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EVALUATION OF GROUNDWATER QUALITY FOR DRINKING AND IRRIGATION BY CALCULATING SPECIFIC QUALITY INDEXES. CASE STUDY: BAIA MARE MINING AREA, ROMANIA

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ABSTRACT. Baia Mare region is one of the most polluted areas from our country due to extraction and processing of ores with high content of Cd, Cu, Pb, Zn and precious metals. The main objectives of the present study were: to assess the groundwater quality by determine the physico-chemical parameters values, dissolved ions and heavy metal concentration and to evaluate if those groundwater sources can be used for irrigation and drinking purposes by calculating 10 specific quality indexes.

A total of 70 groundwater samples were collected from 14 private wells and springs from Baia Mare and surrounding areas (November 2013 and December 2013, June 2014, September 2014 and December 2014).

In situ a portable multiparameter WTW Inolab 320i respectively a portable turbidimeter were used to determine the physico-chemical parameters like: pH, ORP, EC, TDS, DO, salinity and turbidity.

The dissolved ions (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) were analysed in laboratory by using an ion chromatograph IC DIONEX 1500. An atomic absorption spectrometer ZEENIT 700 was used to determine the heavy metals concentrations like: Cd, Fe, Mn, Ni, Pb and Zn.

After calculating the specific quality indexes (WQI, MI, HPI, PI, SAR, % Na, SSP, MH, MR and KR), the obtained results indicated that the majority of the investigated water sources are not recommended for drinking and most of them are suitable to be used only like irrigation waters.

Key words: *Baia Mare, mining area, groundwater, specific quality indexes, irrigation, drinking.*

INTRODUCTION

Unfortunately, the mining activities have an important impact on water quality even if the mining practice has improved in recent years.

STUDY AREA

Baia Mare town is the residence of Maramureș County and it is an important urban center from the North-West part of the country.

The town is located in the Baia Mare depression, on the middle course of the Săsar River, at the foot of the Gutâi Mountains.

The most important mining centers of Maramureș County are located in the territories surrounding the city of Baia Mare.

Baia Mare region is known not only for its underground riches, but also for the fact that is one of the most pollution areas from our country due to extraction and processing of ores with high content of Cd, Cu, Pb, Zn and precious metals (Filip, 2008).

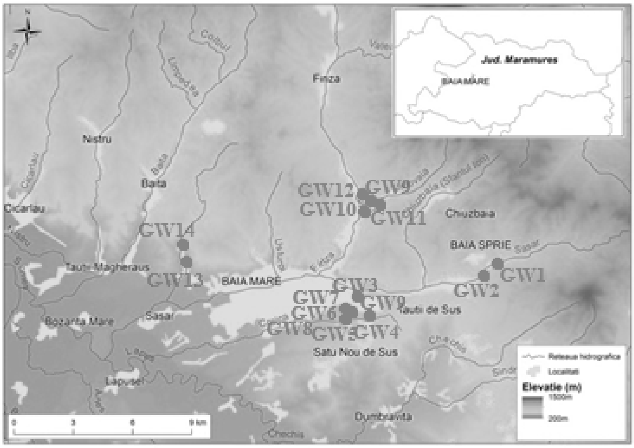

Fig. 1. *Study area (Baia Mare mining area) with sampling points*

AIMS AND OBJECTIVES

The present study aimed to investigate the groundwater quality, from Baia Mare mining area, for drinking and irrigation purposes by calculating specific quality index.

A total of 70 groundwater samples were collected from 14 private wells and springs from Baia Mare and surrounding areas (November 2013 and December 2013, June 2014, September 2014 and December 2014).

MATERIALS AND METHODS

In situ a portable multiparameter WTW Inolab 320i respectively a portable turbidimeter were used to determine the physico-chemical parameters like: pH, ORP, EC, TDS, DO, salinity and turbidity.

The dissolved ions (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) were analysed in laboratory by using an ion chromatograph IC DIONEX 1500. An atomic absorption spectrometer ZEENIT 700 are used to determine the heavy metals concentrations like: Cd, Fe, Mn, Ni, Pb and Zn.

Water Quality Index (WQI)

Using water quality index (**WQI**), a single value can be obtained to expresses the general quality of the surface/groundwater source, based on several quality parameters.

