GeoTerrace-2026-073

Features of Chemical Composition of Drainage Waters of St Andrew's Church and Kyiv-Pechersk Lavra Territories

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SUMMARY

The article examines the features of the chemical composition of drainage system waters and groundwater in the area adjacent to St Andrew's Church and drainage system Kyiv-Pechersk Lavra. Hydrochemical water types were determined, a preliminary assessment of ion-exchange processes was performed using chloride-alkaline indices (CAI, CAI2), and a preliminary analysis of the probable mechanisms of formation of the chemical composition of the studied waters was carried out by comparing the major cations and anions. A comparative analysis was made of the chemical composition of drainage waters of the St Andrew's Church territory with groundwater from observation wells (Quaternary and Paleogene aquifers), as well as with the drainage waters of Kyiv-Pechersk Lavra. The drainage waters of St Andrew's Church and Kyiv-Pechersk Lavra are similar in composition to each other and to the groundwater of a number of wells in hydrochemical type, namely chloride-calcium or mixed-calcium with a significant proportion of chloride ions in the chemical composition. In the drainage waters of St Andrew's Church and Kyiv-Pechersk Lavra, reverse cation exchange processes were established (Ca and Mg are displaced from rocks by Na and K). In the waters of other wells of the St Andrew's Church territory, direct cation exchange processes were established (Na and K are displaced from rocks by Ca and Mg). Apparently, there is an anthropogenic source of input of Cl^- into the groundwater of a number of wells and the drainage waters of St Andrew's Church and Kyiv-Pechersk Lavra. There is also an alternative source of input of Ca^{2+} ions, or an input of Na^+ into the soils and ion exchange of Na^+ for Ca^{2+} during infiltration through the rock layer.

Keywords: St Andrew's Church; National Preserve "Kyiv-Pechersk Lavra"; Drainage System; Drainage waters; Groundwaters; Chemical composition; Hydrogeochemical type; Ion-exchange mechanisms.

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Introduction

Cultural heritage sites located on the slopes of the right bank of the Dnipro River within the historical center of Kyiv – St Andrew's Church and the National Preserve "Kyiv-Pechersk Lavra" are characterized by complex engineering-geological and hydrogeological conditions. Slope territories are under the constant influence of groundwater, which necessitates the operation of drainage systems to prevent flooding and the development of landslide processes that threaten the stability of historical structures.

The drainage systems of these sites are traditionally regarded as purely engineering structures for protection against flooding, while the chemical composition of drainage waters and their relationship with the groundwater of adjacent aquifers remain insufficiently studied.

The aim of this study is a comparative analysis of the chemical composition of drainage waters of the St Andrew's Church territory with the groundwater from observation wells (Quaternary and Paleogene aquifers), as well as with the drainage waters of Kyiv-Pechersk Lavra, in order to establish common and distinctive hydrochemical processes, assess their hydrochemical similarity, and preliminarily evaluate the probable mechanisms of their formation. The obtained results may be useful in developing recommendations and a set of measures to prevent contaminants from entering groundwater.

Methods

According to archival documents (Sushchuk et al., 1987; Molochkova et al., 2017), the drainage adit of St Andrew's Church is embedded in the NpS layer (Novopetrivska series of the Neogene), in grey clay with dark-red mottling, dark-cherry in the roof, sandy, kaolinitic. The adit lies directly beneath the regional confining layer (variegated, brownish-yellow clay with carbonate inclusions) and above the sandy aquifer, from which it is separated by an additional thickness of clay.

Water samples were collected from observation wells No. 3', 5', 9' and the well of the Paleogene (Kharkiv suite) aquifer P_3hr.

Wells 3', 5', 9' were drilled in 2025 next to wells from 1982 and 1995 that had gone out of service, to depths of 10.5 m, 12.5 m and 7.0 m respectively, with a diameter of 160 mm. They are fitted with a plastic casing string with a perforated filter (wound with mesh wire) and a sand-gravel pack; the filter sections are located in the water-saturated Quaternary deposits (lacustrine-glacial, fluvioglacial, aeolian-deluvial silty loams). The established groundwater levels were: well 3' – 6.80 m (165.65 m a.s.l.), well 5' – 10.70 m (165.24 m a.s.l.), well 9' – 5.32 m (160.62 m a.s.l.).

