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# Distribution of heavy metals in potable groundwater of Dnieper-Donetsk artesian basin northwestern slope (as an example of Kyiv groundwater deposit)

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## SUMMARY

The research is devoted to investigation of potable groundwater of Dnieper-Donetsk artesian basin as an example of Kyiv groundwater deposit. The authors conducted the study aimed at identifying the features of the distribution of individual trace elements (heavy metals) in Cenomanian-Callovian groundwater complex and Bayos aquifer. During the research a set of analytical methods was used: atomic adsorption, absorption spectrophotometry, and mass spectrometry with inductively coupled plasma (ICP-MS). Statistical processing of chemical analysis of Kyiv well-rooms water by the content of individual trace elements indicated a slight exceedance of Maximum Allowable Concentration for lead. In addition, it was found that the average concentrations of heavy metals in groundwater of a deeper, Bayos aquifer are higher than the similar values of the above-lying Cenomanian-Callovian groundwater complex. The authors suggest that in this case, there is a complementary effect of natural and man-made factors. Meanwhile important role in this process can play intensification of highly mineralized pore solutions flow from weakly permeable layers to potable aquifers during depression funnel formation.

## Introduction

The Dnieper-Donetsk Artesian Basin (hereinafter – DDAB) is the largest hydrogeological structure in Ukraine – near 40% of all exploitable groundwater resources of Ukraine is attributed to this storey system of aquifers and complexes that determine its hydrogeological conditions (Shestopalov et al., 2009). It is a classic type of artesian basin, which is characterized by spatial endurance of aquifers and confining strata of over large areas, which determines the storey character of the aquifers. The sedimentary rocks are saturated with groundwater and are the unified system of the aquifers, interconnected with each other and with surface waters through weakly permeable layers of rocks. Kyiv groundwater deposit is located on the northwestern slope of the DDAB. The regional weakly permeable layers distributed within this deposit help to reduce the intensity of vertical water exchange with depth – it is much higher in the upper aquifers and complexes than in the lower ones.

From the point of view of potable water supply within the study area, deep (artesian) aquifers are strategically important: the Cenomanian-Callovian groundwater complex, which is timed to sands, sandstones with layers of limestone, flint, clay, siltstone, marl, and Bayos aquifer, which is timed to variegated sand with clay layers and brown coal lenses. Nowadays, the reduction of piezometric levels in Cenomanian-Callovian groundwater complex has reached an average of 50 m in Kyiv. This led to pressure relief in some areas of the Dnieper coast. In the greater part of the city, the pressure above the roof of Cenomanian-Callovian deposits is not higher than 20 m and is increasing in the northeast direction. Depression funnel is common throughout all the urban Kyiv area. As a result of Cenomanian-Callovian groundwater complex piezometric regime violation, the inversion of water exchange conditions with the above deposited aquifers in the southern part of Kyiv and on the left bank of the Dnieper river occurred. The aquifer is now being recharged by downstream filtration with an intensity of 0,1-1,0 l/sec·km$^2$ (3-32 mm/year of water layer) (Litvak et al., 1972). The anthropogenic restructuring of water exchange in the aquifer of Kaniv and Buchach Eocene sediments and in Cenomanian-Callovian aquifer has also led to changes in cretaceous-marl confining layer of the upper Cretaceous, which separates them (Shestopalov et al., 1991).

According to E.O. Yakovlev (Yakovlev, 2011), in the formation of the depression funnel, the diffusion-convective motion of salts and microcomponents from the weakly permeable (separating) layer is a significant factor in influencing the hydrogeochemical composition of the waters of operational aquifers. Thus, it became necessary to conduct a study aimed at identifying the features of the distribution of individual trace elements (heavy metals) in Cenomanian-Callovian groundwater complex and Bayos aquifer, in order to find out how long-term operation (over 100 years) and changing the regime of hydrogeofilter system have reflected on groundwater chemical composition.

## Method and Theory

During the research, the authors used a set of analytical methods: atomic adsorption, absorption spectrophotometry, and mass spectrometry with inductively coupled plasma (ICP-MS). Laboratory studies using the first two methods were performed at the A.V. Dumanskiy Institute of colloid chemistry and water chemistry of NAS of Ukraine, analytical studies by the ICP-MS method were carried out at M.P. Semenenko Institute of geochemistry, mineralogy and ore formation of NAS of Ukraine. In total, 123 water samples were investigated, 68 of them from Cenomanian-Callovian groundwater complex, 55 – from Bayos aquifer. Sampling was performed in November-December 2017 together with scientists from the State Enterprise "Ukrainian Geological Company". Sampling was carried out according to the interstate standard GOST 31861-2012 "Water. General requirements for sampling». The results of chemical analyses of water were processed by using of mathematical statistics in Microsoft Excel environment.

