Journal homepage: www.fia.usv.ro/fiajournal
Journal of Faculty of Food Engineering,
Ştefan cel Mare University of Suceava, Romania
Volume XIV, Issue 3 - 2015, pag. 276 - 281

ASSESSMENT OF POTENTIAL CONTAMINATION AND HEALTH RISK ASSOCIATED WITH METALS IN DRINKING WATERS FROM COPSA MICA REGION

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Received September 5th 2015, accepted September 29th 2015

Abstract: *Metal contamination of drinking water sources from Copsa Mica region (Copsa Mica village, Tarnava villages and Medias Town, Sibiu County, Romania) was assessed using the Metal Index, while health risk associated with metals from the drinking water sources was assessed using the Chronic Daily Intake and the Hazard Quotient. The MI values increase in following order S1>S3>S2>S4>S5, indicating a possible metal contamination of three drinking water sources from the studied area. However, according to the Hazard Quotient and the Total Hazard Quotient, the studied drinking waters are safe for human consumption. The calculated Hazard Quotients for studied metals decrease in the order: As>Cd>Mn>Zn≥ Cu>Ni ≥ Pb>Cr for sample S1, As>Cu ≥ Mn ≥ Pb>Cd ≥ Ni>Zn>Cr> for sample S2, Cd ≥Mn ≥ Pb>Cu ≥ Ni>As>Cr ≥Zn for sample S3, Zn>Cd ≥ Cu>Mn ≥ Ni>Cr>Pb for sample S4 and Cd ≥Ni>Cu>Mn>Cr ≥Pb ≥Zn>As for sample S5.*

Keywords: *drinking water, Metal Index, Chronical Daily Intake, Hazard Quotient*

1. Introduction

Drinking water contamination with metals represents a significant issue for the environment and human health [1-3]. Metals content in water sources have anthropogenic (industrial, agricultural activities) and natural origins (weathering, rock erosion) [1-4]. The use of unnapropriate or poorly monitorized water sources (well water, surface water) as drinking water exposes the population to potential health risks. The raise of population awarenes related to the risk of metal contaminated water consumption could avoid noumerous health problems (cancer, kidney damages, heart disease) [4-6].

Drinking water quality monitoring with respect to chemical compounds (metals, pesticides, nitrogen compounds) is important due to the pollution exposure issues which implies potential negative effects on health [7, 8]. For that purpose increasing numbers of studies all over the world were performed [9, 10]. Studies on metal pollution are important due to the metals toxicity, ubiquity and persistence in the environment [11, 12]. Thus, different indices (metal index, chronic daily intake, hazard quotients) for metal pollution, risk assessment and drinking water quality were elaborated and applied in order to assess the chemical status of drinking water soursec [3, 4, 13].

The Metal Index (*MI*) is an arithmetical tool used to assess the metal pollution status and represents the sum of the ratio between the monitored concentrations and the maximum admissible concentrations (*MACs*) of the studied metal [4, 13].

To assess the non-carcinogenic risk posed by metal contaminated drinking waters, healh risk indices such as the Chronic Daily Intake (*CDI*), the Hazard Quotient (*HQ*) and the Total Hazard Quotient (*THQ*) are used [3].

Copsa Mica is known as a "hot spot" of pollution, due to the metal industry and its negative effects on human and animal health and on plants, soil, air and water qulity [14]. Presently, the industrial activities ceased, but the chemical compounds still persist in the environment [14].

The aim of the present study is to evaluate the metal contamination status of drinking water sources using the *MI* and to assess the potential human health risk of metal contaminated waters using the *CDI,* the *HQ*, and the *THQ* indices.

2. Materials and methods

Study area and sampling

Well water samples from Tarnava village (S2, S3), Copsa village (S4, S5) and a public spring water sample (S1) from the vicinity of Medias Town, Sibiu County, Romania used by inhabitants as drinking water sources were studied (Figure 1).

Fig. 1. Study area and drinking water sampling points

These villages are close to Copsa Mica Town, known for the environment pollution with Cu, Fe, Zn, Cd, Cu [14].

All water samples were colected in August of 2014 in polyethylene bottles (500 ml) and kept at 4 ºC in a refrigerator until analysis.

Chemical analysis

Drinking water samples were filtered using 0.45µm filter membrane and acidified with HNO_3 before analysis of the As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn content using DRC II Perkin-Elmer ICP-MS.

