

Quality and safety of tap water in selected Ukrainian regions

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Groundwater runoff supplies 80% of all drinking water in Ukraine. Their quality and safety differ depending on the biogeochemical zones, the concentration of industrial enterprises, and the state of treatment plants, creating problems in different regions of Ukraine. At the same time, Ukraine's accession to the European Community requires a gradual approximation of national legislation to that of the EU, including regulations on drinking water. Many monitoring studies on drinking water quality have been conducted in Ukraine; however, they concern individual pollutants and require evaluation according to the new drinking water standard criteria. Many monitoring studies on drinking water quality have been conducted in Ukraine; however, they concern individual pollutants and require evaluation according to the new drinking water standard criteria. For the first time, we analyzed 23 indicators of water quality and safety of tap water in the northern, central, southern, and western regions of Ukraine according to national and European standards.

Our studies have shown that the mercury content exceeds the MPC (maximum permitted concentration) 1.25 times according to the requirements of Drinking water standards of Ukraine in the tap water of certain settlements in the Odesa region, the manganese content is three times higher in the Sumy region, in Chernihiv region, iron 1.35 times exceeds its MPC according to the DSTU 7525:2014. These results indicate the need to improve the drinking water treatment system in certain oblasts of Ukraine. The pollution of tap water in the settlements of the northern, central, southern, and western regions of Ukraine with nitrogen compounds (ammonium, nitrates, nitrites), sulfates, and chlorides have not been detected. Trace elements such as manganese, iron, and copper are also essential, and they play a significant role in ensuring the vital activity of people and animals, and their deficiency causes no less dangerous disturbances in the body than their excess. Tap water in the settlements of Volyn, Chernihiv, Kyiv, and Odesa oblasts has increased concentration of manganese; the water of Sumy, Odesa, and Volyn regions have high concentration of iron; the water of Kyiv, Chernihiv, Sumy, Cherkasy, Odesa, and Volyn regions had increased concentration of copper; the water of all Ukrainian regions has a low fluorine content, which is consistent with the data of epidemiological studies of microelements diseases in these territories. This water indicates the need for its additional mineralization according to the mentioned trace elements.

Keywords: heavy metals, trace elements, tap water, quality, safety

Introduction

Water is the foundation of life, and not only the future of humanity but also the Earth itself depends on its quality and safety (Sharma and Bhattacharya, 2017). Only fresh water is suitable for human consumption, the water reserves are unevenly distributed across the planet, and available sources are rapidly declining due to population growth, pollution of significant natural lands with industrial waste, and irrational use of natural resources (Cominelli et al., 2009).

In Ukraine, surface and underground fresh water are used for the drinking water supply. Ukrainians drink mostly water from rivers, which is 80% of water; the remaining 20% is taken from groundwater. Excluding the occupied territories (Crimea, separate settlements of Lugansk and Donetsk regions) during 2015, 9.7 million km were taken from natural sources and cube water. The treatment plant's capacity is 5.8 million km. a cube of water, that is, just over half of the water taken away is purified, and the rest is fed to consumers uncleaned or partially purified. In general, freshwater water resources in Ukraine are considered insufficient (National Report on drinking water quality, 2017).

Central water supply is used by more than 70% of the population of Ukraine. These are all cities, almost 90% of urban settlements and 23% of villages. The water of the Dnieper, Desna, Dniester, Southern Bug, Siverskyi Donets, and Danube rivers is the primary source of drinking water (Kravchenko, 2015). Water treatment plants of Ukraine use the classical system of reagent purification of water with settling and filtration, and its disinfection is carried out by ozonation and chlorination. The main number of water treatment plants in Ukraine has been built for more than 40-50 years and needs reconstruction. Most sewage treatment plants use imperfect technologies, reagents, and materials that cannot prevent the ingress of drinking water into substances that may affect human health. There is also the problem of significant wear and tear of the pipeline water delivery system, during which about 25% of water is lost. Pollution of surface, underground, and groundwater is also caused by wastewater discharges from petrochemical

plants containing various refined petroleum products, phenols, heavy metal salts (Rezaei et al., 2019), insecticide destruction and transformation products and other toxic agents (Bondy and Campbell, 2017). The problem of drinking water pollution in Ukraine is associated with the imperfection of wastewater treatment systems of industrial, utility, and agricultural enterprises, soil erosion of the water intake area, and accidents with severe and long-term consequences. Another aspect of water quality in Ukraine is the deficit in some biogeochemical provinces of many essential elements that require the development of actions for its mineralization (Opalov, 2000).

Determination of the presence of mobile forms of trace elements in the soils of Ukraine, conducted by the Institute of Plant Physiology of NASU, made it possible to divide the whole territory of Ukraine into four biogeochemical zones: the Western zone combines Rivne, Volyn, Lviv, Zakarpatska, Ternopil, Chernopil, and Chernobyl. Soils in this geochemical zone are characterized by a deficiency of iodine, cobalt, zinc, manganese, and copper in some places (Rivne and Volyn regions). The water sources of this area are deficient in iodine, especially in the Transcarpathian region. The northeastern zone includes Sumy, Chernihiv, Kyiv, and Vinnytsia regions, Zhytomyr and Khmelnytskyi regions.