There are three steps in order to calculate WQI (Ramakrishnaiah et al., 2009; Ravikumar 2013):

1. A weight (*w_i)* has to be assigned to each of the chemical parameters: 5 which is the highest weight has to be assigned to the most important parameter regarding its impact on human health or water quality and 2 has to be assigned to non-dangerous parameters.
2. Relative weight (*Wi*) of each parameter has to be calculate using the following equation:

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \qquad (1)$$

Where: W_i is the relative weight, w_i is the weight of each parameter and *n* is the number of parameters.

3. For each parameter has to be calculated a quality rating scale (q_i) by dividing its concentration in each water sample by its standard according and multiplied the result by 100:

$$q_i = \frac{C_i}{S_i} \text{ x } 100 \qquad (2)$$

Where: qi is the quality rating, C_i = concentration of each chemical parameter in each water sample in mg/L, S_i = maximum concentration limit (Low 456/2002 regarding drinking water quality).

In order to calculate the **WQI** the water quality sub-index (SI_i) has to be determined:

$$SI_i = W_i * qi \quad (3) \quad ; \quad WQI = \sum SI\ i \quad (4)$$

Table 1. *Water quality based on WQI values (Ramakrishnaiah et al., 2009; Ravikumar, 2013)*

WQI values	Water quality
WQI < 50	Excellent
50 < WQI < 100	Good
100 < WQI < 200	Moderate
200 < WQI < 300	Poor
WQI > 300	Unsuitable for drinking

Metal Index (MI)

Using MI we can classify the quality of the water body, in terms of heavy metal contamination. MI was calculated using the following formula:

$$MI = \sum_{i=1}^{n} \frac{C_i}{(MAC)_i} \quad (5)$$

Where: C_i = the concentration of metal taken into account; MAC = maximum concentration level for the parameter taken into account.

If the MI value is higher than 1 then the warning threshold has been exceeded (Bakan et al., 2010; Goher et al., 2014).

Heavy Metal Pollution Index (HPI)

The heavy metal pollution index is used to indicate the influence of a cumulative number of heavy metals on the overall water quality. The index was developed in 1996 (Mohan et al., 1996) in order to assess the quality of drinking water. Over time, various researchers (Edet and Offiong, 2002; Nasrabadi, 2015; Tiwari et al., 2015; Yang et al., 2015) have adapted the heavy metal pollution index to determine the quality of different types of water.

The heavy metal pollution index is calculated using the following formulas:

Weight of each heavy metal taken into account:

$$W_i = \frac{k}{S_i} \quad (6)$$

Where: k = constant *of* proportionality (k=1); S_i = the legalized value for the heavy metal taken into account.

Quality assessment for each heavy metal considered:

$$Q_i = 100 * \frac{C_i}{S_i} \quad (7)$$

Where: C_i= heavy metal concentration taken into account (μg/L); S_i= the legalized value for the heavy metal taken into account.

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \quad (8)$$

The sign (-) indicates the numerical difference between two values, this must be ignored. The critical value of the HPI is 100, above this value the water source is considered unsuitable for the purposes for which we intend to use it (Yang et al., 2015).

In the present study, in order to calculate the HPI, all the heavy metals investigated and detected in the monitored water sources were taken into account.

Pollution Index, PI

PI is based on the calculation of each metal and its classification into five quality classes (Table 2). In the present study **PI** was calculated for all investigated heavy metals (Fe, Zn, Cr, Cd, Mn, Ni, Pb). **PI** is calculated using the following formula:

$$PI = \frac{\sqrt{\left[\left(\frac{C_i}{S_i}\right)_{max}^2 + \left(\frac{C_i}{S_i}\right)_{min}^2\right]}}{2} \quad (9)$$

Where: C_i = the concentration of metal taken into account; S_i = maximum concentration level for the parameter taken into account (Caeiro et al., 2005; Bakan et al., 2010; Goher et al., 2014).

