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Metal dispersion in groundwater in an area with natural and processed black shale – Nationwide perspective and comparison with acid sulfate soils

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ABSTRACT

Black shale is often rich in sulfides and trace elements, and is thus a potential environmental threat in a manner similar to acid sulfate soils and active or abandoned sulfide mines. This study aims at characterising how exposed and processed (mined and burnt) black shale (alum shale) in Degerhamn, SE Sweden, affects the chemistry (Al, As, Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Si, Na, Sr, S, U, V and Zn) of the groundwater. There were large variations in groundwater chemistry between nearby sampling points, while the temporal variations generally were small. Acidic groundwater (around pH 4), found in deposits of burnt and carbonate-poor shale where the conditions for sulfide oxidation were favourable, was strongly elevated in Al, U and several chalcophilic metals (Cd, Co, Cu, Ni and Zn). Cadmium and U were also, together with Mo, abundant in many of the near-neutral waters, both in the non-mined black shale bedrock and in the deposits of burnt shale. An extrapolation to a national level suggests that the dispersion of Ni from naturally occurring black shale is similar to that from anthropogenic point sources, while for Cd and As it is assessed to be approximately one tenth of that from point sources. The processed shale was, however, a much larger source of metals than the black shale bedrock itself, showing this material's potential as a massive supplier of metals to the aquatic environment. A comparison of waters in contact with the processed Cambrian–Ordovician black shale in Degerhamn and acid sulfate soils of the region shows that these two sulfide-bearing materials, in many respects very different, delivers basically the same suite of trace elements to the aquatic environment. This has implications for environmental planning and protection in areas where these types of materials exist.

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1. Introduction

Black shales are found worldwide, with especially large occurrences in Russia, USA, Australia, China and Brazil (Hessland and Armands, 1978). In the Baltoscandian area, an approximately 500 Ma old black shale formation is visible in parts of Sweden, Norway, Estonia and also in western Russia. This shale formation is often referred to as alum shale, presumably since it historically has been used for production of alum [$KAl(SO_4)_2 \cdot 12H_2O$] (Andersson et al., 1985). Black shale is formed from sediments deposited in stagnant aquatic environments with a high supply of organic material, leading to a high content of sulfides and also an enrichment of potentially toxic elements such as As, Cd, Mo, U and V (e.g. Brumsack, 2006, and references therein).

If the shale is exposed to O_2 and water, the sulfides can oxidize to H_2SO_4 and thus produce acidic drainage water rich in metals (e.g. Jeng, 1991; Salomons, 1995; Puura, 1998; Evangelou, 2001). Anthropogenic activities such as mining can enhance the weathering and metal dispersion from this material by increasing the oxidation rate, as e.g. in the alum production process where the shale was crushed, burnt and leached with water (Eklund et al., 1995, 1996). The shale has also, due to its high organic content, been used as a fuel in the alum production as well as in lime production (Hessland and Armands, 1978), and in the 20th century it was utilized as a U ore and for production of oil. These processes have left large deposits of processed shale in the former mining areas where it now, if not protected from infiltration and oxidization, can constitute a potential environmental hazard due to acid and metal leaching (e.g. Allard et al., 1991; Kalinowski et al., 2004; Carlsson and Büchel, 2005). Such areas thus have much in common with sulfide mines producing acid mine drainage (AMD), a well known and relatively well studied phenomenon causing metal dispersion to soils and waters (e.g. Evangelou and Zhang, 1995). The production of AMD is an often powerful process but usually relatively limited in space. Less attention has been drawn to the potential metal dispersion from naturally occurring black shale. In such areas the oxidation processes are likely to have a lower intensity than those associated to mining activities, but they can potentially be of high relevance due to the often widespread occurrences of the material. Some studies have pointed out weathering of black shales and black schists as a likely source for metal contamination of soils, sediments, waters and biota (e.g. Lee et al., 1998; Loukola-Ruskeeniemi et al., 1998; Dalai et al., 2002; Peng et al., 2004), and it has

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even been suggested that some high incidences of endemic diseases possibly can be connected to the distribution of black shale bedrock (Loukola-Ruskeeniemi et al., 2003; Peng et al., 2004, and references therein).

The geological precursor of black shale is fine-grained sediments covering areas with restricted circulation at the bottoms of modern seas. As a result of isostatic land uplift and fluctuations in sea-water level in the Quaternary period, such sediments are widely spread on many coastal lowlands worldwide. These sediments are attractive for a variety of reasons, including agricultural and residential development, and have thus been extensively drained leading to formation of acid sulfate soils (Dent and Pons, 1995; Andriesse and van Mensvoort, 2005). This soil type is an environmental analogue to oxidizing black shale, as its runoff is often acidic and metal rich, and affects on the environment are more diffuse than point source (Joukainen and Yli-Halla, 2003; Sohlenius and Öborn, 2004). Thus, when the dispersion of potentially toxic elements is addressed, not only industrial processes and wastes are of interest, but also the diffuse load from naturally occurring sulfidic materials.

Black shale was mined and burnt on site in Degerhamn, SE Sweden, for production of alum and lime, from the 18th century into the 20th century, leaving behind a large quantity of crushed and burnt shale together with exposed surfaces of the bedrock. In 1999 high Cd concentrations were found in sewage sludge in a local wastewater treatment plant, and it was soon realized that the abandoned mining area was the source of the metal pollution. Small-scale monitoring of groundwater at this site showed occurrences of both acidic water with elevated metal concentrations and neutral water usually not elevated in metals (Falk et al., 2006). That study, however, included only As, Cd, Cu, Ni and Zn. Since the shale is known to hold high concentrations of several other potentially toxic metals, the study by Falk et al. (2006) deserves extension both in terms of sampling strategy and chemical analyses.

The main aim of this study is to determine how natural as well as processed (burnt) black shale delivers major and trace elements to the groundwater (study located in Degerhamn). Further, the results are put in a nationwide perspective and a qualitative comparison with metal dispersion from acid sulfate soils is made. Elements included are Al, As, Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Si, Na, Sr, S, U, V and Zn.

2. Study area

The study area, Degerhamn, is located in the south-western part of the island Öland in SE Sweden (Fig. 1). The bedrock is composed of sedimentary rocks with beds gently dipping towards the east. The black shale formation, formed from sediments deposited during late Cambrian and early Ordovician, is an approximately 15 m thick bed, outcropping in a belt a few hundred meters wide along the south-western coast of the island. To the east it is covered by Ordovician limestone, and to the west, closest to the shoreline, the underlying Cambrian siltstone is visible. The non-mined bedrock is usually covered by only a thin soil layer. The annual precipitation for the area is ca. 600 mm (SMHI, 1994).

