

## Heavy metal and metalloid mobilisation and rates of contamination of water, soil and bottom sediments in the Chiprovtsi mining district, Northwestern Bulgaria

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**Abstract.** Geochemical studies of seasonally collected mine, stream and drinking waters, bottom sediments (mine and stream) and soil samples from all mining sections were carried out in order to assess the rates of pollution in the immediate proximity to underground mining facilities and related waste rock dumps. The determined concentrations of studied elements in water (As, Pb, Cu, Zn and Sb) show spatial distribution corresponding to ore mineralisation in different sections. Arsenic concentrations show gradual decrease in west-east direction, whereas Pb concentrations peak in the central and eastern sections. Arsenic and, to a lesser extent, Pb proved to be major pollutants in mine and surface waters, as well as in bottom sediments and soils. Detailed geochemical study of soils revealed strong spatial relation with host rocks and ore mineralogy. Comparisons with state guidelines for harmful elements revealed that alluvial and meadow soils in close proximity to waste dumps contain As, Pb, Cu, Zn and Cd above maximum permissible levels. It was also found that, compared to other Bulgarian and world alluvial (fluvisol) soils and the upper continental crust, the soils in Chiprovtsi mining district are enriched in Te, Re, W, Pd, Au, Ag, Mo, Ti, Mn, Co, Se, Sb, Bi and Cs. Since the processes of weathering and oxidation of mine waste remaining in the area continue naturally, the pollution with As and Pb will presumably carry on with decreasing effect.

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**Keywords:** Chiprovtsi and Martinovo mines, water, soil, bottom sediments, trace elements, pollution.

### INTRODUCTION

Mining of raw materials (ore, coal, industrial minerals) is fundamental for the development of modern industry, economy and technological progress. Metals and industrial minerals are used in various productions essential in providing goods, used in our everyday life and the functioning of our civilisation, although most people do not even think of their great importance for our existing. That is one of the reasons that the EU Commission has done a detailed report on certain raw materials that have critical meaning for the development of EU industry. Common people do not realise that the real cost of using modern technologies is namely the impact on the environment, caused by mining activities. Despite the efforts and precautions

taken in the past 2–3 decades to study and limit the effect of mining activity on the environment, it still has an enormous impact, even on human health.

Mining of certain metals, such as gold, silver, copper, iron, tin, lead, etc., has driven the development of human civilisation since ancient times, and thus has had strategic importance for ancient and modern societies. The region of NW Bulgaria has been a known mining centre for production of silver, lead and gold since Roman times, located in the present-day vicinity of the town of Chiprovtsi and the villages of Martinovo, Govezhda, Kopilovtsi and Diva Slatina. Mining in NW Bulgaria reached its highest intensity during the 1950s–1990s, as Chiprovtsi and Govezhda mining districts were considered as major producers of lead, silver and gold in the country. However, the main waste

products from mineral processing of the ores were arsenopyrite and pyrite. Thus, mining has increased the initial geochemical background of As and Pb related to local ore mineralisation in the area, by tens of times. The first studies on the pollution potential of the two tailing ponds in Chiprovtsi mining district (Mechi Dol and Golyam Bukovets), where the mineral processing waste was deposited, as well as the impact on the local vegetation and soils, were conducted by Vesselinov *et al.* (1996). Later on, more detailed research, outlining the heavy metal and arsenic pollution of the Ogosta River basin, was done by Kotsev (2001, 2003) right after mine closure. These studies were aimed to assess the load of heavy metal and arsenic pollution in the Ogosta River waters and floodplains, as well as in one of its main tributaries, the Chiprovtska Ogosta River. These studies continued on: 1) soils and vegetation in close proximity to the Golyam Bukovets tailing dam and its waters (Mladenova and Zlatev, 2004; Mladenova *et al.*, 2010); 2) the Chiprovtska Ogosta River waters and stream sediments (Kotsev *et al.*, 2010; Mladenova *et al.*, 2011; Ivanova *et al.*, 2011); 3) downstream Ogosta River floodplains (Mladenova *et al.*, 2008; Jordanova *et al.*, 2013; Mandaliev *et al.*, 2014; Simmler *et al.*, 2016; Senila *et al.*, 2016); and 4) bottom sediments of the Ogosta Reservoir (Ivanova *et al.*, 2011; Ivanova, 2013).

Our study, done in 2005–2007, aims to assess the pollution impact of mine waters and waste rock dumps on stream and drinking waters and soil in their immediate proximity, which has not been done previously. The use of modern analytical techniques, such as inductively coupled plasma atomic emission spectrometry (ICP-AES) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), allow us to obtain reliable and extensive data on geochemical composition of water, soil and bottom sediments (stream and mine workings) in the area. This information has implications for the post-mining current and future status of the environment in the area. Detailed geochemical studies on soil composition are rarely done, mainly in cases of mineral deposit prospecting, but not in most environmentally orientated researches. These studies will widen the knowledge of trace element composition of particular soil types in different areas in the world.

## MATERIALS AND METHODS

### Study area

The studied area is located in the vicinity of the town of Chiprovtsi and the village of Martinovo, Northwestern Bulgaria. A lead-silver and an iron deposits are located in the area (Chiprovtsi and Martinovo). The ore deposits are hosted by low-grade metamorphic rocks (marbles, meta-diabases and schists) of the Diabase Phyllitoid Complex (Precambrian–early Ordovician

age) (Kalvacheva, 1986; Carrigan *et al.*, 2003). The formation of the Martinovo skarn deposit is related to the intrusion of the Sveti Nikola granite ( $311.9 \pm 4.1$  Ma, Carrigan *et al.*, 2005), whereas the formation of the Chiprovtsi Ag-Pb deposit is still questionable, as both hydrothermal intrusion relation and strata-bound telethermal origins have been proposed (Atanassov and Pavlov, 1982; Dragov, 1993). The mineralisation in both deposits comprises Mo-W (molybdenite-scheelite), Fe (magnetite-pyrrhotite-arsenopyrite-löllingite-pyrite-siderite), Ag-Pb (galena-tetrahedrite-Ag-Sb sulphosalts) and fluorite-barite-calcite (with minor constituent of cinnabar) (Atanassov and Pavlov, 1982).

The mines that operated the two deposits underground for almost five decades ceased their operation after producing 4.79 Mt at 1.84% Pb and 14.0 Mt at 30.7% Fe (Milev *et al.*, 1996). Reclamation activities were carried out in the area in 2000–2008, covering the three tailing ponds and the numerous mine waste dumps. By the end of 2007, the lower-levelled waste rock dumps located in the Perchinki, Mali Dol, Zhazhkov Dol and Velin Dol mine sections were partially or completely remediated, while those in Yavorov Dol, Rupski Dol, Lukina Padina and Dolich mine sections were left untouched. The reclamation was carried out by stabilisation of the steep slopes and ground with slope erosion control grids and mesh, consolidating the 20-cm thick topsoil cover and subsequent grassing, mainly with clover. Our monitoring during 2006–2008 showed that the reclamation of the dumps was incomplete and inefficient. In most cases, the steep slopes of the waste rock dumps were not stabilised well or covered everywhere, thus pouring rainfalls during wet season (spring and late summer to early autumn) caused waste material slides, as most of the cover of the remediated slopes (mesh, grids and topsoil) were also torn and slid. Such events are relatively frequent because of the mountainous relief where the waste rock dumps are located, as well as of their very steep slopes with height about 30–50 m. Stream waters in some mine sections wash away the base of the dumps (Yavorov Dol). The fluorite mining, started in Lukina Padina mine section in 2010, was ceased in the beginning of 2016, due to quality fluorite reserve exhaustion. During operation, mine waste rocks were disposed in front of the audits, while flotation waste was mainly dumped at the Golyam Bukovets tailing impoundment.

