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Hydrochemical composition, conditions and formation factors in the Pontian aquifer groundwater within the Odesa city territory

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Abstract

This study examines the hydrochemical characteristics of groundwater formation in the Pontian aquifer located beneath the city of Odesa, Ukraine, in the context of prolonged and intensive anthropogenic influence. Drawing on over 300 hydrochemical analyses conducted between 1971 and 2014, the research identifies significant changes in the chemical composition of groundwater over time. Key findings indicate a wide range of mineralization levels (0.7–10 g/dm³) and a consistent dominance of sulfate and sodium-magnesium ions. A noticeable upward trend in mineralization has been recorded in the majority of wells, suggesting increased anthropogenic stress caused by domestic wastewater infiltration, leakage from water supply systems, and inter-aquifer flow. Furthermore, the study highlights a strong correlation between elevated sulfate concentrations and the intensification of karst formation processes in limestone formations. These findings carry important implications for the management of underground infrastructure and the development of effective water resource protection strategies for the Odesa city.

Key words: pont; aquifer; chemical composition; anthropogenic activities; karst; Odesa.

**Умови та фактори формування гідрохімічного складу підземних вод pontичного
водоносного горизонту на території міста Одеси**

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Резюме

У статті досліджено гідрохімічні особливості формування підземних вод pontичного водоносного горизонту на території м. Одеси в умовах інтенсивного техногенного впливу. Особлива увага приділяється змінам у хімічному складі вод у період з 1971 по 2014 роки на основі аналізу понад 300 гідрохімічних досліджень. Встановлено, що води горизонту характеризуються значною мінливістю мінералізації ($0,7\text{--}10 \text{ г/дм}^3$) та домінуванням сульфатних і натрієво-магнієвих компонентів. Простежується зростання мінералізації у більшості свердловин, що вказує на посилення техногенного навантаження, зокрема через інфільтрацію господарсько-побутових стоків, витоки з водогонів та перетікання з інших горизонтів. Виділено зв'язок між підвищеним вмістом сульфатів і активізацією процесів карстоутворення у вапняках. Отримані результати мають важливе значення для оцінки ризиків для підземних комунікацій і планування охорони водних ресурсів Одеси.

Ключові слова: pont; водоносний горизонт; хімічний склад антропогенний вплив; карст; Одеса.

Introduction

In the Odesa city, the growing impact of anthropogenic factors on the geological environment has been observed for a long time. This is manifested in the intensification of engineering-geological processes, rising groundwater levels, and the deterioration of water quality. These challenges necessitate a comprehensive study of the geological and hydrogeological conditions, particularly aquifers of strategic regional importance. Special attention is warranted by

the Pontian aquifer, formed within the same-named Upper Miocene regional substage. This aquifer is utilized by certain enterprises in the city for technical and production purposes and is relevant for the study of karst formation processes in urban conditions.

The hydrogeologically active layer of the Pontian aquifer primarily consists of shelly limestones with an average thickness of 10–13 meters, which lie almost horizontally. These rocks exhibit porous and fractured textures that facilitate groundwater accumulation and filtration. Minor interlayers of fine-grained sands also occur. The aquifer is overlain by reddish-brown Pliocene-Pleistocene clays serving as a confining layer, while its base is formed by greenish-gray Meotian clays. This geological configuration determines the confined nature of the aquifer, in which saturation is observed only in the lower part of the limestone strata, while the upper part typically remains unsaturated.

The Pontian aquifer covers a significant area of the urban territory and is characterized by high water saturation. The productivity of water supply sources within this horizon varies: the yields of wells and shafts range from 1.5 to more than 5.5 liters per second. This variability is associated with heterogeneity in fracturing, porosity, and the degree of karst development in the limestones (Zelinsky 1993).

The formation of groundwater volumes in the Pontian aquifer is mainly ensured by atmospheric precipitation, infiltration through disturbed clay zones, and inflow from the Quaternary aquifer. Recharge is also partially supported by anthropogenic factors — in particular, leakages from water supply systems, industrial effluents, and sewage networks.

The mineral composition of the waters in the Pontian aquifer shows wide variations in mineralization — from 0.7 to 10 g/dm³. In the cation composition, sodium and magnesium ions predominate, while sulfate compounds dominate among the anions. Groundwater pollution, mostly of a local nature, is often caused by the operation of absorbing and filtration structures through which wastewater from the upper layers enters. Unfortunately, to date, insufficient attention has been paid to the hydrochemical characteristics of the aquifer waters, although they significantly influence both environmental pollution factors and the formation of aggressive chemical environments for underground communications.

The aim of the study is to analyze the hydrochemical conditions of groundwater formation in the Pontian aquifer and to assess the factors affecting their qualitative and quantitative state.

To achieve this goal, the following *tasks* were set:

1. To identify reference testing points and collect materials from hydrogeochemical studies over the maximum time depth to obtain continuous observations.
2. To create tables based on the data of analyzed chemical groups and perform statistical processing of the information in coordinates of parameter value versus time.
3. To formulate conclusions corresponding to the resolution of the set tasks.