Table 2. *Water classification based on PI values (Bakan et al., 2010; Goher et al., 2014)*

Class	Values	Status
1	< 1	no effect
2	1-2	slightly affected
3	2-3	moderately affected
4	3-5	strongly affected
5	>5	seriously affected

Sodium Adsorption Ratio (SAR)

In order to calculate sodium adsorption ratio (**SAR**) we used the sodium, calcium and magnesium concentrations (where all ionic concentrations are expressed in milli equivalent per liter) using the following equation (Harront et al., 1983; Sisir and Anindita, 2012).

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \qquad (10)$$

Table 3. *Water classification based on SAR values (Sudhakar and Narsimha, 2013)*

SAR values	Status
SAR < 10	Excellent
10 < SAR < 18	Good
18 < SAR < 26	Doubtful
SAR > 26	Unsuitable

Kelley Ratio (KR)

The Kelley index indicates whether the investigated water sources can be used for agricultural purposes (Ravikumar and Somashekar 2011).

The Kelley index was calculated using the following calculation formula:

$$KR = \frac{Na^{+}}{Ca^{2+} + Mg^{2+}} \qquad (11)$$

The ionic concentrations are expressed in mEq / L (Reddy, 2013)

Sodium Percentage (%Na)

%Na was calculated using the equation (12). The ionic concentrations are expressed in mEq / L (Roşu et al., 2014).

$$\% Na = \frac{(Na^{+} + K^{+}) * 100}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}} \qquad (12)$$

Table 4. *Water classification based on % Na values (Wilcox, 1995)*

% Na values	Status
< 20	Excellent
20 - 40	Good
40 - 60	Permissible
60 - 80	Doutful
> 80	Unsuitable

Magnesium Ratio (MR)

Based on the Mg/Ca ratio, the investigated water sources can be classified as recommended for use in agriculture.

Table 5. *Water classification based on MR values (Ravikumar and Somashekar, 2011)*

Magnesium Ratio value	Status
< 1.5	Excellent
1.5 - 3	Moderate
> 3	Unsafe

Soluble Sodium Percentage (SSP)

SSP was calculated using the formula (13). The ionic concentrations are expressed in mEq/L (Ravikumar and Somashekar, 2011).

$$SSP = \frac{Na^{+}}{Na^{+}+Ca^{2+}+Mg^{2+}} * 100 \qquad (13)$$

Table 6. *Water classification based on SSP values (Le Breton and Berg, 1965)*

SSP value	Status
0 - 20	Excellent
20 - 40	Good
40 - 60	Permissible
60 - 80	Doubtful
80 - 100	Unsuitable

„Magnesium hazard" (MH)

MH was calculated using the equation (14). The ionic concentrations are expressed in mEq/L.

$$MH = \frac{Mg^{2+} * 100}{Ca^{2+}+Mg^{2+}} \qquad (14)$$

If the "magnesium hazard" index exceeds 50%, it is considered that the use of that water source will increase the alkalinity of the soil, affecting the crops growth (Ravikumar and Somashekar, 2011; Sudhakar and Narsimha, 2013).

RESULTS AND DISCUSSIONS

As can be seen in figure 2, two groundwater samples (14 %) are not suitable for drinking. GW3 was collected from a private well which is very close to Tautii de Sus tailing pond and GW9 was collected from a private well as well, but this downstream of Herja Mine, near Herja creek.

If we are taking into account only the concentration of heavy metals, due to high values 71 % of groundwater samples are not suitables for drinking (figure 3), because HPI > 100. GW9 was collected from a private well, near Herja creek and has the higher value.

Regarding the MI all the groundwater samples exceeded the warning thresdold, are not recommended to be used as drinking water sources (figure 4), because MI > 1.

As can be seen in figure 5, regarding PI for Pb non of the ground water samples are seriously affected, because PI < 1. If we take into consideration the PI for Zn – only GW9 is strongly affected, PI for Ni – GW1, GW3, GW7, GW9, GW10, GW11, GW12 and GW13 are moderately affected, PI for Mn – GW2, GW3 and GW13 are seriously afected; PI for Fe – GW2, GW3, GW10, GW11 and GW13 are seriously afected and PI for Cd – only GW9 is seriously afected (figure 4).

