

Mobility of trace elements in black shale assessed by leaching tests and sequential chemical extraction

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ABSTRACT: This study focuses on the abundance and mobility of Ca, Fe, S and trace elements (As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, U, V and Zn) in black shale (alum shale) in SE Sweden. Samples of non-weathered, weathered and burnt black shale were chemically characterized and the potential element release from them was assessed by standard water-based leaching tests and pH/redox-regulated availability tests. Sequential chemical extractions provided further information on the phases in which the elements are bound. Results show that the shale is very rich in As (88–122 ppm), Cd (0.4–4.6 ppm), Mo (64–176 ppm), U (27–71 ppm) and V (496–1560 ppm). Cadmium and Mo, bound mainly in sulphides or organic matter, are very mobile in the non-burnt shale, with mobilization rates of up to 19% (190 µg/kg) and 25% (16 mg/kg), respectively, using only water as extraction medium. The non-weathered shale is also relatively rich in Cu (113 ppm), Ni (100 ppm) and Zn (304 ppm), the latter two in particular showing behaviour similar to that of Cd, but with lower mobilization rates. In all samples U and V are found mainly in weathering-resistant mineral phases and thus have a lower mobility, but due to the high abundance in the material, significant amounts of U can be released on longer time scales (up to 6 mg/kg, as indicated by the pH/redox-regulated test). Less than 1% of the As is released in all the leaching tests, indicating that upon oxidation it is retained in the solid phase. The overall conclusion is that this material has a high potential for releasing Cd, Mo, Ni, U and Zn during weathering.

KEYWORDS: *black shale, alum shale, leaching, sequential extraction, metal mobility*

INTRODUCTION

Black shale is a rock formed from sediments deposited in stagnant aquatic environments and as such usually has a high content of organic material and sulphides. Black shale is also known to be rich in many potentially toxic elements such as As, Cd, Mo, U and V (e.g. Brumsack 2006, and references therein). Due to its content of sulphide and organic material, black shale is easily weathered when exposed to air and water, producing acidic drainage water, rich in metals (e.g. Jeng 1991; Salomons 1995; Puura 1998; Evangelou 2001). During the weathering process the sulphide minerals are oxidized into free metal ions and sulphuric acid, which in turn attacks other minerals and the organic material, resulting in further release of elements and production of secondary minerals (Jeng 1991, 1992). The acidity of the drainage water also enhances the solubility and mobility of many metals. If calcite (CaCO₃) is present the produced acid may be buffered, and dissolved metal ions can precipitate as metal hydroxides and/or carbonates.

In Sweden black shale has historically been used as a raw material for the production of alum [KAl(SO₄)₂·12 H₂O], and it is often referred to as 'alum shale'. In the process the shale was mined, burnt and then leached with water from which the alum was precipitated (Eklund *et al.* 1995, 1996). It was also extensively used as a fuel in the alum production process as well

as in lime production (Hessland & Armands 1978). The remains of the shale were then usually deposited in the mining area where today it can constitute a potential environmental hazard due to metal leaching, as in other areas affected by acid mine drainage from sulphide-mineralized rock (e.g. Evangelou & Zhang 1995) and acid sulphate water from acid sulphate soils (e.g. Joukainen & Yli-Halla 2003; Sohlenius & Öborn 2004). Laboratory-scale leaching procedures are widely used for making risk assessments of such deposited waste materials. The leaching methods, however, have been developed for different purposes and thus provide different information. Some relatively simple methods, such as batch tests and availability tests providing information of leachable amounts of elements on shorter or longer time scales, are employed mainly for industrial waste materials (e.g. Quevauviller *et al.* 1996). Other methods have been developed for more scientific or exploratory purposes, such as sequential chemical extractions which can provide information about the phases in which elements are bound (e.g. Li *et al.* 1995; Carlsson *et al.* 2002), or different kinetic leaching procedures which aim to imitate natural conditions and processes (e.g. Holmström *et al.* 1999).

In Degerhamn, on the island Öland in SE Sweden, black shale was mined in opencast mines and burnt on site from the eighteenth to the twentieth centuries, leaving behind exposed bedrock surfaces together with deposits of burnt shale in an

Table 1. Summary of the leaching methods used.

Test	Leaching medium / reagent	Target phases
Single leaching tests		
ST1	H ₂ O (L/S 2)	
ST2	H ₂ O (L/S 10)	
ST3	H ₂ O + HNO ₃ (L/S 200)	
ST4	H ₂ O + HNO ₃ + H ₂ O ₂ (L/S 200)	
Sequential extractions		
SE5	CH ₃ COONa	Surface positions and carbonates
SE6	Na ₄ P ₂ O ₇	Labile organic material and organic ligands
SE7	NH ₂ OH·HCl (0.25 mol/l)	Amorphous Fe-oxyhydroxides and Mn-oxides
SE8	NH ₂ OH·HCl (1 mol/l)	Crystalline Fe-oxides
SE9	KClO ₃ + HCl	Organic material and sulphides
SE10	HNO ₃ / LiBO ₂	Silicates and other poorly dissolved minerals

L/S, Liquid to solid ratio (l/kg)

area covering a total of *c.* 0.8 km². In 1999 high Cd concentrations were found in sewage sludge in a local wastewater treatment plant, and it was soon realized that the former mining area was the source of the metal pollution (Falk *et al.* 2006). In this study we use different leaching procedures to characterize the mobility and forms of Cd, and also of other potentially associated elements including As, Ca, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, S, V and Zn, in unoxidized, weathered and burnt black shales that exist in the Degerhamn area. The aim of the study is thus to provide information on metal abundances and mobility in non-weathered, naturally weathered and industrially processed black shale. By applying different extraction methods on the same materials, information can also be provided on what procedure is suitable in environmental studies concerning similar types of black shale material, occurring worldwide.

