DRINKING WATER QUALITY IN WELLS FROM AN AREA AFFECTED BY FLOOD EVENTS: CASE STUDY OF CURVATURE SUB-CARPATHIANS, ROMANIA

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ABSTRACT. - Drinking water quality in wells from an area affected by flood events: case study of Curvature Sub-Carpathians, Romania. The present study evaluates the chemical parameters (inorganic anions and metals) of drinking water of twenty-four wells and the presence of *Escherichia coli* in ten selected wells located in two villages from Buzau and Prahova Counties, in Curvature Sub-Carpathians, Romania, a rural area frequently affected by flood events. Water samples were collected in July 2014. Concerntrations of fluorides, nitrites, chlorides and phosphates were below the maximum allowable concentrations (MACs) for drinking water established by European legislation (Drinking Water Directive 98/83/CE) in all the analysed samples. Concentration of nitrates exceeded MAC (50 mg L^{-1}) in five samples, while concentration of sulphates exceeded MAC (250 mg L^{-1}) in two samples. Among the analysed metals, Mn exceeded MAC (50 µg L^{-1}) in two samples, while Cu, Pb, Zn, Fe, Na, Cd, Cr, Cu, Ni and As concentrations did not exceeded the corresponding MACs. *E. coli* (over 2000 UFC 100 mL^{-1}) was found in six water samples. The results show that majority of the studied parameters were below the threshold limits, however in some of the studied wells the water was found to be contaminated both by some chemical pollutants and by *E. coli*, which prepresent a risk for local population health.

Keywords: drinking water quality, well water, inorganic contaminants, Curvature Sub-Carpathians, *Escherichia coli*, flood events

1. INTRODUCTION

The environmental quality is varying constantly due to unfavorable environmental changes, mainly as a result of anthropogenic activities (Zobrist et al., 2009; Kataria et al., 2011). These modifications affect living organisms directly, or through the food-chain. Chemicals such as toxic metals and anions (sulfates, nitrates, nitrites, chlorides and phosphates) along with the microbiological load are the major sources of pollution for well waters.

Inadequate water supply represents a major challenge in rural areas, where domestic wells are the main drinking water sources. In addintion, in areas affected by flood events, well water quality can be seriously damaged. Drinking water

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quality has a direct effect on humans because is consumed as it is withouth any treatement (Celebi et al., 2014). The negative effects of contaminants depend on their toxicity but also on their concentrations, thus even elements that are essential in low concentrations, may become toxic above the concentration of threshold limits. In order to protect human health, the Drinking Water Directive request the control of public water systems to ensure that the water produced for human consumption can be consumed safely, do not contain microorganisms and toxic chemical substances are below specific threshold values (EU Directive 98/83/EC).

According to World Health Organization (WHO) guidelines, there is a need of safe drinking water sources to provide at least 20 liters of water per person per day, up to 1 km radius of the user's home (Calin and Rosu, 2011). It is estimated that, in rural areas of Romania, near 50% of households have their own wells as primary source of drinking water, while only 28% of households are connected to public water supply sytems (Both and Borza, 2011). Due to the anthropogenic activities, in conjunction with flood events, in some areas, the water from wells is increasingly contaminated.

The present study evaluates the drinking water chemical parameters (inorganic anions and metals) from twenty-four wells and occurrence of *Escherichia coli* (*E. coli*) in ten wells located in two villages from Buzau and Prahova Counties, in Curvature Sub-Carpathians, Romania.

2. MATERIALS AND METHODS

2.1 Study area and sampling

The study area is located in the Curvature Sub-Carpathians of Romania, in two willages from Buzau and, respectively, Prahova Counties (Figure 1). A number of 24 representative water samples (14 from Cerasu (CE) and 10 from Chiojdu (CH)) were collected from household and public wells, in July 2014. Because the sampling process is one of the key stage in the evaluation of water physco-chemical characteristics, the sampling followed the recommendations of SR ISO 5667-11 standard. On site, 100 ml of sample were filtered (0.45 µm cellulose acetate filters) for the measurement of anions, while 100 ml sample were filtered and acidified with a few drops of concentrated nitric acid (to obtain $pH<2$) for the determination of metals. The pH and electrical conductivity (EC) were determined on site using a portable Multi 340i analyzer (WTW, Germany). For *E. coli* determination, water samples from 10 wells were collected in sterile containers.

2.2 Materials

Ultrapure water obtained using a Millipore system was used for all dilutions. All used chemical reagents were of analytical grade. Ultrapure grade 65 % (m/m) HNO_3 (Merck, Germany) was used for on site acidulation and digestion of water samples before metals determination. Stock multi-element solutions of

1000 µg mL^{-1} containing all the analysed metals (Merck, Germany) were used to calibrate spectrometers for metals determination. Stock multicomponent solutions containing Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-} of 1000 µg mL^{-1} (Merck, Germany) were used to calibrate ion chromatograph.

