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Technical Communication

The Chemistry of Waters Associated with Metal Mining in Macedonia

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Abstract. Pollution from current and past mining is a significant problem in several parts of the former Yugoslav Republic of Macedonia. Water from six different mining areas in Macedonia was analysed to assess the effects of metalliferous mining activities. Drainage sediments at all locations show evidence of physical and chemical contamination; water compositions, however, were more variable. Low pH water associated with mining has led to the dissolution of minerals and the mobilization of metals from the ores and the host rocks. Only Sb was noted to exhibit enhanced mobility in higher pH waters. The Zletevo Pb-Zn mine discharges low pH water that has high levels of several metals, including Al, Zn, Cd, and Fe; sediment concentrations are grossly elevated for several km downstream. Toranica and Sasa Pb-Zn mines exhibit similar sediment contamination of Pb, Zn, Cd, and other ore-related metals. However, concentrations of metals in waters are far lower at both of these mines, due to less pyrite in the ore and the buffering of the acid waters by carbonate host lithologies. At the Buchim copper mine, waters are both acidic and high in dissolved solids; Cu concentrations exceed 100 mg/L. Krstov Dol and Alshar are small, disused As-Sb mines that discharge waters that exceed potable values for some contaminants (e.g. As), but this may be related to the mineralization of the bedrock rather than the mines. In general, metal concentrations decreased downstream from the source due to dilution from other rivers and co-precipitation of metals on other mineral phases (e.g. Fe-, Al- and Mn-oxides, and hydroxides).

Key words: Antimony, arsenic; heavy metals; Macedonia; metal pollution; mine waters; thallium

Introduction

Despite increased awareness and understanding of the potential threats to the environment, there are many areas around the world where pollution from mining operations is still taking place. Preventative measures are often minimal, untreated mine waters discharge into local watercourses, and water quality monitoring is non-existent. In such situations, understanding the environmental impact of these processes is crucial.

Metal mining has traditionally been an important part of the economy of the Republic of Macedonia, though it has recently declined in importance. The government is trying to stimulate mining through renewed exploration and development and by the sale of state mining assets, though the country relies on its agriculture and must safeguard its soil and water resources. Given the minimal level of environmental regulation previously applied to the mining industry (Midzic and Silajdzic 2005), the nation needs to establish an environment baseline so that any future liabilities are clear. The aim of this study was to quantify the chemistry of surface waters in the important mining areas in order to assess the environmental impacts of current and past mining activities. There are a variety of metal deposits in the country and thus there was also an opportunity to contrast the environmental legacy of different deposit types and the behaviour of different metals in the surficial environment.

Area of Study

The Republic of Macedonia is predominantly mountainous with a highly developed hydrographic net containing numerous springs and rivers (Figure 1). The principal river is the Vardar, which flows from northwest to southeast across the country and into Greece. Its main tributaries are the Bregalnica, Treska, Pcinja, and Crna. These rivers and the associated reservoirs are a principal source of water for human consumption and agricultural irrigation, and also supply fish for local consumption.

In general, the environmental situation in Macedonia is comparable to that of other countries in which a centrally-planned economy required increased production by the industrial and energy sector with little regard for the environment (UNEP 2000). Further ecological degradation occurred during the conflict in the Balkan Peninsula during the 1990s. With increased stability in the region, environmental concerns are emerging as a priority. However, water pollution is still a serious problem (particularly in lowland rivers), and wastewater generated in ore processing and discharge seeping from tailings deposits receive no water treatment at all.

