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ASSESSMENT OF GROUNDWATER QUALITY FROM BAIA MARE MINING AREA, ROMANIA

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Abstract

Baia Mare mining area is one of the most important mining areas from our country. Even if all the mines were closed in 2007 they continue to pollute the environment. In the present study, the water quality from 14 groundwater sources from Baia Mare was investigated. The water sources are located in both rural and urban areas. The samples were collected in March 2014. A portable multiparameter (WTW 320i) and portable turbidimeter (WTW pHotoFlexTurb) were used in order to measure in situ the fallowing parameters: pH, total dissolved solids (TDS), electrical conductivity (EC), temperature, oxidation-reduction potential (ORP), salinity and turbidity. In laboratory, the water samples were analyzed by ion chromatography (DIONEX ICS-1500 system) in order to quantify the following dissolved ions: lithium (Li^+), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), ammonium (NH_4^+), fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrite (NO_2^-), nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}). The laboratory analyses indicated that the waters had a low mineralization and low concentrations of dissolved ions. We calculated the sodium adsorption ratio (SAR) to see if these groundwaters can be used in agriculture. The SAR values ranged between 0.01 and 4.61, being considerably lower than 10, which mean that all the groundwater samples can be classified as excellent waters. As a consequence they can be safely used in agriculture purposes.

Key words: *Baia Mare, mining area, groundwater, major dissolved ions, sodium adsorption ratio*

INTRODUCTION

In the last decades groundwater pollution has become an increasing problem.

Mining activities have an important negative impact on environment because during mining operations (exploitation, ore processing) are produced wastewater, mine tailings and a lot of dust which contains a great amount of heavy metals. [14], [3], [6]

The formation of acid mine drainage is the biggest environmental problem associated with mining activities.

It is a slow process and it continues even after the mining operations were closed and it can affect the air, soil, surface water and groundwater, as well. [8]

The present study was conducted in Baia Mare town, seat of Maramures County, located in the western part of Romania, in Baia Mare Depression, on the middle of the Săsar River, at the foot of Igniş Mountains. [2], [4]

Baia Mare is one of the most important mining areas from our country; it is an important centre of Romanian non-ferrous metallurgy (gold-silver ores, copper, lead, zinc).

The mining activities developed in Baia Mare for over 100 years led to water, soil and air pollution. [5]

We have chosen this area because even the mining activities (extraction, processing and preparation) were closed in 2007 they left behind tens of tailings dumps and tailing ponds which are located near settlements (Fig. 1).

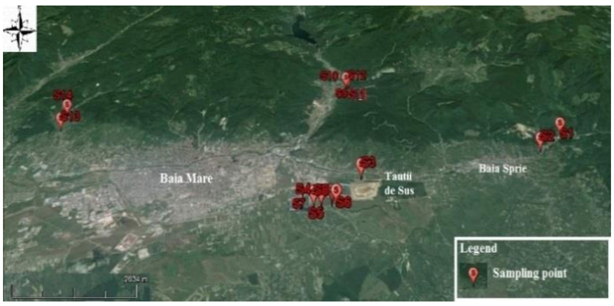


Fig. 1. Study are with sampling points
Source: Google Earth

MATERIALS AND METHODS

Drinking water samples were collected, in March 2014, from various part of Baia Mare mining area. They have been taken from 11 private wells and 3 natural springs.

Using a portable multiparameter WTW INOLAB 320i respectively a portable turbidimeter WTW pHotoFlexTurb we determine the physico-chemical parameters like: pH, temperature, redox potential, electrical conductivity, total dissolved solids, salinity, dissolved oxygen and turbidity. Those determinations were done *in situ* because the physico-chemical parameters values can be changed by climate conditions.

Water samples were stored in fridge and were analyzed for major dissolved ions in 24 hours after sampling. The major dissolved ions like: lithium (Li^+), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrite (NO_2^-), nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulphate (SO_4^{2-}) were determined using a ion chromatograph (DIONEX ICS1500).

Sodium content is an important factor in irrigation water quality assessment. The sodium adsorption ratio (SAR) was calculated is order to assess the possibility to use these waters in agricultural purposes. SAR influences the infiltration rate of water.