Regional low-permeability layers contain large volumes of groundwater and dissolved salts of many chemical elements. During operational pressure relief in permeable layers, decompaction of adjacent weakly permeable layers occurs, and slow migration of mineralized pore solutions develops. The

longtime of development of depression funnels and their large areas in operational aquifers determine the significant influence of low-permeability layers on the formation of ecological-hydrogeological conditions of underground withdrawals (Yakovlev, 2011). Reduction of groundwater level in the operational aquifer, adjacent weakly permeable (separating) layers or confining beds and adjacent aquifers are the main factors of the technogenesis of the hydrogeofiltration system in the influence area of water intake. Under conditions of operational decrease in pore water pressure, there is an increase in the equilibrium pressure of the mineral skeleton, part of the compression deformation of which is transferred to a weakly permeable (separating) layer in the form of initial decompaction and subsequent partial compression (Bolton-Jackson effect). According to researchers, the impact of the aforementioned changes in the stress state of hydrogeofiltration system reaches 1-2% of its total volume. However, during long-term operation of water withdrawal (10-20 years and more), a stable diffuse-convective transfer of porous solutions salts from confining layer is formed, the mineralization of which up to 1-2 orders of magnitude can exceed the mineralization of operational aquifers water. According to existing hydrogeofiltration model, the separating layers have a double structure of pore space due to the existence of weakened linear zones of high permeability and stable weakly permeable blocks. Therefore, in the case of vertical water exchange, boundary sections of the above zones acquire stable flow rates and slow molecular diffusion. At the same time, the contact zones of weakly permeable areas, as long as they are compressively decompacted and the depression funnel gradual develops, is a practically stable source of highly mineralized pore solutions flow (Yakovlev, 2011).

**Results**

Given the urgency of the problem of groundwater contamination with heavy metals, the authors investigated the content of such elements as Pb, Mo, Cu, and Zn within Kyiv potable groundwater deposit. In general, the chemical composition of water in Cenomanian-Callovian groundwater complex is hydrocarbonate calcium-magnesium-sodium with mineralization of 100-680 ppm, in Bayos aquifer – hydrocarbonate calcium-magnesium-sodium and chloride-hydrocarbonate calcium-magnesium-sodium with mineralization of 300-600 ppm. The results of water chemical analysis were processed by using of statistical methods for 123 wells, 68 of which operate Cenomanian-Callovian groundwater complex, and 55 – Bayos aquifer. The results of statistical processing are presented in Table. 1. As a result of the research and calculations, it was found that distribution law was not established for trace element samples in most cases. Lognormal law was established for Cu in the Cenomanian-Callovian groundwater complex and for Mo, Cu, and Zn in Bayos aquifer. The graphical representation of the sample distribution is shown in diagram form (Figure 1).

***Table 1*** *Results of the statistical analysis of the data on the content of heavy metals in well-room water of Kyiv*

| *Cenomanian-Callovian complex* | Average value, ppm | Median, ppm | Mode, ppm | Maximum, ppm | Minimum, ppm | Maximum Allowable Concentration (by Sanitary Regulations and Norms 2.2.4-171-10) |
|---|---|---|---|---|---|---|
| Pb | 0,0014 | 0,0007 | 0,0007 | 0,01 | 0,0003 | 0,01 |
| Mo | 0,0003 | 0,0003 | 0,00025 | 0,002 | 0,0001 | 0,07 |
| Cu | 0,0033 | 0,003 | 0,002 | 0,014 | 0,0007 | 1 |
| Zn | 0,0198 | 0,01 | 0,008 | 0,094 | 0,0014 | 1 |
| *Bayos aquifer* | | | | | | |
| Pb | 0,002 | 0,001 | 0,0005 | 0,04 | 0,0003 | 0,01 |
| Mo | 0,0004 | 0,0003 | 0,0002 | 0,001 | 0,0001 | 0,07 |
| Cu | 0,004 | 0,003 | 0,002 | 0,014 | 0,001 | 1 |
| Zn | 0,024 | 0,012 | 0,008 | 0,126 | 0,001 | 1 |