The object of the study is the aquifer in the Pontian limestones within the industrial-urban agglomeration of Odesa city.

The subject of the study is the hydrochemical features of the groundwater composition.

Materials and research methods

For this study, hydrogeological observation data from 1954 to 2014 (a total of 301 chemical analyses) were used. These observations were conducted within the industrial-urban agglomeration of Odesa city and the adjacent territory by the PrychornomorDRGP (Karavan 1993, Kogan 1963), as well as materials from the Department of Engineering Geology and Hydrogeology of I.I. Mechnikov Odesa National University. The data set was processed using Microsoft Excel statistical software.

To analyze the spatial-temporal changes in the chemical composition of waters within the Pontian aquifer, comprehensive graphs of mineralization dynamics and the content of anions and cations in the Pontian waters were constructed for 11 shaft wells (Fig. 1) over the period 1971–2014. Additionally, graphs showing the dependence of groundwater chemical composition on the discharge of drainage adits were developed.

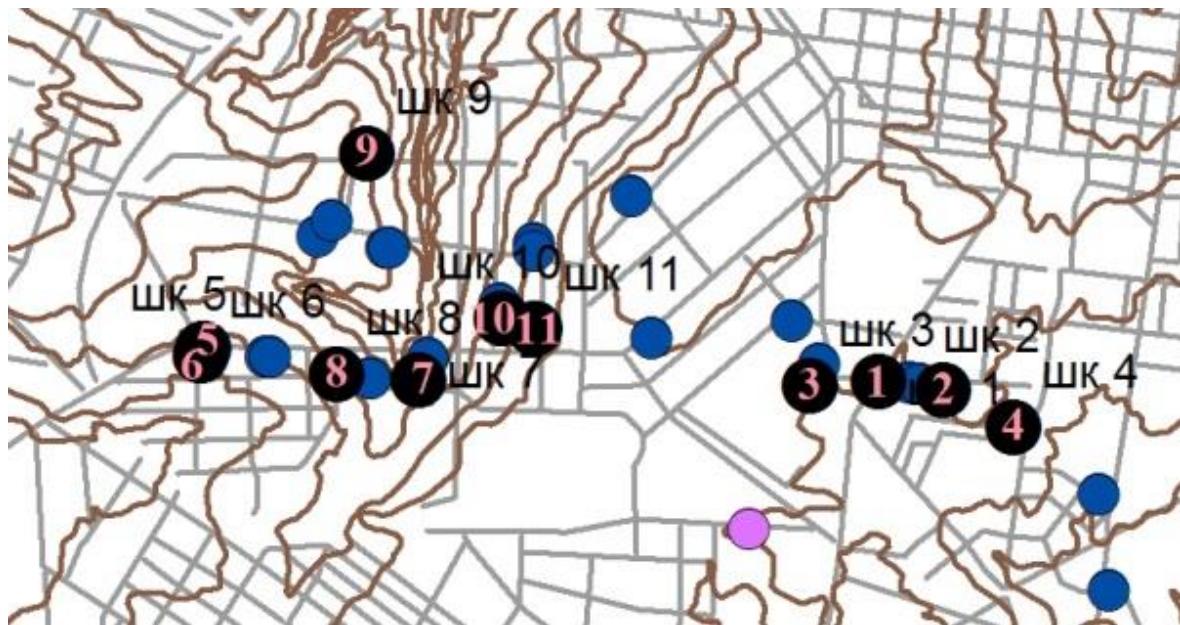


Figure 1. Layout scheme of shaft wells (SW) in Odesa city.

Table 1. Distance between shaft wells (SW) in meters

№ SW	2	3	4	5	6	7	8	9	10	11
1	278,8	302,8	622,1	3017,0	2993,4	2036,3	2412,0	2482,0	1689,5	1539,6
2		595,8	343,4	3303,1	3284,6	2317,1	2693,3	2768,1	1976,0	1873,1
3			916,3	2711,8	2693,6	1730,2	2093,3	2213,5	1392,1	1240,4
4				3627,6	3601,7	2652,7	3012,1	3115,7	2325,3	2167,8
5					56,1	971,0	611,3	1190,0	1354,5	1495,2
6						959,7	592,3	1127,4	1327,0	1469,1
7							367,3	1041,2	456,5	552,4
8								985,4	774,9	907,4
9									942,6	1080,2
10										158,3

The results of chemical analyses, collected from the archives of the aforementioned organizations, were compiled into thematic tables, which were used for conducting statistical analysis.

Research results

A comparative analysis of the chemical composition indicators of groundwater in the Pontian limestone aquifer wells within the city of Odesa shows that over a 40-year period, no signs of groundwater freshening have been observed overall (Fig. 2). In most wells, mineralization either

remained stable or increased. At several observation points, mineralization values exceed 1000 mg/dm³, indicating an increasing influence of anthropogenic pressure or a natural rise in salinity.