SAR was calculated using the sodium, calcium and magnesium concentrations (where all ionic concentrations are expressed in milliequivalent per liter) using the following equation. [7], [1], [11]

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$

Table 1. Water classification based on SAR values

Sodium adsorption ratio (SAR)	Status
<10	Excellent
10-18	Good
18-26	Doubtful
>26	Unsuitable

Source: [12]

%Na was calculated using the sodium, calcium, magnesium and potassium concentrations (where all ionic concentrations are expressed in milliequivalent per liter) using the following equation:

$$\%Na = \frac{(Na^+ \ + K^+)\ x\ 100}{Ca^{2+} + Mg^{2+} + Na^+ + K^+}$$

RESULTS AND DISCUSSIONS

The results are presented in Fig. 2 – 4.

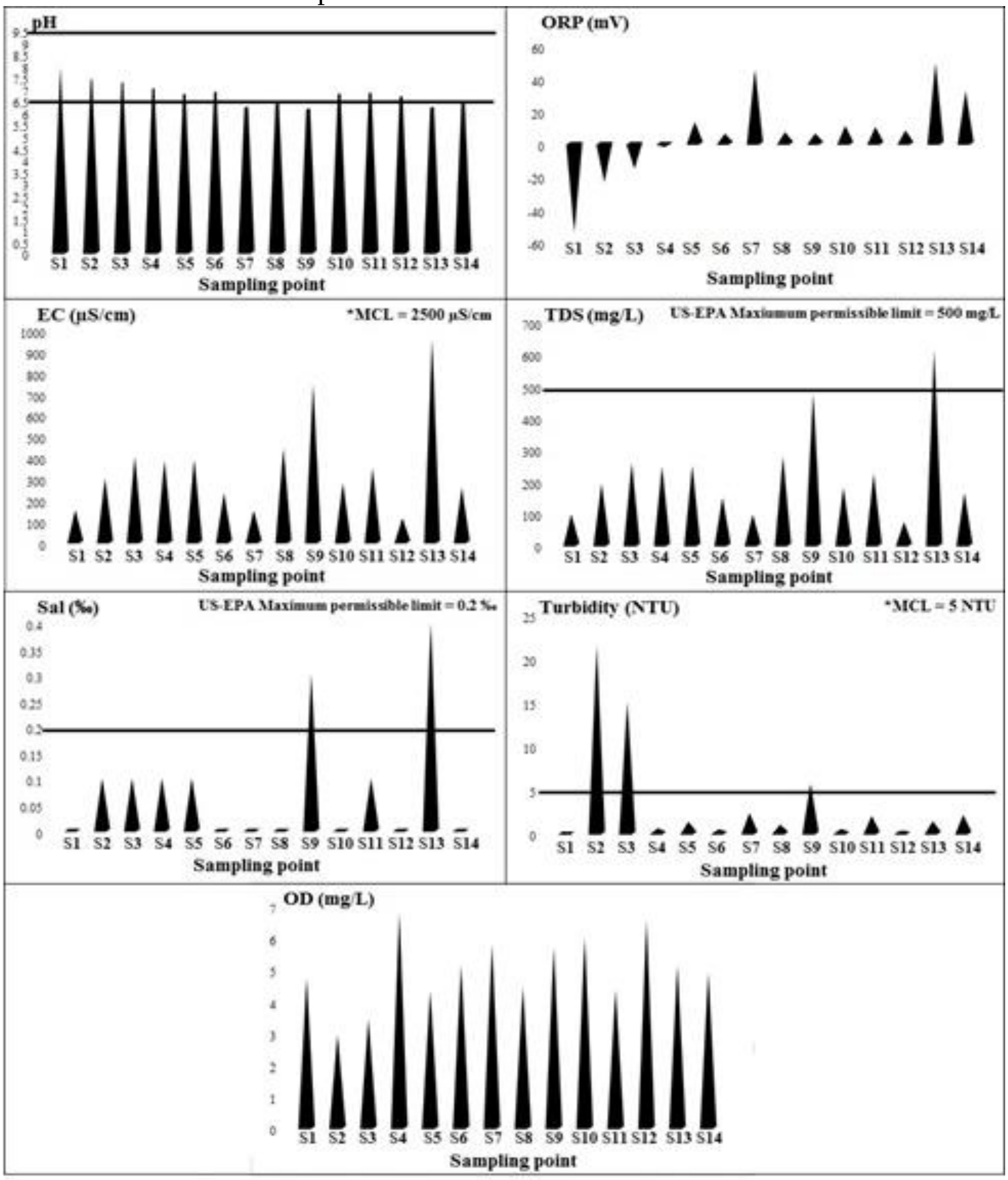
As we can notice in Fig. 2, 36% from samples have a **pH** value below the minimum permissible limit, they are slightly acidic. Regarding the **ORP** values 21.4% from drinking water samples have a negative value that indicates a reducing medium while 78.6% have a positive ORP values that indicates an oxidizing medium.

