Study of microelement composition of potable groundwater in Korostyshiv district of Zhytomyr region in hydrogeochemical monitoring system

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SUMMARY

The purpose of the research was to study microelement composition of potable groundwater in Korostyshiv district of Zhytomyr region in terms of potential threats to human health. The study was conducted as part of general monitoring studies set of groundwater quality in the region in July 2020. Microelement analysis of water samples was performed by use of modern highly sensitive method of mass spectrometry with inductively coupled plasma (ICP-MS). Comparison of biologically significant concentrations (BSC) of the main groundwater trace elements with the content of microelements determined during the study, allowed to identify features: in the studied waters there is an excess of such elements as Sr and Ba. Cr is present in sufficient quantity. Instead, insufficient elements such as Li, V, Mn, Co, Ni, Cu, Zn, As, Cd and Pb were detected. The established features of groundwater microelement composition allowed to outline the range of probable negative consequences for public health. It was concluded that there are risks of some microelementosis deseases occurence in investigated area. The results obtained may be useful to justify the need to adjust the diet of local residents through the additional use of vitamin and mineral complexes.

Introduction

Potable water mineral composition is not only an indicator of its quality, but also an important factor in developing the health of population, because both excess and deficiency of biologically (physiologically) significant chemical elements provoke specific human diseases, such as microelementosis, namely diseases (symptoms) caused by insufficiency, excess or imbalance of trace elements in the body. Biologically (physiologically) significant chemical elements are divided into: 1) structural (C, O, H, N, Ca, Mg, Na, K, S, P, F, Cl), which form the elemental composition of human organism for 99 %; 2) essential (Fe, I, Cu, Zn, Co, Cr, Mo, Ni, V, Se, Mn, As, F, Si, Li); 3) nominally essential; 4) elements which role is little studied or unknown at all (*Avitsyin and Zhavoronkov, 1991*). According to current theories, a number of chemical elements (Fe, Cu, Zn, Mn, Cr, Se, Mo, Co, I,) are absolutely necessary (essential) for human body, the optimal state of its health; they are the part of body general regulatory system and maintain homeostasis. Essential chemical elements enter the human body as part of food and potable water. According to the literature, the contribution of trace elements in the human body with potable water is from 2-4 to 20-25% (according to the WHO – 6-8%) (*Ivanov et al., 2012*). Currently, special attention is paid to the study of endemic diseases caused by trace elements associated with natural and man-made geochemical factors, as well as to determine their role in human pathology. In this context, investigations aimed at studying the mineral composition and content of physiologically significant chemical elements in potable groundwater in different regions of Ukraine, become particularly relevant. It is a particular problem in regions with high level of man-made load on underground hydrosphere and/or negative trends in the dynamics of morbidity (*Kuraieva et al., 2020*).

As the object of the research Korostyshiv district of Zhytomyr region was chosen. This region, along with Kherson and Chernihiv regions, is characterized by the maximum growth rate of cardiovascular diseases in Ukraine. Also, this area has a high dynamics of malignant neoplasms spread. In general, according to the scoring of trends in the dynamics of various population diseases Zhytomyr region, along with Kirovograd, Mykolaiv, Kharkiv and Kherson regions, belongs to the regions with a predominance of negative characteristics of morbidity dynamics (*Mezentseva et al., 2018*). These areas are characterized by an increase in the number of malignant neoplasms cases, cardiovascular and respiratory diseases (Figure 1).

The study area is located in the north-western part of Hydrogeological region of fractured waters of Ukrainian Shield and is characterized by the presence of mostly sandy sedimentary rocks complex with low thikness (up to 20 m), multi-storey aquifers in conditions of free water exchange. Water samples from shafts and wells were taken within the Korostyshiv district of Zhytomyr region, to which Korostyshiv potable groundwater deposit is timed. In general, potable and industrial water supply in Korostyshiv is carried out due to the operation of aquifers in Buchach deposits of Eocene ($P_2bč$) and in the fractured zone of crystalline rocks and their weathering crust (PR_1). The last aquifer has the best water quality indicators in the study region, its hydrogeological characteristics are well studied and described in the literature in detail (*Grebenyuk and Tsymbal, 2020*). Aquifer in fractured zone of crystalline rocks and their weathering crust (PR_1) is regionally sustained in area. Fractured waters are not confined to any stratigraphic complex, and regardless of the composition and age of water-bearing rocks form a single hydraulically coupled system. Crystalline rocks lie at a depth of 5,0-25,8 m and are represented by gneisses, crystalline shales and granites. In the roof of crystalline rocks lies their weathering crust with a thickness of 5-10 m to 20 m, which is represented by kaolin and crushed stone, with the parent rock preserved structure. In places where the weathering crust is blurred, in the roof of the aquifer in fractured zone of crystalline rocks and their weathering crust lie Holocene and Middle Neopleistocene aquifers in alluvial deposits, forming a layered hydraulic system. Formation of groundwater chemical composition of the aquifer in fractured zone of crystalline rocks and their weathering crust is mainly determined by physical and geographical factors, where the leading role is played by the process of rock leaching. Leaching water is formed in free water exchange zone. Residents of nearby villages mostly consume water from homestead shafts