### Sampling and sample preparation

Sampling took place during both wet (high water – May 2006, June 2007) and dry seasons (low water – September 2005, August 2006, and September 2007) in all mine sections in the vicinity of the Martinovo and Chiprovtsi mines. Samples were collected from: 1) mine waters discharging from the main adits in the Perchinki, Mali Dol, Zhazhkov Dol, Sinya Voda,

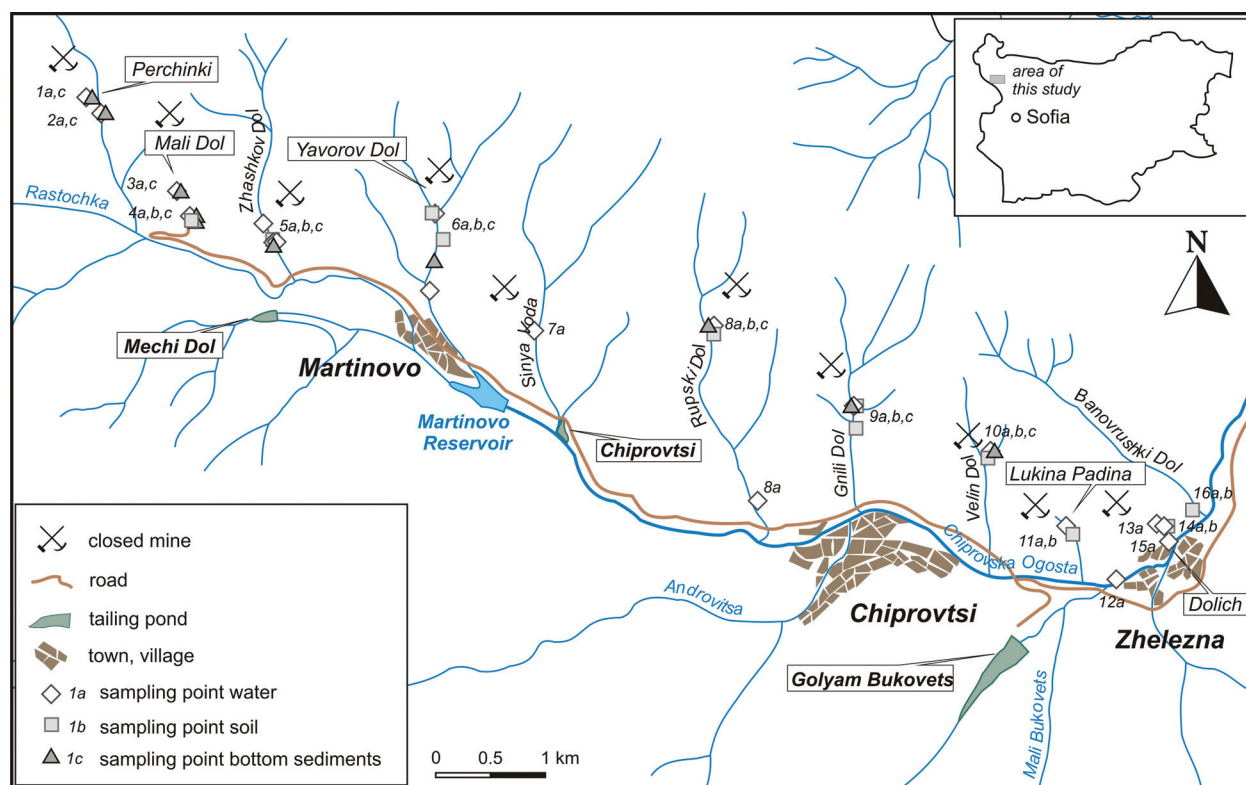
Gnili Dol, Velin Dol, Lukina Padina and Dolich mine sections and from stream waters in the Yavorov Dol and Rupski Dol mine sections; 2) drinking water from public fountains in the village of Zhelezna; 3) soils (meadow and cultivated) in close proximity to the waste dumps and streams from depth 0–20 cm; 4) bottom sediments from the adits and streams (Figure 1, Table 1). Sample locations were recorded with a hand-held Garmin-GPS device. Physico-chemical parameters of waters (pH, temperature, TDS and EC) were measured *in situ* with Combo HANNA and Ludwig Seibold portable equipment (pH-meter and conductivity meter). All water samples were collected according to the international water sampling guidelines (WHO, 1996), ISO 5667-3:1994 and ISO 5667-14:1998, updated versions in 2012 and 2014, respectively. Each 100-ml water sample was: collected in polyethylene bottle with a 50-ml syringe; *in situ* filtrated through 0.45 µm pore diameter membrane filters; and acidified separately with Merck Suprapur® acids: 5 ml HCl (for preservation of As and Sb), and 1 ml HNO<sub>3</sub> (for preservation of Pb, Cu, Zn and Cd). Mean and range of values of the physico-chemical parameters of waters measured during the five seasonal samplings are given in Table 1.

Soil samples (2.5–3 kg) were taken, using small shovel, and preserved in polyethylene bags. They

were dried at room temperature and subsequently dry sieved to fraction <0.063 mm. Fine-grained fractions were pulverized in agate mortar and 1 g of each sample was then digested several times in Merck Suprapur® HNO<sub>3</sub>, HF, HClO<sub>4</sub> and HCl to 25-ml solutions for analysis. In 2016, from the remaining quantities of some soil fractions <0.063 mm (5b2, 5b\*, 6b\*, 8b\*, 9b\*, 10b\*, 11b\*, 14b\*) were made Li-tetraborate fused pellets at 1050 °C for extended analysis of major and trace elements. Samples of bottom sediments were also dried at room temperature and pulverized in agate mortar.

## Analytical techniques

Water samples, separately acidified in the field with HNO<sub>3</sub> and HCl for preservation of Pb, Cu, Zn, Cd, As and Sb species, were analysed at the Geological Institute, Bulgarian Academy of Sciences, by inductively coupled plasma atomic emission spectrometry using HR-ICP-AES Jobin Yvon Ultima 2 in agreement with ISO 11885:1996 (updated in 2007 and referenced herein). Duplicate analyses of three water samples were performed by ICP-AES equipment at the Geochemistry Laboratory, University of Mining and Geology (Sofia). The solutions of digested soil samples were also analysed for concentrations of



**Fig. 1.** Location of the Chiprovtska Ogosta River basin, showing the mining area, tailing ponds and sampling points.

Table 1  
Sampling points, type of samples, parameters and description. For water parameters, mean values from five samplings are listed

Sample No.	Sampling place, coordinates	Water (a)				Soil (b) (0–20cm) <sup>a, b</sup>			Bottom sediments (c) <sup>b</sup>
		pH	TDS (ppm)	Eh (mV)	T (°C)	EC (μS/cm)	Distance (m)	Mineral composition (<0.063mm)	
1	Perchinki, 980 m, adit N 43°25'4.2" E 22°47'58.1"	7.7	193.0	185.3	8.4	364–570			Fine sand to coarse silt
2	Perchinki, 935 m, adit N 43°25'8.5" E 22°47'52.9"	7.7	209.5	197.2	7.2	382–722			Fine sand to coarse silt
3	Mali Dol, 860 m, adit N 43°24'42.8" E 22°48'26.6"	7.8	208.0	214.2	9.9	313–798			Coarse sand to coarse silt
4	Mali Dol, 810 m, adit N 43°24'35.7" E 22°48'33.5"	7.8	205.0	201.7	9.4	403–600	50 m from adit <sup>a</sup>	Qz, KFs, Chl, Ilt, Gth, OM	Coarse silt to coarse sand
5	Zhazhkov Dol, 760 m, adit N 43°49'27.7" E 22°49'5.0"	8.1	294.0	195.0	8.5	567–960	20 m from waste dump <sup>a, c, b</sup>	Qz, Ab, Chl, Amp, Ilt, Cal, Ank, Gth, OM	Coarse sand to coarse silt
6	Yavorov Dol, stream N 43°24'28.4" E 22°50'11.5"	8.0	106.0	176.2	14.3	209–410	30 m from waste dump <sup>a, c, b</sup>	Qz, Ab, Chl, Amp, Ilt, Sme, Cal, Ank, Gth, OM	Coarse sand
7	Sinya Voda, 620 m, adit N 43°24'2.16" E 22°50'46.54"	8.4	304.0	183.3	9.2	638–780			
8	Rupski Dol, stream N 43°24'1.5" E 22°51'57.1"	8.1	143.5	202.6	16.7	241–496	15 m from waste dump and 1.5 m from stream <sup>b</sup>	> 50% dump material, Qz, Ab, Ms, Chl, Amp, Ilt, Sme, Gth, OM	Very coarse sand
9	Gnili Dol, 570 m, adit, pond N 43°23'35.3" E 22°52'52.6"	8.2	161.0	215.0	15.8	344–575	Near pond <sup>d, c</sup> Near waste dump <sup>b</sup>	Qz, Ab, Chl, Amp, Ilt, Py, Gth, OM; Qz, Ab, Chl, Ms, Kfs, Ilt, Gth, OM	Coarse sand
10	Velin Dol, 550 m, adit N 43°23'27.1" E 22°53'43.7"	8.1	204.3	228.0	14.1	416–658	10 m from waste dump <sup>a, b</sup>	Qz, Ab, Chl, Ms, Kfs, Ilt, Sme, Gth, OM	Coarse sand to coarse silt
11	Lukina Padina, 495 m, adit N 43°23'5.0" E 22°57'17.2"	8.0	318.7	241.2	11.5	650–1200	3 m from waste dump <sup>a, b</sup>	Qz, Ab, Chl, Ms, KFs, Cal	