METHODS

Samples

Four composite samples representing the four types of shale material present in the area were used: (1) non-weathered black shale gathered from five drillcores (NBS); (2) weathered black shale gathered from six points at the walls of the old shale quarry exposed for more than a century (WBS); (3) acidic burnt black shale, gathered from the upper horizon (0–30 cm) at three points in >100-year-old waste deposits from previous alum production (BBS); and (4) lime-mixed burnt black shale gathered from the upper horizon (0–30 cm) at two points in *c.* 100-year-old waste deposits from previous lime production (LBBS).

The samples were crushed and air-dried at room temperature for several days, whereafter portions were sieved or milled according to the test procedures' respective requirements (see below). By careful mixing of the respective samples during the preparation procedure, the chemical and mineralogical compositions were considered to be the same in all tests.

General analyses

Mineralogy

Mineral compositions of the samples were investigated by X-ray diffraction (XRD). Milled samples were analysed by a D5005 X-ray diffractometer (interval 5–65°C at 30 rpm), and the main minerals were identified with the Siemens DIFFRACplus-D5005 software. Quantification of the identified minerals was made with the software SIROQUANT V 2.0.

pH

The pH values of the samples were measured by a method adapted from Balsberg-Påhlsson (1990), in which 15 g of milled sample were agitated in 50 ml of deionized water for 2 hours and then left to settle for *c.* 1 hour, after which the pH of the supernatant was determined.

Elemental analysis

The samples were digested and analysed for total (or near-total) concentrations of major and trace elements by ICP-AES and ICP-SFMS at an accredited commercial laboratory. For determination of Al, Ca, Cr, Fe, K, Mg, Mn, Mo, Na, Si, U and V, the samples were fused with lithium metaborate followed by dissolution in dilute nitric acid. For the more volatile elements As, Cd, Co, Cu, Ni, Pb, S and Zn, dried samples were leached with 7 mol/l nitric acid in closed vessels in a microwave oven. In addition to the four composite samples, another ten samples of unoxidized black shale collected from five separate drillcores (later taken in the area) were analysed.

Carbon

Concentrations of total carbon (C) were determined using Leco analysis (infra-red detection). Graphite C was determined after ignition (600°C) and HCl leaching, and carbonate C by direct CO₂ evolution and Leco analysis. Concentrations of organic C were calculated by difference: total C – graphite C – carbonate C.

Metal leachability tests

In all single tests (ST1–ST4) and sequential extractions (SE5–SE10) described below, the collected solutions were acidified with HNO₃ (1 ml per 100 ml) and analysed for As, Ca, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, S, U, V and Zn with ICP-AES and ICP-SFMS at an accredited commercial laboratory. A summary of the different metal leachability tests used is given in Table 1.

Two-stage batch test (ST1, ST2)

A two-stage batch test, developed to investigate the potential immediate leaching properties of inorganic waste material, was conducted according to EN 12457-3 (European Committee for Standardization 2002). Sample material of 175 g, crushed to grain sizes <4 mm, was agitated with distilled water at a liquid to solid ratio (L/S, l/kg) of 2 for 6 hours, whereafter the eluate was filtered (0.45 µm membrane filter) and later analysed. The procedure was immediately continued by adding another

Table 2. Mineralogy of the samples, as identified by XRD.

Mineral	NBS	WBS	BBS	LBBS
Quartz (%)	49	48	48	48
Orthoclase (%)	13	19	8	13
Microcline (%)	5	5	11	4
Muscovite (%)	23	24		
Pyrite (%)	10	4		
Hematite (%)			33	27
Calcite (%)				8
Glauconite (%)	Identified	Identified		
Jarosite (%)			Identified	
Gypsum (%)				Identified

The percentages given are overestimates since some minerals as well as organic matter were not included in the calculations

portion of water at an L/S ratio of 8 and agitation for 18 hours. The eluate was filtered and analysed. The results are reported as L/S 2 (ST1) and L/S 10 (ST2), where the latter is the cumulative element release during the two steps.

Availability tests (ST3, ST4)

An availability test (ST3), developed for granular waste materials (especially ashes and slags) is a batch test designed to give a rough estimation of the totally leachable amounts of elements after disintegration of the material and loss of acid neutralizing capacity (Nordtest 1995). Eight grams of sample material, milled to a particle size of <125 µm, were mixed with distilled water at a high L/S ratio (100) in order to minimize solubility limits and provide a good water contact, whereafter the suspension was stirred for 3 hours. If required, nitric acid was added to maintain the pH at a maximum of 7 in order to gain optimal leachability of oxyanionic species. After settling of the particles, the eluate was filtered (0.45 µm membrane filter). The procedure was immediately repeated with another portion of water (L/S 100), but the suspension was now stirred for a longer time period (18 hours) and its pH kept at 4 or lower. The two eluates were then combined before analysis.

