

## THE QUALITY OF WATER AND SOIL IN HANEȘ MINING AREA, ALBA COUNTY, ROMANIA

**George ISPAS<sup>1</sup>, Carmen ROBA<sup>1\*</sup>, Ramona BĂLC<sup>1</sup>, Mihaela COADĂ<sup>1</sup> &  
Delia GLIGOR<sup>1</sup>**

*<sup>1</sup>Babeș-Bolyai University, Faculty of Environmental Science and Engineering, 30 Fântânele Street, 400294,  
Cluj-Napoca, Romania: carmen.roba@ubbcluj.ro*

**Abstract:** The mining activities from Haneș area caused a severe pollution of the environment, affecting human health. In this study, a number of 52 samples (both water and soil) have been collected over a period of three years from Haneș mining area and along the Turnului Creek (which crosses the Haneș locality). Physico-chemical (pH, redox potential, electrical conductivity, and salinity) and chemical parameters consisting of dissolved anions ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $NO_2^-$  and  $S^{2-}$ ) and heavy metals (Cr, Pb, Ni, Cu, Zn, and Fe) have been analyzed in order to evaluate the quality of the environment. For some of the analyzed wastewaters, the concentration of Ni, Zn, Pb, Fe,  $F^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $SO_4^{2-}$ , and  $S^{2-}$  exceeded the maximum permissible limits (MPL) imposed by the Romanian legislation regarding the discharge in surface water. As a consequence, most of the analyzed surface waters were classified as 5<sup>th</sup> quality class, corresponding to a bad quality. High levels of Zn, Cu, and Pb have been identified in investigated soil samples, exceeding the alert thresholds and even the intervention threshold, for Cu and Pb. The obtained results indicate the presence of several toxic elements, which may represent a risk factor for the ecosystems and human health in the investigated area.

**Keywords:** mining, heavy metals pollution, environmental assessment, Haneș, Romania

### 1. INTRODUCTION

Mining activities are some of the most polluting human activities, severely affecting all the environmental components (water, soil, air) (Donkor et al., 2005; Getaneh & Alemayehu, 2006; González et al., 2007). Ore mining causes the destruction of natural ecosystems through the removal of soil and vegetation and burying them in waste dumps (Cooke & Johnson, 2002). The extraction of ore consists in the grinding of minerals and rocks, extracting useful elements, and storage of waste in tailing ponds or waste dumps (Ledin & Pedersen, 1996).

Romania is one of the countries known for mining, industrial and agricultural pollution; a total of 14 hot-spot areas (Copșa Mică, Baia Mare, Zlatna, Ploiești-Brazi, Onești, Bacău, Suceava, Pitești, Târgu Mureș, Turnu Măgurele, Tulcea, Ișalnița, Brașov and Govora), with a severe degree of contamination with toxic elements (mainly heavy metals) have been identified across the country (Paulette et al., 2015).

The polymetallic ores containing Au and Ag

mineralization from Apuseni Mountains began to be exploited since the Roman time at Roșia Montana (Alburnus Maior) and Zlatna (Ampellum). During the communism time, the mining and related activities had a particular development, producing severe pollution, especially along the Ampoi and Arieș Rivers (Mac & Ripeanu, 1996).

SC Ampellum SA from Zlatna (Alba County) produced a major atmospheric pollution by gaseous emissions ( $SO_2$ ,  $SO_3$ ,  $NO_x$ ) and dust, but also through wastewater discharged into the surface waters. Even if the mining activities have been interrupted in 2004, the pollution sources are still present, being represented by three tailing ponds and a copper smelter (Gamarra et al., 2014). The pollution degree from Zlatna area is exceeded only in Baia Mare and Copșa Mică areas (Șerban et al., 1993). The mining activities from Zlatna area had a significant impact on the quality of Ampoi River, which flows through Zlatna town and joins Mureș River near Alba Iulia city (west-central Romania). The geographical factors, especially the west and north-west winds had

enhanced the pollution along the Ampoi River (Ileana & Popa, 2001), by carrying significant amounts of dust contaminated with heavy metals. It was estimated that the contaminated dust affected 30,000 ha of farmlands and 49,000 ha of forests in Zlatna area (Abrudan & Turnock, 1999). The SO<sub>2</sub> atmospheric emissions reached 150 – 450 tons per year, while the contaminated dust reached around 3,498 tons per year (Șerban et al., 1993; Damian et al., 2008). The Ampoi River represents a hot-spot regarding the Pb contamination and some studies carried out in the area (Gamarra et al., 2014), predicted an increase of Pb concentrations caused by the mobilization of lead, present in the river sediments, if no remediation measures will be applied.

