



APPLICATION OF MACRO AND TRACE ELEMENT ANALYSES TO IDENTIFICATION OF UPWARD FLOW OF WATER FROM MIOCENE AQUIFER INTO THE WARSAW–BERLIN ICE-MARGINAL VALLEY AQUIFER (ŚREM, POLAND)

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Abstract. The upward flow of Miocene aquifer waters into the Quaternary aquifer in the Wielkopolska region can negatively affect the quality of the recharged waters. One example of such an area is the Śrem region, where previous studies indicated the occurrence of groundwater upward flow. Accordingly, research was conducted to confirm the current occurrence of upward flow, determine its impact on the water quality of the Warsaw–Berlin ice-marginal valley aquifer, and assess the relationship between selected trace elements (TEs) and the migration of Miocene aquifer waters. For this purpose, cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+}) and anions (Cl^- , NO_3^- , NO_2^- , SO_4^{2-} , PO_4^{3-}) were determined using ion chromatography (IC), and TEs (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) were measured using inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ-MS). The results confirmed the continuous occurrence of upward flow in the Śrem area. This was determined based on the increasing concentrations of Cl^- , Na^+ , and K^+ , whose rising levels in the waters of the Warsaw–Berlin ice-marginal valley aquifer are associated with the upward flow of Miocene aquifer water. Additionally, it has been shown that the upward flow of Miocene aquifer waters does not significantly affect overall water quality in the Warsaw–Berlin ice-marginal valley. It was also found that the increase in As, Cr, Cu and Zn concentrations with depth in Quaternary groundwater is likely associated with the migration of these TEs from Miocene aquifer waters as a result of upward flow.

Key words: groundwater quality, hydrogeochemistry, Quaternary aquifer, ICP-QQQ-MS, chloride migration, multilevel piezometer

Introduction

The upward flow of Miocene aquifer waters into Quaternary aquifers in the Wielkopolska region, particularly within the Wielkopolska Buried Valley and the Warsaw–Berlin ice-marginal valley aquifers, is a well-documented phenomenon (e.g., Górski 1989; Dragon, Górski 2003; Dragon *et al.* 2003, 2005, 2006, 2007; Górski 2021). This phenomenon occurs in areas where the piezometric pressure of the Miocene aquifer exceeds the pressure of overlying aquifers (Górski 1989; Dow-

giałło *et al.* 2002). The upward flow in these areas can happen through several mechanisms: (1) seepage of water under elevated piezometric pressure through weakly permeable or even near-impermeable formations into the overlying aquifer (Górski *et al.* 2014), (2) the formation of localised hydraulic connections between aquifers along hydraulically active tectonic faults (Górski 1989), or (3) poorly constructed wells and hydrogeological boreholes (Dragon *et al.* 2009; Górski 2021).

The upward flow phenomenon in the Wielkopolska region crucially requires monitoring and thorough understanding, as it can lead to a de-

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crease in the usability of the recharged aquifers (Dragon, Górski 2003; Dragon *et al.* 2006, 2007; Górski 2021). This is due to the characteristic features of Miocene aquifer waters (Macioszczyk *et al.* 1972; Macioszczyk 1973; Ziętkowiak 1988; Dragon *et al.* 2005, 2007; Kotowski, Kachnic 2007; Siepak *et al.* 2010; Górski *et al.* 2012, 2014; Latour *et al.* 2015; Drobnik, Latour 2016). These waters are primarily characterised by a high humic acid content and their stability in dissolved form (Drobnik, Latour 2016), as well as elevated chloride concentrations (>20 mg/L), and low manganese concentrations (<0.1 mg/L) (Górski *et al.* 2012). Due to their specific composition, they often exhibit a brown coloration. Waters are classified as coloured when their hue exceeds 80 mg Pt/L, as observed in the Śrem region (Górski 1989; Drobnik, Latour 2016). Because of these properties, coloured Miocene aquifer waters are considered unsuitable for municipal use (Drobnik, Latour 2016). Depending on the mechanism of upward flow, varying degrees of Miocene water constituents may be transported to the recharged aquifers.

Research conducted by Dragon *et al.* (2005) in the Śrem area using a multilevel piezometer revealed that with increasing depth, elevated concentrations of Cl^- , Na^+ , and total dissolved solids were observed in the waters of the Warsaw–Berlin ice-marginal valley. Additionally, in the sediments collected during piezometer drilling, an increase in organic matter content with depth was observed. This was associated with the occurrence of Miocene water upward flow in this area.