Table 1 (continued)

12	Zhelezna 1, fountain water N 43°22'52.2" E 22°54'33.6"	6.9	144.3	232.5	15.5	284–390	
13	Dolich, 445 m, adit N 43°23'7.8" E 22°54'49.9"	7.9	269.7	273.9	12.1	532–745	
14	Dolich, 410 m, drainage N 43°23'7.3" E 22°54'52.6"	8.3	251.0	225.0	21.3	534–599	3 m from waste dump <sup>b</sup> Qz, Ms, Illt, Chl, Ab, Cal, Illt, Sme, Py, Gth, OM
15	Zhelezna 2, fountain water N 43°23'3.2" E 22°54'54.3"	6.9	144.3	232.5	15.5	284–390	
16	Banovruski Dol, flood-plain N 43°23'13.2" E 22°55'9.12"					10 m from stream <sup>a</sup>	Qz, Ab, Chl, Illt, Kln, Gth, OM

Abbreviations of mineral names: Qz – quartz; Ab – albite; KFs – K feldspar; Chl – chlorite; Amp – amphibole; Ms – muscovite; Illt – illite; Kln – kaolinite; Sme – smectite; Gth – goethite; Ank – ankerite; Cal – calcite; Py – pyrite; OM – organic matter.

<sup>a</sup> samples taken in September 2005;

<sup>b</sup> samples taken in May 2006;

<sup>c</sup> two soil samples marked as **nb1**, **nb2** in the following text and figures, where **n** is sample number in Table 1. Samples taken from the same place during both sampling stages are referred as **nb\*** for May 2006 in figures.



Fe, Cu, Zn, Cd, Ag, Pb, Hg, As and Sb, using atomic absorption spectrometry (AAS) and ICP-AES at the Geological Institute. Mineral and phase composition of soil fractions was examined by X-ray diffractometry, using SIEMENS D 500 and DTA (Geological Institute, BAS). Major element composition of the soil fractions analysed in 2016 was determined by wet chemical analysis at the Geochemistry Laboratory of the Faculty of Geology and Geography, Sofia University. Major and trace element composition of these soil fractions was determined on Li-tetraborate pellets by LA-ICP-MS, using a New Wave UP193-FX excimer laser ablation system connected to PerkinElmer ELAN DRC-e ICP-MS. The laser was operated at constant 10 Hz pulse rate; laser energy was 10.05–10.30 J/cm<sup>2</sup> on the sample for 100 µm spot size. The following 61 isotopes were monitored: <sup>23</sup>Na, <sup>25</sup>Mg, <sup>27</sup>Al, <sup>29</sup>Si, <sup>31</sup>P, <sup>34</sup>S, <sup>39</sup>K, <sup>42</sup>Ca, <sup>45</sup>Sc, <sup>49</sup>Ti, <sup>51</sup>V, <sup>53</sup>Cr, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>59</sup>Co, <sup>62</sup>Ni, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>69</sup>Ga, <sup>73</sup>Ge, <sup>75</sup>As, <sup>77</sup>Se, <sup>85</sup>Rb, <sup>88</sup>Sr, <sup>89</sup>Y, <sup>90</sup>Zr, <sup>93</sup>Nb, <sup>95</sup>Mo, <sup>105</sup>Pd, <sup>107</sup>Ag, <sup>111</sup>Cd, <sup>115</sup>In, <sup>119</sup>Sn, <sup>121</sup>Sb, <sup>125</sup>Te, <sup>133</sup>Cs, <sup>137</sup>Ba, <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>146</sup>Nd, <sup>147</sup>Sm, <sup>151</sup>Eu, <sup>157</sup>Gd, <sup>159</sup>Tb, <sup>163</sup>Dy, <sup>165</sup>Ho, <sup>166</sup>Er, <sup>169</sup>Tm, <sup>173</sup>Yb, <sup>175</sup>Lu, <sup>178</sup>Hf, <sup>181</sup>Ta, <sup>182</sup>W, <sup>185</sup>Re, <sup>197</sup>Au, <sup>205</sup>Tl, <sup>208</sup>Pb, <sup>209</sup>Bi, <sup>232</sup>Th, <sup>238</sup>U. NIST SRM 610 glass standard was used as external standard. Data reduction was done, using SILLS ver. 1.1.0 software (Guillong *et al.*, 2008) and Si as internal standard. Element concentrations were determined in three spots in each sample and then averaged. Major and trace ele-

ments (29 elements) in bottom sediments were studied, using X-ray fluorescence (XRF), at the National History Museum in Berlin, Germany.

## RESULTS

### Waters

The measured *in situ* physico-chemical parameters of stream, drinking and mine waters during all five sampling seasons are similar. In Table 1 are given mean (for pH, Eh, TDS and temperature) and range (for EC) values. An increase of TDS and EC values was noted during dry season (August 2006 – Dimitrova *et al.*, 2006, 2007; and September 2007), which is probably a result of decreased water capacity. pH varies in close range between 6.90 (public fountain in the village of Zhelezna) and 8.76 (drainage water in Dolich section), around neutral pH. This is a result of the carbonate rocks (marbles) that host the ore mineralisation. Their large volume present in the waste dumps neutralises acid mine drainage formation and keeps the sulphide solubility low. Among the elements monitored in our study, only As and Pb were repeatedly detected in mine, and less in stream, waters (Table 2). They show concentrations that are above the maximum permissible levels (MPL) adopted in state regulations for

Table 2

Concentrations (µg/l) of elements in mine, stream and drinking waters determined during 2005–2007 monitoring. Sample numbers are as in Table 1

Sample No.	Sampling season <sup>a</sup>	Cu	Zn	Cd	Pb	As	Sb	Fe	Mo	Mn
1a	May 2006	14	8	9	275	119	–	–	70	8
	August 2006	–	–	–	–	149	–	–	109	3
	June 2007	–	–	–	–	254	–	10	–	5
	September 2007	–	–	–	–	203	–	14	–	120
2a	May 2006	14	9	9	265	71	–	–	46	4
	August 2006	–	–	–	–	77	–	–	50	–
	June 2007	–	–	–	–	111	–	6	–	–
	September 2007	–	–	–	–	98	–	–	–	–
3a	May 2006	68	12	4	34	140	–	–	5	3
	August 2006	24	19	–	–	144	–	2	219	–
	June 2007	–	–	–	–	198	–	7	–	–
	September 2007	–	–	–	–	187	–	6	–	–
4a	September 2005	–	1	3	26	162	3	131	–	9
	May 2006	14	332	–	–	114	4	–	24	5
	August 2006	–	–	–	–	147	–	–	221	–
	June 2007	–	10	–	–	86	–	9	–	343
	September 2007	–	–	–	–	240	–	12	–	19
5a1 <sup>b</sup>	September 2005	–	2	3	28	105	–	114	–	5
	August 2006	–	–	–	–	170	–	–	33	2
	June 2007	–	–	–	–	164	–	4	–	–
	September 2007	–	–	–	–	177	–	–	–	–

Table 2 (continued)

