundated. Reducing conditions prevail at the bottom of the lake, but twice a year the seasonal overturn mixes the oxidative surface water with the hypolimnetic waters, causing degradation and dissolution of the material. However, the main metal sources in the surface waters are the tailings areas above ground. According to Carlson et al. (2002), toe seepage occurs in all directions from the larger tailings area and there is surface drainage to Lake Parosjärvi. The surface waters originating from the mining area are transported in a 7 km long watercourse through Lake Vähävahantajärvi to Lake Näsijärvi (Fig. 1).

Comprehensive remediation measures have not been undertaken at the Ylöjärvi mine area. Though, over decades the ditch leading from the larger tailings area to the Lake Parosjärvi has been limed in order to increase the pH and enhance the precipitation of Fe(III) hydroxides.

2.1.2. Haveri

The Haveri Au–Cu formation is a Cyprus-type volcanogenic massive sulfide (VMS) deposit consisting of tholeiitic basic metalavas, metalava breccia, metatuff and metatuffite (Mäkelä, 1980). Chemical sediments, such as limestone and chert, appear in the Haveri formation. Other main rock types described in the surrounding area are calc-alkaline

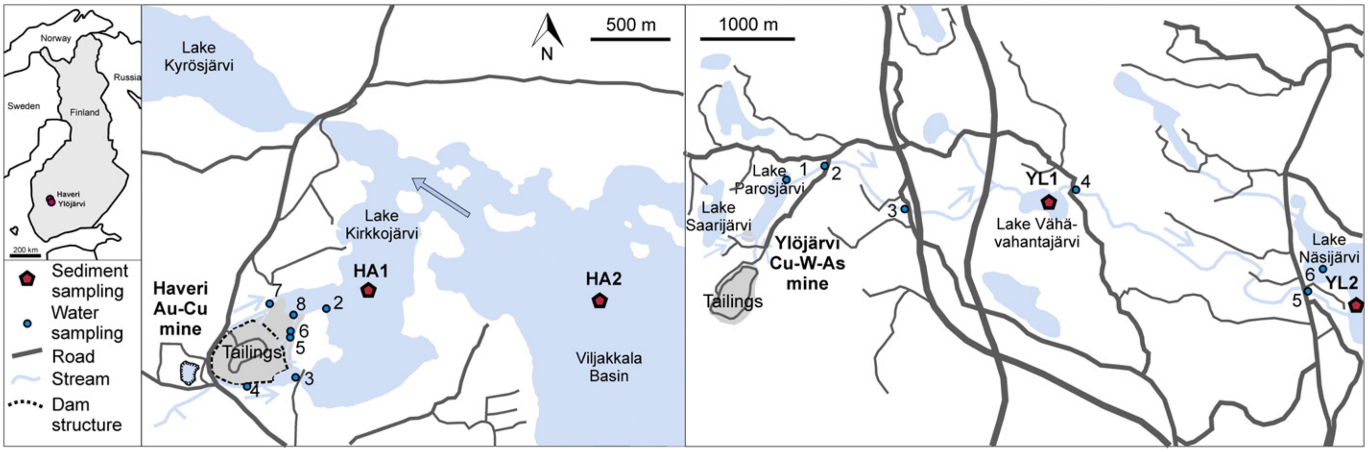

Fig. 1. An index map presenting the location of Ylöjärvi and Haveri mines and site-specific maps of the study areas indicating lake sediment and water sampling points.

Table 1
Ore type, sulfide and carbonate content, mineralogy, ore processing methods and waste management, as well as the expected environmental impacts of these factors at the Ylöjärvi and Haveri mine sites.

Mine	Ore type	Sulfide and carbonate content	Major and minor sulfides and oxides	Mining and mineral processing methods	Waste management
Ylöjärvi Cu–W–As 1943–66	• Tourmaline breccia embedded in tuffites with porphyrite intercalations[1]	• Sulfide content <1% on average[1] • Low carbonate content (calcite)[1]	• Major: pyrrhotite $[Fe_{(1-x)}S]$, chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS)[1] • Minor: pyrite (FeS_2), sphalerite (ZnS), galena (PbS), cubanite ($CuFe_2S_3$), mackinawite $[(Fe,Ni)S_{0.9}]$, molybdenite (MoS_2), magnetite (Fe_3O_4), ilmenite ($FeTiO_3$), cassiterite (SnO_2), uraninite (UO_2)[1]	• Open pit and underground galleries[3] • 1943–1966 Cu flotation[3] • 1948–1961 WO3 flotation with tall oil + hydrochloric acid leach for elimination of apatite[3] • 1949–53 As flotation with $CuSO_4$ activator under acidic conditions[3]	• Total of ca. 4 Mt of tailings[9] • 1943–52 a 4 ha waste area in the southern end of Lake Parosjärvi • 1953–66 a 17 ha waste area on peat bog with no dam structure • 1960–66 underground galleries were filled with coarser tailings (ca. 1.1 Mt) • Lake water used in ore processing. In the 1950s the waste waters were discarded into an outlet of Lake Parosjärvi[3]
	Expected environmental impacts				
	• Near neutral pH and varying metal contents in drainage water	• Moderate to low neutralization potential[2] • Sulfide oxidation and metal release under near neutral conditions[2]	• Release of Fe, Cu, As, SO_4 and minor Ni, Zn and Mo • Moderate acid generation	• Tailings and impurities in process waters occur as particulate matter • At neutral to basic pH values heavy metals are not soluble • HCl only used in small amounts; no great acidifying effect expected • $CuSO_4$ is dissolved, but only used in small amounts as a contributory chemical	• Waste waters in the outlet affect the elemental load of the catchment • Leachates and meteoric water can freely drain from the tailings pile • After mining ceased, tailings material in constant contact with surface waters in Lake Parosjärvi
Mine	Ore type	Sulfide and carbonate content	Major and minor sulfides and oxides	Mining and mineral processing methods	Waste management
Haveri Au–Cu 1942–61	• Cyprus-type volcanic-exhalative massive sulfide (VMS) deposit consisting of tholeiitic basic metalavas, metalava breccia, and metatuffite[4]	• Sulfide content 1–6% (average 3%)[6] • Low carbonate content (<2% calcite and dolomite)[6]	• Major: pyrrhotite, pyrite, chalcopyrite[4,7] • Minor: cobaltite (CoAsS), glaucodote [(Co,Fe)AsS], gersdorffite (NiAsS), arsenopyrite, sphalerite, molybdenite, scheelite, tellurobismutite (Bi_2Te_3) and hessite (Ag_2Te), magnetite and ilmenite[4,7]	• Open pit and underground galleries • Bulk sulfide flotation[8] • Cu flotation[8] • In early production, Au was only recovered as raw enrichment[8] • 1948–1961 Au cyanide leach, with precipitation of Au by Zn and removal of Zn by HCl[8]	• Total of 1.5 Mt tailings[9] • A 18.4 ha waste area in a bay of Lake Kirkkojärvi restricted with a dam that was broken in the mid-1950s • In later stages (mid-1950s), tailings were also piled in the lake with no dam restriction
	Expected environmental impacts				
	• Varying pH and metal contents in drainage water[5] • Generally high metal contents, but Cyprus-type deposits exhibit lower pH than Kuroko-type[5]	• Low neutralization potential[6] • Sulfide oxidation and AMD[6]	• Release of Fe, Cu. SO_4 and minor Zn, Ni, Co and As • Acid generation	• The tailings and impurities in process waters occur as particulate matter after sulfide flotation • pH 9.5 in cyanide leach and neutral to basic pH in Cu flotation • Cyanide leach dissolves the host minerals of Au. Zn of the treatment process is also dissolved	• A break in the dam and the deposition of tailings outside the dam allowed the transport of waste material into Lake Kirkkojärvi
Reference	Himmi et al., 1979[1]; Parviainen and Loukola-Ruskeeniemi, 2009[2]; Kukkonen et al., 1967[3]; Mäkelä, 1980[4]; Plumlee et al., 1999[5]; Parviainen, 2009[6]; Paarma, 1947[7]; Kesti, 1985[8]; Puustinen, 2003[9]				

intermediate metavolcanic rocks, graywacke-slate and mica schist and granite. Ore-forming sulfide minerals mainly consist of pyrrhotite, chalcopyrite and minor pyrite (Table 1). Sulfarsenides are found as accessory minerals containing native Au as small grains along grain boundaries and as fine-grained, nebulous disseminations in cobaltite. In addition, minor sulfides and oxides are found (Paarma, 1947) (Table 1).

