ORIGINAL PAPER

HEALTH RISK ASSESSMENT OF HEAVY METALS IN DRINKING WATERS

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Abstract. *Heavy metal concentrations of Pb, Cd, Zn, Ni, Cr, Mn, and Cu in drinking water collected from capture groundwater stations were determined. These values were correlated with physicochemical indicators. Concentrations of all metals were lower than maximum admitted limits established by Romanian Law 311/2004. The health risk index values for all determined elements (Pb 0.029±0.009, Cd 0.008±0.011, Zn 0.012±0.002, Ni 0.003±0.001, Cr 0.012±0.009, Mn 0.006±0.001, and Cu 0.017±0.004) were also found to be lower than the safe limit values.*

Keywords: *heavy metal, drinking water, health, ICP-MS.*

1. INTRODUCTION

The air and water contamination with heavy metals represents one of the major problems caused by environment pollution. Slow assimilation of these elements implies major risks for human health, producing chronic changes in physiological systems [1-4]. In drinking water, heavy metals can reach through domestic installations, and their presence in high concentrations can seriously damage human health [5, 6].

The heavy metals are naturally present in soil and water [7-9], some are considered indispensable for life, but, in high concentrations, those may become toxic; copper, zinc, manganese, iron, etc. are just a few examples. However, in low concentrations, some elements like cadmium, mercury, lead, nickel, and chromium are considered also toxic and are included in another category of heavy metals,

As particularities, heavy metals are defined by their specific weight, which is at least 5 times greater than that of water. Therefore, if water has a specific weight of 1, heavy metals have much higher values: arsenic 5.7, cadmium 8.6, iron 7.9, lead 11.3 and mercury 13.5 [10-13]. These metals are not degradable and are retained in the human body, including in the fat and nerve tissues [10, 14]. Their toxicity depends on the dose accumulated in the cells [14, 15]. One of the causes for some neurodegenerative diseases, such as Alzheimer's disease, sclerosis or Parkinson's disease is given by mercury [16-18]. The toxicity level caused by

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heavy metals presence inside the human body is closely related to the amount of metals accumulated in the cells [19], but also to the individual tolerance degree [20, 21].

According to the Romanian Regulation (i.e., Law no. 311 of June 28, 2004) the admitted value in drinking water samples for cadmium is 5.0 μg /L, for copper of 0.1 mg /L, for nickel of 20.0 μg /L, for chromium 50 μg /L, and for lead of 10.0 μg/L [22]. Cadmium (Cd) is a toxic metal with a half-life of 10-30 years, being classified in the first group in list of carcinogens [23]. The main source of cadmium contamination is food. A disease caused by cadmium is *Itai Itai* disease, first occurring in Japan [24]. The first symptoms of this disease are manifested by back pain, and after that, the illness develops through disruptive bone fractures [25]. In Japan, the results of studies showed a strong link between the cadmium concentrations that causes the disease and the cadmium concentration in rice [24]. Cadmium is associated with breast cancer, chronic kidney disease, and prostate cancer [26, 27], as well. In this respect, studies have shown that people who work in cigarette factories have had kidney problems being contaminated with cadmium [27, 28]. Also, smokers are the most susceptible to illnesses by neck or brain cancer [29]. There is no known treatment for cadmium intoxication, but recent studies in rats have shown that the *Tinospora cordifolia* extract attenuates histological and biochemical changes induced by cadmium [30]. Exposure to cadmium has been associated with increased inflammatory plasma marker *suPAR (soluble urokinase-type plasminogen receptor activator)* in the population, independent of smoking and cardiovascular diseases [30]. Nickel (Ni) is a metal widely distributed on the Earth's surface. This metal is present in food and drinking water as a result of natural and anthropogenic activity. Nickel has a biological role, but in higher quantities is toxic; nickel salts cause allergies and even cancer [31, 32]. Chromium (Cr) is an essential element for life; the daily requirement is 0.05-0.2 mg / day for humans. In high concentrations, it has toxic effects [32, 33]. The metallic shape is not toxic, but the salts are toxic. Chromium accumulates in living organisms (10,000 times in fish) [33], which lead to increased risks. Lead (Pb) is commonly found among pollutants and is a potent neurotoxin, harmful to central nervous systems for children below six years of age [34]. In this respect, lead exposure leading to acute lead poisoning or chronic health effects is known to impair children's cognitive and behavioral development [35]. Drinking water, if stagnates in lead pipes or has certain physicochemical characteristics, can dissolve lead and cause different illnesses, and sometimes is suspected by carcinogenic effects [35, 36]. Copper (Cu) in concentrations too high in water is toxic [37]. It does not bioaccumulate in the human body. It may come from copper pipes, which are attacked by soft or acidic waters.

