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MIGRATION OF HEAVY METALS FROM MINE WASTE ROCK DUMP END ENVIRONMENTAL IMPACT ON GROUNDWATERS AND SEDIMENTS

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ABSTRACT

The environmental impact of mine waste rock dump, located in the region of Srednogorie, Bulgaria on groundwaters and sediments was studied. The acid mine drainage with low pH (2.43 - 3.53), high electrical conductivity (1500 - 4400 $\mu S\ cm^{-1}$), content of Fe, Mn, Cu, Zn, Al, As and high concentration of sulfates (540 - 6905 $mg\ L^{-1}$) are formed after heavy rainfall. The content of heavy metals, except manganese, in groundwater was significantly lower than that in the acid mine drainage, and the pH was in the range of 5.43 to 6.62. Sediments in the non-consequential vicinity of the mine waste rock dump had a pH in the range of 2.86 - 4.53 and contained heavy metals and As at concentrations higher than those in the mineral waste due to precipitation, co-precipitation and sorption reactions. An increase in the copper and zinc content in the exchangeable and organic matter fractions was found in the sediment sample. A relationship was found between arsenic and iron concentration in the sediments, which was mainly due to the retention of arsenic in the Fe and Mn oxides fraction. The concentration of total Mn in the sediments was lower than that in the mining waste due to the high mobility of manganese.

Keywords: *mine waste rock dump, acid mine drainage, heavy metals, arsenic, sediments pollution.*

INTRODUCTION

Acid mine drainage (AMD) generation continues to be the main environmental impact nowadays regarding to mining during exploration and exploitation activities and after closing period. AMD sources can present in two basic groups – primary (geochemical characteristics of rocks, underground and open pit mine, tailings, mine rock dumps, diffuse seeps) and secondary (rock chips, concentrate spills, emergency ponds and stockpiles). A typical composition of AMD includes high concentrations of sulphates and heavy metals (Fe, Zn, Mn, As, Cr, Ni, Cu, Cd, Al, Pb) and high or extremely high acidity, which promotes migration of toxic elements in generated flows [1 - 3].

Type of mineral waste, mineralogical and chemical composition, the climatic conditions in the area and the activity of the chemolithotrophic bacteria determine the chemical composition of AMD in general [1, 4, 5].

AMD generating process incorporates direct (direct interaction) and indirect (by microbial produced Fe^{3+}) mechanism of oxidation of sulfide minerals (pyrite (FeS_2), chalcopyrite ($CuFeS_2$), marcasite (FeS), arsenopyrite (FeAsS), cinnabarite (HgS), sphalerite (ZnS), millerite (NiS), chalcocite (CuS_2), galena (PbS), pyrrhotite ($Fe_{(1-x)}S$), gersdorffite (NiAsS), etc.) in the presence of atmospheric oxygen and water under the influence of sulfur- and iron-oxidizing bacteria, such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* as well as the bacteria of the genera

Thiobacillus (*T. thioparus, T. neapolitanus*) and Ferroplasma (*F. acidarmanus, F. thermophilum*), which enhance the sulfide oxidation stage [6, 7]. The number and composition of microbial communities strongly depends on the environmental conditions, such as pH, temperature, concentration of metals and sulfate [8 - 11].

The sulfide minerals oxidation is demonstrated by reaction of direct interaction of oxygen and water with pyrite via acidophilic chemolithotrophic bacteria (reaction 1):

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

The oxidation of the other sulfide minerals proceeds in a similar scheme, producing AMD with high concentrations of heavy metals according to reaction 2:

$$2MeS + O_2 + 2H_2SO_4 \rightarrow 2MeSO_4 + 2H_2O + 2S^0 \quad (2)$$

where Me can be Fe, Zn, Hg, Ni, Cu, Pb, etc.

The same microorganisms can oxidize the elemental sulphur (S^0) obtained according to the previous reactions to SO_4^{2-}, through which mechanism additional amounts of sulphates transfer into the AMD (reaction 3) [12, 13]:

$$S^0 + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (3)$$

Microbial produced ferri-ions have high oxidizing efficiency and in an extremely acidic and anoxic conditions react spontaneously with larger amounts of FeS_2 according to reaction 4 [14]:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

The concentration of Fe^{3+} determines the oxidation rate reaction of sulfide minerals at low values of pH at this mechanism. The regeneration of Fe^{3+} by bacterial oxidation of Fe^{2+} is the rate-limiting stage of pyrite oxidation as follows (reaction 5) [15]:

$$4Fe^{2+} + O_2 + 2H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (5)$$

The main factor that controls the rate of pyrite oxidation process in mine waste dump and tailings is the accessibility of oxygen and water to the mineral surface [16]. The change of weather conditions in mine regions has a huge influence on geochemical processes and factors of AMD formation [17]. The migration of contaminants in mining areas enhances during heavy rainfall period that contributes to their spread in surface and groundwater and soils [18]. On the other hand, increasing in the metal concentrations occurs during long term dry period [19].

