# Groundwater and surface water contamination in the area of the Hitura nickel mine, Western Finland

P.M. Heikkinen · K. Korkka-Niemi · M. Lahti · V.-P. Salonen

Abstract Tailings-derived mine drainage water that is neutral in character, has a high electrical conductivity and contains elevated sulphate, chloride and nickel concentrations, has caused deterioration in groundwater and surface water quality in the mining area of Hitura in Western Finland. This deterioration, and thereby the location of the contaminant plume, was recognized in the water chemistry in the form of a gradual change in ion composition from Ca-HCO<sub>3</sub>-type water towards a Mg-SO<sub>4</sub>-rich type. It was possible to define the extent of the pollution by using cluster analysis to distinguish between hydrochemically different regimes and performing an electrical sounding survey. The results indicated that contamination is most intense close to the tailings impoundment and is related to an esker complex running across this area. Nevertheless, the water in the eastern and southern parts of the area upgradient of the hydraulic head is uncontaminated and suitable for water supply purposes.

**Keywords** Finland · Groundwater contamination · Mine drainage · Nickel mine tailings · Surface water contamination

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# Introduction

The impacts of base-metal mining activities on groundwater and surface water have been widely studied around the world (e.g. Rösner 1998; Lottermoser and others 1999). One of the major concerns related to sulphide mines is acid mine drainage (AMD) caused by the oxidation and hydrolysis of metal sulphides. This generally results in elevated heavy metal concentrations, a high sulphate content, an increase in electrical conductivity and a lowering in the pH of water in the mining area (Emrich and Merritt 1969; Williams and Smith 2000). A number of reports have also been published in Finland concerning the effects of mine effluents on surface waters and stream sediments (e.g. Sipilä and Salminen 1995; Angelos 2000), but little attention has been focused on groundwater contamination caused by mining activities (see, however, Cody 1998). On the other hand, about 65% of the country's water supply is reliant on groundwater or artificial groundwater, mostly derived from shallow, unconfined, unconsolidated aquifers. Altogether, there are 7,141 classified groundwater basins, of which just over 20% are already in use as active water resources (Britschgi and Gustafsson 1996). Pollution of aquifers and depreciation of groundwater quality is thus prohibited under the Finnish Environmental Protection Act (86/2000), which also increases the ecological demands on mining activities and the requirements for restoration, especially where the mining activities are located in the vicinity of groundwater reservoirs. There are three sulphide mines in operation at present, and more than 25 abandoned, but mostly unremediated ones in Finland.

One of the active sulphide mines is that of Hitura in the western part of Finland, which has been operating for approximately 30 years and has ore reserves that are estimated to warrant production for about 3 more years. Thus, the planning of reclamation has come to the fore in recent times. An essential part of this will be focused on the prevention of impacts on groundwater reserves. Elevated concentrations of sulphate and nickel have been detected in private wells and monitoring wells around the tailings impoundment from the 1980s onwards. Furthermore, the south-eastern edge of the impoundment borders on an aquifer classified as a class I groundwater area for water supply (Britschgi and Gustafsson 1996). Minor elevation in sulphate concentration has also been discovered recently in a water intake plant located in this aquifer,

resulting in its closure in autumn 1998 (Heikkinen and others 2000).

The present paper describes changes in groundwater and surface water geochemistry resulting from the disposal of tailings of the Hitura mine. Monitoring data collected by the mining company suggest that the tailings-derived water does not reflect the typical impacts of acid mine drainage because there have been only occasional observations of lowered pH. Thus, the first aim of this work was to characterize the main indicators of pollution and to discuss whether this pollution could be attributed to acid mine drainage. Bearing in mind the demands for reclamation, another purpose was to assess the present extent of the contamination. Four approaches to this assessment were examined. Firstly, the areal distributions of individual variables were studied, and secondly, water samples collected from different locations in the area were analysed for major ion concentrations in order to identify the natural water type of the area and detect possible indications of the mixing of tailings-derived water with the natural waters. Thirdly, a cluster analysis was performed on the chemical data to distinguish hydrochemically different regimes and thus to differentiate uncontaminated areas from contaminated ones. Finally, the applicability of an electrical resistivity sounding survey for delineating the contaminant plume was tested. This method has not been used earlier for mining impact assessment under Finnish conditions, but, for example, Merkel (1972) has proved it to be viable

for assessing pollution caused by acid mine drainage in sedimentary rock environments. The method has been successfully employed in Finland for monitoring chloride plumes caused by the de-icing of roads (Vanhala 1998).

### Site characterization

The Hitura nickel mine and concentrating plant are located in Western Finland, at approximately 63°50'N, 25°02′E (Fig. 1). The mine started operation in 1970, and its average annual production of nickel concentrate (containing  $\sim$ 7.0% Ni, 1.7% Cu and 23.0% S) has been around 3,000 tons (t). The low-grade Ni-Cu ore bodies are hosted by an ultramafic complex composed mainly of serpentinite. The main ore minerals are pentlandite, chalcopyrite and pyrrhotite, but mackinawite, cubanite and valleriite are also abundant in places (Isohanni and others 1985). A detailed description of the structure and geochemistry of the ore deposits has been presented by Papunen (1970) and Isohanni and others (1985). The average chemical composition of the ore is given in Table 1. The ore, extracted by open pit mining until 1991, when underground production was initiated, is processed by onsite milling, in which the nickel concentrate is separated in three phases: crushing, grinding and flotation. The main

Fig. 1
Location of the Hitura area and its Quaternary deposits, with sampling sites

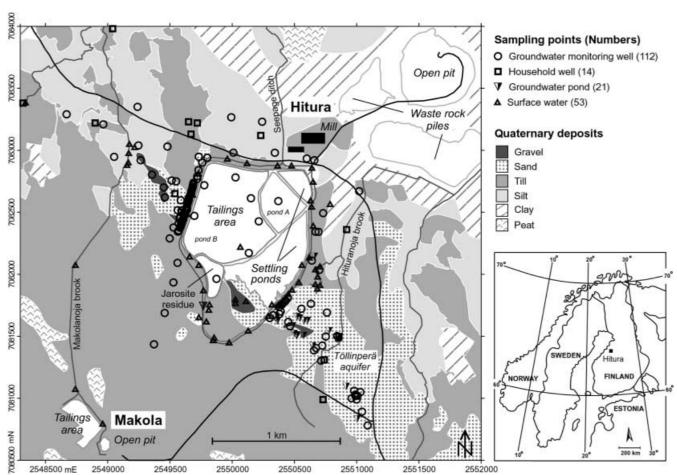


Table 1 Average chemical composition of the ore and tailings in 1993-1998 (source: Archives of Hitura mine)

Comp.	Ore			Tailings	Tailings				
(%)	Min.	Mean	Max.	Min.	Mean	Max.			
SiO <sub>2</sub>	39.1	40.0	41.0	40.1	40.9	41.8			
$Al_2O_3$	2.4	3.1	3.4	2.4	3.2	3.6			
MgO	30.6	33.3	36.0	31.3	33.7	36.7			
FeO	15.1	15.7	16.2	12.9	13.5	14.4			
CaO	0.61	0.82	1.1	0.63	0.83	1.1			
MnO	0.14	0.14	0.15	0.14	0.15	0.15			
S	2.5	2.9	3.2	1.5	1.7	1.8			
(ppm)									
Ni	6,030	6,810	7,170	2,230	2,370	2,600			
Cu	2,360	2,630	2,870	1,260	1,520	1,860			
Co	250	300	360	120	130	140			
Cr	2,480	2,590	2,690	2,570	2,680	2,810			
Cl	1,090	1,580	2,020	1,120	1,610	2,150			
Zn	90	100	110	80	90	100			
Pb	10	14	20	<10	10	20			

reagents used in the flotation process are xanthate, raw pine oil and sulphuric acid, the latter in order to regulate A (Fig. 1), which is no longer in use, has become slightly the pH. Nowadays, flotation normally takes place at pH 5.5-6.5. After flotation, the concentrate is de-watered, filtered and transported to the smelters. The waste water and the tailings formed in the process are pumped as a slurry into the tailings pond situated 700 m south of the mill. Approximately 500,000-600,000 t of tailings are formed in a year. After settling and clarification, the water from the tailings disposal area is recycled back to the mill, which also receives the water pumped out of the mine and an input from the local water supply. Data on the chemistry of the mine water and the recycled process water are presented in Table 2.

