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Spatial and temporal features of water chemistry changes in the quaternary unconfined aquifers of the Dnipro River basin

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The article deals with the chemical composition of uppermost aquifers water in the Dnipro River basin. Its study is necessary not only in connection with the implementation the requirements of the EU Water Framework Directive methodological documents in the groundwater monitoring, but primarily because of water supply from these aquifers to rural areas. Unconfined aquifers water is characterized by a complex and heterogeneous chemical composition due to natural and anthropogenic factors. Natural hydrochemical zoning is distinctly visible on the territory of the Dnipro basin. A number of chemical elements and compounds in the water are contained in concentrations exceeding the standards for drinking water established by the State sanitary norms and rules 2.2.4-171-10 "Hygienic requirements for drinking water intended for human consumption" in the natural state. In addition, unconfined aquifers are subject to significant anthropogenic impact, as they are unprotected from pollution. Comparison of the data on total dissolved solids (TDS) and anionic composition of groundwater obtained during hydrogeological surveys in the period 1965–1975 and 2009–2013 on three sheets of the hydrogeological map (scale 1:200,000) in different sub-basins of the Dnipro River showed the widespread deep changes in groundwater chemical composition. In addition to a significant anthropogenic pressure, groundwater is significantly affected by climatic factors. Over a forty-year period, TDS in the north of the Dnipro basin increased by 50 %, in the central and southern parts – twice, due to an increase in the content of sulfates and chlorides. Within the analyzed areas in the Middle and Lower Dnipro sub-basins, nitrate pollution of unconfined aquifers is almost widespread. Thus, in a large area, waters of these aquifers are unsuitable for drinking water supply due to the excessive content of chemical elements and compounds of natural and anthropogenic origin. Therefore, one of the priorities of the post-war reconstruction of Ukraine should be the transfer of the rural population to water supply from protected confined aquifers and the improvement of sanitary conditions in rural areas.

Keywords: *groundwater; unconfined aquifers; conditions of formation; qualitative state; TDS; Dnipro River basin.*

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Introduction

One of the urgent tasks of Ukraine in the near post-war future will be the State groundwater monitoring system reforming, taking into account international experience and the requirements of European Water Framework Directive 2000/60/EC. In the European Guidelines for Groundwater Monitoring (CIS…, 2007), considerable attention is paid to studying the status of unconfined aquifers, given their vulnerability to pollution, as well as the close connection with surface ecosystems and underlying confined aquifers. For Ukraine, the research of unconfined aquifers qualitative status is of particular importance, since they are widely used for individual water supply in rural settlements.

Unfortunately, representative State groundwater monitoring network of observation wells existed from the 1950s to the 1990s, as of 2023 has suffered significant losses due to insufficient funding over the past few decades and was finally liquidated as a result of the russian aggression. Therefore, adaptation of monitoring to European requirements should occur simultaneously with the restoration of the monitoring network.

Materials and methods

To ensure the representativeness of the observation network and scientifically based planning of monitoring program activities, it is necessary to collect and analyze available information on the groundwater status. This work was initiated in 2019–2021 as part of the Water Initiative Plus program for the Eastern Partnership countries, which aimed to create a framework for the resumption of groundwater monitoring, considering the requirements of the European methodological documents, especially the implementation of the basin principle of water resources management. In particular, groundwater bodies in the Dnipro basin were identified and their qualitative and quantitative status, vulnerability and risks of failure to achieve their environmental objectives were preliminarily characterized (Goshovsky et al., 2019; Lyutyi et al., 2021; Lyuta, Sanina, 2022). The information support of these works was carried out on the basis of data accumulated in geological enterprises of Ukraine, published maps of different scales and the hydrogeological information database created in the Ukrainian State Geological Research Institute.

In the absence of monitoring data, water quality changes were estimated approximately by comparing the multi-temporal data from the 1:200,000 scale hydrogeological surveys of the 1970s and the results of the subsequent hydrogeological follow-up study conducted in 2009–2013. The minimum, maximum and mean TDS values were compared. Waters were grouped according to the predominant anions and the minimum, maximum and median TDS were determined for these groups (Tables 1–3).

Table 1. **Changes in TDS and anionic composition of groundwater in the Pripyat sub-basin (hydrogeological map at scale 1:200,000, sheet Korosten)**

Year	TDS (g/l), $\frac{\text{min–max}}{\text{mean}}$	TDS in groups of waters with predominant anions (g/l), $\frac{\text{min–max}}{\text{median}}$				
		HCO_3^-	HCO_3^- Cl^-	HCO_3^- SO_4^{2-} Cl^-	SO_4^{2-} Cl^-	Cl^-
1971	$\frac{0.1–1.2}{0.39}$	$\frac{0.2–0.4}{0.4}$	$\frac{0.1–1.2}{0.3}$	$\frac{0.2–0.7}{0.4}$		$\frac{0.3–0.7}{0.4}$
		Number of wells				
		8	16	8	0	5
2010	$\frac{0.1–2.9}{0.59}$	$\frac{0.4–0.9}{0.6}$	$\frac{0.2–0.5}{0.4}$	$\frac{0.3–2.9}{0.6}$	$\frac{0.4–1.1}{0.7}$	$\frac{0.2–1.0}{0.6}$
		Number of wells				
		7	8	15	5	6
		Contaminated with nitrates (above 50 mg/l)				
		0	0	4	2	2

