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Estimation of leakage of chemical elements from boreal acid sulphate soils

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The amount of element leakage from young Finnish (boreal) acid sulphate soils was investigated using hydrochemical and geochemical approaches. These approaches gave similar results for S, Na, Mg, Al, Mn, Zn, Sr, Ni and Co, while Ca, La, Cd, U and Fe displayed higher leakage figures when using the hydrochemical approach and K, Cu, Ba, Ga, Sc, Ti, Pb, Th and Tl higher ones when using the geochemical approach. Total reducible sulphur (TRS) was the dominant sulphur species in the parent sediment and in the transition zone, while in the upper oxidised zone it had to a substantial extent been oxidised into sulphuric acid and subsequently leached, giving rise to typical AS soils and waters. However, also in this zone there was a reservoir of TRS left, which shows that the soils still have a great oxidation and acidification potential. The combination of the two approaches gave a clear picture of the qualitative and quantitative leaching of chemical elements from the soils with more reliable results than if only one approach would have been used. The method applied here can therefore be recommended for future studies and environmental monitoring in areas affected by acid sulphate soils.

Introduction

Acid sulphate soils (AS soils) occupy worldwide an area of ca. 17 million ha (Andriesse and van Mensvoort 2002), and cause significant environmental problems due to release of acidity and metals during oxidation of naturally occurring sulphur species. On the coastal plains of Finland these soils are according to Palko (1994) distributed over an area of 336 000 ha, but more recent and rigorous classification work indicates a somewhat lesser distribution (43 000–130 000 ha) (Yli-Halla *et al*. 1999). In Finland, the parent sediments of the AS soils were deposited during the relatively warm Litorina period and are characterised by a matrix of clay and silt sized aluminosilicates and variable amounts of humus, trapped salt and metal sulphides. Due to isostatic land uplift these sediments are now situated as far as 100 m above the present sea level (Palko 1994). When the sulphides in these sediments are oxidised due to oxygen penetration often caused by drainage for agricultural purposes, acidity is produced, which commonly lowers the pH below 4 and occasionally even below 3. This leads to an initial release of elements from sulphides (e.g. pyrite and monosulphides) and subsequent alteration of silicates and dissolution of associated metals (e.g. Palko 1994, Åström and Björklund 1997, Österholm and Åström 2002,

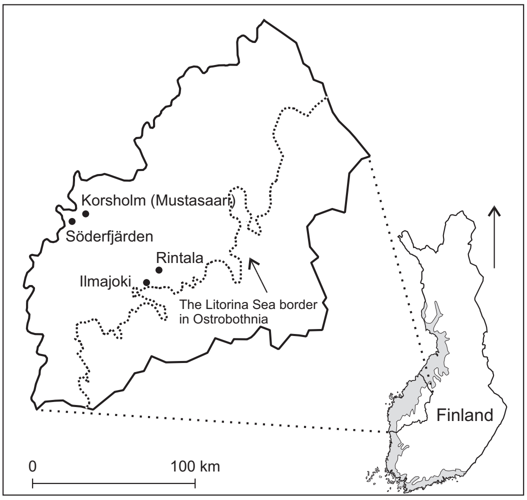

Fig. 1. Location of western Finland, the study sites therein, and the highest shoreline of the Litorina Sea (shaded area).

Joukainen and Yli-Halla 2003, Sohlenius and Öborn 2004). These weathering products are flushed into drains, resulting in elevated concentrations and loads of acidity and metals in downstream rivers (Åström and Björklund 1995, 1996, Åström and Åström 1997, Edén *et al.* 1999, Åström and Spiro 2000, Roos 2005) and estuaries. This, in turn, is harmful for the aquatic flora and fauna, and several mass kills of fish have been documented along the Finnish coast where these soils exist (e.g. Hudd 2000).

The main aims of this study were to: (1) estimate the quantities of multi-element leakage from young Finnish (boreal) AS soils (risen above sea level approximately one century ago), (2) compare the element leakage from Finnish AS soils developed on sediments very recently risen above the sea level to those developed in sediments risen above the sea level several millennia ago, and (3) determine the distribution of reduced-, organic- and sulphate sulphur in Finnish AS soils and sediments.

Material and methods

Field sites

Acid sulphate soil fields in Korsholm (in Finnish Mustasaari) (63°2.8´N, 21°42.9´E) and Söderfjärden (63°0.4´N, 21°33.3´E) were chosen as study sites since they represent young agricultural areas situated close to the present sea level, and since nearly half of the AS soils in Finland are located within this region (Fig. 1). They are compared with corresponding soils and sediments being in similar agricultural use in Rintala (62°47.5´N, 22°42.0´E) and Ilmajoki (62°43.2´N, 22°31.8´E). These sites are situated ca. 40 m above sea level i.e. they emerged from the sea as a result of land uplift some 4000 years ago (Fig. 1).

The Korsholm field is located in a polder area which was constructed in the end of the 1950s and pipe-drained to a depth of 1.1 m in 1969. In 1998, the old subsurface drainpipes were blocked and new ones were installed at a depth of 1 m. The Söderfjärden field was about 200 years ago a bay connected with the sea. However, in the 1820s most of the bay had risen above sea level due to the land uplift and the farmers started to excavate a large ditch in order to turn the area into arable land. The first pumping station was built in 1926 and in the 1950s the area was pipe-drained. The physical, chemical and biological soil forming processes at both sites have been fast and therefore resulted in rather deep soil profiles. It is fair to assume that the AS soil development was slow and marginal before the artificial drainage, since the areas were waterlogged prior to that activity, which prevented oxygen from penetrating and reacting with the inherent sulphides (Pons and Zonnenveld 1965). Hence, the AS soils in Korsholm are about 50 years old, and those in Söderfjärden about 80 years assuming marginal AS soil development before water pumping.

Sediment

A total of 19 vertical profiles (9 in Korsholm and 10 in Söderfjärden) were sampled with an auger to a depth of at least 0.5 m into the black parent sediment. They were immediately divided into 10 cm sub samples, placed in airtight plastic bags and analysed for pH with a Mettler Toledo inlab 426$^{®}$ sediment electrode. The samples were stored in a freezer before further treatment. Later, based on pH and agricultural influence, the profiles were divided into four sections: (1) a plough layer (0–40 cm), (2) an acidified zone (down to a depth where pH rises above 4.2), (3) a transition zone (pH > 4.2 to 6.5), and (4) a parent sediment (pH > 6.5) (Table 1).