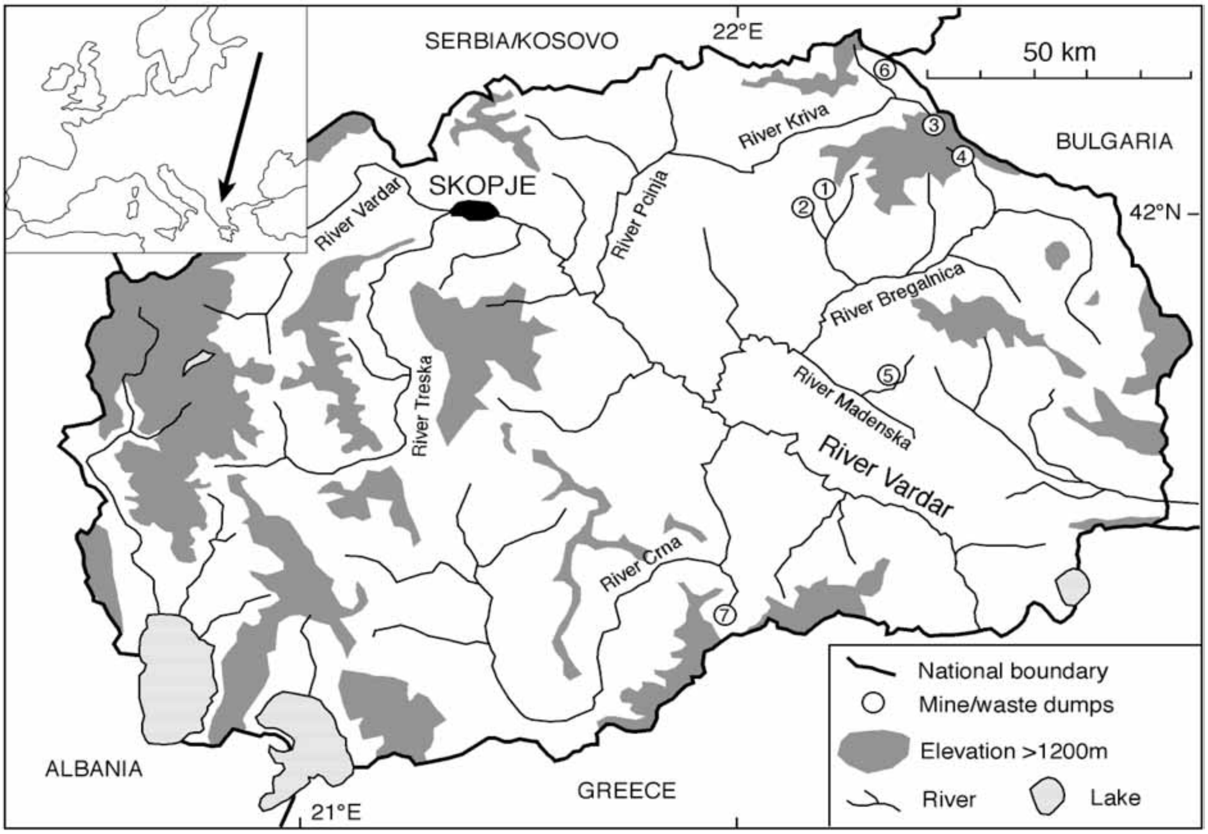

Figure 1. Map of the Republic of Macedonia showing the major rivers and mining locations used in this study; 1: Zletovo (mine), 2: Zletovo (tailings dam), 3: Toranica, 4: Sasa, 5: Buchim, 6: Krstov Dol, 7: Alshar

The most important Macedonian metal deposits are linked to regional magmatic activity that occurred in the southern parts of the Carpatho-Balkanides from the Eocene to the Pliocene (Serafimovski et al. 1995). We studied three types of mineralization and mining at six separate localities (Figure 1): lead-zinc mines, at Zletevo, Sasa, and Toranica; a copper mine at Buchim, and arsenic-antimony mines at Krstov Dol and Alshar.

The Zletevo Pb-Zn Deposit

The Zletevo mine is located near the town of Probistip in northeastern Macedonia. The mine started operation in 1940 but production ceased in 2002 and at present the mine is under 'care and maintenance'. The mineralization is related to Tertiary (mostly Miocene) calcalkaline magmatic rocks (dacites and andesites). Mineralization is found in a dacitic volcano-sedimentary suite that has been altered to clays and micas (Serafimovski and Aleksandrov 1995; Serafimovski and Boev 1996). Ore bodies are located in sub-vertical veins, commonly found sub-parallel to each other and extending for several km in length and to depths of 500 m below surface. The main ore minerals are galena and sphalerite, but tetrahedrite, pyrrhotite, magnetite, chalcopyrite, pyrite, and Mn oxides are also common. Production reached 300,000 t of ore per annum, with ore grades of 9% Pb and 2% Zn, and significant concentrations of Ag, Bi, Cd, and Cu. Ore was concentrated by flotation at Probistip and tailings were disposed of in two impoundments situated in adjacent valleys. The river Kiselica drains the flotation plant at Probistip and the river Reko drains the area containing the main workings of the Zletovo mine (locations 1 and 2 in Figure 1). Both of these rivers join the River Zletovska, which flows down to meet the River Bregalnica (16 km from the tailings dam and 22 km from the mine workings).

The Sasa Pb-Zn Deposit

The Sasa deposit is situated in northeastern Macedonia, 12 km north of the town of Kamenica. The mine has been in production since 1962, yielding about 500,000 t of Pb-Zn ore annually and 14 Mt in total (Aleksandrov et al. 1998; Serafimovski and Aleksandrov 1995). Mineralization is localised along the contacts between Miocene calcalkaline igneous bodies (latites and dacites) and graphite-chlorite-sericite schists, gneisses, and limestones. The ore consists of pyrite, galena, and sphalerite, with additional magnetite and chalcopyrite. Ore grades are about 10% Pb + Zn with additional elevated concentrations of Ag, As, Bi, Cd, Mn, and Sb. Ore is concentrated at the mine by flotation, and tailings are stored in a dam in a narrow valley just below the mine.

The Kamenica river is culverted beneath the tailings dam and flows 12 km until it meets the Kalimansko reservoir at Kamenica. A major collapse of the culvert in the summer of 2003 allowed 4 m t of tailings to enter the river and discharge all the way down to the reservoir (Midzic and Silajdzic 2005).

The Toranica Pb-Zn Deposit

The Toranica deposit is situated in northeastern Macedonia, close to the Sasa deposit, but in a separate watershed. Production of Pb and Zn from the mine occurred between 1987 and 2000. The deposit is geologically similar to Sasa but production has been less. There are elevated concentrations of Cd, Cu, Mn, Ag, and Bi in the ore (Serafimovski et al. 1997). Milling and flotation occurred at the mine and there is a tailings dam below the mine site with a culvert directing the River Toranica beneath the dam.

The Buchim Cu Deposit

The Buchim copper mine is located in eastern central Macedonia, 10 km west of the town of Radovis. The mine started production in 1980 and produced 400,000 t of ore annually; currently it is under care and maintenance. The deposit is a porphyry copper type deposit (Serafimovski et al. 1996) and mineralization is related to Tertiary sub-volcanic intrusions of andesite and latite in a host of Pre-Cambrian gneisses and amphibolites. Four ring-shaped ore bodies are located within and around the magmatic bodies. The main (Centralen del) ore body is approximately 500 m in diameter and 250 m in vertical extent and has been worked in a large open pit. The ore consists of 0.3% Cu, 0.3 g/t Au, 1 g/t Ag, 13 g/t Mo, and 1- 4% pyrite; the igneous rocks have been altered to clays and micas. The important metallic minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite, hematite, and cubanite. Ore was concentrated by flotation on site and tailings were disposed to a dam in an adjacent valley. The original river is culverted beneath this dam. This river and water from the mine workings combine to form the River Madenska, which joins the River Bregalnica. Standing water in the open pit is a vivid blue-green colour.

The Krstov Dol Sb Deposit

Krstov Dol is a small antimony deposit located in northeast Macedonia, near the town of Kriva Planka and close to the Bulgarian border. The old mill, flotation plant, and small waste dumps are situated in the valley of the small Krstovska River, below the mine workings. The Krstovska joins the River Lucka, which then joins the River Kriva. The mine was operational during the 1970s and 1980s and worked a small vein in schists, but mineralization is thought to be related to quartz latites of Oligo-Miocene age (Mudrinic and Serafimovski 1997). The most abundant minerals are stibnite (Sb_2S_3), berthierite ($FeSb_2S_4$), realgar (AsS), pyrite, quartz, and calcite. Minor amounts of Cu-, Zn-, and Pb-bearing sulphides also occur. In addition, the stibnite and berthierite have relatively high (up to 0.3%) thallium concentrations.

