ASSESSING OF WATER QUALITY POLLUTION INDICES FOR HEAVY METAL CONTAMINATION. A STUDY CASE FROM MEDIAS CITY GROUNDWATERS

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Abstract. Three documented methods: Contamination index (C_d), the Heavy metal potential index (HPI) and the Heavy metal evaluation index (HEI) were evaluated for their suitability for contamination monitoring of underground water (water wells) from Medias. In addition, ions and physico-chemical analysis were elaborated. Results show that the concentrations of heavy metals found in the wells from Medias are below the permissible levels of drinking water quality standards. The data have been used for the calculation of C_d, HPI and HEI. All seven samples were classified as low using the C_d, HPI and HEI, whereas nitrogen compounds (nitrate, nitrite and ammonia) exceed the maximum admissible concentration, salinity as well (0.7‰ for F2, F3, F4, F5 and F7, while the MAC is established at 0.1‰, EPA). As a short conclusion, water samples do not present heavy metal pollution, furthermore there is an organic pollution, regarding nitrogen compounds and salinity.

Keywords: pollution indices, heavy metals, nitrogen compounds, groundwater, Medias

INTRODUCTION

Medias is a small town with inhabitants (a small part of them, especially residential inhabitants) that still use water from wells for housework: washing, gardening, and also for drinking and cooking. Groundwater is a very important water supply, especially when it is the only water source for humans, animals and plants. Where humans and animals live, there are also leavings, where anthropic activities bechance there are also pollution indicators. Because of the lack of sewage systems and short distance between the water source and dry toilets, coops or stables, the water composition has been compromised and modified, receiving high concentration of anions, cations and metals. Heavy metals are prime environmental pollution contaminants with remarkable properties (persistence, bioaccumulation, high toxicity) and negative influence for the living organisms. Heavy metals have a vast distribution starting with rocks, soil, water (potable, wastewater, surface, groundwater, seawater), plants (leaves, fruits, flowers), animal tissues.

For heavy metal contamination evaluation several methods were elaborated, methods that develop and apply water quality pollution indices. The contamination index (C_d), the Heavy metal potential index (HPI) and the Heavy metal evaluation index (HEI) are pollution indices which help assessing the present level of pollution.

Pollution indices are valued in obtaining an amalgam influence of parameters of overall pollution and they combine all the pollution parameters into some easy approach (Prasad and Bose, 2001).

This paper work will present a water quality pollution evaluation study of seven water wells from a small town, Medias, with the help of heavy metal indices.

GENERAL DESCRIPTION OF THE STUDY AREA

Medias is a small town with almost 44,000 inhabitants and a 62.60 km^2 surface situated in the central part of the country, between latitude 46°9'50" N and longitude 24°21'3" E, in the north part of the Hartibaciu Plateau (Fig.1).

The Hartibaciu Plateau has soft cliffs hill relief, Miocene and Pliocene sediment deposition and rich underground resources of natural gas, salt, iodine and sulfur and clays marls operation – in pits or quarries. The plateau is a classical earth flow area with glimee relief.

The main physiographic features of the area include medium high hills (highest hills are between 450-600 m).

The annual rainfall mean is in excess of 800 mm with annual mean of 636 mm and the annual temperature mean is between 7°C and 8°C. Humidity presents an 87%annual mean.

Groundwater aquifers can be found between 1.2 and 10 m depth, with flow rates ranging from 0.2 to 8 m/s. The highland areas present a 5 to 10 m in depth ground waters and 5 m depth aquifers in the meadow areas (Chira and Malacu, 2008) and at 250-300 m bedding depth water have been found, but only in the sediment area. Ground waters are very important water sources regarding their housework duty. Two large classes are included in this category:

1. Phreatic aquifers – represent a direct spring source for the hydrographic networks. They can be found at low depths and are directly influenced by the climatic conditions.
2. Depth aquifers - do not supply rivers and are independent regarding the climatic conditions (Horhoi, 2001).

The samples were taken from a residential district (almost 764 years old) of the town, from private wells. This district is inhabited by almost 13% of population, 97% of it has a private house and at least one well.

