

## DISTRIBUTION AND MOBILITY OF ARSENIC AND ANTIMONY AT MINE SITES IN FYR MACEDONIA

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**Abstract:** Soils, river sediments and waters from former As-Sb mining sites in FYR Macedonia have been chemically analysed to assess their impact on the local environment. Soils and river sediments contain very high concentrations of As and Sb (medians 117 and 37 mg kg<sup>-1</sup>), but values are heterogeneously distributed. These values are far in excess of various statutory thresholds and at the largest deposit, Lojane, the area is grossly contaminated. Sequential extraction has demonstrated that a large proportion of the As (50-90%) and Sb (20-60%) in these soils is in a weakly-bound form and is thus available for further mobilization. Surface and groundwaters are neutral to alkaline because of interaction with host lithologies (e.g. serpentinite, dolomite and limestone). Surface waters appear to have higher concentrations of As (55;33) and Sb (2.1;0.6) than the groundwaters (medians, µg/l). For all samples there is a close positive correlation between As and Sb, but As contents are generally much higher than those for Sb. Most of the waters have As concentrations which exceed the 10 µg l<sup>-1</sup> value accepted for safe drinking water whereas most Sb concentrations are much lower and appear to be within the acceptable limits for this element. The alkaline waters have been able to mobilize the As and Sb directly from the primary ore minerals and the lack of pyrite in the ores has minimized the production of secondary Fe oxides which could adsorb and immobilize these elements. These sites are environmental 'hotspots' and need remediation. The reservoir of As and Sb which is able to be released over a long time period threatens a much larger area. Remediation strategies would have to take the mobility of these elements under alkaline conditions into account.

**Keywords:** Lojane, Macedonia, pollution, arsenic, antimony, sequential extraction

### 1. INTRODUCTION

In spite of increased awareness and understanding of the potential threats to the environment from mining activities, there are many examples around the world where pollution from such 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 it is crucial to understand the impact of these processes on the environment.

In common with several other countries in the Balkans of southeastern Europe, metal mining has traditionally been an important part of the economy of the former Yugoslav Republic of Macedonia, but environmental issues have not always been paramount and in many cases there is a widespread legacy of pollution of soils, sediments and waters.

Furthermore, recent conflicts in the region have increased local ethnic tensions and these have hampered efforts for environmental remediation. Although now declining in importance, continued exploration and development indicate that mining will remain an important part of the economy of the country for the near future. In addition, the country has a great reliance on agriculture and it is critical to safeguard the soils and water resources. Therefore a clear understanding of the environmental impact of these activities is crucial.

A previous survey (Alderton et al., 2005) described and quantified the chemistry of waters and river sediments associated with the most important metal mines in Macedonia. These have been worked predominantly for copper, lead and zinc, and the abundance of pyrite has resulted in widespread acid mine drainage; this has led to the mobilization of a variety of metals and the subsequent contamination

of the environment on a large scale. However, the region also contains some disused arsenic and antimony mines which display very different geological and mineralogical characteristics, but at the time of this initial survey these were only subjected to a cursory study. The preliminary results from this earlier study indicated that these sites exhibited very different environmental geochemical characteristics. Furthermore, initial assessments of post-conflict, environmental 'hotspots' in Macedonia by the United Nations Environmental Programme (UNEP 2000) highlighted mining activities (including the Lojane As-Sb mine) as a significant, potential threat to the environment.

Even though the behaviour of arsenic and antimony in the environment has been studied in great detail, there are still unresolved issues about the mobility of these elements under natural conditions and in different environments. The aim of this study was to extend the earlier work and focus specifically on the arsenic and antimony deposits, with a view to assessing their impact on the local environment and elucidating the behaviour of these elements in the environment. This study has concentrated on the largest deposit, Lojane, but these results will be combined with those from two other, smaller deposits which were part of a preliminary investigation during the earlier study.

## **2. GEOGRAPHICAL AND GEOLOGICAL SETTING**

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

The major metalliferous mineral deposits (Fig. 1) are closely associated with igneous rocks of Eocene – Miocene age. These are mostly of an intermediate, calc-alkaline/high K composition (especially granodiorite, quartz monzonite, quartz diorite, andesite and dacite; Boev & Yanev 2001). The present level of erosion is such that the igneous rocks currently exposed are mostly high-level volcanics and pyroclastics.

Several styles of metalliferous mineralization are present in Macedonia (Jankovic 1982; Jankovic et al., 1997a; Serafimovski 1993; Serafimovski et al.,

1995). Of these, the most important economically have been polymetallic Pb-Zn veins (Zletovo), Pb-Zn skarns (Sasa, Toranica) and porphyry copper deposits (Bucim). Most exploitation in the past has been from the Pb-Zn deposits, but most current exploration interest is in polymetallic, Cu-Au deposits. Also present, but as a distinct and separate group, are epithermal, vein deposits containing arsenic and antimony. These are a characteristic feature of the whole Balkan region (Jankovic 1960; 1980) and three Macedonian deposits which were formerly worked for As and Sb (Lojane, Alshar, Krstov Dol) are the subject of this study.

## **3. MINES**

### **3.1. Lojane**

The Lojane deposit is located in the north of Macedonia, close to the border with Kosovo and between the villages of Lojane and Vaksince (Fig. 2). The mine exploited As, Sb and Cr during the period 1923-1979. The geology of the deposit area consists of a package of NW-SE striking lithologies, including serpentinite (containing chromite bodies), flysch and limestone, which were intruded by granite and andesite. Further east there is extensive alluvial cover (gravels). Sb and As were mined from steeply dipping, NW-SE trending veins, often located at the junction of the andesite and serpentinite (Jankovic 1960; Antonovic 1965). The exploitable veins extend for about 0.5km and their thicknesses vary between 1-2m. The main ore minerals were the sulphides of As and Sb (orpiment, realgar, stibnite), but bravoite ((Fe, Ni, Co)S<sub>2</sub>), vaesite (NiS<sub>2</sub>), cattierite (CoS<sub>2</sub>), pyrite, marcasite, molybdenite and pitchblende (UO<sub>2</sub>) also occur in minor quantities. The gangue consists of quartz and minor dolomite. Some oxidation of the primary sulphides has resulted in the formation of secondary oxides and hydroxides.

The mined ore was transported by rail from the underground workings to the mill and flotation plant and then exported by rail. These former workings are spread over a large area and are currently in a very poor state of maintenance. Waste material is estimated at 20,000t at the mine site and 15,000t of arsenic concentrate and 3,000,000t of tailings at the concentration facility (Antonovic 1965). The tailings dam (42°13'02"N, 21°39'52"E) is completely unprotected and its orange colour (clearly visible from satellite images) suggests a high concentration of arsenic sulphides.