Heavy metals from mine drainage are immobilized in sediments due to precipitation, co-precipitation and sorption reactions [20, 21]. At presence of oxygen the capability sequence of minerals for buffering the AMD is carbonate > aluminosilicate > (hydr)oxide minerals. Aqueous metal species tend to precipitate as hydroxide, oxyhydroxide or hydroxysulfate phases at increased pH of the environment and adsorb on the surfaces of these newly formed mineral precipitates [22, 23]. The contact of mine drainage with calcite, dolomite and limestone and the dissolution of gypsum leads to the processes described above [17].

Metals behavior in sediments associated with acid mine drainage were the subject of several studies [23 - 25]. The bioavailability and mobility of metals in sediments, their behavior and impact on the environment depends on their distribution in different geochemical phases (exchangeable and water-soluble, carbonate, organic, Fe-Mn (hydro) oxide and residual) [26]. Boukhalfa and Chaguer reported that the composition of the sediments polluted by acid mine drainage is mainly dominated by iron and sulphur. In the vicinity of the mine, the main mineral in sediments with a highly acidic pH (< 3) is jarosite. Downstream, sediments with a pH above 3 contain the minerals schwertmannite, goethite and lepidocrocite [24]. Nasr et al. reported that the spatial distribution of heavy metals in the sediments of Aden Port was controlled by the association of heavy metals with carbonate, fine particles (silt-clay) and organic matter content [27]. According to Equeenuddin et al., distribution of Mn, Ni, Pb, Cu and Zn into exchangeable part is significantly dependent on pH and metals become more mobile under strongly acidic condition [25].

The composition of sediments affected by mining activity and the geochemical behavior of heavy metals and metalloids sorbed in them are the subject of various studies [23 - 25, 27]. Jung et al. studied the transport and sediment-water distribution of trace metals (Cr, Co, Fe, Pb, Cu, Ni, Zn, Cd) in acid mine drainage in the Kwangyang Au-Ag mine area, southern part of Korea [28]. The authors reported that the sediment-water distribution coefficients for metals were dependent on the water pH and decreased in the following order Pb ≈ Al > Cu > Mn > Zn > Co > Ni ≈ Cd, the coefficients values for Al, Cu and Zn were very sensitive to changes in pH and that among non-residual fractions, Fe-Mn oxides are most important for retaining trace metals in the sediments. Equeenuddin et al. also reported that metal mobilization from sediments around Makum coalfield in North-eastern India is significantly influenced by pH [25]. The pH value affects the distribution of metals in different geochemical fractions, as in moderate to slightly acidic sediments, Cd and Cu are mainly associated with exchangeable and organic fractions, respectively; Zn fractionated into Fe-Mn oxyhydroxides while Cr, Ni, Mn, Pb - mostly into residual part.

Luo et al. have studied the impact of Dabaoshan Mine Site, the largest polymetallic mine in South China on Hengshi River, groundwater, fluvial sediments, and soils, with a focus on As due to its high toxicity [29]. The authors reported that the behavior of As and other heavy metals is a complex and dynamic process where several factors play a role. After application of lime in discharge water, most heavy metals were removed from surface water and the water quality during the dry season has improved. During the rainy season, the overflow of acid mine drainage and remobilization of metals from sediments are responsible for increasing the concentration of metals and decreasing the pH of the water.

The objective of the present study is to investigate the environmental impact of mine waste rock dump by (1) analyzing the chemical composition of the formed acidic drainage waters, (2) investigation of groundwater and sediments contamination with heavy metals and arsenic and (3) determination geochemical speciation of heavy metals and As in mining waste and sediments to assess the changes of their distributions and the potential for their remobilization.