The Alshar As-Sb Deposit

The Alshar deposit is located in a remote and rugged part of southern Macedonia close to the border with Greece and in the steep-sided valley of the River Majdanska. Mining of arsenic and antimony took place between 1881 and 1913, but there has been extensive exploration for Sb and Au during the last few decades (Jankovic et al. 1997). Mineralization is hosted by a Pliocene volcanic-intrusive complex (altered latite, dacite, and andesite) and Triassic carbonates (dolomites and marble). The most abundant minerals in the ore are realgar, stibnite, pyrite, marcasite, and other sulphides, including various Tl-bearing sulphides (e.g. lorandite, $TlAsS_2$).

Methods

Samples were collected during the months of April and May in 2002 and 2003 from the six mining areas outlined above. River water levels were at an average height; rainfall was low, but snow in the mountainous regions was melting. Sampling at Sasa, Zletovo, and Buchim took place when the mines were operating, and at Toranica, Alshar, and Krstov Dol when the mines had ceased all activities.

At each location, streams were sampled downstream as well as upstream of the mining sites to assess the contributions to the drainage from the mining activities. Samples were taken progressively downstream, and in some locations, in receiving waters. All the streams sampled close to the mines were small first or second order streams. Receiving waters were larger rivers, and samples were taken downstream of the confluence. Sampling density varied from a few metres to several kilometres, depending on the situation; in general, sampling density was lower further downstream. Several of these rivers join the River Bregalnica, which is important for agricultural irrigation and water supply (e.g. the city of Stip).

Water was collected in polythene syringes, passed through a 0.45µm filter and transferred into polythene tubes. Water was acidified with 0.4 ml of 50% nitric acid. Conductivity and pH and were measured in the field for all water samples. Samples were stored in a cool and dark place until they were returned to the U.K. for laboratory analysis. River sediment samples were also collected at several locations. For these, a hot (80°C) concentrated nitric acid digest was used to leach elements from the sediment.

Solutions were analysed by ICPAES or ICPMS, depending on concentrations. A large number of analytes were determined but only those that are likely mining related and environmentally significant are presented and discussed here. The concentrations were compared to reference guidelines to assess their significance. The U.S. National Oceanographic and Atmospheric Administration (NOAA) data are used for screening purposes, while the World Health Organization (WHO) data are guidelines for drinking water quality. These values are for different purposes, so there are some large differences in some values for particular elements; however, they are sufficient to assess the significance of levels found in this study.

Results

The compositions of the waters are presented in Table 1 (major constituents) and 2 (minor constituents).

Zletevo (Pb-Zn)

Sediments in the Rive Reko below the adits and mine workings are a deep brown colour and have Fe and Mn levels up to 6 wt % and 1.5 wt % respectively. Elevated levels of a distinctive suite of several other elements occur in the sediments below both the mine workings and the tailings dam. These include values up to (all in mg/kg): Ag (7), As (190), Bi (51), Cd (29), Co (22), Pb (8000), S (11,000), Sb (4), Tl (2.5), U (156) and Zn (2500). Zinc concentrations in sediments above the mine workings are high (1100 mg/kg), indicating that the mineralized area extends beyond the immediate mine workings. This element is also the best indicator of the effects of mining; even at the confluence between the Zletovska and Bregalnica, the sediment still contains 990 mg/kg Zn, indicating that the effects extend along the entire watercourse.

Water composition from Zletovo suggests that there is additional mineralization upstream of the mine; two water samples taken above the mine adit discharges (Z1, Z2) show compositions that are slightly alkaline and generally below water drinking and screening maxima, though some metal levels are relatively high (e.g. Zn at 330 μg/L and Mn at 900 μg/L).

Several adits at the Zletevo mine contribute significantly to the Reko River. Water from the main adit (Z5) is turbid with a pale brown colour, and flows directly into the Reko. Concentrations exceed water standards for most analytes and the pH of the discharge is low, at 3.4. Further downstream, concentrations of Al, Fe, Mn, Cd, Zn, and U are all grossly elevated above fresh and drinking water standards. For example, the Al concentrations reach 52.9 mg/L and Zn concentrations reach 70 mg/L. High values are maintained until sample Z11, approximately 3 km below the mine area, and then dilution reduces the concentrations markedly.

Further downstream, the waters are diluted by non-contaminated waters in the river Zletovska (down to background values at 8 km). Water in the culvert (Z21) below the tailings dam has fairly low concentrations of metals, with the exception of Mn, which at 29.6 mg/L is present at levels far in excess of the water quality standards. Zinc concentrations are slightly elevated but are similar to background values. Concentrations of metals are generally low and the water is alkaline all the way down to the confluence with the river Bregalnica, where the levels of some metals (e.g. Cu) increase.

Sasa (Pb-Zn)

Although there is some indication that the sediments above the main mine workings have elevated levels for some metals, the large contaminant increases in the sediment below the adits and tailings dam point to major contributions from the mining and processing activities (all values in mg/kg): As (127), Cd (73), Cu (650), Pb (4600) and Zn (8500); Ag (10), Bi (45) and U (9) are also high. These elevated values occur all the way down to the reservoir, Lake Kalimansko; for instance, high concentrations of Zn (2200) and Pb (2200) occur where the river discharges into the lake. Furthermore, the river Bregalnica, below the reservoir, also has elevated sediment metal concentrations (e.g. Zn = 120-1460, Cd = 2 -11, and As = 1-14 mg/kg).

In marked contrast to the composition of the associated river sediments, the water contaminant concentrations do not appear to be particularly elevated. The river waters are mostly near neutral, with the water discharging from only one of the main adits (S2) being slightly acid (pH = 5). This water has a dark grey colour, due to transported sulphide particles, and has very elevated concentrations of (in μg/L): Al (9490), Cd (90 mg), Pb (1340), and Zn (14,330). However, most values decrease quite rapidly downstream. Below the tailings dam, the concentrations of Mn and to a lesser extent Zn remain high for at least 8 km downstream from the mine, but by the time the river reaches the lake, these too have decreased to background values.