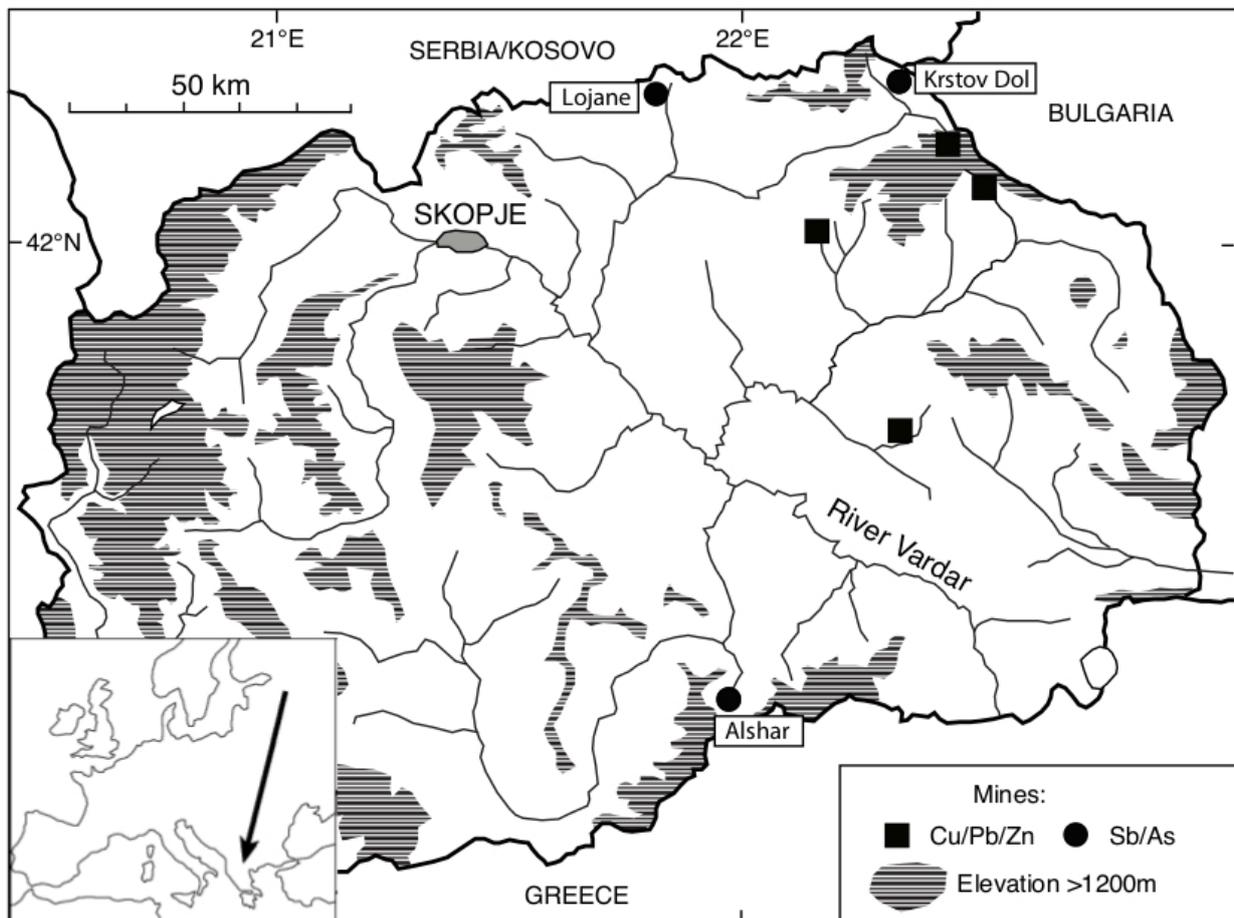


Figure 1. Map of Macedonia, showing the locations of the main mines and principal rivers. Inset shows location of Macedonia in Europe.

(Some of the orange arsenic concentrate has also been used to mark out the local football pitch.) The concentrate was then taken by small gauge railway across the agricultural area to a location next to the main railway line at Civluk (Fig. 2). At this location (42°13'27.77"N, 21°41'43.34"E) there are also the remains of the old arsenic smelter. The smelter site contains a large pile of arsenic concentrate and is also covered with numerous heaps of black and white powder (Fig. 3). These consist of stibnite concentrate and refined 'white arsenic' (arsenolite,  $As_2O_3$ ; see Fig. 4) and are reputed to be the remains of 2500 wooden barrels of processed material which were abandoned during the recent conflict and left to rot.

There is extensive agriculture in the adjacent area, particularly in the flat region between the mine and the smelting facility. Water for irrigation or domestic use is extracted from the rivers and springs, or from numerous private wells (mostly sited in the river gravels, at depths of 5-10m below surface). The soils and sediments in this area contain variable proportions of primary minerals derived

directly from the eroded host rocks (quartz, calcite, dolomite, plagioclase, K-feldspar) and secondary minerals related to weathering (smectite, illite, serpentine/chlorite).

### 3.2. Alshar

The Alshar deposit is located near the hamlet of Majdan (41°09'11.77"N, 21°56'36.21"E) in the Kozuf Mountains, a remote and rugged part of southern Macedonia. Mining of As and Sb took place during the late 1800s and early 1900s but there has been extensive exploration for Au during the last few decades, particularly because of some geological similarities to Carlin-type gold mineralization (Jankovic et al., 1997b; Percival & Radtke 1994; Volkov et al., 2006). Mineralization is closely associated with a Pliocene volcanic complex (altered latite, dacite, and andesite) and the host rocks are dominated by Triassic carbonates (dolomite and marble) overlain by a Tertiary volcano-sedimentary sequence of tuffs and dolomites.

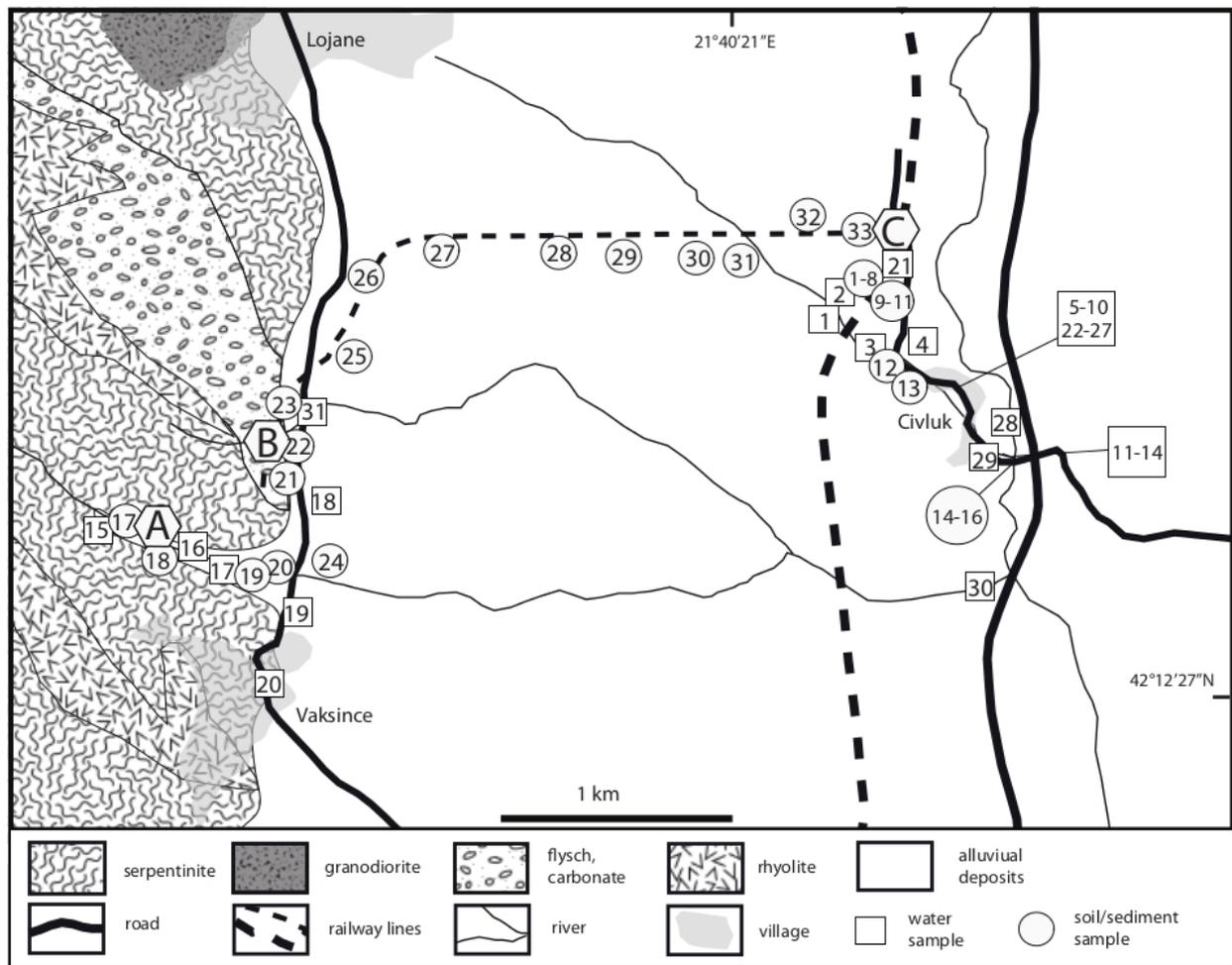


Figure 2. Geological map of the Lojane area, showing the locations of samples and the mine workings (A), mill and tailings dam (B) and arsenic smelter (C).