The tailings disposal area is about 110 ha in size and 25 m in depth, being notably elevated from the surrounding terrain. It is encircled by an earth dam constructed originally of fine-grained till, although this has recently been raised gradually using the tailings material itself. The total amount of tailings in the pond at the moment is  $\sim$ 8,700,000 t. The tailings consist mainly of Mg serpentinites and amphibolites with small amounts of sulphides (S 1.7%). The main metal concentrations in the tailings are Ni 2,370 ppm, Cr 2,680 ppm and Cu 1,520 ppm, and high concentrations of Cl<sup>-</sup> also occur (Table 1). Most of the surface of the tailings is unoxidized because the mine is still actively working and mill residue is being continuously deposited in the area. Nonetheless,

the surface in the oldest part of the impoundment, pond oxidized, as evidenced by the formation of reddish brown iron oxide precipitates. In addition to tailings, jarosite residue, which is formed in the smelting process at the Kokkola zinc plant and contains primarily iron, sulphur, magnesium, calcium, silica, nickel, copper and chromium with minor cobalt, zinc and lead has been transported to Hitura and stored in one part of the tailings area (Fig. 1). The surface water in the tailings impoundment, referred to as process water, is characterized by a near-neutral pH and high concentrations of sulphate and chloride (Table 2).

There is also another mine in the area: the exhausted and abandoned Makola nickel-copper mine located approximately 2 km south-west of the Hitura tailings area (Fig. 1). The Makola mine was exploited in the 1940s and 1950s and, at present, its small-diameter deep open pit has filled with water and all the mining facilities have been demolished. The tailings deposited in a nearby peat area have nevertheless remained untreated, so that their surface has become oxidized and surface runoff has affected water quality in the surrounding brook of Makolanoja, lowering its pH and increasing its electrical conductivity and Ni, Cu, Mg and Mn concentrations (Sipilä 1996). The Makolanoja brook also runs close to the Hitura mine tailings disposal area (Fig. 1) and, according to Wihuri and Ikäheimo

Composition of the mine water and recycled process water in 1996-2000 (source: Archives of Hitura mine)

	Mine wa	ter		Process wa	ater	
	Min.	Mean	Max.	Min.	Mean	Max.
pH	7.6	7.8	8.3	6.1	6.8	7.6
Electrical conductivity (mS/m)	120	160	200	300	510	700
SO <sub>4</sub> (mg/l)	420	460	510	1,320	3,530	5,570
Ni (mg/l)	0.06	0.12	0.16	0.36	1.28	2.4
Cl (mg/l) <sup>a</sup>		150			1,810 <sup>b</sup>	

<sup>&</sup>lt;sup>a</sup>Chloride concentrations represent only one determination made on 15 April 2000

<sup>&</sup>lt;sup>b</sup>Analysis of process water was made of the water pumped into the tailings pond

(unpublished data), water from the latter is also discharging into it.

### Geology and hydrogeology of the area

The bedrock around the Hitura mine consists mainly of Precambrian migmatites, black schists and ultramafic rocks (Isohanni and others 1985). There are no outcrops, but the bedrock is covered by a 5-15-m thick blanket of glacial and postglacial Quaternary sediments (Fig. 1). The lowermost sedimentary unit is in general a Weichselian till that rests directly on the bedrock. According to the maps in Punkari (1980), the area represents an interlobate sedimentary environment between passive and active ice lobes. Consequently, a cover till has been deposited in its south-western part, levelling out the bedrock topography, whereas the till accumulations in the north-east are coarse grained, hummocky moraines deposited during the deglaciation. An interlobate esker complex with gravelly core sets has been deposited in the marginal zone of the two till units, and this runs across both the area as a whole and the tailings pond in a SE-NW direction. The esker complex and the till units are covered in places with shallow peat formations and littoral sands washed out of the morainic material during the early stages in the history of the Baltic Sea (Kukkonen and Korpijaakko 1983; Salonen and others 2001). The surface sediments in the northern part of the area consist of postglacial clays and silts deposited in the Yoldia Sea or Ancylus Lake (Fig. 1). The Quaternary deposits of the area were mapped in detail by means of test pits, geophysical measurements and drillings in conjunction with the present work, and a 3D-model of these deposits together with a groundwater flow model were created. Preliminary results have been published in Heikkinen and others (2000) and Salonen and others (2001).

The main aquifer in the area is hosted by the interlobate esker complex. Its eastern part, the Töllinperä aquifer, located to the north-east side of the tailings area (Fig. 1), has been defined by the environmental authorities as an important groundwater area for water supply purposes (Britschgi and Gustafsson 1996). The aquifer is to a large extent unconfined, with a specific yield of some 870 m<sup>3</sup>/day (Britschgi and Gustafsson 1996). The Töllinperä aquifer was at one time exploited by a small water cooperative for the use of 20 households, but its use was discontinued in autumn 1998 because of a steady increase in sulphate concentration from the background value of 5 mg/l up to ca. 70 mg/l in less than 2 years (Korkka-Niemi and others 1999). It has been suggested that the deterioration in water quality may have been the result of a rise in water level in the tailings area, leading to increased hydraulic pressure and a more pronounced flow towards the Töllinperä aquifer (Korkka-Niemi and others 1999).

# Sampling and analytical methods

The fieldwork was carried out during summer and autumn 1999, when 51 monitoring wells constructed of PVC or PE

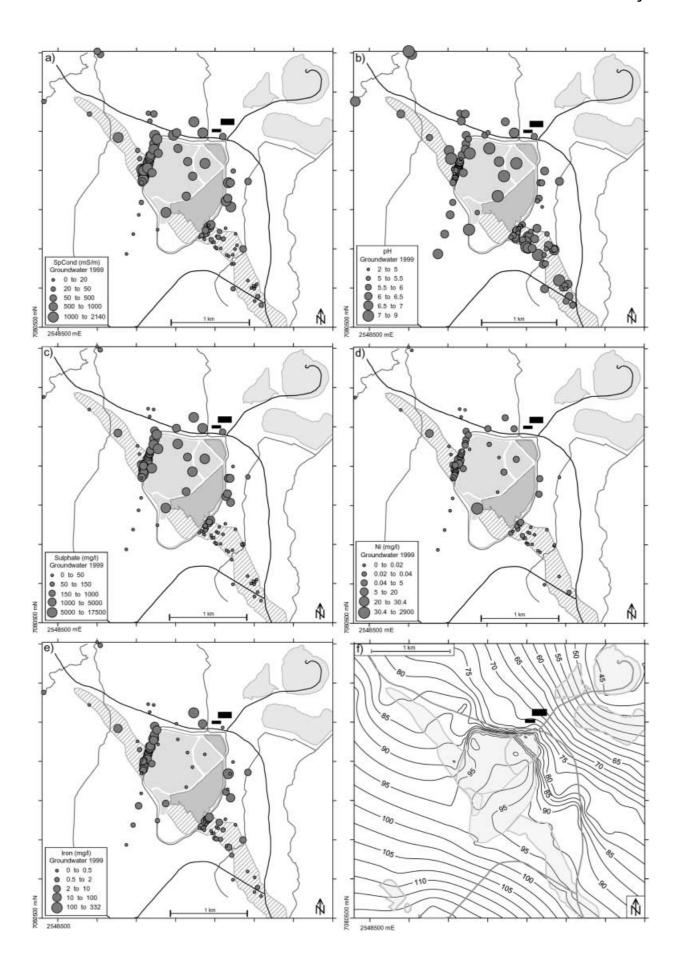
tubing were installed in the area to expand the previous monitoring network. The screens of these wells (Ø 3 mm) were placed at least 1 m below the observed groundwater table and ca. 0.5 m above it. Eight of the monitoring wells were drilled into the tailings area, ranging from the top of the tailings to the bottom, their screens (also Ø 3 mm) being placed from 0.5 m below the surface of the tailings to the bottom of the tailings. Because of an interruption in the operation of the mill in 1999, no new tailings were deposited at the site during the fieldwork.

A total of 167 samples were collected from the groundwater-monitoring wells, local household wells, groundwater and surface water ponds, brooks, the seepage ditch surrounding the tailings area and the settling ponds in the tailings area itself. The groundwater samples were taken with a Teflon tube bailer or a small battery-driven submersible pump, while the surface water samples were collected by submerging a bottle sampler 5 cm below the water surface. About three well volumes of water were removed from each monitoring well prior to sampling. The samples were collected in polyethylene bottles once the water table had stabilized, and the hydraulic head at each site was recorded in conjunction with sampling. The sampling locations are indicated in Fig. 1. Further sampling was carried out the following summer using the same techniques in order to analyse chloride and alkalinity. All the sampling points were analysed in the field for pH, specific conductivity and temperature with a multi-parameter recording device (YSI 610-DM). Filtered (1.2 µm), unacidified samples were used for determination of the major anions with a spectrophotometer (Hach DR2000). Total alkalinity was titrated with sulphuric acid to an end point of pH 4.5. Major cations and trace metals were measured by flame atomic absorption spectrometry of filtered (0.45  $\mu$ m), HNO<sub>3</sub><sup>-</sup> acidified samples. To ensure the quality of the analyses, replicate samples were analysed in all the sets. Checks were also made in an accredited laboratory at the Geological Survey of Finland by inductively coupled plasma spectrometry (ICP-AES/ICP-MS) for cations and by ion chromatography for anions. To detect faulty analyses, charge balance calculations were made using the Aquachem groundwater geochemistry data analysis package (Anon 1998).