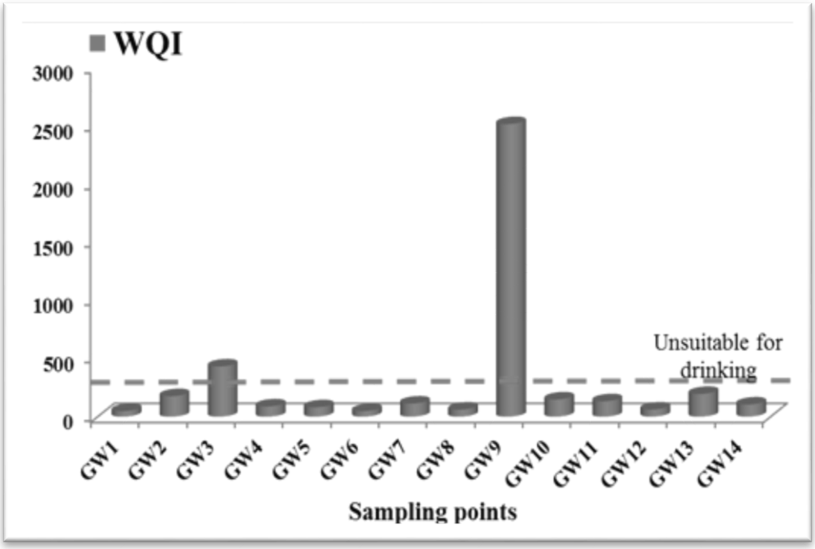

Fig. 2. *Water Quality Index values, depending on the sampling point*

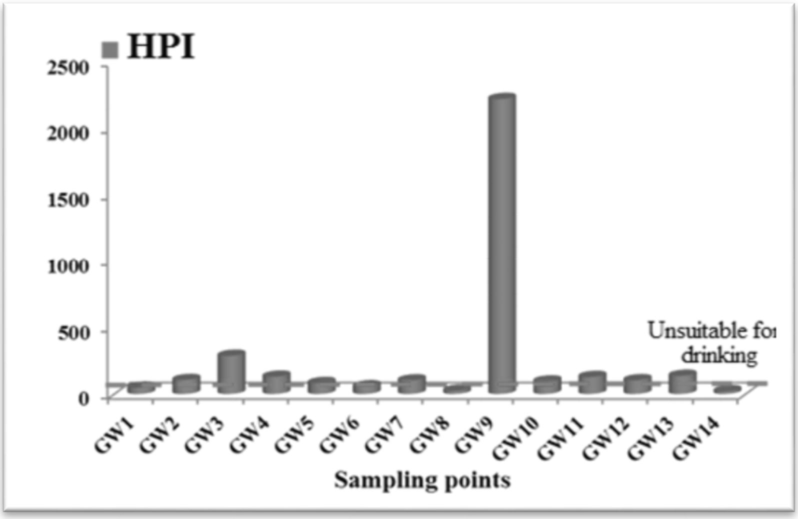

Fig. 3. *Heavy Metal Pollution Index values, depending on the sampling point*

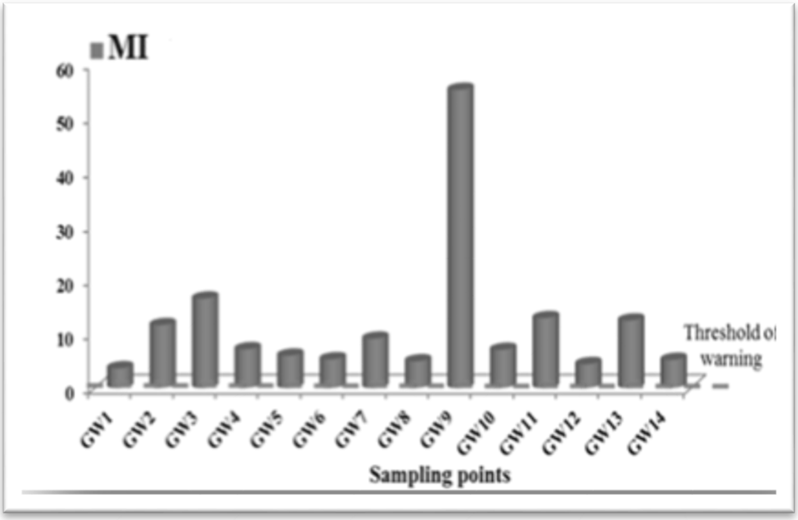

Fig. 4. *Metal Index values, depending on the sampling point*

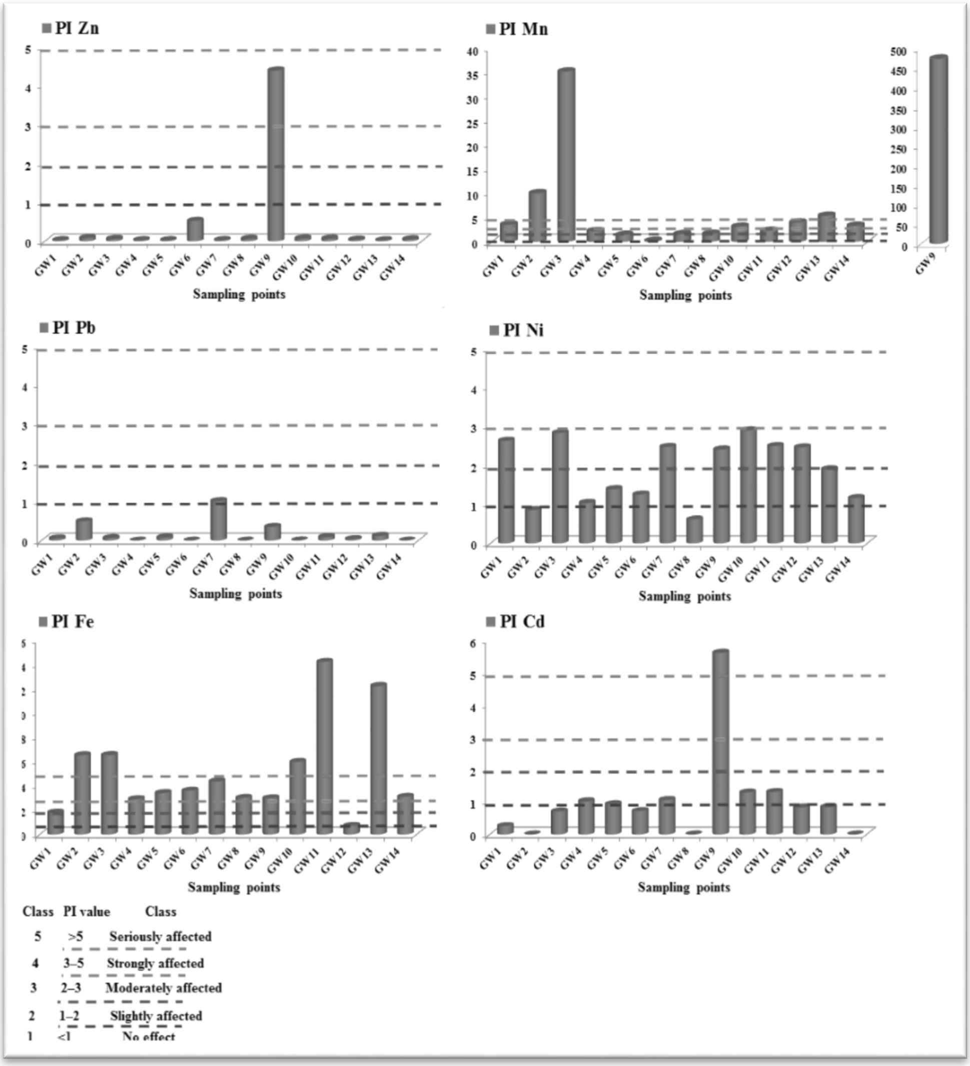

Fig. 5. ***P**ollution **I**ndex (PI) values, depending on the sampling point*

Irrigation

Six specific quality indexes were calculated in order to evaluate if those groundwater sources can be used for irrigation (KR, %Na, MR, MH, SSP and SAR).

Regarding **K**elley **R**atio (Fig. 6) only one groundwater sample (GW13) is not suitable for irrigation, this sample being collected from a pomp downstream of Herja Mine.