EXPERIMENTAL

Site description

The object of the study is a mine waste rock dump with area 41 000 m^2 and volume 38 000 m^3, located in the region of Srednogorie, Bulgaria. The region is characterized by a moderate continental climate. Milder winters and cooler summers are characteristic compared to other regions of Bulgaria, as well as temperature inversions, mainly during the winter. The average annual rainfall is 617 mm. The maximum of rainfall is observed in June, and the minimum - in January-February. Winter is the driest season of the year, with a seasonal average of 104 mm of precipitation, 50 % of which is from snow.

The following minerals have been identified in previous mining waste studies: quartz (28 %), albite (26 %), microcline (14 %), muscovite (10 %), goethite (4 %), calcite (2 %) and pyrite (2 %).

Sample collection

An average composite sample of mineral waste was prepared from 40 unit samples after quartering. Sediment samples were collected from the top 1-2 cm of bed sediment at eight locations in March 2019 (Fig. 1). Samples were air dried, powdered, sieved and stored in polyethylene packets for laboratory study.

AMD samples were collected at five locations

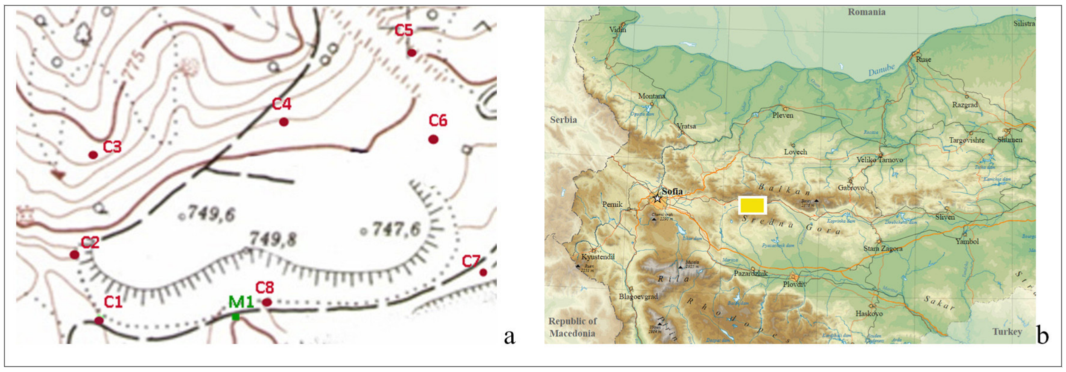

Fig. 1. (a) Sample location map (● – AMDs and sediments, ■ - groundwater) and (b) its geographical location in Srednogorie, Bulgaria.

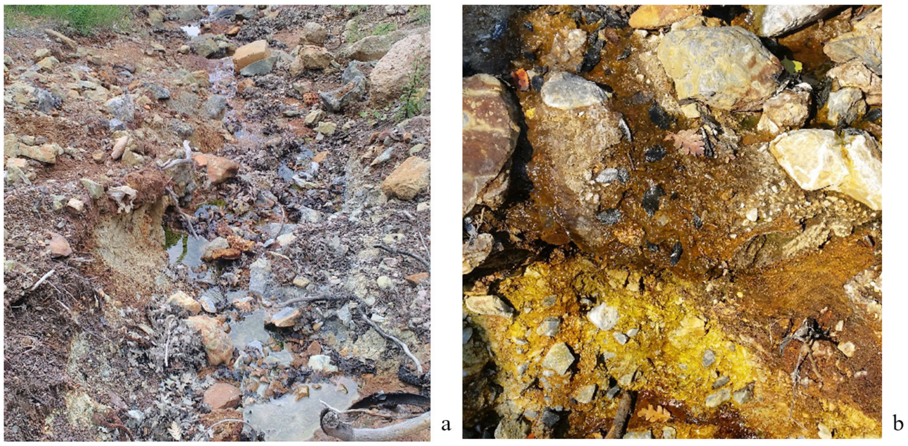

Fig 2. (a) Acid mine drainage from the western part of the rock dump; (b) Sediment from point C1.

C1, C2, C6, C7 and C8 in March and June 2019 (Fig. 1). Measurements of physical parameters such as pH, electrical conductivity and Eh were made in the field on the sampling site.

An observation well for groundwater with a depth of 10 m was constructed in early 2020. The well is located adjacent to the mine waste rock dump in a southerly direction (point M1). Groundwater samples were collected in February 2020, June 2020 and November 2021.