The pollution of Ampoi and Arieș Rivers is caused, in equal measure, by the mining exploitation of Zlatna and Haneș. Haneș mining area is located in Apuseni Mountains, at a distance of 9 km north-west from Zlatna town, and belongs to the same metallogenetic field, where gold-silver and polymetallic ores were extracted. The studies regarding the pollution degree in the Haneș mining area are scarce. Grawunder et al. (2014) studied the pyrite from Haneș mining, pointing out the presence of middle rare elements into acid mine waters. These elements are related to complexation processes and oxidation of intermediate-S species from pyrite. Thus, the acid waters can be formed by mining activities and by natural causes as well.

The studies carried out on the above mentioned areas, pointed out the presence of heavy metals into the soil, waters, air and vegetation. There are many studies focused on the heavy metals contamination of soil and water in the area, using different analytical techniques like the flame atomic spectroscopy (Lăcătușu et al., 2001; Damian et al., 2008; Suciu et al., 2008; Măicăneanu et al., 2013), X-ray fluorescence spectroscopy (Weindorf et al., 2013), or coupled plasma atomic emission spectrometry (Pope et al., 2005; Găgiu et al., 2015). Among the studies, focused on the presence of heavy metals in vegetation in the mining areas of Zlatna and Haneș, it should be mentioned those of Pope et al. (2005) and Lăcătușu & Lăcătușu (2008), who had studied the vegetables and fruits contamination with heavy metals. Rusu et al. (2006) have performed a study of environment quality biomonitoring near the Zlatna area using lichen *Hypogymnia physodes* and bark samples. Most of these studies are focused on Zlatna area and only few emphasize the environment pollution with heavy metals in Haneș mining area.

In addition, some other studies have been carried out on contaminated soils from Zlatna in order

to establish the phytoremediation capability of some microbial community (Sprocati et al., 2014) or to understand the tolerance mechanisms, adaptive response and evolution of some lichens (Purvis, 2014). A conceptual model of catchment-scale remediation of Zlatna area has been proposed by Gamarra et al. (2014), based on the contaminant source degree, the ratio between contaminated and non-contaminated sediments and the frequency of sediment transport.

The aim of this study is to evaluate the quality of soil (with sensitive and less sensitive usage) and water (wastewater, surface water and drinking water) in Haneș mining area. In order to assess the pollution degree, some physico-chemical (electrical conductivity, salinity, pH, and redox potential), chemical parameters consisting of dissolved ions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup> and S<sup>2-</sup>) and heavy metals (Cr, Pb, Ni, Cu, Zn, and Fe) have been investigated. The physico-chemical parameters, NO<sub>2</sub><sup>-</sup> and S<sup>2-</sup> were monitored over a period of three years (2013 – 2015), while the content of heavy metals, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and SO<sub>4</sub><sup>2-</sup> was analyzed during 2013.

## 2. MATERIALS AND METHODS

### 2.1. Study area

Zlatna town is located into the Apuseni Mountains, in Zlatna Depression, at 450-500 m altitude and 38 km west from Alba-Iulia city (Fig. 1). A mineral processing plant and a copper smelter have been opened close to the center of the city. The processing plant has processed base metals ores from the Haneș area. Copper smelter began operating in 1747 and produced copper (between 3,000 and 10,000 tons per year) and iron-silicate slags (Manea et al., 2013). All these activities produced an intense pollution with Cu, Zn, Pb, Sb, Cd, Bi, Cd, and SO<sub>4</sub><sup>2-</sup> (Williamson et al., 2003).

Haneș mine is located in Apuseni Mountains, at a distance of 9 km north-west from Zlatna town, at 700 m altitude. The gold deposit is related to a quartziferous andesitic body, situated in Iepure Hill (Udubașa, 1970).

A vein of Larga deposit (which belongs to Zlatna mining area), very rich in pyrite (FeS<sub>2</sub>), sphalerite (ZnS), galena (PbS), chalcopryrite (CuFeS<sub>2</sub>), pyrrhotite (FeS), gold and gang minerals (quartz, calcite, dolomite, clay minerals) (Măicăneanu et al., 2013) has been exploited until 2004 (Cook & Ciobanu, 2004; Cook et al., 2009), even if the production was around 80,000 tons of ore per month with a combined Zn/Pb grade of 5% with 1 g Au and 30 g Ag (Drew,

1998). The ore extracted from Haneş mine was transported by trucks, and processed into the Zlatna plant. The acid mine waters are discharged into the surface waters, reaching the Turnului Creek, then Almaş and Ampoi rivers.

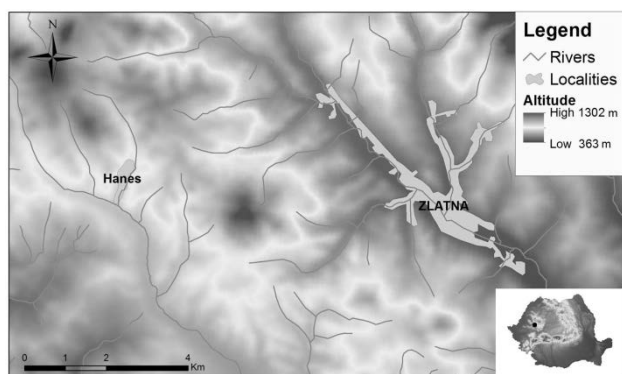


Figure 1. Location of the investigated area.

