ASSESSMENT OF HEAVY METAL CONTENT (Mn, Zn, Cu AND Fe) IN CRIŞUL REPEDE RIVER WATER (NW ROMANIA) UPSTREAM AND DOWNSTREAM OF ORADEA AND SÎNTION

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Abstract:
This work characterizes Crisul Repede River water (NW Romania) upstream and downstream of Oradea city and SÎntion village, before and after confluence with Peţea, an important tributary which flows through the Oradea City, in terms of content of 4 heavy metals (Mn, Zn, Cu and Fe). The monitoring period, the sampling performed from January to April 2011. During the study it was found that drinking water source for Oradea City (Crişul Repede River), corresponds to the requirements of drinking water Law, on ccharacteristics of surface water intended for drinking water (Law 458/2002, amended by Law 311-28 June 2004). In content terms of Zn, Cu and Fe the water fit to A1 category. The measured Mn concentration was higher during January and February water therefore the Crişul Repede River water fit in the A2-3 quality category.

Key words: heavy metal assessment, Crişul Repede, water

INTRODUCTION

Spreading of the metals in water, sediment and atmosphere result from their presence in crust. In their natural concentrations the metals plays an essential role in many biochemical processes, but in exceed concentration over background can become toxic. As a result of human activities, the metals current levels are higher than under natural conditions, representing a threat to organism, because many metals become harmful even in moderate concentrations (Laane, 1992).

The metals potential toxicity depends on their bioavailability and their physico-chemical properties. Examples of metals which are a greater relevance to the environment in terms of toxicity are: Cd, Cr, Co, Cu, Pb, Hg, Ni, Sn, V and Zn (Sarkany-Kiss et al., 1997; Petrovici, Pacioglu, 2010).

General sources of the aquatic environment pollution are: cities and industries, wastewater and industrial residues, domestic waste and storm water, transportation, discharge of waste into surface waters, atmospheric deposition (Damian et al., 2008).

Terrestrial sources that generate heavy metals are mainly represented by waste water treatment plants, industries, mining, agriculture (Adriano, 2001; Vanek et al., 2005). Rust and other forms of corrosion leading to metals spread into the environment (Todoran et al., 2010), during use or storage of various metal equipment. Burning fossil fuels and various categories of waste release into the atmosphere also metals.

Once the metals spread in to the aquatic environment, they can follow different paths: to be dissolved in the water column, stored in sediment, volatilize into the atmosphere, and accumulated in living organisms (Fodor et al.; 2011, Petrescu-Mag et al., 2010).

Nature of the different forms of metals in the aquatic environment remains a variable that is not fully understood. Dissolved or insoluble forms of metals have different ways to receive and storage, so that require further studies.

Specific ways of metals accumulation in ionic forms, free or coordinate with organic ligands, have identified and characterized. It is unknown if specific mechanisms exist for different oxidation states of metals and for different types of inorganic ion complexes (Roesijadi & Robinson, 1994).

Excess of heavy metals have inhibitory effects on the development of aquatic organisms (phytoplankton, crustaceans, insects, fish, etc.) (Bryan, 1971; Viarengo, 1989). It can affect shellfish growth, oxygen consume, bissus formation, reproductive process, and other.

Fishes and crustaceans exposed to high concentrations of metals occur following effects: histological and morphological changes in tissues (the aspect change of gills, necrosis or fatty degeneration of the liver), physiological changes (slowdown in growth and development, decrease in water movement performance, changes of flow), changes in body chemistry (enzyme changes), behavioral changes, changes in reproduction (Authman, 2008; Bryan, 1971; Connell et al., 1984).

We purpose in this work to evaluate the content of heavy metals (Mn, Zn, Cu and Fe) in the Crişul Repede River water, before leaving Romania, after he crosses Oradea and SÎntion, given that this river is the source of drinking water of Oradea City and also of other localities beyond border, in Hungary.