The resistivity sounding survey was conducted using AGI's Sting-Swift multi-electrode resistivity imaging system with three cables and 14 electrodes at a spacing of 5 m per cable. A dipole–dipole electrode configuration was used and the data were interpreted with the RES2DINV program (Loke and Barker 1996). Two profiles were measured, each of length about 200 m, the first running to the west of the tailings dam and the second across the south-western corner of the tailings impoundment.

Fig. 2

Areal distribution of a electrical conductivity, **b** pH, **c** sulphate, **d** nickel and **e** iron in the groundwater of the Hitura area, and **f** a contour map of the hydraulic head. For items on the base map see Figs. 1 and 7



# Results and discussion

### Groundwater flow pattern

The main direction of groundwater flow in the area is SW-NE following the slope of the land surface (Fig. 2f). In the north, however, the flow pattern has been affected by the pumping of water from the mine shafts, turning the flow towards the open pit. Furthermore, disposal of the tailings has resulted in a mounding of the groundwater table under the tailings area. This means that the tailings impoundment forms a regional groundwater recharge area discharging tailings-derived water into the surrounding surface water and groundwater systems. As suggested by the hydraulic head measurements, the groundwater table is below the surface water level in the disposal pond, whereas it is on the same level as the surface water in the settling ponds. Consequently, a perched water table of a kind has formed in the disposal pond. The unsaturated zone varies in depth between 0.6 to 9.4 m, being shallowest in the oldest part of the tailings area, pond A, from which it follows that the oxidized zone in pond A is fairly shallow. The hydraulic head was measured during a break in the operation of the mill, however, so that the unsaturated zone would be thinner during the active disposal of tailings. The hydraulic gradient is steepest in the northern part of the impoundment, where seepage through the tailings dam was also observed during the fieldwork. Pumping for groundwater protection purposes just outside the impoundment causes the cone-shaped feature visible beside the western flank of the tailings area (Fig. 2f), whereas the southernmost part of the tailings area has not yet been taken into use, so that no gradient towards the surrounding area has formed. It is notable that the hydraulic gradient is very small outside the tailings area, in the eastern part of the interlobate esker, resulting in a slow rate of flow regardless of the high hydraulic conductivity  $(K=10^{-2} \text{ m/s})$  reported by Salonen and others (2001). In the western part of the esker a gradient towards the northwest is clearly observable.

### **Nature of contamination**

A statistical summary of the chemical data on the groundwater is presented in Table 3 and on the surface waters in Table 4. In both tables the waters that are in contact with the tailings have been separated from the rest of the data, which will be later on referred to as 'natural waters'. Half the detection limit value was used in the statistical calculations to represent the observations falling below the detection limit. For comparison, Table 3 also lists the median values for Finnish sand/gravel aquifers and till aquifers (Lahermo and others 1990) and Table 4 the median values for Finnish stream waters (Lahermo and others 1996). The recommended values for drinking water for Finnish household wells and small water cooperatives (Anon 2001) are also shown.

The natural water data show a wide overall variation with respect to all the variables studied, and the distributions of the variables are mostly positively skewed (Tables 3 and 4). Especially large variation can be seen in electrical

conductivity (EC) and in the concentrations of sulphate, chloride, iron, alkaline earths, nickel, cobalt and zinc, the maximum values for which are many times greater than the reference values for Finnish aquifers (Lahermo and others 1990) and stream waters (Lahermo and others 1996) and clearly exceed the recommended maxima for drinking water (Anon 2001). Sulphate concentrations of up to 8,200 mg/l, chloride concentrations of 700 mg/l and nickel concentrations as high as 30.3 mg/l were measured in the groundwater, for example. These variables have high maximum values in both the process water and the groundwater of the tailings area.

Apart from iron, however, the median values for the above variables in the natural waters meet the requirements set for drinking water, although they are still somewhat higher than the reference values. This suggests that the pollution is local and that the natural background level in Hitura is somewhat higher for these ions than is generally the case in Finland. The reason for the latter is apparently because sulphide mining environments are commonly characterized by anomalous elevated concentrations of heavy metals and sulphates, etc., because of their geological setting. Salminen and Tarvainen (1997), for example, report Ni concentrations in till in Finland to be typically several times higher in areas of mafic and ultramafic rocks similar to Hitura than in areas of acid rocks. Furthermore, Lahermo (1970) notes that groundwater in mafic rock environments is richer in dissolved solids than that in felsic environments.

The most significant statistical correlations in the whole data were detected between EC, sulphate, magnesium and calcium ( $r_{\text{Spearman}} < 0.923$ , p < 0.001), whereas the correlations of these variables with iron and nickel were also significant but very much weaker ( $r_{SNi}$ <0.796, p<0.001;  $r_{SFe}$ <0.403, p<0.001). In addition, pH showed only a weak negative correlation with heavy metals, e.g. with nickel ( $r_S$ =-0.506, p<0.001). These observations are consistent with the results presented by Gray (1996), who concluded that sulphate and EC are more reliable indicators of mining effluents than are pH or heavy metals. According to him, this is true firstly because sulphate is quite a conservative anion in mining environments and is less affected by sorption processes or fluctuations in pH than are heavy metals, and secondly because conductivity and sulphate are usually closely associated in mining environments. Aside from the fact that the occurrence of nickel and iron is influenced by the pH-Eh conditions, some of the elevated iron concentrations in the Hitura area are presumably caused by natural anomalies.

### pH and neutral mine drainage

In contrast to several other case studies concerning the impacts of mine drainage on water quality (e.g. Emrich and Merritt 1969; Lottermoser and others 1999), the groundwater and surface water chemistry in Hitura is exceptional with respect to pH. Whereas acid mine drainage normally has very low pH values associated with it, the pH around the tailings area was mainly close to neutral in both the groundwater (median pH 5.9) and the

Table 3
Statistical summary of chemical data on the groundwater of the Hitura area in 1999. Note that Cd concentrations are presented in µg/l. National drinking water limits (DWL) for household wells and small water cooperatives (Anon 2001) and median values for Finnish sand and gravel aquifers (Sd/Gr. aqf.) and till aquifers (Till aqf.; Lahermo and others 1990) are presented for reference purposes