Metal Index (MI)

The Metal Index (*MI*) is based on total trend assessment of present status [15, 16]. A high metal concentration associated with its *MAC* indicates a low water quality [15]. The formula (*Eq 1*) for the *MI* rating is [16, 17]:

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

Where C_i represents the metal concentration and *MAC* is the maximum allowable concentration according to Moghaddam [18].
According to the *MI* results, waters can be classified as potable (*MI*< 1), non-potable (*MI*> 1) and water on the threshold of danger (*MI*= 1) [17, 18]. If *MI*> 1 it represents a threshold of warning, even if the *Ci* does not exceed the *MACs* for all metals [17].

Human health risk assessment indices

Chronic Daily Intake (CDI)

The *CDI* was calculated in order to estimate the health risk for adults associated with the consumption of contaminated drinking water. The *CDI* raiting was calculated using *Eq 2* [3, 19, 20]:

$$CDI = \frac{C \times DI}{BW} \quad (2)$$

Where, *C* represents the metal concentration in water samples (µg/l), *DI* is the average daily intake rate (2L/day) and the body weight is represented by *BW* (72 kg) [2, 3].

Hazard quotient (HQ)

The *HQ* is a human health risk assessment index, which quantifies the non-carcinogenic risk (*Eq 3*) [2, 21].

$$HQ = \frac{CDI}{RfD} \quad (3)$$

Where, *CDI* is the Chronic Daily Intake and *RfD* is the oral toxicity reference dose. For the *HQ* computation the used *RfD* values were 1.5mg/kg-day for Cr, 5.0×10^{-4}mg/kg-day for Cd, 3.7×10^{-2}mg/kg-day for Cu, 1.4×10^{-1}mg/kg-day for Mn, 2.0×10^{-2}mg/kg-day for Ni. 3.6×10^{-2}mg/kg-day for Pb, 3.0×10^{-1}mg/kg-day for Zn and 3.0×10^{-4}mg/kg-day for As [2, 3, 22].
If *HQ*< 1, the safety of the exposed population is assumed [2, 3, 23, 24]. In case of HQ>1, there might be non-carcinogenic risk and potential for toxic effects for the population [24].

3. Results and discussion

For the *MI* rating, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were selected in order to evaluate the possible metal contamination of drinking water sources in Copsa Mica region.
The *MI* values revealed possible metal pollution of drinking water samples S1, S2 and S3 with *MI* values higher than the critical value of 1 (Table 1).

Table 1.

Metal Index (*MI)* of the drinking water samples

	S1	***S2***	***S3***	***S4***	***S5***	***MAC****
Cr	5.0	1.5	4.6	3.8	3.4	50
Cd	0.3	0.03	0.1	0.04	0.04	3
Cu	5.8	6.9	6.2	2.8	1.5	1000
Fe	151	94	94.7	50.4	27.2	200
Pb	4.2	0.7	0.8	0.4	0.6	1.5
Zn	38.6	40.9	58	176	21.7	5000
Ni	2.5	1.6	3.9	0.9	1.4	20
As	1.0	0.3	0.9	<LQ	<LQ	50
Mn	7.3	6.6	7.7	4.9	0.7	50
MI	***4.1***	***1.2***	***1.5***	***0.79***	***0.71***	-

*according toMoghaddam et al., 2014 [18]
<LQ – values are bellow the Limit of Quantification

Thought, the measured concentrations for studied metals do not exceed the *MACs* used for the *MI* count. The drinking water samples with *MI*<1 are suitable for drinking.

The *CDI* values (Table 2) for the studied metals in S1 water source situated near Medias decrease in the order of Cd<As<Ni<Pb<Cr<Cu<Mn<Zn.

For samples collected from Tarnava village (S2 and S3) the calculated *CDI* increase in the order Cd<As<Pb<Ni≤Cr<Mn<Cu<Zn and Cd<Pb<As<Ni<Cr<Cu<Mn<Zn, respectively.

Table 2.

Chronic Daily Intake (CDI), Hazard Quotient (*HQ*) and Total Hazard Quotient (*THQ)* for drinking water