Well P_3hr reveals a deeper, Paleogene (Kharkiv suite) aquifer and is used to compare the chemical composition of the waters of the upper (Quaternary) and lower (Paleogene) aquifers with the chemical composition of the drainage waters.

Analytical chemistry methods:
- *Potentiometric method*: determination of pH and the concentration of Ca^{2+}, Mg^{2+}, Cl^- ions, using a DL AI-125 ion meter and a set of glass and ion-selective electrodes.
- *Flame photometry method*: determination of the concentration of Na^+ and K^+ using an Elico CL-22D flame photometer.
- *Titrimetric method*: determination of the concentration of CO_3^{2-} (indicator – phenolphthalein) and HCO_3^- (methyl orange).
- *Gravimetric method*: determination of the concentration of SO_4^{2-} by precipitation with a 10% solution of $BaCl_2$ and weighing the precipitate of $BaSO_4$ on an Ohaus Adventure analytical balance.

Results

The hydrochemical type of the drainage and groundwater of the St Andrew's Church territory and the drainage waters of Kyiv-Pechersk Lavra was determined using a Piper diagram (Fig. 1). By cation composition, the following are classified as: 1) calcium waters – the drainage system waters of St Andrew's Church, collected in 2026 – samples No. 1, 2, 3, and the waters of wells No. 5', 9', P_3hr and all the waters of the Kyiv-Pechersk Lavra drainage system (2025); 2) mixed-type waters – the drainage system waters of St Andrew's Church, collected in 2024 – samples No. 3, 4/40; 3) sodium-type – the groundwater of well 5'. By anion composition: 1) bicarbonate waters in wells 3' and 9' (2025); 2) chloride waters – the drainage system waters of St Andrew's Church – samples collected in 2026 No. 1, 2, 3, and in 2024 No. 3, 4/40, as well as the water of well P_3hr; 3) sulphate-type – the water of well 5' in all sampling years; 4) mixed-type – the water of well 9' during sampling in 2024.

In summary, it can be said that the waters of the drainage systems of St Andrew's Church and Kyiv-Pechersk Lavra, as well as the waters of wells 5', 9' and P_3hr as of 2026 have a similar hydrochemical type – chloride-calcium or mixed-calcium with a significant proportion of chloride ions in the chemical composition.

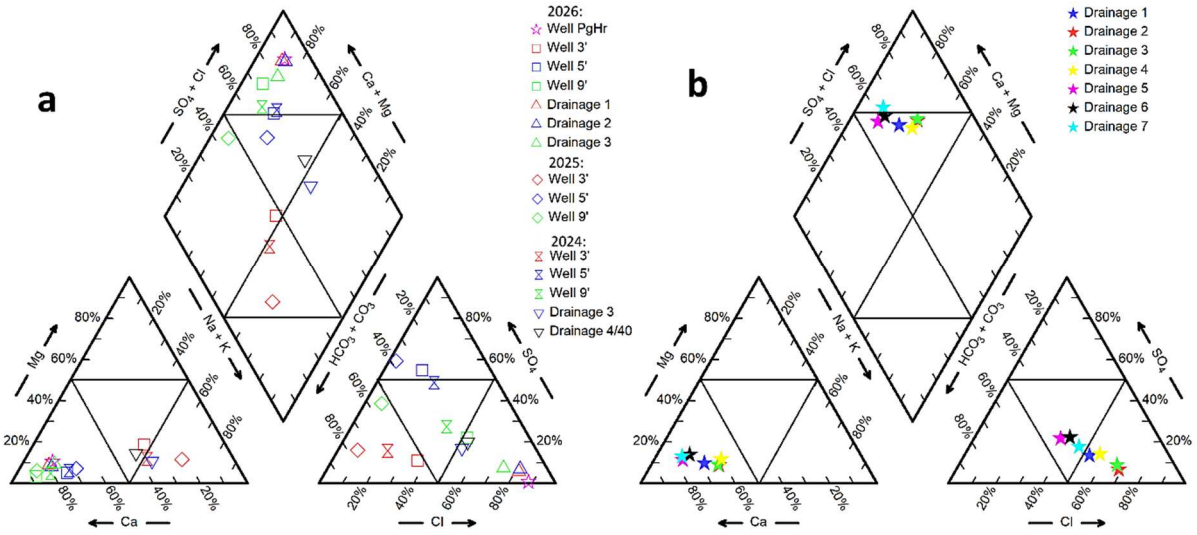

Figure 1 *Piper diagram of groundwater chemical composition from a) wells and drainage system on St Andrew`s church territory; b) drainage system of Kyiv-Pechersk Lavra*