Study methods

Chemical analysis of AMDs and groundwater

The pH was measured using pH electrode (VWR) and pH meter HANNA HI 9021. The Eh was measured using Electrode Sen Tix ORP (WTW). The sulfate concentration was determined using spectrophotometric method by $BaCl_2$ as reagent at a wavelength of light of 420 nm. The determination of ferri- and total iron concentrations are made using spectrophotometric method by 5-sulfosalicylic acid at 425 nm and 500 nm [30]. The concentration of heavy metals in water samples was measured by ICP-spectroscopy.

Microbiological analysis of AMDs

The number of Fe^{2+}-oxidizing acidophilic hemolitotrophic bacteria was determined using medium 9k [31]. A three-tube most-probable number technique was applied for estimation of the number of bacteria.

The pH and electrical conductivity (EC) were determined from 2 mm fraction in a slurry of 1:5 sediment:water suspension.

Total concentration of metals in sediments and mineral waste were determined by ICP-spectroscopy after *aqua regia* digestion. Fractionation of metals in sediments was carried out through sequential extraction process following Tessier et al. method [32]. The procedure consisted of extracting the metals in five forms: (1) exchangeable fraction (1 M $MgCl_2$), (2) carbonate-bound (1 M HOAc), (3) Fe-Mn oxide fraction (0.04 M $NH_2OH.HCl$ in 25 % HOAc), (4) organic bound (30 % H_2O_2, 0.02 HNO_3 and 3.4 M NH_4OAc), and (5) residual fraction (HNO_3 and HCl).

RESULTS AND DISCUSSION

Analysis of the AMDs

Acid mine drainage samples were collected after heavy rains. It should be noted that due to the high sediment filtration rate their amount was negligible (the points C3, C4 and C5 were dry).

All samples of AMDs with the exception of the sample from point C7 are characterized by an extremely acidic pH (Table 1). The obtained results show that there are many zones in the whole area where acid mine waters are formed. Acid mine drainages are formed in the western, southern, and northeastern parts of mine waste rock dump. These data indicate that due to the contact of the mining material with air, water and the presence of acidophilic chemolithotrophic bacteria, conditions have been created for intense oxidation of the sulfide minerals present in the waste.

Another proof of the presence of oxidation processes in mineral waste are the high values of the oxidation-

Table 1. pH, electroconductivity and redox potential of AMDs.

Sample point	pH		EC, μS cm^{-1}		Eh, mV	
	March 2019	June 2019	March 2019	June 2019	March 2019	June 2019
C1 (aq)	2.99	3.04	1810	1730	576	572
C2 (aq)	3.29	3.37	1570	1500	552	557
C6 (aq)	2.43	2.75	6130	4400	521	532
C7 (aq)	6.68	6.62	779	817	312	330
C8 (aq)	3.53	3.47	2340	2580	443	436

Table 2. Concentration of total Fe, Fe^{3+} and sulfate of AMDs.

Sample point	Total Fe, mg L^{-1}		Fe^{3+}, mg L^{-1}		SO_4^{2-}, mg L^{-1}	
	March 2019	June 2019	March 2019	June 2019	March 2019	June 2019
C1 (aq)	86.32	71.0	57.54	47.79	567	540
C2 (aq)	53.20	56.59	36.13	32.32	595	570
C6 (aq)	1085.23	511.9	864.72	354.56	6905	3611
C7 (aq)	0.45	0.5	<0.05	<0.05	355	370
C8 (aq)	11.15	32.55	6.24	8.86	2170	2477

Table 3. Concentration of heavy metals and metalloids of AMDs.

Element, mg L^{-1}	C1 (aq)		C2 (aq)		C6 (aq)		C7 (aq)		C8 (aq)	
	March 2019	June 2019	March 2019	June 2019	March 2019	June 2019	March 2019	June 2019	March 2019	June 2019
Al	65.12	62.02	40.55	40.47	440.4	425.3	0.09	0.1	77.23	213.1
As	0.063	0.055	0.062	0.051	5.09	2.26	<0.005	<0.005	0.012	0.018
Cd	0.042	0.035	0.016	0.028	0.228	0.186	0.005	0.006	0.039	0.111
Cr	0.024	0.029	0.026	0.023	0.129	0.247	<0.005	<0.005	0.007	0.023
Cu	28.59	26.47	19.98	22.76	141.9	134.4	0.166	0.178	18.55	36.05
Fe	89.42	71.13	55.26	57.51	1095	510.3	0.45	0.56	11.04	34.01
Mn	8.44	7.25	4.87	5.23	56.21	53.43	0.467	0.598	5.86	13.28
Ni	0.02	0.02	<0.01	<0.01	0.34	0.33	<0.01	<0.01	0.07	0.1
Zn	9.98	9.61	8.11	7.28	44.56	40.73	1.23	1.44	9.35	24.75

reduction potential (above +430 mV) in a large part of AMD samples. The highest conductivity was found at point C6, which suggests that the concentrations of heavy metals and sulfates in these surface waters will be high.