	Groundw	ater around	Groundwater around the tailings area	rea			Groundwai	roundwater of the tailings area	ilings area				Finnish ref	innish reference values	es
	Min.	Med.	Mean	SD	Max.	и	Min.	Med.	Mean	SD	Мах.	и	DW limit	Sd/Gr. aqf. med.	f. Till aqf. med.
EC (mS/m)	4.4	40	490	630	2,140	109	550	910	950	260	1,360	∞	250	15.0	19.5
, Hd	2.8	5.9	5.9	0.8	8.7	74	5.4	7.5	7.2	0.9	8.3	8	6.5-9.5	6.4	6.3
Alk. (mmol/l)	0.24	1.07	1.32	1.51	5.40	6	0.74		1.59		2.44	7		0.57	0.77
Alk. (mmol/l)	0.14	0.71	1.51	1.53	5.99	15	0.43	1.04	1.20	99.0	2.41	8			
SO <sub>4</sub> (mg/l)	<1	33	1,480	2,120	8,200	26	3,900	5,850	7,440	4,270	17,250	8	250	10.6	13.0
Cl (mg/l)	1.57	13.6	110	220	200	6	840		920		1,090	8	100	7.2	0.6
$(mg/1)^a$	1.70	68	220	260	260	15	23	720	200	530	1,760	8			
Fe (mg/l)	<0.02	69.0	21.1	48.1	330	91	<0.02	<0.02	1.18	1.70	4.63	8	0.2	0.07	0.07
Ca (mg/l)	0.31	22.5	200	240	260	74	390	520	200	53.8	550	8		12.4	16.5
Mg (mg/l)	0.32	10.0	300	390	1,170	74	780	1,240	1,440	570	2,680	8		2.6	3.5
Na (mg/l)	4.41	8.65	30.6	42.7	120	6	180		200		230	7		5.4	6.9
K (mg/l)	1.23	3.27	13.1	19.9	61.9	6	100		170		250	7		3.1	4.3
Mn (mg/l)	< 0.01	0.75	2.59	3.43	19.5	74	1.71		3.53		5.35	7	0.05	0.02	0.02
Ni (mg/l)	<0.02	<0.02	1.48	5.18	30.3	74	<0.02	0.04	360	950	2,860	8	0.02	0.003	0.003
Al (mg/l)	<0.01	0.05	0.02	0.02	0.23	6	<0.01		<0.01		<0.01	7	0.2		
Cd (µg/l)	<0.2	<0.2	0.29	0.38	1.21	6	<0.2		0.2		0.3	7	5.0	0.5	0.5
Co (mg/l)	<0.03	<0.03	09.0	2.16	12.3	74	<0.03	<0.03	330	860	2,610	8			
Cu (mg/l)	< 0.01	<0.01	0.03	90.0	0.46	74	<0.01	<0.01	0.03	0.02	0.21	8	2.0	900.0	0.007
Pb (mg/l)	<0.05	<0.05	<0.05		0.05	64	0.14		0.14		0.14	7	0.01	0.001	0.001
Zn (mg/l)	<0.05	0.02	0.13	0.19	96.0	74	<0.05	<0.05	94.7	250	260	8		0.050	0.050
Si (mg/l)	5.93	7.30	7.64	1.34	9.92	6	0.68		1.28		1.88	7			
Sr (mg/l)	0.05	0.09	0.30	0.42	1.25	6	0.88		1.07		1.26	7			
Br (mg/l)	<0.1	<0.01	0.93	2.13	6.88	6	8.23		9.87		11.5	7			
F (mg/l)	<0.1	<0.1	<0.1	ı	0.18	7	2.90		4.30		5.69	7	1.5	0.10	0.10
NO <sub>3</sub> (mg/l)	<0.2	1.82	2.82	2.59	8.17	∞	1.43		2.37		3.31	7	50	4.0	6.7

<sup>a</sup>Data collected and analysed in 2000

Statistical summary of chemical data on the surface waters of the Hitura area in 1999. Note that Cd concentrations are presented in µg/l. Median values for Finnish stream waters (Lahermo and others 1996) are presented for reference purposes Table 4

Min. Med. Dec. 10	urface waters in the Hitura area				Surface wat	arface waters (=process waters) in the tailings area	waters) in th	e tailings area	3		Reference
250 6.3 0.07 1,120 42.9 140 1.23 59.6 87.3 18.0 12.2 0.83 0.22 0.37 0.01 0.01 0.01 0.01 0.05 0.005	Mean	SD	Max.	и	Min.	Med.	Mean	SD	Max.	и	waters Med.
2.9 6.3	490	260	1,770	46	530	830	810	210	1,030	4	4.4
<ul> <li>&lt;0.002</li> <li>&lt;0.002</li> <li>&lt;0.002</li> <li>&lt;0.40</li> <li>&lt;1</li> <li>1,120</li> <li>3</li> <li>42.9</li> <li>1.4</li> <li>140</li> <li>0.07</li> <li>59.6</li> <li>0.26</li> <li>87.3</li> <li>4.43</li> <li>18.0</li> <li>1.76</li> <li>12.2</li> <li>&lt;0.01</li> <li>&lt;0.02</li> <li>&lt;0.01</li> <li>&lt;0.02</li> <li>&lt;0.03</li> <li>&lt;0.01</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.01</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.01</li> <li>&lt;0.05</li> <l< td=""><td>5.8</td><td>1.2</td><td>7.3</td><td>45</td><td>6.3</td><td>6.4</td><td>6.4</td><td>0.1</td><td>9.9</td><td>4</td><td>5.91</td></l<></ul>	5.8	1.2	7.3	45	6.3	6.4	6.4	0.1	9.9	4	5.91
(40.02   0.40   1,120   3   42.9   1.40   1.40   1.40   1.23   0.07   1.23   0.07   1.23   0.07   0.26   0.83   0.22   0.02   0.22   0.00   0.23   0.00   0.23   0.00	0.10	0.10	0.24	4	0.22					1	0.20
<ul> <li>(1) 1,120</li> <li>3 42.9</li> <li>1.4 140</li> <li>0.07 1,23</li> <li>0.07 59.6</li> <li>0.26 87.3</li> <li>4.43 18.0</li> <li>1.76 12.2</li> <li>&lt;0.01 0.83</li> <li>&lt;0.02 0.22</li> <li>&lt;0.01 0.3</li> <li>&lt;0.02 0.5</li> <li>&lt;0.03 0.5</li> <li>&lt;0.03 0.05</li> <li>&lt;0.005 0.01</li> <li>&lt;0.05 0.01</li> <li>&lt;0.05 0.01</li> <li>&lt;0.05 0.01</li> <li>&lt;0.05 0.01</li> <li>&lt;0.05 0.01</li> <li>&lt;0.07 0.01</li> <li>&lt;0.08 0.01</li> <li>&lt;0.09 0.01</li> <li>&lt;0.01 0.01<!--</td--><td>0.43</td><td>0.34</td><td>0.94</td><td>6</td><td>0.16</td><td>0.22</td><td>0.28</td><td>0.14</td><td>0.51</td><td>4</td><td></td></li></ul>	0.43	0.34	0.94	6	0.16	0.22	0.28	0.14	0.51	4	
3 42.9 1.4 140 0.07 59.6 0.26 87.3 4.43 18.0 1.76 12.2 <0.01 0.83 <0.02 0.22 <0.01 0.83 <0.02 0.22 <0.01 0.3 <0.03 0.5 <0.03 <0.03 <0.03 <0.03 <0.04 <0.05 <0.05 <0.05 <0.01 0.01 <0.05 <0.07 <0.01 0.01 <0.05 <0.01 0.01 <0.05 <0.01 0.01 <0.05 <0.01 0.01 <0.05 <0.05 <0.01 0.01 <0.05 <0.05 <0.07 <0.01 0.01 <0.05 <0.05 <0.07 <0.01 0.01 <0.05 <0.05 <0.05 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0.07 <0	1,650	1,850	5,900	40	1,400	2,700	2,620	880	3,680	4	3.5
1.4     140       0.07     59.6       0.06     87.3       4.43     18.0       1.76     12.2       <0.01	170	250	009	4	780					1	1.4
0.07 1.23 0.07 59.6 0.26 87.3 4.43 18.0 1.76 12.2 <0.01 0.83 <0.02 0.32 <0.01 0.37 0.3 0.5 <0.03 <0.03 <0.01 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.05 <0.05 <0.05 <0.05 <0.05 <0.07 <0.07 <0.07 <0.01 <0.07 <0.01 <0.01 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05	270	270	029	10	450	640	640	150	840	4	
0.07 59.6 0.26 87.3 4.43 18.0 1.76 12.2 <0.01 0.83 <0.02 0.22 <0.01 0.37 0.3 0.01 <0.03 0.01 <0.03 0.01 <0.05 0.05 <0.05 0.00 <0.01 0.01 <0.05 0.01 <0.05 0.01 <0.01 0.01 <0.05 0.01 <0.01 0.01 <0.05 0.01 <0.01 0.01 <0.05 0.01 <0.01 0.01 <0.05 0.01 <0.01 0.01 <0.05 0.01 <0.01 0.01	3.83	6.37	27.2	40	<0.02	<0.02	0.04	0.04	0.11	4	89.0
0.26     87.3       4.43     18.0       1.76     12.2       <0.01	200	240	650	38	420		460		200	7	4.06
4.43 18.0 1.76 12.2 <0.01 0.83 <0.02 0.22 <0.01 0.37 0.3 (0.5 <0.03 <0.03 <0.03 <0.03 <0.01 0.01 <0.05 <0.05 <0.01 0.01 <0.05 <0.05 <0.01 <0.01 <0.05 <0.01 <0.01 <0.05 <0.01 <0.01 <0.05 <0.01 <0.01 <0.05 <0.00 <0.01 <0.05 <0.00 <0.01 <0.01 <0.05 <0.05 <0.00 <0.01 <0.05 <0.05 <0.05 <0.00 <0.01 <0.05 <0.05 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.00 <0.	280	340	1,030	38	550		730		910	7	1.39
1.76 12.2 <0.01 0.83 <0.02 0.22 <0.01 0.37 0.3 0.5 <0.03 0.5 <0.03 0.01 <0.01 0.01 <0.05 <0.05 <0.05 <0.01 <0.01 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <	32.8	34.0	6.06	4	99.5					1	2.1
<ul> <li>&lt;0.01</li> <li>&lt;0.02</li> <li>&lt;0.02</li> <li>&lt;0.03</li> <li>&lt;0.3</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.04</li> <li>&lt;0.19</li> <li>&lt;0.11</li> <li>&lt;0.19</li> <li>&lt;0.19</li> <li>&lt;0.11</li> <li>&lt;0.19</li> <li>&lt;0.11</li> <li>&lt;0.19</li> <li>&lt;0.10</li> <l< td=""><td>18.3</td><td>17.2</td><td>47.1</td><td>4</td><td>53.3</td><td></td><td></td><td></td><td></td><td>1</td><td>0.70</td></l<></ul>	18.3	17.2	47.1	4	53.3					1	0.70
<ul> <li>&lt;0.02</li> <li>&lt;0.01</li> <li>&lt;0.3</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.01</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.01</li> <li>&lt;0.14</li> <li>&lt;0.19</li> <li>&lt;0.1</li> <li>&lt;0.11</li> <li>&lt;0.19</li> <li>&lt;0.10</li> <li>&lt;0.10</li> <li>&lt;0.10</li> <li>&lt;0.11</li> <li>&lt;0.10</li> <l></l></ul>	1.36	1.72	7.71	38	0.78		1.73		2.67	7	0.03
<ul> <li>&lt;0.01</li> <li>0.3</li> <li>0.3</li> <li>0.5</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.03</li> <li>&lt;0.003</li> <li>&lt;0.005</li> <li>&lt;0</li></ul>	7.58	23.4	117	38	1.57		1.73		1.88	7	0.0005
0.3 0.5 <0.03 <0.03 <0.01 <0.01 <0.05 <0.05 <0.05 <0.10 4.37 8.04 0.14 0.19 <0.1	5.29	8.73	20.4	4	<0.01					1	0.095
<0.03	280	480	1,120	4	90					1	<0.02
<ul> <li>&lt;0.01</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.10</li> <li>4.37</li> <li>&lt;0.19</li> <li>&lt;0.1</li> <li>&lt;0.1</li> <li>&lt;0.1</li> </ul>	3.17	9.91	49.9	38	0.15		0.22		0.29	1	0.0002
<ul> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.05</li> <li>&lt;0.10</li> <li>&lt;0.14</li> <li>&lt;0.19</li> <li>&lt;0.1</li> <li>&lt;0.1</li> </ul>	0.37	1.49	7.51	38	<0.01		0.01		0.02	7	0.0006
<ul> <li>&lt;0.05</li> <li>4.37</li> <li>8.04</li> <li>0.14</li> <li>0.19</li> <li>&lt;0.1</li> <li>&lt;0.1</li> <li>&lt;0.1</li> </ul>	<0.05		0.11	38	<0.05		<0.05		<0.05	7	0.0002
4.37 8.04 0.14 0.19 <0.1 0.40 <0.1	0.58	2.23	13.8	38	0.10		0.24		0.38	7	0.004
0.14 0.19 <0.1 <0.1 <0.1 <0.1 <0.1	11.0	7.42	23.6	4	1.55					1	
<0.1 0.40 <0.1 <0.1	0.33	0.27	0.80	4	1.03					1	0.022
<0.1	1.88	2.78	29.9	4	8.89					1	<0.5
	0.12		0.28	7	2.07					1	80.0
0.91 0.96	1.12	0.26	1.49	3	1.64					1	0.50