Another related test (ST4), referred to as an oxidized availability test (Nordtest 1999), was carried out in an identical manner, with the exception that hydrogen peroxide was continuously added to maintain a redox potential equivalent to that of demineralized water of the same pH as that of the sample suspension, and in equilibrium with the atmosphere.

Sequential chemical extraction (SE5–SE10)

In the sequential extraction procedure, which was a modification of that described in Hall *et al.* (1996a, b) and Land *et al.* (1999), the samples were leached stepwise with different chemicals preferentially displacing elements from: (SE5) surface positions (adsorbed, exchangeable) and carbonates; (SE6) labile organic material and organic ligands; (SE7) amorphous Fe-oxyhydroxides and Mn-oxides; (SE8) crystalline Fe-oxides; (SE9) organic material and sulphides; and (SE10) silicates plus other poorly dissolved minerals.

SE5: 0.80 g of the sample was shaken in 20 ml of 1.0 mol/l CH₃COONa (pH 5) for 6 hours and then centrifuged at 10 000 rpm for 10 min, whereafter the supernatant was decanted. This procedure was repeated once, but with only 10 ml of reagent. The remaining residue was rinsed twice with 10 ml of water, which after centrifugation was collected and added to the reagent solution to be analysed.

SE6: To the residue, a volume of 40 ml of 0.1 mol/l Na₄P₂O₇ was added, whereafter the suspension was shaken for 1 hour and then centrifuged, and the supernatant decanted.

This procedure was repeated once, but only with 30 ml of reagent. The rinsing procedure was carried out as in SE5.

SE7: To the residue, a volume of 20 ml of 0.25 mol/l NH₂OH·HCl in 0.10 mol/l HCl was added, whereafter the suspension was heated in a water bath (with loosened cap) at 60°C for 2 hours with vortexing every 30 minutes and then centrifuged, and the supernatant decanted. The procedure was repeated once, but with only 10 ml of reagent and for only 30 minutes. The rinsing procedure was carried out as in SE5.

SE8: To the residue, a volume of 20 ml of 1.0 mol/l NH₂OH·HCl in 25% CH₃COOH was added, whereafter the suspension was heated (with loosened cap) in a water bath at 90°C for 3 hours while vortexed every 20 minutes and then centrifuged, and the supernatant decanted. This procedure was repeated once, but with only 10 ml of reagent and heating for 1.5 hours. The rinsing procedure was carried out as in SE5, but with 25% CH₃COOH instead of water.

SE9: To the residue, 750 mg of KClO₃ and 5 ml of 12 mol/l HCl were added, whereafter the suspension was vortexed and another 10 ml of HCl added. After 30 minutes, the suspension was diluted with 15 ml of water and then centrifuged, and the supernatant decanted. To the residue, 10 ml of 4 mol/l HNO₃ were added, the suspension heated in a water bath at 90°C for 20 minutes and centrifuged, and the supernatant decanted. The rinsing procedure was carried out as in SE5.

SE10: After drying at 50°C, the residue was digested in 7 mol/l HNO₃ in closed vessels in a microwave oven, and analysed for As, Cd, Co, Cu, Ni, Pb, Zn and S. For the determination of Ca, Cr, Mo, U and V, another portion of the residue was fused with lithium metaborate followed by dissolution in dilute nitric acid.

RESULTS AND DISCUSSION

The bulk mineralogy of the samples is presented in Table 2, pH and concentrations of major silicate forming elements in Table 3, and the results from the metal leachability tests in Table 4.

Mineralogy

The main mineral in all four samples is quartz, constituting approximately half of their weight (Table 2). Orthoclase and microcline were identified in all the samples, and in the non-burnt samples (NBS and WBS) also muscovite and glauconite. The similarity of the samples in terms of bulk mineralogy is supported by the similar concentrations in the samples of Si, Al, K, Na and Mg (Table 3). According to the XRD quantification, pyrite (FeS₂) constitutes c. 9% in NBS and 4% in WBS. In the burnt samples (LBBS and BBS) no sulphide minerals were detected, but instead they contain large amounts of hematite, 26% and 33%, respectively. Gypsum, a secondary

Table 3. pH and total concentrations (%) of Si, Al, K, Mg, Na and organic C in samples of non-weathered (NBS), weathered (WBS), burnt (BBS) and lime mixed burnt (LBBS) black shale, together with concentrations in average shale.

	NBS	WBS	BBS	LBBS	Shale*
pH	8.1	3.3	5.9	7.6	
Organic C	6.8	12.6	2.2	0.86	1.2 [†]
Si	24.2	21.7	23.9	23.1	27.5
Al	6.77	7.14	8.1	7.41	8.8
K	4.43	4.19	4.03	3.79	2.66
Mg	1.15	0.546	0.694	0.621	1.5
Na	0.131	0.108	0.13	0.125	0.59

* Li & Schoonmaker (2005)

[†] Total C

mineral known to form from oxidizing sulphides, was identified in the LBBS and BBS samples. The LBBS sample contains *c.* 8% of calcite. The presence of organic material was not adjusted for in the calculations.

pH, Ca and C

The pH values of the NBS, WBS, BBS and LBBS samples are 8.1, 3.3, 5.9 and 7.6, respectively (Table 3), which is entirely in line with expected results, as in the first sample sulphides are as yet unoxidized, in the second they have oxidized to sulphuric acid, in the third the burning has lowered the pH, and in the fourth there was an abundance of lime.