Organic matter content was estimated as loss on ignition (LOI) by combusting 1.0 g of dried sample (105 °C) in a muffle oven at 500 °C for 4 hours (Radojević and Bashkin 1999). According to Ball (1964), Radojević and Bashkin (1999), Heiri *et al*. (2001) and Boyle (2004), LOI is proportional to the amount of organic carbon (OrgC) and is a rapid and reasonably accurate method for estimating the organic matter concentration. LOI might be somewhat overestimated due to loss of structural water from clay minerals, CO_2 from carbonates (Ball 1964) and SO_2 from sulphur species during combustion. However, due to the lack of carbonates in the study area (Åström 1998), loss of CO_2 during combustion is unlikely, but as the sediments contained S, the amount of this element lost during combustion (unpublished results) was taken into consideration when OrgC was calculated from the LOI data.

Particle size distribution in selected profiles, five from Korsholm and eight from Söderfjärden, was determined with a hydrometer after removal of organic matter with H_2O_2 and HCl, subsequent dispersion of soil particles with $Na_4P_2O_7$ and mechanical shaking for over 16 hours (Elonen 1971). Since large iron hydroxide flakes can be mistaken for sand, they were removed with a sieve (1.4 mm) prior to the measurement.

For sulphur speciation, frozen samples were thawed in a nitrogen filled glove bag in order to minimise oxidation of the samples. The oxidation front that had developed during sampling/storage was removed, keeping only the inner un-oxidised core of the sample for subsequent analysis. Five profiles from Korsholm and nine from Söderfjärden were analysed following the procedure by Backlund *et al*. (2005) with respect to total reducible sulphur (TRS), sulphate sulphur (SO_4^{2-}) and organic sulphur (OrgS). Shortly, the determination of TRS was carried out by boiling the sample in a solution of HCl and $CrCl_2$, and released H_2S was collected as Ag_2S which was determined gravimetrically. The solution remaining after TRS extraction was filtered and the filtrate was used for determination of SO_4^{2-} (precipitation with $BaCl_2$) and the residue for OrgS (combustion with Eschka's mixture at 800 °C and subsequent precipitation with $BaCl_2$).

The chemical elements in the soil/sediment samples were determined in a commercial accredited laboratory, with an ICP/ES & MS. Prior to the analysis the samples were oven dried at approximately 50 °C, comminuted in a vibrating disk mill (model RS 100), and for each profile, merged into four composite samples representing the sections described in Table 1. A 1.0-g portion of the dried and pulverised composite sample was partially digested in 6 ml 2:2:2 $HCl:HNO_3:H_2O$ (aqua regia) for one hour at 95 °C, diluted to 20 ml and thereafter analysed for Ag (the analytical precision for 23 replicates calculated according to the method in Gill (1997): 6.7%), Al (3.3%), As (10.0%), B (8.0%), Ba (3.8%), Bi (8.3%), Ca (2.5%), Cd (15.4%), Co (2.1%), Cr (1.4%), Cu (3.4%), Fe (2.5%), Ga (2.7%), Hg (15.9%), K (3.3%), La (3.1%), Mg (1.3%), Mn (4.0%), Mo (3.0%), Na (3.8%), Ni (3.6%), P (3.6%), Pb (2.7%), S (3.8%), Sc (1.6%), Se (8.7%), Sr (1.9%), Th (2.4%), Ti

Table 1. The minimum, median and maximum lower boundaries and pH of different sections in the Korsholm and Söderfjärden AS soils. Note that the data for the parent sediments are only determined for the section sampled and not for the entire sediment layer extending several metres below the surface.

Section		Korsholm		Söderfjärden	
		Lower boundary (m)	pH	Lower boundary (m)	pH
Plough layer					
	Min	0.4	4.0	0.4	3.9
	Median	0.4	6.5	0.4	5.4
	Max	0.4	7.4	0.4	6.9
Acidified zone					
	Min	0.9	3.5	1.1	3.2
	Median	1.1	4.0	1.4	3.8
	Max	1.3	5.5	1.7	5.0
Transition zone					
	Min	1.3	4.1	1.5	4.1
	Median	1.5	4.7	1.8	5.6
	Max	1.6	6.5	2.1	6.6
Parent sediment					
	Min	2.0	6.6	2.0	6.6
	Median	2.2	7.4	2.0	7.0
	Max	2.5	7.9	3.0	8.0

(1.9%), Tl (3.3%), U (3.6%), V (1.9%) and Zn (2.4%).

Water

Water sampling was conducted 26 times, from April to December 2000 from a drainpipe draining a known (24 × 30 m) and representative part of the Korsholm field. Filtered water samples (0.45 μm; Membrane Filters, Millipore HAWP 04700) collected in new polyethylene bottles and acidified with ultra pure HNO_3 (0.2%) were analysed, in a commercial accredited laboratory, with ICP-MS for Al (the analytical precision for 10 replicates calculated according to the method in Gill (1997): 4.7%), Ba (1.1%), Ca (3.7%), Cd (1.7%), Co (8.4%), Cu (5.3%), Fe (4.8%), K (6.5%), La (1.8%), Mg (3.7%), Mn (6.2%), Na (3.9%), Ni (4.5%), Pb (1.9%), Sc (8.2%), Sr (4.3%), Th (7.4%), Ti (7.0%), Tl (2.2%), U (3.0%) and Zn (8.8%).

Calculations

In order to evaluate the quantities of elements leached from the AS soils in the study area, two different approaches were applied. Soil geochemical data were utilised in the first approach, with the aim of obtaining the absolute total amount of elements leached from the soils. In the second approach, hydrochemical data for the year 2000 was used with the intention of estimating the total historical amounts leached in the area.

In the geochemical approach, the leakage/loss of elements was estimated as:

$$\text{Elements lost (kg ha}^{-1}\text{)} = (C_{i,\mathrm{PS}} - C_{i,\mathrm{soil}}) \times \varrho \times V \quad (1)$$

where, $C_{i,\mathrm{PS}}$ is the concentration of element i in the parent sediment, and $C_{i,\mathrm{soil}}$ is the volume weighted average concentration of element i in the acidified and transition zones. The plough layer was not taken into account in this calculation because of the alteration by agricultural activities. ϱ is the soil bulk density (900 kg m^{-3} in a similar soil (Österholm and Åström 2002) and V is the average volume (m^3) of the soil profile (plough layer excluded) per hectare.