<sup>a</sup>Data collected and analysed in 2000

surface water data (median pH 6.3). Furthermore, pH values above 7 were measured in the groundwater of the tailings area itself, even in the monitoring well placed in the oldest part of the impoundment (pond A). Moreover, these near-neutral waters contained elevated concentrations of sulphate and also iron and nickel in places. The occurrence of this type of mine drainage, termed neutral mine drainage (NMD), has been described earlier by Nesbitt and Jambor (1998) and by Pettit and others (1999), both of whom concluded that it results from buffering of the acid produced in the oxidation of sulphides with the neutralizing minerals present in the waste.

In the Hitura case, the observed NMD with elevated sulphate levels may be assumed to be caused by both the sulphate-rich, neutral process water (see Tables 2 and 4) and neutralization of the acid produced in sulphide oxidation. The former factor can be regarded as more probable, however, because the surface of the tailings was observed to be only slightly oxidized, suggesting relatively low acid production. Nevertheless, the lack of visible evidence of sulphide oxidation, i.e. the absence of iron oxide precipitates, could also be a result of incomplete oxidation of ferrous iron (Fe<sup>2+</sup>) caused by the limited oxygen supply (Larsen and Postma 1997). In that case, oxidation of sulphides could occur, resulting in an excess of protons, but this would be mineralogically visible only under a microscope. Further research would be needed to confirm

However, even if some oxidation of sulphides were to occur, the acid production would apparently be neutralized because the Hitura tailings are composed mainly of Mg serpentinite and contain only small amounts of sulphides. Nesbitt and Jambor (1998) concluded that mafic minerals are effective in neutralizing tailings-derived acid mine drainage. Moreover, Saari (unpublished data) has reported that the Hitura tailings are non-acid generating, in the light of the ratio between the measured neutralizing and acid production potentials (NP/AP), which was as high as 10.1. According to Price and others (1997, in Jambor and Blowes 1998) NP/AP ratios higher than 4 generally indicate that the potential of the mine waste for causing acid drainage is nil. In addition, alkalinity values measured in the groundwater of the tailings area were relatively high compared with the median values for Finnish groundwater (Table 3), also reflecting the buffering capacity of the tailings. A predictive geochemical model would nevertheless be needed to assess further the future geochemical behaviour of the tailings. Pettit and others (1999) have demonstrated that such models are capable of predicting the long-term effects of mine drainage over periods as long as the next 100 years. They further discovered that current neutral mine drainage may become acid in the long term.

Nevertheless, low pH values, even below pH 3.0, were detected in natural waters in the area. pH values below 5.0 were measured in the brook of Makolanoja, at a point adjacent to the jarosite pile in the tailings area and on the western border of the tailings area (Figs. 2b and 3b). The

result of acid mine drainage from the abandoned tailings area of the Makola mine. A decrease in pH values downstream in the brook was also noticed by Sipilä (1996), who maintained that it was caused by further oxidation of the seepage water. However, the Makolanoja brook also receives water from the surrounding peat areas, which may result in decreased pH readings.

The lowest pH value for surface waters (2.9) was measured in a pond that is in contact with the jarosite pile, and that for groundwater (2.8) to the west of the tailings area. Before the year 2000, the jarosite pile was only partly covered with clay and till and, therefore, was prone to weathering. According to Nordstrom and Munoz (1985), hydrolysis of jarosite produces protons, and thereby acidity. This results in leaching of metals into both groundwater and surface water. This has evidently also occurred in Hitura, as the highest concentrations of nickel (2,860 mg/l), cobalt (2,610 mg/l) and zinc (760 mg/l) were measured in the monitoring well drilled into the jarosite pile. Furthermore, the highest concentrations of these variables in surface waters were measured in the pond adjacent to the jarosite pile. These relations are shown with respect to nickel in Figs. 2 and 3, in which the areal distribution of nickel concentrations is presented.

