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ENVIRONMENTAL RISKS DUE TO HEAVY METAL POLLUTION OF WATER RESULTED FROM MINING WASTES IN NW ROMANIA

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Abstract

The mining waste facilities in the Baia Mare region, Romania, resulted from the extraction of poly-metallic ores (including Au, Ag). Metal sulphide minerals from the mining waste facilities have a potential to produce acid rock drainage (ARD) and to generate risk for the environment, including for the water resources. Some of the mining waste deposits from the region are located near the town of Baia Mare, close to the residential areas, the agricultural lands and the surface water. The short migration path between the sources and the sensitive receptors is causing an increased environmental risk. The main contaminants found in the area are heavy metals and metalloids, such as: Pb, Zn, Cd, Cu, Ni and As. Their concentrations measured in the water samples from the area exceeded the pollution thresholds. Moreover, there were measured high concentrations of heavy metals in the groundwater from the wells in the villages located downstream of the mining waste facilities. This water is used partly as drinking water for humans and domestic animals and for other agricultural activities (ex: irrigation). The aim of the paper is to identify and to analyse the most polluted water supply sources in the area and to draw conclusions about the environmental risk due to the mining waste facilities. The results show high concentrations of heavy metals downstream the waste facilities, leading to an increased environmental risk.

Keywords: environmental risks, heavy metals, mining waste facilities, water pollution

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1. Introduction

The mining industry is known to cause important environmental pollution, while mining waste heaps are recognized as sources of long term contamination of water and, in generally, of the environment. The mining wastes generate environmental problems because of their characteristics, such as: their high volumes, occupying large areas (estimated as representing approx. 70% of the total excavated material from mining activities (Younger, 2003)); the landscape damages; the impact on ground and surface water; the impact on local ecosystems, vegetation, fauna and on human beings. The mining waste heaps containing metal sulphides, in contact with the atmospheric oxygen and humidity, generate acid rock drainage (ARD) rich in sulphate ions. These acid waters can dissolve and mobilize heavy metals (Pb, Zn, Cu, Ni, Cd), transport and release them into the environment. Mining wastes mainly contain poly-metallic sulphides and minerals including silicates, oxides, hydroxides, carbonates, the most common minerals existing in the mineral gangue.

The mineralogy of the wastes containing sulphides is heterogeneous and their exposure to the action of the environment induces chemical instability, initiating spontaneously a series of chemical reactions (Lottermoser, 2007). The most common sulphide mineral is pyrite (FeS_2) and it is probably the most significant ARD source. The reactions used in the literature to describe the

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mechanism of the pyrite oxidation (Lottermoser, 2007) are as follows:

$$FeS_{2\,(s)} + 7/2\ O_{2\,(g)} + H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + 2\ SO_4^{2-}{}_{(aq)} + 2\ H^+_{(aq)} + Q \quad (1)$$

$$Fe^{2+}_{(aq)} + ¼\ O_{2(g)} + 4\ H^+_{(aq)} \rightarrow 4\ Fe^{3+}_{(aq)} + ½\ H_2O_{(l)} + Q \quad (2)$$

$$FeS_{2\,(s)} + 14\ Fe^{3+}_{(aq)} + 8\ H_2O_{(l)} \rightarrow 15\ Fe^{2+}_{(aq)} + 2\ SO_4^{2-}{}_{(aq)} + 16\ H^+_{(aq)} + Q \quad (3)$$

These reactions are all exothermic. The oxidizing agents can be the atmospheric oxygen or the ferrous ions (Fe^{3+}), depending on the pH of the solution. The Fe^{3+} ion concentration decreases with increasing pH, and its solubility is limited by the precipitation as ferric hydroxide, $Fe(OH)_3$:

$$Fe^{3+}_{(aq)} + 3\ H_2O_{(l)} \rightarrow Fe(OH)_{3\,(s)} + 3\ H^+_{(aq)} \quad (4)$$

The $Fe(OH)_3$ precipitate is a reddish-yellow colloidal suspension, characteristic for the ARD (Fig. 1) and for the acidic mine water (AMD), resulted around the mining waste dumps or around the mines (Younger, 1995).

Fig. 1. $Fe(OH)_3$ in the stream from Aurul and Bozânta tailing ponds - Bozânta Mare Village, August 2012

Usually, during long dry periods, the water acidity and the concentration of the released metals into the environment increase in the vicinity of mining waste heaps. The contaminants may infiltrate in the groundwater, or may reach the surface waters by surface runoff (Gandy and Younger, 2008; Younger et al., 2002), and may suffer different processes as: migration, accumulation, adsorption, transformation, dissolution, desorption and ion exchange (Wang et al., 2008). The areas covered by the mining waste heap or by the tailings dams facilities may be considered hot spots due to the diffuse pollution generated in their surroundings. The specific location of the mining waste facilities in a particular area may increase the vulnerability of that area, due to some physical-mechanical processes (possibility of slipping / breaking of the tailing dam), and due to some geochemical and physical processes (ARD generation, erosion, leakage, air dispersion) (Álvarez-Valero et al., 2009; Banks, 1997).

In the proximity of Baia Mare, Romania, there are located several mining waste heaps or tailings dams, newer or older, and in different stages of preservation. These dumps contain minerals gangue, resulted from the mining exploration and ore exploitation, or fine coarse tailings with different particle sizes resulted from the mineral processing, which intensify the geochemical weathering processes.

The water from the wells situated in the vicinity of these mining waste facilities is used partly as a drinking water resource for humans and domestic animals and for agricultural activities (irrigation). Therefore, the existence of the pollutants in the groundwater represents a direct route of exposure for the population and the environment, generating an increased health risk for humans and environmental risk for biocenosis. The polluted surface water is also dangerous for the aquatic biota, and also for the agriculture, fauna and livestock.

The aim of the paper is to identify and to analyse the pollution of the surface and groundwaters, downstream the mining waste facilities, - used for different purposes, sometimes for the household consumption -, and to draw some conclusions about the environmental risks, through the development of the following general objectives: site investigation, water sampling, instrumental analysis, data interpretation and the conceptual environmental risk model description.