Table 2. **Changes in TDS and anionic composition of groundwater in the Middle Dnipro sub-basin (hydrogeological map at 1:200,000 scale, sheet Pereyaslav-Khmelnytskyi)**

Year	TDS (g/l), min–max / mean	TDS in groups of waters with predominant anions (g/l), min–max / median				
		HCO_3^-	HCO_3^- SO_4^{2-}	HCO_3^- Cl^-	HCO_3^- SO_4^{2-} Cl^-	HCO_3^- NO_3^-
1965	0.2–4.0 / 0.84	0.2–2.0 / 0.5		0.6–4.0 / 1.8		
		Number of wells				
		39	0	10	0	0
2009	0.3–9.2 / 1.8	0.3–1.7 / 1.1	1.2–9.2 / 1.8	2.4–2.6 / 2.5	1.6–4.3 / 3.2	0.9–2.8 / 2.3
		Number of wells				
		21	4	2	6	5
		Contaminated with nitrates (above 50 mg/l)				
		14	4	1	6	5

Table 3. **Changes in TDS and anionic composition of groundwater in the Lower Dnipro sub-basin (hydrogeological map at scale 1:200,000, sheet Dnipropetrovsk)**

Year	TDS (g/l), min–max / mean	TDS in groups of waters with predominant anions (g/l), min–max / median				
		HCO_3^-	HCO_3^- SO_4^{2-}	SO_4^{2-} HCO_3^-	SO_4^{2-}	SO_4^{2} Cl^-
1973	0.2–3.6 / 1.46	0.2–0.7 / 0.4	0.4–1.2 / 0.7	0.9–2.2 / 1.3	1.2–3.6 / 2.8	-
		Number of wells				
		4	11	8	9	0
2012	0.8–9.1 / 2.7	1.0–1.7 / 1.3	1.2–1.6 / 1.4	1.3–2.5 / 2.0	2.0–7.0 / 3.9	2.4–9.1 / 4.3
		Number of wells				
		3	6	11	10	6
		Contaminated with nitrates (above 50 mg/l)				
		1	3	6	8	6

Natural conditions of the territory

The area of the Dnipro basin in Ukraine is 291,400 km^2, or 48 % of the total area of the country, the basin fully or partially covers the territory of 19 administrative regions. Its territory is characterized by complex natural and anthropogenic conditions. The Dnipro basin is located within three sublatitudinal bioclimatic zones – Polissya (marshy woodlands), Forest-Steppe and Steppe. The territory of the basin is the southwestern part of the East European Plain, which consists of upland and lowland areas. In the north of the basin the surface absolute marks are 135–500 m, in the south – 10–150 m. The climate is generally temperate continental, from moderately cold in the north to moderately warm in the south. The geological structure of the Dnipro basin area is complex, consisting of the Ukrainian Shield, Volyno-Podilska Plate, Dniprovsko-Donetska Depression, South Ukrainian Monocline and the Folded structure of the Donbas.

Quaternary sediments cover almost the entire territory of the Dnipro basin and form the upper floor of the geological cross-section. The uppermost aquifers are confined to them. According to the lithological and genetic characteristics of the Quaternary rocks, aquifers are distinguished in the territory of the Dnipro basin in marsh, alluvial, water-glacial sediments, water-glacial and aeolian-deluvial sediments and in aeolian-deluvial sediments.

Unconfined aquifers in Quaternary sediments

The aquiferin marsh Quaternary sediments is widespread in Polissya, in floodplains and relief depressions (Fig. 1). Water-bearing sediments are represented mainly by peat, fine-grained sands, sandy loams and loams. The thickness of the aquifer is 0.5–6.0 m; the depth is 0.4–0.7 m. This aquifer is hydraulically connected with the aquifer in Quaternary alluvial sediments and with surface water bodies.

The chemical composition of water is mixed: anions are represented by sulfates, chloride, hydrocarbonates and nitrates in various proportions. The water is unpleasant in taste and smell, yellow-brown in color, contains a large amount of iron and ammonia. TDS is 0.1–0.7 g/l; hydrogen index from 5.2 to 6.8; total hardness is 1.9–5.4 mmol/l. Poor quality of groundwater makes the aquifer unsuitable for drinking water supply.

The aquifer in alluvial Quaternary sediments is common within the floodplains and terraces of the Dnipro River and its tributaries (see Fig. 1). Water-bearing rocks are fine- and medium-grained sands. The thickness varies from 10–20 m in the valleys of small rivers to 50–60 m in the Dnipro floodplain. Depth of occurrence depending on the relief varies from 2–4 to 5–15 m. Well flow rates reach 173–432 m^3/day.

