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ASSESSMENT OF INORGANIC CONTAMINANTS IN WELL WATERS FROM NONFERROUS MINING AND URBAN AREAS IN NORTH-WEST AND CENTRAL ROMANIA

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Abstract: *The levels of inorganic contaminants in well waters used as drinking water sources from urban and nonferrous mining areas were studied. Well water samples from mining area are circumneutral and present high concentrations of metals (1.0-132 µg/l As, 20-73 µg/l Cr, 4.0-272 µg/l Mn), in some samples exceeding the maximum admissible concentrations set by Romanian Law 311/2004, regarding the drinking water quality, while well water samples collected from urban area are circumneutral to alkaline and show high nitrates (31-271 mg/l), nitrites (0.1-3.3 mg/l) and sulphates (51-245 mg/l), but low metal concentrations. The metal contamination reflects the influence of nonferrous mining activities, while household activities and agriculture imprint high values of* NO_2^-, NO_3^- *and* SO_4^{2-}.

Keywords: *well water, inorganic contaminants, mining area, urban area, metal contamination, nitrite, nitrate.*

1. Introduction

Water is an essential resource for maintaining life. Well waters sources are used as drinking water sources in areas with lack of other fresh water sources or water distribution supply.

The main pollution sources of well waters are anthropogenic activities, such as mining activities (exploiting and metallurgy), industry, household (dry toilets, collecting tanks), impairment of wastewater treatment systems (sewage discharges) and agricultural practices (use of fertilizers, manure deposits) [1-3].

Nitrate and nitrite contamination of well water is found in many urban areas, because of leak from sewage effluent, dry toilets, collecting tanks, cattle manure [4, 5], while metal contamination of well waters is determined mostly by mining activities.

Drinking water contamination by mining activities represents a significant problem worldwide [6, 7]. In African countries, such as Ghana, Tanzania the mining activities impact on water resources quality is serious; well waters being unsuitable to be used as drinking water due to their high toxic metal contents [8]. Asian countries

(China, India) are also confronting with exposure to toxic metals by well waters near mining areas [2, 9]. In Romania the mining activities determined local pollution of aquatic systems, especially in the north-western part of the country [10, 11].

2. Matherials and methods

2.1. Study area and sampling

The studied mining area is localized near Oas Mountains, part of the north-western volcanic chain, Romanian Carpathian. The area is nearby (about 50 km) Baia Mare, the main centre for nonferrous metallurgy and mining (Cu, Zn, Pb, Au, Ag) and metals pollution "hot spot" [12-14]. The nonferrous complex ores are exploited from three main ore deposits (Ghezuri, Penigheri-Turt and Socea-Tarna Mare) [15]. Ghezuri and Penigheri-Turt mines are localized near Turt village, 20 km away from Satu-Mare. Socea - Turt mine is situated near Tarna Mare, and 8 km North West from Turt village [16]. Turulung is situated at 8 km South-West from Turt and 16 km South from Tarna Mare. Inhabitants of the three small localities use well water as drinking water source, because of lack of other fresh water sources. Mining activities started in 1973, as modern exploiting; but since Middle Ages ores containing precious and nonferrous metals were exploited from the volcanic Oas Mountains [16]. Surface water pollution assessment studies of the area indicate acidic pH and pollution with highly toxic elements as As, Cd, Pb, Mn and Zn [11].

The studied urban area is Medias, a medium size town situated in the Northern part of Sibiu County, in central Romania. Although the town has water supply system, not all households have access to it. Thus, private water wells are used as drinking water supply.

The aim of the present study is to assess and compare the inorganic contaminants of well water from nonferrous mining (Tarna Mare, Turulung and Turt, Satu Mare County) and urban areas (Medias, Sibiu County).

From the nonferrous mining area five well water samples (M1-M5) were collected from Tarna Mare, one sample (M6) from Turt and two (M7, M8) from Turulung. Nineteen well water samples (U1-U19) were collected from urban area, Medias. All samples were collected in August 2014 in clean 500 ml bottles and stored at 4 °C until analysis. The pH was measured on site and samples were filtered using 0.45 µm acetate cellulose membrane filters. The anions were measured directly in filtered samples, while for the determination of metals; samples were and acidified to pH ≤ 2 with 63% HNO_3.

2.2. Instrumentation

Elements (Cr, As, Zn, Mn) were measured using inductively coupled plasma mass spectrometry (ICP-MS) using an ELAN DRC II (Perkin-Elmer, Canada) spectrometer. The content of NO_2^-, NO_3^- and SO_4^{2-} were analysed by ion chromatography using a 761 Compact (Methrom A.G., Switzerland) ion chromatograph. The pH was measured by a 350i multiparameter (WTW, Germany).

3. Results and discussion

The pH value of well water samples was circumneutral in the mining area and circumneutral to alkaline in the urban area. Mean pH values for water samples from the mining area was 6.73, while that from the urban area was 7.42. The SO_4^{2-} concentrations for all well water samples were below acceptable limits set by

Romanian Law 311 [17], with highest values for urban well waters (Figure 1).