In present, the existing information about the occurrence of heavy metals in the water designed to be used by the urban population from Targoviste area is insufficient. In this respect, the present inquiry aims to provide a water-quality data set by using consistent sampling methods and analysis, correlated with health index risk data and potential influence on human health.

2. MATERIALS AND METHODS

In this study 360 samples (i.e., 1 sample/day, for 3 months, in 4 points) were collected between September and November 2018, from capture groundwater stations (coded A1-A4), which deserved the urban area. The sampling sites are presented in Fig. 1 and Table 1.

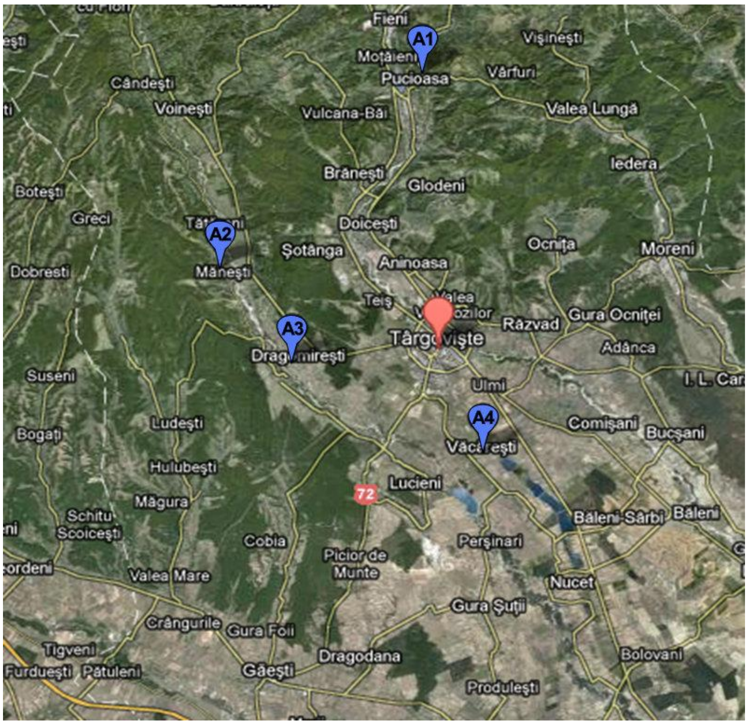

Figure 1. Investigation area.

Table 1. Geographical coordinates of sampling points.

Sample code	Coordinates	
	Latitude	Longitude
A1	45° 05' 31" N	25° 25' 36" E
A2	44° 57' 55" N	25° 17' 12" E
A3	44° 52' 42" N	25° 32' 58" E
A4	44° 54' 52" N	25° 20' 35" E

Sampling was performed following the EPA Groundwater Sampling – Operating Procedure [38]. The measurements of water temperatures, pH, electrical conductivity (EC), TDS, and salinity were performed using a multiparameter Consort 3030. Alkalinity was determined by titration methods in order to quantify the carbonate species in the water sample. The samples were filtered through 0.45-μm cellulose membranes and then transferred into pre-washed HDPE bottles. Samples used for the analysis of heavy metals (i.e., Cd, Cr, Ni, Cu, Pb, Zn, and Mn) were acidified to pH < 2 by adding a few drops of ultrapure nitric acid. 25 ± 1 mL sub-sample and an acid mixture (HNO_3 67%, high purity, Merck and HCl 37%, Merck) were dispensed into a digestion vessel, and then were digested on a hot plate by using a TOPwave Microwave-assisted pressure digestion. All chemical reagents were of analytical grade. Deionized water (resistivity of 18.2 MΩ cm) was obtained with a Milli-Q System.