## 2.2. Sampling and analytical methods

In order to evaluate the impact of the former mining activities developed in the area, a total of 34 water samples and 18 soil samples were collected during three campaigns (autumn 2013, autumn 2014 and spring 2015). The samples consisted of surface waters (18), wastewaters (12), drinking waters (4), soils with sensitive usage (12) and soils with less sensitive usage (6). The classification of soil type was made according to Romanian legislation (Order 756 from 3 November 1997), which states that soils with sensitive usage are soils used for residential areas, recreational purposes, for agricultural purposes, as protected areas, or sanitary areas, while soils with less sensitive usage are soils used for industrial or commercial purposes.

Some of the sampling points were located in the close vicinity of pollution sources (abandoned mine galleries, explosive deposit), while other sampling points were located upstream and downstream from the pollution sources (Fig. 2).

The physical parameters of soil samples were analyzed using current national standard protocols, as follows: determination of organic matter - STAS 7107/1-76; determination of moisture - STAS 1913/1-82; determination of grain size-sedimentation and sift method - STAS 1913/5-85 EN 14688-2 and SR: 2005 determination of density land-hydrostatic immersion method - STAS 1913/3-76 and determination of free swelling - STAS 1913 / 2-88.

The soil pH, redox potential, electrical conductivity and salinity, were measured in aquatic suspension (1:5 v:v) according to SR ISO 10390:2015, by using a portable multiparameter (WTW Multi 350i).

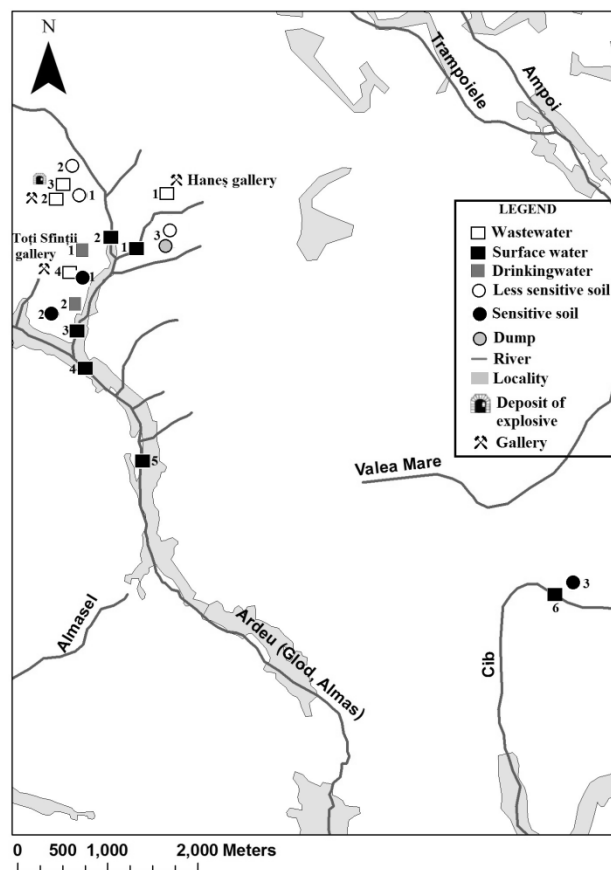


Figure 2. Sampling points (modified map in Google Earth).

The physico-chemical parameters of water samples (electrical conductivity, salinity, pH, and redox potential) were measured *in situ* with a portable multiparameter (WTW Multi 350i). The dissolved ions ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ) were analyzed by ion chromatography (IC 1500 Dionex), while  $NO_2^-$  and  $S^{2-}$  were analyzed by electrochemical methods. The electrochemical determination of nitrites (in water and soil) was performed using carbon paste electrodes (CPEs) modified with zeolite adsorbed with Toluidine Blue (CPE-Z-TB) and the sulphide determination was performed using carbon paste electrodes modified with zeolite adsorbed with Methylene Blue (CPE-Z-MB). The electrochemical experiments (amperometry) were carried out using an AUTOLAB electrochemical analyzer (Autolab-PGSTAT10, Eco Chemie, Utrecht, Netherlands); all measurements were performed at room temperature. The obtained amperometric sensors CPE-Z-TB and CPE-Z-MBs were used for the detection of nitrite and sulphide, respectively, using the standard addition method.

Heavy metals were analyzed by flame atomic absorption spectrometry (AAS-F) using an AAS ZEEnit 700 system (Analytik Jena). Before instrumental analysis the water samples were acidified with  $HNO_3$  (65%) and soil samples were mineralized with *aqua regia*.