MATERIAL AND METHODS

Sampling points for the water on Crişul Repede River course were determined as follows:

Site 1. Upstream Oradea. This point is located approximately 10 km upstream of Oradea (Fughiu), to monitoring the river water quality before Crişul Repede River entry into the urban and industrial center of Oradea.

Site 2. Downstream Oradea. This point is located downstream from Oradea City, to monitoring the water quality of Crişul Repede River, before its confluence with Pețea, an important tributary that crosses the city of Oradea.

Site 3. Upstream Sîntion. In this sampling point the water quality is monitored on Crişul Repede River, downstream of the confluence with the tributary Peța, located upstream of another urban center - Sintion.

Site 4. Downstream Sîntion. This sampling point was chosen to monitor the water content of heavy metals in Crişul Repede water, downstream of both localities (Oradea and Sîntion) and the confluence with his tributary Pețea.

GPS coordinates for the sampling points are showed in table 1 and their location in the figure 1.

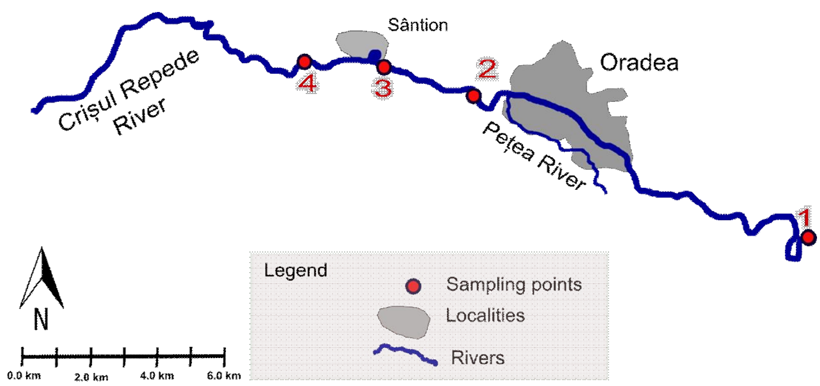

Fig. 1. The map of location and sampling points.

Table 1

Sampling points - GPS coordinates

Sampling points	**GPS coordinates**	
Site 1. Upstream Oradea City	N 47°03’38,1”	E 22°02'32,1"
Site 2. Downstream Oradea City	N 47°04’21,22”	E 21°52'31,11"
Site 3. Upstream Sîntion	N 47°04’17,87”	E 21°52'42,29"
Site 4. Downstream Sîntion	N 47°04’52,5”	E 21°48'26,2"

Sampling was done weekly during the period: January-April 2011, and a total 17 campaigns were done.

Water Sampling and preparation of material were made following the Guidelines for sampling program and analyzing waste water samples (NTPA 004/1997, Annex 2 to the Ordinance of Minister of Waters, Forests and Environmental Protection No. 1097/1997 and ISO 5667.-10), Guidelines for wastewater collection and ISO5667-6 (Water quality-

Sampling-Part 6). The sampling showed turbulence in order to ensure a proper mixing. Water samples were taken in plastic bottles immersed in a third of total high of the water course. Samples were acidified with HNO_3.

Water analysis was done using atomic absorption spectrometry with electro thermal atomization in graphite furnace and flame, according to EN ISO 15586/2003, ISO 8288/2001 and SR 13315/1996.

A total of 68 samples were analyzed (sampling during 17 campaigns from 4 sites- sampling points) using atomic absorption spectrometer type ANALYST 700 for Ni, Cr, Zn, Cu and DUO Varian 240 FS for Fe.

Due to relatively high concentrations of dissolved salts in complex matrix samples and water samples, the method based on atomization in graphite furnace is susceptible to various types of interference (molecular absorption, chemical and matrix effects). To eliminate interference due to the possible presence of chloride in water samples, they are treated with HNO_3 to transform the chlorides in more volatile nitrates, which can eliminate in the calcination step by the selective volatilization of the matrix. It is necessary to perform a control in parallel to eliminate interference due to impurities in the reagents used.