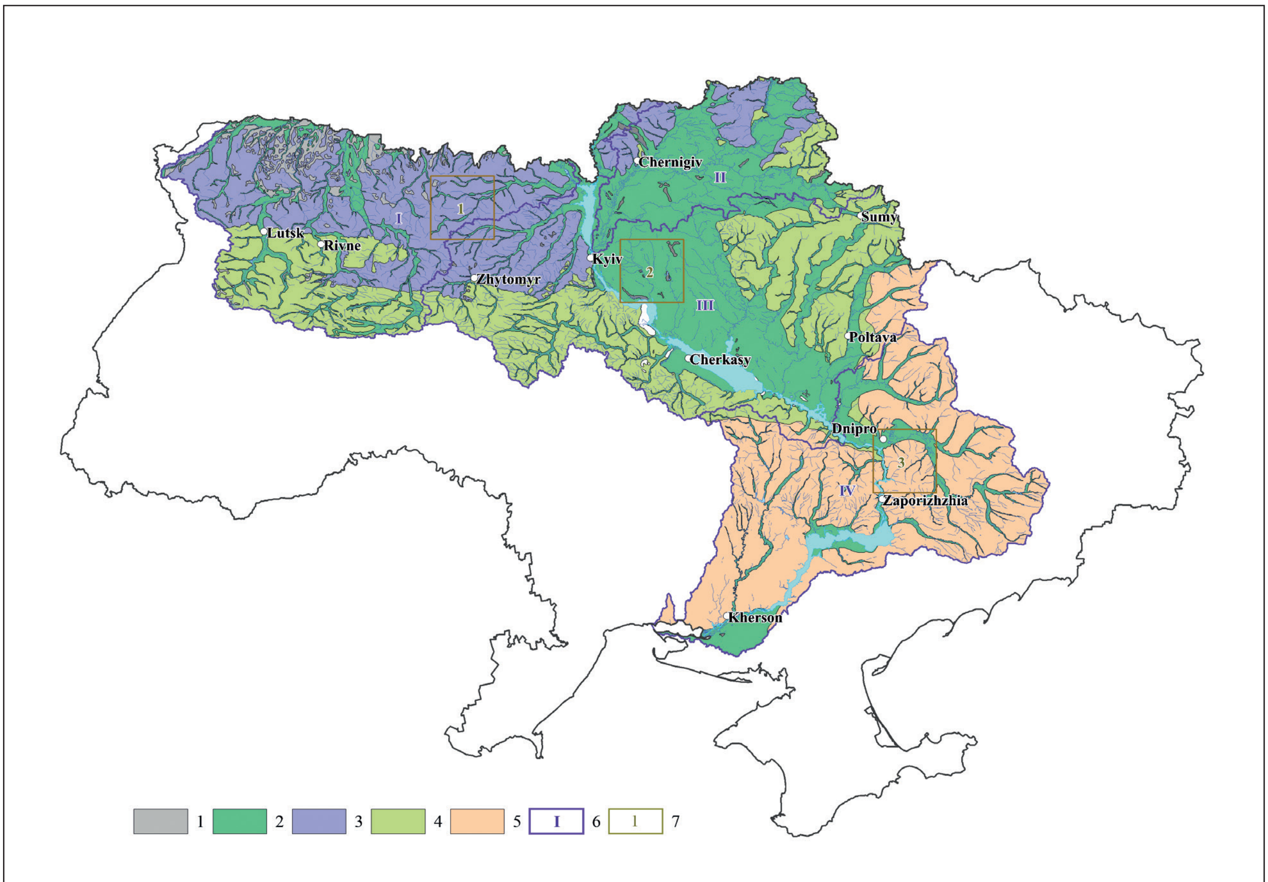

Fig. 1. Unconfined aquifers in the Dnipro River basin

Unconfined aquifers: *1* – aquifer in marsh Quaternary sediments; *2* – aquifer in alluvial Quaternary sediments; *3* – aquifer in water-glacial Quaternary sediments; *4* – aquifer in water-glacial and aeolian-deluvial Quaternary sediments; *5* – aquifer in aeolian-deluvial Quaternary sediments. *6* – Sub-basin boundaries: *I* – Prypiat; *II* – Desna and Upper Dnipro; *III* – Middle Dnipro; *IV* – Lower Dnipro. *7* – Areas of the sheets of the hydrogeological map at a scale of 1:200,000: *1* – Korosten; *2* – Pereyaslav-Khmelnytskyi; *3* – Dnipropetrovsk

The predominant components of the chemical composition are hydrocarbonate, magnesium and calcium, TDS ranges from 0.1 to 1.3 g/l. The water is characterized by high iron content – up to 2–3 mg/l.

The aquifer in water-glacial Quaternary sediments is widespread within the moraine and sand plain in the north of the basin (see Fig. 1). Water-bearing rocks are sands of different grains, mostly fine-grained. The thickness varies from 3–25 m on the right bank to 70 m on the left bank. The water table depth is mainly 2–7 m. Water abundance depends on lithology of water-bearing rocks; well flow rates vary from 0.4–216 to 259–1000 m^3/day.