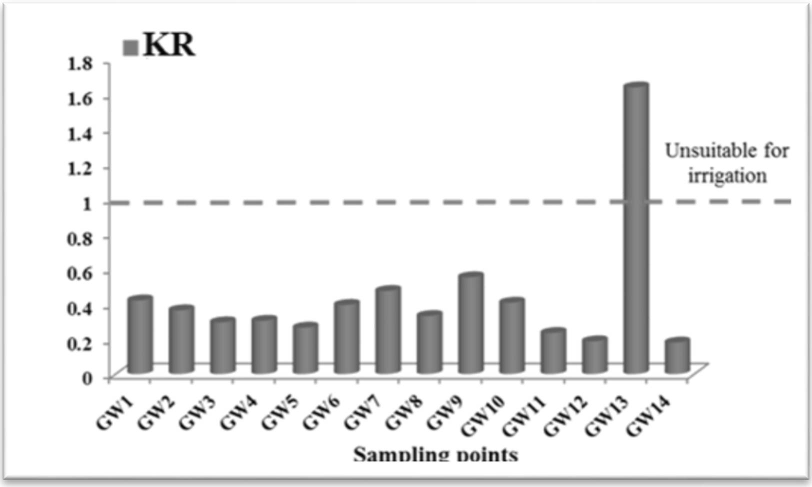

Fig. 6. ***K**elley **R**atio values, depending on the sampling point*

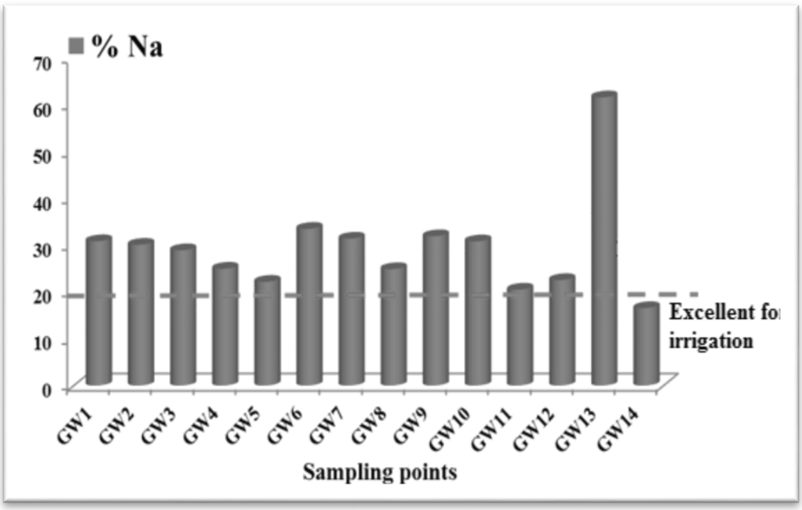

Fig. 7. *Sodium Percentage values, depending on the sampling point*

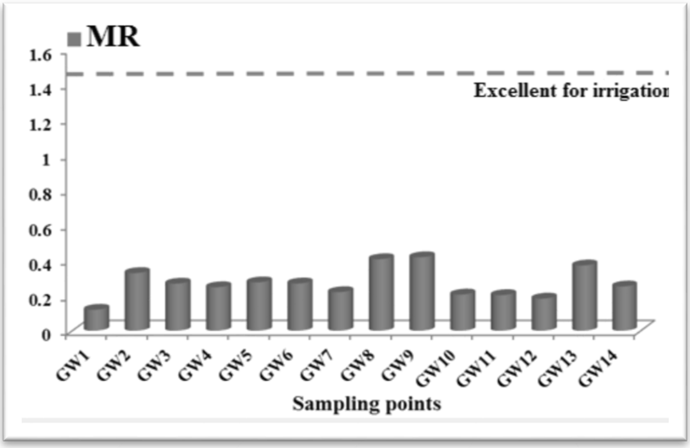

Fig. 8. ***M**agnesium **R**atio values, depending on the sampling point*

In terms of Sodium Percentage (figure 7) only one groundwater samples belong to excellent category, GW14.

Magnesium Ratio (**MR**) and Magnesium Hazard (**MH**) values indicates that all groundwater samples belong to excellent category, this is due to the fact that in order to calculate this index is necessary only the magnesium and calcium concentration (figure 8 and figure 9).