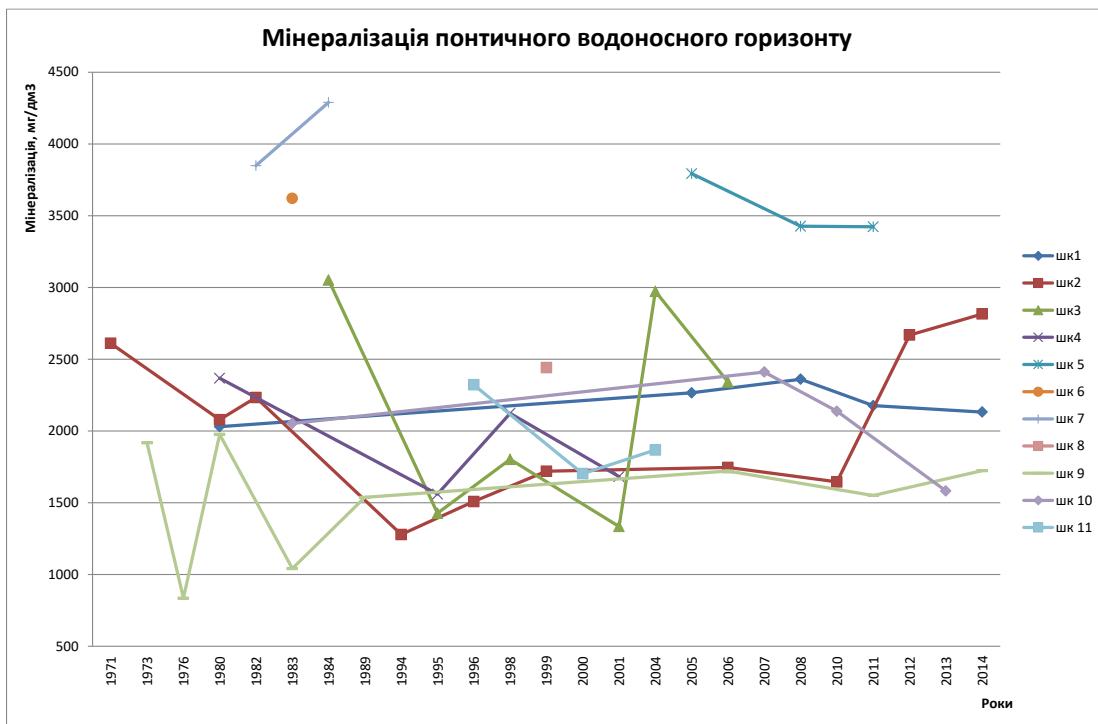


Figure 2. Graph of mineralization changes (mg/dm³) over the period 1971–2014.

Based on changes in the percentage ratio of ions in the chemical macrocomponent composition of the water, the following materials were obtained. Among the anions (Figs. 3, 4, 5), sulfate ion and mixed types predominate. A clear trend of decreasing chloride ion content is observed in most wells, accompanied by an increase in the proportion of sulfates. At the same time, several points retain elevated bicarbonate levels, which may indicate enhanced atmospheric recharge and inflow of fresher waters from the Quaternary aquifer. The accumulation of operating enterprises in the central part of the city likely contributes to the inflow of sulfate ions into the groundwater.

Particular attention in the context of karst formation analysis in the region is drawn to the detection of increased sulfate ion concentrations in the waters of the Pontian aquifer. This parameter can be of key importance in understanding the intensity of chemical dissolution of carbonate rocks within confined aquifer systems. According to studies conducted in the Odesa area (Klimchuk 2010), the formation of karst cavities and a developed network of fractures occurred under the influence of ascending groundwater within zones of elevated pressure. It is likely that

the aggressiveness of these waters increased in some areas due to the presence of hydrogen sulfide, which, upon contact with oxygenated waters of higher horizons, underwent oxidation. As a result, sulfuric acid may have formed, activating the process of sulfate (sulfuric acid) dissolution of limestone formations. A potential source of hydrogen sulfide in deeper layers is the microbiological or geochemical reduction of sulfates in the presence of dispersed hydrocarbons or organic matter (Klimchuk 2010).

In the cationic composition of groundwater (Figs. 6, 7, 8) of the Pontian aquifer, sodium and magnesium predominate, indicating a shift toward the sodium-magnesium type. The share of calcium decreases during periods of intense anthropogenic impact but locally increases in zones of karst activity.