Chemical composition is varied: hydrocarbonate, chloride-hydrocarbonate, sulfate-hydrocarbonate. The predominant cations are calcium, occasionally magnesium and sodium. TDS varies from 0.3 to 1.8 g/l, mostly does not exceed 0.5 g/l, iron content in the water is up to 0.1–0.8 g/l.

The aquifer in water-glacial and aeolian-deluvial Quaternary sediments is widespread in the watersheds of the Middle Dnipro sub-basin and in some areas of the Volyn Upland (see Fig. 1). The lower part of the water-bearing rocks is represented by water-glacial multi-grained sands, the upper part – by aeolian-deluvial loams and sandy loams. Thickness of water-bearing sediments is unstable and varies from 2 to 32 m. The depth of groundwater level is mainly 5–12 m. The lower part of sediments is more water abundant. Specific flow rates of wells vary from 0.9 to 345.6 m^3/day.

Water is calcium hydrocarbonate, calcium hydrocarbonate-chloride and calcium-magnesium with TDS of 0.3–0.7 g/l.

The aquifer in aeolian-deluvial Quaternary sediments is located in the watersheds of the southern part of the Dnipro basin (see Fig. 1). Water-bearing are loams, sandy loams, loess-like loams with thickness from 1 to 30 m. Depth of water table is from 1 to 21 m. The aquifer is low-water-bearing. Well flow rates vary from 0.77 to 20.3 m^3/day. The aquifer is distributed in a zone of insufficient moisture, so there is a natural process of continental salt accumulation in the soils and rocks of the aeration zone, which, in turn, causes an increase in water TDS. Sulfates and chlorides predominate among anions, and TDS often exceeds the normative value, up to 3–10 g/l.

All the listed aquifers (except for marsh waters) are used for domestic needs of the rural population, mainly by means of shallow wells.

Peculiarities of formation, contamination and trendof water quality change

All unconfined aquifers are recharged by infiltration, mainly by precipitation; overflow from surface water bodies, as well as from adjacent aquifers.

According to long-term observations at 12 meteorological stations in the Dnipro basin (Osadchyi et al., 2008), the TDS of atmospheric water ranges from 10.0 to 36.0 mg/l, mainly 20.0 mg/l. The chemical composition of atmospheric water is sustained and characterized by the following ratio of the main ions, %-eq:

SO_4^{2-} 60 > HCO_3^- 25 > NO_3^- 8 > Cl^-4; Ca^{2+} 33 > Na^+ 23 > Mg^{2+} 18 > NH_4^+ 12 > K^+ 10.

No spatial patterns of TDS distribution and chemical composition of precipitation in the Dnipro basin are observed.

As for surface waters, they are subject to a clear natural geographical zonation, and their TDS in the Dnipro basin varies widely. In water of the Pripyat River tributaries, the Ubort and the Uzh rivers, TDS is the lowest – 0.2 g/l. TDS of the Dnipro tributaries elevates significantly from north to south, in the northern part of the basin it is 0.32–0.38 in the Desna water, while in the Sula, the Psel and the Vorskla it reaches 0.7–0.9 g/l (Vyshnevskyi, Kosovets, 2003). Thus, even the lowest TDS of river water is ten times higher than that of atmospheric water.

The map of surface water TDS (Fig. 2) evidences in favor of the climatic factor in the formation of their qualitative composition. The boundary between surface waters with TDS lower and greater than 1.0 g/l corresponds to the boundary of leaching and continental salinization zones, or the boundary of insufficient and sufficient moisture zones. The chemical composition of surface waters in the north of the basin is hydrocarbonate calcium, in the southern part it changes to variegated with predominance of sulfate and sodium ions.

It should be noted that the nature of the distribution of macro- and microcomponents in surface waters is significantly different; it is quite natural that macrocomponents are distributed much more evenly both in space and time. Based on long-term observations (Osadchyi et al., 2008), in the water of the Dnipro cascade reservoirs over a 15-year period, the minimum average annual TDS differed from the maximum by 30 %, while for zinc and copper this