The direction of cation exchange processes was assessed using the chloride-alkaline indexes CAI, CAI2, which are widely used (Elkoholly et al., 2017; Tay et al., 2018; Ravikumar et al., 2015; Hu, & Zhou, 2021). These indices were calculated based on the concentrations of macro-cations in the water, in mg-eq/dm^3 using the formulas:

$$CAI = \frac{Cl^- - (Na^+ + K^+)}{Cl^-}; \quad CAI2 = \frac{Cl^- - (Na^+ + K^+)}{SO_4^{2-} + HCO_3^-}$$

When CAI (CAI2) > 0 – Ca and Mg are displaced from the rocks by the cation exchange mechanism with Na and K (reverse cation exchange); when CAI (CAI2) < 0 – the process proceeds in the opposite direction – Na and K are displaced from the rocks by Ca and Mg (direct cation exchange).

Based on the results of this method (Fig. 2), for the waters of wells 3' and 5', and occasionally for the water of well 9' (only in 2025), the CAI (CAI2) indices < 0, which indicates the occurrence of direct cation exchange processes – Na and K are displaced from the rocks by Ca and Mg. For the water of well 9' (in 2024 and 2026), P_3hr as well as for the waters of the drainage systems of both the St Andrew's Church territory and Kyiv-Pechersk Lavra, CAI (CAI2) > 0, which indicates the occurrence of reverse cation exchange processes – Ca and Mg are displaced from the rocks by Na and K.

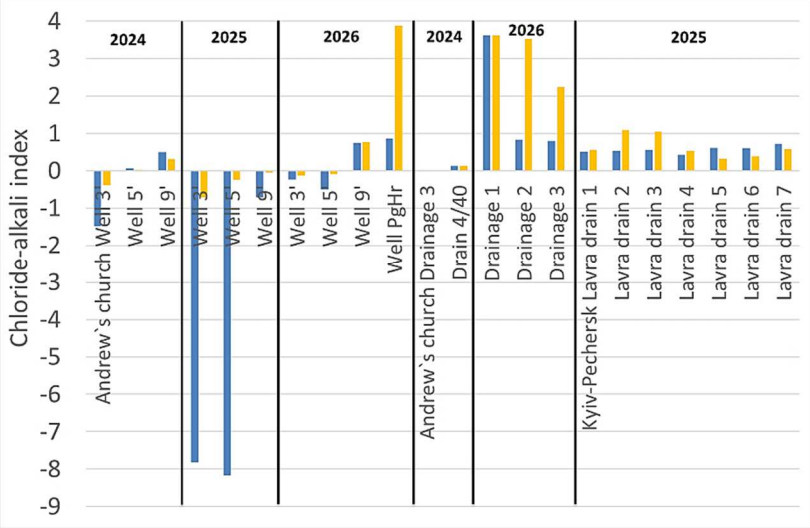

Figure 2 *Chloride-alkali indexes of water from wells and drainage system on St Andrew`s church and drainage system of Kyiv-Pechersk Lavra*