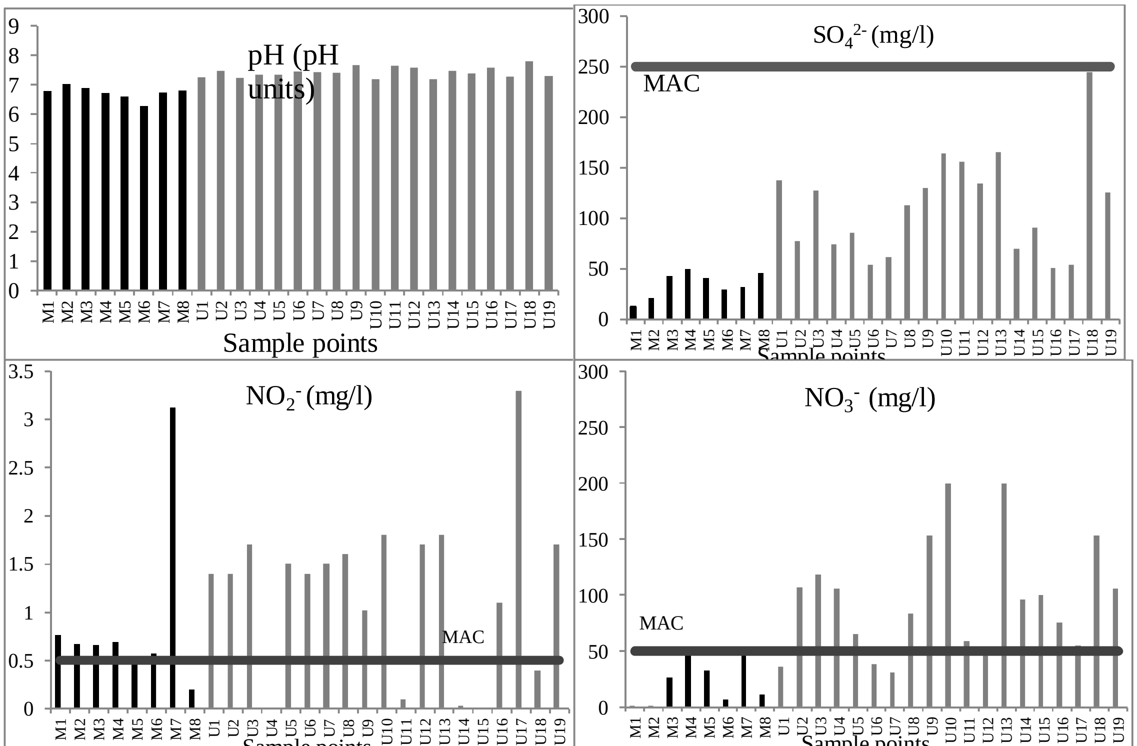

Fig.1 The pH values and SO_4^{2-}, NO_2^-, NO_3^- concentrations in well water samples

There are several regulations that set guideline values for drinking waters, such as the Romanian Law 311/2004, WHO (World Health Organization), and U.S. EPA (Environmental Protection Agency), guidelines [17-19]. The source of nitrites and nitrates could be the collecting tanks, dry toilets, cattle manure localized near water wells used as drinking water source. Except five samples (U4, U11, U14, U15, U18) all water samples from Medias exceed MAC (Maximum Admissible Concentration) for NO_2^-, while only one water sample from mining area (M7 from Turulung) exceeds the MAC (Figure 1).

Table 1

Measured and guideline concentrations of inorganic contaminants in studied well water samples used as drinking water

Chemical parameters		**Measured concentrations**				**MAC**	**Guideline**	**Threshold**
		Min	**Sample**	**Max**	**Sample**	**Law 311/2004**	**WHO**	**U.S. EPA**
pH	**pH units**	6.27	M6	**7.81**	U18	6.5-9.5	6.5-8.5	6.5-8.5
As	**µg/l**	<0.8	U2-U4, U6, U12, U17-U19, M3-M6	**132**	M8	10	10	10
Cr		0.90	U12	**73**	M2	50	50	100
Mn		<1.0	U2, U9,U18, M5	**272**	M1	50	-	50
Zn		7.1	U3	549	M6	5000	-	5000
NO_2^-	**mg/l**	<0.05	U4, U14	3.3	M17	0.5	3.0	1.0
NO_3^-		0.92	M2	271	U10	50	50	10
SO_4^{2-}		13	M1	245	U18	250	-	-

The NO_3^- concentrations are higher for well water samples (range 31 - 271 mg/l, mean 101 mg/l) from the urban area than for well water samples (range 0.92 - 50 mg/l, mean 22 mg/l) from the mining area (Figure 1).

The elements considered in the current study include As, Cr, Mn and Zn. The elements content for well water samples from nonferrous mining area present higher concentrations that those from the urban area. As, Cr and Mn concentrations in waters from mining area exceed the MACs set by drinking water guidelines [17 19] while those from urban area do not exceed the corresponding MACs (Table 1). Chromium concentrations ranged between 0.90 µg/l and 73 µg/l. Well water samples from Medias present lower Cr concentrations than the well water samples from Turulung and Tarna Mare. One water sample (M2) from the mining area shows contamination with Cr, exceeding MAC, while other seven samples indicate Cr concentrations between 20 µg/l and 42 µg/l (Figure 2).