Data on total Fe, Fe^{3+} and sulfate concentrations in AMDs are presented in Table 2. From the data presented, it can be seen that in most cases the generated acid mine waters are characterized by high concentrations of total iron, and in the points with high values of oxidation-reduction potential, a large part of the iron is in the third valency. This is due to the fact that ferrous iron is a preferred energy source for ferro-oxidizing chemolithotrophic bacteria, playing a key role in the generation of acidic drainage waters.

Table 3 presents the results of the ICP analysis for the concentration of heavy metals in the sampled AMDs. In the majority of the samples, aluminum, arsenic, cadmium, copper, iron, manganese and zinc are present in high concentrations. The highest concentrations of heavy metals and toxic elements are contained in the water samples from points C6 and C8. The presence of the heavy metals iron, copper, zinc and arsenic is due to oxidation processes of various sulfide minerals containing these elements in their structure. The entry of aluminum and manganese into the AMDs is related to the contact of the acidic waters with clays and minerals containing manganese. Mineral waste had the weakest impact on AMD quality at point C7, located in the southeastern part of rock dump.

The obtained results for the content of heavy metals in AMDs and their high oxidation-reduction potential also correlate with the results of the microbiological analysis for the presence and number of Fe^{2+}-oxidizing acidophilic hemolitotrophic bacteria (mainly the mesophilic species *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*) (Table 4).

Table 4. Number of chemolithotrophic bacteria, cells/ml in the surface waters of the studied area.

Sample point	Number of Fe^{2+}-oxidizing chemolithotrophic bacteria, cell mL^{-1}	
	March 2019	June 2019
C1 (aq)	5.5×10^3	1.3×10^4
C2 (aq)	5.0×10^3	6.0×10^3
C6 (aq)	6.0×10^3	6.0×10^5
C7 (aq)	5.0×10^1	2.5×10^1
C8 (aq)	2.5×10^3	5.0×10^4

Analysis of the groundwater

Data on basic groundwater parameters are presented in Table 5. It should be noted that the location of point M1 was chosen to provide information on the impact of mineral waste on groundwater, which has a north-south direction. In the autumn and winter period, groundwater is characterized by a pH above 6, while in June the pH values were lower - 5.78. During the summer, the waters had higher electrical conductivity (2130 µS cm^{-1}) and higher sulfate concentrations (1185 mg L^{-1}). Concentrations of Al, Cu, Cr and Fe in groundwater were significantly lower, compared to that of AMDs. Due to its high mobility, manganese was present in high concentrations (0.673 - 6.55 mg L^{-1}) in groundwater.

From the obtained results, it can be concluded that the rainwater passes through the mineral waste, becomes contaminated with heavy metals, arsenic and sulfates and drains, forming streams and gullies in accordance with the unevenness of the area in three directions - west, south and east. Because the filtration rate of the mining waste and sediments is high, surface water flows rapidly to depth, which also leads to contamination of groundwater below and south of the mine waste rock dump with heavy metals and sulfate.

The physical, geochemical, and microbiological processes involved in the formation of AMDs from waste rock and mine tailings have been the subject of a few studies and reviews [6, 33, 34]. Many studies show that regardless of the similar processes that occur in mining waste rocks, differences in mineralogical composition, water, gas and heat transport mechanisms influence the chemical composition of the generated acidic drainage waters. The processes of chemical weathering and physical transport depend on the physical and chemical heterogeneities and internal structure of a waste-rock pile. The mineralogical composition affects the oxidation

Table 5. pH, electroconductivity and concentration of heavy metals, metalloids and sulfate of groudwater.