Figure 3. Waste material at the Lojane smelter site. The orange material is As sulphide concentrate; black is stibnite concentrate; white is processed arsenic ore ('white arsenic', arsenolite).

The mineralogy of the deposit is very complex, but the most abundant ore minerals are realgar, orpiment, stibnite, pyrite and marcasite, together with a gangue of quartz, goethite, calcite,

dolomite, barite and gypsum. Hydrothermal alteration consists of argillization, sericitisation, silicification and decalcification of the carbonates. Oxidation products of the ore include various Fe and Sb oxides/hydroxides, sulphates and arsenates.

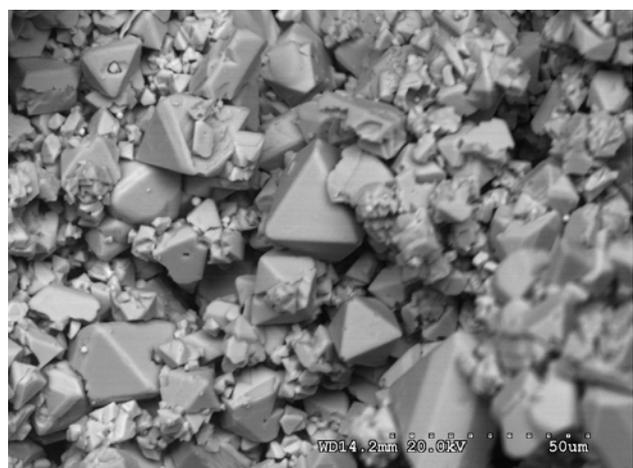


Figure 4. Scanning electron microscope image of arsenolite from the Lojane smelter site.

It is estimated that remaining reserves amount to 15000t As and 20000t Sb (Volkov et al., 2006). A distinctive feature of Macedonian As-Sb mineralization is an enrichment in thallium, but this feature is particularly marked at Alshar. Some of the ores here contained up to 2 weight % Tl and thallium-bearing minerals (e.g. lorandite,  $\text{TlAsS}_2$ ), many unique to this location, are relatively abundant. Current thallium reserves are estimated at 500t. The mine workings and waste dumps are located in the steep-sided valley of the River Majdanska.

### 3.3. Krstov Dol

This deposit is located in the far north-east of Macedonia ( $42^\circ 18' 55''\text{N}$ ,  $22^\circ 18' 29''\text{E}$ ) in a wooded, rural area near the town of Kriva Palanka. The mine was relatively small and extracted antimony ore during the periods 1962-1970 and 1986-1988. The deposit consists of some steeply-dipping, narrow (few cm to 0.5m) veins with a NW-SE trend and which extend for a distance of about 1km. The veins are mostly hosted by Palaeozoic sericite-chlorite schists, but mineralization is thought to be related to quartz latites of Oligo-Miocene age (Mudrinic & Serafimovski 1997). The most abundant minerals are stibnite ( $\text{Sb}_2\text{S}_3$ ), berthierite ( $\text{FeSb}_2\text{S}_4$ ) and pyrite, in a gangue of quartz and carbonates (calcite and siderite). Minor amounts of As-, Cu-, Fe-, Pb- and Zn-bearing sulphides have also been identified. Some weathering of the ore minerals has resulted in the presence of limonite, valentinite and senarmontite. Lithochemical exploration has shown that the mineralized rocks have enrichments in several elements: Pb, Ag, Sb, As, Mo, Ba, Tl and Zn. Thallium appears to be concentrated in the Sb minerals and stibnite and berthierite have Tl concentrations up to 0.3%. A small stream, the Krstovska, passes through the mine area and also receives the discharge from the drainage adit. The old mill, flotation plant, tailings dam and waste dumps are situated further down the valley.

## 4. METHODS

Samples were collected from the three locations outlined above, with a greater emphasis placed on Lojane. Sample locations are given either on a map (for Lojane; Fig. 2) or in Alderton et al. (2005) (for Alshar and Krstov Dol). (At Lojane there was limited sampling in the central, agricultural area, partly due to access issues, but also because the streams here are ephemeral and tend to dry up in the summer months when sampling took place.)

Triplicate sample points were also selected and the analytical determinations were used to assess sampling precision. Samples were taken progressively downstream from the mining sites and, at some locations, in receiving waters. Sampling density varied from a few metres to several kilometres, depending on the situation; in general, sampling density was lower further downstream. Water was collected in polythene syringes, passed through a  $0.45\mu\text{m}$  filter and transferred into polythene tubes. Water was acidified with 0.4 ml of 50% nitric acid. Conductivity and pH were measured in the field for all water samples. Samples were stored in a cool, dark place until they were returned to the U.K. for laboratory analysis. Soil and river sediment samples were also collected at several locations. These were dried, ground in a 'tema'-mill and then dissolved using a hot  $\text{HF-HClO}_4$  digestion.

Solutions were analysed by ICPAES or ICPMS, depending on concentrations. A large number of analytes were determined but only those that are likely to be mining-related and environmentally significant are presented and discussed here. The accuracy of the soil and sediment results was assessed by routinely analysing standard soil samples. There was some concern that As and Sb might be lost by volatilization during the solid dissolution procedure, so selected samples were also analysed by X-ray fluorescence. It was found that some As does get lost, but this only becomes significant at levels greater than about  $100 \text{ mg kg}^{-1}$  and then the amount lost equates to about 10%.

The concentrations of As and Sb in the soils, sediments and waters were compared to various national screening and reference guidelines to assess their significance (EU, 1998; WHO, 2011; USEPA, 2009; Tighe et al., 2005; Buchman, 2008; CCME, 2012; UKEA, 2009; NMIE, 2009). There is some variation in the values for these guidelines and the data for Sb are not as comprehensive as those for As. This is partly because the values may be set for local conditions, but also because they have been derived using different ecotoxicological tests or for different applications (e.g. drinking water, irrigation, environmental well-being, intervention).

Selective/sequential extraction of arsenic and antimony from four samples of soil (agricultural area, Lojane) and two samples of river sediment (Alshar) was achieved using a 5-step procedure based on the method described by Wenzel et al. (2001). This used: 1) Ammonium sulphate solution (for non specifically sorbed components), 2) Ammonium dihydrogen phosphate (specifically sorbed), 3) Ammonium oxalate buffer (amorphous hydrous oxides of Fe and Al), 4) Ascorbic acid plus

ammonium oxalate buffer (well-crystallised Fe and Al hydrous oxides), and 5) Hydrofluoric acid (residual phases).

## 5. RESULTS

The chemical analyses of waters, soils and sediments from the Lojane area are presented in Tables 1 and 2.

### 5.1 Lojane

Surface and groundwaters collected from the Lojane area are all alkaline with a pH of 7.0 to 8.6 (Table 1). A distinctive feature of their chemistry is that for most samples  $Mg > Ca$  and high conductivities (mostly  $>600 \mu S cm^{-1}$ ) point to a high dissolved solid content. These characteristics are

likely due to the interaction with certain underlying, relatively reactive lithologies, particularly serpentinite (containing abundant Mg silicates) and dolomite/limestone.