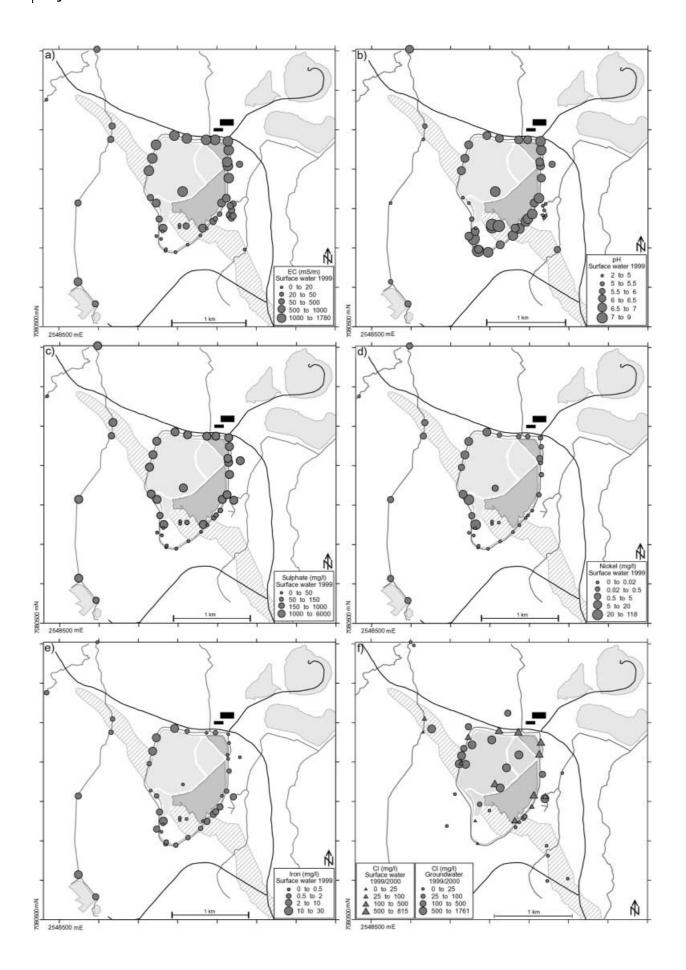
### Chloride

In contrast to the results of Gray (1996), for example, chloride also seemed to reflect well the impact of the tailings-derived water in Hitura. Johnson and Thorton (1987) reported that the chloride concentration was a good tracer for mine water in a river system in the west of England that was contaminated with AMD, and maintained that the chloride was of subterranean origin, resulting either from the infiltration of seawater into the mine or from juvenile water emanating from the granitic rocks. In the Hitura case, the source of chloride is most probably the ore rocks and their fluid inclusions. According to Aulanko (1970), the chloride concentration of the mine water was as high as 2,670 mg/l in the past, whereas it is nowadays  $\sim$ 150 mg/l (Table 2). Additionally, Papunen (1970) discovered that the X-ray fluorescence spectrum of the Hitura serpentinites showed a distinct peak for chlorine, and speculated that the chloride might be of connate origin, introduced into the rock during serpentinization. In the same connection, however, he also suggested that fossil marine water from the postglacial stages was circulating in the Hitura ore massif, resulting in anomalously high sodium concentrations in whole rock serpentinite analyses. Nonetheless, chloride can in this case be considered a good indicator of contamination by tailings-derived water.

# Assessment of the extent of contamination

### Individual variables

The distributions of EC, sulphate and chloride in the surface waters show clear patterns, with the highest concentrations occurring in the northern half of the seepage low pH values in the brook Makolanoja are presumably a ditch (Fig. 3), where the hydraulic gradient outwards from



### 4

### Fig. 3

Areal distribution of a electrical conductivity, b pH, c sulphate, d nickel and e iron in the surface waters of the Hitura area, and f areal distribution of chloride in both surface and groundwater. For items on the base map see Figs. 1 and 7

the tailings area is steepest and seepage occurs through the tailings dam. In contrast, the highest concentrations of nickel and iron are focused on the western part of the seepage ditch, coinciding with the point of protection pumping discharge and with the jarosite pile, as mentioned above. Upstream of the tailings area, all the above variables appear to reflect the natural background. On the other hand, in the brook Makolanoja the impact of the Makola mining area has resulted in elevated EC and of sulphate, nickel and iron concentrations, as reported by Sipilä (1996). These elevated concentrations steadily become dilute downstream towards Hitura because of precipitation and surface runoff (Fig. 3), but further downstream a sudden increase in electrical conductivity is detected, accompanied by high concentrations of sulphate, magnesium, calcium, manganese and cobalt, etc. Furthermore, chloride concentrations increase almost tenfold from less than 1 to 75 mg/l (Fig. 3f). This indicates that tailings-derived water from the Hitura mining area does eventually discharge into Makolanoja, as proposed by Wihuri and Ikäheimo (unpublished data), and that chloride is a good indicator for differentiating the effects of the Hitura tailings from the impact of the Makola mining area. The areal distribution of EC, sulphate and chloride in the groundwater is quite similar to that in the surface waters (Figs. 2 and 3), except that elevated concentrations can also be observed outside the south-eastern corner of the impoundment, adjacent to the tailings dam and to the west of the impoundment, close-to the Makolanoja brook. The elevated concentrations to the north-west and south-east of the tailings area coincide with the interlobate esker. According to Salonen and others (2001), the gravelly core of the esker still exists underneath the tailings dam, even though it should have been removed during construction of the dam, and it thus provides a good hydraulic connection from the tailings area to the surrounding groundwater. To the north-west of the dam this effect is further enhanced by hydraulic pressure from the tailings area and by the protection pumping. It is apparent from Figs. 2 and 3 and from observations made during the fieldwork that the esker complex enables the migration of tailings-derived water into the Makolanoja brook as well. The overburden to the north and west of the tailings area consists of fine-grained till (Fig. 1). According to Salonen and others (2001), the hydraulic conductivity of this till unit is much lower than that of the gravelly core of the esker, varying between 10<sup>-6</sup> and 10<sup>-4</sup> m/s. Nonetheless, EC and sulphate concentrations in its groundwater are even higher locally, especially adjacent to the dam, than in the waters of the tailings area itself (Figs. 2 and 3). In addition, increased concentrations of nickel and lowered pH values occur. In view of the low oxidation rate and the low hydraulic conductivity of the tailings and the till over-

burden, this implies that loading from the tailings area must have been more pronounced in earlier times. This can be attributed to the use of sulphuric acid in the enrichment process, the amounts of acid involved having been at least twice as large in the late 1970s than in the 1990s. Consequently, process water sulphate concentrations will have been of the order of 8,000 mg/l in the late 1970s, as opposed to less than 4,000 mg/l in recent times. Correspondingly, the average pH of the process water has changed from 4.8 to 6.3. Thus, the elevated concentrations in the groundwater around the north-western part of the tailings area are more likely to reflect the historical impact of tailings disposal than the present effect of acid mine drainage.

## Water types

In addition to looking at single variables, major ion-based water types were determined in order to distinguish the contaminated waters better from the waters reflecting the natural background. It has been reported on a number of occasions that deterioration in water quality can be assessed by examining major ion compositions (e.g. Piper 1944; Zubari 1999). Interestingly, Finnish groundwater areas contrast with many others by being predominantly of the Ca-HCO<sub>3</sub> type, whereas other types (e.g. the Na-Cl or Ca-SO<sub>4</sub> type) occur only rarely (Lahermo and others 1990). Any deviations from the Ca-HCO<sub>3</sub> type can thus be considered anomalous under Finnish conditions. The major ion composition was assumed to be a more sensitive tool for detecting incipient pollution than the concentrations of individual elements because it was impossible to determine the distinct background levels for the elements. In addition, evidence of mixing of different water types can be used to delineate the boundaries of the contaminant plume. The main water types were identified by calculating the major ion compositions of 16 samples from different parts of the area and plotting these results on a Piper diagram (Piper 1944, Fig. 4). Major ion compositions for water types characteristic of Finnish sand-gravel aquifers and till aguifers (Lahermo and others 1990) and for streams (Lahermo and others 1996) were calculated for comparison. It may be seen from the figure that the samples arrange themselves in two distinct groups. The first represents waters of the Mg-SO<sub>4</sub> type and is characterized by high total dissolved solids and specific conductivity and large amounts of chloride, calcium, nickel and cobalt in addition to high sulphate and magnesium concentrations. This type represents the tailings-derived water because the process water and groundwater in the tailings area belong to this group (Fig. 5). According to Lahermo and others (1990), Mg-rich groundwater is very rare in Finland. Evidently, therefore, Mg-SO<sub>4</sub>-type waters indicate pollution of the natural waters of the Hitura area. Waters of this type were detected in the seepage ditch and also to the north and west of the dam and in the brook of Makolanoja. The other group of samples, reflecting the most common water type in Finnish sand-gravel and till aquifers (Lahermo and others 1990), can be characterized as being of the Ca-HCO<sub>3</sub> type, containing a small quantity of total dissolved solids and having a low specific conductivity

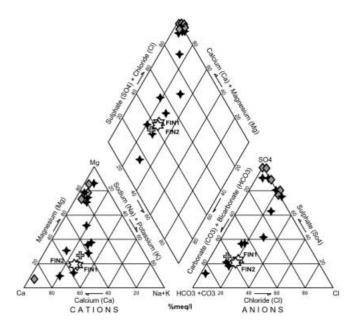


Fig. 4
Piper plot showing the chemical compositions of groundwater and surface water samples. Groundwater samples are indicated with black stars and surface water samples with grey diamonds. Median values for Finnish sand–gravel aquifers (FIN1) and till aquifers (FIN2) are shown with white stars (Lahermo and others 1990) and median values for Finnish stream waters with grey crosses (Lahermo and others 1996)

and, therefore, also low concentrations of the abovementioned ions. Water samples belonging to this group occurred approximately 1 km away from the tailings pond to the south-east, and can be interpreted as uncontaminated waters representing the natural background of the area (see also Fig. 5).