The Haveri mine was active from 1942 to 1961. A total of 1.5 million-tons of ore were mined from an open pit and underground galleries

(Puustinen, 2003). The tailings were piled in a bay of Lake Kirkkojärvi covering an area of about 18.4 ha (Fig. 1). The tailings were constrained by a dam constructed of the subsoil covering the ore and of a wall rock. However, in the later stages of exploitation the tailings were directly piled in the lake outside the dam structure, leaving tailings material in direct contact with lake water. The water in the ditches surrounding the tailings impoundment and in the seasonal gullies on top of the tailings flows into Lake Kirkkojärvi, which is connected to the larger Lake Kyrösjärvi through a very narrow inlet.

After mine closure, rye was planted on the tailings area in order to prevent dusting during drier periods. However, after few failed attempts no more remediation measures were implemented at the Haveri mine area. The central area of the impoundment was used as a rally track in the 1980s to 1990s and was backfilled with gravel and partially covered with asphalt for this end.

2.2. Metal and metalloid contamination sources in sulfide mining

Dissolved metals, metalloids, chemicals, and small particulate matter are found in the ore processing waters, tailings feed and sludge during ore processing. Hence, a peak in pollution in the surrounding water systems may occur when mining operations are active.

At both localities, copper froth flotation was used as an enrichment process, in which Cu is recovered from the sulfide ore by chemically attaching the ground Cu mineral grains to a chemical bubble and by collecting the Cu concentrate separated from the gangue minerals. The process uses various chemicals, including collectors (e.g. xanthates), frothers (pine oil, alcohols) and pH regulators (lime, acids) (Nagaraj and Ravishankar, 2007). At both mines, Cu was merely recovered as a concentrate and was not smelted on site (Kesti, 1985; Kukkonen et al., 1967). At the Ylöjärvi mine, WO_3 and arsenic concentrates were also recovered by flotation (Kukkonen et al., 1967) (Table 1).

In the first years of production at the Haveri mine, Au was recovered as raw enrichment and refined at the Harjavalta enrichment plant, but in 1948 an enrichment plant for cyanide leach was built (Kesti, 1985). Au was dissolved (and possibly also the host minerals) in cyanide solution under an alkaline pH, precipitated with Zn powder, and Zn was separated from Au using an HCl leach (Kesti, 1985).

The tailings impoundments are commonly maintained water-saturated during mine operation, inhibiting active oxygen transport for sulfide oxidation. However, after mine closure the unremediated and drying tailings and waste rock piles are prone to sulfide oxidation, generating acidic or neutral mine drainage, and forming a source of pollutants. During extended breaks in the operation, paleosurfaces may form as the sulfide oxidation process starts in the absence of a fresh cover of tailings material.

Under tailings conditions, the relative resistance of sulfide oxidation generally follows the increasing order of pyrrhotite → sphalerite, galena → pyrite, arsenopyrite → chalcopyrite, but the susceptibility to alteration varies under different conditions and due to grain size variations and other factors (Jambor, 1994). The dissolved elements may be retained by secondary precipitates such as Fe (oxy)hydroxides and Fe (oxy)hydroxysulfates. However, these accumulations may be transitory and the potentially toxic elements may be released again (Moncur et al., 2005).

3. Materials and methods

3.1. Tailings sampling and analysis

The tailings samples from the Ylöjärvi and Haveri mines described in this study have previously been investigated by Parviainen and Loukola-Ruskeeniemi (2009) and Parviainen (2009), respectively. Vadose tailings samples were collected and studied for mineralogy by scanning electron microscope and electron microprobe analysis, and for geochemical distribution of the elements by sequential extraction method attacking water-soluble, adsorbed-exchangeable-carbonate (AEC), Fe(III) (oxy)hydroxides, Fe oxides and residual sulfide fraction. The detailed sampling and analysis methods applied are described in the above mentioned papers.

3.2. Water sampling and analysis

Up to twelve water samples were collected at the Ylöjärvi mine area from March to December 2005 in monthly sampling campaigns and in systematic monitoring samplings performed under the supervision of the Pirkanmaa Centre for Economic Development, Transport and the Environment. The sampling points (1–6) correspond to the regular monitoring stations sampled since 1975 to provide longer temporal datasets (Fig. 1). At two lake sites (1 and 6), samples were collected from both the surface and the bottom (at 10 m and 17.5 m depth, respectively). Two sets of samples were collected: (1) filtered water samples (0.45 μm membrane filter) for analysis of dissolved metals and (2) non-filtered water samples for total concentrations of metals and for anion analysis. Both samples were acidified with HNO_3 (Suprapur), and analyzed by graphite furnace atomic adsorption spectroscopy (AAG) for As, Fe and Mn. The systematic monitoring samples from the same period were also analyzed for Cu and Ni by inductively coupled plasma optical emission spectroscopy (ICP-OES). Additionally, the SO_4 concentration was analyzed by a nephelometric method and total phosphate by a colorimetric method. The pH was measured in situ with a Mettler Toledo portable pH/Eh meter and electrical conductivity (EC) and dissolved oxygen content (DO) with a WTW multiline Pocket Meter.

The surface water results for Haveri mine presented here were analyzed and described in detail by Parviainen (2009). A total of 12 samples were collected in two sampling campaigns in 2006 and 2007. The results of ten samples taken from the adjacent lake (samples 2 and 3), from the immediate surroundings of the tailings (4 and 8), and from ditches in direct contact with tailings (5, 6, and 7) are presented here (Fig. 1).

This paper focuses on the results for relevant elements in non-filtered water samples.

3.3. Lake sediment sampling and analysis

Lake sediment cores were collected in March 2005 from the recipient lakes at both mine sites using a Kajak-type gravity corer (66 mm inner diameter, 500 mm tube length; Renberg and Hansson, 2008). At Ylöjärvi, cores were collected from two lakes: Lake Vähävahantajärvi (core YL1, water depth 2 m, 3 km downstream from the mine) and Lake Näsijärvi (core YL2, 11 m, 7 km from the mine) (Fig. 1). At Haveri, one coring site was located in the basin immediately outside the tailings area (core HA1, 7 m, Lake Kirkkojärvi), while another one was located in the deepest part of the Viljakkala basin (core HA2, 24 m, 2.3 km from the mine) (Fig. 1). The Haveri results have previously been used as environmental variables to explain changes in sediment biota by Kihlman and Kauppila (2010).