None of the drinking water samples exceeded the maximum permissible limit for **electrical conductivity** according to Romanian Drinking Water Law (Law 458/2002).

In terms of **total dissolved solids** in Romania we do not have a maximum permissible limit but regarding the US-EPA limit we can notice that one drinking water samples had a value above 500 mg/L. Total dissolved solids affect water clarity and the water balance in the cells of aquatic ecosystems.

In terms of **salinity**, as we can see in Fig. 2, two drinking water samples (S9 and S13) exceeded the maximum permissible limit imposed by US-EPA. S13 sampling point is a pomp and S9 sampling point is a private well downstream of Herja Mine, near Herja creek. In Herja creek all mine waters from Herja mine are discharged without being treated. The water from these sources is used for drinking, cooking and irrigation. Salinity can include hundreds of different ions and high levels of salinity can destroy fertile agricultural land, can damage crops and can directly affect the plant growth.

The **turbidity** can be definite as the amount of cloudiness in the water. It is very important to measure the groundwater turbidity because a high turbidity can fill the pipes with mud and silt especially during the rainy season. [15], [16] A high turbidity in drinking water is an aesthetic problem and it can also represent a health concern because it can provide food and shelter for pathogens.



* MCL - maximum concentration limit, from Low no. 458 - 08/07/2002 regarding the quality of drinking water

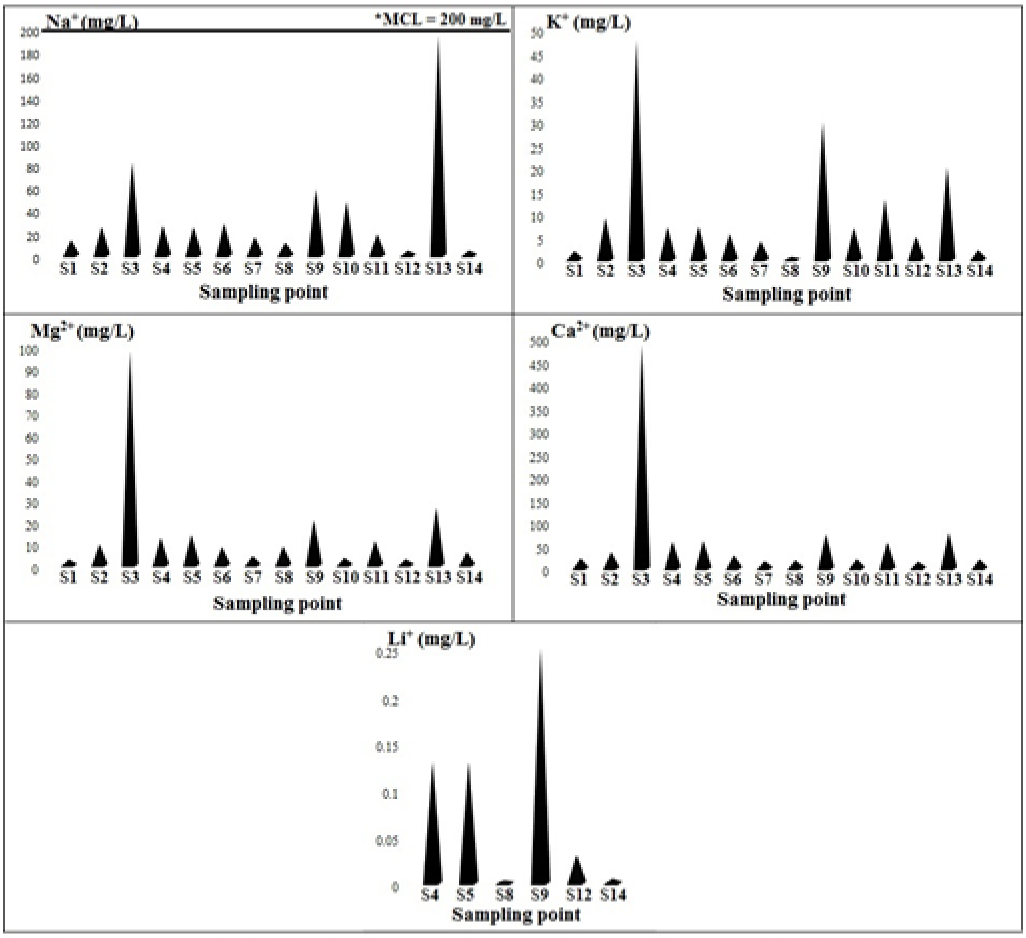
Fig. 2. The physico-chemical parameters values
Source: Own calculation.