5a2 <sup>b</sup>	September 2005	–	1	5	66	12	–	115	–	4
	May 2006	–	–	–	–	–	–	–	1	1
5a3 <sup>b</sup>	May 2006	36	13	31	484	121	–	–	199	4
	August 2006	–	–	–	–	168	–	–	12	5
	June 2007	–	–	–	–	149	–	3	–	–
	September 2007	–	–	–	–	166	–	–	–	–
6a <sup>c</sup>	September 2005	1	–	4	30	1	–	136	–	9
	August 2006	–	–	–	–	10	–	–	–	15
	June 2007	–	–	–	–	–	–	33	–	6
	September 2007	–	–	–	–	45	–	8	–	19
7a	September 2005	–	18	5	61	21	13	124	–	55
	May 2006	27	15	8	171	31	–	–	9	23
	August 2006	–	–	–	–	23	–	–	24	8
	June 2007	–	15	–	–	69	2	11	–	23
	September 2007	–	9	–	–	88	–	82	–	175
8a	May 2006	24	4	7	142	14	–	–	–	1
	August 2006	–	–	–	–	–	–	–	–	2
	June 2007	–	–	–	–	–	–	13	–	7
	September 2007	–	–	–	–	29	–	17	–	–
9a1 <sup>d</sup>	September 2005	–	5	7	106	5	8	149	–	11
	May 2006	17	7	10	277	9	17	–	3	26
	August 2006	–	–	–	–	–	–	–	–	17
	June 2007	–	–	–	–	–	–	8	–	10
	September 2007	–	–	–	–	25	–	7	–	140
9a2 <sup>d</sup>	September 2007	–	–	–	–	45	46	14	–	21
10a	September 2005	–	3	4	47	–	–	118	–	5
	May 2006	14	8	11	264	7	–	9	–	7
	September 2007	–	–	–	–	23	–	–	–	–
11a1 <sup>e</sup>	September 2005	3	3	5	54	29	25	136	–	10
	May 2006	19	25	47	1456	34	18	–	9	29
	August 2006	–	–	–	–	20	–	–	16	5
	June 2007	–	–	–	–	44	27	8	–	15
	September 2007	–	–	–	93	58	43	7	–	–
11a2 <sup>e</sup>	June 2007	–	–	–	–	–	–	2	–	–
12a <sup>f</sup>	September 2005	2	7	7	90	–	–	124	–	3
	May 2006	4	6	–	–	–	–	–	–	3
13a	May 2006	11	10	11	431	8	25	–	37	1
	August 2006	–	–	–	–	13	–	–	58	–
	June 2007	–	–	–	–	–	28	15	–	4
	September 2007	–	–	–	77	35	–	1	–	–
14a	May 2006	8	7	8	259	7	21	–	42	11
15a	June 2007	–	–	–	–	–	–	9	–	–
	September 2007	–	–	–	–	–	–	5	–	–
16a	September 2005	4	–	2	–	–	–	144	–	20

“–” element not determined at limit of detection: 1) Sampling seasons September 2005, June and August 2006: Cu – 5 µg/l; Zn, Fe, Mn, Cd – 2 µg/l; Pb, Mo, Sb – 10 µg/l; As – 7 µg/l; 2) June 2007: As, Sb, Pb – 7 µg/l, Cu – 5 µg/l, Zn, Cd, Fe, Mn – 2 µg/l; 3) September 2007: Sb, Pb – 15 µg/l, As – 8 µg/l, Cu, Fe, Mn, Zn – 5 µg/l, Cd – 3 µg/l.

Samples 1a, 2a, 3a, 8a and 13a were not taken during September 2005 sampling. Concentrations of elements reported for 5a1–3, 9a2, 10a, 11a2, 14a, 15a and 16a are only for the season when they were taken.

<sup>a</sup> Concentrations of some elements determined in the analysed waters during September 2005, May and August 2006 sampling were initially reported in two conference papers (Dimitrova *et al.*, 2006, 2007).

<sup>b</sup> 5a1 – water sample from the adit, 5a2 – drainage water sample, 5a3 – water sample from ore chute.

<sup>c</sup> elements not determined at limit of the detection during May 2006 sampling.

<sup>d</sup> 9a1 – water sample from the adit, 9a2 – stream water.

<sup>e</sup> 11a1 – water sample from the adit, 11a2 – drainage water.

<sup>f</sup> elements not determined at limit of the detection during August 2006, June and September 2007.

surface and irrigation waters (Table 3), ranging from below detection limits (<d.l.) to 254 µg/l for As and up to 1456 µg/l for Pb. Arsenic was detected in mine and stream waters during all samplings, with gradual decrease of measured concentrations from west (71–254 µg/l) to east (5–88 µg/l) (Table 2). Lead concentrations in water samples were determined during the first two samplings, while later they were only occasionally detected. Such extremely high contents measured in wet season were probably related to high water capacity washing away bottom sediments enriched in lead precipitates. Other monitored elements, such as Cu, Zn, Cd, Mo, Mn, Fe and Sb, were also detected only in the course of 2–3 samplings. Copper and Zn contents are highest in 4a from Mali Dol section (Table 2). However, these contents are below the MPL for irrigation waters. On the other hand, the concentrations of Mo measured in samples collected in May and August 2006 are higher than the MPL for irrigation waters. Cadmium concentrations are relatively low. Their highest value was determined in mine water in the adit (11a1). Manganese and iron were rarely determined in water samples. Their concentrations are considered low, since MPL is much higher and they are most likely related to host rocks rather than ore mineralisation. Antimony in waters was measured for the first time in this study, since this element is not even included in the list of monitored elements in state regulations. Antimony was determined several times in samples from the central and eastern sections (7a, 9a1, 9a2, 11a, 13a, 14a) (Table 2). The detected concentrations of these elements correspond very well to the spatial distribution of different ore mineralisations within the area: 1) As-rich iron ore with arsenopyrite, löllingite and As-bearing pyrite (in the western mine sections: Perchinki, Mali Dol and Zhazhkov Dol) and molybdenite mineralisation (Perchinki section), explaining the high contents of As and Mo; 2) Pb-Zn-rich ore with galena, Pb sulphosalts, sphalerite and tetrahedrite-tennantite (in the central and eastern mine sections: Sinya Voda, Yavorov Dol, Rupski Dol, Gnili Dol, Velin Dol, Lukina Padina and Dolich), determining high Pb and moderate As contents, as

well as Sb. The concentrations of the monitored elements in the studied samples of drinking water were always below detection limits, with the exception of Cu and Zn, which were determined twice (in September 2005 and May 2006) in 12a, and Cd and Pb, which were determined once (September 2005) (Table 2).

Most of the studied mine waters discharging from adits flow into streams, which are tributaries to the Chiprovska Ogosta River (Fig. 1). In some cases, they form small ponds, as in Gnili Dol section, and are used both for irrigation and livestock watering place. Stream waters are often used for irrigation of small private gardens along them. Mine waters that eventually flow into stream waters dilute in them, thus concentrations significantly decrease, perhaps with the exception of As, which is the most mobile among them.

## Soils

Soils in the study area are classified as fluvisols and luvisols according to the Food and Agriculture Organization (FAO) (Ninov, 2002), but sampled soils belong mainly to fluvisol category. The mineral composition of all soil fractions (<0.063 mm) is similar (Table 1). Major minerals in all samples are quartz and albite/K-feldspar, in some samples (5b, 6b) chlorite, and around 5–10% of organic matter and iron hydroxides (goethite type). Minor minerals are chlorite, illite, amphibole, muscovite, kaolinite, smectite clay, calcite and ankerite. This corresponds to the rocks present in the area. Pyrite (<1%) was also identified in samples from Gnili Dol (9b) and Dolich (14b) sections. Particle size analysis shows that almost 50% of the particles in soil are with diameter less than 0.1 mm.

Soil samples collected in September 2005 and May 2006 were analysed for Cu, Zn, Pb, Fe, As and Ag. In 2016, an extended geochemical data (61-element concentrations) was obtained for eight samples (mainly collected in May 2006), using LA-ICP-MS analysis. The concentrations of Cu, Zn, Pb, As, Ag and Sb determined using the two different analytical techniques were similar, even almost equal for Ag; therefore, they were averaged in order to avoid ambiguity.

Table 3

*Maximum permissible levels (MPL) (µg/l) of Cu, Cd, Zn, Pb, As and Sb for drinking, surface and irrigation water and water parameters published in state regulations and by the World Health Organization (WHO)*

	pH	EC <sup>a</sup>	Fe	Cu	Zn	Cd	Pb	Mo	As	Sb	Reference
Semi-mountainous river surface water	6.0–8.5	750	50	5.2	40	–	–	–	25	–	Regulation No. N-4, 2012
Irrigation water	6.0–9.0	2000	5000	200	2000	10	50	10	100	–	Regulation No. 18, 2009
Drinking water	6.5–9.5	2000	–	2	4000	5	10	–	10	–	Regulation No. 9, 2001
Drinking water	6.5–8.5	–	300 <sup>b</sup>	2000	3000 <sup>b</sup>	3	10	70	10	20	WHO (2011)

<sup>a</sup> electrolytic conductivity measured in µS/cm at 20 °C.

<sup>b</sup> WHO (1996).



Major element composition of soils includes (in wt.%): SiO<sub>2</sub> (43.5–54.3), Al<sub>2</sub>O<sub>3</sub> (12.3–18.6), Fe<sub>2</sub>O<sub>3</sub> (4.1–10.1), FeO (0.4–2.8), MgO (2.1–3.4), CaO (0.8–4.1), Na<sub>2</sub>O (1.0–4.4), K<sub>2</sub>O (1.0–2.4), TiO<sub>2</sub> (0.64–1.09), MnO (0.09–0.26), P<sub>2</sub>O<sub>5</sub> (0.36–0.56). The relatively high content of Fe is probably related to chlorite, amphibole, Fe hydroxides and Fe-bearing carbonate, such as ankerite. Calcium content is mostly related to carbonates (calcite-ankerite). The other elements reflect major and minor mineral composition.