2. Case study - description of the studied region

The content of the region's subsoil, rich in metals The content of the region's subsoil, rich in metals, determined the mining to be one of the basic occupations in this region, from the ancient times. Since the last century the mining activities in the area were gradually increasing, according to the development of new techniques for the ore processing. The volcanic rocks in the region contain important concentrations of metals, as shown in Table 1 (Bird et al., 2009; Donis et al., 2000; Lăcătuşu et al., 1996; Turekian and Wedepohl, 1961).

As a consequence of the evolution of mining activities, mining wastes tailing heaps or dams appeared, covering large areas, even in the vicinity of the Baia Mare town. These mining waste facilities are the following: Aurul tailing dam, Bozânta Nou and Bozânta tailing dam, in the Western part of the town; Tăuţii de Sus and Central Flotation tailing dams, in the Eastern part of the town; several mining heaps situated on the Northern part of the town, such as those of Herja Mine, Valea Roșie, Băița, Borcuț Mine in Baia Sprie etc. (Figs. 2 and 3).

Their ages are variable, beginning from the end of the 18th century since starting the exploitation of Pb, Zn, Au and Ag ores from Baia Sprie mine, as far as the last one, the Aurul tailings dam, put into operation in 1999. Presently none of these mining waste deposits situated in the proximity of Baia Mare are active, all of them being totally or partially rehabilitated or being in various stages of the preservation.

Table 1. Mean concentrations of metals in the volcanic rocks from the Baia Mare region (Bird et al., 2009)

Metal	**Granitic rocks** average concentration (Turekian and Wedepohl, 1961)	**Baia Mare Region, geogenic background**, average concentration (Lăcătușu et al., 1996)	**Baia Mare Region, andesites**, range concentration (Donisa et al., 2000)
Cd	0.13	1.2	-
Cu	30	39.7	8-70
Pb	15	68.4	10-31
Zn	60	93.2	58-136

The metallurgical plant Romplumb is also located in Baia Mare and the waste resulted from their technological processes is located near to the plant, as a slag heap. In the Baia Mare region, the natural pH of the background is acidic due to the geological substrate containing acidic rocks, and covered by acidic soils. The main soil types in the area are luvisoils, cambisoils, intrazonal soils, and generally undeveloped leachate soils (Damian et al., 2008), and these acidic conditions determine the type of vegetation that grow in the area.

3. Experimental

The water samplings were performed in two campaigns: the first in August 2012, after a dry summer; the second in May 2013, at the end of a wet spring. The main contaminants found in the proximity of the mining waste facilities were heavy metals, as: Pb, Zn, Cd, Cu, Ni. In some of the groundwater samples and surface water samples near the inhabited areas of the the villages located downstream to mining waste facilities the heavy metal concentrations were exceeding the pollution thresholds.

The sampling points are presented in Figs. 2 and 3. For the determination of the natural background concentrations of metals, groundwater samples were also, taken upstream of the pollution sources (GW6, GW7). The sampling points for the groundwater are located in the Baia Mare and in some villages around the city, as Bozanta Mare, Sarar, Tăuții Măgherăuș, Baia Sprie. The groundwater samples were taken from the wells situated in the vicinity of the vulnerable receptors, as schoolyard, or private courtyards

The water from these wells are occasionally used as drinking water for humans or for livestock, and usually used for irrigation. The surface water samples were taken from some Rivers in the region, for example, Săsar, Lăpuș, Băița, Firiza River, and from some polluted creek downstream the tailing dams facilities as Valea Rosie, Herja etc.

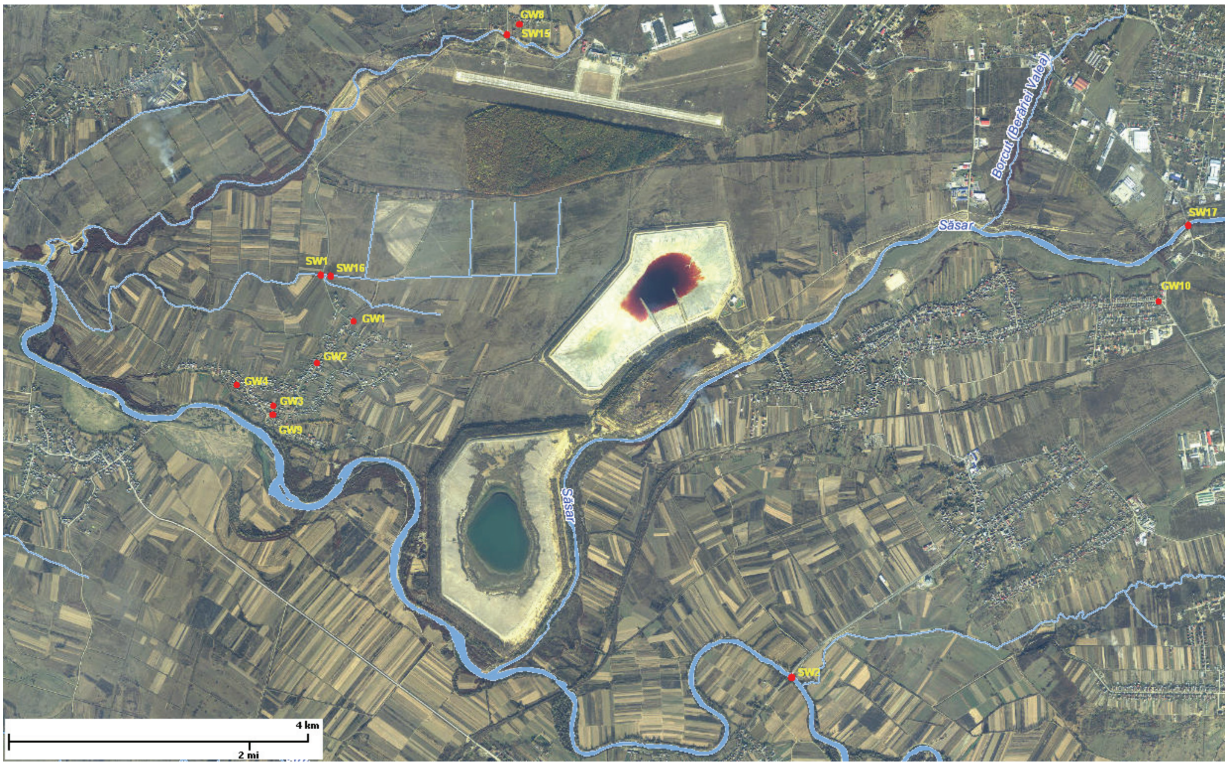

Fig. 2. Water sampling points in the Western part of Baia Mare; SW – surface water; GW – ground water