Table 1. Major constituents in waters associated with metal mining activities in Macedonia and relevant reference values; all values in mg/L (except pH)

Sample	Al	Ca	Fe	Mn	S	pH	Notes
Zletovo							
Z1	0.0	121.3	0.2	0.94		8.1	Stream above adits
Z2	0.1	38.2	0.2	0.01		8.1	Small tributary
Z3	0.2	95.3	0.8	12.80		7.1	1st adit
Z4	2.2	48.3	5.8	1.28	35.9	6.5	Between 1st and second adit
Z5	49.2	90.1	98.2	25.98	417.0	3.4	2nd adit
Z10	52.9	95.3	103.3	34.35	465.2	3.5	River Reko below mine workings
Z11	37.2	127.4	37.1	114.90	612.0	3.4	River Reko; much ochre present
Z13	0.7	216.1	1.4	0.70	316.3	6.1	Small tributary
Z20	0.0	21.2	0.1	0.28		7.5	Confluence with River Zletovska
Z21	0.1	148.4	0.0	29.63		7.3	Below tailings dam. River Kiselica
Z27	0.1	23.1	0.2	0.22		7.6	River Zletovska; 11km from mine
Z29	0.1	37.2	0.1	0.21		7.6	River Zletovska; 15km from mine
Z31	0.4	72.9	0.6	1.11	76.3	6.7	Confluence with Bregalnica
Sasa							
S1	0.06	4.5	<0.05	0.05		6.9	Stream above adit
S2	9.49	44.7	0.28	4.17		5.0	Water coming out of adit
S3	<0.02	157.2	<0.05	3.47		6.5	Below tailings dam
S4	<0.02	137.5	<0.05	3.57		6.7	Kamenica river
S6	0.03	45.4	<0.05	0.72		6.8	Kamenica river
S15	0.02	49.9	<0.05	0.05		7.7	Kamenica river
Toranica							
T1	0.30	42.8	0.72	0.06	50.2	7	Water coming out of upper adit
T2	0.11	20.6	0.81	0.15	27.2	7	Stream above adit
T4	0.04	20.3	0.4	0.05	11.7	7.2	Tributary, no connection with mine
T5	0.20	33.5	1.46	0.18	38.1	6.9	Immediately below lower adit
T6	0.10	22.9	0.69	0.19	26.3	7	Stream below lower mine adit
T7	0.07	42.9	0.43	0.12	30.5	6.9	Below tailings dam. Small stream
T8	0.11	13.2	0.32	0.08	11.7	7	River Toranica; culvert under tailings
T11	0.18	15.1	0.65	0.15	14.5		River Toranica; 10 km from mine
T13	0.43	18.5	1.03	0.11	12.3		River Kriva; 1km above Kriva Palanka
Buchim							
B1	0.1	180.5	0.0	1.40		7.8	Culvert from below tailings dam
B4	54.9	214.5	0.3	46.35		5.1	Stream from mine
B5	0.3	156.8	0.0	0.21		6.8	Upstream of meeting with mine stream
B6	15.5	189.6	0.8	23.82		5.3	Downstream of confluence
B7	75.2	173.6	1.9	61.00	1232	4.5	Mine stream by road/bridge.
B10	0.3	199.5	0.2	4.44		7.1	River Madenska; 8 km from mine
B14	0.6	210.6	0.2	3.52		7.8	River Madenska; 11 km from mine
B19	0.3	159.4	0.1	0.03		7.2	Confluence with River Bregalnica
Alshar							
A1	0.0	23.3	0.1	0.04	19.9	7.7	Small tributary above workings
A2	0.0	8.3	0.1	0.02	7.1	7.6	Majdanska river - above workings
A4	2040	367	7886	315.03	19688	2.3	Standing water in adit
A5	0.1	10.5	2.0	0.05	8.7	6.7	Majdanska river - below workings
A7	0.0	11.3	0.9	0.05	9.3	7.1	Majdanska river - below workings
A8	0.0	14.6	0.6	0.03	10.1	7.2	Majdanska river - below workings
Krstov Dol							
K1	0.1	63.1	0.13	0.04	23.5	7.5	Upstream of adit
K2	0.1	96.7	0.02	0.03	176.3	7.7	Discharge from adit
K3	0.1	75.4	0.22	0.05	78.3	8.5	Small tributary through mine waste
K5	0.9	63.8	2.66	0.42	18.8	8.2	Upstream of tailings dam
K6	0.0	65.3	0.43	0.11	29.1	8.4	Below tailings dam.
K7	0.1	62.0	0.18	0.04	59.2	8.3	Approx 0.5 km below K6
K9	0.1	40.7	0.19	0.04	16.2	8.4	River Lucka; 8km from mine
Reference values							
WHO	0.2		2	0.4			Drinking water (WHO 1993, 2004)
NOAA	0.75						NOAA 'SQuiRTs' (Buchman 1999)

Table 2. Minor constituents in waters associated with metal mining activities in Macedonia and relevant reference values; all values in μg/L