Determined concentrations of trace elements were compared to maximum permissible levels for cultivated soils (Regulation No. 3, 2008), concentrations in Bulgarian alluvial soils (fluvisols) (Naydenov and Travesi, 1977), other Bulgarian soils, world concentrations in fluvisols published by Kabata-Pendias (2001, 2011) and upper continental crust (Grigoriev, 2009; Rudnick and Gao, 2014) (Table 4) in order to assess their coefficient of enrichment (CE) in the studied samples.

In state regulation No. 3 (2008), as harmful elements subject to monitoring are listed Cr, Cu, Zn, Cd, As, Hg and Pb. Our results, excluding Hg, which was not measured due to absence in the used external standard, show that only As has concentrations (22.3–791 ppm) equal or higher (from 0.9 up to 31.6 times) compared to MPL (Table 5b, Fig. 2). The highest As contents (791 ppm) were measured in sample 6b1 (Yavorov Dol), which was collected from a place very near to a waste dump and was probably highly contaminated with ore-containing waste rock, since the determined concentrations of Cu (239 ppm), Zn (396 ppm), Pb (3900 ppm) and Ag (19.5 ppm) were also very high. Very high concentrations of these elements (Cu – 279 ppm, Zn – 279 ppm, Pb – 1720 ppm, As – 498.4 ppm) were determined in sample 6b2, which was also collected in the area, but much closer to the stream. As it is seen in Table 5b, As contents in soil samples also correspond to spatial distribution of ore mineralisation: highest in west sections, due to arsenopyrite-bearing ore, and relatively high in east sections, probably due to As-containing pyrite and tetrahedrite-tennantite (Dimitrova *et al.*, 2013). Lead exhibits higher concentrations than MPL also in 6b\* (CE = 4.4, 437 ppm) and 8b\* (CE = 5.7, 564.8 ppm) (Rupski Dol), and is almost equal to MPL in 14b\* (95.3 ppm) (Dolich). In other samples, it varies in the range of 24–81.9 ppm. Copper and Cd also have CE ≥ 1: Cu in 5b1 (179 ppm), 6b1 and 6b2 (239–279 ppm). Cd in 8b\*, 9b\*, 10b\*, 11b\* and 14b\* (2–4.1 ppm). Zinc concentrations vary between 69.1 ppm and 396 ppm, but only in 6b1 they are higher than MPL (CE = 1.2). Concentrations of Cu, Zn, Cd and Pb are also in agreement with ore mineralisation.

Data about most trace elements in different types of soils in Bulgaria is scarce. This study presents an extended geochemical data of eight soil samples (<0.063 mm) from the area. Comparisons with concentrations for elements reported in alluvial or other

Bulgarian soils and world soils (Table 4, Fig. 3a) highlighted specific features of these soils. Apart from the heightened concentrations of Cu, Zn, Cd, Pb and As, a result of local geochemical anomaly related to the mineral deposits and extensive mining, other trace elements also revealed considerable enrichment.

In Fig. 3a is seen that 42 elements have CE ≥ 1.5. Among them, 19 elements (Mo, Cs, W, Re, Ti, Mn, Co, Cu, Zn, As, Se, Cd, Sb, Te, Pb, Bi, Pd, Ag and Au) have CE ≥ 5 in some or all samples. The highest CE is exhibited by Te (up to 941), followed by Re (CE = 309), W (CE = 308 in one sample), Pb (up to 243), As (up to 233), Pd (up to 180), Ag (up to 167) and Au (up to 152). With the exception of Pd, the other elements have direct relation with the ore mineralisation. Their respective concentrations are given in Table 5. High Ag content is mainly due to Ag-bearing tetrahedrite-tennantite and other Ag sulphosalts in the ore mineralisation. Gold was determined rarely in the mineralisation as native gold associating with rare bismuth minerals (Dimitrova and Kerestedjian, 2006) or related with pyrite (Dimitrova *et al.*, 2012, 2013). Although economic reserves of Au were not determined during mining operation, concentrations in the range of 0.08–0.46 ppm seem quite high for soils (Table 5a). Tellurium content (2.8–5.6 ppm) is most likely also related to the mineralisation, although Te-bearing minerals were not found in the deposits. So far, data about Pd concentrations in minerals exist only for sphalerite (9.36 ppm) (Dimitrova, 2009). Thus, Pd could be also connected to the mineralisation or the host rocks. Antimony has the highest CE in 14b\* (14.6) and 10b\* (10.7), also related to the specific ore mineralisation there. As it can be presumed, most of the other elements with CE ≥ 5 are either connected to the mineralisation and host rocks (Ti, Mn, Fe) or the host rocks (Cs) (Table 5, Fig. 3a). Concentrations of other trace elements with CE ≤ 1.5 are given in Table 5. It appears that sample 14b\* is enriched in most of the elements, which is probably a combined influence of the host rock and the ore mineralisation.

Comparisons to the upper continental crust concentrations (Grigoriev, 2009; Rudnick and Gao, 2014; Table 4) revealed very similar picture as that to world and Bulgarian soils (Fig. 3b). However, Pd has the highest CE (up to 6904), followed by Te (up to 1946), Re (623), W (up to 276), Pb (up to 229), Ag (up to 413), As (up to 164), Au (up to 274), Se (up to 120), Cd (up to 46), Bi (up to 34), Sb (up to 30), Cu (up to 10) and Mn (up to 9). The elements with CE 1.5 ≤ 7 are: Cu, Zn, Ge, Ga, In, Sn, Co, Mn, S, Ni, Cs, Mo, P, Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, V, Cr.

### Bottom sediments

The concentrations of major (Si, Al, Ti, Fe, Mn, Ca, Mg, Na, K, P, S) and trace (As, Ba, Bi, Co, Cu, Zn, Mo, Pb, Th and Zr) elements in bottom sediments were determined (Table 6). Since these are bottom

Table 4

Element contents in the upper continental crust and soils, as well as maximum permissible levels (MPL) in soils used for comparisons. Concentrations of major elements (Na, Mg, Al, K, Ca, Si, Ti and Fe) are given in wt.%; all others are in ppm

Element	Lithophile elements <sup>a</sup>																					
	Na	Mg	Al	K	Ca	Rb	Sr	Y	Zr	Nb	Mo	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	
Content in soil <sup>b</sup>	–	–	1.0–5.0	–	–	173.5 <sup>c</sup>	147	12	300	12	0.3–4.6 <sup>d</sup>	2.58 <sup>c</sup>	691.5 <sup>c</sup>	20.1 <sup>c</sup>	31.9 <sup>c</sup>	13.4–5.0 <sup>d</sup>	14.9 <sup>c</sup>	3.38 <sup>c</sup>	0.74 <sup>c</sup>	10.3–11.0 <sup>d</sup>	0.66 <sup>c</sup>	
Upper crust <sup>e</sup>	2.43	1.50	8.15	2.32	2.57	84	320	21	193	12	1.1	4.9	628	31	63	7.1	27	4.7	1.0	4.0	0.7	
Element	Lithophile elements										Non-metals				Siderophile elements							
	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Si	P	S	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	
Content in soil <sup>b</sup>	8.6–11.00 <sup>d</sup>	1.7–2.0 <sup>d</sup>	1.7–4.8 <sup>d</sup>	0.54–0.80 <sup>d</sup>	1.15 <sup>c</sup>	0.24 <sup>c</sup>	3.37 <sup>c</sup>	0.36 <sup>c</sup>	1.7	0.0004	54	–	–	7.65 <sup>c</sup>	0.11 <sup>c</sup>	69 <sup>d</sup>	91 <sup>c</sup>	488	2.13 <sup>c</sup>	6.45 <sup>c</sup>	29	
Upper crust <sup>e</sup>	3.9	0.83	2.3	0.30	1.96	0.31	5.3	0.9	1.9	0.000198	31.15	654.7	621	14	0.38	97	92	774.6	3.92	17.3	47	
MPL <sup>g</sup>																	200				110	
Element	Chalcophile elements										Radioactive elements						Noble elements					
	Cu	Zn	Ga	Ge	As	Se	Cd	In	Sn	Sb	Te	Tl	Pb	Bi	Th	U	Pd	Ag	Au			
Content in soil <sup>b</sup>	38.9	62 <sup>d</sup>	15.2	1.3 <sup>d</sup>	3.4 <sup>d</sup>	0.44	0.42 <sup>d</sup>	0.06	1.7 <sup>d</sup>	0.82 <sup>c</sup>	0.006	0.5	16–22 <sup>d</sup>	0.42	5.05 <sup>c</sup>	1.9–4.4	0.02	0.13	0.003			
Upper crust <sup>e</sup>	28	67	17.5	1.4	4.8	0.09	0.09	0.056	2.1	0.4	0.0029 <sup>f</sup>	0.9	17	0.16	10.5	2.7	0.00052	0.053	0.0015			
MPL	150	320			25		2						100									