In the LBBS the Ca concentrations are considerably higher, and the vast majority is soluble in the acidic ST3 and in the SE5 (adsorbed/carbonates) step (Table 4), which shows that the dominating form is calcite, also identified by XRD (8%, which is in line with the Ca concentrations). In the other samples, *c.* 50% of the Ca is soluble by ST3 and SE5. Very little Ca is associated with silicates (SE10).

The concentrations of organic C in the NBS, WBS, BBS and LBBS samples are 6.8%, 12.6%, 2.2% and 0.86%, respectively (Table 3). This shows that, as expected, the organic matter has oxidized during the burning process. The difference in concentration between the two unburnt samples likely reflects the heterogeneity of the shale bedrock.

Iron

The total Fe concentrations in NBS and WBS are <5% which is similar to that in average shale (Table 4) and only marginally lower than the average and median for the Degerhamn black shale in general, as shown in Table 5. In contrast, in both burnt samples the concentrations are >10%, which is higher than the maximum for the 11 black shale samples (Table 5). The enrichment of Fe in these samples cannot alone be explained by the loss of organic material caused by the burning process. Since the silicate mineralogy in all samples is both qualitatively and quantitatively similar, the only reasonable explanation for the Fe abundance in the burnt samples is that these were originally very high in pyrite.

In the burnt samples, most of the Fe (>7% by weight) is associated with SE10 (residual) and hematite was abundant (26 and 33%), which shows that during the burning process, the Fe(+II) was converted to hematite, which is not soluble by the Fe-oxide attacking reagents of SE7 and SE8. Approximately 50% of the Fe in NBS is soluble in SE9, indicating association with sulphides and to some extent organic material, and *c.* 40% is found in the residual fraction (SE10) certainly dominated by Fe-bearing silicates such as glauconite and chlorite. In the naturally weathered sample (WBS), in contrast to the burnt ones, there are relatively high Fe concentrations in SE8

(crystalline Fe-oxides) and SE9 (sulphides/organics) and little in SE10 (residual), indicating association with both Fe-oxides and sulphides/organics and less with chemically resistant minerals (silicates, hematite). Iron is highly insoluble in water (ST1, ST2), although slightly more soluble in the acidic sample (WBS) than in the others (Table 4).

Sulphur

The total S concentration in NBS is 2.7%, which is *c.* 12 times higher than in average shale (Table 4), but considerably lower than the average and median values for the Degerhamn black shale in general (Table 5). This means that the unoxidized sample used in the leaching tests (NBS) is relatively low in S considering the characteristics of this material. In the oxidized samples, the S concentrations are lower than in NBS as a result of oxidation and leakage (Falk *et al.* 2006) and, consequently, the original S abundances in these are unknown.

In NBS, the majority of the S (>80%) is soluble in SE9 (sulphides/organics) which is due to an abundance of pyrite in the sample (identified by XRD), while the concentrations are very low in the water-based (ST1, ST2) and pH-regulated (ST3) tests (Table 4). In ST4, which is the same as ST3 plus added hydrogen peroxide, the S concentration increases considerably, but is still only 12% of the total S and 15% of the SE9-extractable (pyrite) S (Table 4). This shows that pyrite has not been fully dissolved by the hydrogen peroxide treatment. Borah *et al.* (2005) found a pyrite dissolution of up to 31% when leaching pulverized pyrite with hydrogen peroxide (1:1) for 24 hours, a figure which somewhat increased (up to 35%) by the addition of metal ions to the solution. Dimitrijevic *et al.* (1999) found that the dissolution of pyrite in acid solution was enhanced by higher hydrogen peroxide concentrations but was decreased by stirring. The large difference between ST4 and ST3 thus indicates that hydrogen peroxide has released S from organic matter and some sulphides.

Although the S concentrations in the oxidized samples are lower, they are very high considering the oxidized nature of the materials (Table 4). In LBBS the S is highly soluble: *c.* 30% and >50% (absolute abundance of 0.85%) is released by ST2 and ST3, respectively. In contrast, the concentration in SE9 (sulphides/organics) is relatively low (25%) and the difference between ST4 and ST3 is very small (Table 4). These data show that in this sample, i.e. a burnt black shale with additional lime, the S is abundantly adsorbed on mineral surfaces and/or occurs as soluble gypsum. In WBS and BBS, the S concentrations are most abundant in SE9 (*c.* 50% and 60%, respectively), which is caused by binding to sulphides and to some extent organic material. In the hydrogen peroxide extractable fraction (difference: ST4–ST3) S concentrations are similar to that in NBS, and in the water-based tests (ST1, ST2) in general between those of NBS and LBBS (Table 4).

Table 4. Total and partial concentrations (mg/kg for Ca, Fe and S; µg/kg for all others) of elements in samples of non-weathered (NBS), weathered (WBS), burnt (BBS) and lime-mixed burnt (LBBS) black shale.