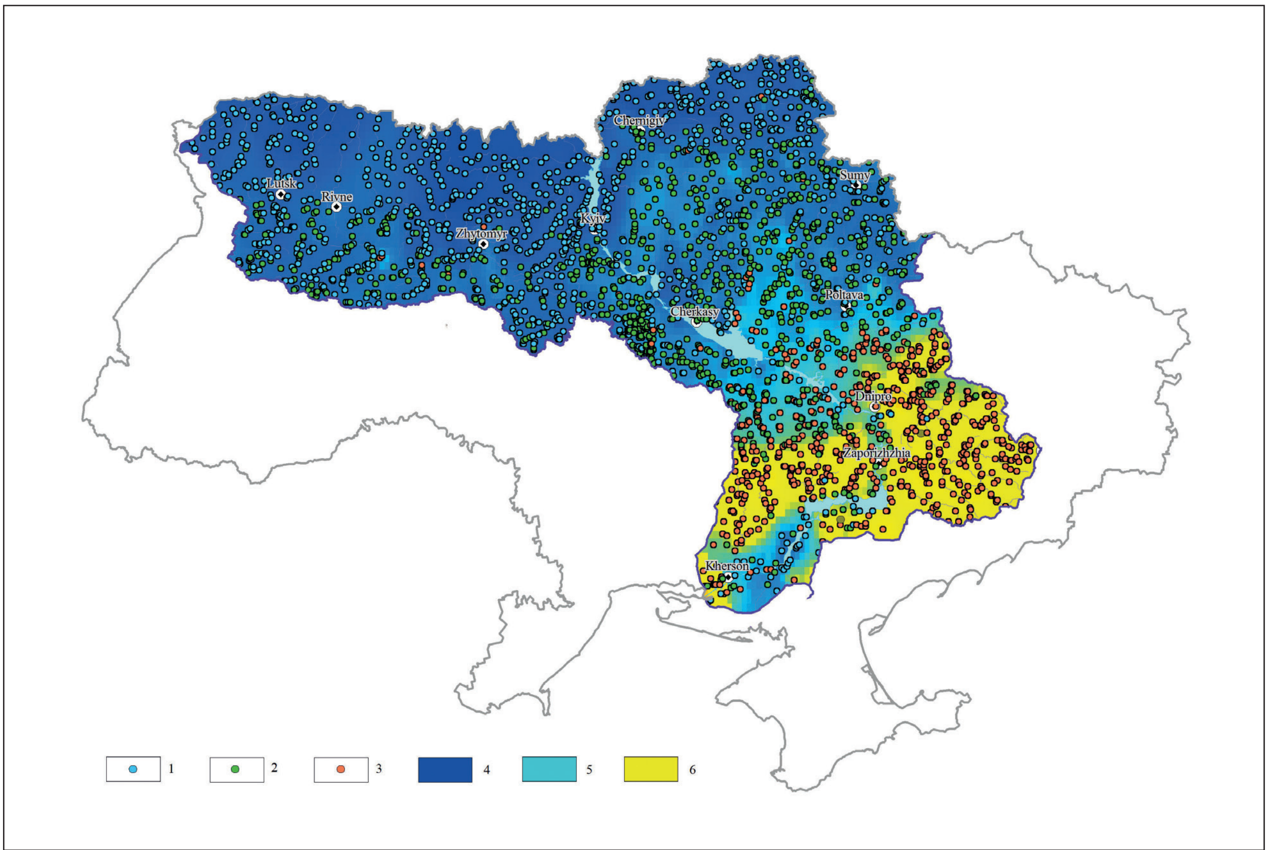

Fig. 2. Surface water TDS in the Dnipro River basin
Sampling points of surface watercourses with TDS: *1* – < 0.5 g/l; *2* – 0.5–1.0 g/l; *3* – > 1.0 g/l
Area distribution of surface water with TDS: *4* – < 0.5 g/l; *5* – 0.5–1.0 g/l; *6* – > 1.0 g/l

indicator is 6 and 15 times, respectively. This feature is explained by purely natural factors – uniform distribution of macrocomponents in rock-forming minerals and extremely uneven distribution of microcomponents, in particular metals.

In groundwater, the natural geographical hydrochemical zonation is even more contrasting, reflecting the additional influence of the basin's rocks material composition. In the groundwater of Polissya, TDS is lower than 0.5 g/l, while within the Lower Dnipro sub-basin it is more than 3.0, sometimes up to 10.0 g/l.

In addition to TDS and macrocomponent content, groundwater often contains elevated natural concentrations of microcomponents that exceed the standards established by the State sanitary norms and rules 2.2.4-171-10 "Hygienic requirements for drinking water intended for human consumption". This primarily concerns iron and manganese within the Ukrainian Shield, which are widespread in organic-rich groundwater of Polissya. In addition, within the Ukrainian Shield, groundwater sometimes contains elevated content of lead (up to 0.032–0.09 mg/l) and beryllium (up to 0.29–0.64 μg/l), which corresponds to the hydrogeochemical specification of this region.

The varied natural conditions of groundwater quality formation are complicated by intensive anthropogenic impact. An important aquifers characteristic is their protection from the surface pollution. To assess the protection of the uppermost aquifer the authors analyzed the aeration zone thickness and lithological structure and compiled a GIS-map of Ukraine's territory, a fragment of which is shown in Fig. 3. According to the existing criteria (Migulya et al., 1981), all uppermost aquifers in Ukraine are unprotected because they are not overlain by a clay layer of more than 10 m, and differ only in the time of pollutants penetration from the surface. Using the data on the thickness of various lithological layers of the aeration zone and filtration coefficients, the time of penetration of neutral contaminant with infiltration flow was approximately determined. According to these