In order to evaluate the pollution degree of the environment in the area and the potential effects upon human health, the values of the investigated quality parameters were compared to the maximum permissible limits imposed by Romanian legislation for surface waters (Order no. 161/2006), drinking water (Law no.458 of 8 August 2002), wastewaters (GD no. 352/21 April 2005), and soils (Order no. 756/3 November 1997).

### 3. RESULTS AND DISCUSSION

#### 3.1. Physico-chemical parameters of water samples

The annual variation of the measured physico-chemical parameters for the waters sampled from Haneş area are presented in figure 3.

##### 3.1.1. Wastewaters

Except for sample 4 (from the entrance to the Toţi Sfinţii mine galery), the wastewaters had a highly acidic pH, between 2.3 and 3.5, considerably lower than the limits imposed by Romanian legislation (6.5 – 8.5) (GD 352/21 April 2005), for the discharge of wastewaters in

surface waters (Fig. 3). These waters are mining waters coming from the former mining galleries (samples 1 and 2) and an explosive deposit (sample 3) and are discharged into the surface water (Turnului Creek) without any treatment. The wastewater sampled from point 4 had a considerably higher pH (6.9 – 7.2), possibly due to the fact that at the mine gallery entrance there is a wall containing some limestone material. It is well known that the limestone is successfully used for wastewater decontamination (Aziz & Mohd., 1998; Popescu et al., 2008; Srivastava & Goyal, 2010; Macias et al., 2012; Ayora et al., 2013; Yoshida et al., 2016).

The redox potential was generally positive (-7.4 – +236.0 mV) (Fig.3) indicating the presence of oxidizing agents, enhancing the solubility of heavy metals. The EC (405 – 4280  $\mu\text{S}/\text{cm}$ ) and salinity (0.2 – 2.3 ‰) levels were relatively high in the wastewater samples, especially during 2014, reflecting the presence of high contents of organic and inorganic salts (Kremer, 2014).

##### 3.1.2. Surface waters

The discharge of highly untreated mining waters into the Turnului Creek is reflecting in the more acidic pH of the creek close to the discharging

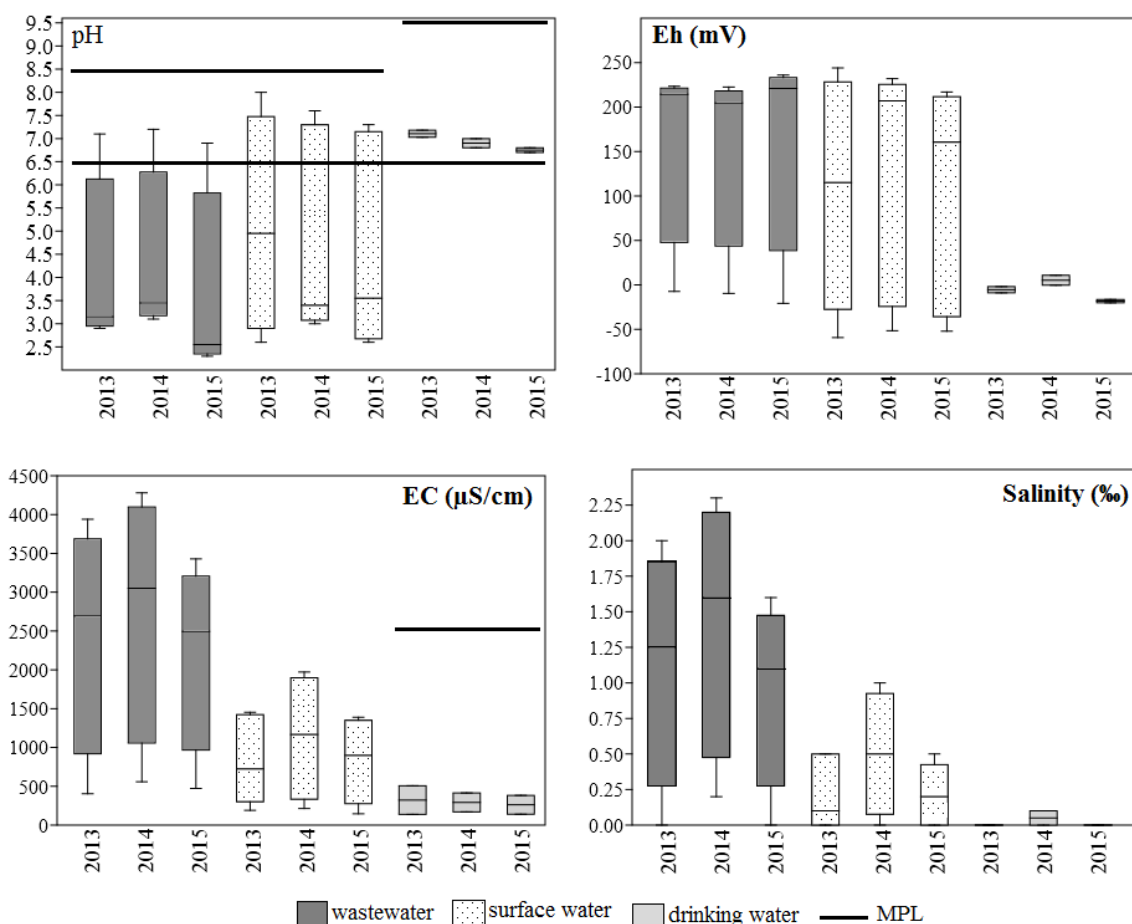


Figure 3. Physico-chemical parameters of analyzed surface waters (n=18), wastewaters (n=12), and drinking waters (n=4) during 2013 – 2015.