Element	Sample	Total	Single tests (ST)			Sequential extraction (SE)						
			Water ST1	Water ST2	pH 7/4 ST3	pH 7/4 + H ₂ O ₂ ST4	CH ₃ COONa SE5	Na ₄ P ₂ O ₇ SE6	NH ₂ OH:HCl SE7	NH ₂ OH:HCl SE8	KClO ₃ + HCl SE9	HNO ₃ /LiBO ₂ SE10
Ca	NBS	12900	64	152	5610	5850	4750	559	7060	733	258	na [†]
Ca	WBS	2650	1030	1240	1690	1680	1560	<94	675	77	37	na [†]
Ca	BBS	4280	1230	1580	2430	2450	2280	<94	798	65	38	832
Ca	LBBS	33800	1260	5620	28700	28300	28500	527	1060	247	156	916
Ca	Shale*	16000										
Fe	NBS	49000	0.22	2.00	523	89	616	947	4560	5810	23700	20100
Fe	WBS	31500	216	271	573	2170	725	1030	2230	15500	11700	6700
Fe	BBS	115000	0.01	0.03	277	1240	183	760	5050	22300	9890	74800
Fe	LBBS	104000	0.01	0.06	289	19	238	500	2980	18000	9880	71000
Fe	Shale*	47200										
S	NBS	27700	80	204	190	3380	221	743	639	<12	22900	882
S	WBS	18500	1340	1580	1940	5470	2060	685	968	2610	11200	1550
S	BBS	14200	1070	1360	1920	4230	1590	955	1800	3960	6960	1100
S	LBBS	15700	1120	4880	8510	8920	8230	458	706	2440	3850	966
S	Shale*	2400										
As	NBS	122000	41	200	690	200	1900	6900	<5200	13500	103000	1500
As	WBS	88000	21	63	420	<200	2700	18600	17400	36400	30800	990
As	BBS	109000	<4	<20	<200	<50	390	7200	14600	51400	32300	22300
As	LBBS	109000	16	110	690	500	10000	12500	30100	42600	31400	11300
As	Shale*	13000										
Cd	NBS	4600	20	28	350	2300	350	130	330	440	2700	12
Cd	WBS	1000	150	190	300	460	310	100	170	290	250	13
Cd	BBS	400	3.1	4.2	89	120	100	22	57	180	100	32
Cd	LBBS	1200	1.6	4	500	540	480	98	270	240	130	52
Cd	Shale*	300										
Co	NBS	18000	4.5	11	4000	8400	3800	2300	2700	1600	5800	2400
Co	WBS	5700	1400	1600	2100	3700	2100	470	710	770	2400	180
Co	BBS	8000	200	240	2000	3400	2100	490	1300	2100	1900	2100
Co	LBBS	12000	9.6	20	2800	3400	1900	470	2600	3400	4100	2400
Co	Shale*	19000										
Cr	NBS	108000	1.2	8.2	120	700	540	510	3300	8500	6800	84300
Cr	WBS	81000	78	76	87	1200	740	700	1800	7600	4500	64300
Cr	BBS	98000	0.48	4.6	100	2000	490	480	2700	10500	5200	68300
Cr	LBBS	88000	0.42	5.7	130	250	360	320	2000	9100	4700	67800
Cr	Shale*	90000										
Cu	NBS	113000	1.8	9	4700	22000	4900	8800	8700	8000	74100	2200
Cu	WBS	97000	1000	1300	2300	28000	4600	14100	16000	17900	34400	1700
Cu	BBS	64000	2.1	8.7	5300	20000	3700	6500	15000	21600	9900	3800
Cu	LBBS	75000	12	31	4500	8800	4300	6200	15500	22200	17800	7200
Cu	Shale*	45000										
Mn	NBS	246000	16	42	68000	67000	50800	11800	38800	59000	45400	31000
Mn	WBS	67400	4640	5400	11000	16000	6700	3860	3640	6470	14600	32400
Mn	BBS	169000	1600	2000	30000	35000	9460	4360	6390	18000	9510	120000
Mn	LBBS	293000	490	1000	83000	85000	65200	11700	28500	26400	13900	132000
Mn	Shale*	850000										
Mo	NBS	64000	10400	16000	23000	54000	10600	15700	5900	5300	27400	6300
Mo	WBS	149000	23	42	700	15000	2700	18900	8100	58400	57800	13900