Due to climate change, groundwater levels are declining worldwide (Jasechko *et al.* 2024). This issue also affects Poland (Olichwer *et al.* 2015; Kubiak-Wójcicka, Machula 2020; Kaznowska *et al.* 2024). Considering the infiltration recharge of the Miocene aquifer in Wielkopolska, regular monitoring of upward flow occurrences is recommended (Górski 1989; Dąbrowski *et al.* 2011). Furthermore, due to the demonstrated negative impact on the usability of Quaternary aquifers (Dragon, Górski 2003; Dragon *et al.* 2006; Górski 2021), it is essential to enhance understanding of the identification and effects of the upward flow of Miocene aquifer water in the Śrem area.

This paper aims to: (1) assess the upward flow of Miocene aquifer water based on changes in the hydrogeochemical characteristics of Warsaw–Berlin ice-marginal valley waters in the Śrem area; (2) investigate the vertical distribution of macro element (ME) and trace element (TE)

concentrations (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) in the Warsaw–Berlin ice-marginal valley waters and assess the relationship between their variability and the influence of upward flow; and (3) evaluate the impact of the upward flow of Miocene aquifer water on the quality of the Quaternary aquifer.

Materials and methods

Research area

The location of study area is in Wielkopolska, within the geographical mesoregion of the Śrem Basin (Solon *et al.* 2018). The object of the study was a multilevel piezometer in Śrem, situated at the “Przywale” well-field (Fig. 1). However, it is located outside the depression cone caused by groundwater exploitation (Dragon *et al.* 2005). The piezometer has four individually constructed well screens at depths about 4.5, 11, 16, and 23 meters below ground level (considering the upper edge of the well screen), designated as Sr1, Sr2, Sr3 and Sr4, respectively (Fig. 2; Dragon *et al.* 2005; Siepak 2005). All four well screens were embedded as a set, forming a multilevel piezometer. These screens are installed in sediments of the Warsaw–Berlin ice-marginal valley. The aquifer is divided into two parts: the upper part is mainly composed of fluvial fine- and medium-grained sands, approximately 10 meters thick, containing silty sediment inserts with organic matter and low carbonate content. The lower part consists of fluvio-glacial river formations represented by coarse-grained sands and gravelly sands. At a depth of 25 meters below ground level, there is a layer of Neogene clays, which separate the Quaternary and Miocene aquifers. This clay layer is thick – about 50 meters. The multilevel piezometer is in a grassland area and no significant sources of pollution were found in its surroundings (Fig. 1).

Sample collection and preparation

Fieldwork took place on 17 October, 2022. Samples were taken in order, from the deepest level (Sr4) to the shallowest level (Sr1) relative to ground level. Between each successive sampling, a 30-minute pumping of the piezometer at the level sampled was performed. During the entire pumping process, the depth of the water table at all levels was checked every 5 minutes to ensure that there was no mixing of water from the differ-