In the hydrochemical approach, the leakage/loss of elements was estimated as:

$$\text{Elements lost (kg ha}^{-1}\text{)} = C_{i,\mathrm{w}} \times q \times t \quad (2)$$

where, $C_{i,\mathrm{w}}$ is the runoff weighted average concentration (g l^{-1}) of element i in the drainage water in Korsholm year 2000 (runoff from the nearby Solf River), q is the annual mean runoff for the region (7 l s^{-1} km^{-2}) estimated from Mustonen (1986) and t is the time (33 years) since the pipe drainage has begun in the area. The reason for using the amount of years since the pipe drainage has begun in the area and not the years since the first open ditch was made is because the leakage was probably minimal before the former (Pons and Zonnenveld 1965, Österholm 2005).

Long-term monitoring has shown that due to different meteorological conditions the overall element concentrations in AS soil runoff can vary greatly, by a factor of 5 or more (Österholm 2005). On the contrary, yearly medians, based on many representative samples from each year, tend to vary relatively little within a few years (Österholm 2005). In the short term (few years) variations in the amount of runoff seem to be more important in controlling leakage amounts than variations in concentrations (Österholm 2005). The more runoff that transports the solutes from the soil to the drains, the higher the leakage amount. Taken together, the large number of runoff-weighed samples (n = 26) from the year 2000 and the use of the long-term mean for runoff, we considered the leakage amounts calculated in this study to be representative for the area.

Results and discussion

Characteristics of the parent sediments

The parent sediments in Korsholm and Söderfjärden consisted of approximately 40% clay (Table 2), which is in agreement with previous data of corresponding (Litorina) sediments from Finland and Sweden (Georgala 1980, Joukainen and Yli-Halla 2003). In the same sediment as we investigated, Joukainen and Yli-Halla (2003) found the mean clay concentration to be 49%

which is in accordance with our results as the sedigraph method they used is known to produce a clay fraction 5%–10% higher than the hydrometer method used in this study (Lintinen 1995). The low clay concentration determined in the sediments throughout western Finland by

Table 2. Physicochemical characteristics of parent sediments throughout western Finland and locations therein (Korsholm, Söderfjärden and Rintala).

Determinant	Western Finland1)			Korsholm			Söderfjärden			Rintala2)		
	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max
Clay (%)	4.83)	173)	373)	35	41	43	36	40	44	–	27	–
LOI (%)*	–	–	–	4.5	4.8	5.1	3.5	5.4	7.5	–	–	–
OrgC (%)	0.34	1.4	4.0	1.5**	1.6**	1.7**	1.1**	1.8**	2.6**	0.52	1.3	3.8
S (%)	BD	0.54	1.8	0.77***	0.94***	1.2***	0.45***	1.0***	1.4***	0.04	0.32	1.04
TRS (%)	–	–	–	0.74	0.89	1.1	0.41	0.99	1.3	–	–	–
SO_4^{2-} (%)	–	–	–	0	< 0.01	0.027	0	< 0.01	0.021	–	–	
OrgS (%)	–	–	–	0.023	0.026	0.037	0.010	0.034	0.050	–	–	
Fe (%)	0.78	3.8	5.7	2.8	3.2	3.4	3.0	3.5	4.2	2.9	3.9	4.8
Al (%)	0.35	2.0	3.6	1.6	1.9	2.0	1.7	1.9	2.2	1.7	2.0	2.8
K (%)	0.07	0.60	1.4	0.60	0.65	0.69	0.57	0.63	0.71	0.41	0.56	0.78
Mg (%)	0.12	1.0	1.8	0.87	0.98	1.0	0.91	0.97	1.1	0.87	1.1	1.5
Ca (%)	0.25	0.50	0.75	0.41	0.45	0.52	0.40	0.46	0.48	0.45	0.52	0.61
Na (%)	BD	0.10	0.31	0.20	0.23	0.25	0.17	0.28	0.37	0.060	0.080	0.15
P (%)	0.004	0.064	0.18	0.077	0.087	0.092	0.082	0.094	0.14	0.060	0.080	0.11
Ti (%)	0.07	0.22	0.30	0.15	0.16	0.16	0.14	0.15	0.16	0.17	0.20	0.25
Mn (ppm)	90	448	1147	420	445	468	404	483	602	348	596	793
Ba (ppm)	14	87	229	84	93	100	69	88	103	77	94	211
Zn (ppm)	18	90	142	78	84	88	74	85	98	78	91	117
Cr (ppm)	11	48	76	51	55	57	52	57	63	45	54	71
V (ppm)	12	50	76	48	53	54	50	56	62	50	60	77
La (ppm)	13	38	62	32	36	38	34	34	38	31	37	51
Sr (ppm)	10	36	60	31	34	37	31	37	44	27	33	39
Ni (ppm)	6.0	31	58	28	31	32	27	31	33	24	29	44
Cu (ppm)	2.0	27	65	24	26	27	20	25	28	17	22	43
Co (ppm)	2.0	13	31	12	13	14	12	14	15	11	14	18
Th (ppm)	BD	10	22	8.8	10	11	8.8	9.8	10	6.7	9.3	15
Pb (ppm)	BD	12	25	11	11	12	10	11	12	–	–	–
B (ppm)	–	–	–	11	13	16	12	15	20	–	–	–
As (ppm)	–	–	–	7.9	8.8	9.9	8.6	10	12	–	–	–
Ga (ppm)	–	–	–	7.4	7.9	8.3	7.3	7.9	8.3	–	–	–
Sc (ppm)	–	–	–	6.1	6.7	6.9	6.1	6.7	7.1	–	–	–
U (ppm)	–	–	–	2.1	2.3	2.4	2.2	2.3	2.9	–	–	–
Se (ppm)	–	–	–	1.1	1.2	1.4	1.1	1.8	2.2	–	–	–
Mo (ppm)	–	–	–	1.1	1.2	1.3	1.1	1.4	2.1	–	–	–
Bi (ppm)	–	–	–	0.23	0.25	0.27	0.22	0.25	0.26	–	–	–
Tl (ppm)	–	–	–	0.29	0.34	0.35	0.30	0.33	0.36	–	–	–
Cd (ppm)	–	–	–	0.060	0.080	0.10	0.070	0.090	0.12	–	–	–
Ag (ppb)	–	–	–	55	62	71	52	66	112	–	–	–
Hg (ppb)	–	–	–	12	24	32	13	31	85		–	–

1) Data published in Åström and Björklund (1997).
2) Data in Österholm and Åström (2002).
3) Data in Åström and Rönnback (2005).
* Loss on ignition.
** Estimated from the organic matter concentration.
*** Sum of S species.
– = not analysed.
BD = below detection limit.