The short cores were sliced in the field into 1 cm slices (2 cm slices below 10 cm for HA2) and analyzed for sediment chemistry with inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled mass spectrometry (ICP-MS) after microwave-assisted HNO_3 digestion (modified US EPA method 3051). The method does not provide a complete leach of the sediment samples, but is designed to extract the contaminated fraction of the samples. The leach is suitable for mine impact studies because it does not dissolve major silicates but breaks down sulfides, carbonates, most salts, certain micas, and clay minerals. Analytical quality control was based on the practices and standards of the laboratory (Labtium Ltd., Finas accreditation T025). No project standards or field duplicates were inserted.

The lake sediments were dated with the ^{137}Cs method, which is based on locating the current depth of the distinct 1986 Chernobyl nuclear fallout in the sediment profile. Other radionuclides were not measured from the cores. The cesium activity was determined with an Ortec gamma spectrometer equipped with a four inch NaI(Tl) crystal, two amplifiers and a 2048 channel pulse height analyzer (Äikäs et al., 1994). The final dating was based on linear extrapolation without correcting for sediment compaction, because the focus was on recent events. The estimates of sediment age obtained are presented for both sites in the element profiles (Figs. 2–5).

4. Results and discussion

4.1. Metal mobilization from tailings impoundments

At present, both Ylöjärvi and Haveri mines show extensive sulfide oxidation and release of sulfate and trace elements into the nearby surface water systems (Parviainen, 2009; Parviainen and Loukola-Ruskeeniemi, 2009). This acid mine drainage (AMD) is a continuous source of pollution, in many cases exceeding the recommended threshold values for drinking water during mining and for decades and perhaps for centuries after mine closure (Heikkinen et al., 2009; Moncur et al., 2006; Nieto et al., 2007; Nordstrom, 2011). According to Parviainen and Loukola-Ruskeeniemi (2009), in the Ylöjärvi tailings, the major sulfide minerals (pyrrhotite, arsenopyrite, chalcopyrite, and some pyrite) remain in the unaltered tailings, but they have been consumed from the surface layer (upper 20–65 cm) and moderate alteration can be detected to the depth of ca. 120 cm. Arsenic is retained to some extent by scarce secondary minerals (Fe(III) (oxy)hydroxides and Fe(III) arsenates) that appear as very fine, brown layers and irregular aggregates filling the pore spaces between primary minerals (Parviainen and Loukola-Ruskeeniemi, 2009). Table 2 presents the elemental concentrations for vadose tailings samples, which represent the sum of sequential extractions attacking water-soluble, adsorbed-exchangeable-carbonate (AEC), Fe(III) hydroxide, Fe(II) oxide and Fe sulfide fractions (i.e. excluding more inert silicate minerals) (methodology in Parviainen, 2009). In the Ylöjärvi tailings, the trace elements Cd, Co, Cr, Ni, and Pb exhibit low concentrations (<41 mg/kg on average), whereas As (3355 mg/kg), Cu (240 mg/kg), Fe (5.9 wt.%), Ti (1494 mg/kg) and Zn (147 mg/kg) show higher concentrations and the average S content is <1 wt.%.

At the Haveri tailings impoundment, sulfide oxidation has consumed nearly all sulfide minerals in the top 15 cm layer, and extensive sulfide alteration has generally reached the depth of 50 cm and up to 150 cm in the central tailings (Parviainen, 2009). The acidic ambient of the oxidized surface tailings favors continuous sulfide degradation. Parviainen (2009) also reported that discontinuous cemented layers appear in the lower part of the oxidation layer with secondary minerals (jarosite, Fe(III) (oxy)hydroxides) retaining moderate concentrations of As, Cu, and Zn. The Haveri tailings contain low concentrations of As, Cd, Cr, and Pb (<62 mg/kg on average), but Co (112 mg/kg), Cu (619 mg/kg), Fe (8.1 wt.%), Ni (125 mg/kg), and Zn (142 mg/kg) are present at higher concentrations (Table 2). At Haveri, the S content varies from 0.5 to 5.1 wt.% with an average of 2.1 wt.%.

4.2. Modern trace element load in surface waters

Previous studies by Bilaletdin et al. (2007), Carlson et al. (2002) and the systematic monitoring since 1975 (HERTTA database, unpublished data) have demonstrated that the catchment area of the Ylöjärvi mine is affected by AMD. During the sampling period in 2005, the As, Ni, and SO_4 content decreased along the 7 km long watercourse (from 118 to 3 µg/l, 4 to 2 µg/l, and 35 to 11 mg/l, respectively), whereas Cu, Fe, Mn, and P fluctuated with no clear trend (11–259 µg/l,

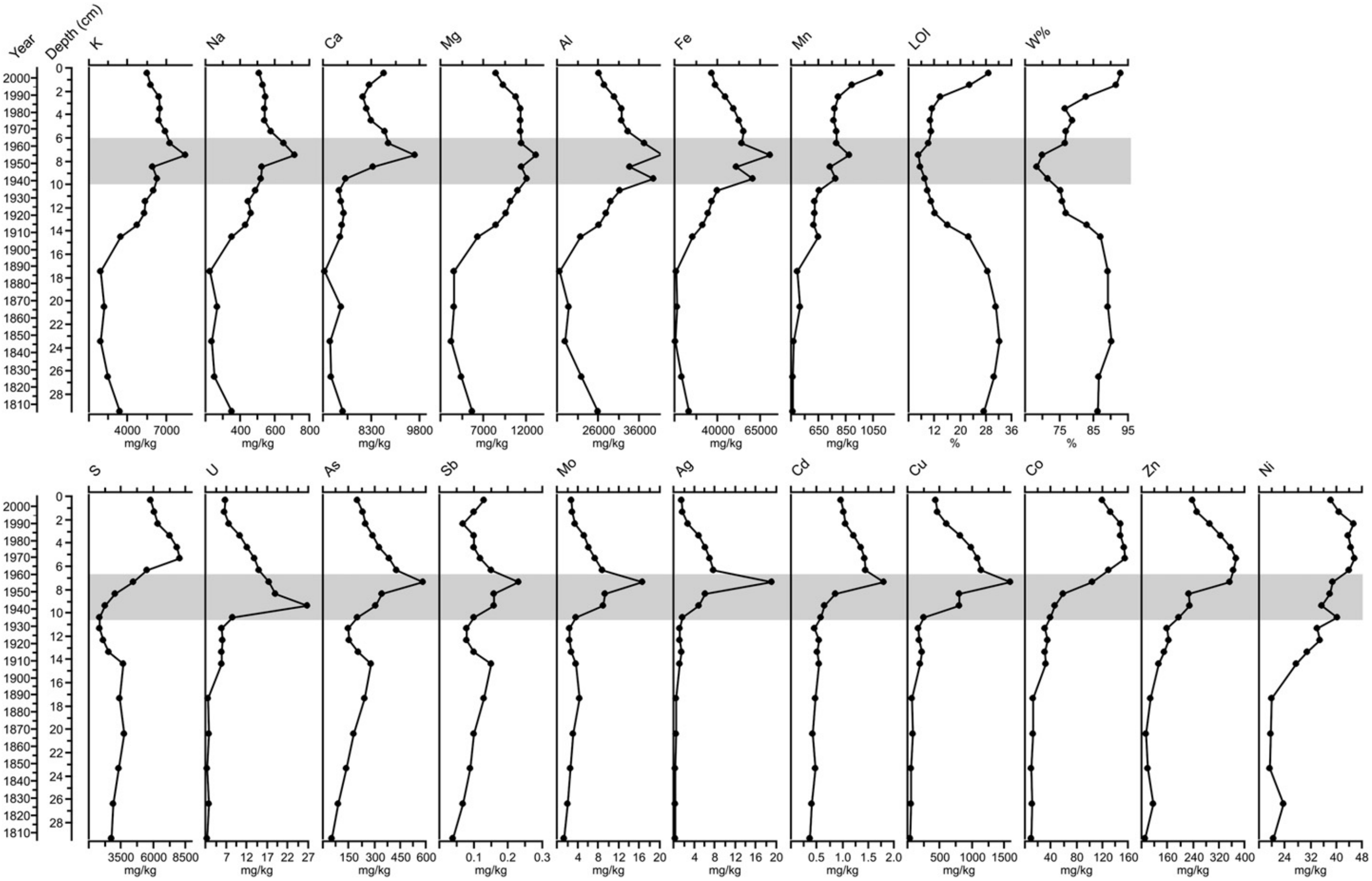

Fig. 2. Elemental, LOI and W% profiles for core YL1 from the Ylöjärvi mine. The highlighted gray area represents the active mining period.