The whole study area stretches approximately 3 km from north to south and 500 m from east to west (Fig. 1). Historical mining activities have had a large influence on the local landscape. The most characteristic feature is the heaps of burnt shale, covering 0.7 km^2 and having an estimated volume of 2,700,000 m^3. These deposits are to various degrees mixed with lime residues, and also with non-burnt or partly burnt shale, and are thus quite inhomogeneous in character. Further, approximately 60,000 m^2 of the black shale bedrock is visible in the walls and floors of the old opencast mines, and therefore directly exposed to weathering processes, while other parts of the mined bedrock are covered by the deposits of burnt shale. The mining area, from the quarry walls down to the shoreline, has a total area of approximately 1.2 km^2. Between the eastern border of this area and the limestone bedrock further to the east, the drainage divide is located and the bedrock is composed of black shale. This infiltration area is 1.6 km^2 in size and located 19–25 m above sea level. Water infiltrating here flows as shallow groundwater in a westerly direction into the abandoned mining area, where it is mixed with water infiltrating directly in the mining deposits, and eventually discharges into the Baltic Sea. According to an investigation of the geohydrology of the area (Administrative Board of Kalmar County, 2005), the annual inflow of groundwater from the black shale upstream of the mining area is 75,000 m^3, while the groundwater recharge from infiltration directly in the mining area is estimated to be 153,000 m^3. Thus, the total groundwater flow through the mining area and its deposits is 228,000 $m^3\ a^{-1}$.

3. Material and methods

3.1. Groundwater sampling and analyses

A total of 16 groundwater monitoring tubes of high density polythene (HDPE), Ø 63 mm, were installed in the area during August 2002 (GW1–GW5) and November 2003 (GW6–GW15). The tubes were installed with NOEX drilling to depths between 3.5 and 12.5 m, after which the holes were filled with filler sand (Ø 1.2–2 mm) and sealed with bentonite at the ground surface. Thirteen tubes were installed in the former mining area: two directly in the exposed black shale bedrock (GW1 and GW4), seven in the deposits of burnt shale (GW2b, GW5, GW6, GW9, GW12, GW13 and GW14) and four extending through the deposits and into the underlying black shale bedrock (GW2a, GW3, GW8 and GW10). Three tubes were located in the infiltration area upstream of the mining area, in the black shale bedrock covered by 1–3 dm of organic soil (GW7, GW11 and GW15). The precise locations of the tubes are indicated in Fig. 1. During the first month after installation, the water in the tubes was exchanged several times by a submersible pump. This was also done one day before every sampling event. Samples were taken once a month, from December 2003 to July 2004, with HDPE bailers. Electric conductivity (EC) and pH was determined in situ immediately after extraction (WTW pH/Cond 340i/SET with WTW SenTix 41 pH electrode and WTW TetraCon 325 EC electrode). On four sampling occasions (March, May, June and July) also the redox potential was measured (WTW pH/Cond 340i/SET with Hamilton Profitrode Pt ORP electrode). Filtered (0.45 μm) water samples were collected and, the day after sampling, sent to an accredited commercial laboratory for elemental analysis according to EPA Methods 200.7 and 200.8. The samples were in the laboratory acidified with HNO_3 and analysed for Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, S, Si, Sr, U, V and Zn, by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma sector field mass spectrometry (ICP-SFMS). On one of the sampling occasions (January 2004), samples were also taken and sent for analysis of dissolved organic C (DOC; according to SS-EN 1484) and Cl^- (according to ISO 10 304-1:1995).

3.2. Analysis of solid shale material

From drill-cores taken in the area, 11 samples of unoxidized black shale (depths 0–3 m) and 44 samples of the burnt shale material (depths 0–7 m) were collected. The samples were sent to an accredited commercial laboratory where they were digested and analyzed by ICP-AES and ICP-SFMS. For determination of As, Cd, Co, Cu, Ni, Pb, S and Zn dried samples were leached with 7 M

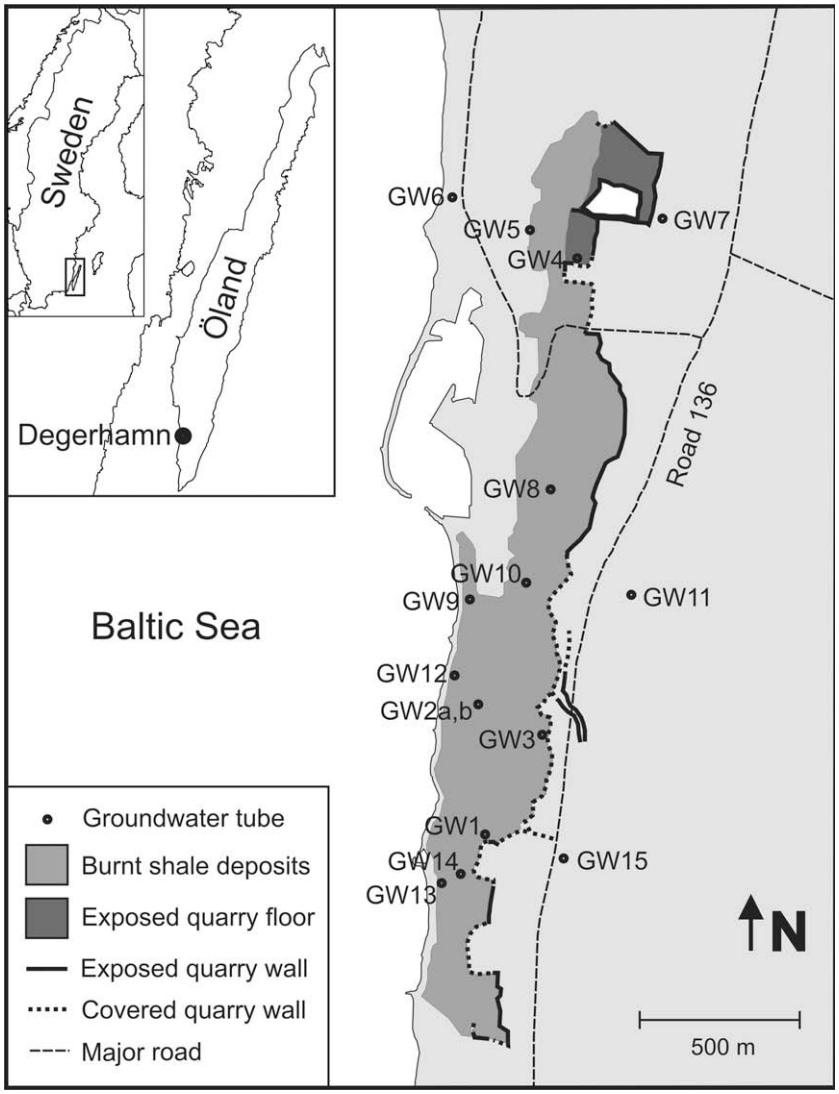

Fig. 1. Map of the abandoned mining area and groundwater sampling points, Degerhamn, SE Sweden.

HNO_3 in closed vessels in a microwave oven (according to SS 028150). For determination of Al, Ba, Ca, Cr, Fe, K, Mg, Mn, Mo, Na, Si, Sr, U and V, the samples were fused with lithium metaborate and dissolved in dilute HNO_3 (according to ASTM D3682).