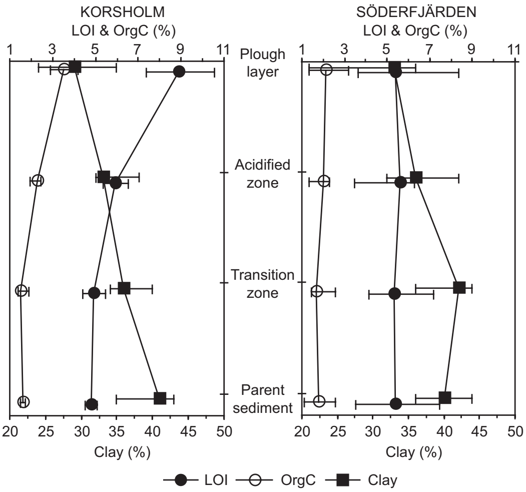

Fig. 2. The distribution of median concentrations of loss on ignition (LOI), organic C (OrgC) and clay fraction. Minimum and maximum values are shown as vectors.

Åström and Rönnback (2005) (Table 2) is due to the fact that the laser method they utilised underestimates the clay concentration in this type of sediment (e.g. Beuselinck *et al*. 1998, Lehman *et al*. 2004). The sediments in Rintala (Table 2) and Ilmajoki (Bärlund *et al*. 2004) had a somewhat lower clay concentration than those in Korsholm and Söderfjärden.

The median LOI concentrations in the parent sediment in Korsholm and Söderfjärden were 4.8% and 5.4%, respectively (Table 2). Based on these figures and on results in Håkansson and Jansson (1983), Heikkilä (1999) and L. Nordmyr (unpubl. data), the median organic carbon concentration (OrgC) was estimated to be 1.6% in Korsholm and 1.8% in Söderfjärden. These results are in agreement with previously published data for the Korsholm area (Bärlund *et al*. 2004, Sohlenius and Öborn 2004). The sediments in Korsholm and Söderfjärden contained slightly more organic matter than corresponding sediments in Rintala (OrgC 1.3%) (Table 2) and Ilmajoki (~0.7%) (Bärlund *et al*. 2004).

TRS was abundant in both Korsholm (median 0.89%) and Söderfjärden (0.99%), and constituted 97.0% and 96.2%, respectively, of the total sulphur (Table 2). OrgS and SO_4^{2-} were present only in minor concentrations at both locations (Table 2). The concentration of OrgS in these sediments constitutes approximately 0.8% of the organic matter, which indicates an origin in assimilatory sulphate reduction (Kaplan *et al*. 1963). The occurrence of SO_4^{2-} in the parent sediment may be an artefact from the distillation process. The low total S concentration in Rintala (0.32%) as compared with that in Korsholm (0.94%) and Söderfjärden (1.00%) may be related to the coarser grain size (Purokoski 1956, 1959) and the lower organic matter concentration in that area.

The median element concentrations in the parent sediments in Korsholm and Söderfjärden are remarkably similar to those in related sediments collected from the entire region by Åström and Björklund (1997) (Table 2). This indicates that the relatively small areas Korsholm and Söderfjärden are regionally representative. According to Sohlenius and Öborn (2004), sulphide-containing sediments, like the ones of this study and in Rintala, do not contain more metals than sulphide-free clays. A negative and significant correlation ($n = 13$) was observed between the median grain size and the concentrations of Al, As, Co, Cr, Fe, Ga, K, Mg, Mn, P, Sc, Sr, U, V and Zn ($r_s = 0.56–0.85$). Elevated element concentrations in the finer fractions of the sediments are a result of high concentrations of small-sized metal-bearing phyllosilicates (Deng *et al*. 1998).

Grain size and organic matter in the soil

The soil profiles in Korsholm and Söderfjärden demonstrated a weak decrease in clay concentration from the parent sediment towards the sediment surface (Fig. 2). This might either be due to natural inhomogenity or leakage of clay minerals. The organic matter concentration, on the other hand, increased towards the plough layer in almost all profiles in Korsholm, but not in Söderfjärden, where the organic matter concentration was generally stable throughout the profiles (Fig. 2).

Loss of chemical elements from the soil

Sulphur

The current rate of S leaching from the soil seems to be somewhat higher than in the past, as indicated by the higher leakage amounts based on the hydrochemical data than the soil geochemical data (Table 3). This might be due to a slower oxidation in the beginning of the drainage when the hydraulic conductivity of the soils was extremely low (Österholm 2005). In the acidified zone and plough layer, the S concentrations were much lower than in the transition zone and the parent sediment (Fig. 3; *see* also Appendix). This is due to the oxidation of TRS and formation and leakage of sulphate from the former. For reasons not investigated in this study, the S concentrations were higher in the transition zone than in the parent material in several profiles (Fig. 3). There is also a considerable amount of TRS left in the acidified zone comprising approximately 61% of the total sulphur in Korsholm and 46% in Söderfjärden, and some is even left in the plough layer (Fig. 3a). This sulphur presumably consists of large pyrite grains, or pyrite covered with e.g. a layer of clay or other cements and/or overgrowths, leading to greater resistance towards oxidation. OrgS concentrations in the profiles were low (< 0.1%) and decreased slightly upwards, due to oxidation. The acidity produced from OrgS was negligible compared to the acidity released from TRS.