The metal concentrations determination were performed by inductively coupled plasma mass spectrometry (ICP-MS) using an iCAP™ Q ICP-MS. The relative standard deviation (RSD) for analyzed parameters was 0.01%-2.66%. Limit of quantification (LOQs) was performed by standard curve. Metals calibration curves showed good linearity over the concentration range (0.05 to 10.0 mg/L) with R^2 correlation coefficients in the range of 0.992 to 0.999.

The health risk index (HRI), by consumption of analyzed water samples, was estimated from ratios of the daily intake of metals (DIM) to oral reference dose (RfD) values, according to equation (1) [39-41].

$$HRI = \frac{DIM}{RfD} = \frac{C_{water} \times I}{BM \times RfD} \quad (1)$$

where: C_{water} represents the metal content in water samples; I represents the daily intake (I = 2 L); BM represents the average body mass of an adult (BM = 70 kg); RfD represents the average reference dose, values for each metal is presented in Table 2.

Table 2. The values for average reference dose (RfD) [$mg \cdot kg^{-1} \cdot day^{-1}$] [41-50].

	Pb	Cd	Zn	Ni	Cr	Mn	Cu
RfD	0.0035	0.0010	0.3000	0.0200	0.0030 (Cr^{VI}) 1.5000 (Cr^{III})	0.1400	0.0400

3. RESULTS AND DISCUSSION

The Romanian regulation requires the determination of the level of contaminants in the drinking water with a strict accuracy by using physicochemical investigation in order to eliminate the potential negative effects on the health. These unavoidable health goals, based solely on potential health risks, are called maximum admitted levels (MAL).

Lately, cardiovascular diseases are partially generated by water mineralization [7-11, 22]. Statistical investigations in different countries have indicated the existence of an inverse relationship between water hardness and deaths caused by cardiovascular diseases [30]. It has been found that the number of deaths caused by these conditions is higher in the localities where the water is soft and that this number decreases in proportion to the increase in water hardness. In this respect, the water hardness values shown in Table 3 can give important information about the presence of cardiovascular illness in the urban area.

Table 3. The average values of the quality indicators of the water sources in the water catchment areas during September to November of the year 2018

Sampling point	Month	Physico-chemical indicators						
		pH	Conductivity [μS/cm]	Salinity [‰]	Turbidity [NTU]	Total hardness [mg echiv/dm^3]	TDS [mg/mL]	Alkalinity [mg echiv/dm^3]
A1	September	7.9	743	0.1	0.1	18.2	361	13.1
	October	8.2	752	0.2	0.1	17.9	371	15.2
	November	7.6	703	0.1	0.1	12.6	352	12.4
A2	September	7.5	650	0.1	0.0	10.9	323	10.8
	October	7.2	689	0.1	0.0	10.5	349	10.1
	November	7.4	678	0.1	0.1	10.8	337	10.9
A3	September	7.6	674	0.1	0.0	11.2	336	11.1
	October	7.8	649	0.1	0.0	10.3	327	10.8
	November	7.5	625	0.1	0.0	10.1	311	9.6
A4	September	7.7	661	0.1	0.0	11.8	331	12.7
	October	7.4	602	0.1	0.0	11.4	351	11.6
	November	7.8	692	0.1	0.0	10.7	343	11.2
Maximum Admitted Limit (MAL) according Law 311/2004		6.5 - 9.5	2.500	-	5	Minimum 5.0	-	-

In the Romanian Regulation is stipulated that the 5.0 mg echiv/dm^3 as the minimum value for water hardness, and maximum not more than 15.00 mg echiv/dm^3. In Table 3 can be seen that the source A1 presented slightly higher average values than the maximum accepted value, in September and October of the year 2018. In the case of turbidity, the best values (i.e., the lowest) were obtained at the collection points A2 and A4, both at high and lower temperatures.

It is well known that the role of calcium is very important from the hardness point of view of the water, and calcium deficiency leads to arrhythmias [22, 30], as well. On the other hand, the hardness of the water favors the dissolution in the water of a chain of metals: cadmium, nickel, chromium, manganese which, in turn, has a toxic effect on the cardiovascular system [30, 32-37]. Water hardness affects the washing process, but positively influences cardiovascular pathology, hard water is considered a protective factor. More recent studies [35-37] indicate that hardness itself is not beneficial, but that Ca and Mg, whose compounds are the major determinant of hardness. Clinical studies indicate a favorable effect of Ca, Mg, Cr, Mn, and Zn; instead, Na, Cu, and Co are suspected of adverse effects.