3.3. Reference groundwater

Overburden groundwater from a typical Swedish setting with glacial till overlying Proterozoic granite was used as reference material. This data was retrieved from the Swedish Nuclear Fuel and Waste Management Company's (SKB) database (Order # SICADA 06_128), and included water collected between September 2004 and December 2005 from 27 groundwater tubes located at Simpevarp on the east coast of Sweden, approximately 120 km north of Degerhamn. The samples were taken in the overburden about 1 m above the bedrock surface, filtered (0.45 μm) and analyzed by ICP. For further details regarding sampling and analyses, see Nilsson and Borgiel (2005). Median values of this entire set of groundwater samples (n = 65) were used as reference.

3.4. Transport calculations

For calculations of the total amounts of element transported by the groundwater flowing through the investigated site and eventually discharging into the Baltic Sea, the mining area with its deposits of burnt shale was divided into 4 sub-areas. From north to south, sub-area 1 included GW5 and GW6; sub-area 2 included GW8 and GW10; sub-area 3 included GW2a, GW2b, GW 9 and GW12; and sub-area 4 included GW13 and GW14. Three groundwater tubes (GW1, GW3 and GW4) were excluded in the transport calculations since they were located near the eastern (upstream) boundary of the mining area and thus most likely not significantly affected by the deposits of burnt shale. The average concentrations of all samples taken in the respective sub-area were multiplied by the calculated annual groundwater flow (originating from the eastern infiltration area and from direct infiltration) through the shale deposits in that sub-area: 42,000 m^3 for sub-area 1; 81,000 m^3 for sub-area 2; 68,000 m^3 for sub-area 3; and 37,000 m^3 for sub-area 4. To estimate the contribution from the black shale bedrock, average concentrations in the eastern (non-mined) infiltration area (including GW7, GW11 and GW 15) were used.

In the transport calculations, when the analyses showed concentrations below analytical detection limits, half of the numerical value of the reported detection limit was used for calculating average values. This was the case for Al in one sample, As in 68 samples, Cr in 15 samples, Cu in two samples, Ni in one sample, Pb in 11 samples, V in one sample and Zn in one sample, of the 104 samples in total used in the calculations.

Table 1
Median values of pH, EC, redox potential and element concentrations in 16 groundwater tubes in Degerhamn, Sweden, and in reference groundwater in granitoidic till. The tubes are arranged by material and in order of decreasing pH.

Material		Black shale bedrock					Deposits of burnt black shale							Both material types				Reference
Tube		GW15	GW7	GW1	GW4	GW11	GW6	GW5	GW14	GW9	GW13	GW2b	GW12	GW3	GW8	GW10	GW2a	
pH		7.4	7.2	6.9	6.9	6.1	7.7	7.35	7.15	7.05	6.7	4.1	4.05	7.7	6.8	5.9	4.2	6.69
EC	$\mu s\ cm^{-1}$	684	897	1910	1720	201	3030	893	1850	1980	1080	2760	2200	702	2480	2680	2410	380
Redox	mV	184	144	198	142	148	168	164	208	−90	232	379	382	−138	174	236	345	n.a.
DOC[a]	$mg\ L^{-1}$	14	19	23	8.6	26	8.5	15	6.3	26	5.2	n.a.	1.6	9.1	11	n.a.	1.8	8.9
Chloride[a]	$mg\ L^{-1}$	15	51	55	21	7.8	380	24	48	34	69	n.a.	20	26	36	n.a.	24	13
Ca	$mg\ L^{-1}$	123	160	403	394	26.0	216	160	379	324	143	466	370	119	556	559	412	32.3
K	$mg\ L^{-1}$	4.38	4.17	5.52	2.36	2.90	36.4	11.1	18.0	42.7	51.5	45.8	39.6	3.56	60.6	146	42.6	4.57
Mg	$mg\ L^{-1}$	3.70	7.96	31.6	18.0	2.28	57.6	7.42	17.8	51.8	9.92	41.0	24.6	9.48	24.4	31.2	32.0	8.2
Na	$mg\ L^{-1}$	11.4	18.5	11.15	8.88	3.78	321	20.0	17.6	41.9	15.2	12.4	13.0	9.94	10.2	14.4	11.3	26.7
S	$mg\ L^{-1}$	25.4	71.0	294	263	20.6	176.5	82.6	288	288	106	662	490	8.85	484	559	550	7.15
Si	$mg\ L^{-1}$	3.12	4.08	4.34	5.74	4.53	6.78	6.03	2.64	6.70	5.35	13.2	36.3	3.06	7.25	12.8	14.6	13.5
Al	$\mu g\ L^{-1}$	3.53	4.82	42.8	7.165	320	5.51	4.10	5.38	1.02	11.9	128,000	83,800	30.2	9.48	1140	73,500	1700
As	$\mu g\ L^{-1}$	0.754	1.16	<0.4	<0.36	0.565	9.49	<0.6	<0.6	<0.5	<0.6	<0.9	<0.8	<1	<0.56	<0.9	<0.6	0.6
Ba	$\mu g\ L^{-1}$	55.0	38.5	13.3	12.4	22.2	34.8	18.0	21.6	11.5	5.94	10.14	13.2	673	21.6	35.6	13.0	54.3
Cd	$\mu g\ L^{-1}$	1.22	0.694	0.351	0.125	4.20	0.292	0.150	0.152	0.011	0.198	19.8	10.6	0.027	0.595	1.64	12.3	0.0379
Co	$\mu g\ L^{-1}$	0.212	2.22	16.1	12.2	4.45	0.189	0.103	0.908	0.051	1.18	892	341	0.460	3.08	30.4	366	1.98
Cr	$\mu g\ L^{-1}$	0.075	0.105	0.036	<0.01	0.374	0.172	0.038	0.015	<0.01	0.297	9.46	11.3	0.022	<0.01	0.085	4.84	3.74
Cu	$\mu g\ L^{-1}$	4.92	2.40	3.34	1.19	23.4	2.47	4.3	1.10	0.145	0.970	552	482	0.330	1.26	8.99	320	7.13
Fe	$\mu g\ L^{-1}$	4.70	10.2	6.30	206	260	1.70	1.55	0.600	999	3.4	464	506	4.85	6.90	28.4	124	5650
Mn	$\mu g\ L^{-1}$	1.12	118	634	506	68.5	1.19	0.256	40.5	462	3.22	1860	1760	30.4	225	1010	1380	397
Mo	$\mu g\ L^{-1}$	36.4	228	0.460	16.4	32.6	118	58.3	4.15	5.38	14.6	0.248	0.484	0.065	90.6	15.4	0.292	0.869
Ni	$\mu g\ L^{-1}$	34.2	104	47.4	45.6	130	3.80	4.83	4.80	0.136	5.97	1640	650	0.766	27.2	65.4	754	4.1
Pb	$\mu g\ L^{-1}$	0.023	0.0400	0.067	<0.01	0.180	0.034	0.047	0.031	<0.01	0.02	0.442	0.868	0.02	0.033	0.044	0.901	2.53
Sr	$\mu g\ L^{-1}$	124	244	799	292	30.5	628	171	320	1830	177	344	309	431	438	597	364	132
U	$\mu g\ L^{-1}$	30.7	97.5	9.38	34.8	6.58	60.8	56.8	43.8	0.162	5.51	183	196	0.294	59.4	16.4	108	2.7
V	$\mu g\ L^{-1}$	2.06	0.512	0.017	0.015	1.74	8.89	0.218	0.078	0.025	0.654	0.03	0.062	0.053	0.174	0.388	0.053	8.06
Zn	$\mu g\ L^{-1}$	33.1	115	61.2	80.6	147	2.76	5.32	6.26	1.70	8.37	1580	875	3.85	22.9	207	903	12.4

[a] Determined only once (January 2004).