Wells that were studies are at least 50 years old with similar structures: concrete roles covered with a metal sheet and a depth of 3 m to 8 m. All wells were constructed nearby dry toilets, emptying collector for dejection, stables or coops with feces settlement (activities stopped a couple of year ago, people stopped raising animals: porcine, cattle, horses or sheep). Albeit people know the influence of the sources mentioned before, they still use the water well for consumption, furthermore for drinking. It has been observed the influence of precipitation referring to the water volume, which increases while the precipitation quantity grows (Hoaghia, 2013).

MATERIAL AND METHOD

SAMPLE COLLECTION

Seven wells were subjects of the study. Samples were collected at every two months starting with November 2012 and finishing in the month of May 2013. So eight sampling sessions were made, following the International Standard ISO 5667-11:1993, regarding the underground water quality. Water samples were collected with the help of every wells bucket, drowned 10-20 cm under the mirrors water, except one well whom sample was taken with help of a house water supply plant. Samples were collected in 100 mL polyethylene bottles, without air bubble and deposited in a freezing combine at 4 °C until analysis.

PHYSICOCHEMICAL AND ELEMENTAL ANALYSES

Physico-chemical analysis likewise pH and electrical conductivity measurements were performed with WTW Multi 350i portable multiparameter.

For the ions determination, Ion Cromatograph model IC Dionex with high sensitivity conductivity detector and a mobile phase conductivity suppressor system was used. Cations and anions were define as cations: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Li^{+} and NH_4^{+} and anions: Cl^{-}, Br^{-}, F^{-}, NO_2^{-}, NO_3^{-}, SO_4^{2-}, PO_4^{3-}.

In order to elaborate the chemical analysis, samples were acidified at 2 pH units with nitric acid. The samples were filtered using a plastic filter unit equipped with a 0.45 μm filter membrane for the elemental analysis.

Concentrations of heavy metals in water samples were determined with an ICP-MS model PE/20139 CEEX Module IV, heavy metals like: As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were analyzed. No replicates were analyzed for these samples.

EVALUATION METHODS

The evaluation methods used in the study are quality methods using arithmetical equations based on heavy metal values obtained after sampling and standard, ideal values.

Pollution evaluation indices are determined for the purpose of evaluation surface water quality. Those quality pollution indices are estimated for a specific use of the water under consideration. The indices used in this study are the degree of contamination index (C_d), heavy metal pollution index (HPI) and the heavy metal evaluation index (HEI) computed for the intent of evaluating drinking water quality. Methods are described below:

THE CONTAMINATION INDEX (C_D)

The contamination index method uses the degree of contamination (C_d) that calculates the quality of water and is computed as follows using the equation from below and "it summarizes the combined effects of a number of quality parameters regarded as unsafe to household water" (Prasanna and all, 2012).

$$Cd = \sum_{i=1}^{n} Cfi$$

$$Cfi = \frac{CAi}{CNi} - 1$$, where

C_{fi}-the contamination factor for the *i*th component

C_{Ai}- analytical value for the *i*th component

C_{Ni}- upper permissible concentration of the *i*th component (N denotes the "normative value") (Edet and Offiong, 2002)

C_d is calculated for every sample independently, values are grouped into three categories regarding contamination level as follows: low contamination if C_d values are lower as one (C_d<1), medium contamination when C_d = 1-3, and when C_d is higher as three (C_d>3) contamination is high (Beckman and al. 1998) in case of water samples, but for the sediment samples there are other categories as: low degree of contamination if the C_d is lower than 8, moderate degree of contamination if the C_d is higher than 8 and lower then 16, values between 16 and 32 mean that there is a considerable degree of contamination and results higher than 32 refers to a very high degree of contamination indicating serious anthropogenic pollution, for the sediment samples (Hakanson, 1979).

HEAVY METAL POLLUTION INDEX (HPI)

The pollution index represents the total quality of water regarding heavy metals. The HPI is developed in two steps by assigning a weightage (W_i) for each chosen indicator and is based on weighted arithmetic quality mean method. The weightage or rating is an arbitrary value between zero and one and it reflects the relative importance of individual quality esteems and can be defined as inversely proportional to the standard permissible (S_i) value for all and each parameter (Horton, 1965; Mohan and al. 1996; Reddy, 1995).