Metal	*S1*		*S2*		*S3*		*S4*		*S5*	
	CDI	*HQ*	*CDI*	*HQ*	*CDI*	*HQ*	*CDI*	*HQ*	*CDI*	*HQ*
Cr	$1.4 x10^{-4}$	$0.1x10^{-3}$	$0.4x10^{-4}$	$0.3x10^{-4}$	$1.2x10^{-4}$	$0.1x10^{-3}$	$0.1x10^{-3}$	$0.1x10^{-3}$	$0.9x10^{-4}$	$0.1x10^{-3}$
Cd	$0.1x10^{-4}$	$0.2x10^{-1}$	$0.1x10^{-5}$	$0.2x10^{-2}$	$0.3x10^{-5}$	$0.6x10^{-2}$	$0.1x10^{-5}$	$0.2x10^{-2}$	$0.1x10^{-5}$	$0.2x10^{-2}$
Cu	$1.6x10^{-4}$	$0.4x10^{-2}$	$1.9x10^{-4}$	$0.5x10^{-2}$	$1.7x10^{-4}$	$0.5x10^{-2}$	$0.8x10^{-4}$	$0.2x10^{-2}$	$0.4x10^{-4}$	$0.1x10^{-2}$
Mn	$2.0x10^{-4}$	$1.0x10^{-2}$	$1.8x10^{-4}$	$0.5x10^{-2}$	$2.1x10^{-4}$	$0.6x10^{-2}$	$1.4x10^{-4}$	$0.1x10^{-2}$	$0.4x10^{-4}$	$0.3x10^{-3}$
Ni	$0.7x10^{-4}$	$0.3x10^{-2}$	$0.4x10^{-4}$	$0.2x10^{-2}$	$1.1x10^{-4}$	$0.5x10^{-2}$	$0.3x10^{-4}$	$0.1x10^{-2}$	$0.6x10^{-3}$	$0.2x10^{-2}$
Pb	$1.2x10^{-4}$	$0.3x10^{-2}$	$0.2x10^{-4}$	$0.5x10^{-2}$	$0.2x10^{-4}$	$0.6x10^{-2}$	$0.1x10^{-4}$	$0.3x10^{-3}$	$0.2x10^{-4}$	$0.1x10^{-3}$
Zn	$10.7x10^{-4}$	$0.4x10^{-2}$	$0.1x10^{-2}$	$0.1x10^{-3}$	$1.6x10^{-3}$	$0.1x10^{-3}$	$4.9x10^{-3}$	$0.2x10^{-1}$	$0.2x10^{-4}$	$0.1x10^{-3}$
As	$0.3x10^{-4}$	$0.9x10^{-1}$	$0.1x10^{-4}$	$0.3x10^{-1}$	$0.3x10\text{-}^{4}$	$0.4x10^{-3}$	-	-	-	-
THQ	***0.13***		***0.05***		***0.03***		***0.02***		***0.01***	

For samples from Copsa Mica village (S4 and S5) the calculated *CDI* increase in the order As<Cd<Zn<Cr<Pb<Ni<Cu<Mn for sample S4 and Cd<Pb≤Zn<Cu≤Mn<Cr<Ni for sample S5.

The highest *CDI* values were obtained for Zn in samples S1, S2, S3 and S4, followed by the *CDI* for Ni in sample S5 and Cr in sample S4. Samples S2, S3, S4 and S5 present the lowest *CDI* for Cd.

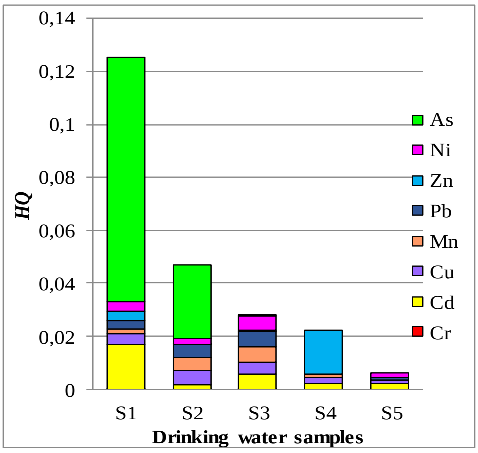

Fig. 2. The Hazard Quotient (*HQ*) variation for drinking water

According to the *HQ* values, the sample S1 and S2 present the highest risk exposure to metals, mainly As and Cd. Sample S4 is characterized with the highest Zn concentration. The lowest *HQ* values were obtained for sample S5, as shown in figure 2.

The *THQ* ranged from 0.01 (S5) to 0.13 (S1).

According to the *HQ* and the *THQ* results, the inhabitants using the studied water samples as drinking water sources do not present potential non-carginogenic risk.

4. Conclusion

The *MI* indicates a possible metal contamination of drinking water samples from Medias Town and Tarnava village, respectively water samples S1, S2 and S3. However the metal concentrations do not exceed the *MACs* used for the *MI* calculation. The health risk assessment (*CDI, HQ* and *THQ* indices) indicates that the studied drinking water samples do not present potential non-carcinogenic risk, adverse or toxic effects for the inhabitants.

5. Acknowledgments

The research is financed by Romanian financial authority CNCS-UEFISCDI, Partnership project VULMIN, Contract No. 52/2012 and the Sectorial Operational Programefor Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project POSDRU/159/1.5/S/133391 - *"Doctoral and postdoctoral excellence programs for training highly qualified human resources for research in the fields of Life Sciences, Environment and Earth".*

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