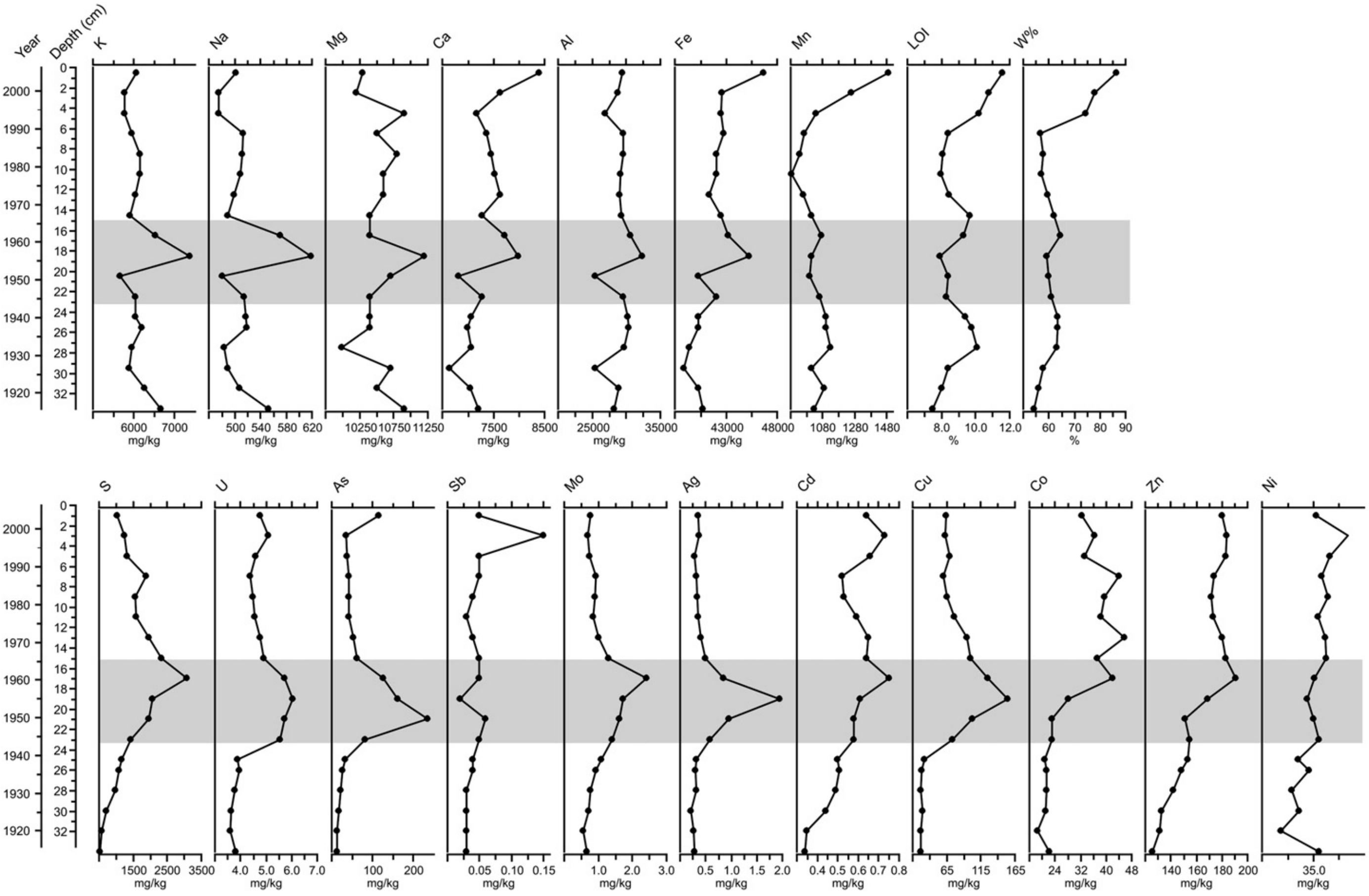

Fig. 3. Elemental, LOI and W% profiles for core YL2 from the Ylöjärvi mine. The highlighted gray area represents the active mining period.

361–1903 μg/l, 116–260 μg/l, 30–55 mg/l, respectively) (Table 3). The pH values increased from 5.7 to 7.1 further away from the mining area, and electric conductivity increased (from 106 to 157 μS/cm) along the watercourse. The dissolved oxygen content varied from 6.2 to 10.3 mg/l, and in the lake bottom sample from sampling point 6 a value of 1.8 mg/l was recorded.

Carlson et al. (2002) reported low pH values (average 4.0) for toe seepages from the Ylöjärvi tailings pile. However, the ditch leading from the tailings to the Lake Parosjärvi presented a near neutral pH (6.4) because of liming to prevent the acidification of the lake and to accelerate Fe precipitation. Here, elevated concentrations of As (1480 μg/l), Fe (58,200 μg/l), Mn (2780 μg/l), and SO_4 (633 mg/l) were recorded, but the authors reported low concentrations for Cd, Cu, Ni, and Zn (<5 μg/l).

At the Haveri mine site, no long-term monitoring results are available. According to Parviainen (2009), the surface waters in the ditches in close contact with the tailings material contain elevated concentrations of Ni, Co, Zn (<1000 μg/l of each element), Cu (<1880 μg/l), and sulfate (<1170 mg/l) (Table 3). However, other detrimental elements such as As (<3.0 μg/l), Cd (<6.1 μg/l), and Pb (<1.3 μg/l) were reported to occur at low concentrations. The water affected by AMD in these ditches flows into Lake Kirkkojärvi. However, the lake water samples exhibited low average concentrations of trace elements (<1.2 μg/l of As, Cd, Pb, and <19 μg/l of Ni, Co, Cu, and Zn) and SO_4 (<122 mg/l). The pH of water in the ditches affected by AMD ranged from 3.4 to 4.4, electric conductivity from 1330 to 2020 μS/cm, redox potential from 464 to 701 mV and oxygen saturation from 3.0 to 9.6 mg/l, whereas in the lake water samples the respective values ranged from pH 7.1 to 7.8, 77 to 303 μS/cm, 398 to 406 mV, and from 8.4 to 8.9 mg/l.