points (samples 2 – 5) than upstream (sample 1) (Fig. 3). Due to the high dilution, in sample 6, collected from Almaş River (which collects the Turnului Creek) at approximately 6.5 km downstream of the mine galleries, the pH is neutral to slightly basic (7.1 and 8.0), being within the range of 6.5 – 8.5 imposed by the Romanian legislation (Order 161/16 February 2006) (Fig. 3).

The redox potential ranged between -15.3 and 244.1 mV (Fig. 3), reflecting the presence of high concentrations of oxidizing agents especially during 2013 campaign, enhancing the solubility of heavy metals.

The EC (146.1 – 1972.0  $\mu\text{S}/\text{cm}$ ) and salinity (0.5 – 1.0 ‰) (Fig. 3) levels were considerably lower than in the wastewaters, reflecting the contribution of high dilutions after the wastewater discharging.

### **3.1.3. Drinking waters**

The drinking water pH was within the limits (6.5 – 9.5) (Fig. 3) required by the Romanian legislation (Law 458/08 July 2002).

Generally, the drinking waters had a stable redox potential, fluctuating between -20.1 and 10.8 mV (Fig. 3).

The analyzed drinking water samples were weakly mineralized, having low levels of EC (139.0 – 507.0  $\mu\text{S}/\text{cm}$ ) (Fig. 3), being for all samples below the maximum permissible limit (MPL) of 2500  $\mu\text{S}/\text{cm}$  (Law 458/08 July 2002).

## **3.2. Dissolved ions and heavy metals concentrations in water samples**

The content of dissolved anions and heavy metals in the analyzed water samples is shown in Fig. 4. The dominant anions proved to be sulphate, chlorine and nitrate, while the abundance of metals was dominated by the presence of Fe, Zn, Cu and Pb.

### **3.2.1. Wastewaters**

The level of chlorine and nitrite was within national standards for all the wastewater samples (Fig. 4). Some of the analyzed wastewaters had a high content of fluorine (1.2 – 13.8 mg/l), nitrate (9.8 – 48.8 mg/l), sulphate (155.5 – 4118.8 mg/l) and sulphides (0.03 – 2.04 mg/l) (Fig. 4); in some cases, these parameters exceeded the MPL imposed by the Romanian legislation for wastewaters discharging in surface water (GD 352/21 April 2005). Fluorine is a very common element in nature, being present in rocks, soil, water, plants and air. A high amount of fluorine in former mining areas has been reported (Colbourn & Thornton, 1978; Geeson et al., 1998) as a result of aerial and fluvial dispersion of waste

material. Through weathering processes of fluorine-based minerals, significant amounts of fluorine can be released into the environment (Geeson et al., 1998). The mobility of this element is directly influenced by the water or soil acidity, migrating much easily in acidic environments (Larsen & Widdowson, 1971; Omuetti & Jones, 1980). Having such a high mobility, fluorine can be spread far from the place where it has been released at the terrestrial surface (De Rita et al., 2011).

A considerably high content of nitrate (48.8 mg/l) was registered in wastewater from sampling point 1 (Fig. 4), exceeding the MPL (25 mg/l) for wastewater discharge in surface water. The water sample was collected at the entrance of the mining gallery where stagnant water forms a small pond, then flows into Turnului Creek. The stagnant regime of water may have increased the nitrate concentration. A possible source of  $\text{NO}_3^-$  in the sample 1 could be the explosive usage in underground mining for Haneş mine (Fig. 2). Most of the explosive used in mining is based on ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) which is highly soluble in water and dissociates into  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . The high content of sulphates and sulphides from the mining waters reflect geological features of the area, especially the deposits rich in pyrite ( $\text{FeS}_2$ ), sphalerite ( $\text{ZnS}$ ), galena ( $\text{PbS}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), pyrrhotite ( $\text{FeS}$ ), gold and gang minerals (quartz, calcite, dolomite, clay minerals) (Măicăneanu et al., 2013). The high content of  $\text{SO}_4^{2-}$  can be correlated with the low pH of wastewaters which enhance the oxidation of metal sulphides from the area. The study showed high annual fluctuations of sulphides, the concentrations being considerably lower during 2014 and 2015 (Fig. 4). One of the factors which influenced this fluctuation could be the high dilutions caused by the rains registered at the end of September 2014 and 2015, before the sampling campaigns.