As can be observed in Fig. 3 none of collected drinking water samples has a **sodium** concentration above the maximum concentration level required by Romanian drinking water law (Law 458/2002). Sodium does not have negative effects on human health; more than an adequate level of sodium are required for a good health. In Romania we do not have a maximum permissible concentration regarding the potassium, magnesium, calcium and lithium.

As we can see in Fig. 3, S3 sampling point has the highest **potassium, calcium** and **magnesium** concentrations. This drinking water was collected from a private well which is near the Tăuții de Sus tailing ponds. The water from the well is used for drinking, coking and for watering the plants. Calcium and magnesium are the most common sources of water hardness and they are essential elements for plants growth.[10]

In general potassium is a nutrient for plants at low concentrations; a high potassium concentration can indicate the presence of pollution from fertilizers or other contaminants.

Lithium was found in 42.8% from drinking water samples. It doesn't occur naturally as a pure element, it occurs in salts and stable minerals. [9]



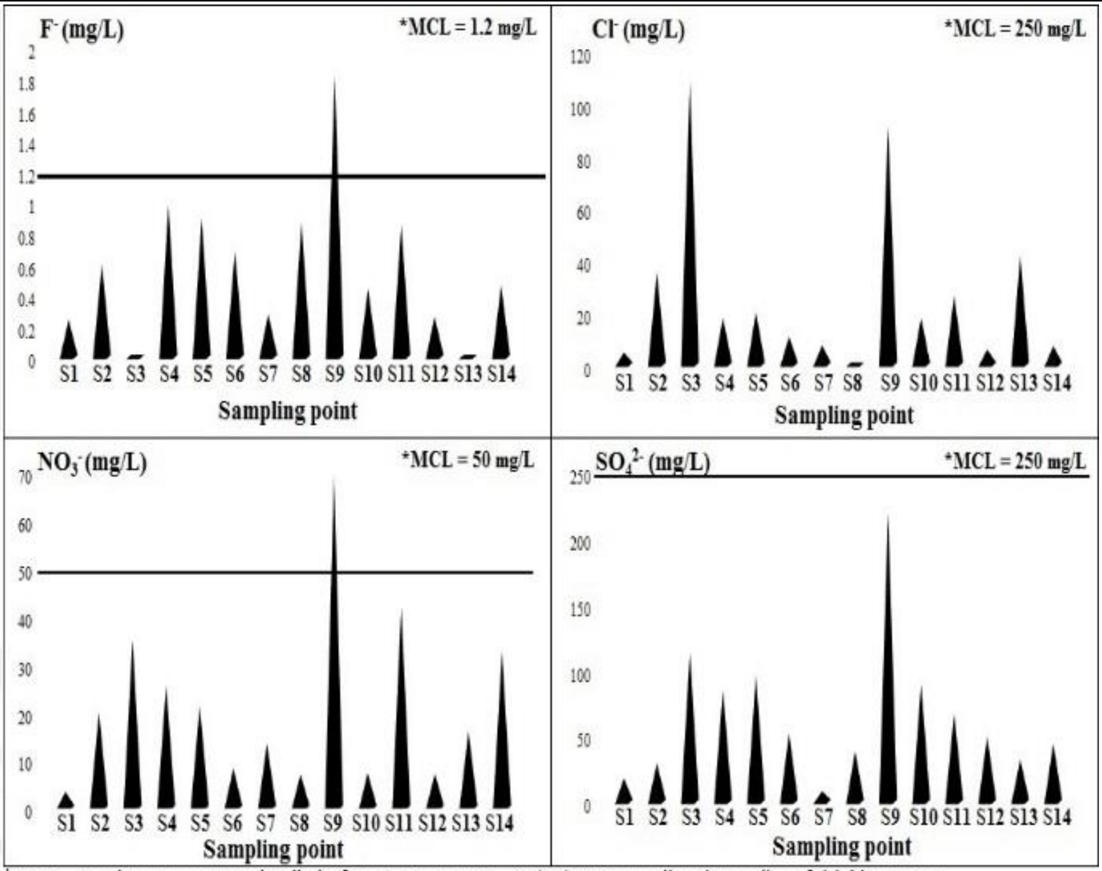
* MCL - maximum concentration limit, from Low no. 458 - 08/07/2002 regarding the quality of drinking water