Table 4. *continued.*

Element	Sample	Total	Single tests (ST)			Sequential extraction (SE)									
			Water ST1	Water ST2	pH 7/4 ST3	pH 7/4 + H ₂ O ₂ ST4	CH ₃ COONa SE5	Na ₄ P ₂ O ₇ SE6	NH ₂ OH·HCl SE7	NH ₂ OH·HCl SE8	KClO ₃ + HCl SE9	HNO ₃ /LiBO ₂ SE10			
Mo	BBS	155000	9.1	86	150	1700	240	6600	6500	66600	15700	56900			
Mo	LBBS	1760000	500	1600	4600	12000	2300	6800	6500	59000	26400	63700			
Mo	Shale*	2600													
Ni	NBS	1000000	24	50	8400	29000	8500	12500	10700	6100	41100	24800			
Ni	WBS	460000	5100	6200	8800	14000	6900	3000	4900	8200	14300	10900			
Ni	BBS	210000	640	820	4500	7400	3800	1200	2900	7800	5900	9800			
Ni	LBBS	430000	34	76	5000	7000	3500	1800	8300	15500	11800	9700			
Ni	Shale*	50000													
Pb	NBS	370000	0.56	2	330	700	7600	2100	11200	2700	14900	560			
Pb	WBS	270000	1.6	3.2	26	130	300	500	2300	18700	6300	460			
Pb	BBS	300000	0.2	3.5	22	35	1600	960	8600	17200	2700	2300			
Pb	LBBS	160000	0.07	1	10	20	730	340	2000	9300	3600	2100			
Pb	Shale*	20000													
U	NBS	270000	240	340	980	2000	4800	540	4700	2200	6100	14000			
U	WBS	590000	320	350	380	6100	4900	3700	1300	4000	20600	39400			
U	BBS	590000	12	11	390	3900	2500	1200	1800	2300	5300	69100			
U	LBBS	710000	440	780	3000	3700	6900	2800	4500	5000	5700	60000			
U	Shale*	2700													
V	NBS	8760000	84	480	2300	21000	2300	5100	13000	13000	62800	767000			
V	WBS	15600000	100	110	240	25000	2000	14600	20400	51400	201000	1180000			
V	BBS	4960000	0.66	1.9	5	4100	350	4600	26700	58400	31100	361000			
V	LBBS	5670000	31	150	940	25000	8000	11500	35000	50600	29900	415000			
V	Shale*	1300000													
Zn	NBS	3040000	2.1	11	10000	98000	10800	6800	20400	18000	145000	2800			
Zn	WBS	4000000	3400	4100	6100	7900	3700	1800	5300	8800	10900	1200			
Zn	BBS	510000	20	34	3700	5700	2200	970	6000	10000	8400	7600			
Zn	LBBS	490000	2.7	7.7	9100	9700	7100	2400	9400	7500	8000	10200			
Zn	Shale*	95000													

For further description of samples and leaching methods, see text

* World average shale (Li & Schoonmaker 2005)

† Not analysed

Table 5. Element concentrations in 11 black shale samples (NBS plus ten separate samples) from Degerhamn, Öland, Sweden.

Element	Average	Median	Min.	Max.
Al (g/kg)	65.5	67.7	38.6	80.4
Ca (g/kg)	9.38	3.29	0.357	48
Fe (g/kg)	53.9	53	23.3	92.3
K (g/kg)	33.6	35.7	12.7	44.4
Mg (g/kg)	7.4	7.54	2.71	11.5
Na (g/kg)	1.03	1.19	0.185	1.31
S (g/kg)	65.2	59.1	11	210
Si (g/kg)	228	206	178	393
As (mg/kg)	121	122	4.58	248
Cd (mg/kg)	5.81	3.02	0.005	15.9
Co (mg/kg)	24.6	20.4	6.39	44.5
Cr (mg/kg)	80.8	85.5	37.8	108
Cu (mg/kg)	157	173	22.2	240
Mn (mg/kg)	232	207	153	454
Mo (mg/kg)	97	96	3	240
Ni (mg/kg)	163	99.5	17.7	371
Pb (mg/kg)	27.1	26.6	9.96	43.1
U (mg/kg)	72.4	72.6	2.11	227
V (mg/kg)	1,150	441	47.6	3,240
Zn (mg/kg)	297	241	20.8	563

Trace elements occurring abundantly in shale (As, Cd, Mo, U, V)

In comparison to the geochemistry of average shale, the studied samples are strongly enriched in As (up to 9 times), Cd (up to 15 times), Mo (up to 68 times), U (up to 26 times) and V (up to 12 times). Arsenic is approximately equally abundant in all samples, Cd is higher and Mo and U lower in NBS, and V is higher in WBS (Table 4). In NBS, the Cd concentration (4.6 ppm) is typical for the Degerhamn black shale (Table 5), while the lower Cd concentrations in the others are caused by leaching (Falk *et al.* 2006). The lower concentrations of Mo and U in NBS and the high abundance of V in WBS (Table 4) are most likely caused by inherent geochemical heterogeneities in the black shale, supported by the large concentration variations that exist among the 11 samples of this material (Table 5). The abundance of As, Mo, U and V in the oxidized samples indicates, overall, limited relative leaching from the shale.

In NBS, the largest Cd pool (*c.* 60%) is found in SE9 (Table 4), which is dominated by sulphide. A high proportion of Cd, however, also occurs in the peroxide-extractable fraction (difference: ST4–ST3) (42%) in comparison to the corresponding one for S (12%). This shows that the sulphide-carrying Cd, possibly greenockite (CdS), is more easily soluble than pyrite, which implies that when the shale becomes exposed to atmospheric O₂, Cd is more rapidly released than Fe and leaching into groundwater is possible (Falk *et al.* 2006). The area of black shale currently directly exposed to weathering at the walls and floors of the old quarry is *c.* 60 000 m². Assuming a Cd-leaching percentage of 80% (approximately the difference between the concentration in NBS and the weathered samples) and an average Cd concentration similar to that of NBS (well representative for the Degerhamn shale), the amount of Cd lost (leached) is *c.* 6 kg for every centimetre of weathering depth. The drillcores show that the shale, having been exposed for *c.* 100 years at the quarry floor, is clearly affected by weathering to a depth of *c.* 0.6 m. The natural shale bedrock, covered by 0.5 m of topsoil, is heavily affected by weathering down to more than 1 m and to a lesser degree to *c.* 2 m below the ground surface. This indicates that during the 12 000 years since the last glaciation, oxidation has occurred at a vertical distance of at least 1.5 m. In WBS, Cd is very mobile (15–23%)

in the water-based tests (ST1, ST2). Thus, the Cd released from easily weathered sulphides is partly leached into ground (or surface) water and partly trapped by sorption onto mineral surfaces. In the burnt samples, in contrast, only small amounts of Cd are released by water (Table 4), indicating that the burning process has either depleted the most easily mobilized fractions, or increased the strength of surface-binding of Cd.