Surface waters appear to have higher concentrations of As, Sb and Mo than in the groundwaters. In the surface waters the concentrations (in  $\mu g l^{-1}$ ) are: As 7-335, median 55; Sb 0.2-75, median 2.1; Mo 0-5.8. In the groundwaters, the concentrations are: As 16-402, median 33; Sb 0.1-166, median 0.6; Mo 0.3-3.5. For all samples there is a close positive correlation between As and Sb, but As contents are generally much higher than those for Sb (Fig 5a). There appears to be no major variation in concentration of either As or Sb with pH (Figs. 5b and 5c).

Table 1. Chemical analysis of waters from the Lojane area. g = groundwater, a = adit. All others are surface water.

| LW  | Al<br>mg/l | As<br>$\mu g/l$ | Ca<br>mg/l | Fe<br>mg/l | K<br>mg/l | Mg<br>mg/l | Mn<br>mg/l | Mo<br>$\mu g/l$ | Na<br>mg/l | Sb<br>$\mu g/l$ | Tl<br>$\mu g/l$ | pH  | C<br>$\mu S/cm$ |
|-----|------------|-----------------|------------|------------|-----------|------------|------------|-----------------|------------|-----------------|-----------------|-----|-----------------|
| 1   | 0.1        | 117             | 39.9       | <0.1       | 53.8      | 60.5       | 0.5        | 5.8             | 12.5       | 7.0             | <0.5            | 8.6 | 856             |
| 2g  | 0.1        | 20.5            | 47.1       | <0.1       | 18.8      | 64.6       | <0.1       | 0.1             | 7.3        | 0.8             | <0.5            | 7.7 | 610             |
| 3   | 0.2        | 110             | 52.6       | 0.3        | 0.7       | 69.8       | 0.3        | 0.6             | 7.3        | 6.6             | <0.5            | 7.9 | 630             |
| 4   | 0.1        | 87.5            | 50.4       | <0.1       | 0.6       | 69.6       | <0.1       | 1.1             | 7.4        | 2.6             | <0.5            | 8.0 | 645             |
| 5g  | <0.1       | 19.9            | 44.8       | <0.1       | 1.5       | 64.1       | <0.1       | 0.3             | 7.8        | 0.1             | <0.5            | 7.6 | 630             |
| 6g  | 0.1        | 40.5            | 71.2       | <0.1       | 6.0       | 114.0      | 0.3        | 1.2             | 16.5       | 0.5             | <0.5            | 7.7 | 1100            |
| 7g  | 0.1        | 26.1            | 68.1       | <0.1       | 1.2       | 101.6      | <0.1       | 0.6             | 10.8       | 2.0             | <0.5            | 7.7 | 940             |
| 8   | 0.1        | 14.8            | 52.1       | <0.1       | 8.0       | 68.4       | <0.1       | 0.1             | 8.1        | 0.2             | <0.5            | 7.6 | 720             |
| 9   | 0.1        | 11.1            | 55.8       | <0.1       | 5.8       | 75.4       | <0.1       | 0.3             | 8.1        | 0.6             | <0.5            | 7.8 | 760             |
| 10  | 0.1        | 63.0            | 53.4       | <0.1       | 8.3       | 73.5       | 0.1        | 1.1             | 8.6        | 2.5             | <0.5            | 8.3 | 760             |
| 11g | 0.1        | 29.8            | 63.6       | <0.1       | 18.6      | 81.8       | <0.1       | 1.5             | 13.0       | 0.6             | <0.5            | 7.8 | 860             |
| 12  | 0.1        | 13.3            | 43.4       | <0.1       | 9.2       | 60.0       | <0.1       | 0.0             | 10.8       | 0.7             | <0.5            | 7.4 | 630             |
| 13  | 0.1        | 54.8            | 59.9       | <0.1       | 3.9       | 62.8       | <0.1       | 0.9             | 11.0       | 3.0             | <0.5            | 8.3 | 670             |
| 14  | <0.1       | 61.7            | 62.5       | <0.1       | 4.0       | 63.4       | <0.1       | 1.0             | 11.3       | 2.1             | <0.5            | 8.1 | 640             |
| 15a | 0.1        | 4598            | 25.3       | <0.1       | 3.0       | 121.9      | <0.1       | 39.8            | 6.0        | 1685            | 1.0             | 8.3 | 827             |
| 16  | 0.1        | 216             | 29.8       | <0.1       | 1.4       | 100.8      | <0.1       | 3.1             | 4.6        | 74.8            | <0.5            | 8.3 | 720             |
| 17  | 0.1        | 6.7             | 28.2       | <0.1       | 0.4       | 81.1       | <0.1       | 0.0             | 6.0        | 1.4             | <0.5            | 8.6 | 624             |
| 18g | 0.1        | 70.4            | 29.1       | <0.1       | 7.4       | 82.4       | <0.1       | 2.2             | 5.4        | 8.0             | <0.5            | 8.3 | 705             |
| 19g | <0.1       | 402             | 25.4       | <0.1       | 4.5       | 110.4      | <0.1       | 3.5             | 4.0        | 166.3           | <0.5            | 8.2 | 875             |
| 20g | 0.1        | 54.6            | 71.6       | <0.1       | 49.0      | 78.4       | <0.1       | 0.7             | 19.0       | 5.7             | <0.5            | 8.0 | 1050            |
| 21  | 0.1        | 90446           | 316        | <0.1       | 12.3      | 45.5       | 0.1        | 61.6            | 44.2       | 3350            | 0.8             | 7.7 | 1609            |
| 22  | 0.1        | 298             | 52.5       | 0.2        | 0.9       | 69.2       | 0.3        | 0.6             | 6.4        | 4.5             | <0.5            | 7.8 | 688             |
| 23g | <0.1       | 60.4            | 64.7       | <0.1       | 1.6       | 100.6      | 0.3        | 1.3             | 10.6       | 0.8             | <0.5            | 7.6 | 958             |
| 24g | <0.1       | 26.1            | 49.0       | <0.1       | 1.0       | 67.7       | 0.1        | 0.8             | 5.8        | 0.5             | <0.5            | 7.8 | 668             |
| 25g | <0.1       | 35.9            | 46.0       | <0.1       | 1.6       | 62.4       | 0.1        | 0.6             | 6.8        | 0.6             | <0.5            | 7.8 | 621             |
| 26g | <0.1       | 22.7            | 44.7       | <0.1       | 1.6       | 62.9       | <0.1       | 0.6             | 6.5        | 0.6             | <0.5            | 7.8 | 683             |
| 27g | <0.1       | 16.4            | 51.4       | <0.1       | 3.2       | 68.2       | <0.1       | 0.4             | 6.3        | 0.4             | <0.5            | 7.7 | 682             |
| 28  | 0.2        | 21.3            | 90.1       | 0.3        | 2.8       | 37.3       | 0.1        | 0.2             | 14.9       | 0.3             | <0.5            | 7.8 | 660             |
| 29  | <0.1       | 45.4            | 66.2       | <0.1       | 8.4       | 53.8       | <0.1       | 0.6             | 11.1       | 1.4             | <0.5            | 7.6 | 685             |
| 30  | 0.2        | 22.1            | 91.1       | 0.2        | 3.3       | 39.1       | 0.1        | 0.2             | 14.8       | 0.4             | <0.5            | 8.0 | 662             |
| 31  | <0.1       | 335             | 77.9       | 0.8        | 0.7       | 24.1       | <0.1       | 1.9             | 4.3        | 114.4           | 0.7             | 7.7 | 463             |

Table 2. Chemical analyses of soils and sediments from the Lojane area. \* = river sediments; r=replicates.