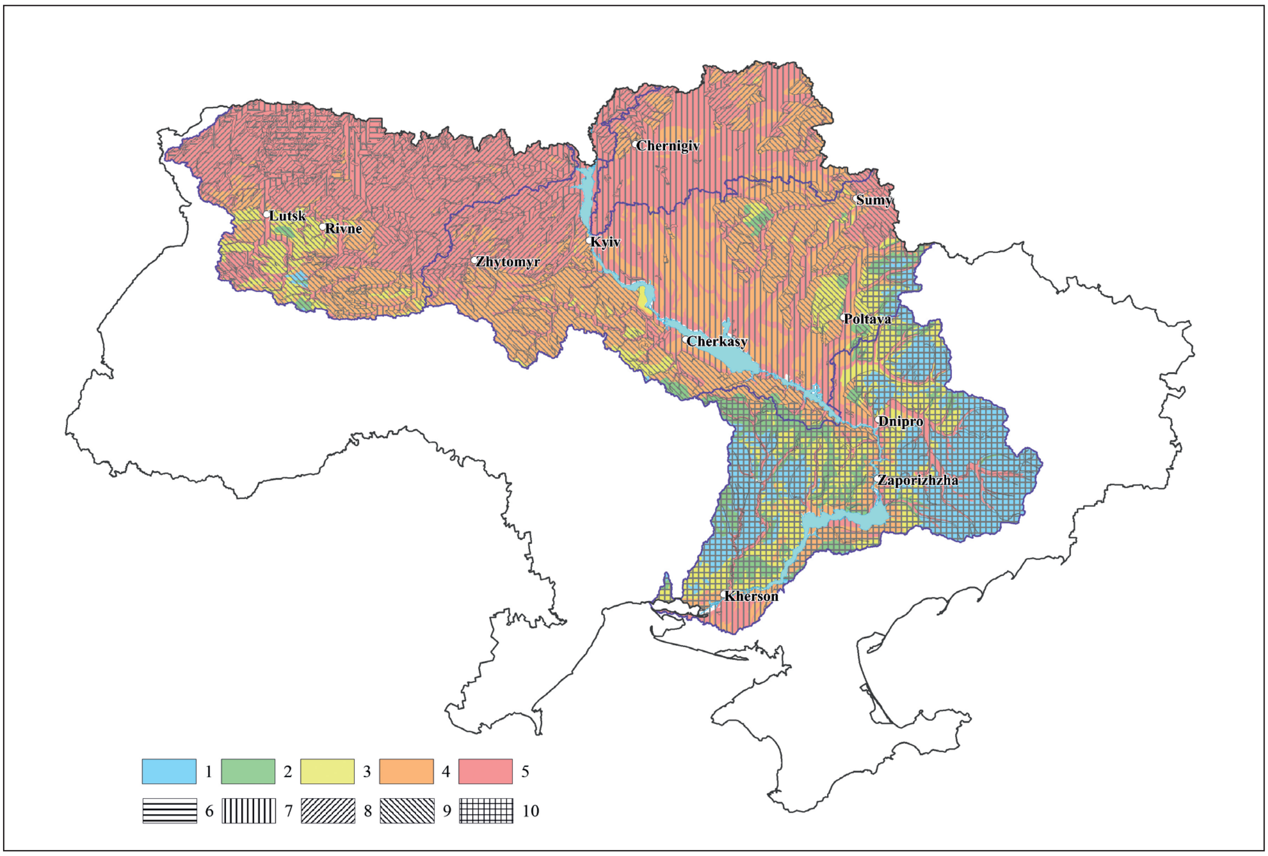

Fig. 3. Time of possible penetration of pollutants into groundwater, days: *1* – > 3000; *2* – 1000–3000; *3* – 250–1000; *4* – 50–250; *5* – 0–50. Unconfined aquifers: *6* – aquifer in marsh Quaternary sediments; *7* – aquifer in alluvial Quaternary sediments; *8* – aquifer in water-glacial Quaternary sediments; *9* – aquifer in water-glacial and aeolian-deluvial Quaternary sediments; *10* – aquifer in aeolian-deluvial Quaternary sediments

estimates, the uppermost aquifers vary in the time of penetration of pollutants from the surface with infiltration water (see Fig. 3): from 0–50 days in the north to 2000–3000 days in the south of the Dnieper basin (Sanina et al., 2005). Such natural conditions combined with intensive and long-lasting anthropogenic pressure resulted in large-scale groundwater pollution.

The most significant anthropogenic impact on unconfined aquifers throughout the Dnipro River basin is caused by diffuse sources of pollution within agricultural lands due to the use of mineral fertilizers and pesticides, irrigation and discharges of polluted wastewater into surface water bodies.

The detection of large areas of nitrate pollution indicates a steady trend towards their accumulation in groundwater. Given the significant demand for food products on the world market, the volume of agricultural production will grow and the use of fertilizers and pesticides will increase. Therefore, we should expect an increase in the pressure from diffuse sources of pollution within agricultural lands.

The problem of pollution with organic compounds and nitrates is exacerbated within rural settlements, where the population uses decentralized wastewater disposal systems (septic tanks and cesspools). According to the regional centers for disease control and prevention in different regions of Ministry of Health in Ukraine, cases of acquired methemoglobinemia are periodically reported due to the use of water from wells for the preparation of infant formula, and in such cases the nitrate content exceeded the standard (50 mg/l) by 10 or more times. Considering open-source information (Nitrate…, 2018) that cases of an acquired methemoglobinemia also occur at fairly low nitrate levels (above 10 mg/l), this situation looks threatening.