Total Dissolved Solids (TDS) represents the total concentration of dissolved substances in water, made up of inorganic salts, and a small amount of organic matter. The inorganic salts found commonly in water include cations (e.g., calcium, magnesium, potassium and sodium), and anions (e.g., carbonates, nitrates, bicarbonates, chlorides, and sulfates). Usually, a high concentration of dissolved solids is not a health hazard and is strong correlated with conductivity. World Health Organization concluded that can be accepted five preferable levels of TDS for drinking water [51] presented in Table 4.

Table 4. Taste of drinking water with different TDS concentrations [50].

Level of TDS[mg/L]	Rating
Less than 300	Excellent
300 - 600	Good
600 - 900	Fair
900 – 1,200	Poor
Above 1,200	Unacceptable

It is well known that a high concentration of TDS of drinking water is an indicator that harmful contaminants, such as iron, manganese, sulfate, bromide, and arsenic, are present in the water and can produce hard water. On the other hand, a very low concentration of TDS has to be assigned for the water with a flat taste. The conductivity and TDS data presented in Table 3 are in accordance with Romanian Regulation and WHO requirements (Table 4). The pH of the water samples calculated as averages, presented in Table 3 are in according to Romanian Law 311/2004, with a single amendment from the World Health Organization part, who recommends that the pH of the water be less than 8.0 because basic water does not allow for effective chlorination (i.e., source A1: the average of the pH values of samples collected in October 2018).

The water not only has the potential to expose people to unwanted contaminants, such as lead (Pb) but also potentially beneficial metals, such as iron (Fe) and zinc (Zn). These metals are nutritionally important because their deficiency or overloading is harmful to human health. There is also some evidence that Fe and Zn could compete with Pb for human intestinal uptake, suggesting that deficiencies may lead to increased Pb uptake or possibly other changes in Pb biokinetics. Fig. 2 shown the average concentrations of seven metals, including lead, cadmium, chromium, nickel, manganese, copper, and zinc, collected in the period from September to November of the year 2018.

Cadmium has high mobility, is poorly retained by soil and water and is readily absorbed by living cells. The normal cadmium content in plants is between 0.1 and 0.8 ppm, values greater than 1 ppm being considered toxic. The toxic effects in humans have been observed following repeated consumption of some plants whose cadmium content is around 3 ppm. Cadmium toxicity is manifested by disruption of enzymatic activity, an effect explained by its affinity to thiol (-SH) groups of enzymes or proteins. On the other hand, due to its high half-life, cadmium accumulates in the human body with the age. According to medical research, the human body contains about 30 mg of total cadmium, of which about 10 mg is found in the kidney and 4 mg in the liver. Starting from these data, the monitoring of cadmium in drinking water must be done very carefully. In the investigated urban areas of drinking water supply (Fig. 2) was concluded that there is no exceedance of the maximum concentration allowed of cadmium in accordance with the Romanian legislation. Although, in the case of source A1 during the entire sampling period and in all the water samples were determined slightly higher concentrations than in the other three sampling points (A2-A4, Fig. 1 and Table 1).