Here the deficiency of mobile forms of zinc and cobalt is found, and in some places - manganese and copper. Iodine deficiency was found in soils and water sources of Zhytomyr, Chernihiv, northern regions of Kyiv, and Sumy regions. The central geochemical zone is the southern regions of Vinnytsia, Kyiv, Chernihiv and Sumy regions, Cherkasy and Poltava regions, and the northern regions of Odessa, Kirovograd, and Kharkiv regions. Southern geochemical zone - covers Mykolaiv, Kherson, Dnipropetrovsk, Zaporizhia, Donetsk, Luhansk regions, southern and central regions of Odessa, and Kirovograd regions. The soils of the central and southern zones are comparatively better provided with trace elements, but here a deficiency of mobile forms of zinc and in some places - cobalt, excess of manganese, and boron.

The quality and safety of drinking water are closely linked to chronic diseases in humans and animals. The danger is presented by water pollution with heavy metals (Burke et al., 2016) in dissolved and suspended states in water and have a high potential to cause negative consequences and a shortage of essential elements in water (Bhattacharya et al., 2016). The latter affect the vital biochemical reactions in animals and humans, acting as cofactors of many enzymes and acting as centers for stabilizing the structure of enzymes and proteins. The functions of trace elements have a dual role. They are essential for stabilizing cellular structures while at an average level in the body, but in conditions of deficiency, they can cause diseases (Prashanth et al., 2015).

Describing the presence of various chemicals in the water, we took as a basis their classification according to the biological function in animals and humans, which is as follows: 1) essential – Fe, I, Cu, Zn, Co, Cr, Mo, Se, Mn; 2) relatively essential – As, B, Br, F, Li, Ni, V, Si; 3) toxic – Al, Cd, Pb, Hg, Be, Ba, Vi, Tl; 4) potentially toxic – Ge, Au, In, Rb, Ag, Ti, Te, U, W, Sn, Zr (Avtsyin et al., 1991). The presence of nitrogen compounds, including nitrates, in drinking water at concentrations below the maximum tolerable risk of cancer (Ward et al., 2018) and sulfates and chlorides - urolithiasis and hypertension in humans (Scheelbeek et al., 2017).

Many European Union (ISO) regulations on quality and safety of drinking water have been implemented in Ukraine, but some of the standards still approved in the Soviet Union (GOST) remain in force. Following the entry into force of the Association Agreement, Ukraine undertakes to gradually approximate its legislation with EU legislation within a specified timeframe to provide an objective assessment of the state of drinking water supply and possible ways to improve it to plan further modernization of this area through investment.

To this end, the National Standard of Ukraine DSTU 7525:2014 was developed. Requirements and methods for controlling the quality of drinking water, which according to the list of indicators is the closest to the standard of the European Union. To solve the problem of obtaining high-quality drinking water, it is necessary to regularly monitor its quality according to the list of indicators regulated by national standards and in the conditions of integration into the European Community, the requirements of Council Directive 98/83/EC.

The study objective was to determine the compliance of the tap water chemical composition in some areas of Ukraine with quality and safety requirements following regulatory documents of Ukraine and the European Union.

Materials and Methods

Research area

The samples of tap water that were supplied to the laboratory during 2018 from the settlements of the northern – Kyiv (n = 18), Chernihiv (n = 6) and Sumy (n = 13); central – Vinnytsia (n = 5) and Cherkasy (n = 6); southern – Odessa (n = 6); and western – Volyn (n = 4) regions of Ukraine (Fig. 1)



Fig. 1. Map of tap water sampling in the regions of Ukraine (settlements are marked with points).

Sample collection

Samples of tap water were taken for analysis according to DSTU ISO 5667-3:2001. Samples of tap water were taken for analysis according to ISO 5667-3:2003. The research was carried out based on the scientific research chemical-toxicological department of the State Scientific and Research Institute of Laboratory Diagnostic and Veterinary Sanitary Expertise in Kyiv.

Sample preparation and instrumental analysis

Working multi-element and single-element standard solutions for atomic emission spectrometry by Merck (Germany) with a certified ion content were prepared by diluting them in a way to obtain concentrations of the same order with the upper limits of the element content range. For dilution of standard solutions, a 2% solution of nitric acid is used. According to the following scheme, sample preparation was carried out: a 1000 mL sample was filtered through a 0.45 µm Sartorius membrane filter (France) immediately after sampling. The first samples from 50 cm³ to 100 cm³ were used to flush the filter device. The filtrate was acidified with 0.5 cm³ of nitric acid for every 100 cm³ solutions to ensure a pH < 2 according to protocol ISO 5667-3:2003.

The study of the lead, cadmium, arsenic, copper, iron, manganese, chromium, aluminum, boron, sodium, nickel, selenium, and antimony content in water was carried out on an inductively coupled plasma-optical emission spectrometer (ICP-OES) by PlasmaQuant PQ 9000 (Analytik Jena, Germany) according to DSTU ISO 11885:2005.