|     | Fe <sub>2</sub> O <sub>3</sub> | MgO   | CaO   | MnO  | As    | Ba    | Cr    | Cu    | Mo    | Ni    | Pb    | Sb    | Tl    | Zn    |
|-----|--------------------------------|-------|-------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| LS  | wt%                            | wt%   | wt %  | wt % | mg/kg |
| 1   | 3.46                           | 1.71  | 4.43  | 0.05 | 414   | 547   | 82    | 16    | 0.6   | 82    | 25    | 201   | 1.5   | 42    |
| 2   | 5.67                           | 1.91  | 1.33  | 0.12 | 1635  | 509   | 140   | 28    | 1.3   | 128   | 39    | 625   | 2.2   | 73    |
| 3   | 5.47                           | 1.80  | 1.21  | 0.12 | 298   | 525   | 135   | 25    | 0.3   | 105   | 38    | 60    | 0.7   | 67    |
| 4   | 5.20                           | 1.59  | 1.09  | 0.11 | 115   | 501   | 130   | 26    | 0.3   | 100   | 37    | 23    | 0.5   | 64    |
| 5   | 4.95                           | 1.44  | 0.94  | 0.10 | 95    | 515   | 135   | 24    | 0.1   | 99    | 33    | 11    | 0.4   | 56    |
| 6   | 3.44                           | 5.18  | 1.03  | 0.12 | 147   | 491   | 109   | 30    | 0.1   | 272   | 26    | 12    | 0.2   | 53    |
| 7   | 5.32                           | 8.50  | 2.07  | 0.11 | 47    | 405   | 330   | 37    | 0.1   | 428   | 37    | 7     | 0.2   | 62    |
| 8   | 3.81                           | 4.86  | 1.32  | 0.09 | 31    | 359   | 301   | 30    | 0.1   | 280   | 39    | 6     | 0.3   | 52    |
| 9r  | 4.94                           | 1.65  | 1.62  | 0.11 | 655   | 499   | 130   | 31    | 1.0   | 112   | 44    | 72    | 0.6   | 82    |
| 9r  | 4.65                           | 1.68  | 1.20  | 0.11 | 567   | 481   | 134   | 25    | 0.1   | 121   | 34    | 37    | 0.5   | 57    |
| 9r  | 4.51                           | 1.51  | 1.16  | 0.10 | 688   | 474   | 127   | 24    | 0.2   | 112   | 37    | 29    | 0.6   | 55    |
| 10  | 5.10                           | 2.19  | 1.46  | 0.10 | 937   | 444   | 126   | 37    | 1.3   | 124   | 47    | 596   | 2.2   | 76    |
| 11  | 10.32                          | 1.75  | 1.47  | 0.08 | 10838 | 391   | 162   | 105   | 24.0  | 144   | 134   | 7593  | 32.4  | 110   |
| 12* | 3.43                           | 4.59  | 1.97  | 0.07 | 90    | 525   | 768   | 24    | 1.9   | 180   | 44    | 44    | 0.6   | 46    |
| 13* | 3.37                           | 5.01  | 1.52  | 0.10 | 51    | 562   | 144   | 25    | 0.5   | 266   | 24    | 13    | 0.2   | 47    |
| 14* | 3.11                           | 4.62  | 1.70  | 0.06 | 37    | 527   | 198   | 24    | 0.3   | 205   | 23    | 28    | 0.3   | 61    |
| 15* | 2.95                           | 4.53  | 2.28  | 0.06 | 24    | 569   | 150   | 19    | <0.1  | 213   | 23    | 6     | 0.2   | 42    |
| 16* | 4.46                           | 9.16  | 2.23  | 0.07 | 24    | 489   | 660   | 25    | 0.1   | 356   | 20    | 8     | 0.1   | 45    |
| 17* | 6.53                           | 23.44 | 2.26  | 0.11 | 17    | 106   | 559   | 30    | 0.0   | 1148  | 8     | 9     | <0.1  | 45    |
| 18* | 6.63                           | 19.16 | 2.59  | 0.12 | 56    | 137   | 672   | 30    | 0.0   | 980   | 52    | 27    | <0.1  | 48    |
| 19* | 5.96                           | 20.44 | 2.94  | 0.10 | 118   | 147   | 729   | 24    | 0.0   | 1006  | 16    | 37    | 0.1   | 44    |
| 20* | 6.30                           | 22.35 | 2.61  | 0.12 | 283   | 148   | 651   | 40    | 1.6   | 872   | 13    | 541   | 2.3   | 50    |
| 21* | 5.80                           | 13.85 | 6.88  | 0.12 | 23828 | 143   | 276   | 37    | 16.0  | 833   | 24    | 10687 | 35.5  | 81    |
| 22  | 6.46                           | 18.32 | 8.49  | 0.09 | 1009  | 196   | 428   | 25    | 0.8   | 1119  | 101   | 605   | 5.5   | 59    |
| 23  | 4.65                           | 7.80  | 19.67 | 0.10 | 1611  | 234   | 231   | 34    | 0.9   | 485   | 32    | 749   | 2.5   | 72    |
| 24  | 6.47                           | 16.57 | 6.20  | 0.11 | 81    | 252   | 320   | 31    | 0.2   | 895   | 39    | 35    | 0.1   | 89    |
| 25  | 6.03                           | 3.76  | 2.57  | 0.24 | 117   | 413   | 464   | 56    | 0.6   | 379   | 51    | 104   | 3.3   | 80    |
| 26  | 4.94                           | 3.30  | 13.90 | 0.14 | 94    | 305   | 269   | 39    | 0.6   | 403   | 36    | 107   | 1.5   | 72    |
| 27  | 6.49                           | 3.84  | 2.27  | 0.26 | 333   | 467   | 595   | 41    | 1.5   | 776   | 43    | 837   | 3.3   | 72    |
| 28  | 6.59                           | 3.01  | 1.60  | 0.16 | 42    | 434   | 381   | 38    | 0.5   | 582   | 35    | 35    | 0.9   | 70    |
| 29  | 5.45                           | 6.80  | 2.65  | 0.14 | 74    | 395   | 345   | 30    | 0.4   | 575   | 27    | 74    | 0.7   | 58    |
| 30  | 5.53                           | 3.72  | 2.43  | 0.11 | 51    | 403   | 345   | 35    | 0.4   | 364   | 34    | 31    | 0.9   | 61    |
| 31  | 5.79                           | 3.61  | 1.95  | 0.10 | 48    | 477   | 398   | 29    | 0.5   | 384   | 33    | 21    | 0.9   | 58    |
| 32  | 4.10                           | 3.40  | 2.56  | 0.06 | 161   | 441   | 387   | 19    | 0.6   | 202   | 33    | 128   | 1.1   | 50    |
| 33  | 5.07                           | 2.80  | 1.73  | 0.10 | 216   | 531   | 243   | 28    | 0.8   | 203   | 41    | 174   | 1.2   | 66    |

Concentrations of Cu, Pb and Zn are low, being either close to or below the detection limits. Most of the waters have As concentrations which exceed the 10  $\mu\text{g l}^{-1}$  value accepted for safe drinking water. In contrast, most Sb concentrations are much lower than 10  $\mu\text{g l}^{-1}$  and appear to be within the acceptable limits for this element. Waters discharging from adits or in close proximity to the tailings and smelting sites have higher concentrations of the elements As, Sb, Mo and Tl (and two samples are so high that they have been excluded from the above compilations). Some waters sampled from wells (and number LW19 from Vaksince in particular) have contents of As and Sb

which are significantly above the drinking water limits set by the various regulatory agencies.