Fig. 3. The level of major dissolved cations

Source: Own calculation.

Regarding the **fluoride** and **nitrate** concentration, S9 sampling point exceeded the maximum concentration level imposed by Romanian legislation. Fluoride has negative health effects especially on bones. Fluoride can be absorbed by plants via their roots and after this it is store in their leaves. If the plant is sensitive to chloride can appear toxic symptoms (scorching or abscission of leaves). Nitrate is a naturally occurring form of nitrogen found in soil and nitrogen is an essential nutrient for plant growth.

As it can be seen in Fig. 5, SAR has the values between 0.01 (S3) and 4.61 (S10). 92.85 % from collected groundwater samples have a value below 3 what means that it is no threat to vegetation and these groundwater sources can be used safely as irrigation waters. Sampling point S10 has the highest SAR value. It may be due to the fact that this point is located near Herja mine.



* MCL - maximum concentration limit, from Low no. 458 - 08/07/2002 regarding the quality of drinking water

Fig. 4. The level of major dissolved anions
Source: Own calculation.

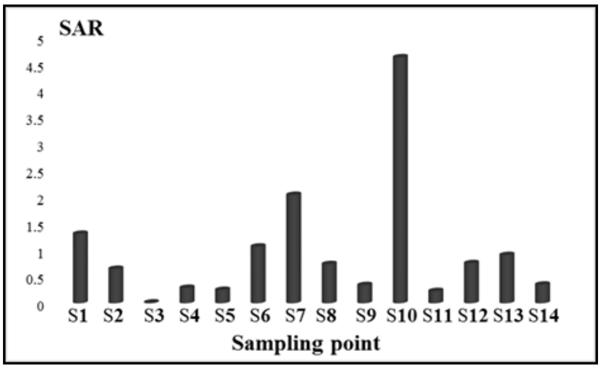


Fig. 5. The level of sodium adsorption ratio (SAR) for the groundwater samples
Source: Own calculation.

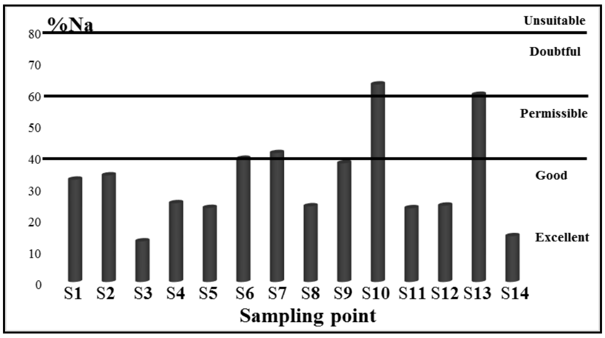


Fig. 6. The percent of Na for the groundwater samples
Source: Own calculation.

Based on %Na, 71.4% of the investigated groundwater sources belong to the excellent category, 14% belong to permissible category and 14 % from samples belong to doubtful category (Fig. 6). [13]

CONCLUSIONS

S3 sampling point has the highest potassium, calcium and magnesium concentrations. This groundwater was collected from a private well which is near the Tăuții de Sus tailing ponds. The water from the well is used for drinking, coking and for watering the plants. While the highest lithium, fluoride, nitrate and sulfate concentrations were determined in S9 sampling point. S9 sampling point is a private well downstream of Herja Mine, near Herja creek. In Herja creek all mine waters from Herja mine are discharged without being treated.

Regarding the SAR values and Na percentage almost all collected water sources may be used as safe source of irrigation.

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