In all samples, the majority of U and V is associated with the residual fraction, SE10 (Table 4), and thus primarily reside in relatively weathering-resistant minerals. The solubility of U in the water-based tests (ST1, ST2) varies but is, in relative terms, low (Table 4). Because of the U abundance in the material, however, the absolute values released by various partial extractions are not negligible. For example, in WBS the U concentration in SE7 (amorphous Fe-oxides) is nearly half that of average shale (Table 4). It is clear, however, that from the oxidized samples the U has not been extensively leached (*cf.* Cd). The NBS sample is low in U (Table 4), so it is not possible to make any quantitative estimations of leaching losses for this metal. Vanadium occurs in very low concentrations in the water-based (ST1, ST2) and pH-regulated (ST3) tests, and in relatively low concentrations also in the weak extractions. The high amounts of V occurring in the shale and its oxidation products are thus largely immobile.

Approximately 85% of As in NBS is associated with SE9 (Table 4), which certainly is due to an abundance of As-bearing sulphides such as realgar (As₄S₄) or arsenopyrite (FeAsS) in the material. In this sample, as well as in the others, the As concentrations are very low in all single leaching tests, which shows that irrespective of redox potential and pH, As does not occur in easily mobilized forms. In the oxidized samples only *c.* 30% of the As reports to SE9 (Table 4) which is explained by its release from oxidized sulphides. In WBS the As pool released from sulphides is lower than in NBS, and it is instead disseminated through SE6 to SE8 (labile organic complexes and Fe-oxides), while in the burnt samples the residual pool (SE10) is also quantitatively important indicating strong As association with poorly soluble hematite. As has been reported to be abundantly associated with hematite, especially under acidic conditions (*e.g.* Zhang *et al.* 2004; Giménez *et al.* 2007), but to a lesser extent in the presence of organic matter (*e.g.* Redman *et al.* 2002; Ko *et al.* 2007). Arsenic is thus, upon oxidation, transferred from sulphides to various oxides and possibly to organic molecules.

Molybdenum in NBS is exceptionally soluble in the water-based tests (ST1, ST2), the pH/redox-regulated tests (ST3, ST4) and in SE5 (adsorbed/carbonates), both in relation to the total concentrations in the sample (10–84%) and to the absolute concentrations in the oxidized samples that have much higher total Mo concentrations (Table 4). In comparison to the concentration in average shale, the ST2, as an example, releases Mo concentrations that are six times higher (Table 4). In black slates high Mo concentrations have been found to correlate with high carbon concentrations (Jeong 2006), and studies by Helz *et al.* (1996) and Erickson & Helz (2000) suggest that a major mechanism in the accumulation of Mo in euxinic sediments is formation of (non-reduced) thiomolybdates and subsequent binding to organic matter. Thus, a possible explanation for the very high solubility of Mo in NBS could be that, due to alterations of the organic matter during diagenesis, Mo now occurs in the shale as water-soluble organic complexes or possibly as thiomolybdates that are easily transformed to mobile molybdate ions (MoO₄²⁻) even under mildly oxidizing conditions. In the sequential extraction of NBS, 43% of the Mo is released by SE9 (sulphides/organics), and a similar

proportion (48%) with hydrogen peroxide (difference: ST4–ST3). This fraction most likely represents sulphides (e.g. molybdenite, MoS_2) as well as Mo bound to organic matter. In WBS, the major fraction of the Mo is extracted by SE9 (sulphides/organics) and SE8 (crystalline Fe-oxides) and in the burnt samples by SE8 and SE10 (residual). The burning process thus seems to have transformed some of the Mo into a more insoluble form, probably hematite-associated. The high solubility of Mo in the non-weathered shale is an intriguing feature, which deserves further investigation. In an *in situ* study of weathering profiles of black shales in China, Peng *et al.* (2004) observed extensive leaching of Mo from some profiles and enrichment of Mo in others, indicating a complex behaviour of this element in this type of material.

Trace elements weakly enriched in the shale (Cu, Ni, Zn)

In NBS, which is the sample with the highest concentrations of Cu, Ni and Zn, these metals are, in comparison to average shale, enriched by 2.5 times, 2 times and 3.2 times, respectively (Table 4). The concentrations in NBS are good representatives for the Degerhamn black shale in general (Table 5).

The pattern for Zn is similar to that for Cd. NBS has a Zn concentration which, in comparison to the oxidized samples, is 6.0–7.6 times higher, and *c.* 50% is extracted by SE9 and 29% by hydrogen peroxide (Table 4). Hence, in a manner similar to Cd, the Zn sulphide is quantitatively important and more easily oxidized than pyrite (i.e. to a large extent dissolved by hydrogen peroxide). In the oxidized and Zn-poor samples, only a small portion of Zn is available by the oxidizing agents (SE9 and difference: ST4–ST3), which is evidence of extensive release and removal from sulphides during oxidation. In WBS, the water-soluble Zn fraction (ST1–ST3) is high (9–19%), like that of Cd, which shows that a significant proportion of Zn exists in the weathered shale in easily leachable forms.