<sup>a</sup> element arrangement according to Solodov *et al.* (1987)

<sup>b</sup> average concentrations of elements in world soils (Kabata-Pendias, 2011)

<sup>c</sup> concentrations of elements in alluvial soils from Bulgaria (Naydenov and Travesi, 1977)

<sup>d</sup> average or range of concentrations for alluvial soils in the world and concentration of Mo, Zn, As and Cd in soils from Bulgaria (Kabata-Pendias, 2001)

<sup>e</sup> concentrations of elements in upper continental crust (Rudnick and Gao, 2014)

<sup>f</sup> concentration of Te in upper continental crust (Grigoriev, 2009)

<sup>g</sup> maximum permissible levels of concentration (Regulation No. 3, 2008)

Table 5

Concentrations of trace elements<sup>a</sup> in soil fractions (<0.063 mm) determined by: a) only LA-ICP-MS (ppm); b) ICP-AES (4b, 5b1, 6b1, 6b2, 9b, 10b, 11b, 16b) (µg/l) and mean values of ICP-AES and LA-ICP-MS measurement (5b2, 5b\*, 6b\*, 8b\*, 9b\*, 10b\*, 11b\* and 14b\*)

a)

Sample No.	5b2	5b*	6b*	8b*	9b*	10b*	11b*	14b*
Rb	53.44	42.19	52.40	51.46	49.11	65.77	61.47	106.68
Sr	312.60	164.53	131.30	134.38	113.84	124.30	163.19	103.95
Y	22.69	13.98	15.18	21.90	19.47	16.89	23.90	37.85
Zr	152.85	112.88	105.96	154.57	155.46	129.50	172.80	171.77
Nb	6.66	4.88	4.12	7.40	7.38	4.66	7.92	8.93
Mo	2.41	1.23	1.12	1.94	<1.02	1.37	4.05	2.78
Cs	4.36	3.27	5.53	8.29	6.80	14.35	9.93	23.93
Ba	461.67	332.98	549.15	392.00	368.53	467.58	464.23	655.99
La	27.49	15.22	13.93	20.42	18.23	15.99	21.77	31.42
Ce	57.70	32.29	28.67	43.75	38.19	33.95	46.52	66.55
Pr	6.81	3.68	3.56	5.09	4.50	4.04	5.56	8.18
Nd	28.21	14.89	15.68	21.14	18.70	17.25	23.76	35.15
Sm	5.34	3.01	3.23	4.58	3.70	3.57	5.36	8.25
Eu	1.54	0.84	0.93	1.18	1.00	0.92	1.44	2.29
Gd	4.96	2.74	3.31	4.30	3.55	3.36	4.92	8.93
Tb	0.69	0.44	0.43	0.62	0.55	0.48	0.73	1.29
Dy	4.12	2.34	2.50	3.93	3.14	2.80	4.21	7.39
Ho	0.75	0.48	0.52	0.77	0.70	0.60	0.83	1.35
Er	2.34	1.47	1.51	2.25	2.17	1.87	2.40	4.05
Tm	0.31	0.20	0.22	0.31	0.26	0.26	0.32	0.57
Yb	1.98	1.48	1.39	2.15	2.09	1.54	2.28	3.63
Lu	0.29	0.20	0.19	0.31	0.28	0.24	0.37	0.48
Hf	3.60	2.94	2.75	3.84	3.84	3.29	4.28	4.27
Ta	0.43	0.29	0.27	0.49	0.50	0.36	0.49	0.63
W	6.10	27.50	12.30	3.89	3.84	522.94	5.20	12.14
Re	<0.13	<0.11	0.12	<0.14	<0.16	<0.23	<0.11	<0.13
S	2613.15	1931.61	2059.62	2644.07	1563.95	1694.91	1520.84	2328.04
Sc	24.54	20.69	19.32	18.89	21.83	22.14	25.03	31.68
V	138.92	124.73	131.61	125.13	136.36	139.07	143.05	177.18
Cr	135.91	117.99	129.19	110.41	123.28	152.07	118.21	158.11
Co	21.47	16.30	21.12	19.62	20.17	56.09	22.96	27.43
Ni	49.67	47.75	65.50	42.83	49.74	63.38	52.85	83.53
Ga	21.50	20.36	26.42	17.97	23.79	26.92	25.00	31.90
Ge	3.71	2.36	2.41	<3.00	<4.12	<3.62	3.50	4.80
Se	5.61	<6.23	<6.03	<5.89	<7.14	10.80	<5.33	9.02
In	0.14	0.08	0.13	0.13	<0.09	0.08	0.09	0.16
Sn	2.02	1.93	2.55	2.36	2.10	3.60	1.74	3.05
Sb	3.22	1.99	7.66	7.12	7.26	15.82	7.76	15.56
Te	3.07	2.85	4.70	4.31	3.92	5.58	3.10	5.65
Tl	0.31	0.27	0.31	0.30	0.37	0.54	0.36	0.95
Bi	5.46	0.86	0.40	0.25	0.49	0.48	0.24	0.41
Th	4.83	3.27	2.72	3.85	4.14	2.67	5.04	7.56
U	1.79	1.56	1.22	2.12	1.61	1.45	2.22	3.28
Pd	0.18	0.26	3.59	<0.15	<0.19	2.05	0.37	0.19
Au	0.41	0.27	0.41	0.08	0.38	0.40	0.28	0.46

<sup>a</sup> element arrangement according to Solodov *et al.* (1987)

Table 5 (continued)

b)

Element	4b	5b1	5b2	5b*	6b1	6b2	6b*	8b*	9b	9b*	10b	10b*	11b	11b*	14b*	16b
Cu	59.00	179.00	106.31	51.25	239.00	279.00	110.95	70.72	49.00	38.03	40.00	92.67	71.00	56.28	71.21	65.00
Zn	–	–	119.38	62.38	396.00	279.00	91.38	116.24	88.00	69.12	90.00	98.81	94.00	84.40	117.69	–
As	63.25	359.34	402.22	86.97	791.00	498.38	121.65	49.31	22.31	40.61	33.28	38.52	130.73	107.47	158.83	72.68
Cd	–	–	1.90	1.97	–	–	1.98	2.00	–	4.14	–	4.09	–	3.41	2.49	–
Pb	52.00	24.00	81.87	25.20	800.00	800.00	437.30	564.84	55.00	38.92	69.00	67.17	23.00	42.97	95.31	54.00
Ag	5.23	6.90	1.86	0.54	19.54	21.90	3.03	2.64	2.69	0.66	2.20	0.76	1.86	0.80	1.32	7.87

“–” element not determined at limit of detection: Cu – 5 µg/l; Zn, Fe, Mn, Cd – 2 µg/l; Pb, Mo, Sb – 10 µg/l; As – 7 µg/l

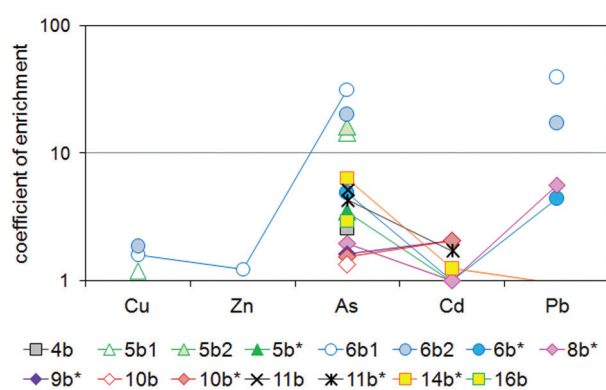


Fig. 2. MPL normalised patterns for Cu, Zn, As, Cd and Pb in soils.