Figure 4 also demonstrates that a few samples differ from the major groups and plot in the Ca-SO<sub>4</sub> and Mg-HCO<sub>3</sub> sectors of the diagram. These results, especially with regard to the Mg-HCO<sub>3</sub> type, indicate mixing of different types of water and thus provide evidence of migration of the tailings-derived contaminant plume. This situation was typical especially of the south-eastern side of the tailings area near the dam (Fig. 5).

Examples of the groundwater types discussed above are placed on a map in Fig. 5 and their major ion compositions are illustrated by means of radial plots. A gradual change in water chemistry from Mg-SO<sub>4</sub>-dominated water through the mixed type to Ca-HCO<sub>3</sub> water occurs within 500 m from the tailings area. Based on the above results, it can be concluded that the major ion composition seems to be a good tool for delineating the extent of contamination in the Hitura area.

### Hydrochemical regimes

Because the major ion composition was not measured for all samples, the contaminant plume could only be delineated with low resolution. Therefore, following the example given by Suk and Lee (1999), hierarchical cluster analysis was applied to the data to distinguish the hydrochemically different regimes in the area, although with the difference that it was applied to the original observations instead of the factor scores. A total of 12 variables with the widest number of cases without missing values (119 groundwater and surface water samples) were selected for the analysis, as shown in Table 5. Data on the groundwater and surface water of the tailings area were included. To reduce the effect of non-normal distributions on the analysis, a log10 transformation was performed on selected variables and the log-transformed data were further standardized to equalize the scale differences between the variables. The clusters were separated computing Euclidian distances and using Ward's method as the linkage rule.

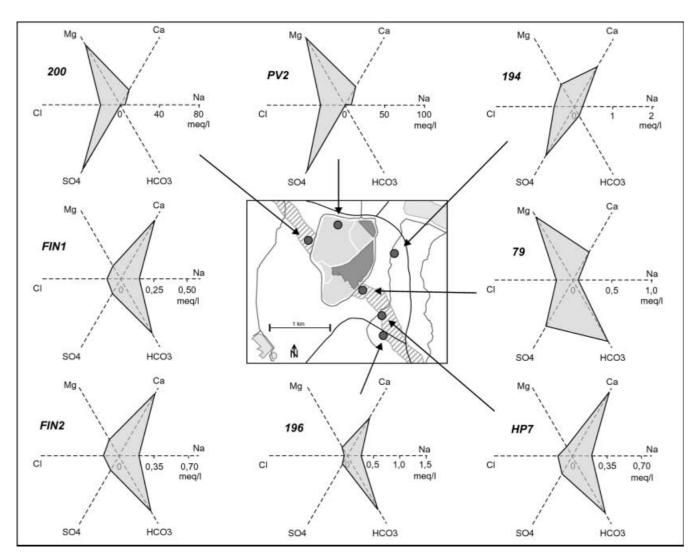
Cluster analysis divided the data set into two main groups (A and B in Fig. 6), basically corresponding to the grouping of water types according to the Piper diagram, with sulphate, chloride and nickel concentrations being approximately 20 times higher in group B than in group A. Thus the cluster analysis appears to divide the data roughly into uncontaminated, i.e. Ca-HCO<sub>3</sub>-type waters (A) and waters affected by the tailings area, i.e. Mg-SO<sub>4</sub>type waters (B). Both groups included a combination of groundwater and surface water samples. Group A could then be further divided into three subgroups (1-3) and group B into four subgroups (4-7; Fig. 6). The chemical characteristics of the groups are presented in Table 5. In the light of these data and the areal distribution of the clustering groups, presented in Fig. 7, the subgroups can be described as follows:

### Cluster A – uncontaminated waters

- Cluster 1 (n=25): waters resembling the natural geochemical background of the area; concentrations of sulphate and nickel are below the national drinking water limits (DWL) and the medians of the parameters analysed correspond to those recorded for Finnish sand-gravel and till aquifers.
- Cluster 2 (n=17): like cluster 1, but with a somewhat higher electrical conductivity and manganese concentration.
- Cluster 3 (n=15): waters representing minor impacts of the tailings-derived water or reflecting naturally high concentrations of Mn and Fe; concentrations of SO<sub>4</sub>, Mg, Ca, Mn and Fe are two to ten times higher than in clusters 1 and 2, but concentrations of Ni and SO<sub>4</sub> are still below the DWL, except that iron exceeds the limits about tenfold; the cation-anion proportions indicate slight mixing.

### Cluster B - contaminated waters

- Cluster 4 (n=24): mainly tailings-derived surface water diluted to some extent with rainwater and overland flow; high concentrations of heavy metals and a somewhat lower pH than in the other subgroups in cluster B.
- Cluster 5 (n=21): resembles cluster 4, but consists primarily of groundwater samples containing more iron, manganese and sulphate than those in cluster 4; heavy metal concentrations are well above the DWL.
- Cluster 6 (*n*=6): groundwater samples in the tailings area, with heavy metal concentrations mostly below the detection limit.



**Fig. 5**Radial plots of the major ion compositions of the groundwater in the tailings area and its surroundings. *FIN1* and *FIN2* represent the medians of the major ion compositions of Finnish sand/gravel and till aquifers (Lahermo and others 1990). For items on the base map see Figs. 1 and 7

• Cluster 7 (n=11): the most contaminated waters of all, with high electrical conductivity and extremely high concentrations of heavy metals; associated partly with the jarosite landfill.

When these clusters are plotted on the map (Fig. 7), contamination is seen to be most intense to the north and west of the tailings area, reaching the Makolanoja brook in the west and apparently being limited by it, and presumably extending all the way to the open pit in the north, controlled by the groundwater flow direction (Fig. 2). The latter is further evidenced by the cluster of uncontaminated observation sites north-west of the impoundment. Interestingly, samples representing cluster 7 occur to the west of the tailings area as well as in the vicinity of the jarosite pile. This seems to provide further evidence of the good hydraulic connection existing via the esker core underneath the dam, as suggested earlier.

Despite the intense pollution near the impoundment, the southern and south-eastern parts of the area appear to be uncontaminated. There are indications of initial pollution directly beside the south-eastern part of the tailings dam, however, where the dam crosses the interlobate esker, and this is apparently the route taken by the tailings-derived water that brought about the slight pollution of the Töllinperä water intake reported by Korkka-Niemi and others (1999). Salonen and others (2001) have nevertheless proposed that, on the basis of sedimentological investigations and a groundwater flow model, this hydraulic connection is only available when the water level rises considerably in the impoundment. This seems to be true since the Töllinperä aquifer has largely remained unpolluted.

# Electrical resistivity sounding survey

Finally, resistivity soundings were performed in order to test the applicability of this method for locating tailingsderived aquifer pollution in a terrain in which the overburden consists of complex Quaternary sediments typical of Finnish conditions. The target was to test the method firstly for identifying an observed leakage and secondly for

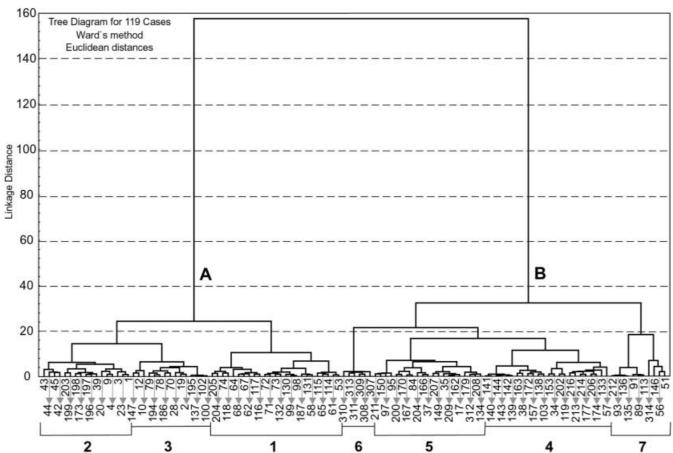
**Table 5**Mean and median values for the groups distinguished by hierarchical cluster analysis. The italicized data represent the medium and mean values for the whole groups A and B. Group A thus corresponds to

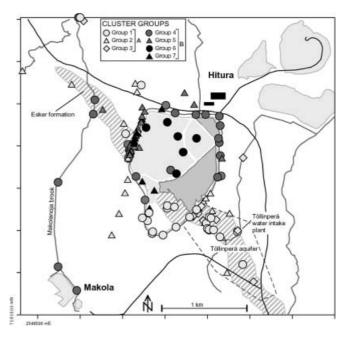
the uncontaminated waters and includes the subgroups 1, 2 and 3. Similarly, med. and mean values for group B are the med. and mean for the contaminated waters comprising subgroups 4–7