Table 2
Spearman rank correlation coefficients (r_S) for chemical parameters in 128 groundwater samples collected in Degerhamn, Sweden. The r_S values for As are calculated from the 43 samples with concentrations above the (for this element varying) analytical detection limit, and the r_S values for redox potential are calculated from the 64 measurements performed.

	pH	Redox	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Pb	S	Si	Sr	U	V	Zn
pH		−0.68*	−0.65*	0.49*	0.61*	−0.50*	−0.63*	−0.78*	−0.50*	−0.53*	−0.58*	−0.36*	−0.29*	−0.74*	0.45*	0.28*	−0.69*	−0.53*	−0.67*	−0.63*	0.03	−0.28*	0.37*	−0.68*
Redox	−0.68*		0.65*	−0.05	−0.40*	0.40*	0.67*	0.66*	0.64*	0.64*	0.28	0.41*	0.22	0.46*	−0.31	0.01	0.67*	0.60*	0.57*	0.48*	−0.15	0.53*	−0.02	0.59*
Al	−0.65*	0.65*		−0.03	−0.21	0.31*	0.66*	0.77*	0.65*	0.65*	0.43*	0.19	0.21	0.62*	−0.48*	−0.39*	0.70*	0.64*	0.46*	0.49*	0.03	0.29*	−0.18	0.65*
As	0.49*	−0.05	−0.03		0.43*	0.01	0.18	−0.08	0.47*	0.10	−0.45*	0.34	0.15	−0.28	0.68*	0.44*	0.09	0.10	0.02	0.16	0.05	0.49*	0.65*	−0.08
Ba	0.61*	−0.40*	−0.21	0.43*		−0.27*	−0.10	−0.31*	−0.22	−0.12	−0.36*	−0.20	−0.28*	−0.32*	0.37*	−0.02	−0.21	−0.19	−0.41*	−0.41*	0.03	−0.05	0.43*	−0.25*
Ca	−0.50*	0.40*	0.31*	0.01	−0.27*		0.26*	0.55*	−0.07	0.16	0.21	0.60*	0.70*	0.66*	−0.21	0.01	0.33*	0.18	0.92*	0.58*	0.57*	0.33*	−0.47*	0.33*
Cd	−0.63*	0.67*	0.66*	0.18	−0.10	0.26*		0.72*	0.74*	0.87*	0.41*	0.19	0.07	0.51*	−0.07	−0.25*	0.88*	0.69*	0.42*	0.50*	−0.26*	0.60*	0.11	0.80*
Co	−0.78*	0.66*	0.77*	−0.08	−0.31*	0.55*	0.72*		0.52*	0.64*	0.53*	0.14	0.28*	0.84*	−0.36*	−0.39*	0.89*	0.54*	0.63*	0.56*	0.03	0.48*	−0.36*	0.80*
Cr	−0.50*	0.64*	0.65*	0.47*	−0.22	−0.07	0.74*	0.52*		0.77*	0.32*	0.19	0.05	0.29*	−0.20	−0.02	0.65*	0.69*	0.19	0.45*	−0.27*	0.42*	0.23*	0.57*
Cu	−0.53*	0.64*	0.65*	0.10	−0.12	0.16	0.87*	0.64*	0.77*		0.37*	0.08	0.01	0.42*	−0.12	−0.16	0.81*	0.74*	0.34*	0.48*	−0.29*	0.62*	0.07	0.77*
Fe	−0.58*	0.28	0.43*	−0.45*	−0.36*	0.21	0.41*	0.53*	0.32*	0.37*		<0.01	0.25*	0.69*	−0.31*	−0.28*	0.55*	0.31*	0.36*	0.49*	0.07	0.09	−0.41*	0.55*
K	−0.36*	0.41*	0.19	0.34	−0.20	0.60*	0.19	0.14	0.19	0.08	<0.01		0.63*	0.25*	−0.05	0.41*	0.02	0.15	0.69*	0.61*	0.47*	0.16	0.03	<0.01
Mg	−0.29*	0.22	0.21	0.15	−0.28*	0.70*	0.07	0.28*	0.05	0.01	0.25*	0.63*		0.54*	−0.34*	0.33*	0.06	0.13	0.77*	0.58*	0.83*	0.13	−0.44*	0.09
Mn	−0.74*	0.46*	0.62*	−0.28	−0.32*	0.66*	0.51*	0.84*	0.29*	0.42*	0.69*	0.25*	0.54*		−0.49*	−0.26*	0.69*	0.44*	0.75*	0.63*	0.36*	0.29*	−0.62*	0.71*
Mo	0.45*	−0.31	−0.48*	0.68*	0.37*	−0.21	−0.07	−0.36*	−0.20	−0.12	−0.31*	−0.05	−0.34*	−0.49*		0.23*	−0.15	−0.29*	−0.34*	−0.19	−0.28*	0.16	0.68*	−0.24*
Na	0.28*	0.01	−0.39*	0.44*	−0.02	0.01	−0.25*	−0.39*	−0.02	−0.16	−0.28*	0.41*	0.33*	−0.26*	0.23*		−0.37*	−0.14	0.09	0.09	0.23*	0.12	0.20	−0.34*
Ni	−0.69*	0.67*	0.70*	0.09	−0.21	0.33*	0.88*	0.89*	0.65*	0.81*	0.55*	0.02	0.06	0.69*	−0.15	−0.37*		0.62*	0.45*	0.49*	−0.23*	0.60*	−0.13	0.89*
Pb	−0.53*	0.60*	0.64*	0.10	−0.19	0.18	0.69*	0.54*	0.69*	0.74*	0.31*	0.15	0.13	0.44*	−0.29*	−0.14	0.62*		0.34*	0.45*	−0.09	0.46*	−0.07	0.69*
S	−0.67*	0.57*	0.46*	0.02	−0.41*	0.92*	0.42*	0.63*	0.19	0.34*	0.36*	0.69*	0.77*	0.75*	−0.34*	0.09	0.45*	0.34*		0.74*	0.50*	0.41*	−0.46*	0.46*
Si	−0.63*	0.48*	0.49*	0.16	−0.41*	0.58*	0.50*	0.56*	0.45*	0.48*	0.49*	0.61*	0.58*	0.63*	−0.19	0.09	0.49*	0.45*	0.74*		0.29*	0.43*	−0.25*	0.49*
Sr	0.03	−0.15	0.03	0.05	0.03	0.57*	−0.26*	0.03	−0.27*	−0.29*	0.07	0.47*	0.83*	0.36*	−0.28*	0.23*	−0.23*	−0.09	0.50*	0.29*		−0.17	−0.39*	−0.18
U	−0.28*	0.53*	0.29*	0.49*	−0.05	0.33*	0.60*	0.48*	0.42*	0.62*	0.09	0.16	0.13	0.29*	0.16	0.12	0.60*	0.46*	0.41*	0.43*	−0.17		0.03	0.53*
V	0.37*	−0.02	−0.18	0.65*	0.43*	−0.47*	0.11	−0.36*	0.23*	0.07	−0.41*	0.03	−0.44*	−0.62*	0.68*	0.20	−0.13	−0.07	−0.46*	−0.25*	−0.39*	0.03		−0.23
Zn	−0.68*	0.59*	0.65*	−0.08	−0.25*	0.33*	0.80*	0.80*	0.57*	0.77*	0.55*	<0.01	0.09	0.71*	−0.24*	−0.34*	0.89*	0.69*	0.46*	0.49*	−0.18	0.53*	−0.23	

* Significant at the 99% level.