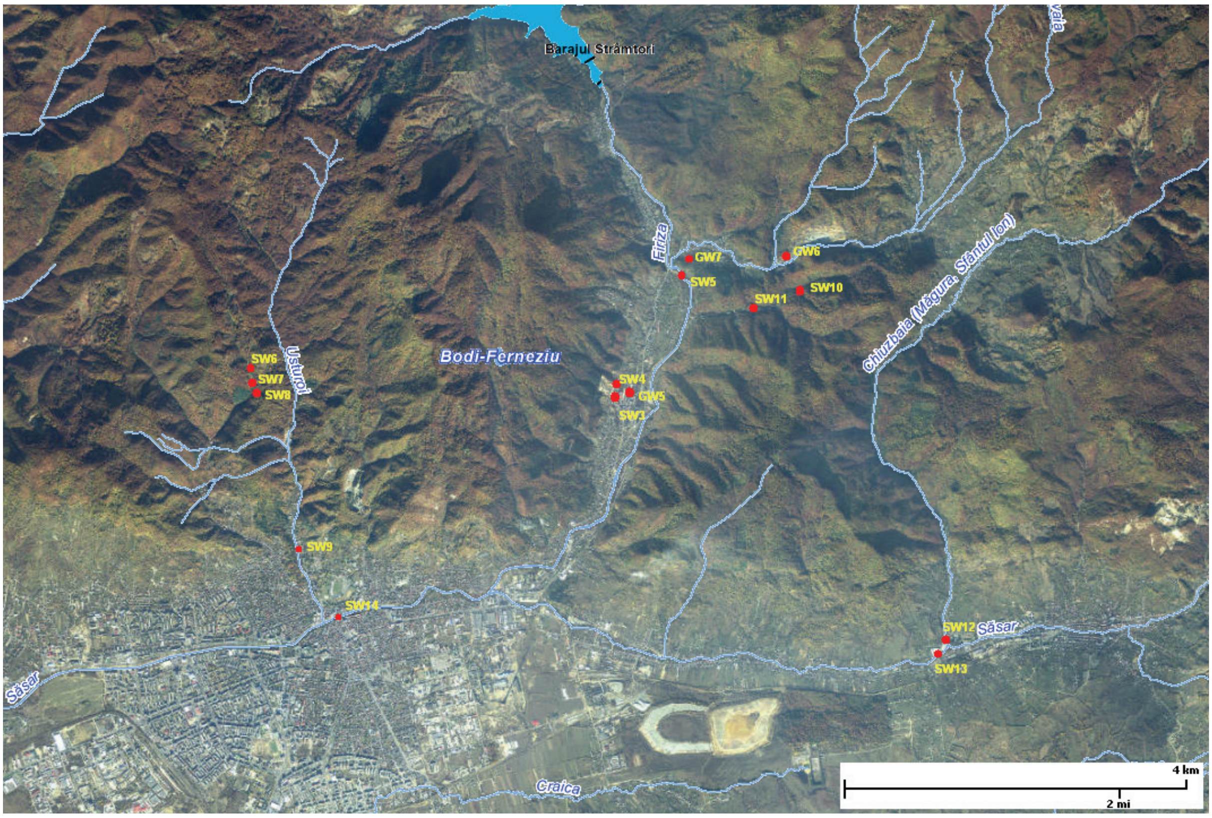

Fig. 3. Water sampling points in the Eastern part of Baia Mare; SW – surface water; GW – ground water

The analyses of the heavy metals were performed using a ZEEnit 700 atomic absorption spectrometer with acetylene–air flame and the adequate cathode lamps at the recommended conditions. The major dissolved ions were analysed using an ion chromatograph IC 1500 Dionex, with IonPac AS23, 4×250 mm (for anions) and IonPac CS12A, 4×250 mm (for cations) columns.

4. Results and discussion

4.1. The analysis of the water samples

The analysed physicochemical parameters were electrical conductivity (EC), salinity, redox potential (Eh) and pH. Their levels were compared with the permissible limits set by the Romanian legislation, which for surface water quality is the Ministry Order, MEWM (2006).

As shown in Fig. 4, the electrical conductivity of the surface waters ranged between 72.7 and 1579 µS/cm, with an average level of 478.03 µS/cm, while in the groundwater the EC was higher, ranging between 251 and 1263 µS/cm, with an average of 664.1 µS/cm. Some of these ground waters are used as potable water and their EC was below the permissible limit imposed by the Romanian legislation which is 2500 µS/cm (RL, 2002).

As in the case of EC, the salinity was slightly higher in the surface water (0-0.7 ‰, with an average of 0.22‰) than in the ground water (0-0.6‰, with an average of 0.25‰), reflecting the high amounts of dissolved salts (Fig. 4). Generally, the surface waters had a higher redox potential (more positive), ranging between -30.5 and 186 mV, compared to the groundwater, which had a lower Eh (negative values), ranging between -40.8 and -0.7 mV (Fig. 4).

The pH level of the groundwater samples ranged between 6.69 and 8.88, having an average value of 7.17 (Fig. 4). The groundwater had the pH within the permissible limits (6.5 – 9.5) set by the Romanian legislation. Contrarily, the pH of the surface waters varied significantly, having values between 3.37 and 7.52, with an average value of 5.91. Generally, the pH of the surface waters was slightly acidic (Fig. 5), and exceeded the limits (6.5 – 8.5) set by the Romanian legislation for the surface waters (MEWM, 2006).