4.3. Lake sediments

The lake sediment cores taken from Ylöjärvi and Haveri mine sites provide an insight into the pre-mining background values and elemental conditions during and after mining. The results indicate that any land use disturbances within a metal-enriched catchment may mobilize the same elements that mining operations would. Due to the lower sedimentation rate (2.6 vs. 6.8 mm/a on average), core YL1 (Lake Vähä-Vahantajärvi, 3 km from the mine) captures a longer period of pre-mining activities in the area than core YL2 (Lake Näsijärvi, 7 km), showing the pre-mining effects of intensified agriculture in the area from the late 19th century onwards. Besides increases in the concentrations of elements derived from silicate mineral inputs (Al, N, K, Mg, Ca etc.; Fig. 2), elements associated with mining (e.g., Ag, Cu, Co, Zn, Ni, and also U) also gradually increased in these pre-mining sediments (Fig. 2). These changes soon also caused a shift in the sediment retention of elements mobile as oxyanions, which can be seen as a decrease in the concentrations of As, Sb and Mo. Similarly, in an ore-potential area in Eastern Finland, Mäkinen et al. (2010) described the impact of soil tillage on a lake detected as increased mineral matter inputs as well as elevated Cu and Ni concentrations in the lake sediment records. Later on, local mining also left its legacy in the accumulated sediments. However, the short sediment cores from Haveri did not allow detection of the effects of pre-mining land use.

Sediment records from both mine sites show temporal trends in the quality and quantity of mine water loading to the receiving water bodies, with concentrations well above the pre-mining sediments and regional background values (Lahermo et al., 1996). The Ylöjärvi and Haveri mines are both low-grade sulfide deposits with low carbonate contents, and are thus prone to generating moderate

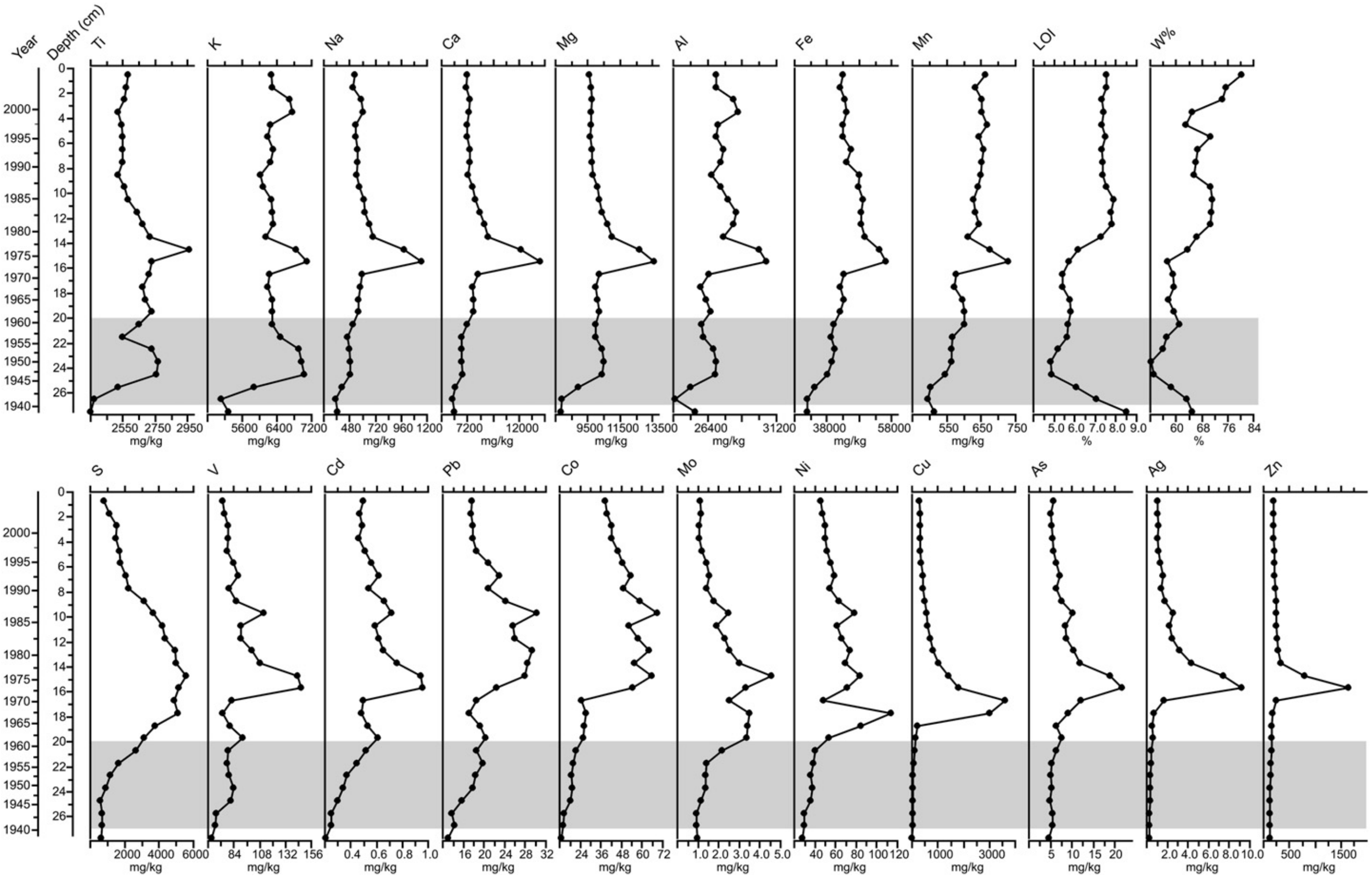

Fig. 4. Elemental, LOI and W% profiles for core HA1 from the Haveri mine. The highlighted gray area represents the active mining period.

metal concentrations in near neutral to acidic drainage waters (Table 1). However, the sequences of events were not identical at both sites due to differences in deposit types, site characteristics and operational histories: in the sediment cores of the Ylöjärvi mine, the sulfide mineral-related elements and also the silicate-related elements strongly increased and peaked during active mining, whereas at Haveri the concentrations increased more gradually when the mine was operating and peaked approximately 5 to 15 years after mine closure.

4.3.1. Ylöjärvi

At the Ylöjärvi mine, the mining-related changes began with a sharp peak in the U profile (up to 27 mg/kg, 10-fold higher than pre-mining values) at the YL1 coring site in the early 1940s, accompanied by somewhat less prominent increases in Cu, As, Sb, Mo, Ag, Co, Zn, and Ni (Fig. 2). This pattern was similar at the more distant YL2 site, but the longer tail of the U peak (2-fold) in core YL2 may be the result of gradual transportation of previously deposited U in the water course to the final receiving lake (Fig. 3). Similarly, the increases in metals such as Sb, Co, and Zn were less prominent in core YL2 than in YL1 (Fig. 3). This was a period of Cu production at the mine, while the recovery of WO_3 and As started 5 to 6 years later, respectively. During this phase, the processing waters were also deposited in Lake Parosjärvi. U concentrations, derived from the small uraninite concentrations of the ore, have since gradually decreased to the same level as in the immediate pre-mining period when the anthropogenic effects on the lake sediments began. $CuSO_4$ was used as an activator reagent in As flotation process in the course of 5 years (Table 1), however its use did not cause a detectable peak in the lake sediment cores, especially considering chalcopyrite as the major source of Cu. The majority of Cu should have been transported in particulate matter in the waste waters from flotation, because of the nature of the flotation procedure. However, the transportation of dissolved Cu cannot be ruled out.