Table 3
Median and (min.–max.) element concentrations in black shale material in Degerhamn, Sweden.

Element		Black shale bedrock (n = 11)		Burnt black shale (n = 44)		Average shale[a]
Al	%	6.77	(3.86–8.04)	6.72	(3.79–8.57)	8.8
Ca	%	0.329	(0.0357–4.80)	5.08	(0.113–16.6)	1.6
Fe	%	5.30	(2.33–9.23)	8.29	(5.40–13.1)	4.72
K	%	3.57	(1.27–4.44)	3.52	(2.01–4.41)	2.66
Mg	%	0.754	(0.271–1.15)	0.621	(0.334–0.790)	1.5
Na	%	0.119	(0.0185–0.131)	0.130	(0.0453–0.413)	0.59
S	%	5.91	(1.10–21.0)	2.36	(0.155–5.33)	0.24
Si	%	20.6	(17.8–39.3)	21.2	(13.9–27.0)	27.5
As	ppm	122	(4.58–248)	111	(34.3–241)	13
Ba	ppm	670	(176–973)	1 006	(606–3 460)	580
Cd	ppm	3.02	(0.0050–15.9)	1.40	(0.402–12.0)	0.3
Co	ppm	20.4	(6.39–44.5)	14.4	(2.53–51.1)	19
Cr	ppm	85.5	(37.8–108)	96.4	(47.0–149)	90
Cu	ppm	173	(22.2–240)	86.8	(19.4–198)	45
Mn	ppm	207	(153–454)	356	(80.5–2 010)	850
Mo	ppm	96.0	(3.00–240)	135	(60.7–198)	2.6
Ni	ppm	99.5	(17.7–371)	55.6	(10.3–215)	50
Pb	ppm	26.6	(9.96–43.1)	21.2	(4.79–258)	20
Sr	ppm	74.8	(27.9–84.1)	111	(41.9–235)	170
U	ppm	72.6	(2.11–227)	74.4	(39.7–166)	2.7
V	ppm	441	(47.6–3 240)	500	(298–821)	130
Zn	ppm	241	(20.8–563)	70.5	(11.5–292)	95

[a] Li and Schoonmaker, 2005.

4. Results and discussion

The variations in concentrations/values over time (December 2003–July 2004) were generally marginal and unsystematic, and much smaller than the variations existing between the tubes. Therefore, first, temporal variations are not presented or discussed except where some relevant deviation from the stable pattern was found and, second, median values for each tube were used to describe the chemical and physical qualities for each of them.

4.1. General features

All the groundwater tubes, except GW11, had much higher EC than the reference groundwater in the nearby granitoidic setting (Table 1). This shows that the black shale material has a large overall impact on the levels of dissolved materials in the groundwater they carry. Only in one tube (GW6), located close to the shoreline, did EC vary considerably over time (1.4–8.5 ms cm^{-1}), indicating occasional intrusion of brackish water from the Baltic Sea.

Three of the groundwater tubes had low pH values with a median of about 4, while in the others pH was near-neutral with median values between 5.9 and 7.7 (Table 1). The three acidic tubes (GW2a, GW2b, and GW12) are located close to each other (Fig. 1) in an area covered by extensive deposits of burnt shale, derived primarily from the production of alum and thus likely to be low in carbonate. In these tubes, the redox potentials were higher (>300 mV) than in any of the other tubes, which indicates more favourable conditions for acid production by sulfide oxidation. In the tubes having negative redox potential, H_2S was clearly smelled and pH was >7. In GW10, extending through both burnt and bedrock shale, there was a decrease in pH from 9.5 to just above 5 during the study period, which is a result of either increased oxidation around this groundwater tube over the study period (occurring naturally or as a result of the tube installation) or a change of water movement and source over time. This decrease in pH was accompanied by an increase in the concentrations of Al, Cd, Co, Cr, Cu, Fe, Ni and Zn by between one and two orders of magnitude, while the concentrations of Mo and V decreased by about one order of magnitude.

DOC, determined only once (January 2004), varied between 1.6 mg L^{-1} and 26 mg L^{-1} with a median value of 10 mg L^{-1}. These values are similar to those in the reference water having a DOC concentration range of 3.9–19 mg L^{-1} and a median of 8.2 mg L^{-1}.

4.2. Alkali and alkaline earth metals

The Ca concentrations were about one order and three orders of magnitude higher (in weight per volume) than those of Mg and Sr, respectively, much higher than the Ca concentrations in the granitoidic reference water (Table 1) and negatively correlated to pH, with a Spearman rank correlation coefficient (r_S) of −0.50 (Table 2). The Na and Ba concentrations were strongly elevated in one groundwater tube each. In the Na-rich tube (GW6), concentrations varied considerably (76–1390 mg L^{-1}) but throughout the period were higher than in any of the other tubes at any sampling occasion. The high Na concentration in this tube, located on the shore, is explained by intrusion of brackish water from the Baltic Sea. Chloride, determined on one occasion (January 2004), was also abundant in this tube with a concentration of 380 mg L^{-1}, in comparison to 7.8–69 mg L^{-1} in the others. In the Ba-rich tube (GW3), the Ba concentrations were high and stable throughout the sampling period (633–845 μg L^{-1}; Table 1) and the S concentrations were much lower (7.33–18.6 mg L^{-1}) than in any other tubes. This indicates that the S concentrations here are governed by precipitation of $BaSO_4$, which is also confirmed by calculations of saturation indices (SI). The SI for $BaSO_4$ was in this tube approximately 1 on all sampling occasions, showing an oversaturation of $BaSO_4$ in the groundwater.

Potassium behaved differently to the other alkali and alkaline earth metals, as it was constantly more abundant in the tubes located in the deposits of burnt shale (11–52 mg L^{-1}) than those in the black shale bedrock (2.4–5.5 mg L^{-1}; Table 1). Of the tubes extending through both materials, three were high in K (43–146 mg L^{-1}) and one was low (3.6 mg L^{-1}; GW3). It is thus plausible that the water in the former dominantly originates in the burnt shale and that of the latter in the black shale bedrock, a reasonable assumption since GW3 is located close to the upstream infiltration area with no deposits of burnt shale. The waters in the black shale bedrock had very similar K concentrations to those in the reference water. This means that K is, in relative terms, particularly soluble in the burnt shale and thus leaves a good finger-print of this material in the groundwater. This could possibly be caused by dissolution of alum still present in the material.