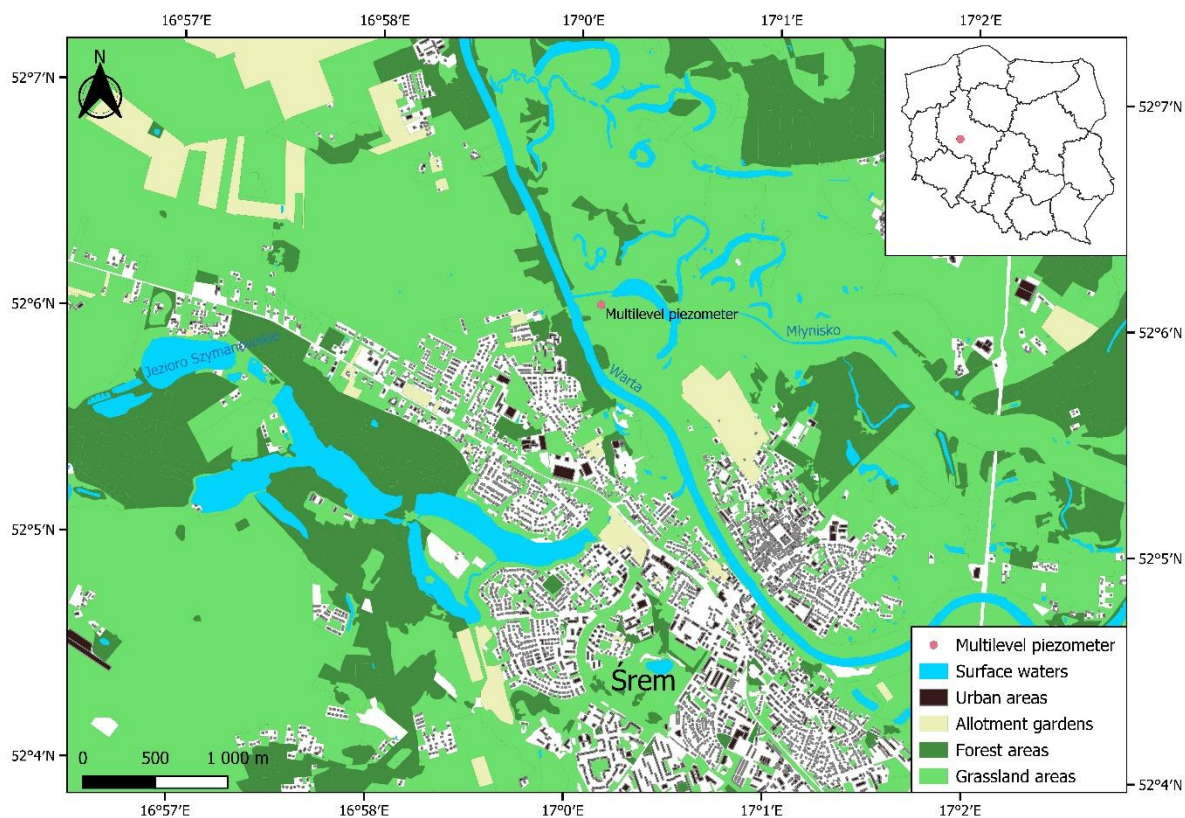


Fig. 1. The location of a multilevel piezometer

ent depths. The Solinst 101 Water Level Meter (Solinst, Canada) was used for this. Temperature, pH and electrolytic conductivity were measured *in-situ* conditions using a Multi 350i multifunctional measuring device, from WTW (Weilheim, Germany). The accuracy of the measured parameters was $\pm 0.2^\circ\text{C}$ for temperature ± 0.004 for pH and $\pm 0.2 \mu\text{S}/\text{cm}$ for electrolytic conductivity, respectively. Three 250-ml water samples from each level were collected into Nalgene® polyethylene (HDPE) bottles. Samples were fixed *in situ* with 60% HNO_3 Ultrapur® (to $\text{pH} < 2$) for TE analysis and CHCl_3 Pro Analysis® (Merck, Darmstadt, Germany) for ion analysis. After collecting, the samples were transported to the chemical laboratory at a temperature of $4 \pm 2.5^\circ\text{C}$.

Chemical analysis

Cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+}) and anions (Cl^- , NO_3^- , NO_2^- , SO_4^{2-} , PO_4^{3-}) were determined in the water samples using an ion chromatograph (IC) from Metrohm (Metrohm, Switzerland), model 881Compact IC Pro (Walna, Siepak 2012; Siepak *et al.* 2023). Determinations of TEs (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were performed using inductively coupled plasma triple

quadrupole mass spectrometry (ICP-QQQ-MS), model 8800 Triple Quad, from Agilent Technologies (Japan) (Siepak, Sojka 2017; Śniady *et al.* 2024ab). Alkalinity (expressing HCO_3^- concentration) was measured by *in situ* titration with HCl (0.1 N) using methyl orange as an indicator. As a quality control measure, the ionic error balance was calculated. The calculated error did not exceed $\pm 3\%$. Chemical oxygen demand (COD) was measured using the permanganate method.

Reagents

Standard solutions from Merck (Merck, Darmstadt, Germany) and CPChem (C.P.A. Ltd Stara Zagora, Bulgaria) were used in the IC determinations. The mobile phase for cations and anions was prepared from Fluka reagents (Sigma-Aldrich, Steinheim, Switzerland). Multi-element standard solutions from VHG Labs (Manchester, USA) with a stock concentration of $100 \mu\text{g}/\text{mL}$ were used for the ICP-QQQ-MS technique determinations. Ultrapure reagents and $18.2 \text{ M}\Omega \cdot \text{cm}$ deionised water purified using a Direct-Q® 3 Ultrapure Water System device (Millipore, France) was used. Certified reference material 1643f (National Institute of Standards and Technology, USA),