Some of the surface water samples were taken from the creeks, downstream of the mining waste deposits or downstream of the old mine and these samples were more acidic (ex.: SW1, SW7, SW12, SW15, SW16). The low pH in the proximity of mining wastes is the result of sulphide mineral oxidation, as pyrite, according to the equations (1)÷(4), resulting in the mobilisation of heavy metals and the pollution of the surface and groundwater resources (Dold, 2008). In the rivers, due to the intake of large amounts of fresh water and due to neutralization reactions with the natural backgrounds, the pH is increasing, and the natural attenuation phenomena appears (Wilkin, 2007).

The concentrations of the major dissolved ions detected in both surface and ground water samples are summarized in Fig. 6. Generally, the ions content was higher in the groundwater than in the surface water. In the surface waters the dominating dissolved ions were Ca^{2+} (9.64 – 206.2 mg/L, with an average value of 58.44 mg/L) and SO_4^{2-} (5.6 – 725.96 mg/L, with an average value of 97.26 mg/L), while in the ground waters the dominating ions were NO_3^- (1.3 – 829.35 mg/L, with an average value of 254.63 mg/L) and Cl^- (4.83 – 342.82 mg/L, with an average level of 84.96 mg/L).

The higher concentration of NO_3^- and NH_4^+ in the groundwater samples is assumed to be a result of the stables for the livestock and the turd hills from the people's yard.

In the surface waters the Na^+ concentration ranged between 2.72 and 18.34 mg/L, with an average level of 7.85 mg/L, being lower than 25 mg/L, the maximum permissible limit for 1st class of quality (Order 161/2006). The Na^+ concentration in the ground water samples was within the maximum permissible limit for potable water (200 mg/L) with the exception of sample GW3 (245 mg/L) (Fig. 6).

The level of Cl- ranged between 1.37 and 36.14 mg/L, with an average level of 6.91 (Fig. 6). The maximum permissible limit for 1st class of quality (25 mg/L) was exceeded only in sample SW1, the rest of surface water samples had a chlorine level under 17.35 mg/L. Generally, the surface water samples had a high level of NO_3^-. The samples SW3, SW6-9, SW12-16 correspond to 1st class of quality, having the NO_3^- content lower than 1 mg/L. The samples SW10 and SW11 correspond to 2nd class of quality (1 mg/L < NO_3^- < 3 mg/L), while the samples SW4, SW5 and SW17 are included in the 3rd class of quality (3mg/L < NO3- < 5.6 mg/L). The highest level of NO3- was registered in the samples SW1 (33.4 mg/L) and SW2 (174.39 mg/L), which considerably exceeded the maximum permissible limit for the 4th class of quality (11.2 mg/L).

The ground water samples GW5-10 had a low level of NO_3^-, below the permissible limit for potable water (50 mg/L), while the samples GW1-4 had a considerably higher level of NO_3^- (between 251.6 and 829.4 mg/L).

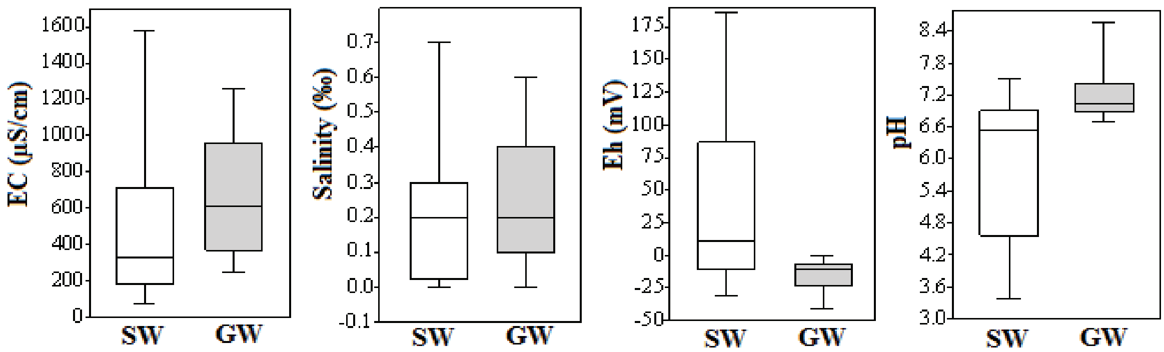

Fig. 4. The levels of the analysed physicochemical parameters in surface water (SW) and groundwater (GW) samples