In the next phase, dating approximately to the late 1950s, concentrations of several mining-related elements peaked at the YL1 coring site: e.g. As (583 mg/kg, 11-fold), Mo (17 mg/kg, 12-fold), Ag (19 mg/kg, 61-fold), Cd (1.5 mg/kg, 5-fold), Cu (1600 mg/kg, 37-fold), and Fe (7.1 wt.%, 3-fold). This short-lived peak coincided with increases in silicate-related elements (Al, K, Na, Ca, Mg, Mn, Na, ca. 2-fold), suggesting that the inputs may have occurred as fine-grained particulate matter. At the same time, the concentrations of Co, Zn, Ni, V, and S (on average 110, 302, 42, 86, and 5190 mg/kg, respectively) began rising, maintaining high levels until the late 1980s. The mine-related metal concentrations were elevated due to sulfide minerals such as pyrrhotite, pyrite, arsenopyrite, chalcopyrite, sphalerite, mackinawite, and molybdenite present in the processed ore (Table 1). Co probably originated from arsenopyrite and mackinawite, as it is a common impurity in these minerals. At some point during the 1950s, Lake Parosjärvi was dewatered as the mine workings proceeded under the lake. The waste waters were redirected to the outlet of the lake, which could be the reason for the considerable increase in metal concentrations in the sediment cores. In core YL2 the peaks were much less prominent, with only some silicate-related elements, Ag and Cu, showing marked concentrations at this time (Fig. 3). Instead, core YL2, with a higher temporal resolution, displayed slight peaks in the profiles of Mo, Cd, Co, Zn, and S after the silicate-related peaks, during the final phase of the mining operations.

After mine closure, Lake Parosjärvi filled up again, allowing the tailings areas and the tailings deposited at the bottom of the lake be communicated through water to the natural catchment area. Both cores record largely consistent post-mining metal inputs, but no post-

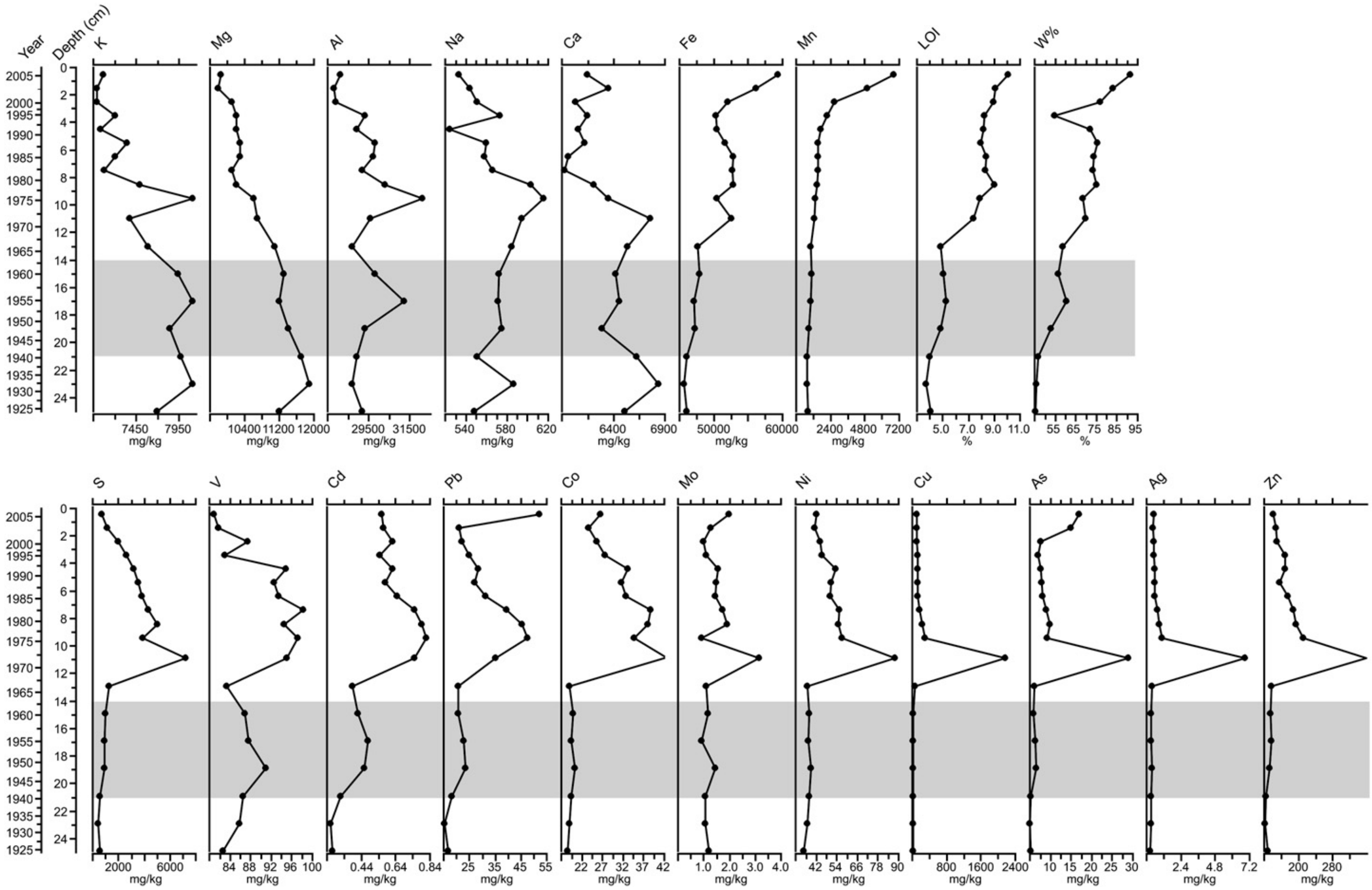

Fig. 5. Elemental, LOI and W% profiles for core HA2 from the Haveri mine. The highlighted gray area represents the active mining period.

closure peaks in the profiles of these elements were detected. While the concentrations of many mining-derived metals show a gradual decreasing trend, other typical sulfide mineral-related elements such as Co, Fe, and Zn, followed by Ni and Cd, deviate from this pattern. Considerable inputs to the sediments still occur, and the concentrations in the recent sediments (e.g. 200 mg/kg As, 446 mg/kg Cu, 121 mg/kg Co, 239 mg/kg Zn, 38 mg/kg Ni, 7 mg/kg U, and 5790 mg/kg S) are higher than in the pre-mining layers, demonstrating that five decades after closure the impact of mining is still reflected in the lake sediment records. This is in accordance with the findings of Parviainen and Loukola-Ruskeeniemi (2009), who described the progress of oxidation of Ylöjärvi tailings. Ni and V appear to be affected by the transportation of fine-grained mineral matter to the sediments, but no signs of major recent increases in inputs of elements related to silicate weathering (K, Al) were seen in either profile.

4.3.2. Haveri

Cores HA1 and HA2 from Haveri demonstrate that the impact of mining on the lake sediment records was moderate during operation, even though from approximately the mid-1950s the tailings were also deposited directly into the lake with no dam restriction (Figs. 4 and 5). In contrast to the short-lived U peak at Ylöjärvi, the early mining phase at Haveri was mainly characterized by clastic inputs, seen as a sharp drop in LOI and increases in Ti, K, Mg, Al, and V. Increases

Table 2
Minimum, maximum, average, and median concentrations for vadose tailings samples from the Ylöjärvi and Haveri mines. The concentrations represent the sum of sequential extractions (water-soluble, adsorbed-exchangeable-carbonate, Fe(III) hydroxide, Fe oxide and sulfide fractions). n = number of samples, bdl = below detection limit. (Parviainen, 2009; Parviainen and Loukola-Ruskeeniemi, 2009).