Generally, the analyzed wastewaters had a low content of Cr (12.7– 49.2  $\mu\text{g}/\text{l}$ ), Cu (21.5 – 104.0  $\mu\text{g}/\text{l}$ ), Pb (82.2 – 201.9  $\mu\text{g}/\text{l}$ ), and Ni (20.7 – 641.3  $\mu\text{g}/\text{l}$ ), being within the national limit for surface water discharging (Fig. 4), with the exception of Pb and Ni content in sample 3 (acid mine drainage from the closed mine gallery), which exceeded the national MPL (200  $\mu\text{g}/\text{l}$  and 500  $\mu\text{g}/\text{l}$  respectively).

The high content of heavy metals from sampling point 3 can be correlated with the acidic pH of these waters (2.3 – 3.4) and the highly positive redox potential (203.8 – 236 mV) which enhance the metals solubility. The mining water coming from Toţi Sfinţii mine gallery had the lowest content of heavy metals, fact that can be correlated with the high pH (6.9 – 7.2), which can enhance the metals precipitation.

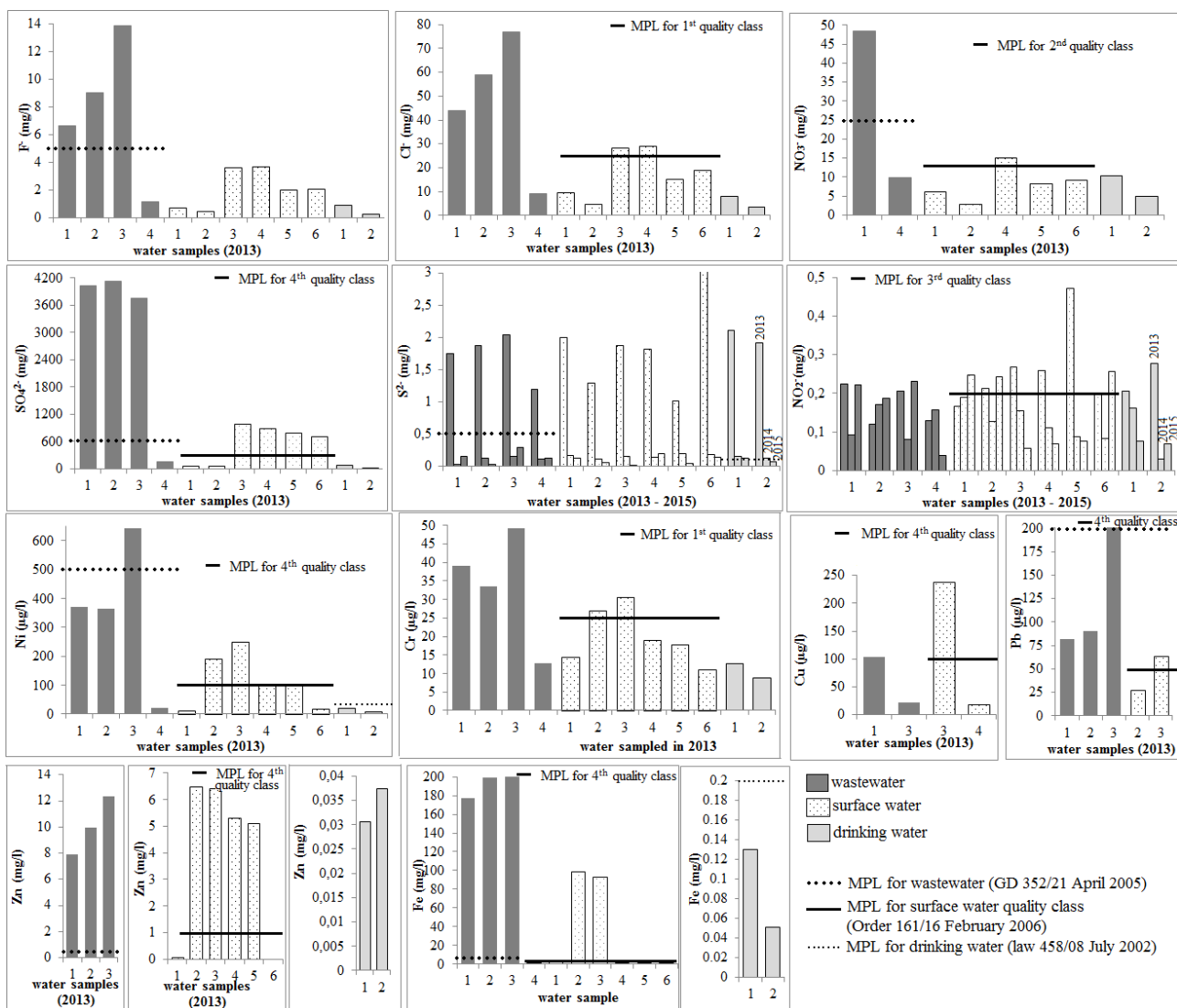


Figure 4. The presence of dissolved ions and heavy metals in the analyzed water samples.