Parameter	Ground water – point M1		
	February 2020	June 2020	November 2021
Water level, m	9.30	6.41	5.78
pH	6.15	5.43	6.62
EC, µS cm^{-1}	1730	2130	1534
Al, µg L^{-1}	<8.0	834	110
As, µg L^{-1}	18	17	<3.0
Cd, µg L^{-1}	-	41	-
Cr, µg L^{-1}	<1.0	<1.0	<1.0
Cu, mg L^{-1}	<0.003	0.15	0.83
Fe, mg L^{-1}	15.6	3.58	0.008
Mn, mg L^{-1}	6.55	6.24	0.673
Ni, µg L^{-1}	22	90	12
Zn, mg L^{-1}	-	5.9	-
SO_4^{2-}, mg L^{-1}	800	1185	700

processes of sulfide minerals, the formation of secondary minerals, as well as the course of acid-neutralizing reactions [6]. The acid generated from the oxidation of pyrite and other sulfide minerals are neutralized to varying degrees by dissolution from carbonate, (oxy) hydroxide, and silicate minerals [34]. The pH value affects the solubility of metals and metalloids produced by the oxidative destruction of sulfide minerals. The acid drainage waters with low pH often contain high concentrations of metals such as Fe (III), Cu, Zn, and Ni. The elements As, Sb, Se, and Mo form (hydr)oxyanions, which have high mobility at the pH of drainage waters around the neutral point.

Analysis of the mining waste and sediments

Data on pH, electrical conductivity, and sulfate concentrations of the mining waste and surrounding sediments are presented in Table 6. The mining waste has a paste pH of 3.24 and a water-soluble sulfate concentration of 1.97 g L^{-1}. The pH values of the sediments in most cases (except points C3, C5 and C7) are below 3.6. From these results, it can be expected that oxidation processes of sulfide minerals take place in almost the entire aerobic zone of the mine waste rock dump, which, by the outflow of both surface water and those passing through the waste, reflect on the chemical composition of the deposited sediments.

Very high concentrations of water-soluble sulfates were measured in sediments in the eastern part (C6) and southern part (C8) of the study area. These data also correspond to the high values of electrical conductivity of the water suspensions of the sediments from these points.

Table 7 presents information on the content of heavy metals and arsenic in mining waste and sediments. From the obtained results, it can be seen that the migration of heavy metals and metalloids leached from the mineral waste takes place in the formed ravines located to the east, west and south of rock dump. Most of the sampled sediments contain higher concentrations of arsenic, copper and zinc compared to their content in the mineral waste.

These data show that precipitation, co-precipitation and sorption processes occur in the sediments, leading to immobilization of heavy metals (except manganese) and arsenic in them. For example, the concentration of arsenic in the sediments from points C1, C2 and C6 is more than three times higher than the concentration of the toxic element in the mining waste.

Table 6. pH, electrical conductivity and sulfate concentrations of the mining waste and sediments.

Sampling points	pH	EC, µS cm^{-1}	SO$_4^{2-}$, mg kg^{-1}
Mining waste	3.23	ND	1940.15
C1 (s)	3.52	544	1340.9
C2 (s)	3.00	771	1573.75
C3 (s)	4.53	141	524.1
C4 (s)	3.45	360	791.95
C5 (s)	5.88	65	1025.95
C6 (s)	3.51	2134	5852.75
C7 (s)	3.90	242	819.6
C8 (s)	2.86	1330	4578.45

Table 7. Concentration of heavy metals and metalloids in mineral waste and sediments in the area of the mine waste rock dump.

Sampling points	Mining waste	C1 (s)	C2 (s)	C3 (s)	C4 (s)	C5 (s)	C6 (s)	C7 (s)	C8 (s)
Al, mg kg^{-1}	19398	20769	15340	42512	32507	15733	13197	25152	16275
As, mg kg^{-1}	253	784	739	138	141	48.5	865	486	639
Cd, mg kg^{-1}	6.4	<1	<1	< 1	<1	<1	1.05	<1	<1
Cr, mg kg^{-1}	1.7	46.2	23.1	18.4	16.3	7.1	32.7	21.2	31.3
Cu, mg kg^{-1}	685	703	764	783	160	104	789	751	611
Fe, mg kg^{-1}	44659	57798	47432	20133	30877	22424	50518	37949	48706
Mn, mg kg^{-1}	480	249	203	351	308	297	302	315	232
Ni, mg kg^{-1}	-	7.11	2.51	6.47	<5	<5	8.24	7.19	10.3
Zn, mg kg^{-1}	120	330	337	110	351	88	202	183	247

High concentrations of iron were found in points C1, C2, C6 and C8. Depending on the pH values, much of the iron is most likely in the form of hydroxides, oxidohydroxides (at pH above 3) and as jarosite and schvetmannite (at pH below 3).