***Note*** *Number of samples (N) = 123.*

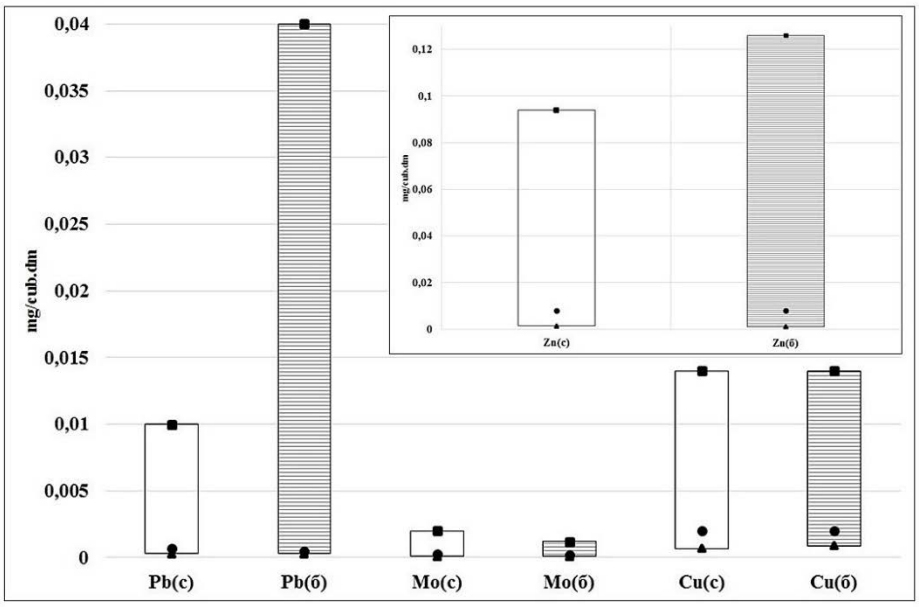


***Figure 1*** *Diagrams of heavy metals content in well-room's groundwater in Kyiv: (c) – Canomanian-Callovian groundwater complex, (б) – Bayos aquifer, ■ – maximum content, ▲ – minimum content, ● – median.*

Within the study area, the low permeability layers, which can potentially be the source of pore solutions flow to potable aquifers – Cenomanian-Callovian complex and Bayos aquifer – are the low permeability deposits of cretaceous-marl layer of the upper Cretaceous (thickness ranges from 10 to 50 m), through which a transit downward recharge from Eocene aquifer proceeds, as well as confining clay-siltstone layer of the middle Jurassic, represented by dense clays (thickness fluctuates within 60-90 m).

**Conclusions**

During the research hydrogeochemical peculiarities of potable groundwater of DDAB northwestern slope (on the example of Kyiv groundwater deposit) were investigated. Statistical processing of chemical analysis of Kyiv well-rooms water by the content of individual trace elements indicated a slight exceedance of Maximum Allowable Concentration for lead. In addition, it was found that the average concentrations of heavy metals in groundwater of a deeper, Bayos aquifer are higher than the similar values of the above-lying Cenomanian-Callovian groundwater complex. The authors suggest that in this case, there is a complementary effect of natural and man-made factors, which affects the content of these trace elements in deep artesian aquifers of DDAB. Natural factors include the lithological composition of water-bearing strata, namely the presence of brown coal lenses in Bayos aquifer. The technogenic factors include the inversion of groundwater hydrodynamic flow, confined to depression funnels, with further intensification of highly mineralized pore solutions flow from weakly permeable layers, the elimination of overlapping confining layers along the Dnieper, and heavy metals soils pollution.

Analysis of groundwater quality changes with long-term exploitation of water withdrawals (Koshliakova and Koshliakov, 2014) makes it possible to conclude that mineralized pore solutions of clay weakly permeable rocks, which form separating regional layers, are involved in formation of groundwater chemical composition from the initial phase of depression funnel formation.

The authors believe that it is promising to carry out further studies aimed at identifying the migration forms of micro- and ultramicroelements in groundwater using the thermodynamic modeling method, based on the principles of partial and local equilibrium and reduced to establishing regularities of chemical composition changes and existence conditions of equilibrium state. It seems appropriate to study the micro- and ultramicrocomponent composition of porous solutions of weakly permeable (separating layers), which enhance the interaction with the downward flows in depression funnels

zones. To expand the range of investigated components of groundwater chemical composition, the authors consider it expedient to use more sensitive analytical methods, namely the method of mass spectrometry with induction coupled plasma.

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