Another concern is the fact that oil products and pesticides have become common pollutants in unconfined aquifers. Pollution by oil products is spotty, and pesticides are mainly recorded in the southern regions, where their appearance is facilitated by irrigation (State…, 2021).

In the area of mining facilities influence in the sub-basins of the Middle and Lower Dnipro (mining areas of Dnipro, Zaporizhzhia, Donetsk and Poltava regions), the violation of natural hydrochemical conditions is associated with discharges of highly saline drainage and mine waters. In areas with a high level of industrial development and dense construction, changes in the quality composition of groundwater are observed. Here, unconfined aquifers are vulnerable to the impact of wastewater from chemical and metallurgical enterprises, industrial sites and tailing dumps of mining and processing plants. In these places (cities of Kamianske, Dnipro, Zaporizhzhia), waters of unconfined aquifers have high TDS (up to 3.4–8.6 g/l), elevated content of sulfates, chlorides, and high water hardness.

The most considerable changes in groundwater quality were recorded as a result of the Kryvyi Rih iron ore deposit development in the Lower Dnipro sub-basin, which affects not only unconfined, but also the underlying confined aquifers. The total area of uppermost aquifers groundwater contamination in the Kryvbas region is 300 km2 with TDS up to 12.3 g/l. Groundwater in this area is characterized by a high concentration of sulfates, chlorides, iron (up to 2.9 mg/l), strontium (up to 16.6 mg/l), bromine (up to 47.4 mg/l), manganese (up to 26.1 mg/l) (State…, 2021).

These data confirm the conclusions of previous studies that the waters of the uppermost aquifer in most of its distribution area do not meet the requirements of current quality standards by one or more indicators (Shestopalov et al., 2005).

Hydrochemical characteristics of the uppermost aquifers are variable both in space and time. To assess changes in water quality over time, we compared the sheets of the hydrogeological map of scale 1:200,000 Korosten, Pereyaslav-Khmelnitsky and Dnipropetrovsk, located respectively in the sub-basins of Pripyat, Middle and Lower Dnipro. It should be noted that different map sheets are unequally provided with hydrochemical information. Therefore, only the data available on all sheets and for both time periods were compared, namely TDS and anionic composition of water.

In the north of the Dnipro basin, in the Pripyat sub-basin, information from hydrogeological maps for 1971 and 2010 was compared for 37 and 41 wells, respectively, in the Korosten sheet (see Fig. 1). Here, the most common aquifers are in water-glacial and alluvial Quaternary sediments. During this period, the mean TDS elevated by 5 0%, increasing from 0.39 (from 0.1 to 1.2 g/l) to 0.59 (from 0.1 to 2.9 g/l). In the natural state, groundwater in this area is characterized by low TDS and predominance of hydrocarbonates and chlorides in the anionic composition. Over the 40-year period, TDS increased mainly due to chlorides and sulfates, the amount of three-component anionic composition doubled (see Table 1). The anthropogenic origin of this growth is evidenced by the fact that nitrate contamination of water, recorded in a quarter of the tested wells, shows a clear correlation with waters of chloride and three-component anionic composition.

Hydrogeological maps of the Pereyaslav-Khmelnytskyi sheet (the Middle Dnipro sub-basin) at a scale of 1:200,000 (see Fig. 1) for 1965 and 2009 were compared for by studying the chemical composition of water in 49 and 38 wells, respectively, which exploit mainly the aquifer in alluvial Quaternary sediments. More significant changes have occurred here, with groundwater TDS more than doubling over a 44-year period, from 0.84 to 1.8 g/l. The anionic composition of water has undergone significant changes. The number of water points with natural hydrocarbonate water composition has almost halved, while the number of wells with water of mixed composition has significantly increased (see Table 2).

Agrarian specificity of the territory affected the significant nitrate contamination. Out of 38 tested wells, 30 contain water with excessive nitrate content. In five wells, the content of nitrates reached such values that they together with hydrocarbonates form the main anionic composition of water. Wells with nitrate content below the maximum permissible concentration spatially tend towards the river network, while in watersheds the nitrate content in water increases.

In the territory of the Lower Dnipro sub-basin (Dnipropetrovsk sheet, see Fig. 1), hydrogeological maps drawn up in 1973 and 2012 were analyzed (respectively, data on 32 and 36 wells were compared, which mainly exploit aquifers in aeolian-deluvial and alluvial Quaternary sediments). The analysis showed that over a 40-year period groundwater TDS increased by an average of 1.8 times (see Table 3). As of 1973, it was 0.2–3.6, mainly 1.46 g/l, and the anionic composition was dominated by hydrocarbonates and sulfates. After 40 years, groundwater TDS is 0.8–9.1, averaging

2.7 g/l, and the role of sulfates and chlorides in the anionic composition increased significantly. Nitrate pollution is widespread, the content of sulfates and nitrates exceeds the MPC in 2/3 of the tested wells.

Thus, changes in the TDS and chemical composition of groundwater over the past 40 years have occurred throughout the Dnipro basin, even in the north, where the highest amount of precipitation and the lowest anthropogenic pressure is observed.