Table 4
Calculated flow of elements in groundwater from the investigated area.

Element	Kg year^{-1}
Ca	91,000
S	89,000
Na	15,000
K	14,000
Mg	7100
Al	4800
Si	2400
Mn	160
Fe	130
Sr	120
Zn	70
Ni	56
Co	29
Cu	24
U	15
Mo	9.7
Ba	5.3
Cd	0.87
Cr	0.44
As	0.27
V	0.24
Pb	0.08

Table 5
Estimated dispersion of elements from black shale bedrock, and emissions from point sources, to the water environment in Sweden (kg year^{-1}).

Element	Black shale	Point sources[a]
Ca	10,300,000	
S	4,200,000	
Na	990,000	
Mg	460,000	
Si	350,000	
K	340,000	
Sr	13,000	
Zn	13,000	580,000
Mn	12,000	
Mo	11,000	
Ni	11,000	15,000
Al	8600	
Fe	7000	
U	4800	
Ba	3700	
Cu	1100	50,000
Co	380	
Cd	270	1800
V	120	
As	88	830
Cr	15	11,000
Pb	8	13,000

[a] Swedish EPA and Statistics Sweden, 2000.

4.3. Sulfur and iron

The S concentrations were high overall with a median for all groundwater samples of 266 mg L^{-1}, which corresponds to 797 mg L^{-1} SO_4. All the groundwater tubes in the burnt shale and the three K-rich ones extending through both materials (GW8, GW10, and GW2a) were high in S (83–662 mg L^{-1}), reflecting oxidation of sulfides present in the material. The median concentration of S in the bedrock shale is approximately 6%, while in the oxidized material it is less than half of that (Table 3). According to sequential chemical extractions performed on the shale materials (Lavergren et al., 2008), 25–50% of the S in the processed shale was extracted by chemicals designated to dissolve sulfides and stable organic material, which shows that sulfides are present in this material. Of the S in the (unoxidized) bedrock shale more than 80% was found in this phase, and an XRD analysis confirmed an abundance of pyrite in the material. Also in the groundwater in the black shale bedrock, in particular at two sites (GW1 and GW4), the S concentrations were high with median concentrations of 294 mg L^{-1} and 263 mg L^{-1}, respectively (Table 1). Since high abundances of sulfate minerals are not expected in the original black shale, the high S concentrations most likely are a result of oxidation of sulfides. Because of the inherently high sulfide concentrations in this material, exposure even of small volumes of rock combined with slow groundwater movement could result in enrichment of dissolved SO_4^{2-}. This means that the source black shale is not entirely reducing, which also is supported by the redox results (Table 1). High S concentrations thus occurred in both acidic and neutral waters and in both types of material. The concentrations of S and Ca were strongly correlated ($r_S = 0.92$; Table 2), indicating that sulfide oxidation results in dissolution of Ca-bearing minerals, most likely calcite, which thus constitutes an important pH buffer.

The Fe concentrations in the groundwater were low, i.e. 0.6–999 μg L^{-1} compared to 5650 μg L^{-1} in the reference water (Table 1), despite high Fe concentrations both in the unoxidized and the

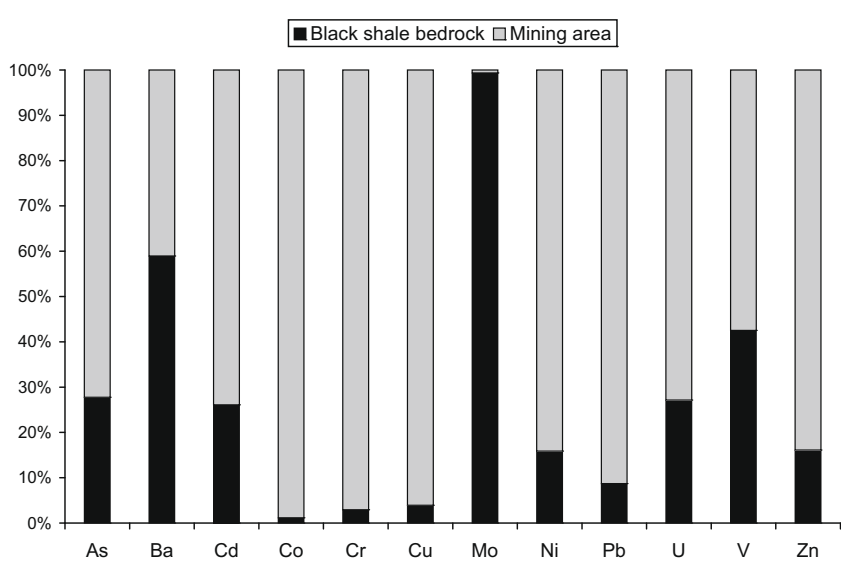

Fig. 2. Calculated fractions of elements in the groundwater originating from the natural black shale bedrock and from the mining area in Degerhamn, SE Sweden.

burnt shale materials (Table 3). Approximately 50% of the Fe in the unoxidized bedrock shale is bound in sulfides and 40% is associated with weathering resistant silicates, while in the processed shale it is predominantly found in weathering resistant minerals (including hematite) and to a less degree (ca. 10%) in sulfides. In both materials, and also in naturally weathered shale, Fe generally exhibits low solubility (0.2–2%) when pH is adjusted to 4.0 (Lavergren et al., 2008). In contrast to S, therefore, Fe is to a large extent retained in the solid materials and not leached into water, which is also observed in other oxidizing, pyrite-rich environments (van Breemen and Harmsen, 1975; Österholm et al., 2005). The low Fe concentrations are also an indication of relatively low levels of colloidal Fe hydroxides in the waters.

4.4. Elements occurring abundantly in the acidic waters

The concentrations of Al, Cd, Co, Cu, Ni and Zn were strongly elevated in the acidic groundwater (GW2a, GW2b, GW12), both in relation to the concentrations found in the near-neutral ones (medians 11,700, 42, 310, 201, 28 and 39 times higher, respectively) and to those in the reference water (medians 49, 325, 185, 68, 184 and 73 times higher, respectively). An additional feature is that Ni and Zn occurred in higher concentrations in the tubes in black shale bedrock (all near-neutral) than in the near-neutral ones in the deposits of burnt shale. Thus, in the burnt shale, it is likely that the most easily mobilized fractions of Ni and Zn have already been depleted. Compared to concentrations in average shale, the black shale in Degerhamn is very rich in Cd, and also relatively rich in Cu, Ni and Zn, but not in Co and Al (Table 3). This shows that the relative enrichment of a metal in the acidic groundwater is poorly correlated with its relative enrichment in the sulfide-rich shale. The chalcophilic metals (Cd, Co, Cu, Ni and Zn) in the investigated black shale are to a large extent associated with sulfides and are, with the exception of Cu, highly mobile in the burnt shale (Lavergren et al., 2008). Only in the acidic groundwater, however, were these metals clearly enriched (Table 1). Therefore, the burnt shale carrying near-neutral groundwater is either already depleted in easily mobilized fractions of these metals, or forms a suitable environment for the precipitation and removal from the solution phase. The exceptionally large difference in Al concentrations between the near-neutral and the acidic waters is caused by the solubility of Al-bearing minerals, probably to a large extent Al hydroxides formed during the burning of the shale.