Random 'grab' samples from the piles of abandoned concentrate material at the disused smelter site contain very high concentrations of As (up to 3%), Sb (up to 1.6%), Tl (up to 400  $\text{mg kg}^{-1}$ ) and Ni (up to 4200  $\text{mg kg}^{-1}$ ). Thirty-three samples of soil and river sediment from locations separate from the mine dumps exhibit some very high concentrations of As (median 117  $\text{mg kg}^{-1}$ ) and Sb (median 37  $\text{mg kg}^{-1}$ ) (Table 2). Two locations (LS11 and LS21) are particularly noteworthy (As > 10,000  $\text{mg kg}^{-1}$  and Sb > 5,000  $\text{mg kg}^{-1}$ ); Mo and Tl values are also particularly high in these samples. Overall, concentrations of As tend to be higher than those for

Sb (Fig. 6). The concentrations of As and Sb across the study area are quite variable and even replicate samples from the same location can have concentrations of both of these elements which vary by at least 50%. Many of the river sediments have As and Sb contents which exceed proposed environmental quality limits (typically around 20 mg kg<sup>-1</sup> for both elements) and for the soils, even if a rather conservative threshold value of 50 mg kg<sup>-1</sup> for both Sb and As is adopted, it is clear that many samples have contents of these elements which are above the ‘intervention’ values and thus classed as ‘contaminated’ and requiring remediation.

Concentrations of Mg, Cr and Ni are also high in many of these samples (MgO up to 22 wt%, Cr up to 770 mg kg<sup>-1</sup>, Ni up to 1150 mg kg<sup>-1</sup>), no doubt illustrating the influence of the serpentinite on the samples. Chromite was noted as being an HF-insoluble phase during the chemical analysis of many of the samples.

## 5.2 Alshar

The waters from the Madanska river area are mostly close to neutral pH and total solute contents are generally low (conductivities < 70  $\mu\text{S cm}^{-1}$ ; Alderton et al. 2005). Increases in levels of some elements (e.g. As, Fe, Tl) are noted where the river first passes the main adit and mine workings and the pH here drops to below neutral (6.7). These elevated contents are maintained for several km downstream from the area of mining. As with the water samples from Lojane, there appears to be little correlation between pH and concentrations of either As or Sb (Fig. 5).

Sediments in the river Majdanska, close to the Alshar mine workings, have markedly elevated concentrations of several elements (maximum found, all in mg kg<sup>-1</sup>): As (860), S (890), Sb (22), Mo (43) and Tl (75). Although there is a clear input from the mine workings, it is apparent that elevated levels of As and Tl also occur in sediments above the workings, suggesting the presence of more mineralization upstream and elevated background values in the area. Elevated concentrations of Co, Cr and Ni are presumed to be related to the background geology (possible erosion of serpentinites further upstream). These high sediment values are also maintained further downstream for at least several km below the mine workings, particularly for the elements As, Sb and Tl. In contrast to the situation at Lojane, there appears to be little correlation between As and Sb contents of the sediments (Fig. 6).

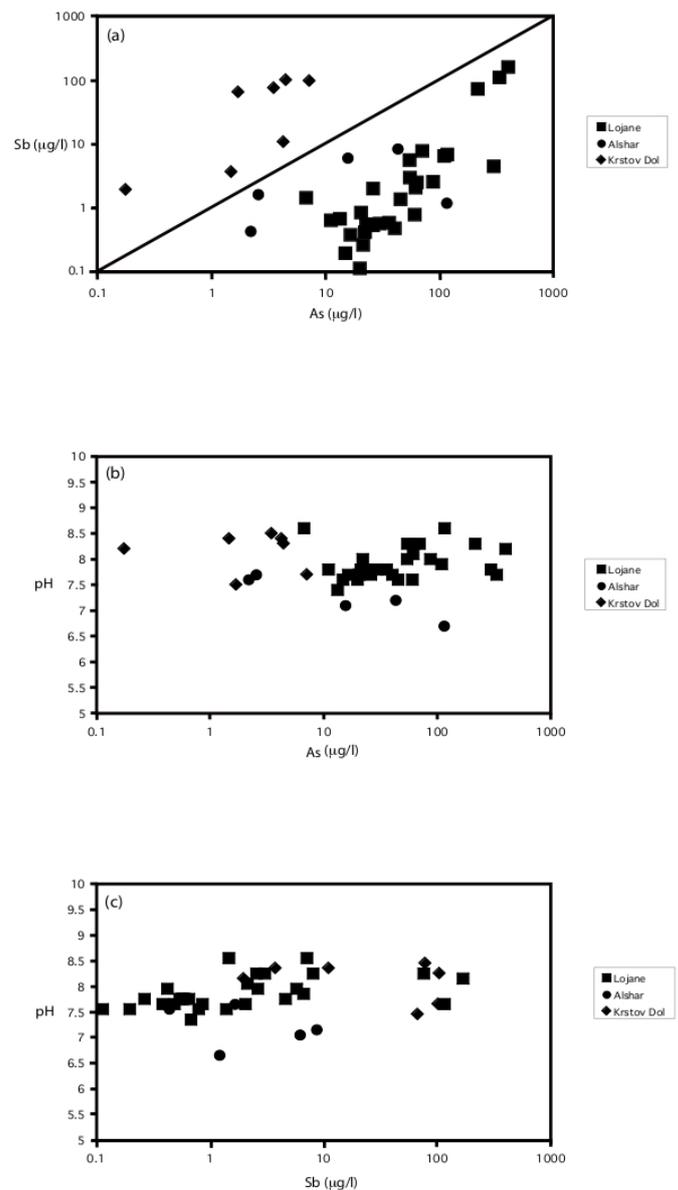


Figure 5. Scatter plots for compositions of waters from Lojane, Alshar and Krstov Dol. a: As vs Sb; b: As vs pH, c: Sb vs pH

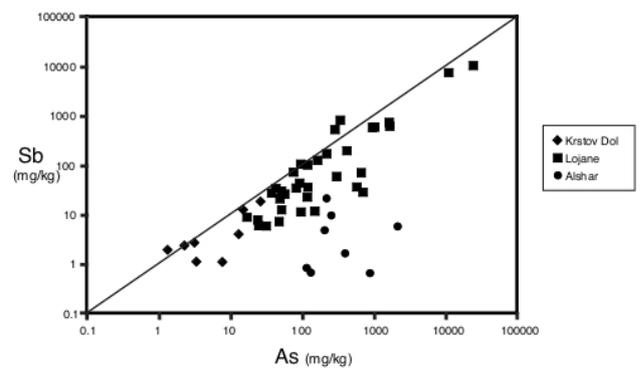


Figure 6. Scatter plot for concentrations of As and Sb in soils and sediments from Lojane, Alshar and Krstov Dol.

Boev & Lepitkova (2005) have presented some analyses of waters and sediments related to the Alshar mineralization and concluded that the mineral deposit and workings are not having a major effect on the ecosystem, particularly downriver in the important reservoir of Lake Tikves. Although their analytical results are similar to those presented here, it is unfortunate that no exact locations for their samples are presented.

### 5.3 Krstov Dol

All of the waters from the vicinity of Krstov Dol are moderately alkaline (pH=7.5 to 8.5) and have relatively low total solute contents (Alderton et al. 2005). An input of elements from the mining and processing activities is clearly visible, with elevated As, Co, Cr, Fe, Mn, Mo, S, and Sb derived from either the adit or the waste material. However, not all elements are consistently associated and in fact some of the highest values are seen in the tributary stream above the tailings dam. In addition, the presence of mineralization in bedrock further upstream is also indicated by the elevated Sb contents of waters from above the mining area. Several of the water values exceed screening values and/or drinking water recommendations but the Sb concentrations are particularly elevated, and remain so until the stream joins the larger river Lucka. However, these enrichments are relatively small and the composition of the water reaches background and 'safe' levels within 7km further downstream.