Sample	Ag	As	Bi	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sb	Tl	U	Zn
Zletovo														
Z1				<2	<4	<4	10.0		<4	<30				330
Z2				<2	<4	<4	<2		<4	<30				60
Z3				30	10	<4	30.0		<4	<30				6070
Z4	0.2	10.9	0.3	10	4.5	0.9	58.5	0.3	10	<30	0.8	0.3	26.0	1090
Z5	0.2	157.3	1.3	140	82.6	4.1	456.4	0.8	30	60	1.4	0.8	408.4	21570
Z10	0.2	173.3	0.9	150	92.0	4.0	521.3	0.6	30	50	1.3	0.7	454.0	26110
Z11	0.2	54.1	0.6	240	153.4	3.7	1054.3	0.3	50	80	0.8	0.6	327.6	70070
Z13	0.1	1.9	0.2	<2	<4	0.5	21.5	0.4	10	<30	0.8	0.2	29.6	1450
Z20				<2	<4	<4	<2		<4	<30				40
Z21				<2	<4	<4	<2		<4	<30				300
Z27				<2	<4	<4	15.0		10	<30				50
Z29				<2	<4	<4	10.0		<4	<30				40
Z31	0.1	6.8	0.2	<2	11.8	1.0	746.6	0.9	10	<30	1.6	0.4	14.2	90
Sasa														
S1				<2	<4	<4	<2		<4	<30				40
S2				90	10	<4	1070		120	1340				14330
S3				10	<4	<4	20		20	90				1360
S4				10	<4	<4	20		10	70				1570
S6				10	<4	<4	66		10	40				1370
S15				<2	<4	<4	10		<4	<30				30
Toranica														
T1	0.1	3.7	0.3	<2	0.6	0.8	54.7	3.3	<4	40	0.4	0.2	18.7	310
T2	0.1	3.5	0.6	<2	1.0	0.8	18.9	0.5	<4	60	0.2	0.2	2.0	670
T4	0.1	1.8	0.1	<2	0.4	0.6	3.7	1.2	<4	<30	0.1	0.2	1.6	70
T5	0.2	14.6	3.2	<2	0.6	1.1	12.4	5.9	10	460	0.5	0.3	5.3	55
T6	0.1	2.2	0.6	<2	1.1	0.6	9.3	0.9	10	70	0.3	0.2	2.1	44
T7	0.1	1.2	0.7	<2	0.5	0.7	7.4	1.5	10	80	0.5	0.2	4.2	80
T8	0.1	0.6	0.4	<2	0.6	0.5	6.9	0.4	10	40	0.1	0.2	1.4	150
T11	0.1	0.8	0.1	<2	0.6	0.6	4.9	0.4	<4	<30	0.1	0.2	2.7	190
T13	0.2	1.3	0.7	<2	0.9	1.2	7.9	0.3	<4	80	0.4	0.2	1.6	120
Buchim														
B1				<2	<4	<4	80		<4	<30				30
B4				<2	1160	<4	139160		620	180				1540
B5				<2	2.12	<4	620		<4	<30				30
B6				<2	590	<4	69690		320	100				720
B7	0.1	7.8	0.2	<2	1162	4.6	141040	11.3	<4	260	0.7	0.4	905	1940
B10				<2	90	<4	940		50	<30				70
B14				<2	60	<4	1270		<4	<30				40
B19				<2	2	<4	520		<4	<30				20
Alshar														
A1	0.1	2.6	0.1	<2	0.3	0.5	2.4	0.5	<4	<30	1.6	0.3	1.1	20
A2	0.1	2.2	0.1	<2	0.4	0.9	3.2	0.2	10	<30	0.4	0.2	0.5	20
A4	0.2	280000	0.1	3650	8700	3230	12200	35	8190	2070	10.8	0.2	541	9830
A5	0.1	115.3	0.1	<2	1.0	1.4	2.8	0.2	10	<30	1.2	1.5	0.8	17
A7	0.1	15.6	0.1	<2	0.7	2.0	1.9	0.1	<4	<30	6.1	0.9	0.7	20
A8	0.1	43.1	0.1	<2	0.4	1.0	1.2	0.2	<4	<30	8.5	0.9	0.7	10
Krstov Dol														
K1	0.1	1.7	0.1	<2	0.5	0.7	4.6	0.2	10	<30	66.3	0.3	2.3	20
K2	0.1	7.2	0.1	<2	0.5	0.2	1.6	0.2	10	<30	100.3	0.4	1.4	30
K3	0.1	3.5	0.1	<2	0.6	0.5	3.0	0.2	4	<30	77.4	0.3	2.1	30
K5	0.2	0.2	0.1	<2	2.6	2.7	5.5	0.0	10	<30	2.0	0.3	0.6	30
K6	0.1	4.3	0.2	<2	0.6	0.4	2.1	1.6	<4	<30	10.9	0.3	0.6	20
K7	0.1	4.5	0.1	<2	0.5	0.6	2.5	2.4	<4	<30	103.2	0.3	1.6	20
K9	0.1	1.5	0.1	<2	0.5	0.7	2.3	0.2	<4	<30	3.7	0.2	1.2	20
Reference values														
WHO		10		3		50	2000	70	20	10	20		15	3000
NOAA	1.7	850		4.3		570	13		470	65	88	1400		120

Toranica (Pb-Zn)

Mining and processing facilities have had a major effect on the chemical composition of river sediments in the river Toranica. Concentrations of Pb, Zn, and S are each >1000 mg/kg. Although present at much lower levels, Ag, As, Bi, Cd, Co, Cr, Cu, Mn, Mo, Ni, and U are also high in the mining area. Concentrations decrease after the confluence with the river Kriva but are still significantly elevated.

Waters from the Toranica area have a near neutral pH and solute contents are generally fairly low. Elevated values for As, Bi, Pb, S, U, and Zn occur in the vicinity of the mining area but rarely exceed reference limits and then only in the immediate vicinity of the adit discharges. High values for some elements (e.g. Bi, Co, Fe, Mn, Pb, Zn) in waters above the adit discharges suggest that more mineralization is present in bedrock upstream of the mine workings and that these values are thus representative of the (relatively high) regional geochemical background.

Buchim (Cu)

Two streams drain the mining and processing area at Buchim: one is culverted beneath the large tailings dam, the other comes directly from the area of the mine and flotation plant. Sediments in the stream that flows in the culvert under the dam and through the village of Topolnica generally appear uncontaminated and concentrations of most metals are not particularly elevated. In marked contrast, the sediments from the stream draining the mine area are bright blue-green, and a white colloidal precipitate of Al sulphate is also present; these characteristics continue to be visible after the confluence of the two streams and for several km downstream and into the river Madenska. These sediments contain elevated concentrations of several elements, with Co (158), Cu (145,000), Mo (25), U (485), and Zn (830) (all values as mg/kg) being particularly high.