Fig. 1. ***Sampling sites in Cerasu and Chiojdu willages Curvature Sub-Carpathians, Romania***

2.3 Instrumentation and analytical determinations

The major metals (Na, Ca, Mg, K, Fe) were determined by inductively coupled plasma atomic emission spectrometry using a ICP-AES Optima 5300 DV Spectrometer (Perkin Elmer, Norwalk, USA) while trace elements (Cu, Pb, Zn, Mn, Cd, Cr, Ni, As) by inductively coupled plasma mass spectrometry using a ICP-MS ELAN DRC II Spectrometer (Perkin-Elmer, Toronto, Canada). For the water samples digestion, 4 mL of concentrated nitric acid was used for in microwave digestion unit (OI Analytical, Canada) with pressure control. Anions were quantified directly in the filtered water by ion chromatography using the 761 Compact IC (Metrohm, Switzerland). *E. coli* was measured according to SR EN ISO 9308-1:2004 method, based on membrane filtration, subsequent culture on a chromogenic coliform agar medium, and calculation of the number of target organisms in the sample. The accuracy of metals determination was checked by analyzing NIST 1643e freshwater (NIST, Canada), while that of anions analysing the BCR 616 artificial groundwater certified reference sample (IRMM, Belgium). Recovery degrees ranged between 97-108 % for metals and 95-114 % for anions, showing a good accuracy for the used analytical methods.

3. RESULTS AND DISCUSSION

3.1. Electrochemical parameters and major anions

The concentration of main analysed indicators in collected water samples and Maximum Allowable Concentrations (MACs) are presented in Table 1.

Table 1. ***Concentration of selected indicators in wells water samples***

Sample	pH	EC	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na	Mn	Cu	Zn	Pb
	pH unit	μScm^{-1}	mg L^{-1}					µg L^{-1}			
CH1*	8.02	471	0.16	2.43	3.20	54.0	11.9	<1.0	3.50	22.4	<1.0
CH2	7.77	620	0.23	2.10	1.41	149	10.6	<1.0	7.31	21.9	<1.0
CH3	8.04	706	0.25	1.19	1.23	101	32.4	1.10	16.9	23.5	<1.0
CH4	7.91	673	0.16	7.26	9.74	108	17.1	<1.0	3.44	33.1	<1.0
CH5	8.09	470	0.16	2.40	0.79	58.8	13.3	<1.0	4.30	38.0	<1.0
CH6	7.61	790	0.14	13.9	29.5	119	23.2	28.2	8.10	129	<1.0
CH7	7.66	860	0.14	23.5	46.7	118	22.4	<1.0	<1.0	14.1	<1.0
CH8	7.70	918	0.14	23.9	**58.6**	123	26.1	<1.0	3.71	37.9	<1.0
CH9	7.53	967	0.18	30.9	28.9	177	33.4	<1.0	1.28	6.40	<1.0
CH10	7.67	691	0.18	11.6	11.6	143	22.9	<1.0	1.30	32.2	<1.0
CE1*	7.08	607	0.24	15.6	7.25	132	22.9	**470**	<1.0	20.8	<1.0
CE2	7.46	1060	0.13	35.5	**65.7**	126	33.8	5.11	3.60	19.7	<1.0
CE3	7.09	364	0.18	2.07	1.64	89.4	25.2	6.72	12.3	112	<1.0
CE4	7.62	494	0.25	5.51	0.72	77.8	26.6	20.3	<1.0	15.5	<1.0
CE5	7.49	1253	0.11	60.3	**118**	101	46.5	20.2	30.2	214	<1.0
CE6	7.54	784	0.13	11.7	8.34	85.0	23.1	5.22	1.10	23.7	<1.0
CE7	7.39	1114	0.12	36.1	**99.9**	104	28.8	1.41	10.3	62.5	<1.0
CE8	7.11	2400	0.18	2.71	<0.1	**1330**	38.5	**285**	<1.0	5.60	<1.0
CE9	7.19	1793	0.17	2.04	1.75	91.4	13.5	3.20	<1.0	98.6	<1.0
CE10	7.34	739	0.23	5.63	<0.1	74.4	12.7	2.22	9.6	66.8	<1.0
CE11	7.55	640	0.22	2.43	0.63	67.4	7.06	9.21	4.1	117	<1.0
CE12	7.22	503	0.15	2.29	6.23	39.2	15.5	1.90	3.3	114	<1.0
CE13	7.31	1658	0.16	82.5	**54.5**	**539**	53.8	1.56	4.4	39.2	<1.0
CE14	7.39	550	0.17	0.66	0.66	13.1	3.57	4.20	<1.0	11.7	<1.0
MAC**	6.5-8.5	-	1.20	250	50	250	200	50	100	5000	10

*CH – Chiojdu; CE – Cerasu
**MAC - maximum allowable concentration

As presented in Table 1, the pH values for water samples in CH and CE were found in the ranges of 7.52 – 8.09 and 7.08 – 7.62, respectively. Thus, the pH values were in the range of values considered normal for drinking water (Drinking Water Directive 98/83/CE). The EC values in CH and CE were in the ranges of 470 – 967 µS cm^{-1} and 364 – 2400 µS cm^{-1}, respectively.