Analytical - Analytical Signal is any manifestation of a chemical or physical property of a substance that is functionally related to its nature and concentration.) signals were processed automatically by spectrometer software, using calibration dependencies taking into account background correction and, if necessary, the mutual influence of the elements under study. The determination of boron and arsenic content was carried out using the PlasmaQuant HS PQ hydride system for ICP-OES PQ 9000 (Analytik Jena, Germany) with the continuous addition of a reducing agent (as a restorer agent used SnCl₂) (which reducing age for the simultaneous determination of hydride-forming elements. Quality control was carried out by using certified reference material (ERM CA 011c), blank and duplicate samples. To control the sensitivity fluctuations of the ICP-OES analysis, an internal standard sample of 20 µg/L indium solution (ROTI®STAR) was used.

Determination of mercury content in water was carried out by a direct method using a Milestone DMA 80 mercury analyzer (Milestone, Italy) without sample preparation according to ISO 12846:2012.

Determination of permanganate water oxidation was carried out according to ISO 8467:1993 Ammonium content in tap water was determined by a spectrometric method using a Ultrospec 2100 spectrophotometer (AMERSHAM, USA) according to DSTU ISO 7150-1:2003, nitrate concentration – using sulfosalicylic acid according to GOST 4078-2001, nitrite concentration – by molecular absorption spectrometric method according to DSTU ISO 6777-2003, fluorides – by the photometric method with lanthanum-alizarin complex according to GOST 4386-89, chlorides – by the Mohr method according to DSTU ISO 9297:2007, sulfates – by the deposition in an acidic medium by barium chloride according to GOST 4389-72.

Water pH was determined by the electrometric method using Merk, Hamilton, LLG, Mettler Toledo, and Mettler Toledo MP 220 reagents (China) (ISO 10523:2008, MOD, water conductivity was measured on a Mettler Toledo Seven Compact S230 B, (Switzerland) according to ISO 3696:1987.

Statistical analysis

The results statistical processing was carried out with the calculation of the arithmetic mean (M) and arithmetic mean error (m) using Microsoft Office Excel, 2016 (USA).

Results and Discussion

Lead. Heavy metals, including lead, belong to the most common pollutants of water supplies. According to the DSTU 7525:2014 and Council Directive 98/83/EC requirements, the lead content in tap water should not exceed 10 µg/L. As the obtained data show, the water in all the studied water supply sources in Ukraine in terms of lead was in the range of 1/13-1/5 of the MPC and was suitable for use (Table 1).

Table 1. Content of heavy metals in tap water in regions of Ukraine, µg/L

Indicator	Region of Ukraine							Reference document	
	Kyiv	Chernihiv	Sumy	Cherkasy	Vinnitsia	Odesa	Volyn	State Standard of Ukraine 7525:2014	Council Directive 98/83/EC
Plumbum	0,867±0,439	0,857±0,391	0,754±0,408	1,853±0,697	1,164±0,165	0,927±0,256	1,132±0,268	10	10
Cadmium	0,191±0,039	0,161±0,113	0,051±0,025	0,057±0,018	0,073±0,018	0,189±0,080	0,235±0,096	1	5
Arsenic	1,626±0,325	0,756±0,306	2,931±1,332	2,186±0,477	1,395±0,304	1,818±0,442	1,590±0,180	10	10
Hydrargyrum	0,127±0,047	0,081±0,036	0,099±0,022	0,270±0,061	0,181±0,037	0,241±0,110	0,053±0,041	0,5	1
Antimony	0,824±0,194	0,707±0,283	0,109±0,028	1,103±0,194	0,496±0,154	0,749±0,341	0,497±0,245	5	5
Nickel	3,887±1,380	4,562±3,292	3,917±3,270	4,128±1,361	2,988±0,642	0,730±0,182	3,433±2,241	20	20
Chromium	1,662±0,395	1,015±0,650	0,894±0,437	1,262±0,282	1,176±0,272	0,883±0,259	0,686±0,315	50	50
Aluminium	10,297±4,005	25,660±2,680	3,223±1,390	8,513±4,396	6,290±5,449	41,115±30,657	5,464±0,175	200	200
Copper, mg/L	0,026±0,008	0,024±0,014	0,018±0,013	0,014±0,003	0,092±0,036	0,025±0,010	0,007±0,002	1	2
Iron	84,277±17,458	102,715±43,837	10,283±2,322	91,044±14,753	75,438±19,710	41,036±15,209	59,588±43,589	200	200
Manganese	8,741±1,295	8,751±8,369	59,336±52,617	22,827±6,286	37,170±7,171	11,090±2,918	2,935±1,563	50	50
Boron, mg/L	0,117±0,094	0,349±0,011	0,031±0,004	0,111±0,099	0,029±0,008	0,074±0,007	0,092±0,001	0,5	1
Selenium	3,529±0,842	2,893±2,435	3,424±0,370	6,538±0,734	1,292±0,552	3,072±1,303	2,254±1,190	10	10
Sodium, mg/L	45,034±19,036	84,835±25,465	67,045±54,956	25,058±22,015	5,472±0,111	64,195±37,234	18,805±0,235	200	200