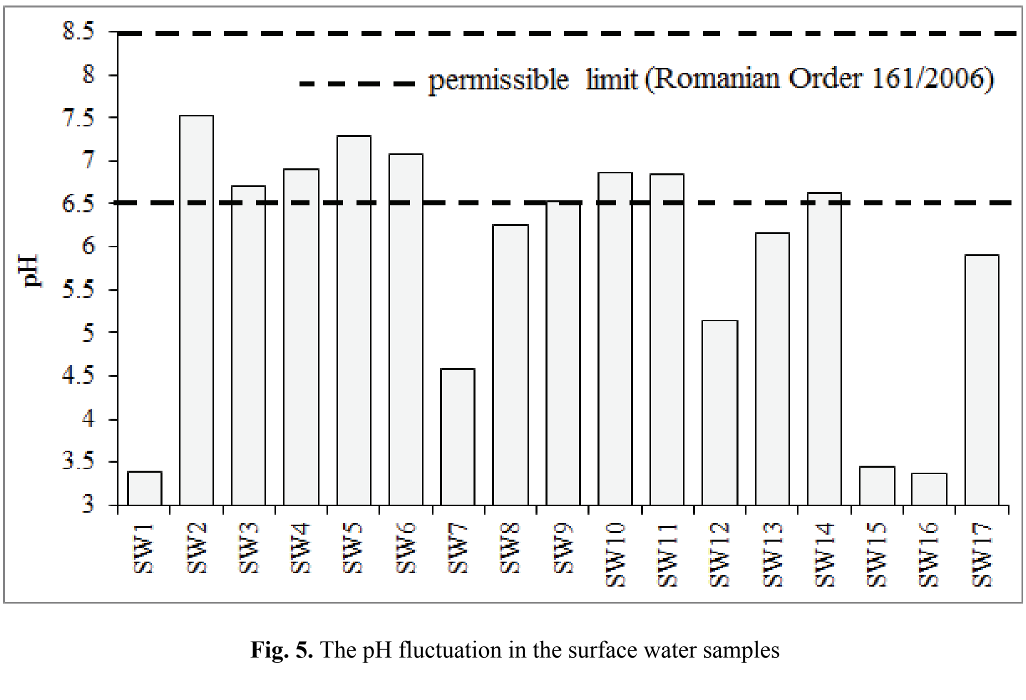

Fig. 5. The pH fluctuation in the surface water samples

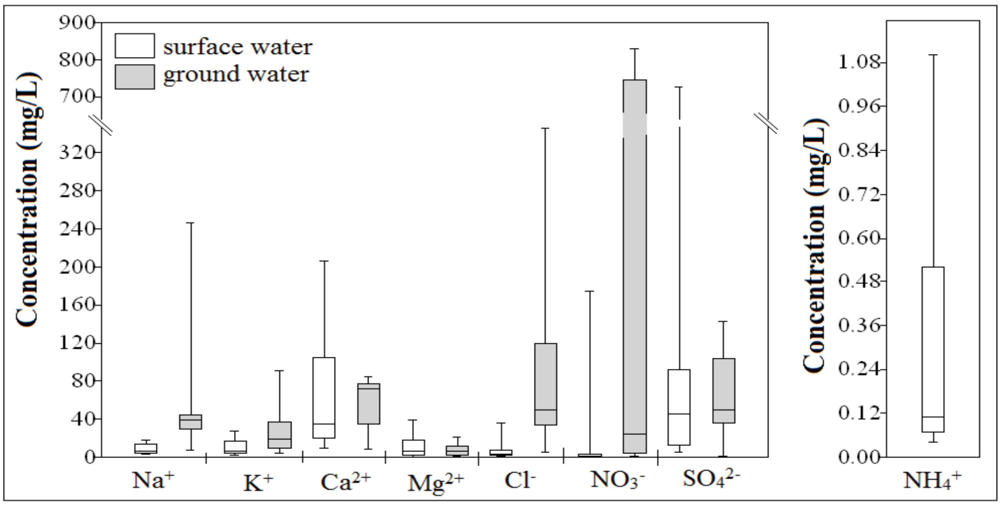

Fig. 6. Major dissolved ions content in both surface and ground water samples

The consumption of these waters by the local people can lead to severe health consequences. The NO_2^- ions were detected only in two ground water samples, GW5 (0.75 mg/L) and GW7 (0.99 mg/L), and their levels of NO_2^- exceeded the maximum permissible limit for potable water (0.5 mg/L).

In the case of Ca^{2+}, two surface water samples (SW3 and SW16) exceeded the level of 50 mg/L for the maximum permissible limit for 1st class of quality, and other three samples (SW2, SW11 and SW12) exceeded the maximum permissible limit (100 mg/L) for 2nd class of quality (Order 161/2006) (Fig. 7). Sample SW9 had the highest concentration of Ca^{2+} (206.2 mg/L) exceeding the maximum permissible limit (200 mg/L) for 3rd class of quality (MEWM, 2006). Five of the surface waters (SW1, SW8, SW10, SW11 and SW13) had a high level of Mg^{2+}, exceeding the maximum permissible limit for 1st class of quality (12 mg/L) (Fig. 8). Generally, the surface waters had a low NH_4^+ level (Fig. 9).

Two of the analysed samples (SW12 and SW14) had the ammonia content higher than the permissible limit for the 1st class of quality (0.4 mg/L), and one sample (SW17) exceeded the permissible limit for the 2nd class of quality (0.8 mg/L).

Some of the surface water samples had a high level of SO_4^{2-} (Fig. 10). Four samples are included in the 2nd class of quality ($60 < SO_4^{2-} < 120$ mg/L), one sample (SW17) belong to 3rd class of quality ($120 < SO_4^{2-} < 250$ mg/L), while sample SW16 belong to 5th class of quality ($SO_4^{2-} > 300$ mg/L).

All the ground water samples had a SO_4^{2-} within the maximum permissible limit (250 mg/L). The higher SO_4^{2-} concentration appears in the surface water samples with low pH values, situated immediately downstream of the mining wastes facilities, and is a result of the sulphide mineral oxidation in the waste rocks, according to equations (1)÷(4) (Dold, 2008; Lottermoser, 2007).