The wastewaters proved to have a high content of Fe (0.2 – 212.0 mg/l) and Zn (7.9 – 12.4 mg/l), considerably exceeding the MPL (50 mg/l and 0.5 mg/l) imposed by national legislation for discharging in surface water (Fig. 4).

### 3.2.2. Surface waters

The chlorine, nitrate and chromium levels from surface water ranged between 4.8 – 29.2 mg/l, 2.9 – 15.03 mg/l and 11.1 – 30.8 µg/l, respectively. Based on Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and Cr content, most of the samples are classified as 1<sup>st</sup> and 2<sup>nd</sup> quality class (Fig. 4). Nitrite content of surface water ranged between 0.06 and 0.47 mg/l, exceeding, for most of the samples collected during 2013, the limit for 3<sup>rd</sup> water quality class. Two of the surface water samples (2 and 3) had a high content of Cu, being classified as 5<sup>th</sup> water quality class (Fig. 4).

Because of the high content of Pb, Ni, Zn, Fe and sulphates in waste waters, the discharge without any treatment of the mining waters into the Turnului Creek

lead to surface water contamination; based on these chemical parameters most of the surface water samples could be classified as 5<sup>th</sup> quality class (Fig. 4).

### 3.2.3. Drinking waters

The content of F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Ni, Zn, Fe in drinking water, was within the maximum allowed concentration for all the analyzed samples, while S<sup>2-</sup> exceeded the national limits for almost all the samples (Fig. 4). Considerably higher levels of S<sup>2-</sup> were registered during 2013 than in 2014 and 2015. The high content of sulphides in drinking water can be correlated with the high level of sulphides in the wastewaters generated from the upstream mine, which could contaminate the groundwater and drinking water.

## 3.3. Physical and physico-chemical parameters of soil samples

The physical parameters indicated that the majority of the investigated soil samples are of sandy

loam type (Table 1). Two of the analyzed soil samples (4 and 5) proved to have high adsorption capacity (Table 1), which means that they can adsorb and retain water rich in toxic compounds. The soil samples 4 and 5 are agriculture soils collected from a residential area and from a small farm, both located in the vicinity of Toți Sfinții mine gallery. The high adsorption capacity of soil samples 4 and 5 is correlated with the high concentrations of  $S^{2-}$ ,  $NO_2^-$ , Cr, Cu, Zn, and Ni identified in these soil samples (Fig. 5).

Table 1. Physical parameters of the soil samples.

Soil	Humidity (W%)	Density ( $g/cm^3$ )	Texture	Adsorption capacity ( $U_L\%$ )	Humus (%)
1	83.19	-	Silty Sand	60	0-1
2	30.62	1.07	Loamy Sand	90	2-5
3	8.52	-		50	0-1
4	76.89	1.06		125	2-5
5	34.67	1.13		110	>5
6	45.35	-		15	>5

Table 2. Physico-chemical parameters of soil samples.

	Soils with sensitive usage	Soils with less sensitive usage
Salinity (‰)		
min	0	0
max		0.9
mean		0.5
pH		
min	6.0	2.4
max	7.8	5.6
mean	7.4	4.1
Electrical conductivity (µS/cm)		
min	25.0	15.1
max	308.0	2100.0
mean	134.0	1098.4
Redox potential (mV)		
min	-50.7	56.6
max	12.9	240.0
mean	-18.3	152.0

The soils with less sensitive usage had a higher salinity (up to 0.9 ‰) and EC (up to 2100  $\mu S/cm$ ) than the sensitive soils, reflecting the impact magnitude of mining activities in the area (Table 2).

Extremely low levels of pH were identified for some of the analyzed soils, especially the soils located in front of the warehouse of explosives and tailing pond (Table 2). The redox potential was positive for the soils with less sensitive usage indicating the

presence of oxidizing agents, enhancing the solubility of heavy metals.

The highest pH values can be observed in soils sampled from the vicinity of the Toți Sfinții mine gallery and from a private garden, which proved to be neutral to slightly basic.

### 3.4. Dissolved ions and heavy metal concentrations in soil samples

The content of dissolved anions and heavy metals in the analyzed soil samples are presented in figure 5.

The nitrite content of soil was generally lower than 500 mg/kg, except for sample 5 (during 2013), where the nitrite level was considerably higher (4009.3 mg/kg), due to the fact that shortly before collecting the soil sample, manure was placed over the soil (Olliver et al., 2013). The sulphides content (70.6 – 188.6 mg/kg) of soils with less sensitive usage was within the maximum limit of Romanian legislations, compared to soils of sensitive usage, where the sulphides content (1.3 – 2362.6 mg/kg) frequently exceeded the alert threshold (200 mg/kg) (Fig. 5). High level of  $S^{2-}$  was registered in the soil S4 sampled in 2013 in the vicinity of the Toți Sfinții mine gallery, exceeding the intervention threshold (1000 mg/kg) (Fig. 5).