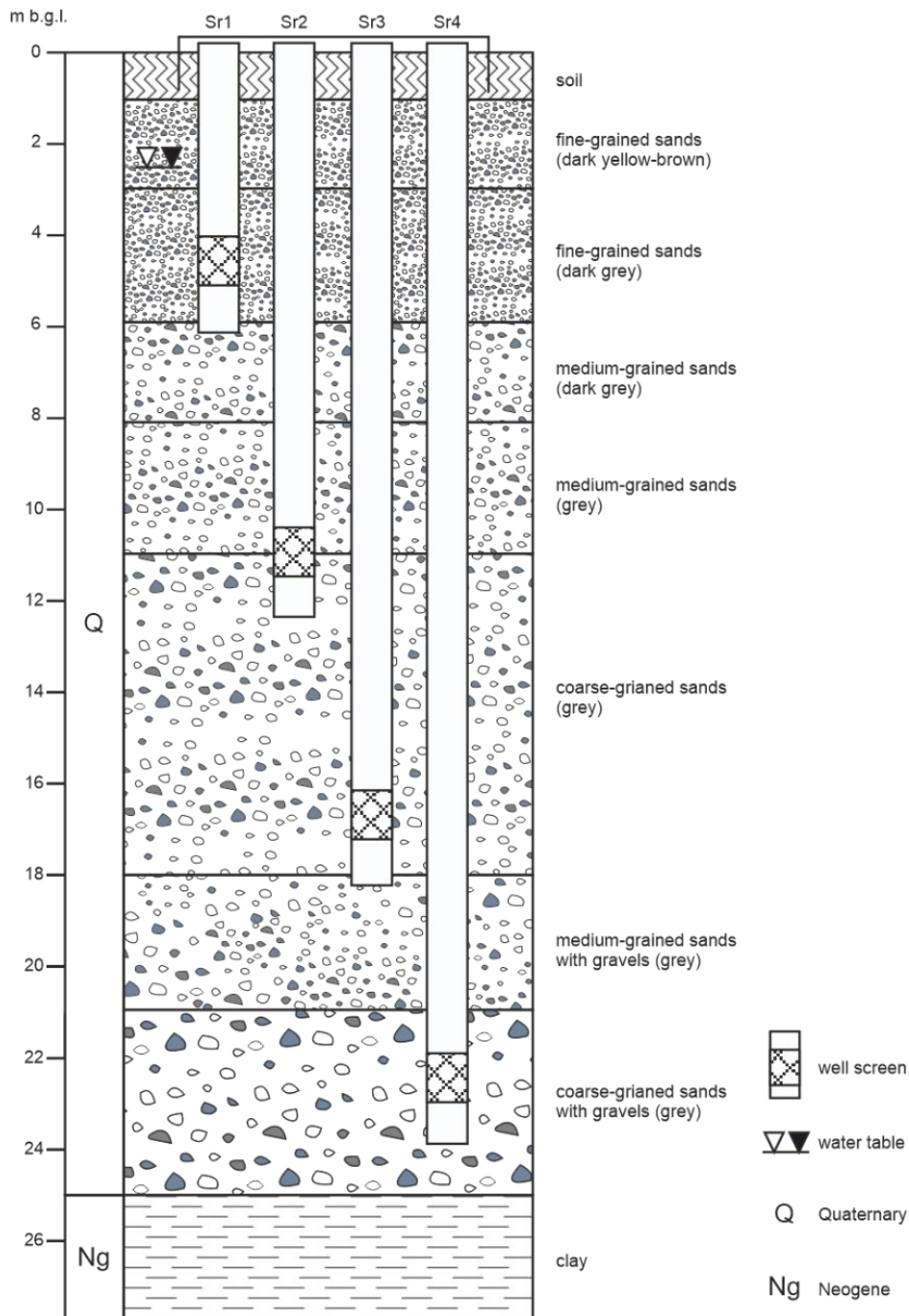


Fig. 2. Scheme of a multilevel piezometer

RAIN-97 and PERADE-09 (Environment Canada) were used to validate the results obtained.

Data analysis and water quality assessment

Based on the obtained results for anions and cations, the waters from Warsaw–Berlin ice-marginal valley aquifer was classified according to the Szczukariew–Prikłński classification (Alekin 1956; Macioszczyk, Dobrzyński 2007). Addition-

ally, the results were presented using a Piper diagram (Piper 1944), prepared with an Excel template developed by Stosch (2022). The data for charting groundwater level changes for the Quaternary and Miocene aquifers were taken from the Polish Hydrogeological Survey's Hydrogeological Annual Reports for 2003–2014 (Kazimierski 2005–2014; Sadurski 2015). Graphical materials were prepared using Microsoft Excel, version 2503 (Microsoft Corporation, Redmond,

WA, USA), CorelDRAW Graphics Suite 2019 (Corel Corporation, Ottawa, ON, Canada), and QGIS version 3.40.5 (QGIS Development Team 2024).

