Heavy metals and metalloids content assessment in mine waters from Martinovo and Chiprovtsi mines, Northwestern Bulgaria

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Introduction

Mine waters are rich source of heavy metals and metalloids in dissolved state with potential toxicity to the environment, especially when they unrestrained discharge in streams and rivers. Although their concentrations decrease, due to dilution by surface waters, or as a result of absorption by channel sediments, for some mobile elements, such as arsenic, they remain much higher compared to the maximum permissible concentration for surface waters. The monitoring of the seasonal dynamics and contents of the potential pollutants in mine waters will help in prediction and prevention of possible surface and drinking water contamination in concentrations above the guideline values. In Chiprovtsi and Martinovo mines vicinity is observed a typical case of mine waters discharging into small streams, which in turn flow into the Chiprovska Ogosta river. This additionally contributes in Chiprovska Ogosta river pollution.

Geology and mining history of the Martinovo iron and Chiprovtsi silver-lead deposits

The Martinovo iron and Chiprovtsi silver-lead deposits are hosted in the low-grade metamorphic rocks (marbles and schists) of the Diabase Phyllitoid Complex (Precambrian — Early Ordovician age) (Kalvacheva, 1986; Carrigan et al., 2003)), intruded by Sveti Nikola granite of 313.8$\pm$3.5 Ma age (Carrigan et al., 2005). The mineralizations in both deposits comprise of Mo-W (molybdenite-scheelite), Fe (magnetite-pyrrhotite-arsenopyrite-loellingite-pyrite-siderite), Ag-Pb (galena-tetrahedrite-Ag-Sb sulphosalts) and fluorite-calcite (with minor constituent of cinnabar) (Atanassov, Pavlov, 1983). Chiprovtsi and Martinovo mines are known to be exploited from Roman times, through Middle Ages, most intensively from 1950 to 1999, when both mines are closed. Remediations activities have been carried out in the region since 2000 year, which covered not only the three tailing impoundments, but the numerous mine spoil heaps too. At present all mine spoil heaps are partially or completely remediated, except those in Rupski Dol, Lukina Padina and Dolich mine sections.

Materials and methods

Sampling took place during both dry (September 2005) and wet seasons (May 2006) in all mine sections in the Martinovo and Chiprovtsi mines. Samples were collected from mine waters discharging from the main adits in the Perchinki, Mali Dol, Zhazhkov Dol, Gnili Dol, Velin Dol, Lukina Padina and Dolich mine sections and from stream waters in the Yavorov Dol and Rupski Dol mine sections. One sample of drinking water was collected from public fountain in the village of Zhelezna, located near Dolich mine section. Sample locations were recorded with a handheld Garmin-GPS device. Physico-chemical parameters of waters (pH, Eh, T and EC) were measured in situ with Ludwig Seibold portable equipment (pH-meter and conductivity meter). All water samples were collected according to the international water sampling guidelines (WHO, 1996). Each 100 ml water sample was collected in polyethylene bottle with 50 ml syringe; in situ filtrated through 0.45 μm pore diameter membrane filters, and acidified separately with supra pure acids: 5 ml HCl (for As and Sb), and 1 ml HNO_3 (for Pb, Cu, Zn and Cd). The contents of As, Sb, Pb, Cu, Zn and Cd in the samples were determined by inductively coupled plasma atomic emission spectroscopy using HR-ICP-AES Jobin Yvon Ultima 2 in agreement with ISO 11885:1996(E) at the Geological Institute, BAS.

Results and Discussion

The measured in situ physico-chemical parameters of mine waters slightly differ during September 2005 and May 2006, but distinct increase of the measured temperature and Eh and decrease of conductivity is observed during wet season for all sampled waters. This is not valid for pH, which ranges from 6.90 (drinking water) up to 8.54 (Zhazhkov Dol, May 2006), but remains almost equal to neutral-circumneutral pH, due to the carbonate-buffering by the host rocks (siderite marbles). This also prevents acid mine drainage (AMD) generation discharge from the mines and retains the sulphides dissolution ability low. The estimated total concentrations of heavy metals and metalloids in the waters collected in May 2006 are insignificantly higher than those collected in September 2005, except for the lead contents, which are several times higher than September contents (table 1, fig. 1).

The observed concentrations of each element show apparent correlation with the particular mineralization in each mine section. The highest arsenic concentrations are determined in the mine waters from Perchinki, Mali Dol and Zhazhkov Dol mine sections, where the ore is strongly enriched with arsenopyrite and loellingite. Similarly to this, the highest lead and antimony concentrations determined in waters from Sinya Voda, Gnili Dol, Lukina Padina and Dolich mine sections are related to the galena-tetrahedrite containing ore in Chiprovtsi mine.