The main part of sulphate minerals in AS soils are usually in the form of water soluble sulphates and jarosite [$KFe_3(SO_4)_2(OH)_6$] (van Breemen 1973, Begheijn *et al.* 1978). Jarosite is often used as a diagnostic for AS soils since it is easily detected due to its pale yellow colour, and is formed under strongly oxidising conditions at pH levels below 3.7 (Palko 1994). During sampling, jarosite was found in most profiles in Söderfjärden but in none in Korsholm. Joukainen and Yli-Halla (2003), however, detected jarosite in this area. The acidified zone in Söderfjärden contains proportionally more SO_4^{2-} than Korsholm (median: 48.5% and 32.0% of the total S, respectively). This can be explained by a more extensive precipitation of jarosite in the former area. The high relative concentration of TRS in the acidified zone in Korsholm, compared to Söderfjärden, is an indication of a shorter oxidation time.

One profile (in Söderfjärden; Fig. 3a) stood out from the rest, as it did not exhibit the typical leaching of sulphur. Instead, the total S concentration was within a narrow range (0.45%–0.51%) throughout the profile. It is possible that SO_4^{2-} in the acidified zone and in the plough layer was more or less completely tied up in jarosite and was therefore not as easily weathered and leached as water soluble sulphates. Potassium

Table 3. The amounts (median, kg ha^{-1}) of chemical elements leached from soils in Korsholm based on hydrochemical data (*see* Eq. 1) and geochemical data (*see* Eq. 2), and from Söderfjärden based on geochemical data. The symbols set in boldface indicate elements that are leached more from AS soil than from other soils (e.g. Åström and Björklund 1995, 1996).

Element	Korsholm		Söderfjärden
	hydrochemical data (kg ha^{-1})	geochemical data (kg ha^{-1})	geochemical data (kg ha^{-1})
S	44000	28000	40000
Na	19000	15000	18000
Mg	13000	17000	19000
Al	7000	5700	n.d.
Mn	990	900	1900
Zn	92	69	100
Sr	87	120	57
Ni	50	44	64
Co	19	19	28
Ca	14000	7300	12000
La	61	23	5.8
Cd	0.23	0.036	0.32
Fe	230	n.d.	n.d.
U	0.41	n.d.	n.d.
K	2100	6800	3200
Cu	2.3	50	13
Ba	0.77	160	n.d.
Ga	0.73	4.1	0.54
Sc	0.59	3.6	0.90
Ti	0.43	940	n.d.
Pb	0.39	6.2	n.d.
Th	0.026	14	n.d.
Tl	0.0066	0.28	n.d.
Cr	–	33	3.4
B	–	68	95
Se	–	2.1	8.46
Bi	–	0.18	0.099
Ag	–	0.063	0.009
As	–	n.d.	0.72
Hg	–	n.d.	n.d.
Mo	–	n.d.	n.d.
P	–	n.d.	n.d.
V	–	2.2	n.d.

n.d. = not detected. – = not analysed.

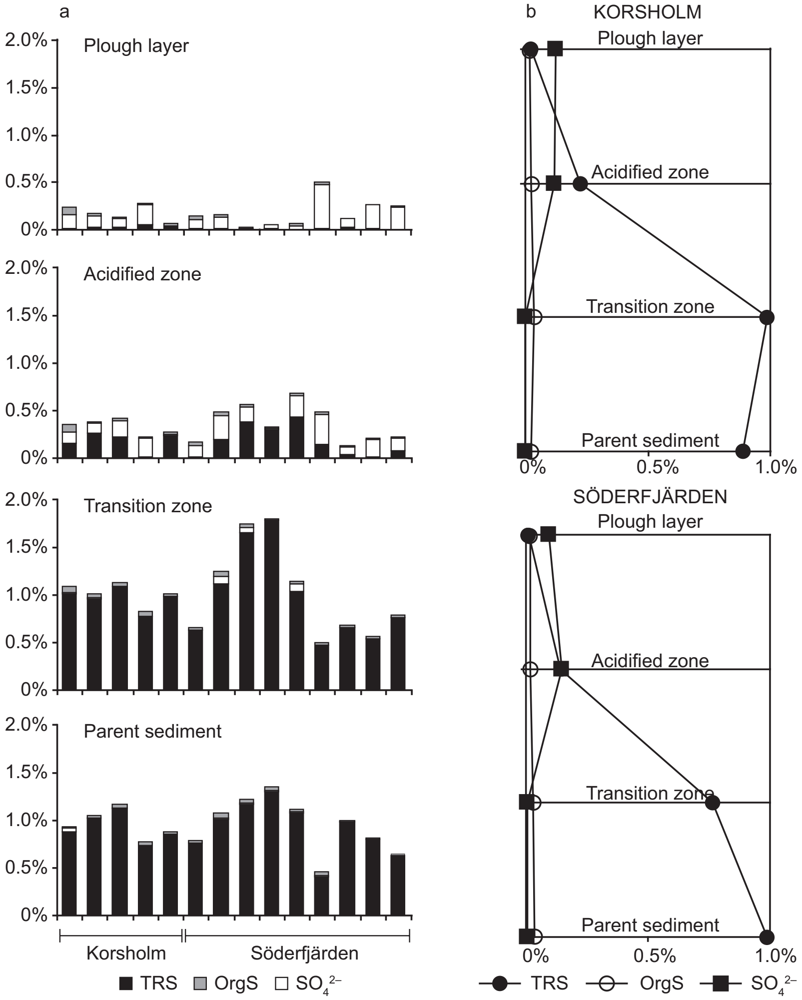

Fig. 3. (**a**) Distributions, and (**b**) median concentrations of total reducible sulphur (TRS), sulphate sulphur (SO_4^{2-}) and organic sulphur (OrgS) throughout the profiles in Korsholm and Söderfjärden.

was not either leached from this profile, which further supports this assumption since K is a substantial element in jarosite. Another explanation for the abnormal behaviour of sulphur in this profile might be related to the hydrology at this site, since this was the lowest point in Söderfjärden, where the ground water table often, even in late spring, is right at the surface.

Metals, As, B, P and Se

The elements have been ordered into four groups based upon the results from two different leakage estimations (Table 3). The groups are presented below.