Ylöjärvi n = 12	As mg/kg	Cd mg/kg	Co mg/kg	Cr mg/kg	Cu mg/kg	Fe wt.%	Mg mg/kg	Mn mg/kg	Ni mg/kg	Pb mg/kg	Ti mg/kg	Zn mg/kg	S wt.%
Min	1289	3.7	0.0	1.0	77	3.4	3628	147	5.0	bdl	678	37	0.0
Max	6612	22	94	29	839	7.6	11,476	620	28	bdl	2378	170	1.3
Average	3355	11	41	14	240	5.9	8204	408	16	bdl	1494	147	0.4
Median	2743	8.9	40	14	133	6.3	9469	473	15	bdl	1571	146	0.3
Haveri n = 14	**As mg/kg**	**Cd mg/kg**	**Co mg/kg**	**Cr mg/kg**	**Cu mg/kg**	**Fe wt.%**	**Mg mg/kg**	**Mn mg/kg**	**Ni mg/kg**	**Pb mg/kg**	**Ti mg/kg**	**Zn mg/kg**	**S wt.%**
Min	0.0	0.0	7.7	21	140	2.8	2278	64	8.0	0.0	914	20	0.3
Max	183	7.4	379	63	2446	15.1	9329	347	429	47	3717	395	5.1
Average	62	1.5	112	38	619	8.1	5716	180	125	8.0	1806	142	2.1
Median	56	0.9	61	31	476	8.4	5282	175	68	5.3	1582	107	1.8

Table 3
Average total concentrations for selected elements, SO_4, P, electric conductivity (EC), pH, redox potential (E_h) and dissolved O_2 in water samples from the Ylöjärvi and Haveri mines. n = number of samples; na = not analyzed; ( ) = concentration of sample from lake bottom; * = single analysis of water in direct contact with tailings.
Results for Ylöjärvi from the HERTTA database and results for the Haveri mine after Parviainen, 2009.

Ylöjärvi n = 81	As µg/l	Cu µg/l	Fe µg/l	Mn µg/l	Ni µg/l	P mg/l	SO_4 mg/l	EC µS/cm	pH	O_2 mg/l
Sampling point 1	118	55	819	179	4.0	37	35	106	5.7	9.6
	(161)	(95)	(1210)	(201)	(5.0)	(41)	(41)	(122)	(5.5)	(5.5)
Sampling point 2	118	60	1258	237	4.2	49	36	112	5.9	9.8
Sampling point 3	102	259	1903	260	3.1	55	28	112	6.5	10.3
Sampling point 4	20	11	676	179	2.0	47	22	150	6.8	6.2
Sampling point 5	7.2	na	1138	254	na	49	18	157	6.8	8.4
Sampling point 6	3.0	na	361	116	na	30	11	101	7.1	6.5
	(24)	na	(1764)	(1853)	na	(52)	(13)	(144)	(6.7)	(1.8)

Haveri n = 10	As µg/l	Cd µg/l	Co µg/l	Cu µg/l	Fe µg/l	Mn µg/l	Ni µg/l	Pb µg/l	Zn µg/l	P mg/l	SO_4 mg/l	EC µS/cm	pH	Eh mV	O_2 mg/l
Sampling point 2	0.4	<0.1	0.5	8.5	550	63	4.0	<0.6	9.3	<0.3	13	77	7.8	398	8.4
Sampling point 3	1.2	<0.1	4.1	17	820	64	19	<0.6	16	<0.3	122	303	7.1	406	8.9
Sampling point 4	0.6	0.2	14	71	4200	1163	31	0.9	28	<0.3	304	923	6.2	389	6.3
Sampling point 5*	0.4	6.1	866	1880	3900	6810	775	0.8	749	<0.3	1030	1880	3.4	701	9.6
Sampling point 6*	1.4	6.1	834	1830	7800	6190	774	0.8	755	<0.3	1170	2020	3.5	675	6.4
Sampling point 7*	1.0	4.1	636	1200	6600	7640	563	0.9	831	<0.3	778	1590	4.4	464	3.0
Sampling point 8*	3.0	5.2	881	110	52,800	2750	956	1.3	764	<0.3	1150	1330	3.9	661	5.2

were also seen in Fe, Mn, Na, and Ca, while the concentrations of S, Cd, Co, Cu, and Pb increased more gradually somewhat later. The elevated Cu concentrations (6-fold) in core HA1 were chiefly accumulated as particulate matter derived from froth flotation as rests of fine chalcopyrite grains. Therefore, this event is not recorded in the distant core HA2. Only V increased in core HA2 in the early mining phase, followed by Cd and Pb. The start of the cyanide leach for Au was not clearly recorded in the sediment cores; only a slight hump was observed in the HA2 As profile. The Zn powder used in the process is not reflected in core HA1, and Zn concentrations peaked in the early 1970s due to sphalerite oxidation. Nevertheless, As, Co, Ni, and S concentrations slowly began to increase after Au extraction started.

The intensive metal accumulation at the HA1 site from the late 1960s after mine closure was probably related to the intensified mineral alteration in the Haveri mine tailings. Some years after mine closure the tailings surface dried up and sulfide oxidation began, lowering the pH and increasing the metal release from the tailings impoundment to Lake Kirkkojärvi. The sequence of main metal release events was the following: Ni (up to 114 mg/kg) (accompanied by an increase in S) → Cu (3600 mg/kg) (S) → As (22 mg/kg), Ag (9.2 mg/kg), Cd (0.92 mg/kg), Fe (5.6 wt.%), Zn (1650 mg/kg), V (147 mg/kg) (S) → Co (66 mg/kg), Mo (4.6 mg/kg) (Fe, S) (Fig. 4). This suggests the alteration sequence of gersdorffite → chalcopyrite → arsenopyrite, sphalerite, pyrrhotite, pyrite → cobaltite, molybdenite, which does not follow the one suggested by Jambor (1994). Small concentrations of Cd are probably derived from traces in altered sphalerite. When the active oxidation front moved downward and some of the minor sulfides were depleted from the surface, the concentrations dropped in the HA1 core as a response to lower concentrations in the runoff waters from the tailings. S did not show a clear peak, but exhibited high concentrations (9-fold) for two decades, while Fe peaked at the same time as many other sulfide-bound metals and afterwards maintained high concentrations up until the late 1980s, when both S and Fe concurrently dropped (Fig. 4). The spreading peak of these elements probably formed because the oxidation of major sulfides, pyrrhotite and pyrite, continued throughout the above-described sequence.

Interestingly, the profile of As does not match that of Ni and Co, even though they were presumably derived from same sulfarsenide minerals. Arsenic concentrations began rising simultaneously with, but more moderately than Ni, and peaked roughly 5 years later, whereas when Co contents were elevated, As substantially decreased. The differences in the profiles may be due to differences in the aquatic chemistry of these elements. According to Parviainen (2009), secondary Fe(III) (oxy)hydroxides formed in the oxidation layer of the Haveri tailings retain As, because under the oxidized and declining pH conditions of the tailings, As is strongly adsorbed by oxide minerals, retaining it from runoff waters (Smedley and Kinniburgh, 2002). This may be the reason for the decreasing As values in this period. The Mo profile lacks a clear peak dating to the late 1960s, but otherwise matches the Ni profile. All the metal peaks were also prominent, although merged due to the lower temporal resolution in the distant HA2 profile, suggesting that these inputs were mainly in a dissolved form. The maximum concentrations of the corresponding elements were somewhat lower in core HA2 than in HA1, except for As and S, which showed concentrations of up to 29 and 7190 mg/kg, respectively. The concentrations in both cores followed a general decreasing trend, but S, V, Cd, Pb, Co, and to a lesser degree As, Mo, and Ni remained elevated until at least the beginning of the 1990s.