Also the concentrations of Cr, Mn, Pb and Si were higher in the acidic groundwater, but not to the same extent as the above listed ones, and they were only weakly elevated (and in the case of Pb even lower) compared to the concentrations in the reference water (Table 1). Compared to concentrations in average shale, the black shale in Degerhamn is poorer in Mn and Si and contains typical concentrations of Cr and Pb (Table 3). This shows that Cr and Pb are not particularly soluble in the acidic groundwater environment, and that the low levels of Si and Mn are partly caused by low concentrations in the source materials and partly by slow weathering of silicates carrying Si and Mn.

4.5. Elements occurring abundantly in the near-neutral waters

The Mo concentrations were low in the acidic groundwater (0.25–0.48 $\mu g\,L^{-1}$) and also in two of the tubes with near-neutral waters (0.46 $\mu g\,L^{-1}$ and 0.065 $\mu g\,L^{-1}$). In the other waters Mo was abundant (4.2–228 $\mu g\,L^{-1}$) with concentrations up to 260 times higher than in the reference water (Table 1). High concentrations thus existed in near-neutral waters in both types of materials (bedrock and burnt shale). Molybdenum occurs in high concentrations in the black shale, with a median concentration of 96 ppm, compared to 2.6 ppm in average shale (Table 3). It is also exceptionally soluble: up to 25% is mobilized by mixing crushed shale with distilled water at a ratio of 1:10 (Lavergren et al., 2008). The high Mo concentrations in the groundwater thus match well with its high solubility in the black shale. Much of the Mo found in black shale occurs in an unknown, dispersed form difficult to characterise, and it has been suggested that formation of (non-reduced) thiomolybdates and subsequent binding to sulfurised organic matter is a major mechanism in accumulation of Mo in euxinic sediments (Helz et al., 1996; Erickson and Helz, 2000). Thus, a possible explanation for the high solubility of Mo could be that, due to alterations in the organic matter during diagenesis, it now occurs in the shale's matrix as water-soluble organic complexes or as thiomolybdates that are readily transformed to mobile molybdate ions (MoO_4^{2-}) when exposed to oxidizing conditions. The low Mo concentrations in all the acidic waters are most likely caused by adsorption (e.g. Adriano, 2001).

Although the highest U concentrations, as for Al, Cd, Co, Cu, Ni and Zn, were found in the acidic groundwater, a characteristic feature of this metal was its high abundance also in the near-neutral groundwater in both bedrock and burnt shale (Table 1). Uranium is a metal which in its reduced state (+IV) is highly insoluble but in the oxidized state (+VI) highly soluble in form of uranyl (UO_2^{2+}) (Langmuir, 1997). The inherently high U abundance in the black shale (median 76 ppm as compared to 2.7 ppm in average shale), combined with generally oxidizing conditions, thus constitutes a favourable environment for extensive U mobilization. The elevated U concentration in several of the groundwater tubes in the black shale is a strong indication that the source of the waters in these tubes is at least suboxic, as was also indicated by the S data. Microbial activity has been shown to enhance the mobilization of U from this type of material, which most likely contributes to the high U concentrations (Kalinowski et al., 2006). By far the lowest U concentrations (median values <0.30 $\mu g\,L^{-1}$) were found in the two tubes (GW3 and GW9) having negative redox potentials, indicating the stability of poorly soluble U(IV) minerals (Langmuir, 1997).

4.6. Elements occurring in low concentrations in the waters

Vanadium and As have several features in common: (1) both are highly enriched in the studied black shale compared to concentrations in average shale (Table 3), (2) they are positively correlated in the groundwater ($r_S = 0.65$; Table 2), and (3) their abundances in the groundwater are on a low to average level (except for As in one tube), in comparison to the reference groundwater (Table 1). The inherently high concentrations of V and As in the black shale are thus not reflected in the groundwater. This is in line with the low extractability of these metals observed in both unoxidized and burnt shale (Lavergren et al., 2008), and also with the limited loss of V and As recorded from the oxidized shale in the area (Table 3). Both V and As have an affinity for Fe oxides (Adriano, 2001), which is why it is likely that any mobilized fractions of these elements were strongly adsorbed by the Fe-rich matrix of the shale material.

4.7. Quantification of impacts on the aquatic environment

The WHO guidelines for drinking water (World Health Organization, 2006) includes values for As (10 $\mu g\,L^{-1}$), Ba (700 $\mu g\,L^{-1}$), Cd (3 $\mu g\,L^{-1}$), Cr (50 $\mu g\,L^{-1}$), Cu (2000 $\mu g\,L^{-1}$), Mn (400 $\mu g\,L^{-1}$), Mo (70 $\mu g\,L^{-1}$), Ni (70 $\mu g\,L^{-1}$), Pb (10 $\mu g\,L^{-1}$) and U (15 $\mu g\,L^{-1}$). In the acidic groundwater in this study, several of these guideline values were exceeded: for Ni and U by about one order of magnitude, for Cd by a factor of five and for Mn by a factor of four. In particular U, but also Ni and Mo, also occurred in concentrations well above the guidelines in several of the near-neutral groundwater tubes in the natural black shale bedrock (Table 1). This shows that

groundwater extracted in black shale areas largely unaffected by anthropogenic activities can also potentially be a health concern if used for drinking water purposes. In addition, fragmentized black shale may be present as quaternary deposits outside the boundaries of the black shale bedrock, e.g. in sand and gravel formations which are often used as a source of drinking water, where it may have a negative effect on the water quality.

The total transport of elements to the Baltic Sea by the groundwater infiltrated in the study area (Table 4) was dominated by Ca and S (approximately 90 tonnes a^{-1}). However, considerable amounts of several trace elements were also transported, such as Zn (70 kg), Ni (56 kg), Co (29 kg), Cu (24 kg), U (15 kg), Mo (10 kg) and Ba (5 kg). For most of the elements, more than 80% is calculated to originate from the deposits of burnt shale, making the historical anthropogenic activities a strong contributor of element dispersion from the area. For several elements, however, the natural black shale bedrock is also a major source. Roughly half of the Ba and V originates from the bedrock, and about a quarter of the As, Cd and U (Fig. 2). Molybdenum almost entirely originates from the black shale bedrock, reflecting the particularly high solubility of this metal in that material.