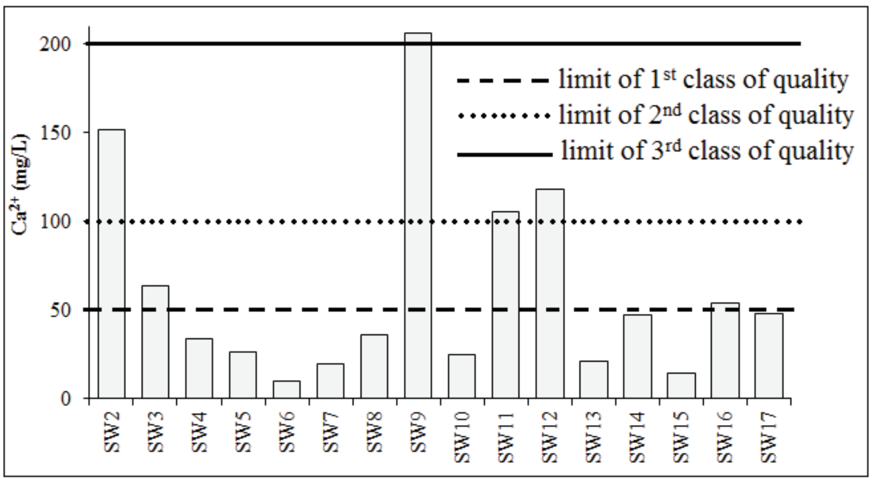

Fig. 7. The concentration of Ca^{2+} in the surface water samples

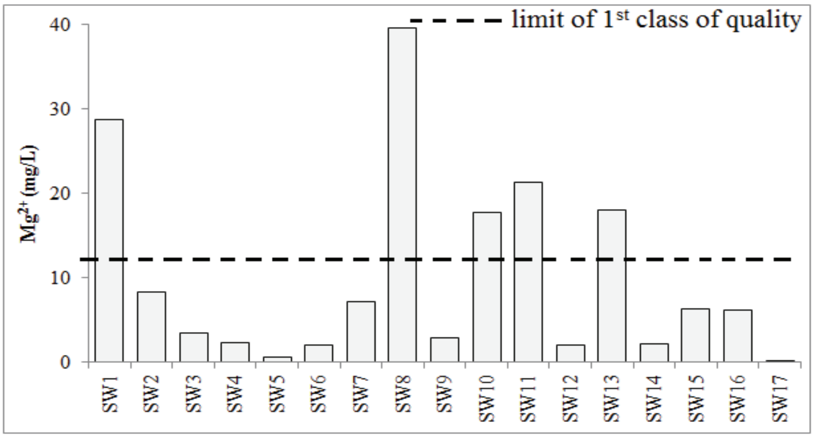

Fig. 8. The concentration of Mg^{2+} in the surface water samples

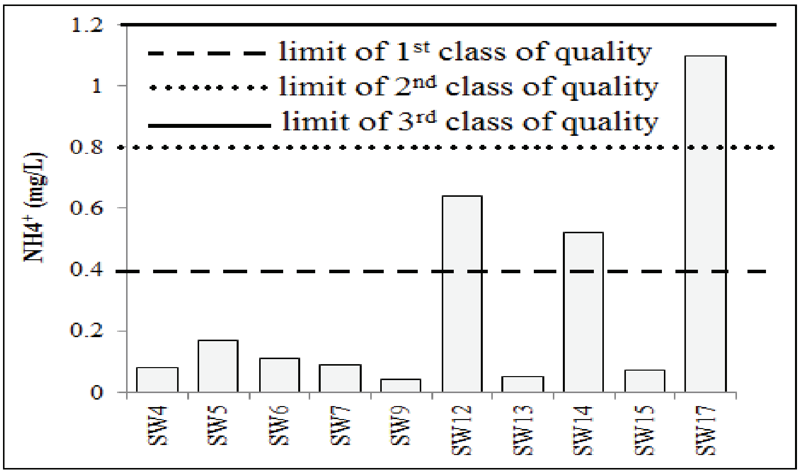

Fig. 9. The concentration of NH_4^+ in the surface water samples

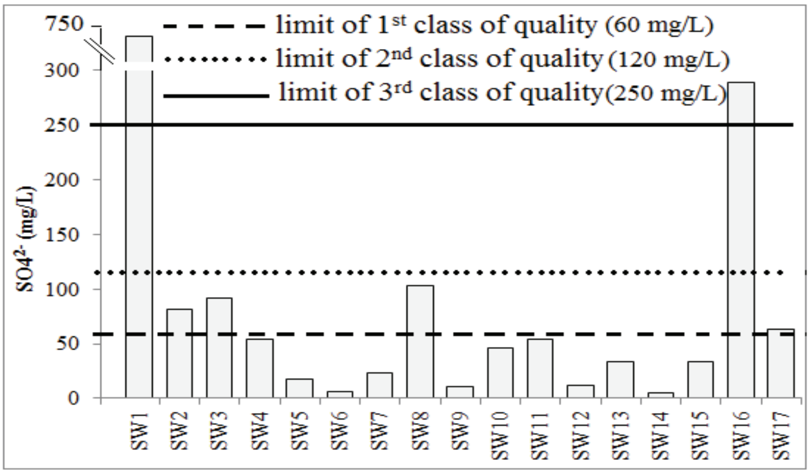

Fig.10. The concentration of SO_4^{2-} in the surface water samples

Besides the physicochemical parameters and dissolved ions, the heavy metals were also analysed in both surface and ground water samples. The decrease of bivalent heavy metals adsorption due to the increase of total dissolved solids (TDS) (or conductivity) levels has been attributed to a variety of factors, including: the competition of cations for the available adsorption sites, the increase in the mineral surface charge, and the formation of strong organic complexes. These factors can lead to an increase in the mobility of the bivalent heavy metals in both surface and groundwater. As a consequence high concentrations of iron, copper or zinc are expected in these waters.

As it is shown in Fig. 11 the dominating heavy metals were iron (0.002 – 11.58 mg/L, with an average value of 3.02 mg/L) and zinc (0.019 – 59.33 mg/L, with an average value of 1.73 mg/L) for the surface waters, while in the ground waters iron (0.007 – 0.011 mg/L, with an average value of 0.009 mg/L) and nickel (0.003 - 0.049 mg/L, with an average value of 0.034 mg/L) were dominating. Considering the copper level, two surface water samples SW1 and SW11 are classified as 2nd class of quality ($0.02 < Cu < 0.03$ mg/L), and one sample (SW16) belong to 5th class of quality ($Cu > 0.1$ mg/L). Otherwise, the other surface water samples are classified as 1st class of quality, with a copper content lower than 0.02 mg/L.

The surface waters had a high level of zinc. Only the samples SW2-4, SW6, S8 and SW 9, are classified as 1st class of quality ($Zn < 0.1$ mg/L), the rest of samples having considerably higher concentrations of zinc. Contrarily, the groundwater had a lower level of zinc, under the maximum permissible limit for potable water (5 mg/L).

With the exception of SW11 (0.006 mg/L) the rest of the surface water samples are classified as 1st class of quality, having the lead level lower than 0.005 mg/L. The lead was detected only in one ground water sample (GW5), which is not suitable for drinking, having a concentration (0.032 mg/L) higher than the maximum permissible limit (0.01 mg/L). The groundwater sample GW5 was taken from a well situated near the metallurgical plant Romplumb. Cadmium was detected in 6 surface water samples: SW1, SW5, SW10 and SW 14 classified as 4th class of quality ($0.002 < Cd < 0.005$ mg/L), and SW2, SW17 classified as 5th class of quality ($Cd > 0.005$ mg/L).