The geochemical and hydrochemical approaches gave very similar leaching amounts for Mg, Ni and Co and rather similar amounts for Na, Mg, Al, Zn and Sr (Table 3). This is interpreted as if the soil currently has a leaching rate close to the average rate since the beginning of drainage, again assuming that the drainage was minimal before pipe-drainage. The elements in this group are all recognized to be leached in large amounts from AS soils as compared with other soils (Åström and Björklund 1995, 1996, Åström and Åström 1997, Edén *et al.* 1999, Åström and Spiro 2000). According to the geochemical data these elements were also leached in similar amounts from Söderfjärden (Table 3) and Rintala (Österholm and Åström 2002), which indicates that the amount of leaching of these elements has been approximately similar in AS-soil landscapes throughout western Finland. These elements might be derived from sulphides (e.g. Mn, Zn, Ni and Co) phyllosilicates (Al and Mg) and/or trapped sea salts (Na, Mg and Sr). Manganese, Zn, Ni and Co are usually associated with sedimentary sulphides, such as FeS, FeS_2 and/or discrete metal sulphides (e.g. Huerta-Diaz and Morse 1992, Huerta-Diaz *et al.* 1998, Morse and Luther 1999). Sohlenius and Öborn (2004) reported that Ni, Co and Mn are to some extent incorporated in pyrite in the parent sediment of AS soils in the same area as we have investigated. In some of the profiles, a concentration peak of Mn, Zn, Ni and Co occurred in the transition zone (Fig. 4), which was observed also in other studies (Åström 1998, Österholm and Åström 2002, Sohlenius and Öborn 2004). It is, however, not known precisely what is causing this peak. One possibility is that it is caused by sulphide precipitation of metal portions transported from the acidic layer above. However, a plot of the relative metal concentration peak and the relative TRS peak in the transition zone for all analysed profiles (Fig. 5) shows that there were no indications in these data of metal accumulation as a result of metal-sulphide precipitation.

The total amounts of Ca, La, Cd, U and Fe leached from the soils in Korsholm were twice as high when estimated with the hydrochemical approach as when estimated with the geochemical approach (Table 3). This implies that the current rate of leaching is considerably higher than the average rate of leaching since pipe drainage has begun. However, these differences may also be caused by extensive external input, which is possible for Cd e.g. via phosphate fertilizers that can contain high amounts of Cd (Förstner 1995), and for Ca as a result of extensive liming of the plough layer. Hence, at least for these two metals the hydrochemical data may have overestimated the rate of current weathering-related leaching. Of the other elements, only Fe was generally not extensively leached from AS soils more than from other nearby less acidic and sulphuric soils. Cadmium, Fe and U were leached in similar amounts in both Söderfjärden and Korsholm. In contrast, Ca was leached in a higher quantity in Söderfjärden compared to Korsholm while for La it was the other way around (Table 3).

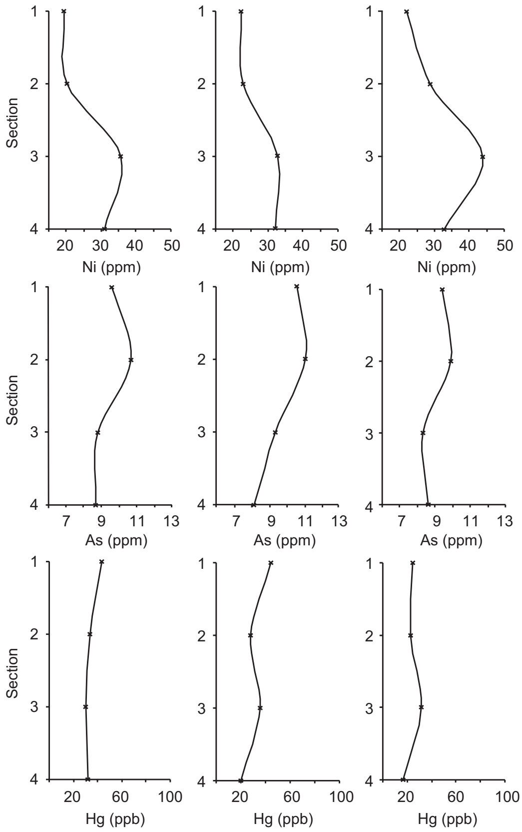

Fig. 4. The vertical distribution patterns of Ni, As and Hg in three selected soil profiles from the study area. Sections: 1 = plough layer, 2 = acidified zone, 3 = transition zone and 4 = parent sediment.

The figures for the total amounts of leaching of K, Cu, Ba, Ga, Sc, Ti, Pb, Th and Tl were much higher when using the geochemical approach than the hydrochemical approach (Table 3). This could in principle be explained by a considerably lower leakage rate during the year 2000 than the average since pipe drainage. This, however, does not make sense as it is unlikely that the pH of the soils has increased since drainage and as none of these elements is likely to exist predominantly in a very mobile form, such as trapped sea salt. Barium, Ga, Sc, Ti, Pb and Th are known not to leach from AS soils more than from other soils, while the elements K, Cu and Tl are commonly to some extent enriched in AS soil waters (Åström and Björklund 1995, 1996, Åström and Åström 1997, Åström and Spiro 2000). Therefore, the relative quantity of each of these elements leached from the soil is not great, which makes even small errors in the leaching estimations significant. We therefore assume that the losses based on the geochemi-