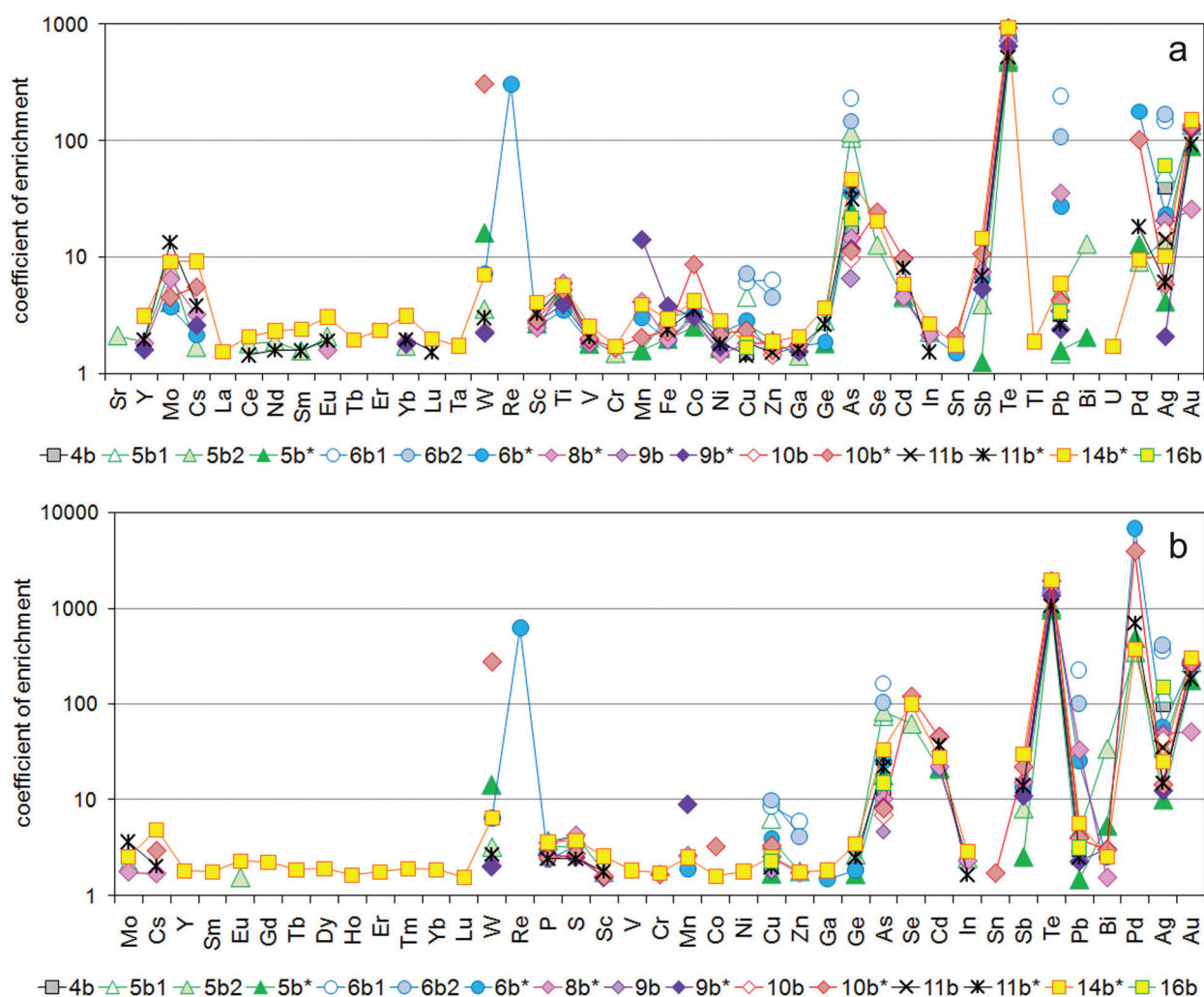
sediments from the adits (1-5c, 9-10c) and streams (6c and 8c), it is most suitable to compare them to the upper crust concentrations. As it is seen in Fig. 4, Bi has the highest CE (1094), followed by As (812), Pb (282), Mo (123), Mn (16), Cu (12), Zn (8) and Fe (6). Major element composition (Table 6) is related mainly to the host rocks. The high-Fe content (13.2–24.4 wt.%) in samples from the western area (1-2c, 4c1, 4c2, 5c) is probably related to the presence of also siderite and magnetite-pyrrhotite-pyrite ore. The contents of S (0.12–0.44 wt.%) and Mn (0.53–1.23 wt.%) support this. The contents of elements related to ore mineralisation (*i.e.*, As, Bi, Mo, Cu, Pb, Zn) in different samples correspond to the spatial distribution of the ore mineralisations: high As concentrations (1850–3900 ppm) mostly in the western area and high Pb concentrations (777–4790 ppm) in the central and eastern parts. Molybdenum also has higher content in bottom sediments from adits in the western area. The concentrations of Cu are 76–337 ppm, while for Zn they are 91–573 ppm. On the other hand, V concentrations increase in the samples from the adits in the

eastern part, probably related to elevated V content in pyrites.

## DISCUSSION

The determined concentrations for elements in waters show considerable decrease compared to the values published by Kotsev (2003), especially for As and Pb. There is no previous data about Sb in water and soil to compare with. Although the solubility of Sb increases in waters with pH 7–9 (Longmuir, 1997; Alderton *et al.*, 2005), the determined concentrations in mine waters (mainly in the eastern mine sections) are closed to guideline values published by WHO (2011) for drinking waters. Although there is no MPL for Sb in soil, the concentrations of Sb could be considered low or at least a geochemical background for the region. The high CE of Sb in 10b\*, 11b\* and 14b\* is most likely related to As- and Sb-bearing pyrite rather than tetrahedrite-tennantite minerals in the waste as in 6b\*, 8b\* and 9b\*.

The main problem in the area (for water and soil) remains As, and to a lesser extent Pb. It was expected that their concentrations would be high in waters discharging from adits. These predominantly vadose waters became saturated with As and Pb while they ran through the abandoned underground mine workings and washed away fine material from the bottom sediments, which revealed to be highly concentrated with As and Pb (Fig. 4, Table 6). Bottom sediments in flooded underground mine workings usually contain large amount of ore particles (with arsenopyrite, pyrite, galena, etc.), remaining during mining operation. Their interaction with water (oxidation) ultimately drives the mobilisation of As, Pb, Sb, Cu, Zn, etc. Since the major source of As are arsenopyrite and pyrite, the rate of As mobilisation in waters and soil would depend on their behaviour during oxidation either in water or in air. Pyrite is considered more susceptible to oxidation in water or air than arsenopyrite. The smaller the pyrite grains are the larger is the reac-



**Fig. 3.** Trace elements in soils: a) normalised to concentrations in Bulgarian and world fluvisols (Table 4); b) normalised to concentrations in the upper continental crust (Table 4).

tive surface (Nicholson *et al.*, 1988). Pyrite oxidation is usually the major reason for acid mine drainage. However, in the studied area, this process is limited by the carbonate host rocks, which retain pH of waters circumneutral (6.9–8.4, Table 1), thus also limiting the oxidation process (Nicholson *et al.*, 1990) through Fe(II) being adsorbed, blocking further reactivity of Fe(III) in the Fe(III) oxyhydroxide (Moses and Herman, 1991; Todd *et al.*, 2003a). However, pyrite oxidation in air results in formation of water-soluble Fe sulphates, which incorporate other metalloids and metals included in pyrite, thus assisting their spreading during sulphate dissolution. In the studied area, the As concentrations detected in waters and soil from the central and eastern mine sections are mainly related to oxidation of As-bearing pyrite (up to 4.8 wt.% As) (Dimitrova *et al.*, 2007, 2013). In the western mine

sections, where arsenopyrite is a major component of the ore, the determined concentrations of As in waters, bottom sediments and soil are related mostly to arsenopyrite oxidation. Arsenopyrite stability is controlled by temperature, pH and Eh of the environment, so are the resulting arsenite and arsenate species. Taking into account the measured temperature, pH and Eh of waters in adits (Table 1), the arsenopyrite dissolution should be lower than that calculated for 25 °C by Craw *et al.* (2003). The formation of micron-scale protective oxide layer on arsenopyrite grain surfaces (Fe(III) oxyhydroxides and scorodite) during initial oxidation passivates further oxidation reactions (Nesbitt and Muir, 1998). At these conditions, the protective layer and dissolved As(V) are stable. However, equilibrium in an open system, like the environment, is impossible, because it changes constantly and the leaching



Table 6

Concentrations of major (Na, Mg, Al, K, Ca, Si, Fe) (wt.%) and trace elements<sup>a</sup> (ppm) in bottom sediments. Manganese, S and P are given in ppm