Previous mine waters investigation carried out by Kotsev (2001, 2003) compared to this study shows considerable decrease in the lead, zinc, copper, cadmium and arsenic contents in mine waters at present, probably resulting from the mining activity end. However, the lack of data about antimony concentration in mine waters, especially from Lukina Padina and Dolich mine sections, did not allow us to correlate the obtained data in this study to previous investigations. Antimony was not examined in mine waters in Bulgaria so far, because of its insignificant quantity in the processed ores. Taking into account its presence in the mined ores from Chiprovtsi mine and its behavior and toxicity to the environment, we decided to examine its concentration in mine waters and explore whether it could be, or is a potential pollutant of the waters in the study area. The determined total antimony concentration in 5 from 15 water samples does not exceed 25 μg/l, which is slightly above the maximum permissible limits (MOEW, 2001) and WHO guideline values (WHO, 2004), but antimony was not found in surface and drinking water (table 1, 2).

Table 1. Physico-chemical parameters of waters and total Cu, Cd, Zn, Pb, As and Sb concentrations (in μg/l) in mine, surface and drinking waters in the region measured in September 2005 and May 2006

Таблица 1. Физикохимични параметри на водите и общи концентрации на Cu, Cd, Zn, Pb, As и Sb (в μg/l) в руднични, повърхностни течащи и питейни води в района измерени през септември 2005 и май 2006

№	Sampling place (mine section and level)	Sampling season	pH	Eh (mV)	T (°C)	EC (μScm^{-1})	Cu (μg/l)	Zn (μg/l)	Cd (μg/l)	Pb (μg/l)	As (μg/l)	Sb (μg/l)
1.	Perchinki, 940, adit	September 2005	-	-	-	-	-	-	-	-	-	-
		May 2006	7.75	157.2	9.7	387	14	08	9	275	119	-
2.	Perchinki, 900, adit	“	-	-	-	-	-	-	-	-	-	-
			7.54	189.3	7.8	382	11	9	9	265	71	-
3.	Mali Dol, 810, adit	“	8.16	184.0	10.0	403	1	1	3	26	162	3
			7.50	238.2	8.4	420	156	332	-	-	114	4
4.	Mali Dol, 850, adit	“	7.91	181.9	9.6	397	-	-	-	-	-	-
			7.33	253.0	9.0	375	68	12	4	34	140	-
5.	Zhazhkov Dol, 760, adit	“	8.36	169.0	8.6	681	-	2	3	28	105	-
			8.43	248.0	8.0	583	36	13	31	484	121	-
6.	Zhazhkov Dol, 740, drainage water	“	7.98	202.0	13.2	131	-	1	5	66	12	-
			7.69	239.0	16.1	200	-	-	-	-	-	-
7.	Yavorov Dol, stream	“	8.05	181.0	14.2	211	1	-	4	30	1	-
			-	-	-	-	-	-	-	-	-	-
8.	Sinya Voda, 620, adit	“	8.42	169.0	10.2	746	-	18	5	61	21	13
			8.54	238.0	8.9	649	27	15	8	171	31	-
9.	Rupski Dol, stream	“	-	-	-	-	-	-	-	-	-	-
			8.15	150.0	15.8	294	24	4	7	142	14	-
10.	Gnili Dol, 570, lake in front the adit	“	8.20	179.0	15.2	344	-	5	7	106	5	8
			8.35	217.0	14.8	391	17	7	10	277	9	17
11.	Velin Dol, 545, adit	“	8.18	150.5	19.3	527	-	3	4	47	-	-
			8.10	259.0	13.1	506	14	8	11	264	7	-
12.	Lukina Padina, 495, adit	“	7.90	154.0	11.9	776	3	3	5	54	29	25
			8.23	266.2	9.4	681	19	25	47	1456	34	18
13.	Dolich, 415, adit	“	-	-	-	-	-	-	-	-	-	-
			7.50	260.5	11.7	596	11	10	11	431	8	25
14.	Dolich, 395, drainage water	“	-	-	-	-	-	-	-	-	-	-
			7.86	225.0	15.5	599	8	7	8	259	7	21
15.	Zhelezna village, drinking water	“	6.90	180.0	16.9	390	2	7	7	90	-	-
			7.16	285.0	12.4	288	4	6	-	-	-	-