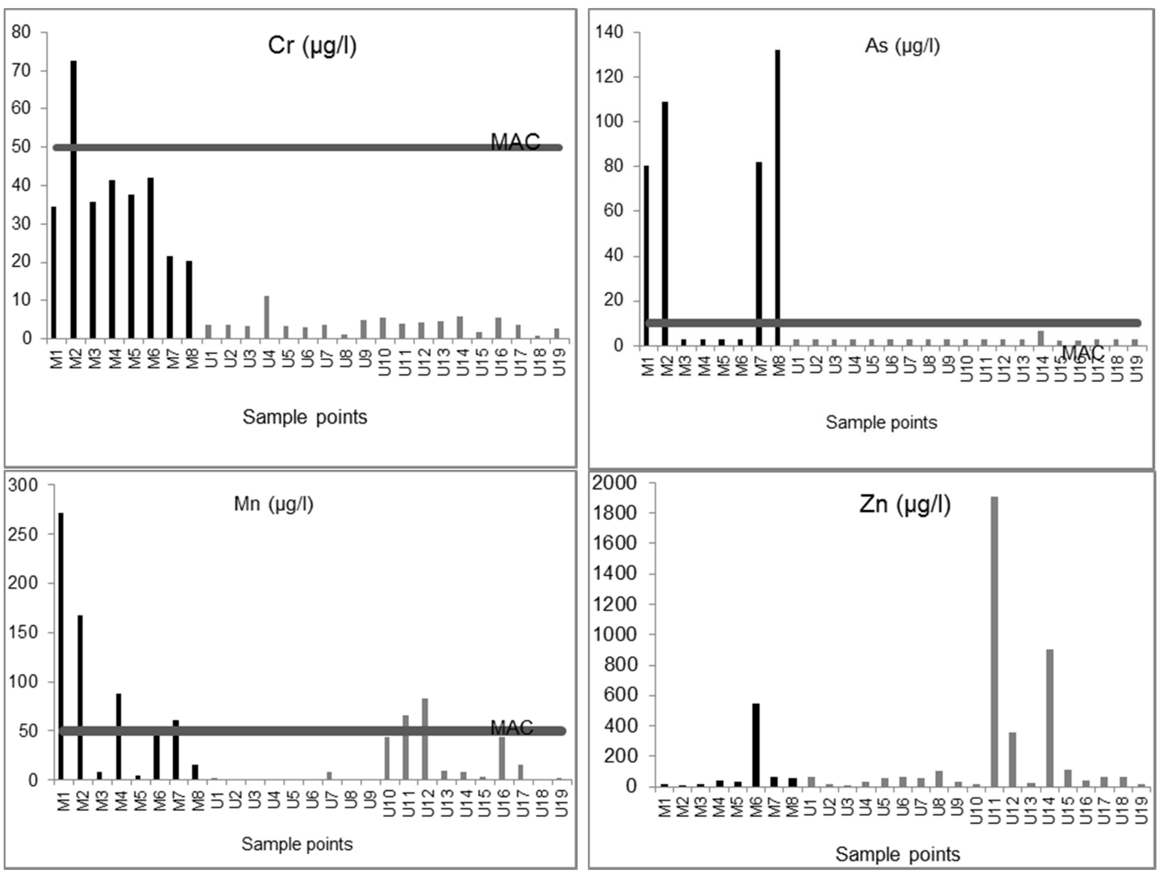

Fig. 2 Cr, As, Mn and Zn concentrations in well water samples

The As content in four well water samples (M1, M2, M7 and M8) were found to be more than ten times higher than the corresponding, while samples from Medias are lower than MAC. Studied well water samples present Mn contamination, two well water samples (U11 and U12) from Medias, three well waters from Tarna Mare (M1, M2, M4) and one sample M7 from Turulung exceeding the MAC (Figure 2).

The Zn concentrations do not exceed MAC, as shown in figure 2. Samples from Medias show generally higher Zn concentrations (mean 207 mg/l) than samples from mining area (mean 97 mg/l As). Source for high Zn concentrations could be a metallurgical facility (Zn, Pb, Sn) localized at about 13 km from Medias.

4. Conclusion

Growing population and anthropogenic activities (mining, industry, agriculture and household) imply interference with the natural ecosystems and influence the well water quality used as drinking water source. In the current study one was found that NO_2^-, NO_3^-, SO_4^{2-}, and As, Cr, Mn concentrations exceed the limits set by national and international drinking water guidelines. Well water samples from Turulung and Tarna Mare present higher Cd, As and Mn concentrations than the well water samples from Medias. The pH values, measured for well water samples from the nonferrous mining area, indicate circumneutral waters, while well water samples from the urban area are characterized by circumneutral to alkaline pH. However, NO_2^-, NO_3^- and SO_4^{2-} concentrations are significantly higher compared with the values measured in the Turt region, especially NO_2^-, NO_3^- values which are noteworthy higher as MAC.

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