Iron concentration was determined using atomic absorptions spectrometry with flame atomization with a Varian 240 FS type DUO spectrometer, with a normal calibration method.

RESULTS AND DISSCUSIONS

Average of heavy metal concentrations measured in a month in the river water Crişul Repede showed different variation depending on the the sampling point and kind of heavy metals analysed.

Thus, manganese, as shown in Figure 1, had higher values in January and February, especially in the points 3 and 4, located downstream of Oradea City and at the confluence with tributary Pețea, it also transports in Crişul Repede polluted water from the city. In February 2011 was recorded maximum value for this heavy metal in water (140 mg /l), so that water is included in A 2-3 category (table 3). This water category means that the river water must be treated intensively physical and chemical to be used like drinking water. Operations of the intensive treatment include loosening and disinfection, chlorination to break point, coagulation, flocculation, decantation, filtration, adsorption (on activated carbon), disinfection (ozone feeding, final chlorination).

The zinc concentrations, unlike manganese, hadn´t disturbing values in any of the measurements performed (figure 1). Its quantities in the surface waters studied were well below permissible level in accordance with STAS rules (table 2). Because the STAS rules limits for the concentration of zinc in water are very high, means that it does not affect drinking water quality in a stressed, only extremely high concentrations.

Table 2

Quality conditions of the drinking water

Parameter/Unit of measurement	**Maximum permitted value**	**Analysis method**
Mn/µg/l	50	STAS 3264/81 SR ISO 6333/96
Zn/µg/l	5000	STAS 6327/81
Cu/µg/l	100	STAS 3224/69
Fe/µg/l	200	STAS 3086/68 SR ISO 6332/96

Table 3

Characteristics of surface water intended for drinking water (according to HG 352/2005 on amending GD No 188/2002, Annex 3 - Table 3 and 4).

Parameter/Unit of measurement	Water Quality Class					
	A1	A1	A2	A2	A3	A3
Mn (µg/l)	50		100		1000	
Zn (µg/l)	500	3000	1000	5000	5000	5000
Cu (µg/l)	20	50	50		1000	
Fe (µg/l)	100	300	1000	2000	2000	
Category A1: Simple physical treatment and disinfection, for example rapid filtration and disinfection.						
Category A2: Normal physical and chemical treatment and disinfection, for example prechlorination, coagulation, flocculation, decantation, filtration, disinfection (final chlorination).						
Category A3: Intensive physical and chemical treatment, extended treatment and disinfection, for example chlorination to break point, coagulation, flocculation, decantation, filtration, adsorption (on activated carbon), disinfection (ozone feeding, final chlorination).						

On copper, we can observe an increase in the concentration of surface waters mentioned, in January (figure 2). If site 4, located downstream of the city Sîntion, copper concentration was also increased in April, probably due to external causes, such as slight pollution. In April, we can say that the pollution source was different from that in January, because in February and March the concentration of copper was lower than in January.