Cadmium. The content of cadmium, which is a highly toxic heavy metal, did not exceed the permissible limit of 1µg/L according to GOST 7525:2014 and 5 µg/L according to the requirements of Council Directive 98/83/EC in tap water in all regions of Ukraine. The concentration of cadmium did not even reach 1/20 of the MPC according to the requirements of Council Directive 98/83/EC in water from settlements of Volyn, Kyiv, Odesa, and Chernihiv regions, and in the water from Vinnitsia, Cherkasy, and Sumy regions its level did not exceed 1/100 of this value indicating the safety of drinking water on this element, according to both national and European standards.

Arsenic, antimony and aluminum. The arsenic content was in the range from 1/13 to 1/3 of the MPC, antimony – from 1/46 to ¼ MPC, nickel – from 1/27 to ¼ MPC, and chromium – from 1/73 to 1/30, and for aluminum pollution – from 1/62 to 1/5 of the MPC in the tap water of the northern, central, southern and western oblasts of Ukraine according to the requirements of DSTU 7525:2014 and Council Directive 98/83/EC, which do not differ among themselves in these indicators confirming its suitability for use. In this case, the high variability of the concentration of the above heavy metals in the tap water of settlements of the Ukrainian regions indicates their different sources and the intensity of their entering the water.

Mercury. The excess permissible mercury level, which is 1.0 µg/L according to the requirements of Council Directive 98/83 / EC, was not found in the tap water of the central, northern, western, and southern regions of Ukraine. However, the mercury content in the tap water of some settlements in the Odesa region was 0.624 µg/L, which exceeds the MPC by 1.25 times according to the DSTU 7525: 2014 standard and indicates point pollution of certain territories of the Dnister and Danube river basins. In each of two tap water samples taken from the settlements of Odesa, Chernihiv, and Volyn regions, as well as 40% of samples from the Kyiv region, the mercury content was below the determination limit, which indicates the absence of primary and secondary pollution of water supply sources in these parts of the country.

Copper, boron, and selenium. Pollution of tap water by copper, as well as boron and selenium, was not detected in the regions under study following the National Standard DSTU 7525: 2014 and Council Directive 98/83/EC, which allows us to consider it safe for human and animal health according to these indicators.

Iron. The iron content in the tap water in most regions of Ukraine varied within the MPC according to the requirements of DSTU 7525:2014 and Council Directive 98/83/EC; however, in one sample of the tap water in the settlement in the Chernihiv region, an excess of the permissible level of iron was 1.35 times, which indicates the danger of such water for human and animal consumption.

Manganese. Manganese pollution of tap water differs both according to regions of Ukraine and within one region. The maximum content of manganese in tap water exceeded the permissible level of 50 µg/L according to the requirements of DSTU 7525:2014 and Council Directive 98/83/EC almost three times in one of the settlements of Sumy region that indicates its unsuitability for drinking.

Sodium. The sodium content in the tap water in several regions of Ukraine was characterized by significant variability associated with the peculiarities of the release of its compounds into the water from industrial and municipal wastewater. However, in the research process, not a single sample of tap water was detected where the MPC exceeded in terms of sodium content (200 mg/L) according to GOST 7525: 2014 and Council Directive 98/83/EC.

Nitrogen compounds. Considering that drinking water supply to settlements in different regions of Ukraine occurs using river flow, the level of surface sources pollution with organic compounds that are mineralized with the formation of ammonium, nitrate, and nitrite compounds at different stages is essential. Their presence and ratio in water indicate both the intensity of pollution and its duration.

Pollution of tap water in the northern regions of Ukraine with nitrogen compounds (ammonium, nitrates, and nitrites) was within the MPC regulated by DSTU 7525:2014 and Council Directive 98/83/EC that coincided in these indicators and did not significantly differ in particular regions.

Sulfates. The level of sulfates in the tap water of the northern regions was in the range of 1/50-1/28 MPC, and in the central, southern, and western regions, it was almost in trace amounts (Table 2).

Table 2. Content of salts in tap water in regions of Ukraine, mg/L.