The HPI is determined using the following expression:

$$HPI = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} W1}, \text{ where}$$

W_i and Q_i are the unit weight and sub-index of the *i*th parameter, and n represents the number of the considered indicators. Q_i, the sub-index can be calculated by the formula below:

$$Qi = \sum_{i=1}^{n} \frac{\{Mi(-)Ii\}}{Si-Ii} \times 100, \text{ where}$$

I_i, M_i and S_i represent the ideal value or standard limits for the same parameters in drinking water (values are presented in table 1), the monitored heavy metal and the standard value of the *i*th indicator or the maximum allowable concentration in drinking water in absence of alternate water sources. The (–) sign denotes numerical difference of the two values ignoring the algebraic sign (Edet and Offiong, 2002).

Table 1

Standard used for the indices computation: W (weightage-1/MAC), S (Standard permissible in ppb, WHO), I (Highest permissible in ppb, WHO), MAC (Maximum admissible concentration/upper permissible), RV (Reference value in ppb) (Edet and Offiong, 2002)

Metal symbol	Unit of measure	W	S	I	MAC	RV
As	µg/l	0.02	50	10	50	0.5
Cd	µg/l	0.3	5	3	3	0.2
Cr	µg/l	0.02	50	50	50	1
Cu	µg/l	0.001	1000	2000	1000	3
Fe	µg/l	0.005	300	200	200	50
Mn	µg/l	0.02	100	500	50	5
Ni	µg/l	0.05	20	20	20	0.3
Pb	µg/l	0.7	100	10	1.5	3
Zn	µg/l	0.0002	5000	3000	5000	5

The weightage of *i*th parameter can be calculated using the following equation:

$$W_i = \frac{k}{Si}, \text{ where}$$

W_i is the unit weightage, k is the constant of proportionality and S_i the WHO recommended standard for the *i*th indicator (Reza and Singh, 2010).

HEAVY METAL EVALUATION INDEX (HEI)

This method gives an overall quality with respect for heavy metals, just like the HEI method, which can be computed with the help of the following equation:

$$HEI = \sum_{i=1}^{n} Hc/Hmac$$, where

H_c reflects the monitored value of the *i*th indicator and H_{mac} the maximum admissible concentration of the *i*th parameter.

This index was used for a better understanding of the pollution indices.

RESULTS AND DISCUSSION

Water well samples that were analysed in this study have an 8.53 maximum value for pH and 7.02 minimum value; results that ingrains to water wells a neutral-alkalinity state of aggregation. pH values rise in the rainy seasons and inherit acid values in the dry season, as the water volume degrees and the dilution rates degrees as well.

Electrical conductivity is almost high, it reaches 1639 µS/cm, while EPA established a 2500 µS/cm value. One of the most outrival physical chemical parameter is the salinity; most of the wells have over 0.6 ‰ salinity (0.1 ‰ MAC, WHO) which means that there is a source of salts that influence this indicator and they are, because researches reveal dry toilets, animal feces deposits and emptying pools.

In case of TDS (Total dissolved solids), there was a considerable amount of dissolved ions in almost all samples. The highest concentration is 864.5 mg/L (1500 mg/L MAC, EPA) obtained in the wet season and in the summer season it ranged between 155-864.5 mg/L.

Nitrogen compounds (ammonia, nitrate and nitrite) determined with help of an IC were analysed and results show that nitrate concentration is distinguished high for F4, F5 and F7 samples, with concentrations that exceed 200 mgN/L, values that is above the maximum admissible concentration established by EPA, a concentration with 40 times higher than the normalized value. A higher concentration as 13.5 mg/L indicates an eventual anthropological influence towards water (Croll and Hayes, 1988).

Nitrites were also detected in high concentrations, above the maximum admissible concentration (0.5 mg/L), results that range between 0.45-5.08 mg/L all study period (November 2012-May 2013).