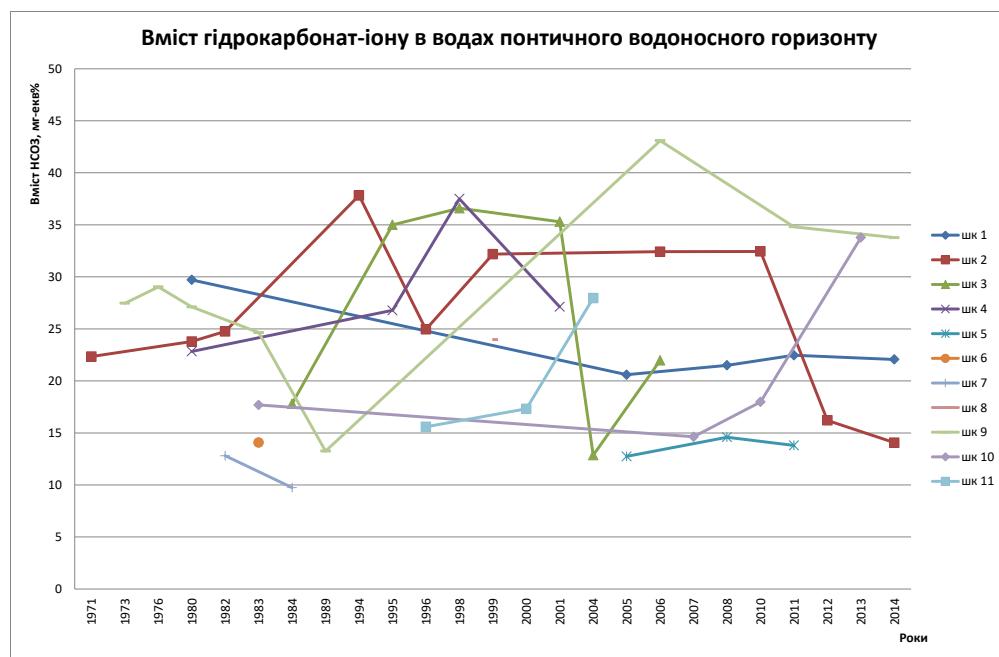


Figure 3. Graph of bicarbonate ion concentration changes (mg-equiv%) over the period 1971–2014.

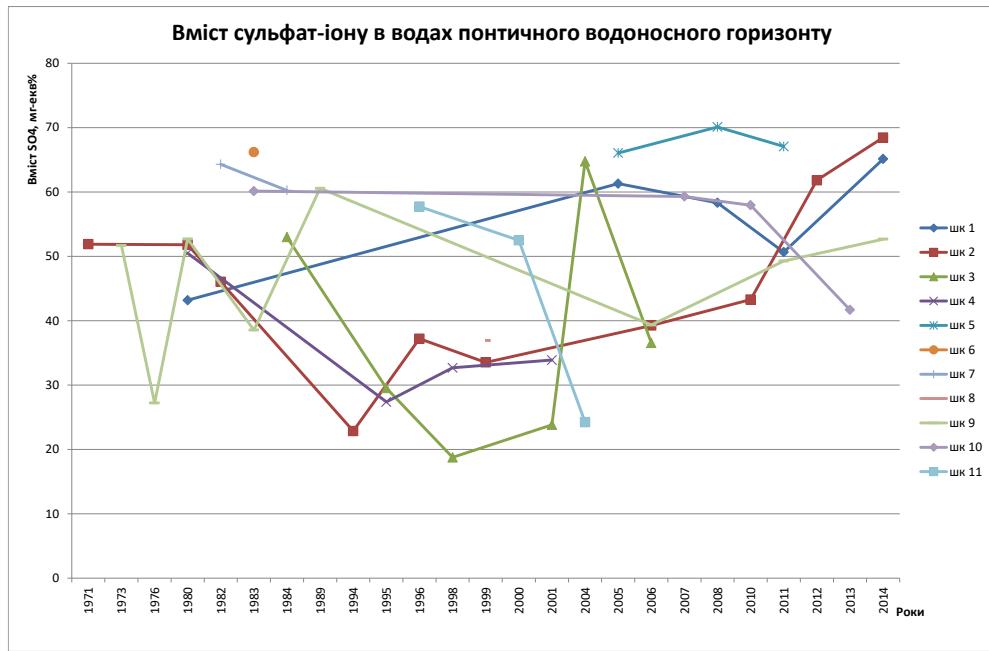


Figure 4. Graph of sulfate ion concentration changes (mg-equiv%) over the period 1971–2014.