The waters in these rivers reflect the sediment chemistry. The water from the culvert is slightly alkaline and is not significantly contaminated with metals. In marked contrast, the water from the mine is acidic (pH <5) and has some dramatically high concentrations of particular elements, for instance (all values in μg/L): Al (75,000), Co (1160), Cu (140,000), Mn (61,000), and U (905). These very high values occur within about 3 km of the mine but the influence of the mine extends downstream. For instance, the Cu concentrations are still elevated (>500 μg/L) 24 km downstream, where the River Madenska joins the River Bregalnica.

Krstov Dol (As-Sb)

Although only a small mine, the processing area and tailings dam at Krstov Dol clearly have had an effect on the adjacent river sediments. Sediments from this part of the valley had elevated concentrations for: Fe (135,000), As (2000), Cd (29), Mo (43), S (54,000), Sb (22), and Tl (75) (all in mg/kg). Highest sediment concentrations occurred below the tailings dam.

All of the waters from the vicinity of Krstov Dol are moderately alkaline and have relatively low total solute contents. However, the effects of mining and processing areas are clearly visible, with elevated As, Co, Cr, Fe, Mo, S, and Sb. Several of these values marginally exceed drinking water recommendations but the Sb concentrations are particularly elevated, and remain so until the stream joins the larger river Lucka. The presence of mineralization in bedrock further upstream is indicated by the elevated Sb contents of waters from above the mining area.

Alshar (As-Sb)

Sediments in the river Majdanska, which flows past the Alshar mine workings, had elevated concentrations of (maximum found, all in mg/kg): As (860), S (890), Sb (22), and Tl (75). Although there is a clear input from the mine workings, it is also apparent that elevated sediment values also occur above the workings (e.g. As at 869 mg/kg), suggesting the presence of more mineralization upstream and elevated background values in the area.

The waters from the Alshar area are mostly close to neutral pH and total solute contents are generally low (conductivities < 70 μs/cm). However, elevated values of As and Sb were found in the vicinity of the workings and both upstream and several km downstream of the mineralization.

Standing water in one of the adits (A4) has a distinct red colour and is very acidic (pH = 2.3). The concentration of As is extremely high (at 280 mg/L) in this sample and there are also elevated levels of Al, Co, Cr, Mo, S, and Sb.

Discussion

Chemical analyses of river sediments in the vicinity of these mines clearly demonstrate that there has been poor control on the discharge of mining-related waste. Physical contamination of sediments from mine waste and tailings is evident at many of these deposits, and the effects can be traced for several kilometres downstream from the mine sites.

In contrast, the composition of the associated waters is more variable. However, and in spite of the (variable) dilution effects of melting snow on the river volumes, the effects of mining and mineralization can be detected in all the waters studied. In particular, waters from the active and recently-worked Pb/Zn and Cu mines have very high concentrations of dissolved metals, derived either from dissolution of 'ore' minerals or host rocks (e.g. Ca from calcite and Al from aluminosilicates, particularly amphiboles and pyroxenes). As such, their compositions are generally comparable to polluted waters from mining regions elsewhere (e.g. Lee et al. 2001; Marqués et al. 2001; Moore et al. 1991; Rösner 1998; Yan Gao and Bradshaw 1995). However, not all of the elevated concentrations are anthropogenic; the regional mineralization increases the local background values of some elements.

The waters at Zletovo have a low pH, no doubt due to the dissolution of pyrite. Sulphate, Mn, Zn, and Fe are all very elevated, and there is widespread precipitation of ferric oxyhydroxide downstream. The host lithology is dominated by silicate minerals and so there is little chemical buffering to counteract the acidity.

The mines at Toranica and Sasa have exploited similar Pb- and Zn-rich minerals to those at Zletovo, and the associated river sediments are contaminated. However, the water contamination at these two localities is small compared to that at Zletevo. There appears to be a moderate but restricted acid mine drainage problem at Sasa, where the lower pH has mobilised some ore-related elements as well as Al and Mn. This problem is most severe near the mine adit, but concentrations only fall to background values downstream of Lake Kalimansko. The reduced drainage acidity and dissolved solid concentration are probably due to the lower volumes of pyrite in the ore, and buffering by the host limestones (as noted in other carbonate-hosted Pb-Zn mineral deposits, e.g. Marqués et al. 2001).

The Buchim waters also have a low pH and high solute contents. Here there are also substantial amounts of pyrite in the ore and the host gneisses and volcanic rocks provide little buffering capacity. In addition, the ore processing operations (e.g. Al sulphate used in the flotation process) affects the water chemistry. The water contains major amounts of Cu, Al, and other ore-related elements, which are subsequently precipitated downstream.

Alshar and Krstv Dol are examples of smaller workings that have been closed for a longer period; solute concentrations are low and contamination problems are consequently more local in scale.

The elevated element concentrations are clearly a consequence of mineral dissolution and strong element correlations provide an indication of the association of these elements. Many of the metals appear to be associated with the main sulphide phases. Thus, there is a distinct association of Ag, Bi, and Cd, with Pb and Zn (Figures 2a and 2b), probably due to solid solution of Cd in sphalerite and Ag and Bi in galena. The correlations of Co and Mo with Cu (Figure 2c) indicate the association of these metals with Cu sulphides. Thallium only shows a close association with As (and not Sb) (Figure 2d).

Decreases in concentration of elements downstream and further away from the mining regions can be explained by a combination of dilution from non-contaminated rivers and removal from solution due to co-precipitation and adsorption on various solid phases in the sediments. These phases are likely to include oxides/hydroxides of Al, Fe, and Mn. Lee et al. (2002) investigated the precipitation of such phases as acidic mine drainage became neutralised by dilution. They demonstrated the control of pH on the precipitation of these phases, such that Fe oxyhydroxide would precipitate first at low pH, while Al hydroxides precipitate at a slightly higher pH. Mn oxyhydroxides precipitate in neutral waters. This predicted pH control on Fe-Al-Mn precipitation can also be demonstrated to be in operation here. There is a correlation between metal solubility (given as the ratio of water to sediment concentration) and water acidity (Figure 3) and at a particular pH value, the relative solubility of these metals is Mn>Al>Fe.