or wells exploiting the aquifer in Upper Neopleistocene alluvial deposits of 1-2 floodplain terraces ($a^{1-2}P_{III}$), and private wells, drilled the aquifer in fractured zone of crystalline rocks and their weathering crust (PR_1). It should be noted that the water intake site of Korostyshiv utility company «Vodokanal» is located in groundwater discharge zone where the river Teteriv plays a role of powerful natural drain. In addition, within the distribution of Holocene aquifer in alluvial deposits, surface water is a source of operational reserves formation of the main aquifer in the fractured zone of crystalline rocks and their weathering crust.

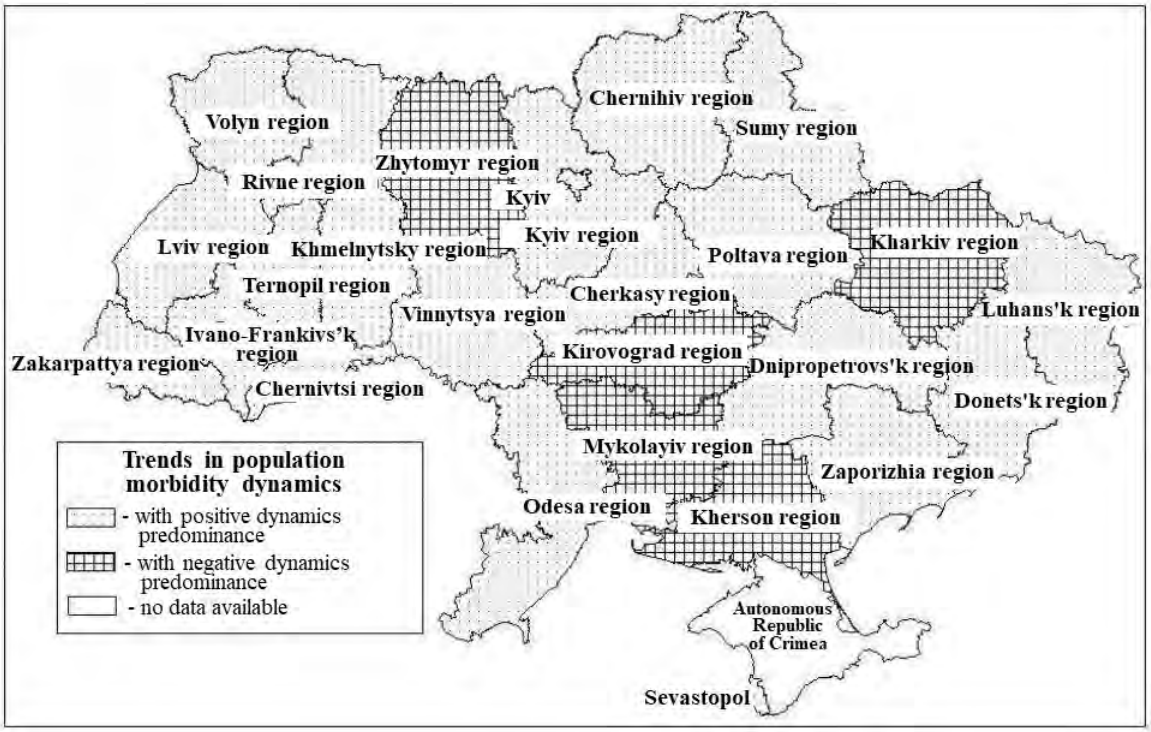

Figure 1 *Trends in population morbidity dynamics in Ukraine regions in 2001-2015 (Mezentseva et al., 2018)*

Method and Theory

Microelement analysis of water samples was performed using the method of mass spectrometry with inductively coupled plasma (ICP-MS) on a mass spectrometer with dual focusing of the ion beam «ELEMENT-2» company «Thermo Scientific» (Thermo Electron GmbH, Bremen), which operates on the basis of M. P. Semenenko Institute of geochemistry, mineralogy and ore formation of the National Academy of Sciences of Ukraine. To obtain «signal-concentration» calibrations, a certified standard (ICP multi-element standard solution VI, manufacturer – Merck KGaA) was used, from which a series of 6 calibration standards from 1 to 1000 ppb was made. Samples and standards preparations were performed by weight. Purified water using Millipore-Q3 (Millipore SA, France) was used to prepare the solutions. To characterize the total groundwater chemical composition in the study region, the results of hydrogeochemical monitoring were used. The monitoring surveys weree conducted by the laboratory of Korostyshiv interdistrict department of Zhytomyr Regional Laboratory Center of the Ministry of Health of Ukraine and the Central Laboratory of Ukrainian Geological Company during 2017-2019 (*Grebenyuk and Tsymbal, 2020*).