The concentration of arsenic in sediments is directly related to that of iron (Fig. 3), because arsenate and arsenite ions have an affinity to be sorbed by formed ferric hydroxides, possessing a highly developed specific surface. It is likely that some of the arsenic in the sediments is also in the form of ferriarsenate.

In order to obtain additional information on the processes of migration and immobilization of heavy metals, a sequential extraction procedure was used to determine the geochemical phases of metals and arsenic in mining waste and sediment from point C6, where the highest concentrations of As and Cu were found (Tables 8 and 9; Figs. 4 and 5).

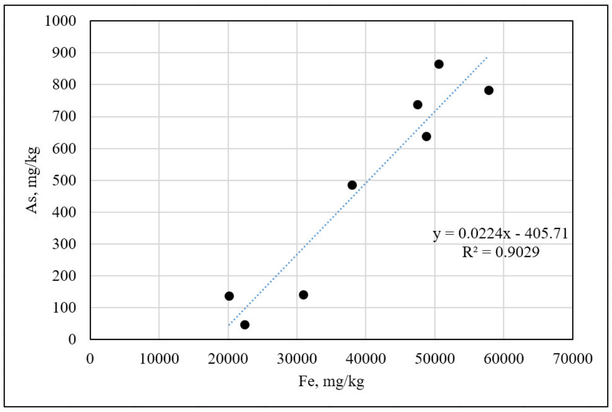

Figure 3. Iron and arsenic concentrations in sediments in the mine waste rock dump area.

Table 8. Concentration of heavy metals and As in mining waste.

Fraction	Cu	Zn	Fe	Mn	Cd	Al	As
	mg kg^{-1}						
Exchangeable	110.65	27.8	21.77	164.12	<0.1	228.05	<0.1
Carbonates	12.5	0.1	6.56	8.72	<0.1	11.1	<0.1
Fe and Mn oxides	124.9	4.6	5355	101.4	<0.1	2548	58.05
Organic matter	110	11.1	639.14	5.3	<0.1	1301	18.94
Residual	323.1	76.1	36961	210.05	5.1	15355	176.1
Total	681.15	119.7	42983.47	489.59	5.1	19443.15	253.29

Table 9. Concentration of heavy metals and As in sediment from point C6.

Fraction	Cu	Zn	Fe	Mn	Cd	Al	As
	mg kg^{-1}						
Exchangeable	135.45	42.5	55.5	33.7	<0.1	583.5	<0.1
Carbonates	26.4	0.1	12.65	3.75	<0.1	38.645	<0.1
Fe and Mn oxides	63.05	7.65	9595	85.75	<0.1	1226.31	242.4
Organic matter	246	21.3	631	5.5	<0.1	895.03	37.85
Residual	286.1	107.15	39925	189.65	0.5	9794.6	540.9
Total	757	178.7	50219.15	318.35	0.5	12538.09	821.35

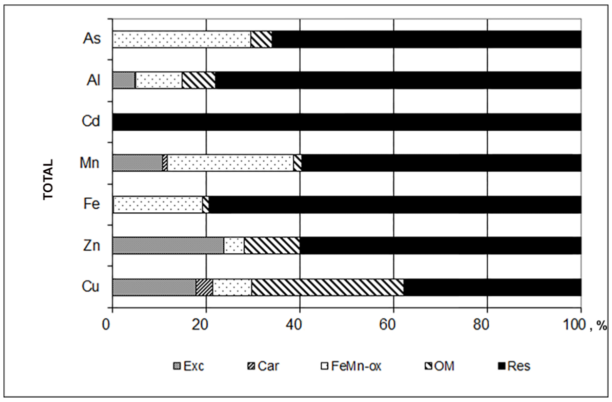

Fig. 4. Relative distributions of As, Al, Cd, Mn, Fe, Zn and Cu in mining waste, according to the sequential extraction procedure: Exc - exchangeable; Car - carbonates; FeMn-ox - Fe and Mn oxides; OM+SS - organic matter + secondary sulfides; Res - residual.