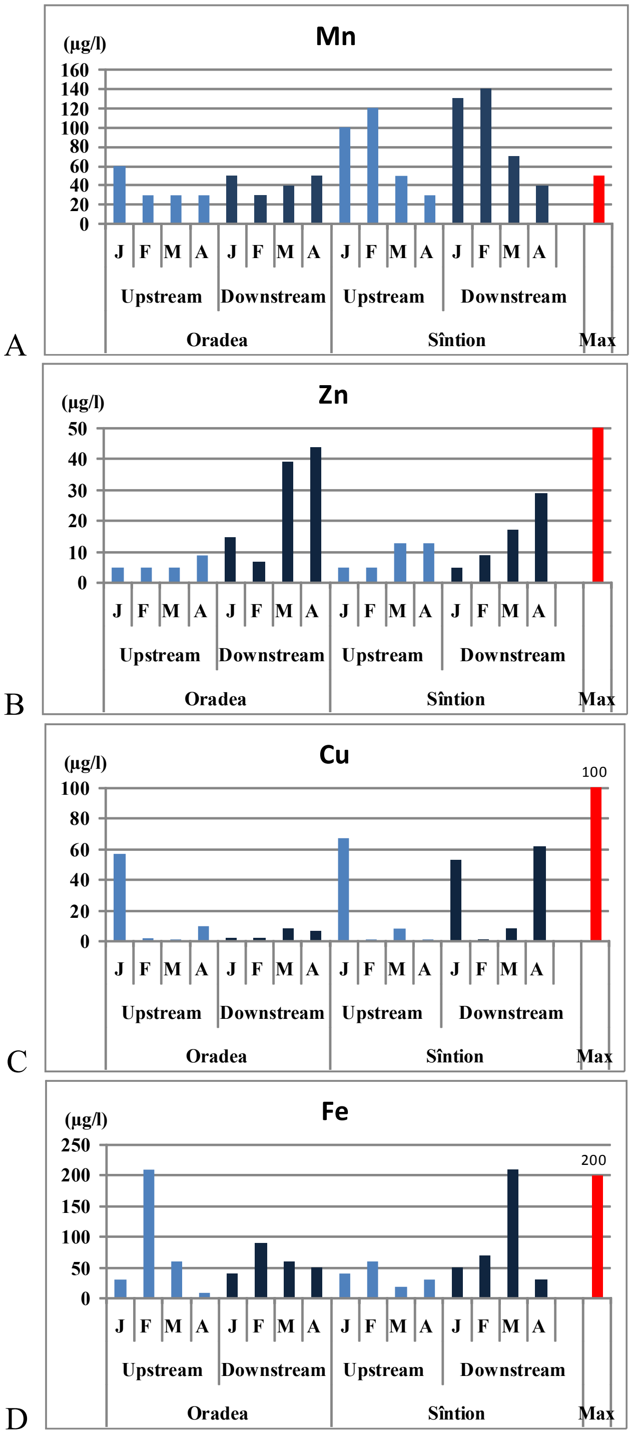

Fig. 2 Manganese (A), zinc (B), cooper (C) and iron (D) concentrations of Crişul Repede River, at sampling points (January – April 2011). Max = maximum permitted value in drinking water.

None of the copper ion concentrations found in surface water is greater than the maximum allowable value for the drinking water in accordance with STAS rules (table 2).

As the amount of iron in surface water can be observed that in February and March, there were increases its concentration at site 1 (upstream Oradea), respectively, at site 4 (downstream SÎntion), so the value maximum allowed (200 mg / l) was slightly exceeded (210 mg / l).

Based on the concentration of iron, Crişul Repede River can be classified as surface water of categories A1, which needs a simple physical treatment and disinfection to be converted into drinking water (table 3).

CONCLUSIONS

Source of drinking water to Oradea (Crişul Repede River), was consistent with the requirements for drinking under Law 458/2002 as amended - Law 311-28 June 2004 on drinking water quality in terms of content of heavy metals: Zn , Cu and Fe. During the monitoring period January-April 2011, except those points, the Crişul Rpede River was within in A1category (requires simple physical treatment and disinfection, for example rapid filtration and disinfection).

Regarding manganese, higher values were recorded in January and February, especially in downstream of Oradea City and at confluence with tributary Peţea, which brought polluted water from the city. In February 2011 was recorded maximum value for the heavy metal (140 mg /l). In terms of manganese concentration in water of Crişul Repede River, this may be included in A 2 or 3 quality category for drinking water requires intense physical and chemical treatment, extended treatment and disinfection, for example chlorination to break point, coagulation, flocculation, decantation, filtration, adsorption (activated carbon), disinfection (ozone feeding, final chlorination).

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