A preliminary analysis of the probable mechanisms of formation of the chemical composition of the studied waters was performed by comparing the major cations and anions, similarly to the previous work of the authors (Koliabina at al., 2026). The results show (Fig. 3) that the imbalance between sodium and chlorine content, with a predominance of chloride ions, is greatest in wells 9' and P_3hr and in the drainage system waters of St Andrew's Church, collected in 2026. Notably, in samples from this drainage system in 2024 a balance between sodium and chlorine content was observed. Also, to a lesser extent, the concentration of chloride ions prevailed over the concentration of sodium in the waters of the Kyiv-Pechersk Lavra drainage system. Such an imbalance, with a predominance of chloride ion concentration, may indicate the presence of a probably anthropogenic source of input of Cl^- into the groundwater and drainage waters. There is also an imbalance between the sum of calcium and magnesium concentrations (Fig. 3), as well as sulphates and bicarbonates, with a predominance of mainly calcium, in the same wells where a predominance of chlorides was observed – well 9' and P_3hr and in the drainage system waters of St Andrew's Church collected in 2026 and the drainage waters of Kyiv-Pechersk Lavra. This may indicate the presence of an alternative source of Ca^{2+} ions, or anthropogenic input of NaCl into the soils and a process of ion exchange of Na^+ for Ca^{2+} during infiltration through the rock layer.

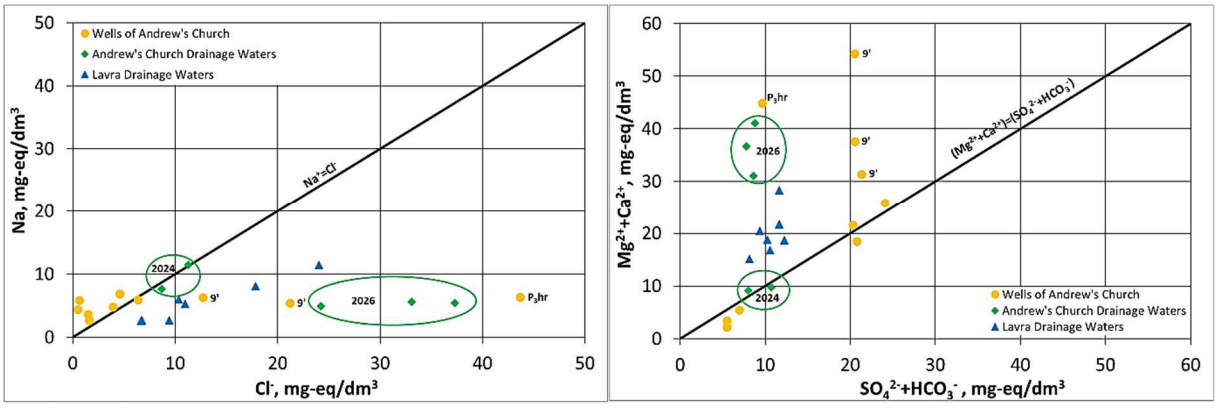

Figure 3 *Comparison of the concentrations of major cations and anions in the wells and drainage system on St Andrew`s church and drainage system of Kyiv-Pechersk Lavra*

Acknowledgements

This study was funded by the budget program CPCEL 6541030 in the framework of the R&D Project "Resource and geoecological aspects of anomalous hydrogeological processes and conditions",

2022-2026 (SRN № 0122U001786) and in the project postgraduate program of junior researcher Dramaretskyi Ye. in the hydrogeological problems department of Institute of Geological Sciences of NAS of Ukraine (scientific supervisor – head of department Koliabina I.).

Conclusions

The waters of the drainage systems of St Andrew's Church and Kyiv-Pechersk Lavra, and the waters of wells 5', 9' and P_3hr have a similar hydrochemical type – chloride-calcium or mixed-calcium with a significant proportion of chloride ions in the chemical composition.

The chloride-alkaline indexes of the collected drainage water samples of St Andrew's Church and Kyiv-Pechersk Lavra have positive values, which indicates the occurrence of reverse cation exchange (Ca and Mg are displaced from rocks by Na and K).

The chloride-alkaline indexes of the groundwater samples from the majority of wells of the St Andrew's Church territory (with the exception of well 9' and P_3hr) have predominantly negative values, which indicates the occurrence of direct cation exchange processes (Na and K are displaced from rocks by Ca and Mg).

The presence of a probably anthropogenic source of input of Cl^- into the groundwater of a number of wells and the drainage waters of St Andrew's Church and Kyiv-Pechersk Lavra has been established. There is also an alternative source of input of Ca^{2+} ions, or an input of Na^+ into the soils and ion exchange of Na^+ for Ca^{2+} during infiltration through the rock layer.

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