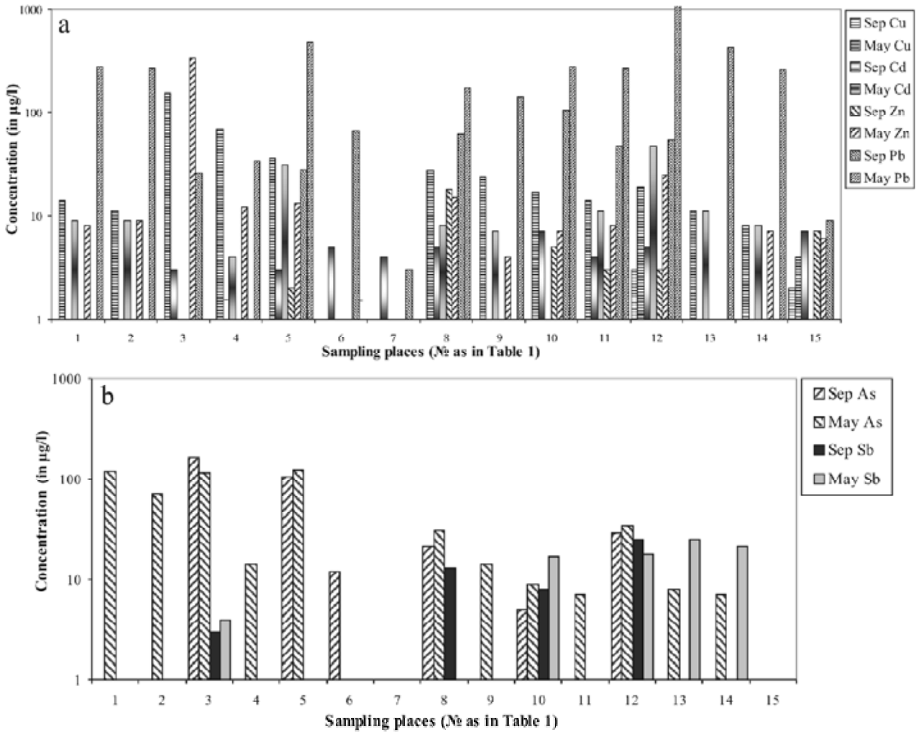

Fig. 1. Comparison between heavy metals and metalloids total concentrations determined in mine, surface and drinking waters collected in September 2005 and May 2006: a) Cu, Cd, Zn and Pb; b) As and Sb

Фиг. 1. Сравнение между съдържанието на тежки метали и металоиди в рудничните, повърхностните и питейни води през септември 2005 и май 2006: a) Cu, Cd, Zn и Pb; b) As и Sb

Table 2. WHO (World Health Organization) guideline values and MOEW (Ministry of Environment and Water) maximum permissible limit (MPL) values of Cu, Cd, Zn, Pb, As and Sb for drinking and surface water

Таблица 2. Пределно допустими и препоръчителни концентрации на Cu, Cd, Zn, Pb, As и Sb възприети от Международната здравна организация и Министерството на околната среда и водите

Organization, guideline values	**pH**	**T (°C)**	**EC (μScm^{-1})**	**Cu (µg/l)**	**Zn (µg/l)**	**Cd (µg/l)**	**Pb (µg/l)**	**As (µg/l)**	**Sb (µg/l)**
MOEW (1986), MPL, surface water, 2nd category	6.0-8.5	20.0	1300	100	5000	100	50	50	-
MOEW (2001), MPL, drinking water	6.5-9.5	20.0	2000	2000	5000	5	10	10	5
WHO (2004), guideline values, drinking water	<8.0	-	-	2000	3000	3	10	10	20

Although some authors consider arsenopyrite as relatively stable mineral under oxidizing conditions, circumneutral pH and comparatively high Eh (Jambor, 1994), it still dissolves in water and its concentration reaches up to 200—300 µg/l. Arsenopyrite decomposes following the reaction: $FeAsS + 7H_2O = Fe^{2+}(aq) + H_3AsO_3(aq) + 11H^+ + 11e^- + SO_4^{2-}$. As far as solubility is a function of the temperature, substance chemistry, pH and Eh, could be assumed, that at 8—10°C and pH — 7—8 of the water in the underground workings, the arsenopyrite solubility would be lower than that calculated for 25°C by Craw et al. (2003), but well enough to produce about 100-150 µg/l dissolved $As^{3+}(aq) + As^{5+}(aq)$ in the waters, as it was determined in mine waters from Perchinki, Mali Dol and Zhazhkov Dol mine sections.

The higher lead contents in mine waters determined during wet season probably result from essential variation in the mine water ionic composition, especially SO_4^{2-} and HCO_3^- concentrations, which control in turn the lead content in mine waters (Blowes, Ptacek, 1994).

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Оценка на съдържанието на тежки метали и металоиди в рудничните води от рудниците Мартиново и Чипровци, Северозападна България

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Резюме. Рудниците Мартиново и Чипровци в Северозападна България са активно експлоатирани в периода от 1950 до 1999 г. От 1999 г. те са в процес на ликвидация и консервация, като до момента са рекултивирани както трите обслужващи хвостохранилища, така и по-голямата част от насипите в отделните участъци на рудниците. Рудничните води от основните извозни галерии в повечето участъци, обаче изтичат навън и се вливат в притоците на р. Чипровска Огоста. Извършените сезонни изследвания на съдържанието на тежки метали (мед, кадмий, цинк, олово) и металоиди (арсен и антимон) в рудничните води и в някои притоци на р. Чипровска Огоста показват незначително сезонно колебание и високи съдържания на тези елементи (до няколко пъти над ПДК по БДС), особено на арсена и оловото, които са основни замърсители на водите и почвите в района, което от своя страна подчертава потенциалната токсичност на рудничните води върху околната среда в непосредствена близост. Изключение правят съдържанията на разтворено олово, които показват значителна сезонна вариация. В участъците Лукина падина и Долич се отбелязва и задоволително постоянно съдържание на разтворен антимон (до 25 μg/l) в изтичащите руднични води.