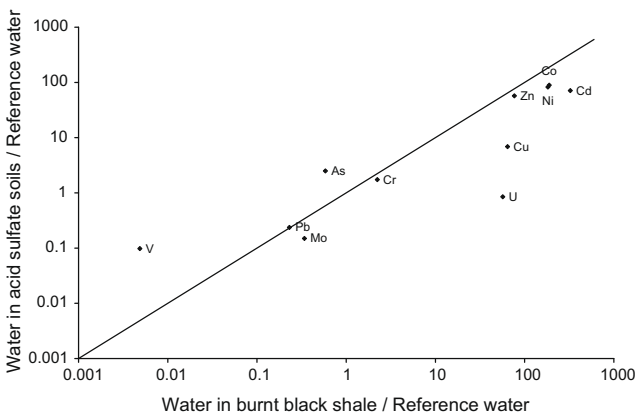

Fig. 3. Element concentrations in surface waters (median values of 30 samples) derived from acid sulfate soils in W Finland (Sundström et al., 2002) versus those in acidic groundwater (median values of 24 samples) in the deposits of burnt shale in Degerhamn, SE Sweden. All concentrations are normalized to a reference groundwater in granitoidic till.

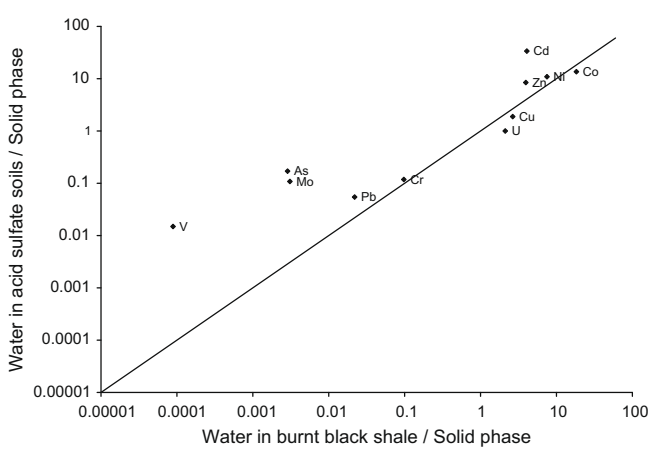

Fig. 4. Element concentrations in surface waters (median values of 30 samples) derived from acid sulfate soils in W Finland (Sundström et al., 2002) versus those in acidic groundwater (median values of 24 samples) in the deposits of burnt shale in Degerhamn, SE Sweden. The former are normalized to concentrations in the unoxidized parent soil material (median values of 9 composite samples; Nordmyr et al., 2006), and the latter to the concentrations in the black shale bedrock (median values of 11 samples; Table 3).

As a rough measure of what this could mean in terms of dispersion of metals on a national level, the area of black shale bedrock exposed to weathering in Sweden was estimated from Hessland and Armands (1978). In the southern half of the country there is a total occurrence of approximately 3300 km^2, and in the north approximately 15,000 km^2 along the western parts of the Caledonian mountain range. In the south a total of about 400 km^2 (12%) is not covered by other types of bedrock and thus most likely exposed to some degree of chemical weathering. Of the occurrence in the north, it was assumed that 10% is exposed to oxidizing processes. This gives a total area of 1900 km^2 of black shale that is currently exposed to chemical weathering and thus potentially affecting the groundwater quality in a way similar to that in Degerhamn. By using the simplified assumption that the concentrations of elements in the black shale groundwater in Degerhamn (upstream of the mining area) is representative for all black shale groundwater in Sweden, this would mean that on a national level, weathering of this type of bedrock annually contributes with approximately 13 tonnes of Zn, 11 tonnes each of Mo and Ni, 5 tonnes of U and 4 tonnes of Ba to the groundwater environment (Table 5). This calculation does, of course, not take into account the variable composition of the black shale or the different hydrological conditions existing throughout the country. Nonetheless, it gives a rough estimate of the magnitude of elements that can potentially be dispersed by groundwater from weathering of black shale.

The total emissions of As, Cd, Cr, Cu, Ni, Pb and Zn to waters from point sources (including mines, mining waste deposits, industries and municipal wastewater treatment plants) in Sweden in 1995 (Swedish EPA and Statistics Sweden, 2000) is shown in Table 5. The calculated amounts of Ni released from weathering of black shale is similar to that from anthropogenic point sources (11 tonnes and 15 tonnes, respectively), while the release of Cd and As are about one tenth of those from anthropogenic point sources. As black shale is widely spread on most continents, this type of material may be a yet underestimated source of metals dispersed in the aquatic systems.

4.8. Comparison with acid sulfate soil

When the median concentrations, normalized to the reference water, of selected trace elements in the acidic groundwater in Degerhamn are plotted against those in acidic waters from acid sulfate soils, there is an overall correlation (Fig. 3). The acid sulfate soil data, derived from Sundström et al. (2002), are median values of water samples collected in 30 ditches draining acid sulfate soils in western Finland. These waters had pH values between 2.9 and 4.7 and are considered to be representative for acid sulfate soil runoff in that region. In detail, the groundwater in the burnt shale was somewhat more enriched in most of the elements, but the overall picture is that the relative abundance of various elements is generally similar in waters in contact with these two types of sulfide-rich materials. This means that upon oxidation, the sulfide-rich bedrock originating in the Cambrian–Ordovician sea and the sulfide-rich sediments deposited in the Holocene brackish Baltic Sea delivers basically the same suite of elements to the aquatic environment. When the geochemistry of the unoxidized parent materials is considered, many of the elements plot rather close to the 1:1 line (Fig. 4). Exceptions are V, As and Mo, which overall are relatively immobile in these acidic materials. This shows that the concentrations in the waters are mainly governed by the abundance in the source material. Because U was, in relative terms, approximately equally mobile in the burnt shale and acid sulfate soil, the much higher U abundance in the water in contact with

the former (Fig. 3) can be explained simply by the U abundance in the source material.

5. Conclusions

The major findings and conclusions are:

(1) Oxidation of sulfides occurs both in the deposits of processed black shale and in the black shale bedrock unaffected by anthropogenic activities, however often to an extent insufficient to produce acidic groundwater. The near-neutral groundwater found in both these materials carries an abundance of U and Mo, and also often has high concentrations of Cd, Ni and Zn.
(2) Sulfide oxidation in the deposits of burnt black shale is, as would be expected, locally sufficient to produce severely acidic groundwater (pH 4), with strongly elevated concentrations of several metals, especially Al, Cd, Co, Cu, Ni, U and Zn.
(3) The behaviour of K was different to that of the other alkali and alkaline earth metals, as it occurred throughout in considerably higher concentrations in the processed black shale, irrespective of pH and electric conductivity, than in the natural shale bedrock. These results show that K, in these kinds of settings, can be used as a tracer of groundwater sources.
(4) On a national (Swedish) level, the metal dispersion from black shale bedrock can possibly be comparable to that from anthropogenic point sources, and deposits of processed shale can strongly enhance this dispersion. Widespread occurrences of black shale bedrock may thus constitute a considerable source of metal dispersion to the water environment.
(5) The deposits of processed black shale deliver a suite of potentially toxic metals (especially Cd, Co, Ni, Zn and Cu) similar to that in runoff from acid sulfate soils. Hence, irrespective of the origin and physical properties of the sulfide-bearing materials, basically the same metals are dispersed in the aquatic environment. This has environmental implications, as in many regions worldwide, different types of sulfidic materials (ranging from soft Holocene sediments to Phanerozoic and Precambrian black shales) will be ever more excavated and drained as a result of expanding human activities.

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