The pattern for Ni is similar to that for Zn and Cd, but it is not as strongly developed (Table 4). In NBS, the Ni concentration is 2.2–4.8 times higher than in the oxidized samples, and a relatively large proportion is extracted by SE9 (41%) and hydrogen peroxide (21%). In WBS, Ni is relatively soluble (13% is leached by ST2). The release and leaching of Ni thus appear to be overall weaker than for Cd and Zn, but occur by a similar mechanism.

In contrast to Cd and Zn (in particular) and also to Ni, Cu is only slightly lower in the oxidized samples (Table 4). In NBS, a high proportion of Cu (66%) is associated with SE9 (sulphides/organics), but only a small percentage (15%) with hydrogen peroxide (difference: ST4–ST3). The difference between these two methods is *c.* 50 ppm, which is approximately the amount of Cu that has been lost in the oxidized samples in the SE9 pool (Table 4). All samples have similar amounts of Cu extracted by ST4, although the amount is lowest in the sample lowest in organic C (LBBS) and highest in the one highest in organic C (WBS). In the oxidized samples, Cu is significantly extracted by SE7 and SE8 (Table 4). These patterns indicate that: (1) Cu-bearing sulphides, probably minerals such as chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4) or chalcocite (Cu_2S), are abundant in the non-weathered shale and are, like pyrite, not dissolved by hydrogen peroxide; (2) in the oxidized samples, the Cu sulphides have to a large extent disappeared and the Cu has been trapped by amorphous and crystalline Fe-hydroxides (not abundantly on hematite); and (3) the hydrogen peroxide extractable pool is dominated by Cu bound to organic compounds.

Trace elements at average or low concentrations in the shale (Co, Cr, Pb, Mn)

Manganese in particular (but also Pb) occurs in relatively low concentrations in the shale and in its oxidation products (Table 4). Relatively high amounts of Mn are extracted by ST3, but only marginally more is released by the addition of hydrogen peroxide (ST4) and relatively small amounts are leached in the SE9 (sulphides/organics) step (Table 4). Manganese is thus not abundantly related to sulphides in the material. In the burnt samples Mn resides, like Fe, to a large extent in the residual fraction (Table 4). Lead is highly immobile in the single tests (ST1–ST4); in NBS it is concentrated in step SE9, followed by steps SE7 (amorphous Fe-oxides) and SE5 (adsorbed/carbonates); and in the oxidized samples it is dominant in SE8 (crystalline Fe-oxides). These patterns indicate a change from sulphide to oxide phases during oxidation and very low solubility, which is a typical feature for this metal in many environments (McBride 1994).

The Cr concentrations are similar in all samples and at a level typical for shale (Table 4). The Cr is, like Pb, highly immobile (low concentrations in ST1–ST4 and SE5–SE7) and strongly associated with the residual fraction. Chromium is thus likely to reside in minerals such as pyroxenes. In NBS, the Co concentration is similar to that of average shale (Table 4), and in the oxidized samples it is lower, indicating leaching, in a manner similar to Cd, Zn and Ni (Table 4).

CONCLUSIONS

The leaching tests applied on non-weathered and different types of oxidized black shale indicate that in areas where this bedrock type is exposed to natural and anthropogenic weathering, dynamic and complex hydrogeochemical processes are involved. Some elements that occur in high concentrations are mobile and easily leached on oxidation (Cd, S) or even by circulating water (Mo), while others are less mobile (U, V) or are transferred to other solid phases during the oxidation (As). Several other chalcophilic elements, such as Zn, Ni and Cu, also occur in relatively high concentrations in the shale. Zinc and Ni are, especially in the weathered shale, relatively mobile, while Cu is more immobile.

The tests using only water as the extraction medium (ST1, ST2) were sufficient to demonstrate considerable immediate leaching of Mo from the unoxidized sample and of Cd (and to some extent also Zn and Ni) from acidic samples. The use of a pH-controlled leaching medium with addition of hydrogen peroxide showed that Cd, Mo, Zn, Ni and U are elements that can, in the long term, be leached in considerable amounts from the shale material. The hematite in the burnt samples was not leached by the reagents intended to dissolve crystalline Fe-oxides (SE8: $\text{NH}_2\text{OH}\cdot\text{HCl}$ in CH_3COOH) but was mainly dissolved in the extraction targeting silicates (SE10), indicating that the hematite in the burnt material is very stable and is dissolved only by very strong reagents.

A comparison of the behaviour of the toxic elements As and Cd underlines an important feature. Both occur in high concentrations in the black shale, but upon oxidation (natural or anthropogenic) the former is transformed from sulphides to other solid phases, while the latter to a large extent is leached and can contaminate surface and groundwaters. This does not, however, mean that As is not an environmental problem in these settings. The burnt shale material is fine-grained and easily dispersed by wind, which means that direct contact with skin or inhalation is a potential threat. These two toxic elements thus affect the environment by different routes.

Black shale can supply considerable amounts of metals to aquatic as well as terrestrial environments. As black shale occurs widely on most continents, this type of bedrock may be a large and possibly underestimated source of potentially toxic elements to ecosystems. In large environmental surveys, or when information is required for an initial environmental risk assessment involving black shale, we recommend determination of total concentrations and utilization of the oxidized availability test. The former gives an indication of the abundance of elements, and the latter a good approximation of the solubility of the potentially hazardous ones.

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