Indicator	Region of Ukraine							Reference document	
	Kyiv	Chernihiv	Sumy	Cherkasy	Vinnitsia	Odesa	Volyn	State Standard of Ukraine 7525:2014	Council Directive 98/83/EC
Ammonium	0,109±0,028	0,126±0,051	0,083±0,017	0,091±0,018	0,104±0,002	0,049±0,018	0,009±0,005	0,5	0,5
Nitrate	0,131±0,094	0,079±0,042	0,206±0,091	0,165±0,045	0,181±0,004	0,307±0,130	0,553±0,244	50	50
Nitrite	0,016±0,003	0,007±0,005	0,006±0,002	0,004±0,003	0,014±0,001	0,008±0,003	0,005±0,001	0,5	0,5
Sulfates	4,725±2,588	8,802±10,076	4,452±3,018	0,179±0,023	0,168±0,001	0,161±0,032	0,215±0,013	250	250
Fluoride	0,219±0,047	0,255±0,148	0,324±0,054	0,287±0,154	0,103±0,006	0,203±0,103	0,186±0,028	0,7-1,5	1,5
Chlorides	20,303±7,960	30,600±12,91	25,130±8,586	27,882±14,392	15,320±0,399	59,800±33,697	44,300±8,503	250	250
Oxidizability, mg/L O ₂	0,109±0,028	0,212±0,012	0,219±0,012	0,202±0,010	0,232±0,011	0,218±0,018	0,230±0,009	5	5
Hydrogen index (pH), pH, units	7,650±0,118	8,250±0,384	7,504±0,110	7,030±0,260	6,710±0,071	7,843±0,058	7,123±0,070	6,5-8,5	6,5-9,5
Conductivity, μS cm ⁻¹ at 20 °C	473,308±47,352	442,667±141,706	636,231±46,975	371,833±55,773	364,600±11,670	687,500±251,188	486,000±67,953	-	2500

Fluoride. Fluorine compounds that are found in water as fluorides are an essential source of fluorine for humans and animals at the optimal concentration. The tap water in the settlements of Ukraine was characterized by the level of fluoride that reached an average of 1/5 of the MPC according to the requirements of DSTU 7525:2014 and Council Directive 98/83/EC.

Chloride. The chloride content in tap water determines its taste and often indicates sewage pollution from industrial, communal, and livestock enterprises. The chloride content in the tap water in settlements of the northern, central, western, and southern regions of Ukraine did not exceed the MPC set by DSTU 7525:2014 and Council Directive 98/83/EC and was at a minimum level that confirms the absence of water pollution with these compounds.

Permanganate oxidizability is one of the indicators characterizing the level of water pollution by organic substances. The data given in Table 2 show that the tap water in the regions of Ukraine was usable according to this indicator.

pH. The tap water in the settlements of the Vinnitsia region had an average pH value characterized and did not go beyond the standard value both according to the requirements of DSTU 7525:2014 and Council Directive 98/83/EC, in other parts of Ukraine, the pH of tap water was neutral (the Cherkasy region) and weakly alkaline (Odesa, Donetsk, Kyiv, Sumy and Chernihiv regions). Conductivity. The conductivity of tap water in all cases did not exceed the normative indicator (2500 μS cm⁻¹) according to the requirements of Council Directive 98/83/EC, and this indicator is not standardized according to GOST 7525:2014.

Analysis and Discussion

The results of the chemical composition analysis of tap water in different parts of Ukraine give reason to assess it by the toxic and essential component contents for compliance with DSTU 7525:2014 and Council Directive 98/83/EC requirements. It is worth noting that for most indicators that were used in the studies, the national regulatory document on drinking water quality differs little from the European Directive. The difference in most cases lies in the stricter requirements of DSTU 7525:2014 on the content of toxicological indicators such as cadmium (5 times lower) and mercury, copper, and boron (2 times lower) than the permissible level established by Council Directive 98/83/EC. Besides, the upper limit of the drinking water pH is lower in DSTU 7525: 2014 for one unit, and there is no national standard of water conductivity compared to the European Directive. Zaitsev et al. (2015) consider that the overestimation of the standards in DSTU 7525: 2014 for the given indicators in drinking water is not sufficiently substantiated and should be brought into compliance with Council Directive 98/83 / EC. The significant variability in the content of heavy metals that we found in our studies of tap water in settlements of different regions of Ukraine testifies to the peculiarities of the chemical composition of both sources of pollution of surface water bodies – rivers water is taken from for drinking water supply, and soils of the water intake territory. This may be connected with separate biogeochemical provinces into which the territory of Ukraine is conditionally divided and characterized by different contents of microcells, macro-elements, and heavy metals in soil and water (Zhovinsky et al., 2009). Other researchers obtained a similar pattern in determining the concentration of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in river sediments collected in the Ave river basin (Portugal), which is divided into five standard zones with different pollution intensities (Soares et al., 1999).

The accumulators of industrial and household liquid and solid wastes, the remains of mineral fertilizers and pesticides, sewage from livestock complexes make a significant contribution to the pollution of surface and groundwater and the geochemical features of the territory of Ukraine. The rivers of Dnipro, Dnister, Pivdennyi Buh, Siverskyi Donets, the Danube with tributaries, and small rivers of the northern coast of the Black and Azov Seas are the primary sources of freshwater in Ukraine (Pakhota 2018). About 1000 filtering reservoirs are located within the Dnipro basin, 80% of which are in the basin's southern part. The total volume of accumulated polluted water in them is about 1 km³ (Opalov, 2000). Wastewater of industrial enterprises polluting soils and groundwater causes a particular risk of drinking water pollution with Pb, Ni, Cu, Zn, Fe (Esmailzadeh et al., 2019), As (Shahid et al., 2018; Masood et al., 2019). The dominant sources of metals in agricultural soils are polluted irrigation water which can cause the accumulation of heavy metals in plants and create both non-carcinogenic and carcinogenic risks for the population (Fakhri et al., 2015; Sun et al., 2018).