Stream sediments show an influence and input from the tailings dam as below this (sample KS6) there is a rise in concentrations of a large number of elements (e.g. As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Sb, Tl and Zn). These mostly decrease as the river flows downstream but there are indications that some element values (e.g. Sb, As) are still elevated and above background several km downstream, indicating physical transport of mining-related material from the mine site. Although the sediments appear to have roughly equal concentrations of As and Sb (Fig. 6) it is interesting to note that water Sb concentrations are higher than those for As.

### 5.4 Selective extractions

The results of the sequential extraction of As and Sb from soils and sediments are presented in Figure 7. These results show that between 40-80% of the Sb is present as a residual phase (Fig. 7a), whilst for As the residual proportion is generally less, around 10-50% (7b). In addition, the amounts

of As released during each subsequent step of the extraction procedure tend to be higher than those for Sb. This demonstrates that in these samples the As has been mobilized more readily than the Sb, supporting the observation of Ettler et al., (2010) that As is more readily mobilized from its sulphides compared to Sb (see also Flynn et al., 2003; Landsberger et al., 2010). However, to a certain extent this is also a function of the amount of each element available, as the amounts mobilised relative to total amount present in the sample remain fairly similar for both elements (Fig. 8). There are however some large differences in values between samples from similar locations, demonstrating that the As and Sb in these samples are present in a variety of forms. Soil conditions and mineralogy (e.g. organic matter and clay mineral content) probably play an important role in controlling the retention of mobilized As and Sb (as noted for example by Krysiak & Karczewska 2007).

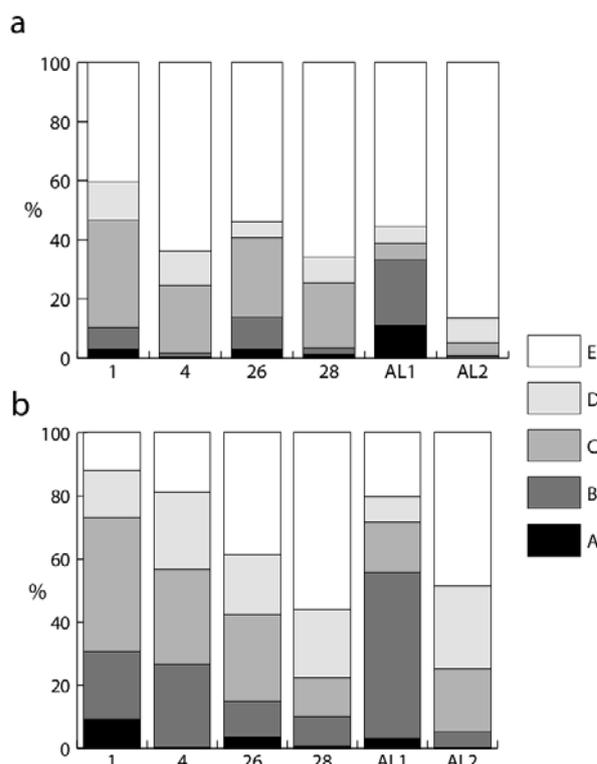


Figure 7. Proportions of (a) Sb and (b) As extracted from samples using the sequential extraction procedures. Samples 1, 4, 26, 28 from Lojane (LS); AL1 and AL2 from Alshar. Letters A to E refer to extraction methods 1 to 5 in the text.

The sequential extraction analyses indicate that in those samples which have high (above background) concentrations of As and Sb, relatively large amounts of the primary sulphides are being eroded and transported in their original, physical

form. However, the results also reveal that a substantial proportion of these elements is also present in a more soluble form, in more weakly bound and adsorbed sites. Breakdown of the primary sulphides and redistribution of these elements have been taking place at both locations and a large proportion of the As and Sb has been mobilised.

## 6. DISCUSSIONS

The results from this study demonstrate that all three of these former As-Sb mines are releasing high levels of these two elements into the environment, either through direct discharge of minewaters from drainage adits or through weathering, erosion and breakdown of mine waste. Many of the waters and sediments at all three locations exceed established thresholds and could therefore promote adverse ecological effects.

Lojane is the main potential threat to the environment, because of the size of the former operation, the close proximity to human activity and the nature of the terrain. The other two mining sites are also a source of pollutant As and Sb, but as they are smaller in size and located in more remote areas it is unlikely that they are currently having a major affect on people or biota. At Lojane the main problem is from As and to a lesser extent Sb, due to

the former element's greater volume, mobility and (probable) enhanced toxicity. There are also some elevated levels of Tl and Mo in these samples. These elements are enriched in the mineralization and have similar transport mechanisms, in particular having increased mobility in alkaline conditions. This behaviour and association have been noted elsewhere (e.g. in Argentina; Smedley et al., 2002) and the mobility of Tl can lead to an enrichment to high levels in plant crops (Xiao et al. 2012). However, the results from this study suggest that Tl and Mo concentrations in water and soils/sediments away from the immediate mine sites are probably not high enough to pose a significant threat. Base metal contents are generally low, as are those for Ni, Co and U (despite there being some enrichments in the ores). There are also some high levels of Cr in the Lojane soils and sediments but these arise from the presence of chromite and they are unlikely to present any problem because of this mineral's stability during weathering.

There is a large amount of waste at Lojane in the form of dumps, tailings and abandoned ore, but none of this is currently protected or managed properly. This material is exposed to the weather for continued physical transport via rivers and wind-blown dust, and chemical weathering and transport in solution.

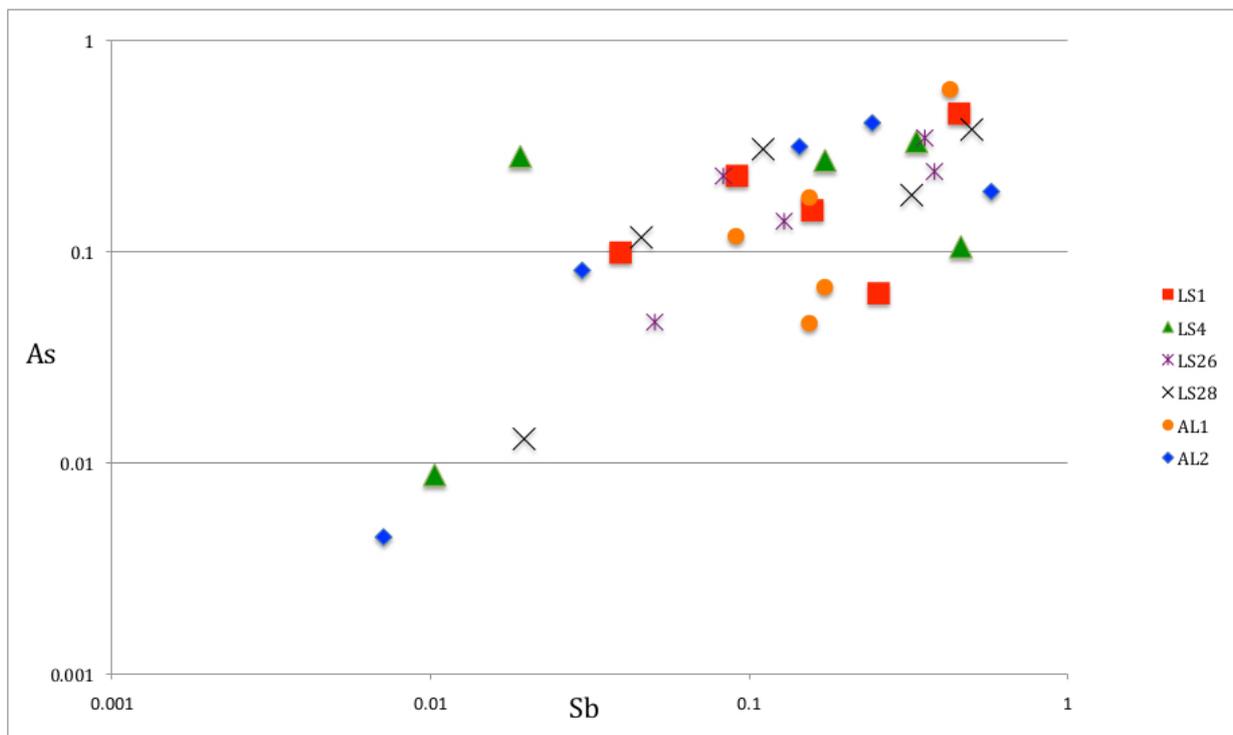


Figure 8. Scatter plot illustrating relative concentrations of As and Sb released during successive phases of extraction. Sample numbers as in Figure 7.