The surface waters had a high level of iron. Only five samples are classified as 1st class of quality (SW2, SW3, SW4, SW6 and SW 14), having the iron concentration lower than 0.3 mg/L. Contrarily, the groundwater had a lower level of iron, under the maximum permissible limit for potable water (0.2 mg/L).

The highest concentrations of heavy metals (Fe, Ni) in the groundwater samples were identified in the wells of Bozânta Mare village, situated downstream to the Aurul and Bozânta tailing ponds.

According to the Dutch Environmental Standards named "Dutch Target and Intervention Value", regarding the metals concentration in the groundwater, some of the groundwater samples exceeded the target values for Zn, Ni, Cu, Cr, Pb, but the intervention value was not exceeded (DTIV, 2000). For the comparison between the natural geochemical background and the polluted ground waters, two samples upstream of the mining wastes areas were taken (GW6 and GW7).

The groundwater sample GW6 taken from near the lime open pit Limpedea was found to be unpolluted, with all of the analysed parameters (including heavy metals) being below the permissible limits. The groundwater sample GW7, taken from the well of a resident's courtyard, presented a small increase of the NO_2^- and NO_3^- values, for which the pollution source is assumed to be the stable for animals in the household. All the other analysed parameters were within the permissible limits.

High heavy metal concentrations were detected in the section of the Săsar River crossing Baia Mare. In this section, the river is polluted as a result of the past mining activities and it was classified in the 4th and 5th quality classes.

4.2. Environmental risks

The environmental pollution generated by the mining activities and the mining wastes facilities is continuous, even during the closure and post-closure phases of the mines, for a long period of time, over many decades (Coynel et al., 2007).

The exposure of mining wastes to the weathering effects can last several decades or more, depending on the ecological rehabilitation actions and their efficiency. Even if the mining waste heaps were properly rehabilitated, accidents such as water infiltrations or landslides may occur and these undesirable events may generate environmental pollution.

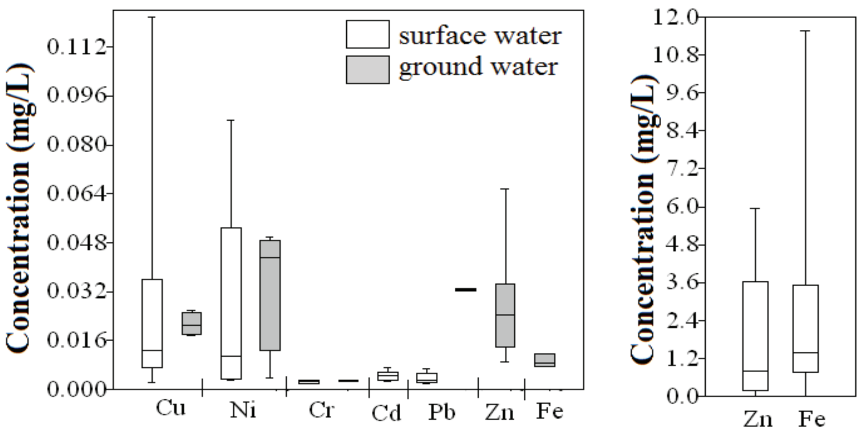

Fig. 11. The concentration of heavy metals in the water samples

Therefore the ecological rehabilitation of the mining waste is a complex problem, for which a possible solution is the risk analysis approach. The negative effects of the pollutants on the environment and on the human health depend on the toxicity, the route, the intensity and the likelihood of exposure. The pollution may affect the groundwater, the surface water, the soil, the vegetation and fauna (Ramirez Andreota et al., 2013). The groundwater is an important source of drinking water, especially for the rural population, and can also be used for agriculture, as water for irrigation, for livestock or for industrial purposes, as an industrial water resource (Rotaru and Raileanu, 2008). The consumption of contaminated water is a direct way of exposure for humans, which may produce serious health prejudices (Briggs, 2003).

The risk is the probability that a pollutant has adverse effects on the population or environment, (Chon et al., 2012; Panagopoulos et al., 2009). Vegetation exposure to soil contaminants depends on the bioavailability of the pollutants (Hlihor et al., 2009; Modoi et al., 2011), on the pollutant concentration and on the exposure time (Järup, 2003). The heavy metals are able to accumulate in living organisms (Chi et al., 2007), either directly through consumption of contaminated water or indirectly by consumption of contaminated plants or meat (Doğan-Sağlamtimur and Kumbur, 2010).

In this case study, the environmental risk assessment is based on a preliminary risk analysis including hazard identification (sampling and chemical analysis), identification of vulnerable areas, pathways of exposure and the qualitative analysis of exposure likelihood. The conceptual risk model for the mining activities in the Baia Mare region is presented in Fig. 12. To determine the impact of the mining waste facilities on the water quality, and also for the development of a suitable decision support for the rehabilitation of the area, a comparative analysis between the unpolluted and polluted water's quality was performed. Mining wastes and mining activities may present different exposure pathways through which the pollutants reach the receptors, such as infiltration, leaking, surfaces runoff, diffuse pollution, wind erosion etc. (Palumbo-Roe et al., 2012).

The exposure of the receptors to contaminants may be aggravated by the short distances between the pollution source and the receptor. For example, the distance between the Western tailing ponds from the Baia Mare area, and the village Bozânta Mare situated downstream is only about 1 km, the village having approx. 600 inhabitants. Some of them, more or less occasionally, use the groundwater from the wells as drinking water, and usually use it for the agricultural purposes. In the villages there are drinking water supply systems, but some of the residents prefer to use the groundwater from the wells, because of various reasons: habits, traditions, tastes etc (Gurzău et.al., 2012). In terms of the metals content the groundwater from the Bozânta Mare village contains high concentrations of heavy metals (Zn, Cu, Ni, Cr), but they do not exceed the limits for the surface drinking water. Nevertheless, the concentrations are higher than the limits established in the Dutch Standards (DTIV, 2000) for the metals in the groundwater.