The only measured species that do not exhibit a negative correlation of concentration with pH are Sb, and to a lesser extent, Mo. Thus, the highest dissolved Sb concentrations occur in alkaline (pH 7-9) waters (in marked contrast to the situation with As). Thus, the concentration of Sb in solution is not just related to its presence in the ore minerals but also to pH. Antimony forms oxyanions, the most common being $Sb(OH)_6^-$ (Langmuir 1997) and the solubility of this species is higher in neutral to alkaline conditions. However, the adsorption properties of this species are also important and Sb can be removed from solution by its strong adsorption on Fe oxides below pH 7 (Jones et al. 1990). Other studies on water associated with As- and Sb-deposits (e.g. Ashley et al. 2003) have indicated that both Sb and As can be mobilised in neutral to alkaline waters.

Even though sphalerite and galena are present in equal amounts in many of these deposits (particularly the Pb-Zn mines), ZnS is much more soluble than PbS (Barnes 1979). Experiments on oxidation of sulphide tailings confirm such differential rates of

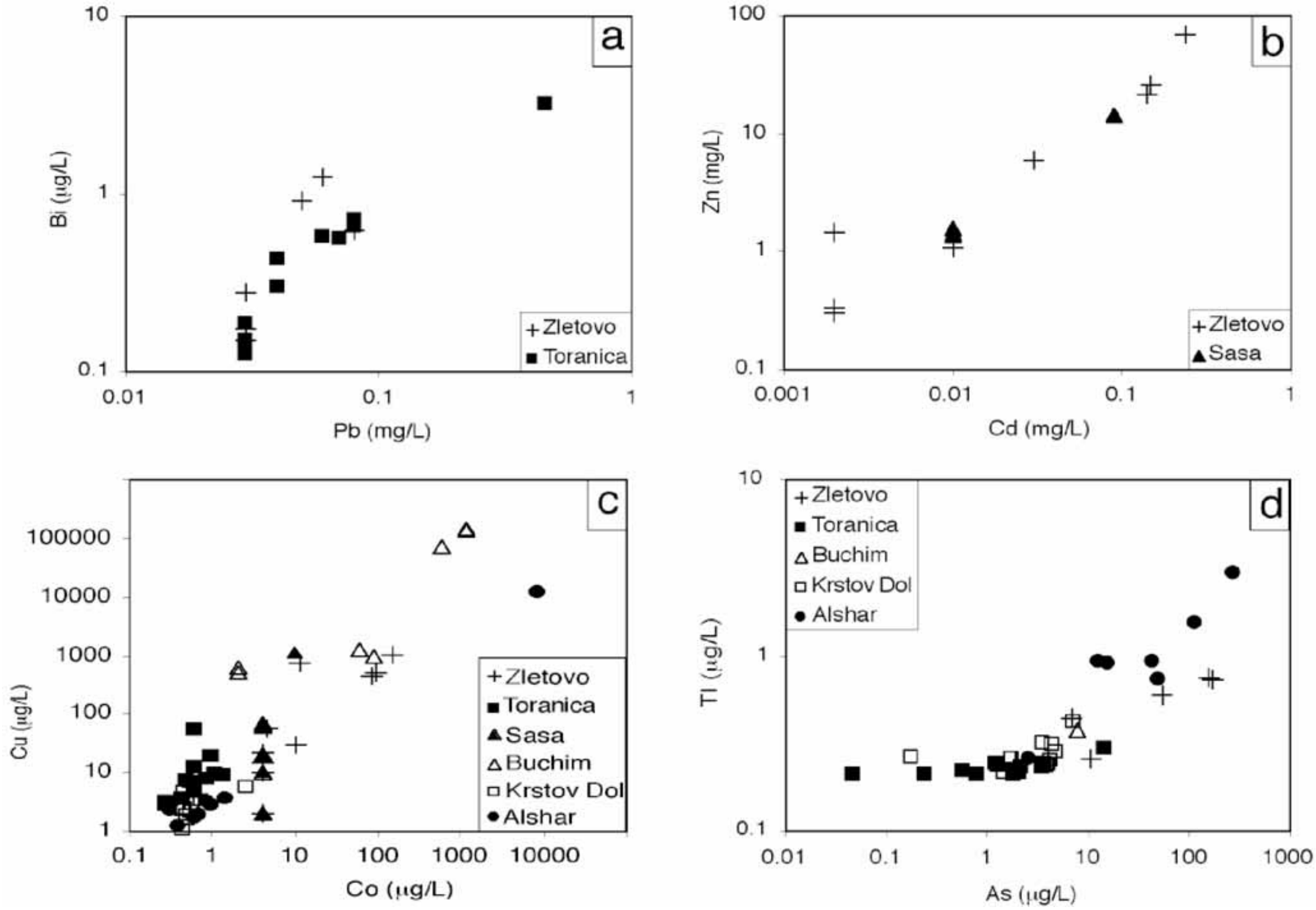

Figure 2. Scatter plots for concentrations of selected elements in waters from mine sites in Macedonia: a.) Bi-Pb for samples from Toranica and Zletovo; b.) Zn-Cd for samples from Zletovo and Sasa; c.) Cu-Co for samples from all sites; d.) Tl-As for samples from all sites (except sample A4 from Alshar)

mineral breakdown (Domènech et al. 2002). In addition, Pb is readily adsorbed by Al and Fe oxide phases and galena dissolves at a much lower pH than other metal sulfides (Lee et al. 2002). Similarly, Sb mobilisation is not expected to be a large problem due to the low solubility of Sb_2S_3 (Krauskopf 1967) and other Sb species. The low bioavailability of Sb in heavily Sb-contaminated soils over a large pH range has also been noted (e.g. Flynn et al. 2003). Low concentrations of As, Bi, and Sb have also been noted in (relatively acidic) rivers draining contaminated mining areas in Korea (Jung et al. 2002). In contrast, Ashley et al. (2003) found that As and Sb can be dissolved at high levels from contaminated sediments in near-neutral waters. Other factors (including complex ion formation and variable local conditions) thus play a part in controlling the solution of As and Sb, and in particular the potential for adsorption on solid phases (e.g. Fe-oxides).