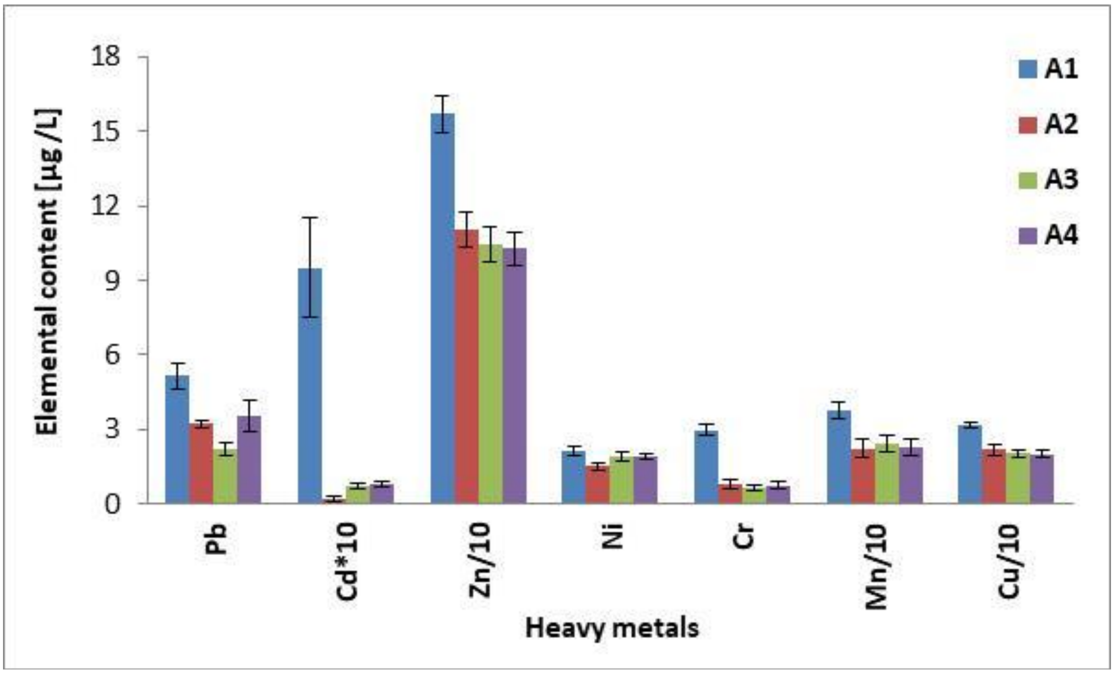

Figure 2. Average concentration of heavy metals [µg /L] (i.e., 90 samples/sampling point) during September to November of the year 2018.

Regarding the concentrations of copper and manganese in the drinking water samples analyzed the values were below the maximum allowed for both metals (i.e., 20.11±1.54 – 31.63±1.25 µg/L for Cu, and 22.28±3.52 – 37.83±3.31 µg/L for Mn, comparative with MAL according to Law 311/2004, that is 100 µg /L for Cu and 50 µg /L for Mn, respectively). The concentrations of chromium and nickel are lower than MAL according to Law 311/2004; the average concentration of Cr were between 0.65±0.10 µg/L (A3) and 2.97±0.21 µg/L (A1) and for Ni ranged from 1.52±0.15 (A2) µg/L to 2.15±0.20 µg/L (A1), comparative with MAL (i.e., Law 311/2004) 50 µg/L for Cr and 20 µg/L for Ni, respectively. The average concentrations of Pb (Fig. 2) in water samples ranged between 2.21±0.25 µg/L (A3) and

5.15±0.52 μg/L (A1) much lower than provided by Romanian Regulation and World Health Organization (i.e., 10 μg/L).

Table 5. Average values of Health Risk Index (i.e., 90 samples/sampling point) during September to November of the year 2018.

Sampling point	Health Risk Index (HRI)						
	Pb	**Cd**	**Zn**	**Ni**	**Cr**	**Mn**	**Cu**
A1	0.042	0.027	0.015	0.003	0.028	0.008	0.023
A2	0.026	0.001	0.011	0.002	0.007	0.005	0.016
A3	0.018	0.002	0.010	0.003	0.006	0.005	0.015
A4	0.029	0.002	0.010	0.003	0.007	0.005	0.014

The average values of Health Risk Index (HRI), calculated for analyzed samples are presented in Table 5. The HRI values were: Pb 0.029±0.009, Cd 0.008±0.011, Zn 0.012±0.002, Ni 0.003±0.001, Cr 0.012±0.009, Mn 0.006±0.001, and Cu 0.017±0.004, respectively. The drinking water samples does not present risk to the local population (HRI<<1).

4. CONCLUSIONS

This study was conducted to evaluate the health risks of exposure to heavy metals from the water supplies in urban areas of Romania. It can concluded that the waters samples collected from the A1-A4 sources are alkaline at 10 °C, with a pH ranged from 7.2 (A2) to 8.2 (A1). Alkaline water has the ability to neutralize and liquefy acid waste from the human body while maintaining its alkalinity, therefore the health and well-being of peoples. The average concentrations of heavy metals (i.e., Cd, Cr, Ni, Pb, Cu, Mn and Zn) were correlated with physicochemical indicators, and for all seven metals the high values were obtained for A1 source. The order of the heavy metals toxicity according to average values of HRI, calculated in drinking water, were: Pb > Cr > Cd > Cu > Zn > Mn > Ni.

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