Taking into consideration the **S**oluble **S**odium **P**ercentage (**SSP**) and **S**odium **A**dsorption **R**atio (**SAR**) none of the groundwater samples belong to unsuitable for irrigation category (figure 10 and figure 11).

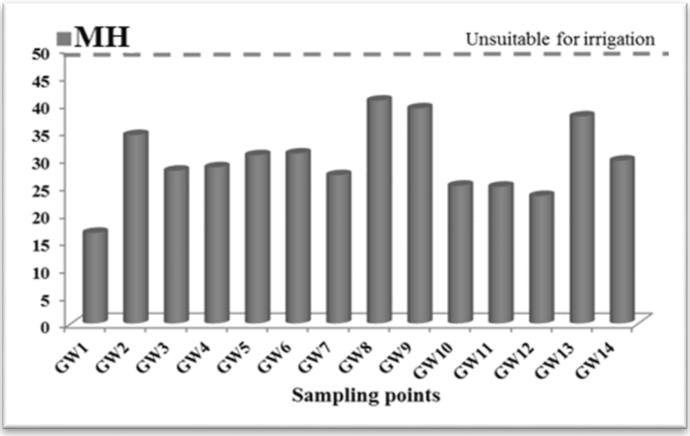

Fig. 9. ***M**agnesium **H**azard values, depending on the sampling point*

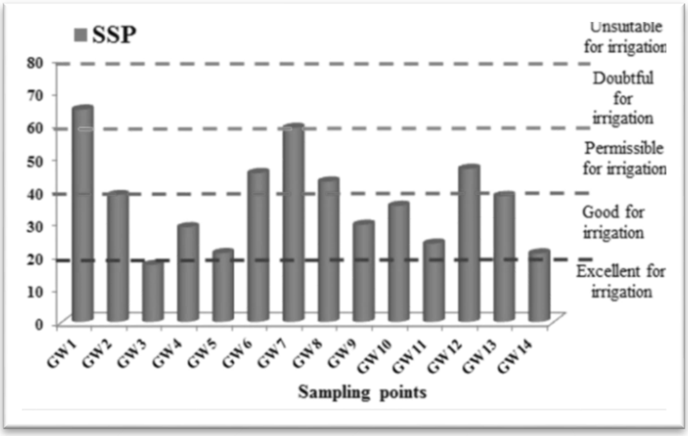

Fig. 10. ***S**oluble **S**odium **P**ercentage values, depending on the sampling point*

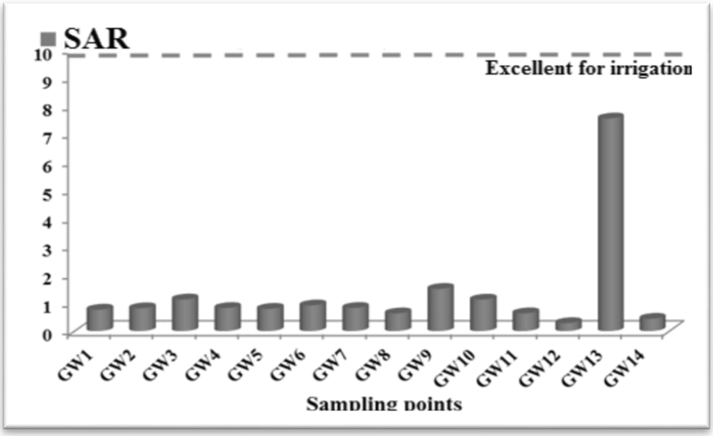

Fig. 11. ***S**odium **A**dsorption **R**atio values, depending on the sampling point*

CONCLUSIONS

The investigated groundwater samples proved to be high polluted with manganese, iron and nickel, these are not recommended to be used like drinking waters. By calculating **WQI**, **HPI** and **MI** it can be seen that the sampling point GW9, which is a private well, is the most polluted. It may be due to the fact that this well is located downstream of Herja Mine, and near the Herja creek where all mine waters are discharged.

After calculating **KR**, **SSP**, **%Na**, **SAR**, **MR** and **MH** it can be concluded that almost all groundwater samples can be used like irrigation water, a special attention should be paid to GW13 sampling point, due to its high sodium content it cannot be used as a reliable source of irrigation.

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