Uranium values also show a negative correlation with pH and a positive correlation with many metals, especially Cu (Figure 4), indicating that this metal is associated in particular with Cu-bearing sulphides. However, the extremely high values found at Buchim

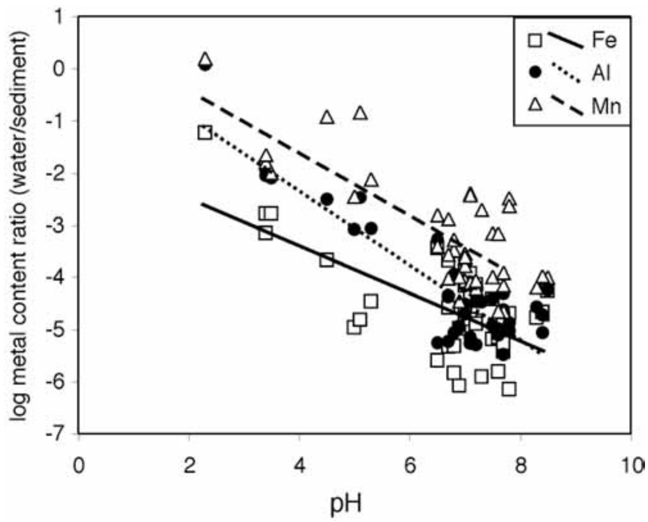

Figure 3. Regression lines illustrating the relationships between pH and Fe, Mn, and Al water/sediment concentration ratios for mine sites in Macedonia; ratios represent the concentration in water (in mg/L) divided by the concentration in sediment (in mg/kg) for each sample location.

are not easy to explain. No U minerals have been identified at the mine and no U mineralization is known

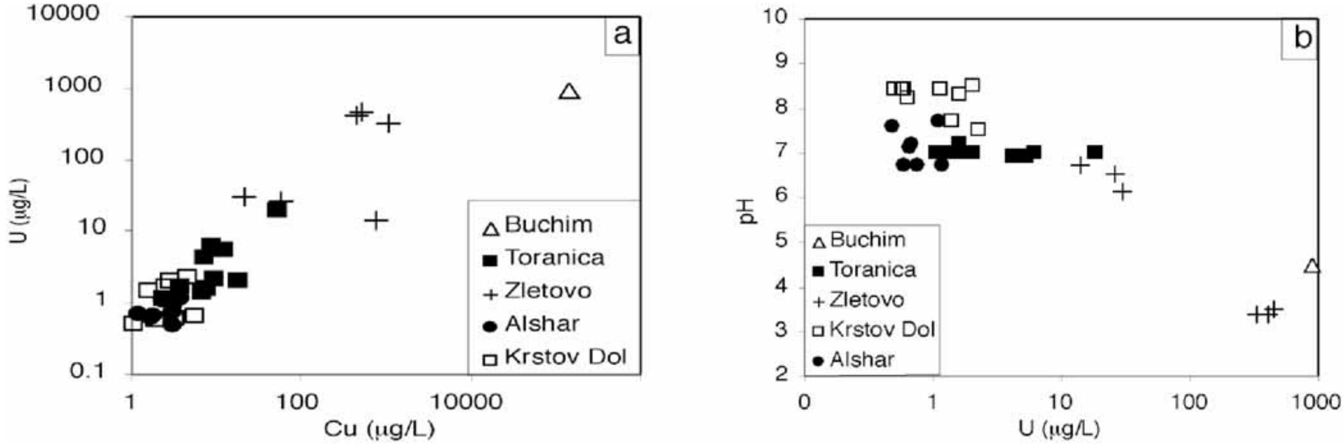

Figure 4. Scatter plots for concentrations of U against Cu (a) and pH (b) in waters from mine sites in Macedonia

in the immediate vicinity of the mine. However, these high U values are very similar to those found in standing water at the old pit at the Butte (Montana) porphyry Cu deposit (Gammons et al. 2003).

Conclusions

There are poor controls in place at many of the mine sites in Macedonia. Thus, there is the potential for contamination of water and river sediments from mine workings, waste/tailings sites, and processing plants. Contamination of sediments and water was high in the immediate vicinity of the mine sites but was reduced to near background levels at distances of 5-25 km from the mines (depending on the size of the operation). The tailings dams are a major potential source of sediment pollution; however, the use of culverts to direct water away from the tailings generally seems to be quite successful and largely prevents the ingress of polluted water to the streams.

All sites are associated with river sediments that are contaminated to some degree and the mining-related particulate material constitutes a large reservoir for potential future contamination. However, water contamination was often only moderate, such as at Sasa and Toranica, where the lack of pyrite and buffering by limestone keep metal concentrations low. In contrast, the waters associated with the Zletovo deposit are acidic and highly contaminated with several metals. Mine water from Buchim is grossly polluting the River Madenska, with copper concentrations in excess of 100 mg/L. Uranium levels there were also high but the ultimate source of this metal is unclear. Water pollution at Krstov Dol and Alshar was low and only Sb and As were found in higher than normal concentrations.

The elevated concentrations of metals found in these waters can usually be related to the mineralogy of the individual deposits, and metallic sulphides appear to be the main primary source of the metals. Mine drainage commonly has a lower pH than background waters and the increased acidity has promoted metal dissolution. Of the elements investigated here, only Sb, and to a lesser extent Mo, exhibited a high mobility in neutral to alkaline waters.

Mining and processing activities in Macedonia have therefore had an adverse impact on the environment, albeit to varying degrees. Some of the mines are small and/or remote, and the effect has been minimal; others, however, have had a greater impact. Sites that are close to areas of habitation, agriculture, irrigation, or water extraction should be monitored on a regular basis. Such sites may need to be remediated and further development of mining activities will need to take this into account.

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