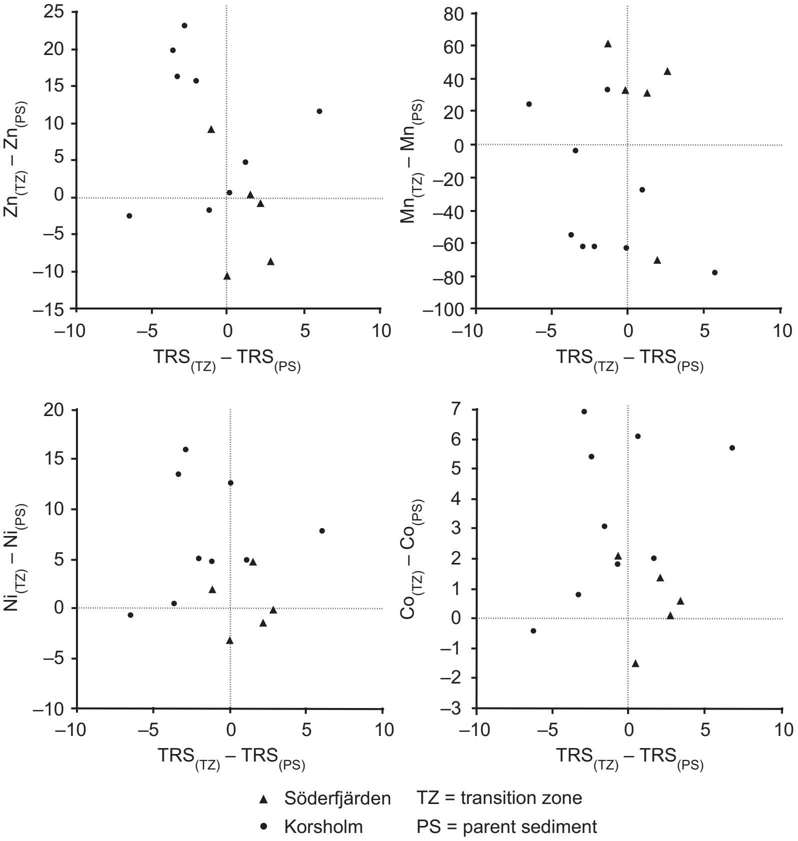

Fig. 5. The relative concentrations in the transition zone for Zn, Ni, Co and Mn versus the relative concentrations of total reducible sulphur (TRS) in the same zone.

cal data were too large for these elements and caused by small but significant inherent heterogeneities highlighted by the slightly coarser grain-size towards the surface in Korsholm. This assumption is also supported by the fact that estimated amounts of leaching for these elements in Söderfjärden (Table 3) and Rintala (Österholm and Åström 2002) were considerably lower. For K and Cu, however, another explanation is possible. These metals may be entrapped in jarosite and oxyhydroxides, respectively. Since Fe and Al oxides are developed when the soil conditions become oxidising and jarosite is developed when pH turns sufficiently low in the soil, extensive entrapment of K and Cu may not have occurred until recently, thus minimising the current amount of leaching. Both jarosite and Fe oxides have been found in the acidified zone in both Korsholm and Söderfjärden.

Hydrochemical data is lacking for Cr, B, Se, Bi, Ag, As, Hg, Mo, P and V (Table 3). In general, B is mobile in AS soils, while the other elements listed here are not (Åström and Björklund 1995, 1996, Åström and Åström 1997, Åström and Spiro 2000). In Korsholm the Cr leakage was quite large, considering its generally low mobility in this type of soil (e.g. Söderfjärden) (Table 3). It is thus likely that the Cr leaching in Korsholm is overestimated and, at least partly, caused by the increasing grain size towards the surface. In many profiles the concentrations of As, Mo, P, U and V were higher in the plough layer and the acidification zone as compared with those in the transition zone and parent sediment (Fig. 4; *see* also Appendix). These elements are often used in agriculture, either as pesticide (As, Hg) or impurities or components in fertilizers (As, P, Hg, V, Mo) (Alloway 1995), and elevated concentrations could therefore be expected towards the surface. Arsenic, Mo and P form oxyanions and have consequently an increasing solubility with increasing pH (Edwards *et al.* 1995, Adriano 2001) and might therefore migrate downwards in the soil profile when the pH rises due to liming in the plough layer. The concentration of Hg was highest in the plough layer from where it decreased downward with depth (Fig. 4), which is a common trend also in other soils (Steinnes 1995). The enrichment in the plough layer may partly be explained by the fact that Hg is readily bound to organic matter.

Conclusions

The results of this study imply that element concentrations are quite similar in the parent sediments of AS soils throughout western Finland, which is of great value for further investigations. Total reducible sulphur is the dominant sulphur species in the parent sediment and in the transition zone, but when the conditions change to oxidising higher up in the profile, TRS is oxidised into sulphate and subsequently leached, giving rise to typical AS soils and waters. Sulphate may, however, be tied up in jarosite which may diminish the leaching of SO_4^{2-} from the soil. There was, however, a significant amount of TRS left in the acidified zone and even in the plough layer, caused by inhibited oxidation. The concentration of OrgS in the sediments constituted approximately 0.8% of the organic matter, which indicates an origin in assimilatory sulphate reduction.

The assessments of the amounts of elements leached from the soils were carried out using both a hydrochemical and a geochemical approach. The two approaches assessing the amounts leached in 1969–2002 were strikingly similar for S, Na, Mg, Al, Mn, Zn, Sr, Ni and Co, indicating that currently the soils have reached the average leakage rate since the beginning of pipe drainage. These elements were lost in similar amounts both from the young soils in Korsholm and Söderfjärden and the “older” soils in Rintala, which implies that the leakage has in general occurred during the same time period throughout the region, no matter of the time elapsed since the parent sediments were brought above the sea level by isostatic land uplift. Some elements were more leached according to the hydrochemical approach (Ca, La, Cd, U and Fe) which is probably partly due to external input from fertilizers and lime, while the leaching amount of other elements (K, Cu, Ba, Ga, Sc, Ti, Pb, Th and Tl) were overestimated by the soil geochemical data. Still other elements, such as Hg and As, were enriched towards the surface (plough layer) most likely as a result of input via fertilizers and pesticides.

The two approaches used in this study, i.e. hydrochemical data combined with hydrological data and soil geochemical data using composites of the various soil profile layers, gave a very clear picture of the qualitative and quantitative leaching of chemical elements from various sites in an area that holds the largest AS soil occurrences in Europe. Since the leaching of several toxic elements from these soils is enormous, the method here developed should provide a useful tool for future studies and environmental monitoring in this and other areas worldwide affected by these nasty soils.

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Appendix. Physicochemical characteristics of the plough layer, acidified zone and transition zone in Korsholm and Söderfjärden.