The concentration of the metals in the shallow groundwater samples is a result of the interactions with the geochemical environment, but also of the proximity of the tailing dams. In the groundwater sample taken from the well GW5, near the metallurgical plant Romplumb, the concentration of Pb was found higher than in the mentioned Dutch document. This groundwater is not used as drinking water, but is used for agricultural purposes. In this case, it would be important to protect the people and to communicate the risk to which they are exposed to. The groundwater located downstream from the mining wastes or other mining activities is not the main drinking water resource for the area. The drinking water source of the region is the Firiza reservoir. The Firiza lake is located upstream of the pollution sources, at a higher altitude than the town, at approx. 8 km from Baia Mare. The water quality in the Firiza Lake is monitored by the Company for Drinking Water "Apele Romane", and the data shows that the quality of the water is proper to be used as drinking water.

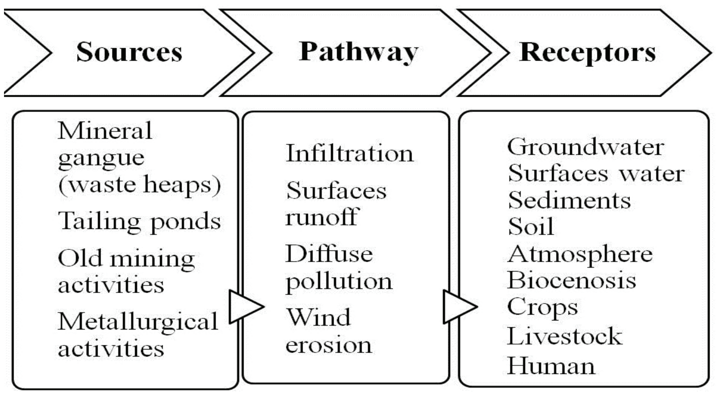

Fig. 12. The conceptual risk model

Not only the mining activities have generated groundwater pollution, but also some agricultural activities (the high concentration of the NO_3^- in some of the groundwater samples and the NH_4^+ in some surface water samples), especially the stables for the livestock in the courtyard, and problems with the sewer system for the household wastewater.

The values of the electric conductivity (EC) in several groundwater samples (eg: GW3, GW4, GW8) were around 1000 µS /cm, which are too high to be used as drinking water in accordance with the World Health Organization and others (Harter, 2003; WHO, 2003). Other previous research studies conducted in the region, for the determination of the concentrations of metals in the soil and in the groundwater and for the assessment of the bioavailability of the metals, had also drawn caution for the use of groundwater in the agriculture or as drinking water in the area (Culicov et al., 2002; Frențiu et al., 2007).

The annual reports of the EPA Maramures mention that the groundwater pollution with heavy metals and cyanide generated by the accident from the Aurul tailing dam (2000) was naturally attenuated. The existence of significant concentrations of heavy metals in the groundwater was detected, especially in the immediate vicinity of the old uninsulated tailings ponds, (BozântaVechi and Bozânta Nou). The same conclusion was drawn from the study of Gurzau et.al. (2012) concerning the groundwater quality in the area and the population exposure to heavy metals from the groundwater. Gurzau et al. (2012) and Neamţiu and Pop (2014) assessed the health of the local population in the region, taking into account the environmental pollution with heavy metals, especially the groundwater pollution. The population exposure to heavy metals was also evaluated taking into account the consumption of the groundwater from the wells from their courtyard as drinking water. Both studies also considered the monitoring of the population health in the region, which was carried out by family doctors in the area, during the interval 2000 - 2009, immediately after the accident in 2000, from the Aurul tailings dam facility.

The measurements in the blood and the urine of the biomarkers for population exposure in the region to heavy metals had usually values below the limits, for the sample of population analyzed, except for a few cases (Neamţiu and Pop, 2014). The general morbidity caused by chronic diseases in the area is not significantly different compared to other places in the area or in the country (Gurzău, 2012).

Regarding the surface water pollution, according to the analyses, a high pollution with heavy metals in some river sectors was observed, classifying these rivers in the lowest quality classes. For example, the Săsar River sector in Baia Mare and immediately downstream of the town is classified in the lower quality classes IV, and V, because of the high concentrations of heavy metals in the water.

In the rivers where the heavy metals concentrations exceed the pollution thresholds, the aquatic biocenosis cannot grow properly. Heavy metals do not only migrate in the environment, but they may expand pollution to the surrounding areas, turn into persistent, highly toxic metal compounds, which may bio-accumulate in living organisms (plant and animal), being amplified in the food chain, and generating threats for human health (Zhou et al., 2008).

The heavy metals in surface waters may be also deposited on the sediments and thus became a long-term pollution source for the benthic organisms, and a contamination source for the higher trophic levels, including the fish. The sediments pollution also presents a potential hazard to the water quality, because the heavy metals may be released in the water, due to some physicochemical aquatic environment changes (Kabata-Pendias and Mukherjee, 2007; Miclean et. al., 2009; Tekin-Özan; 2008). Miclean et al. (2009) determined some significant concentrations of Pb, Cd and Zn in the fish samples taken from the Lăpuș River. The highest values were determined in the samples taken downstream to the tailings dam facilities located in the West of Baia Mare (Bozânta Nou, Bozânta Vechi, Aurul). Long term ingestion of contaminated fish with heavy metals by the population represents a serious health hazard.

5. Conclusion

For the determination of surface and groundwater pollution caused by heavy metals resulted from the mining activities, in the vicinity of the sensitive receptors located downstream of the tailings dams, water samples were taken and analysed. The evaluation of the surface water quality underlined their pollution level with heavy metals, especially in the areas downstream the mining waste facilities around the Baia Mare area. Two reference water samples were also analysed, to determine the influence of the geochemical environment on the groundwater quality. In those unpolluted water samples, taken upstream the mining waste facilities the presence of heavy metals was not detected.

The conceptual risk model used in the study highlighted the fact that there are many sensitive receptors in the studied region: residents and their livestock, crops or surface water. The results of the case study may be used in further studies for the environmental and human health risk assessment, and as a support to decision making for ecological rehabilitation of mining waste facilities.

The area is connected to the water supply network, and the tap water quality is guaranteed through daily monitoring by the public health authority and water management authority.

Therefore, it is also important to inform the local population about the risks of exposure to contaminants by consuming of shallow groundwater from their wells.

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