Among the analysed anions, sulphate was found in the higher concentrations, with values ranges of 54.0 – 177 mg L^{-1} in CH and 13.1 – 1330 mg L^{-1} in CE. In two wells situated close to a watercourse coming from a local stone pit the MAC for sulphates (250 mg L^{-1}) was exceeded. Chlorides concentrations were in the ranges of 1.19 – 30.9 mg L^{-1} in CH and 0.66 – 82.5 mg L^{-1} in CE, all the values being below the MAC of 250 mg L^{-1}. Fluorides concentrations, ranging in the all samples between 0.11 – 0.25 mg L^{-1}, were also below the MAC of 1.20 mg L^{-1}. The concentrations of nitrites and phosphates (data not shown in Table) were, in all cases, below limits of detections (0.05 mg L^{-1}) and below the corresponding MACs. High levels of nitrates concentrations in waters can be a consequence of domestic and agricultural activities. Nitrates concentrations varied significantly in analysed samples, being in the ranges of 0.79 – 58.6 mg L^{-1} in CH and <0.1 – 118 mg L^{-1} in CE. Thus, it was exceeded the MAC for drinking water (50 mg L^{-1}) in five water samples (one in CH and four in CE), collected from private wells located proximate to the agricultural activities.

3.2. Concentrations of metals in wells water

As shown in Table 1, the concentrations of Na were in the ranges of 10.6 – 33.4 mg L^{-1} in CH and 3.57 – 53.8 mg L^{-1} in CE, all the values being below the MAC of 200 mg L^{-1}. For the other major cations (Ca, Mg, K) there are not established maximum values for drinking water. The values of Ca concentrations measured in collected samples were in the range of 25.6 – 423 mg L^{-1}. Mg concentrations ranged between 5.20 – 25.7 mg L^{-1}, while values of K concentrations were in the domain of 0.66 – 50.1 mg L^{-1}. From the analysed trace metals, the concentration of Mn exceeded MAC (50 µg L^{-1}) in two water samples. The concentrations of Cu ranged between <1.0 – 30.2 µg L^{-1}, and were in all cases below MAC (100 µg L^{-1}). The concentrations of Zn were considerably below MAC (5000 µg L^{-1}) ranging between 5.60 – 214 µg L^{-1}, while the concentrations of Pb in water samples were below MAC and below limit of detection in all the analysed samples. The levels of Fe, Na, Cd, Cr, Cu, Ni and As concentratios (data not shown in a Table) did not exceeded MACs in any of the analysed samples.

3.3. Biological indicators of wells water

For public health protection, *E. coli* is considered the best biological drinking water indicator, thus it is not required to investigate drinking water for all pathogens (Edberg et al., 2000). *E. coli* can be found in all mammal faeces, but it does not increase significantly in the environment. *E. coli* subsists in drinking water 4 to 12 weeks, depending on environmental conditions (Edberg et al., 2000). From the 10 analysed water samples, 6 samples were contaminated by *E. coli* with values of concentrations of over 2000 UFC 100 mL^{-1}. Thus, despite the fact that chemical contamination does not raise a high concern in the studied area, the microbiological contamination in over 50% of the analysed samples represents a risk for human health.

4. CONCLUSIONS

The evaluation of drinking water quality in 24 wells from two willages of Buzau and Prahova Counties, in Curvature Sub-Carpathians from Romania, affected by flood events, was carried out in order to have an awareness about the extent of physic-chemical and microbiological contamination in the study area. According to the obtained results the pH values are in normal ranges, while potential toxic anions such as nitrites and sulphates were found above MACs in few samples. Other anions, having permissible limits proposed by drinking water quality standards, such as fluorides, chlorides, nitrites and phosphates are in concentrations lower than MACs or even below limits of detection. For the analysed metals, concentrations higher than MAC were found only for Mn in two samples. However, a more concerning situation is represented by the presence of *E. coli* in more than half of the analysed samples.

The results show that even if many of the analysed inorganic anions and metals were below the maximum limits, the concentrations above MACs of nitrates, sulphates and Mn in some samples as well as the presence of *E. coli* in drinking water represent a risk for the health of local population.

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