The content of Cr, Ni and Zn was relatively low, being for almost all the sample within the normal values for soils (30 mg/kg, 20 mg/kg and 100 mg/kg), according to Romanian legislation (Fig. 5). The soils with less sensitive usage had low levels of Cu and Pb, within the alert threshold, while in some of the soils with sensitive usage the level of Cu (sample S4) and Pb (samples S2, S4 and S5) exceeded the intervention threshold (Fig. 5). High levels of fluorine, nitrate, sulphate and sulphur. The high content of lead from the sensitive usage soils may be a consequence of the geological features of the areas like the presence of minerals rich in lead like galena (PbS) (Măicăneanu et al., 2013).

Sample 4 proved to be highly contaminated with heavy metals, fact that should be correlated with the physical characteristics of the soil sample like the high adsorption capacity (125 %).

## 4. CONCLUSIONS

In this study the concentrations of dissolved anions and heavy metals in the wastewater, surface water, drinking water, and soil have been investigated in Haneș mining area.



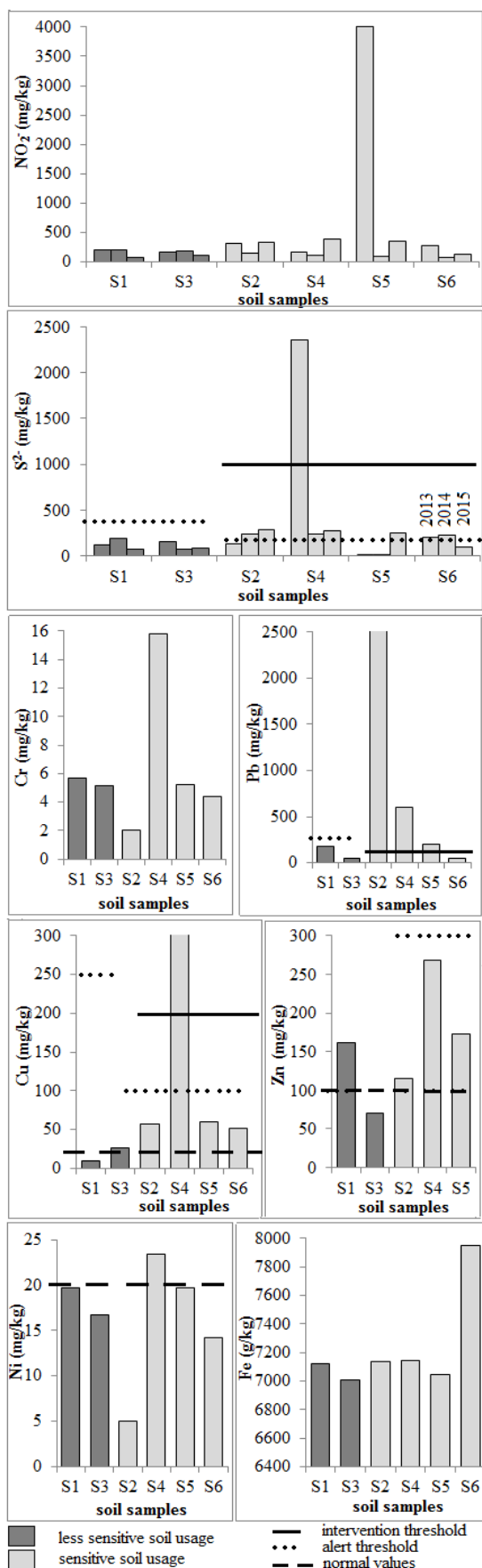


Figure 5. The content of dissolved ions and heavy metals in the analyzed soil samples.

High levels of fluorine, nitrate, sulphate and sulphides have been identified in the analyzed wastewaters. The concentration of heavy metals in these waters is low for Cr and Cu but high for Ni, Pb, Fe, exceeding the permissible limit for discharging in surface waters.

The surface waters can be classified as belonging to the 2<sup>nd</sup> and 3<sup>rd</sup> class (considering the nitrate and nitrite levels); while some of the surface waters can be classified as 5<sup>th</sup> quality class, considering the high content of sulphides, Cu, Pb, Zn and Fe. A high level of sulphides (in samples collected in 2013) has been determined in drinking water. High concentrations of sulphides, Cu and Pb have been identified in some of the soils with sensitive usage, where these elements exceeded the intervention threshold.

Despite the fact that the mining activities in Haneş have been interrupted in 2004, the consequences on the environment are still present. For some of the investigated soil and water samples, there were quality parameters which do not met the requirements imposed by national legislation. As a consequence remediation measures should be applied in order to protect the environment and inhabitants' health.

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