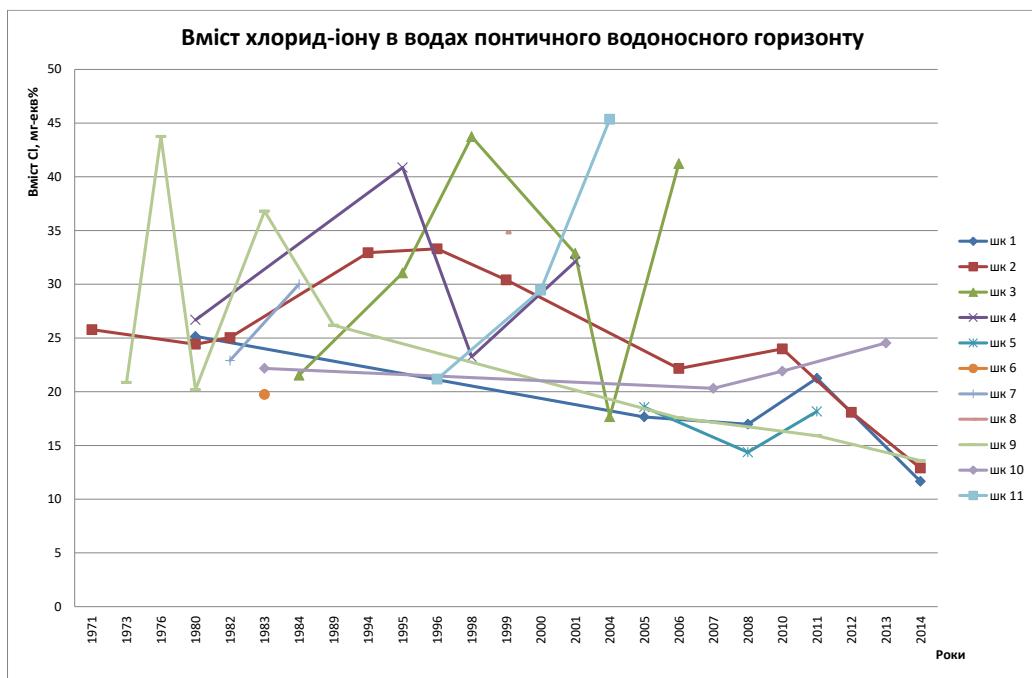


Figure 5. Graph of chloride ion concentration changes (mg-equiv%) over the period 1971–2014.

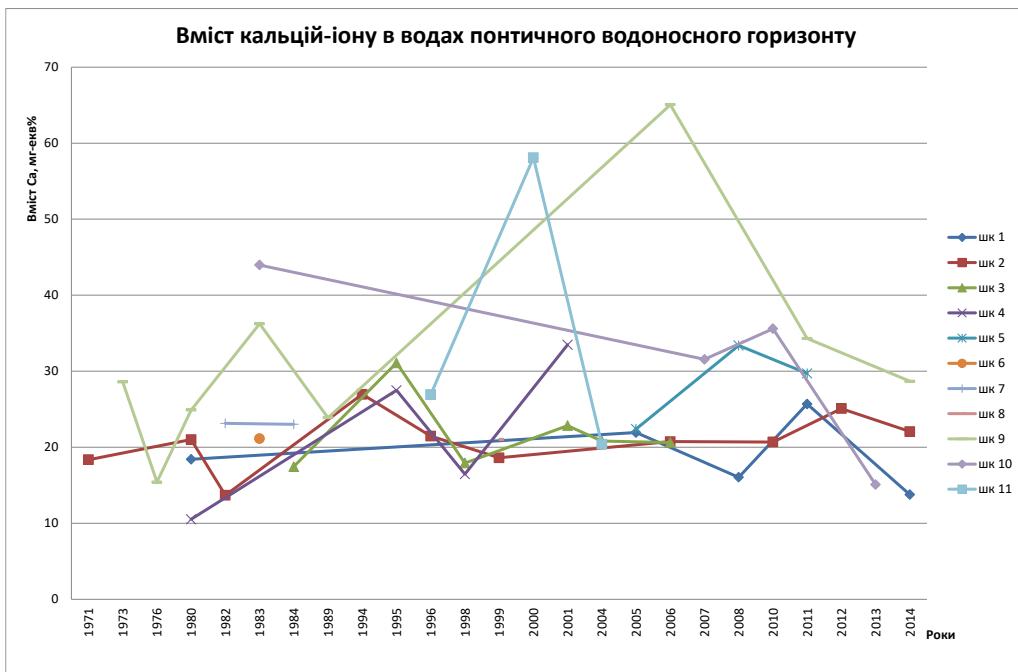


Figure 6. Graph of calcium ion concentration changes (mg-equiv%) over the period 1971–2014.