For each sample ammonia was detected, but not in every set of samples for each and every sample; results (0.11-2.99 mg/L) exceed the MAC (0.5 mg/L),

Presence of nitrites and ammonia is a proof of favorable conditions for the nitrification process. Nitrification and denitrification are natural processes that involve nitrogen, which is one of the most limiting nutrients for ecosystem productivity (Yan and al, 2013) and its compounds.

Concentration of heavy metals in the groundwater (wells) is attributed to geogenic sources. Since major industries or mining activities do not exist in this area, the reasonable explanation for the acidic nature of the groundwater is the leaching of altered rocks by acidic rainwater.

Though, concentration for Zn and Mn exceed 100 (highest value for Zn is 119,35 μg/L, WHO sets a 5000 μg/L maximum admissible concentration, MAC, but Mn MAC is 50 μg/L value exceed by two of the samples, sample well F7 has a 73.91 μg/L and sample F1 119,35 μg/L) other heavy metal concentrations do not grow up 50 μg/L, but in case of Pb with a 1.5 μg/L MAC it has a higher value as the standard one, sample F7 has a 3.93 μg/L concentration of Pb.

Cadmium has the lowest values of the metals, followed by arsenic and lead.

Table 2 details the results for all pollution indices and the values for the unit weightage (W_i) and standard permissible value (S_i) as obtained in the presented study.

Table 2

Results of Water Quality Pollution indicators applied for the groundwater samples from Medias City

Sample ID	C_d	HPI	HEI	Metals	S_i	W_i
F1	-6,17	5,21	2,83	**As**	50	0,02
F2	-7,45	3,71	1,55	**Cd**	5	0,2
F3	-7.06	3,81	1,94	**Cr**	50	0,02
F4	-7,75	2,64	1,25	**Cu**	1000	0,001
F5	-6,44	4,30	2,56	**Fe**	300	0,003
F6	-6,75	3,31	2,25	**Mn**	100	0,01
F7	-4,66	3,48	4,34	**Ni**	20	0,05
Mean	**-6,61**	**3,78**	**2,39**	**Pb**	100	0,01
Minimum	**-7,75**	**2,64**	**1,25**	**Zn**	5000	0,0002
Maximum	**-4,66**	**5,21**	**4,34**			

The calculated C_d values are beneath zero, the C_d value for low contamination, with a maximum concentration of -4.66 for sample F7, -7.75 for the minimum value, for sample F4 and the mean of water samples is -6.61.

The HPI values for all the water well samples are lower than 100, the critical value for drinking water. HPI maximum concentration is 5.21 for sample F1 and HPI minimum has sample F4 with a concentration of 2.64.

The HEI values are divided into three classes: low contamination (HEI < 400), medium contamination (HEI = 400-800) and high contamination (HEI > 800) (Edet and Offiong, 2002). HEI for Medias water wells are beneath 400, a mean of 3.39 with a maximum concentration of 4.34 (F7) and a minimum one of 1.25 (F4), results that denote a fall into the low contamination zone.

We can observe that sample F4 has the lowest concentration for all pollution indices sample F7 has the highest values for HEI and C_d.

CONCLUSIONS

The presented study reveals that most of the water samples of wells from Medias City were found less polluted in heavy metal concentration profile, but shows a trend in seasonal variation regarding other parameters, such as pH, electrical conductivity, TDS and salinity. Results for salinity exceed maximum admissible concentration (WHO). A possible source for those values could be the dry toilets, animal feces deposits and deposits pools placed at a very short distance from the water wells. The impact of named sources can be sustained by the high concentrations of nitrogen compounds (nitrite, nitrate and ammonia).

The C_d (<0) place all the samples as of low contamination level. The HPI method consider the level of contamination as noncritical (<100). HPI method is a very useful pollution evaluation tool of water well samples with respect to heavy metals (Prasad and Kumari, 2008).

The third method, HEI method, developed during the study give a pollution classification for the water well samples which straddle three classes: low, medium and high with more that 99.99% in the low class (<400). All metal concentrations do not overage the standard values, observation that reflects the negative results for the pollution indices.

Conclusively, this water wells from Medias City study do not presents a heavy metal pollution, but high concentration of organic parameters, such as: salinity, TDS, electrical conductivity and nitrogen compounds attests an organic pollution.

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