Sample No.	1c	2c	3c	4c1	4c2	5c	6c	8c	9c	10c
Na	1.06	0.64	2.97	0.64	1.85	0.99	2.31	2.46	1.29	1.30
Mg	1.39	1.45	1.48	1.48	1.49	1.40	1.84	1.32	1.08	0.56
Al	5.19	4.76	8.84	3.44	5.98	4.34	7.46	7.52	7.52	9.48
K	0.99	1.00	1.06	0.58	0.80	0.61	0.80	0.91	1.42	1.66
Ca	5.64	9.15	0.89	9.51	3.82	11.65	4.26	2.64	7.36	6.30
Rb	53	44	60	25	37	34	41	51	69	80
Sr	176	173	149	162	133	239	210	201	126	195
Y	11	10	14	<10	<10	<10	11	23	10	23
Zr	119	85	130	63	99	66	148	292	146	153
Nb	10	10	<10	14	12	10	<10	<10	<10	<10
Mo	135	45	<10	51	28	38	<10	<10	15	<10
Ba	471	782	350	389	456	340	464	388	594	579
Si	17.58	15.80	24.45	11.69	20.24	14.35	22.35	26.55	20.10	20.99
P	1222	1353	698	655	698	873	786	698	829	698
S	1201	2002	400	2403	2403	4405	400	400	801	400
Ti	0.37	0.34	0.29	0.26	0.29	0.28	0.58	0.73	0.50	0.54
V	72	72	124	54	78	62	151	158	120	124
Cr	23	20	81	<15	<15	<15	112	129	83	106
Mn	5887	8598	3950	12316	5267	5500	5190	2246	3408	1627
Fe	13.29	13.92	4.58	24.41	16.29	14.90	5.87	4.71	5.07	4.80
Co	24	25	18	30	20	18	<15	<15	15	25
Ni	24	<15	36	<15	<15	<15	<15	16	<15	50
Cu	189	337	76	185	184	233	197	84	297	102
Zn	377	573	91	154	214	211	199	140	192	106
As	1850	3900	730	2500	3870	2580	775	<30	420	245
Pb	291	144	51	131	221	88	1517	777	4790	160
Bi	<30	125	<30	165	<30	175	<30	150	<30	<30
Th	<10	11	<10	15	<10	15	<10	<10	<10	<10
U	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

<sup>a</sup> element arrangement according to Solodov *et al.* (1987)

of As proceeds. The contamination of soils with As is realised through introducing of As-contaminated water, raw As-bearing mineral particles, or both. In

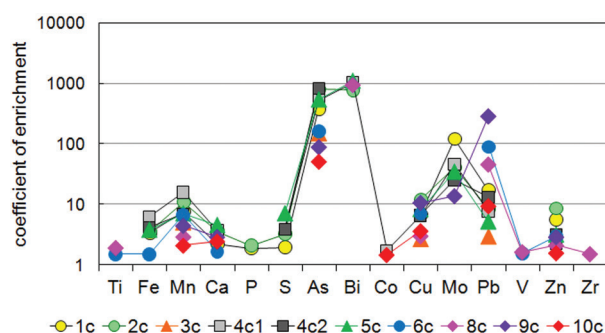


Fig. 4. Upper continental crust normalised patterns of trace elements in bottom sediments.

the area, the contamination occurred both ways, but mostly through water-sludge discharging during earlier mining operation before the construction of tailing dams into the Chiprovka Ogosta River. This caused severe contamination, detected far away from the source in the lower downstream Ogosta River floodplains (Mladenova *et al.*, 2008; Jordanova *et al.*, 2013; Mandaliev *et al.*, 2014; Simmler *et al.*, 2016; Senila *et al.*, 2016). However, soils in close proximity to waste dumps and adit water discharges bear weaker but constant influence of mine waters and arsenopyrite/As-containing pyrite particles distributed by slides now and then. The particle weathering in soils goes either in fairly reduced or in highly oxidic conditions in presence of pore water with some dissolved organic acids and microorganisms in much wider temperature range. Therefore, oxidation in soils would proceed more rapidly due to diffusion of As from bulk to oxidised surface and subsequent leaching, as suggested by Nesbitt

*et al.* (1995), local acidification around weathered particles, causing dissolution of otherwise stable Fe(III) oxyhydroxides (Yu *et al.*, 2007), and influence of biogenic activity (Corkhill and Vaughan, 2009). Disintegration of initial ore grains during weathering into fine particles accelerates the oxidation process and release of As. As it was determined by Mandaliev *et al.* (2014), the dominant As speciation in soils would be As(V) adsorbed to ferrihydrite and/or presence of As(V)-rich hydrous ferric oxides. However, the determined high As contents in 6b1 and 6b2 are probably in larger part related to the presence of fine (micro-scale sized) arsenopyrite/As-containing pyrite particles, as well as of As adsorbed to Fe oxyhydroxides (goethite) identified in all soil samples. Outer-sphere adsorption of As may occur also on clay minerals, such as montmorillonite, carbonates, etc. (Foster and Kim, 2014). The highest As contents in bottom sediments are also a result of the presence of adsorbed As species (arsenates [As(III)] and arsenates [As(V)]) onto clay and Fe oxide-hydroxide particles and partly weathered arsenopyrite grains.

As it was mentioned before, Pb is the other potential contaminant of the environment (water and soil) in the studied area, as it was detected during two seasonal samplings of waters and soils in concentrations several times above the MPL. It is known that galena, as well as the other major sulphides as chalcopyrite and sphalerite, are easily dissolved in low pH conditions, especially in presence of Fe in the form of pyrite (Gleisner and Herbert, 2002). Their behaviour in circumneutral pH solutions, however, would decrease their oxidation rate. Galena weathering leads to formation of a stable  $\text{PbSO}_4$  (anglesite), which initially passivates further oxidation, but in carbonate buffered media this phase is transformed into cerussite (Lara *et al.*, 2011). During progressive weathering of galena, anglesite and cerussite disappear (Keim and Markl, 2015). Ultimately, the concentration of Pb in waters is controlled by the presence of  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  ions in mine waters (Blowes and Ptacek, 1994), which in dry season would likely precipitate. Voegelin *et al.* (2011) concluded that weathering of sphalerite grains in soil at neutral pH and presence of carbonate minerals is quicker, with formation of Zn-bearing layered double hydroxides. Oxyhydroxides ( $\text{FeOOH}$ ) and sulphates are formed during chalcopyrite oxidation at neutral pH; however, sulphates are soluble and do not remain on the oxidised surface in aqueous media (Todd *et al.*, 2003b). Formation of oxyhydroxides is a step in the process of mobilisation of As, Pb, Cu, Zn and Cd (from sphalerite). The quantity of contaminant source minerals in the waste rock dumps and bottom sediments in adits and streams controls the rate of contamination in the area. Since the main waste minerals of mining and processing are arsenopyrite and pyrite (As-bearing), their transformation determines the dominant As contamination in the area.

The comparisons to concentrations of elements in Bulgarian and world fluvisol soils, as well as in the upper continental crust, revealed strong genetic dependence for most of the elements with  $\text{CE} \geq 1.5$  on geological setting, host rocks and mineralisation, respectively. Elements with the highest CE are predominantly related to the ore mineralisation. Not all of them are released due to oxidation process and mobilised. Some of them (Ag, Au) tend to occur as native metal form and undergo passive transportation as particles. Some Ag content is exsolved as native Ag or acanthite from Ag-rich tetrahedrite-tennantite. The introduction of Co, Ni, Ga, Ge, Sn, In, Bi, Se, Sb, Te, Tl, Pd in soils is related to weathering of the major host minerals (*i.e.*, pyrite, arsenopyrite, galena and sphalerite). However, the speciation of their occurrence is not well studied. Supposedly, in ion form, they are adsorbed onto clay and iron oxyhydroxide minerals, form complexes with arsenates, or are included in micro-scale sulphide mineral particles ( $<0.063$  mm).

## CONCLUSIONS

The determined concentrations of main pollutants (As, Pb, Cu, Zn and Sb) in waters (mine and stream), soils and bottom sediments correspond to spatial position of ore mineralisation in a west-east direction. The source of the pollutants remains on site (washed away material from underground workings and waste dumps and extensive weathering), thus causing further contamination, probably not in high extent as during mining operation. The reclamation done in the area is incomplete and failed to diminish and limit the mining impact. The carbonate-containing host rocks of the ore mineralisation prevent acid mine drainage formation and retain pH in circumneutral range, thus affecting the oxidation of sulphide waste and slowing down the mobilisation of pollutants. The extended geochemical data of soils revealed increased concentrations of: 1) elements that are related to soil mineralogy (lithophile and radioactive elements, non-metals, partly siderophile elements); 2) elements related to ore mineralisation (chalcophile, siderophile and noble elements). These characteristics imply specific geochemical background in the area, predetermined by the geological setting.

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