Group		SpCond (mS/m)	pН	SO <sub>4</sub> (mg/l)	Fe (mg/l)	Ni (mg/l)	Mg (mg/l)	Ca (mg/l)	Mn (mg/l)	Zn (mg/l)	Co (mg/l)
Uncontaminated	d waters (A)										
Subgroup 1	Med.	13.3	6.7	1.0	0.44	0.01	1.92	3.93	0.01	0.02	0.02
0 .	Mean	20.0	6.9	8.2	0.78	0.01	3.10	7.99	0.03	0.04	0.02
Subgroup 2	Med.	20.5	6.1	16	0.07	0.01	2.34	3.93	0.15	0.09	0.02
0 1	Mean	22.6	5.9	15.7	1.25	0.01	3.10	8.48	0.16	0.18	0.02
Subgroups 1+	-2 Med.	16.2	6.5	7.5	0.39	0.01	1.95	3.93	0.03	0.05	0.02
0 .	Mean	21.0	6.5	11.2	0.97	0.01	3.10	8.19	0.08	0.09	0.02
Subgroup 3	Med.	59.3	6.0	69	3.78	0.01	11.0	19.8	1.30	0.05	0.02
0 1	Mean	79.9	5.9	150	15.4	0.02	20.3	26.2	1.79	0.06	0.02
Group A	Med.	22.3	6.4	10	0.52	0.01	2.77	5.37	0.12	0.05	0.02
•	Mean	36.5	6.4	46.5	4.76	0.01	7.62	12.9	0.53	0.08	0.02
Contaminated w	vaters (B)										
Subgroup 4	Med.	850	5.9	2,900	0.38	0.36	500	370	1.16	0.10	0.09
0 1	Mean	880	5.7	2,690	1.65	1.44	460	340	1.79	0.16	0.31
Subgroup 5	Med.	1,450	6.0	4,300	37.0	0.28	840	480	5.16	0.11	0.10
0 1	Mean	1,390	5.9	4,630	62.3	0.85	790	490	6.04	0.10	0.32
Subgroup 6	Med.	910	7.8	5,800	0.01	0.01	1,120	500	1.62	0.01	0.02
0 1	Mean	920	7.7	6,580	0.07	0.06	1,070	510	2.03	0.01	0.04
Subgroup 7	Med.	1,730	6.1	5,500	25.5	19.4	950	550	4.68	0.60	9.52
<b>5</b> 1	Mean	1,390	5.3	5,670	28.8	290	840	520	5.08	70.8	250
Group B	Med.	1,180	6.1	4,000	4.04	0.36	740	490	3.71	0.10	0.12
•	Mean	1,150	5.9	4,260	26.8	52.7	700	440	3.84	12.6	44.7

**Fig. 6**Results of the cluster analysis, presented as a hierarchical cluster tree. *Numbers* below the results are sample codes

delineating the unknown extent of the contaminant plume. Based on the information obtained from the chemical analyses, the first transect, therefore, was located to the west of the tailings impoundment, where the contamina-



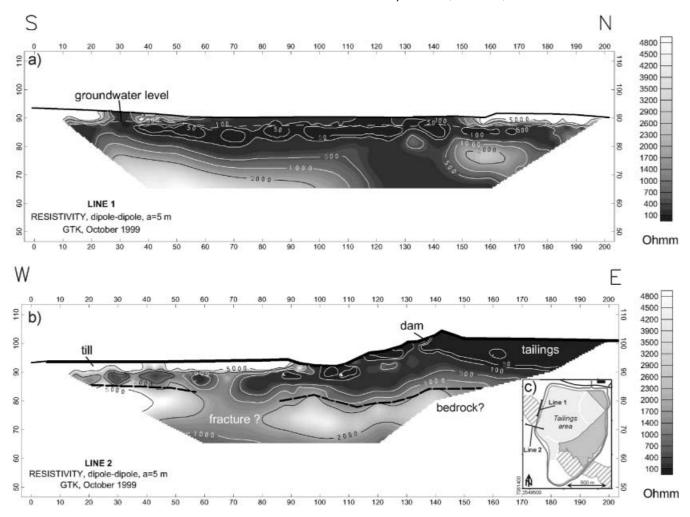


**Fig. 7**Areal distribution of the cluster groups. For items on the base map see Fig. 1

tion was observed to be most severe, and the second across the tailings dam, extending from the impoundment to the till terrain, for which only limited chemical data were available. The selected locations and the resistivity images of the measurements are shown in Fig. 8.

Layers of low resistivity,  $10-50 \Omega m$ , were detected within 10 m of the surface on both transects (Fig. 8). By comparison, saturated soils in Finland in general give values varying between 35 and 2,000  $\Omega$ m (Peltoniemi 1988). The soil of the first transect (profile 1 in Fig. 8) is composed mainly of sand and stony till, i.e. of materials having average resistivity values above 200 Ωm (when saturated). According to Vanhala (2001), a decrease in electrical resistivity can be a direct result of an increase in the ionic content of the water, especially in cases of inorganic contamination of an aquifer. Indeed, the results of the hydrogeochemical study suggest that the low-resistivity layer coincides with the measured hydraulic head and elevated electrical conductivity and sulphate concentrations. Thus, the lowered resistivity of the soil evidently originates from infiltration of tailings-derived water into the aquifer.

Fig. 8
Resistivity sections (2D-models) and locations of transects 1 and 2



The resistivity image for the second transect (profile 2 in Fig. 8) shows that the low-resistivity layer, which has the lowest reading recorded in this survey, is closely related to the tailings area. The image clearly indicates a continuous plume of tailings-derived water advancing from the impoundment to the adjacent groundwater also in this part of the study area. The depression in the middle of the section represents the seepage ditch surrounding the tailings area, which obviously prevents the progress of contamination in relation to surface runoff. The pollution front has nevertheless migrated underneath the ditch approximately 100 m into the groundwater of the till terrain. Resistivity sounding would seem to be a practicable method for delineating groundwater contamination in the Hitura area and would thus be readily applicable to the assessment of groundwater pollution in mining environments under Finnish conditions in general, especially since the natural groundwater in Finland usually has a low TDS content (Lahermo and others 1990).

# **Conclusions**

Deterioration in groundwater and surface water quality has occurred in the Hitura mining area because of the disposal of tailings. The best single indicators of the present contamination are elevated electrical conductivity and increased concentrations of sulphate and chloride. On the other hand, the greatest risk to the use of groundwater is evidently related to the increased nickel levels. Unlike most other mine drainage cases, the pollution from Hitura is neutral in character, since only minor oxidation of sulphides takes place in the tailings and the tailings material is able to neutralize the acidity that is produced. Thus, the tailings-derived water infiltrating into the surrounding surface and groundwater mainly represents the slightly altered, neutral process water pumped into the tailings area. This process water contained more than twice the concentrations of sulphate in the 1970s than it does nowadays and was more acid in character because of the extensive use of sulphuric acid in the mill. This feature is now reflected in the groundwater of the till unit adjacent to the tailings impoundment with increased sulphate and nickel concentrations and lowered pH values. Future research should be focused on modelling of long-term effects of the Hitura tailings.

The waters of this area appeared to be hydrochemically highly complex in nature. The natural waters are originally of the Ca-HCO<sub>3</sub> type, but infiltration of the tailings-derived water has altered their chemical composition towards the Mg-SO<sub>4</sub> type, resulting in a combination of these two main groups, i.e. Mg-HCO<sub>3</sub>-type waters. The complexity is further increased by the naturally high iron concentrations, the presence of surface water derived from the adjacent abandoned Makola mining area, representing traditional acid mine drainage water, and an influx of water affected by weathering of the jarosite waste pile deposited in the Hitura tailings area. The latter has a pH below 4 and contains a hundred times more nickel, cobalt

and zinc, for example, than does the water derived from the Hitura Mg serpentinite tailings. These hydrochemically different regimes could nevertheless be recognized using hierarchical cluster analysis and by reference to their major ion compositions. Tracing changes in ion composition proved to be a good method for delineating the contamination plume, since Finnish groundwater is primarily of the Ca-HCO<sub>3</sub> type. In addition to distinguishing the hydrochemically different regimes, both methods appeared to be well suited for the assessment of the extent of contamination. Aside from these two methods, the plume was also successfully mapped by means of an electrical sounding survey. The results of the assessment indicated that contamination has been most intense to the west and north of the tailings dam, and that uncontaminated waters prevail in an upgradient direction towards the hydraulic head in the southern part of the area and in the Töllinperä aquifer. The pollution is closely related to the esker complex running across the tailings area, which forms a good hydraulic route for water from the tailings area to pass into the surrounding groundwater.

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