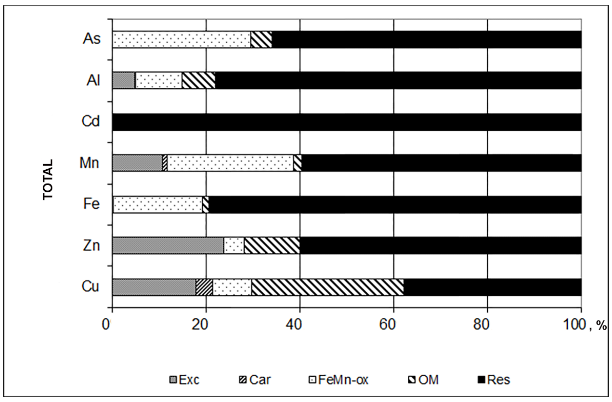

Fig. 5. Relative distributions of As, Al, Cd, Mn, Fe, Zn and Cu in sediment C6, according to the sequential extraction procedure: Exc - exchangeable; Car - carbonates; FeMn-ox - Fe and Mn oxides; OM+SS - organic matter + secondary sulfides; Res - residual.

The content of total Cu in the mining waste was 681.15 mg kg^{-1}, as most of the copper (47.7 %) was found in the residual fraction. Distribution of copper between the exchangeable, the Fe - Mn oxyhydroxides and the organic matter fractions was 16.2 %, 18.3 % and 16.2 %, respectively. The total copper content of the sediment (757 mg kg^{-1}) was higher than that of the mine waste. The partition of copper in the exchangeable and organic matter fractions increases to 17.9 % and 32.5 %, respectively, and that in the residual fraction decreases to 37.8 %. Since the sediment is characterized by high concentrations of sulfates, it is possible that some of the copper is present in the form of the water-soluble mineral chalcanthite ($CuSO_4{}^x5H_2O$).

The content of total aluminum in the mineral waste (19.44 g kg^{-1}) was higher than that in the sediment sample (12.54 g kg^{-1}). The distribution of aluminum by geochemical phases in the mining waste was as follows: Fe and Mn oxides fraction - 13.1 %, organic matter fraction - 6.7 % and residual fraction - 79.0 %. In the sediment, the proportion of aluminum increases with exchangeable and organic matter fractions, being respectively 5.3 % and 7.0 %. Most of the Al (79.2 %) was found in the residual fraction.

The total concentration of Mn in the mining waste was 489.59 mg kg^{-1}. Sequential fractionation of manganese showed that 33.5 % of the total Mn was distributed in the exchangeable fraction, 20.7 % in Fe and Mn oxides fraction and 42.9 % in residual fraction. The high content of manganese in the exchangeable fraction leads to its easy mobilization and transport through mine drainage waters. The concentration of total manganese in the sediment was lower than that in the mining waste - 318.35 mg kg^{-1}. The proportion of manganese in the exchange fraction was 10.6 %, significantly lower compared to the manganese content of the same fraction in the waste, which is due to the high mobility of the element. The distribution of Mn in the Fe and Mn oxides and residual fractions was 26.9 % and 59.6 %, respectively.

The concentration of cadmium in both mining waste and sediment was very low as shown by the results in Tables 8 and 9.

CONCLUSIONS

The mobilization of heavy metals and arsenic from mine waste rock dump, located in the region of Srednogorie, Bulgaria has an impact on groundwater quality and leads to of pollutants deposition in sediments. AMDs containing heavy metals (Fe, Mn, Cu, Zn, Al), As and sulfates are observed in the ravines around the waste rock dump only after heavy rains. Most AMDs are characterized by low pH values (2.43 - 3.53) and high electrical conductivity (1500 - 4400 µS cm^{-1}). The pH values of the groundwater were in the interval 5.43 - 6.62, and the concentrations of Al, Cu and Fe except for manganese were lower, compared to that of AMDs.

Most of the sediments contain higher concentrations of arsenic, copper and zinc compared to their content in the mineral waste due to precipitation, co-precipitation and sorption reactions. Using a sequential extraction procedure, sediments were found to have a higher proportion of heavy metals and As in the non-residual fractions compared to mining waste. Distribution of copper in the exchangeable and organic matter fractions increases to 17.9 % and 32.5 %. Also, an increase in the zinc content of both fractions was found in the sediment sample. The concentration of arsenic in sediments is directly related to concentration of iron. The content of arsenic in the Fe and Mn oxides fraction was 29.5 %. The concentration of total Mn in the sediment was lower than that in the mining waste and the proportion of manganese in the exchange fraction was significantly lower compared to the Mn content of the same fraction in the mining waste.

From the obtained results, it can be concluded that the formed acid mine waters leave a significant imprint on the chemical characteristics of the sediments, and the concentrations of heavy metals in the latter can be used as a criterion for evaluating the intensity of sulfide mineral oxidation processes in different areas of mining areas subject to exploration.

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