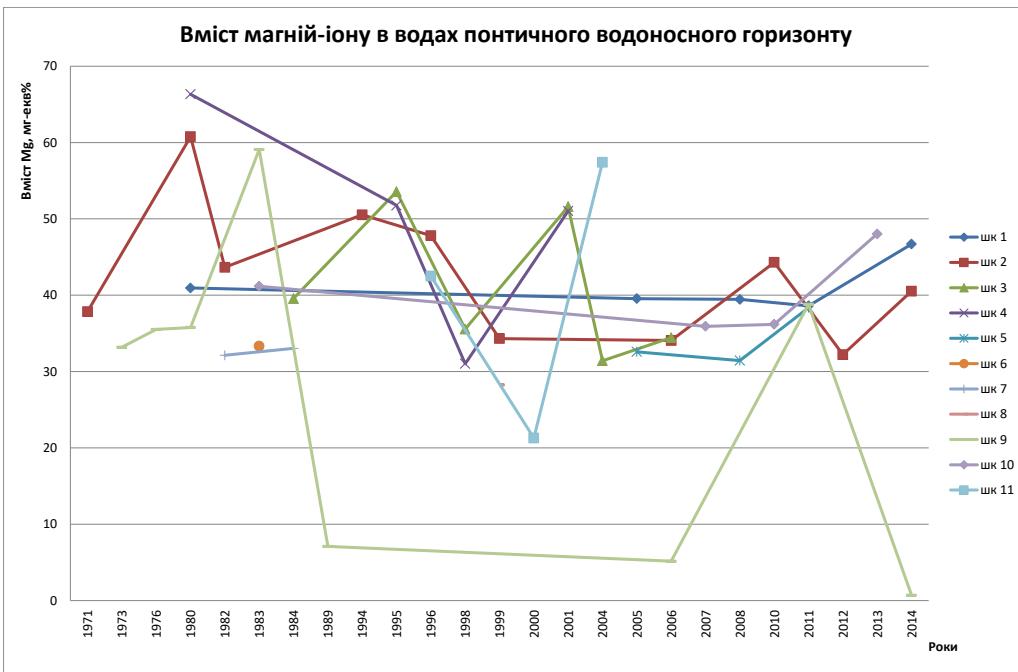


Figure 7. Graph of magnesium ion concentration changes (mg-equiv%) over the period 1971–2014.

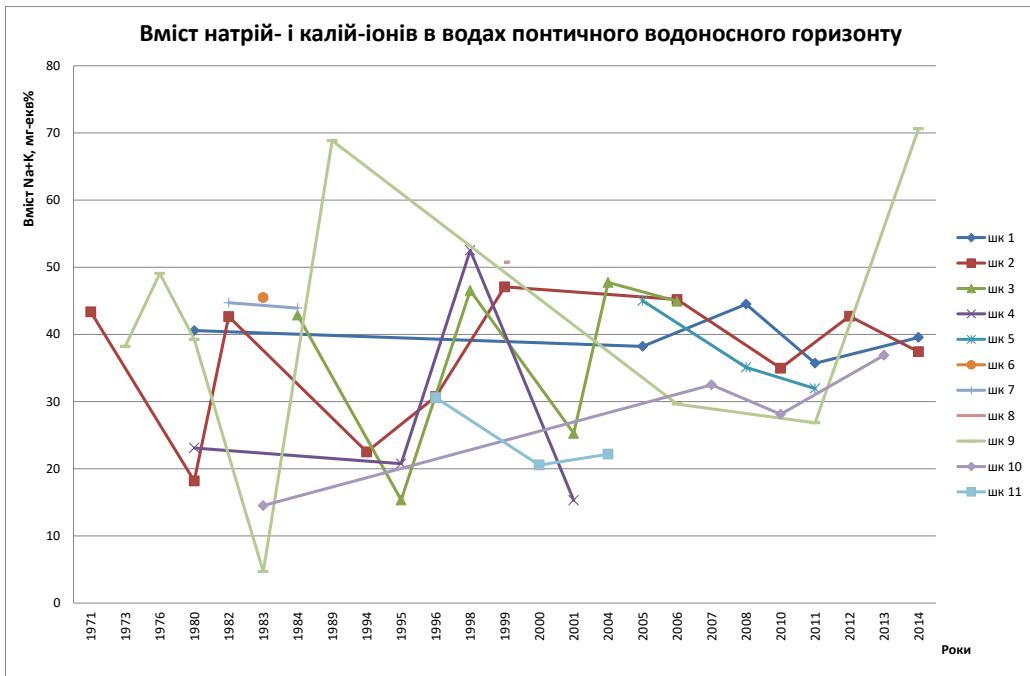


Figure. 8. Graph of sodium and potassium ion concentration changes (mg-equiv%) over the period 1971–2014.

Analysis of the chemical composition results of groundwater from Pontian limestones, sampled between 1971 and 2014 from shaft wells operating within industrial enterprises in the central part of Odesa (Fig. 9), revealed a consistent trend: an increase in mineralization is accompanied by elevated concentrations of sulfate and sodium ions. This correlation indicates a significant role of external factors in shaping the hydrochemical composition of waters within the Pontian aquifer.

The obtained data suggest that the source of changes in mineralization and ion composition is anthropogenic influence, particularly infiltration of water from damaged or worn-out pipelines, increased failure rates of municipal utilities, as well as the operation of drainage infrastructure, which directs part of the water from the Quaternary aquifer into the Pontian horizon. Such seepage conditions facilitate the transport of contaminants and transformation of the natural chemical composition of groundwater.

Monitoring of the chemical composition of drainage waters has been conducted since the beginning of the drainage system's operation, including regular sampling for laboratory analysis. Over a long observation period – approximately from the 1960s to the 1990s – a trend of decreasing total mineralization of groundwater in the Pontian aquifer along the coastline of Odesa was recorded. While average mineralization values were about 5.5 mg/dm³ at the start of this period,

by the late 1990s they had decreased to 2.8 mg/dm³. At the same time, the volume of drainage water discharge gradually increased, which was associated with the growth of overall water consumption within the city limits.