Based on the results of assessing pollution and health risks, Cd, As, Cr, Cu, Pb, and Ni are identified as priority control metals (Järup, 2003; Dogaru et al., 2009; Islam et al., 2018).

Heavy metals belong to the group of toxic substances by the nature of the biological effect on animals and humans and are among the most dangerous pollutants in the aquatic ecosystem for their resistance to degradation in natural conditions (Khan, 2011). As we can see in our data, the content of such heavy metal as mercury in tap water in various parts of Ukraine allows us considering it suitable for use according to the requirements of Council Directive 98/83/EC; however, according to DSTU 7525: 2014 requirements, the exception is the water in separate settlements of Odesa region where its level reached 1.25 MPC. The latter indicates point pollution of certain territories of the Dnister and Danube river basins due to getting the waste and debris containing residual pesticides, oil products, damaged measuring tools (barometers, thermometers), switches, fluorescent lamps, and other electronics in the rivers (Final European Commission Report, 2002).

Mercury poisoning of men is characterized by more than 250 symptoms making diagnosis and treatment difficult, as it exhibits deep cellular, cardiovascular, hematological, pulmonary, renal, immunological, neurological, endocrine, reproductive, and fetal toxicity. The effect of mercury is manifested in a change of membrane permeability, the macromolecular structure through an affinity for sulfhydryl and thiol groups, and DNA damage at the cellular level. It has been proven that mercury causes oxidative stress and mitochondrial dysfunction that can lead to a change of calcium homeostasis and increased lipid peroxidation (Rice et al., 2014).

Even though the content of toxic elements such as As, Cr, Pb, Cd, Ni in the tap water of the regions of Ukraine understudy was within the regulatory values of the national and European standards, they have a potential risk to the health of consumers even in low doses, especially in chronic effect (Saleh et al., 2019), since they are xenobiotics and their positive effect on the body or participation in metabolism has not been proven; therefore they are potentially toxic even in trace amounts (Jafari et al., 2017). The toxicity of heavy metals in trace amounts in drinking water to the human body is related to their compatible action. They can act as pseudo microelements in the body and disrupt metabolism due to the accumulation in the body's tissues, exhibiting a chronic effect. This can cause oxidative stress caused by the formation of free radicals (Jaishankar et al., 2014).

Pollution of tap water in the northern regions of Ukraine with nitrogen compounds (ammonium, nitrates, and nitrites) was within the MPC regulated by DSTU 7525:2014 and Council Directive 98/83/EC that coincided in these indicators and did not significantly differ in particular regions. The primary sources of drinking water pollution with manganese in Ukraine are considered under-treated wastewater of iron and steelworks, municipal wastewater, and outdated wastewater treatment systems having low efficiency (Stanko, 2012).

The high manganese content in drinking water can cause intellectual developmental disorder in children (Rahman et al., 2017; Bouchard et al., 2018; Dion et al., 2018). After rapid absorption in the digestive organs, Mn is rapidly excreted from the blood, but it remains in the tissues for a relatively long time. Recent data indicate that Mn accumulates mainly in the bones, where its half-life is 8 - 9 years. Mn toxicity in humans is associated with dopaminergic dysfunction (O'Neal and Zheng, 2015), and manganese-induced Parkinsonism has also been reported (Zheng, 2005).

As for manganese as an essential trace element in the human body, in most cases, researchers recommend taking the total daily dose that comes with food and water for calculation that is 2.5-7.0 mg for a person weighing 70 kg (Watts, 1990). Given that drinking water covers 1-10% of the daily requirement for manganese (Avtsyn et al., 1991), then a person should receive 0.025-0.7 mg of this trace element when using it. The obtained data show that when 2 liters of water are consumed, people living in the Volyn region can receive about 0.006 mg, Chernihiv and Kyiv regions – 0.017 mg, the Odesa region – 0.022 mg of manganese, which indicates a deficit, while tap water in the Cherkasy region ensures the delivery of 0.046 mg, Vinnytsia – 0.074 mg of manganese, that is, it satisfies the minimum daily intake of water into the human body. The role of manganese in humans and animals consists of its participation in the synthesis and activation of many enzymes (oxidoreductases, transferase, hydrolase, lyase, isomerase, and ligase) and lipid metabolism protein synthesis, vitamin C and B vitamins. Mn metabolites, including arginases, glutamine synthetase, phosphoenolpyruvate decarboxylase, and Mn superoxide dismutase (Mn SOD), also affect the regulation of metabolic processes listed above and reduce oxidative stress induced by free radicals (Li and Yang, 2018).