Determinant	Korsholm									Söderfjärden								
	Plough layer			Acidified zone			Transition zone			Plough layer			Acidified zone			Transition zone		
	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max
Clay (%)	24	29	35	32	33	38	34	36	40	21	33	36	32	36	42	36	42	44
LOI (%)*	7.4	8.9	11	5.4	5.9	6.5	4.5	4.8	5.5	3.6	5.4	8.3	3.5	5.6	6.3	4.2	5.3	7.2
OrgC (%)**	2.9	3.5	4.2	1.9	2.3	2.5	1.4	1.5	1.9	1.4	2.1	3.2	1.3	2.0	2.3	1.4	1.7	2.6
S (%)***	0.063	0.17	0.28	0.23	0.35	0.42	0.83	1.0	1.1	0.035	0.15	0.51	0.13	0.33	0.68	0.50	0.79	1.8
TRS (%)	< 0.01	0.024	0.049	0.010	0.22	0.27	0.78	0.99	1.1	< 0.01	0.010	0.026	0.015	0.14	0.43	0.48	0.77	1.8
SO_4^{2-} (%)	< 0.01	0.13	0.22	< 0.01	0.12	0.20	0	< 0.01	0.017	< 0.01	0.096	0.46	0.016	0.15	0.32	0	< 0.01	0.077
OrgS (%)	0.016	0.020	0.087	0.022	0.025	0.084	0.019	0.038	0.067	< 0.01	0.017	0.046	0.010	0.020	0.041	0.015	0.027	0.054
Fe (%)	3.0	3.6	3.9	3.2	3.4	4.6	3.0	3.2	3.4	2.5	2.7	3.9	2.9	3.5	4.7	3.0	3.2	4.1
Al (%)	1.4	1.8	2.1	1.7	1.8	1.9	1.6	1.8	2.0	1.3	1.5	1.9	1.7	1.8	2.1	1.7	1.9	2.2
K (%)	0.44	0.47	0.56	0.52	0.56	0.60	0.56	0.60	0.65	0.39	0.47	0.67	0.57	0.63	0.67	0.57	0.64	0.71
Mg (%)	0.56	0.73	0.80	0.74	0.77	0.81	0.81	0.90	0.99	0.49	0.66	0.78	0.75	0.81	0.92	0.89	0.96	1.0
Ca (%)	0.43	0.60	1.5	0.32	0.37	0.41	0.36	0.40	0.46	0.32	0.39	0.55	0.29	0.32	0.36	0.40	0.42	0.45
Na (%)	0.030	0.039	0.051	0.046	0.052	0.066	0.070	0.11	0.14	0.026	0.037	0.057	0.052	0.057	0.089	0.10	0.17	0.23
P (%)	0.10	0.13	0.14	0.082	0.12	0.14	0.075	0.087	0.11	0.084	0.094	0.12	0.083	0.095	0.14	0.075	0.095	0.15
Ti (%)	0.096	0.12	0.13	0.13	0.14	0.15	0.14	0.16	0.16	0.11	0.13	0.15	0.14	0.15	0.16	0.14	0.15	0.17
Mn (ppm)	207	264	277	262	302	352	391	484	513	190	238	269	276	294	378	400	452	574
Ba (ppm)	59	67	77	64	75	84	70	81	90	57	69	89	69	81	98	75	85	93
Zn (ppm)	54	72	86	66	72	80	67	88	98	47	59	71	63	72	90	77	95	118
Cr (ppm)	41	49	53	49	52	53	50	53	61	42	50	56	51	57	62	53	57	65
V (ppm)	44	51	54	49	53	58	49	53	55	44	51	63	53	58	63	52	56	61
La (ppm)	34	43	48	30	33	37	33	36	39	28	34	35	28	32	40	34	38	42
Sr (ppm)	18	24	27	17	19	24	21	25	32	27	40	55	25	29	41	30	32	35
Ni (ppm)	19	24	28	20	22	25	25	32	36	14	18	22	19	21	29	26	34	46
Cu (ppm)	18	21	26	18	19	26	22	25	26	16	20	24	18	23	30	22	25	29
Co (ppm)	7.1	9.1	10	8.2	9.5	12	12	14	16	5.6	7.2	8.7	7.8	9.0	12	12	17	20
Th (ppm)	6.4	7.4	8.6	8.3	8.8	9.6	9.2	9.6	11	6.5	8.4	9.6	8.8	9.5	12	9.1	10	10
Pb (ppm)	10	11	12	10	10	14	10	11	12	9.0	11	12	10	12	15	11	11	12
B (ppm)	4.0	5.0	6.0	5.0	6.0	8.0	5.0	9.0	11	3.0	4.0	7.0	6.0	8.0	10	10	12	14
As (ppm)	9.6	11	13	9.0	11	12	7.8	9.2	10	7.5	8.6	11	8.6	9.1	12	8.3	11	11
Ga (ppm)	5.6	6.5	7.4	6.9	7.4	7.6	7.1	7.7	8.4	5.9	6.9	7.9	7.2	7.9	8.4	7.0	8.0	8.6
Sc (ppm)	4.5	5.7	6.4	5.9	6.3	6.6	5.9	6.5	7.1	4.9	5.8	6.8	5.9	6.5	7.1	6.2	6.8	7.5
U (ppm)	2.3	2.8	3.0	2.4	2.7	3.0	2.1	2.3	2.6	2.1	2.4	2.9	2.3	2.8	3.6	2.2	2.5	3.3
Se (ppm)	0.90	1.2	1.2	0.80	0.90	1.2	1.0	1.1	1.2	0.70	0.80	1.1	0.90	1.0	1.2	1.1	1.6	2.1
Mo (ppm)	1.1	1.2	1.4	1.2	1.4	1.7	1.1	1.3	1.6	1.4	1.6	2.1	1.1	1.7	2.4	1.1	1.3	2.3
Bi (ppm)	0.17	0.19	0.24	0.20	0.23	0.25	0.22	0.24	0.27	0.18	0.22	0.28	0.21	0.23	0.27	0.22	0.24	0.27
Tl (ppm)	0.25	0.28	0.32	0.28	0.30	0.32	0.29	0.31	0.35	0.24	0.29	0.34	0.31	0.31	0.38	0.30	0.33	0.35
Cd (ppm)	0.070	0.11	0.15	0.020	0.060	0.19	0.060	0.090	0.16	0.050	0.060	0.080	0.030	0.050	0.10	0.070	0.090	0.15
Ag (ppb)	45	53	61	45	54	62	51	61	71	44	55	80	53	62	84	56	64	74
Hg (ppb)	33	42	51	24	34	52	15	26	36	11	25	48	23	32	50	13	32	60

* Loss on ignition. ** Estimated from the organic matter concentration. *** Sum of S-species.