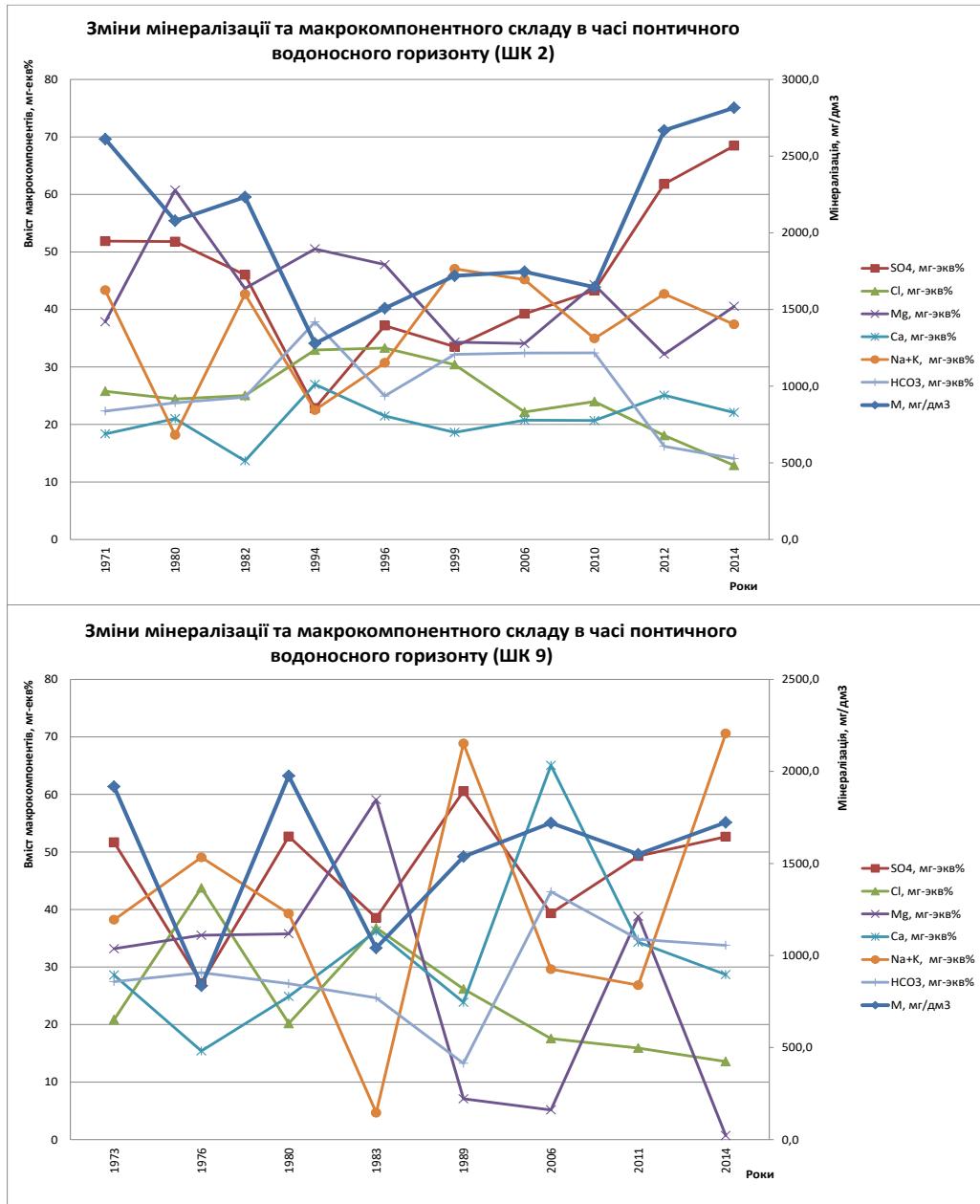


Figure 9. Graphs of mineralization and macrocomponent composition changes over time during 1971–2014. A) in SW 2, B) in SW 9.

A comparative analysis of the hydrochemical parameters of groundwater and the discharge rates of drainage adits (Fig. 10) demonstrated that the spatial distribution of the chemical

composition closely correlates with the level of water saturation within the aquifer. Specifically, drainage adits characterized by increased water inflow generally exhibit a decreased concentration of sodium ions alongside an increased calcium content in the water. This pattern indicates active dissolution processes of carbonate rocks, which does not exclude the development of karst phenomena within the Pontian limestone formations.