Iron is the fourth most common element, accounting for 5.6% of the Earth's crust. An excess of the permissible iron content of 1.35 times in the tap water in one settlement of the Chernihiv region was found, as well as significant variability of its content in several settlements in this region indicate spot pollution of water. The origin of iron in water can be both geogenic and resulting from industrial wastewater, household waste, and the significant deterioration of the water supply system. The intake of iron in humans and animals in high doses causes cancer and cirrhosis, diabetes, heart disease, and infertility. High iron concentrations change the organoleptic properties of water, namely color, taste, smell, leaving stains on clothes and destroying water networks (Colter and Mahler, 2006; Behera et al., 2012).

Considering that iron belongs to essential elements, we can conclude that a pronounced deficiency of this trace mineral was observed in the tap water in the settlements of the Sumy region, which was 1/10 of its desired level (0.1 mg/L) (Khan, 2011), while in other regions of Ukraine, the concentration of iron in tap water on average reached 41-91% of the optimal value (see Table. 1). The physiological role of iron is that it participates in the synthesis of hemoglobin and myoglobin, catalase and peroxidase, in the direct and indirect oxidative processes (part of 72 enzymes), ensuring the normal functioning of the immune system, its deficiency leads to anemia, growth and developmental delay in animals and humans (Avtsyn et al., 1991). Iron deficiency anemia is extremely high in Ukraine, especially among children and women of reproductive age. According to the Ministry of Health of Ukraine (2000), the prevalence of iron deficiency anemia was 1163.9 per 100,000 population, particularly among adults – 610.2, among children – 3598.6 per 100,000 population (Vynnychenko and Orlovskiy, 2006).

If we consider that the desired level of copper in drinking water should be 0.05 mg/L (Khan, 2011), our research results indicate that there is an evident deficiency of this trace mineral in the water of most regions of Ukraine. The exception is only the tap water from the settlements of the Vinnytsia region, where the average copper level was between the desired and maximum permissible concentration. Copper is an essential trace mineral in humans and animals, and it plays the role of a cofactor of many redox enzymes, is a part of ceruloplasmin, and plays an important role in iron metabolism, the function of the immune system, and antioxidant defense. Its deficiency in the body can lead to metabolic disorders, the development of the cardiovascular system, bone growth, and the function of the nervous and immune systems. The toxic copper effect in the body is associated with oxidative damage and cell death (Bost et al., 2016). However, Cu toxicity is not usually considered an ordinary human health problem, probably due to adaptation mechanisms that control its absorption and elimination (Turnlund et al., 2005). This may be one of the aspects the MPC of this indicator is two times increased following Council Directive 98/83/EC requirements compared to DSTU 7525:2014.

The concentration of selenium in the tap water of settlements in the regions of Ukraine in all cases was below the MPC according to the norms of both national and European standards, which are the same for this indicator (10 µg/L). Given that selenium is an essential element, it is essential to determine its toxic concentration and the optimal range in water that will satisfy the needs of human and animal organisms. However, scientists have no consensus regarding the toxicity or usefulness of selenium for the human body. Lafond and Calabrese (1979) question the established normative value for drinking water due to the inadequate rationale of selenium toxicity and consider MPC level of 50 µg/L sufficient. Experimental studies of other researchers on the inorganic selenium that comes with drinking water effect on the human body showed that its toxicity could be seen significantly lower levels than previously assumed. Vinceti et al. (2013) suggest reducing its MPC to 1µg/L to protect human health adequately. The difference in the approach to determining the toxicity of selenium for humans is probably due to the different structure and nature of its compounds and different combinations with other toxic and essential elements that have a mutual influence on the human and animal body. However, most researchers do not doubt that the biological effect of selenium in the body is associated with its participation in the regulation of the myocardium, blood vessels, ensuring immunity, average growth and development, anticarcinogenic and antioxidant action. Due to selenium deficiency in food anemia, cardiomyopathy, growth disorder, and formation of bone tissue, liver, pancreas, male sterility, frequent infectious diseases, and hypercholesterolemia occur in humans and animals. The occurrence of alopecia, arthritis, brittle nails, metallic taste in the mouth, muscle pain, irritability, decreased immunity, impaired renal and hepatic function, skin rashes, and face pallor are symptoms of toxic effects of selenium in the human body (Avtsyn et al., 1991; Lopes et al., 2017).

Based on the boron concentration in the tap water of the regions of Ukraine, we believe that it should be considered in this case from the position of a conditionally essential element that was in the water of the regions of Ukraine within the optimal level. Our assumption is consistent with similar studies by French (Yazbeck et al., 2005) and Chinese scientists (Xu et al., 2010). Due to the insufficiently substantiated boron toxicity that enters the humans and animals with drinking water, there are differences in the regulatory documents of Council Directive 98/83/EC compared to DSTU 7525:2014; in the latter one, the boron MPC is reduced by two times.