Results

As part of groundwater quality monitoring survey in the region in order to study in more detail the trace element composition using modern, more sensitive, laboratory methods, in July 2020 the authors

took samples of potable water from shafts and wells in Korostyshiv district of Zhytomyr region. In total, 15 water samples from wells and 10 samples from shafts located on private plots were taken. The depth of shafts ranged from 10-15 m, wells – 10-20 m. The results of microelement analysis of water samples are presented in Table 1.

As of (Grebenyuk and Tsymbal, 2020), according to water chemical composition of the studied aquifer in fractured zone of crystalline rocks and their weathering crust (PR1) are fresh, have hydrocarbonate, chloride-hydrocarbonate type. The anionic composition of water is calcium and magnesium-calcium. The mineralization varies from 0,3 to 0,6 g/dm^3. The total water hardness is in the range of 2,1-10,8 mmol/dm^3, pH value is 6,8-7,5. The total iron content ranges from 0,2 to 7,0 mg/dm^3, which is characteristic of the fracture-vein waters of the crystalline shield. In areas unprotected from surface contamination, there is an increased content of nitrates (from 76 to 379,40 mg/dm^3), chlorine (354-404 mg/dm^3), and high mineralization value (up to 1,5 g/dm^3). Water chemical composition can be expressed by the generalized formula:

$$M_{0,53}\frac{HCO_3^{1-}55SO_4^{2-}24Cl^{1-}24}{Ca^{2+}62Mg^{2+}22(Na^{1+}+K^{1+})12}pH_{7,1}$$

The water has a slight yellowish tinge, which may be due to the presence of iron salts. Microbiological indicators are characterized by the absence of bacterial contamination, bacteria of the Escherichia coli group are absent. Phenols, pesticides, surfactants and petroleum products in water samples are practically absent. According to the method of M.V. Barvish and O.A. Shvarts (Barvish and Shvarts, 2000) it were determined the values of biologically significant concentrations (BSC) of the main trace elements for studied potable groundwater. Comparison of BSC with the content of microelements determined during the study, allowed to identify features: in the studied waters there is an excess of such elements as Sr and Ba. Cr is present in sufficient quantity. Instead, insufficient elements such as Li, V, Mn, Co, Ni, Cu, Zn, As, Cd and Pb were detected.

Table 1 *Generalized results of microelement analysis of groundwater samples (arithmetic mean) with indication of biologically significant concentrations (BSC) values*

Element, mg/dm^3	Type of water intake facilities		BSC (Barvish and Shvarts, 2000), mg/dm^3
	Shaft	Well	
	Arithmetic mean, mg/dm^3		
Li	0,000922	0,001555	0,025
V	0,001036	0,000122	0,025
Cr	0,003326	0,001729	0,00175
Mn	0,000824	0,000633	0,05
Co	0,000008	0,000017	0,0075
Ni	0,000211	0,000864	0,0075
Cu	0,000197	0,012659	0,025
Zn	0,009309	0,023665	0,3
As	0,000035	0,000008	0,00125
Rb	0,000448	0,000644	–
Sr	0,312244	0,178328	0,05
Cd	0,000023	0,000081	0,0025
Ba	0,063614	0,065276	0,02
Tl	0,000001	0,000003	–
Pb	0,000085	0,000249	0,01
U-238	0,000793	0,000048	–

Note *Number of samples (N)* = 25

Conclusions

Due to the fact that the local population consumes the studied water constantly and this water is the main source of biologically significant chemical elements to human body, there are risks of a number of microelementosis deseases occurence in investigated area. In particular, detected excessive concentrations of Sr and Ba can cause the so-called Urov (Kashin-Beck) disease, which is manifested by severe lesions of the musculoskeletal system – bones curvature, their fragility, joint pain (*Avitsyin and Zhavoronkov, 1991*). Mn deficiency can adversely affect the processes of bone and connective tissue formation, cause imbalance in carbohydrate and lipid metabolism, be accompanied by disorders in the reproductive system. Cu is one of the most important trace elements that is necessary for human life. It is involved in the metabolism of Fe, the processes of human tissues oxygen saturation, stimulates the absorption of proteins and carbohydrates. Clinical manifestations of Fe insufficient consumption can be manifested in form of cardiovascular system and skeleton disorders, in the development of connective tissue dysplasia. Zn is vital for humans because it is involved in nucleic acids, RNA and DNA polymerases biosynthesis, and is a mandatory component of the blood enzyme contained in erythrocytes. Deficiency of this element in human body can manifest itself in the suppression of enzyme activity, as well as in delayed wound healing, can cause anemia, secondary immunodeficiency, liver cirrhosis and sexual dysfunction (*Ivanov et al., 2012*).

Thus, the established features of microelement composition of groundwater used for potable water supply in Korostyshiv district of Zhytomyr region, allowed to outline the range of probable negative consequences for public health. The results obtained may be useful to justify the need to adjust the diet of local residents through the additional use of vitamin and mineral complexes.

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