Despite the fact that all the tested wells are located within settlements, and obviously subjected to intensive anthropogenic impact, we cannot exclude an additional contribution of a powerful natural factor – significant climate change in the deterioration of groundwater quality. The main role of the climatic factor in the formation of surface and groundwaterqualitative composition causes a justified concern about the deterioration of their quality due to climate change. According to the data of meteorological observations, conducted in Ukraine since 1881, the average annual temperature increase over the last 30 years was 1.20 C, and the average annual temperature in Ukraine may rise by another 1–1.50 C during the next 30 years. Aridization of the climate is observed, which may lead to a significant shift of the physiographic zones' boundaries and desertification of large territories in the next 30-40 years. One of the negative consequences of climate change is predicted to be significant changes in the quantitative and qualitative groundwater status (Wilson et al., 2021).

Russian aggression has greatly exacerbated an already difficult situation. Throughout 2022–2023, much of Ukraine was contaminated with oil products, heavy metals, and various chemical elements and compounds that entered the environment as a result of industrial plants destruction. Military activity has been observed in areas of particularly hazardous facilities, including the largest in Europe South Ukraine Nuclear Power Plant, which has been occupied since March 2022. Intense fighting continues in the Lower Dnipro sub-basin. Surface water and soil are heavily contaminated over large areas, which cannot but affect groundwater, and especially the uppermost aquifers, given their unprotected nature. In addition, warfare changes the recharge conditions of unconfined aquifers, especially in places of mass rocket fire, as a result of the formation of sinkholes, as well as soil compaction from the movement of heavy military equipment. These effects have yet to be evaluated after the war is over.

Conclusions

The waters of unconfined aquifers in the Dnipro River basin are characterized by a complex and heterogeneous chemical composition, which is caused by numerous natural and anthropogenic factors. As a result of comparing the different-time hydrogeological maps, long-term trends of pollutants concentrations increasing have been established. During the last four decades there has been a profound metamorphization of unconfined aquifers groundwater chemical composition in the Dnipro basin. Particularly significant changes have occurred within the Middle and Lower Dnipro sub-basins, where TDS has doubled, and the anionic composition in most wells has undergone radical changes.

The priority is to restore groundwater monitoring of unconfined aquifers, taking into account their relationship with surface ecosystems and underlying confined aquifers. Only on the basis of monitoring, necessarily including background areas least disturbed by anthropogenic impact, it will be possible to better understand the contribution of natural and anthropogenic factors in the process of groundwater quality deterioration.

And, above all, one of the important directions of post-war rehabilitation in Ukraine should be to change the water supply sources of the rural population and improve sanitary conditions in rural areas. It is necessary, as noted in the works of previous studies (Shestopalov et al., 2005), to develop and implement a program of rural water supply through the use of water from the second or third from the surface confined aquifers.

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Просторово-часові особливості змін хімічного складу вод безнапірних водоносних горизонтів у четвертинних відкладах басейну Дніпра

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Проаналізовано та узагальнено дані про хімічний склад вод безнапірних водоносних горизонтів у басейні Дніпра. Це проведено не лише у зв'язку з необхідністю впровадження вимог методичних документів Водної Рамкової директиви ЄС у процесі моніторингу підземних вод, а передовсім через те, що ґрунтові води широко використовуються для водопостачання населення у сільських населених пунктах. Ґрунтові води відзначаються складним і неоднорідним хімічним складом, обумовленим комплексом природних і антропогенних чинників. На території басейну Дніпра яскраво виявляється природна гідрохімічна зональність. Низка хімічних елементів і сполук у воді містяться у концентраціях, що перевищують нормативи для питних вод, установлені ДСанПіН 2.2.4-171-10, у природному стані. Крім того, безнапірні водоносні горизонти зазнають суттєвого антропогенного впливу, оскільки є незахищеними від забруднення. Виконане порівняння даних щодо мінералізації та аніонного складу грунтових вод, отриманих під час гідрогеологознімальних робіт у період 1965–1975 і 2009–2013 рр. по трьох аркушах гідрогеологічної карти масштабу 1:200 000 у різних суббасейнах Дніпра, засвідчило повсюдні великі зміни хімічного складу грунтових вод. Крім значного антропогенного навантаження, ґрунтові води зазнають суттєвого впливу кліматичних чинників. За 40-річний період мінералізація на півночі басейну Дніпра зросла на 50 %, у центральній і південній частинах – удвічі, за рахунок збільшення вмісту сульфатів і хлоридів. У межах проаналізованих територій у суббасейнах Середнього і Нижнього Дніпра відзначається практично повсюдне нітратне забруднення грунтових вод. На значній території ґрунтові води через понаднормовий вміст хімічних елементів і сполук природного та антропогенного походження є непридатними для питного водопостачання населення. Тому одним з першочергових завдань повоєнної відбудови України повинне стати переведення сільського населення на водопостачання із захищених напірних водоносних горизонтів і поліпшення санітарних умов у сільських населених пунктах.

Ключові слова: *підземні води; безнапірні водоносні горизонти; умови формування; якісний стан; мінералізація; басейн Дніпра.*