Regarding the concentration of sodium in tap water in settlements of different regions of Ukraine, we can state that there is no risk of poisoning humans and animals through this water, as well as its effect on the organoleptic characteristics of drinking water that meets the requirements of DSTU 7525:2014 and Council Directive 98/83/EC. Regulatory documents have not established the desired level of sodium in water, but as a trace mineral, it plays an essential role in intracellular and cellular metabolic processes; being the principal cation of extracellular fluid, it maintains normal osmotic pressure, regulates acid-base balance, and excitability reactions of neuromuscular fibers. Sodium also enhances the adrenaline action and, together with chlorine ions, promotes the formation of hydrochloric acid in the stomach, activates the activity of digestive enzymes, and stimulates digestion. Most often, sodium enters the body of humans and animals in high doses, so most scientific studies are directed at studying the effect of a high concentration of this element in the water on the risk of hypertension in humans (Strohmann et al., 2018).

The fluoride content occupies a special place in the study of the chemical composition of water since fluorine is one of the trace minerals that have a pronounced biological effect in animals and humans. The optimum fluoride content in drinking water should be at least 0.7 mg/L. The processes of mineralization in the tissues of the teeth and bones are carried out with its participation. It exerts a particularly pronounced effect on cells involved in enamel formation. When a fluorine content is <0.3 mg/L in consumed by humans and animals water, the processes of the teeth mineralization are disturbed and caries occurs. Consumption of water with high fluorine content significantly increases the mineralization processes of tooth and bone, and another specific pathology called fluorosis of teeth and bones occurs (Iheozor-Ejiofor et al., 2015; Tryhub, 2017). As the research results show, the tap water from all settlements of Ukraine used for the study was deficient in fluorine content (see Table 2). Our data are confirmed by the results of an epidemiological study conducted by researchers showing the prevalence of caries in 12-year-old children in different regions of Ukraine between 88.5% and 98.4% (Zadorozhna and Povorozniuk, 2014).

Many nitrogen compounds were found in tap water in various regions of Ukraine, including ammonium, nitrate, and nitrite, in concentrations that do not reach the MPC indicating the safety of drinking water, especially with organic pollution. However, it is known that nitrates, even at low concentrations not reaching the MPC can pose a potential health risk to humans, including adults, children, and especially infants (Qasemi et al., 2018). Nitrate can be converted by the microflora of the digestive apparatus to nitrite in a low stomach pH reacting with amines and amides to form N-nitroso compounds associated with the emergence of various types of cancer (Ward et al., 2018).

The content of sulfates and chlorides in the tap water of various regions of Ukraine does not pose a risk to human and animal health and can be considered safe.

The oxidation of tap water confirms the previously stated assumption that its contamination with organic compounds is insignificant (Oyem et al., 2014), which in our case is consistent with the low content of dissolved salts in water in different settlements in Ukraine.

The results of research by some scientists indicate that the presence of pollutants in water in low concentrations does not necessarily lead to adverse effects on human health; the effect may not be noticeable, and toxicity depends on individual sensitivity (Villanueva et al., 2014). Besides, an essential factor determining the degree of negative impact on animals and humans is the combination of many toxic and deficiency essential substances, including heavy metals, significant nutrients, trace minerals, and others in the water. Therefore, to make a complete picture of the toxic effect of drinking water components on humans and animals, constant monitoring of its quality is required following the requirements of regulatory documents and a comparison of results with the epidemiological situation in some areas of Ukraine.

The effects of contamination of drinking water on the human body are also related to the ability to dissolve and transport in tissues a significant amount of toxic substances, including residues of veterinary drugs that come with food of animal origin (Bayer et al., 2017; Voitsitskiy, et al., 2019; Shevchenko, et al., 2019, Kurbatova, et al., 2016).

The obtained research results indicate that tap water in most regions of Ukraine in terms of toxic substances meets the requirements of both national and European quality standards, to some extent, it may be associated with a severe industrial decline in recent years that affected the intensity of water sources pollution (Nazarov et al., 2004).

Conclusion

The tap water from the settlements of the northern (Kyiv, Chernihiv, Sumy regions), central (Cherkasy and Vinnytsia regions), southern (Odesa region), and western (Volyn region) regions of Ukraine was examined for compliance with the quality and safety requirements of the National (DSTU 7525:2014) and European (Council Directive 98/83/EC) standards. Non-compliance with the

safety requirements of the tap water for the content of heavy metals in certain settlements of the Odesa region, where the mercury content was exceeded by 1.25 times according to the DSTU 7525:2014 standard, the manganese content was exceeded by three times in one settlement of the Sumy region, and one settlement in the Chernihiv region – the iron level was 1.35 times higher according to the standards of DSTU 7525:2014 and Council Directive 98/83/EC. These results indicate the need to modernize the drinking water treatment system in the mentioned oblasts.

The tap water in Volyn, Chernihiv, Kyiv, and Odesa regions does not contain enough manganese that is considered an essential mineral. Significant iron deficiency was noted in the water of some settlements in the Sumy, Odesa, and Volyn regions. A deficiency of copper was found in the water of the Kyiv, Chernihiv, Sumy, Cherkasy, Odesa, and Volyn regions, and all the regions of Ukraine that took part in the study showed fluorine content deficiency. Considering the above results, it is recommended to mineralize water for human consumption in regions with deficient microelements.

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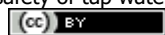
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