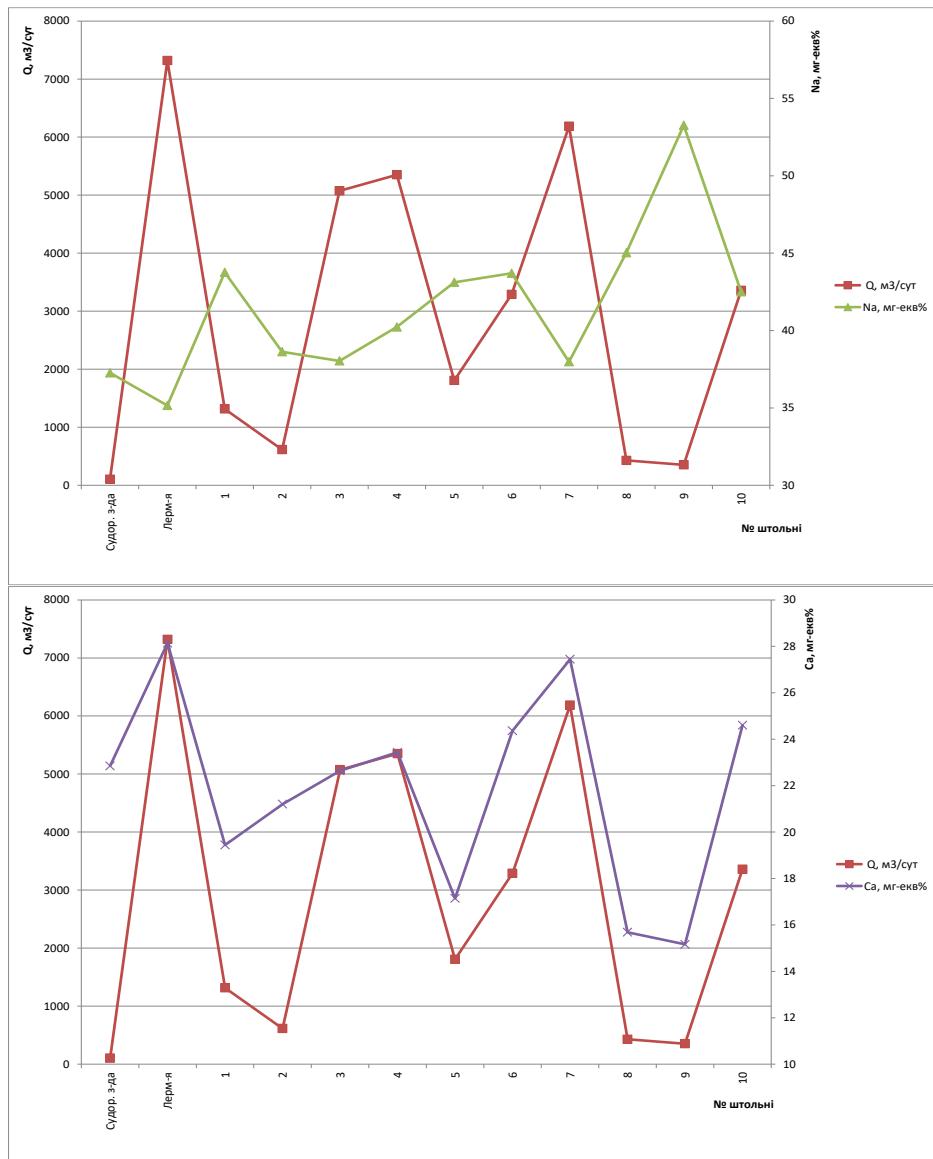


Figure 10. Graphs of the dependence of concentration of 1) sodium ion (mg-equiv%) and 2) calcium ion (mg-equiv%) on drainage adit discharges.

Anthropogenic factors also have a significant influence on the chemical composition formation, particularly through the infiltration of domestic wastewater, leakages from water supply networks, and specialized industrial channels entering the aquifer via vertical engineering structures. These sources contribute not only to the overall increase in water saturation of the system but also alter the dynamics of groundwater levels, which in turn affects mineralization and the concentration of specific ions.

Conclusions

As a result of the study, reference test points that best meet the objectives were identified. Tables were created based on selected data of the analyzed chemical groups from the reports of the PrychornomorDRGP organization and the materials of the Department of Engineering Geology and Hydrogeology of I.I. Mechnikov Odesa National University. The data were statistically processed (11 graphs were constructed), which allowed the following conclusions to be drawn:

1. The formation of the main volume of groundwater in the Pontian aquifer within the urban area is conditioned by the interaction of numerous natural and anthropogenic factors.
2. Waters of the Pontian aquifer are characterized by a complex ionic composition. By mineralization degree, they mostly belong to the weakly brackish ($1-3 \text{ g/dm}^3$) or brackish ($>3 \text{ g/dm}^3$) types. The cation composition is usually sodium-magnesium, while sulfates predominate among the anions.
3. Over the observation period of more than 40 years, no significant signs of groundwater freshening in the Pontian aquifer were detected. At the same time, changes in the relative content of macrocomponents were noted, indicating a transformation of the hydrochemical water type.
4. Spatial variability of water exchange within the aquifer affects the concentration of individual components, particularly the increased levels of sulfate and calcium ions in the waters of some wells.
5. One of the key factors influencing the increase in water saturation and changes in mineralization of the Pontian aquifer is the seepage of water from the Quaternary aquifer.
6. In zones of additional recharge, conditions favorable for the development of karst phenomena are formed. In particular, a high content of sulfate ions can enhance the chemical activity of waters and contribute to the formation of karst cavities, thereby stimulating karst processes.

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