There is a reliance on local water supplies for drinking and irrigation, but some of the water clearly has As and Sb contents which exceed safe levels. Sediments and soils are also a potential source of long-term input for As and Sb. This contaminant material is available for steady transport into and down the rivers, thus increasing concentrations over a larger area (as has been found at other mining sites; Ashley et al., 2007; Tighe et al., 2005).

Although there is now a large amount of information on the mobility of arsenic in the environment, the behaviour of antimony (and in particular the uptake by plants) appears slightly contradictory. Many studies have suggested that Sb shows limited mobility in the environment and low levels in plants, even where the soils contain high levels of this element (e.g. Flynn et al., 2003; Hammel et al., 2000; Gal et al., 2007; Filella et al., 2002; He 2007; Landsberger et al., 2010). Additionally, Ainsworth et al., (1990), although finding high levels of Sb close to an antimony smelter, demonstrated that much of this Sb was from airborne particulate deposition rather than by incorporation of soluble Sb in plant tissue. In any case, and as stressed by several authors, with very high soil concentrations (e.g. >1000 mg kg<sup>-1</sup>) even a low mobility could become important.

However, Ashley et al., (2007) and Baroni et al., (2000) have shown that relatively large amounts of Sb can be taken up by algae and riparian plants. Furthermore, different plant species and even different parts of the plant are able to take in varying amounts of Sb (Murciego et al., 2007; Landsberger et al. 2010; see also O'Neill 1990, and Jung et al., 2002). It is therefore apparent that if soluble Sb is present then some plants can take this element up; thus the form of the element in the soil is clearly important.

In these sediments and soils, primary/resistant As and Sb phases constitute a major component, suggesting that physical transport of primary ore minerals (sulphides) and possibly processed arsenic oxide, is important. Remaining fractions relate to the dissolution of the primary phases and subsequent reprecipitation and adsorption; thus Sb and As mobility and bioavailability will also be dependant on redox conditions, pH and the presence of secondary minerals (especially hydrated Fe oxides) (e.g. Wilson et al., 2004; Palumbo-Roe & Klinck 2007). The alkaline, oxidising nature of these three Macedonian environments, combined with a relative lack of secondary Fe-oxide phases may have contributed to maintaining a high mobility of these elements. Iron arsenates (such as scorodite and

pharmacosiderite) are important in many environments for controlling the mobility of As and there are a large number of other potential phases which could also be important (Drahota & Filippi 2009) but they are unlikely to be present in significant amounts here. The high Ca/Mg – low Fe nature of these waters indicates that Ca and Mg arsenates, such as the Mg arsenate hoernesite (as noted by Voigt et al., 1996) or a Ca arsenate such as pharmacolite, might be present, but none of these phases has so far been identified.

Previous work on the effect of various Macedonian base metal mines on the environment (Alderton et al., 2005) has demonstrated that a large range of elements (including As, Sb, Tl and Mo) has been discharged and mobilized. The abundance of pyrite in these base metal deposits has generated classic, low-pH water and this has enhanced the mobility of these elements. In this respect their situation and behaviour are similar to those in many other deposits worldwide (e.g. for As; Smedley & Kinniburgh 2002). It is important to note that in such low-pH, Fe-rich environments an increase in water pH via rock buffering leads to a decrease in the concentration of these elements; this is partly due to the decreasing solubility of base metal sulphides as water pH increases, but also the effects of dilution by circum-neutral, background waters. This extension of the earlier study has demonstrated that the As and Sb mines are also releasing high levels of these elements, but under conditions that are neutral to alkaline.

Eh-pH diagrams for As and Sb species (Vink 1996; Lu & Zhu 2011) demonstrate that Sb and As can be present in a variety of anionic species in oxygenated waters over a large range of pH.

It has been established that As and Sb are readily adsorbed on to Fe oxides and oxyhydroxides, especially at low to neutral pH (Smedley et al., 2002; Palumbo-Roe & Klinck 2007; Smedley & Kinniburgh 2002; Haffert & Craw 2008; Roddick-Lanzilotta et al., 2002; Howell 1994; Wilson et al., 2004; Gal et al., 2007; Jones et al., 1990; Leuz et al., 2006). Thus As and Sb may not be totally mobilized and bioavailable if in a low pH environment in which Fe hydroxides are present. Studies on water associated with As- and Sb-deposits (e.g. Ashley et al., 2003; Smedley et al., 2002; Krysiak & Karczewska 2007) have indicated that both Sb and As may be desorbed and mobilised if those waters become less acidic.

The alkaline host lithologies (at all three locations) have generated neutral to alkaline waters which have been able to mobilize the As and Sb directly from the primary ore minerals. Furthermore,

the lack of pyrite in the ores (at Lojane) has minimized the production of secondary Fe oxides which could adsorb and immobilize these elements. In addition, arsenolite, produced from smelting of the As ore, is particularly soluble in water, especially if it is alkaline and the low Fe content inhibits Fe-arsenate formation (e.g. Haffert & Craw 2008).

## 7. CONCLUSIONS

Soils and river sediments at all three Macedonian As-Sb mines contain up to several hundred mg kg<sup>-1</sup> of both elements, but values are heterogeneously distributed. These values are far in excess of various statutory thresholds and at the largest deposit, Lojane, the area is grossly contaminated. A large proportion of the As and Sb in these soils is in a weakly-bound form and is thus available for further mobilization.

Metal mining and processing sites are typically acidic to neutral and studies on mining-related pollution tend to focus on these low pH environments. Acid from dissolution of Fe-sulphides can break down As and Sb sulphides and mobilize these elements, but secondary minerals can often then bind and immobilize a significant proportion. Information about the mobility and behaviour of As and Sb in neutral to alkaline conditions is therefore mostly derived from theoretical and laboratory-based experimental work. This study has demonstrated that alkaline waters can also readily break down As and Sb sulphides and that these elements are indeed mobile in naturally alkaline conditions, particularly if there is a lack of hydrated Fe-oxides to adsorb them from solution. The lack of pyrite and the alkaline geological environment mean that mine drainage and local waters are not acidic but alkaline and waters contain up to hundreds of ug l<sup>-1</sup> of both elements. Because the regional background water is also slightly alkaline it is likely that much of the arsenic and antimony can remain in solution and be transported over greater distances. These findings are of particular importance at Lojane because of the reliance on local water supplies and the importance of agriculture for food crops.

This study confirms UNEP's (2000) initial results, but in spite of a realisation that this is an environmental 'hotspot' and the government's commitment to carrying out further environmental impact studies (UNDP 2007), the sensitive location and history of recent conflict hinder any attempts to remediate the problem. The mine site will continue to be a potential problem for the local area but the reservoir of As and Sb which is able to be released over a long time period threatens a much larger area.

Often As and Sb contamination is only local in its effects because of the adsorption of these elements on to secondary minerals in low pH environments. Traditional remediation strategies (such as reed beds or lime dosing) would probably be ineffective at Lojane and alternative strategies, which take the mobility of these elements under alkaline conditions into account, would have to be devised.

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