The silicate-derived elements K, Al, Na, Ca, Mg, and Mn peaked in core HA1 in the mid-1970s, which coincides with the highest sulfide oxidation rate. This suggests an advanced state of weathering and a decline in pH, also resulting in the mobilization of these elements in dissolved form (Fig. 4). The concurrent peak in Al, K, and Na in the more distant core supports soluble discharge from the tailings area (Fig. 5). These indications of intense silicate weathering distinguish the Haveri site from the Ylöjärvi mine, with no post-closure peaks of silicate-related elements in the sediment cores. Again, at the beginning of 2000, Al, K and Na increased in core HA1, but no signs of simultaneously intensified sulfide oxidation were detected.

Although Parviainen (2009) found that some elements are retained in secondary Fe(III) minerals, the author reported that sulfide-bound metals (especially Co, Cu, Fe, Ni, Zn), SO_4, and silicate-related elements (Table 3) are still released and transported from the Haveri tailings to the nearby lake, which is reflected in higher concentrations than the pre-mining values of these elements in the sediment cores. As, Cd, Fe, Mo, Ni, U, S, and Zn exhibit 1.2 to 2.3 times higher concentrations than the pre-mining values, while the concentrations of Ag, Co, and Cu are 4.5, 3 and 17-fold higher, respectively. The increased concentrations of Fe, Mn, Mo, and As in the top layers of core HA2 are a result of redox processes in this profundal core. Metal scavenging by secondary precipitates is thus not enough to stop the loading from the mine site. As the active oxidation front moves downward in the vadose tailings, sulfide oxidation by oxygen decreases and the principal transportation of dissolved oxidation products occurs in the percolating pore water of the tailings pile, ending up in the groundwater body beneath it instead of surface water runoff (Parviainen, 2009; Placencia-Gómez et al., 2010).

In an attempt to identify the main metals released in the environment and to compare the lake sediment records of metal accumulation with studies of metal mobilization from the tailings pile, the elevated (i.e. above the background level) concentrations of each element were summed for the post-operational sediment sections. These extra metal concentrations in the post-closure sediments are probably mainly derived from sulfide oxidation in the tailings areas (Table 4). For core HA1, these accumulated concentrations were compared with the concentrations of sulfide-bound metals and S leached from the Haveri tailings area to date as a consequence of sulfide oxidation (Parviainen, 2009). The main sulfide-derived elements leached from the pile were in the increasing order As, Ni~Co, Zn, Cu, Fe, and S, while the accumulated concentrations in HA1 increased in the order As, Ni ~ Co, Zn, Cu, S, and Fe. Elevated concentrations of Fe in the sediment load are a consequence of the abundance of this metal in various sources of sediment input and are not solely derived from sulfide oxidation. In core YL1 the most abundant elements were Ni, As, Co, Zn, Cu, S, and Fe. The results for cores HA1 and YL1 in Table 4 are not quantitatively comparable, but provide a qualitative indication of the major contaminants mobilized from each mine site after mine closure. Assuming the close relation of the elements leached from tailings pile and accumulated in the lake sediments, during and after mining the concentrations in the surface water, as a means of transport, must have been well above the modern metal loading (Table 3), which still exceeds natural background values. The moderate transport of metal concentrations at the present is reflected as slightly elevated accumulation in the top sediments.

Similar findings to this study have previously been reported. In Lac Dufault in Canada, three different mining operations were distinguished from a lake sediment profile, each with a characteristic metal composition (Couillard et al., 2004). The authors also found that trace element concentrations in the top (recent) lake sediments were well above pre-mining concentrations, up to ~10 (Cu, Zn) and 50 (Cd, Pb) times higher than at Ylöjärvi and Haveri, while the lake water concentrations had diminished to a similar level as that at Haveri. In a similar manner, at Orijärvi in South Finland, the intensive mining of Cu (Zn, Pb) by froth flotation was depicted in a lake sediment record as exceptionally high metal concentrations (Salonen et al., 2006). The sulfide-related metal concentrations were also elevated in the recent sediment layers, with up to approx. 30 mg/kg of As, 2000 mg/kg of Cu, 5 wt.% of Fe, 5000 mg/kg of Zn, and 500 mg/kg of Pb.

Table 4
Concentrations for selected elements leached from the Haveri tailings up to date (Parviainen, 2009) and accumulated in post-mining sediments in core HA1 at Haveri and in core YL1 at Ylöjärvi mine sites.

Element	Leached from Haveri tailings to date (kg)	Accumulated in post-mining sediments HA1 (mg/kg)	Ratio (leached/accumulated)	Accumulated in post-mining sediments YL1 (mg/kg)
Cd	70	8	8.8	4
Pb	110	181	0.6	19
Cr	210	161	1.3	69
Mo	220	25	8.8	8
As	690	88	7.8	595
Ni	4330	720	6.0	92
Co	4500	686	6.6	712
Zn	6000	3872	1.5	999
Cu	14,700	1.7 (wt.%)	0.9	3247
Fe	1330 (t)	28.5 (wt.%)	4.7	10.3 (wt.%)
S	2070 (t)	5.3 (wt.%)	39.1	2.5 (wt.%)

5. Conclusions

The anthropogenic impact on the elemental loading of lake sediment records was clearly detected at the Ylöjärvi and Haveri mines sites in SW Finland.

- The sediment records revealed that mine water loading changes in composition and intensity during and after mining;
- Other land uses (e.g. agriculture) in mining regions often also mobilize mining-associated metals;
- The changes in the evolution of loading depend on the operational history and characteristics of the mine;
- At Ylöjärvi the sulfide-derived metal concentrations already peaked during mining, while the impact was minimal at Haveri;
- At Ylöjärvi, As, Ag, Cd, Cu, and Mo peaked during mining, whereas Co, Ni, Zn, and S exhibited constant high concentrations upon closure and immediately afterwards;
- The Haveri cores revealed prominent post-mining (AMD derived) metal peaks (Ni, Cu, As, Ag, Fe, Zn, Co, Mo, S), but these were lacking at Ylöjärvi, probably due to the spreading of loading around the tailings pile;
- Records of metal accumulation in sediments agreed with calculations of metal losses from the shallow tailings at Haveri;
- Cu was the principal mining-derived metal at both mines throughout the sequence and continues to be a major contaminant, with 10- and 17-fold concentrations in the recent sediments in comparison with pre-mining values;
- The decreasing elemental load (but higher values than in the pre-mining sediments) derived from the tailings may be a result of the attenuating effect of adsorption by secondary Fe(III) minerals and because of the decreasing activity of the downward-moving oxidation front, probably causing the contaminant plume to percolate into the groundwater body beneath.

This study demonstrated that the examination of lake sediment cores allows assessment of the long-term evolution of metal and metalloid drainage from mining areas. When combined with good background information on the mining operational history, mineralogy and characteristics of the ore deposit, as well as other possible random factors, data from sediment cores can more easily be interpreted and the history of events at a mine site can be reconstructed. However, one must bear in mind that the sediments provide a record of the net loading from the mine site with all sources and attenuating mechanisms combined. For future perspectives, sediment records with improved temporal resolution and the use of stable isotopes to help distinguish different sources of contamination are required.

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