The Arithmetic Weight Water Quality Index (WQI) (Tyagi et al. 2013) was used to assess the vertical variability of groundwater in the Warsaw–Berlin ice-marginal valley regarding parameters associated with the occurrence of Miocene aquifer water upward flow in this region. The WQI calculation method was adapted from Zakir *et al.* (2020) and is performed in several steps.

Step I: Parameters potentially related to water upward flow in the Śrem region were selected based on both current and previous studies (Dragon *et al.* 2005; Siepak *et al.* 2010; Górski *et al.* 2012). The following were chosen for calculations: Na⁺ and Cl⁻ ions, and the following TEs: As, Cr, Cu, K⁺ and Zn were excluded from the calculations due to their low harmfulness in drinking water.

Step II: Quality rating scale (Qi) for each selected parameter was computed by the following expression:

$$Q_i = \frac{V_{\text{actual}} \times 100}{V_{\text{standard}}}$$

where, V_{actual} is the calculated value of every one parameter in the analysed water sample. V_{standard} indicates the limit value for a parameter defined according to the “Regulation of the Minister of Health on the quality of water intended for human consumption” (2017) (Zakir *et al.* 2020; Fahimah *et al.* 2024).

Step III: The unit weight (Wi) for each water quality parameter was determined using the following formula:

$$W_i = \frac{K}{V_{\text{standard}}}$$

where, K is the proportionality constant which is calculated using the following equation:

$$K = \frac{1}{\sum(1/V_{\text{standard}})}$$

Step IV: Calculation of WQI following the formula:

$$WQI = \frac{\sum(Q_i \times W_i)}{\sum(W_i)}$$

The groundwater condition assessment scale was adopted from Zakir *et al.* (2020): 0–25 (Excel-

lent), >25–50 (Good), >50–75 (Poor), >75–100 (Very poor) and >100 (Unsuitable).

Results

Water composition

The study of the chemical composition of water using a multilevel piezometer in Śrem demonstrated variation in water chemistry across the vertical profile. The results indicate a transition in water type from HCO₃⁻-Ca²⁺ at point Sr1 to HCO₃⁻-Cl⁻-(SO₄²⁻)-Ca²⁺-Na⁺ at point S3 and below (according to the Szczukariew–Prikłński hydro-geochemical classification). A clear difference in chemical composition was observed between samples Sr3 and Sr4 and samples Sr1 and Sr2 (Fig. 3). The water temperature varied slightly from 10.2°C at point Sr1 to 11.1°C at the other points. pH also did not change significantly and ranged between 6.91 and 7.17. Among the measured parameters, electrical conductivity increased with depth, ranging from 269 to 871 μS/cm. The COD showed an irregular decline, with a peak observed at point Sr2.

Anions such as Cl⁻, SO₄²⁻ and NO₂⁻ also showed an increasing trend with depth. The most significant increase was observed in Cl⁻ concentrations, which rose from 9.13 mg/L at shallower depths to 77.9 mg/L at the deepest point, representing an 8.5-fold increase. NO₂⁻ concentrations remained low, ranging from 0.002 to 0.011 mg/L. SO₄²⁻ concentrations, like Cl⁻, increased substantially from 5.07 to 85.3 mg/L, marking an almost 17-fold rise. In contrast, PO₄³⁻ and NO₃⁻ showed a decreasing trend with depth. PO₄³⁻ concentrations were very low, ranging between 0.08 and 0.12 mg/L. NO₃⁻ peaked at the surface (3.40 mg/L) and gradually decreased to 0.418 mg/L at the deepest piezometer level. HCO₃⁻ was the only major ion that did not exhibit a consistent increasing or decreasing trend, instead showing irregular increasing trend with depth, ranging from 158.6 to 341.6 mg/L.

The concentrations of all analysed cations (Na⁺, NH₄⁺, K⁺, Ca²⁺, Mg²⁺) displayed an increasing trend with depth. This was particularly evident in Na⁺, NH₄⁺, and Mg²⁺, whose concentrations increased to approximately 11, 12 and 3.5 times, respectively. At points Sr3 and Sr4, the NH₄⁺ values were 1.03 and 1.24 mg/l, respectively. K⁺ concentrations slightly increased with depth, from 1.33 to 2.99 mg/L, while Ca²⁺ concentrations doubled, reaching 105.4 mg/L. Detailed results for ions in

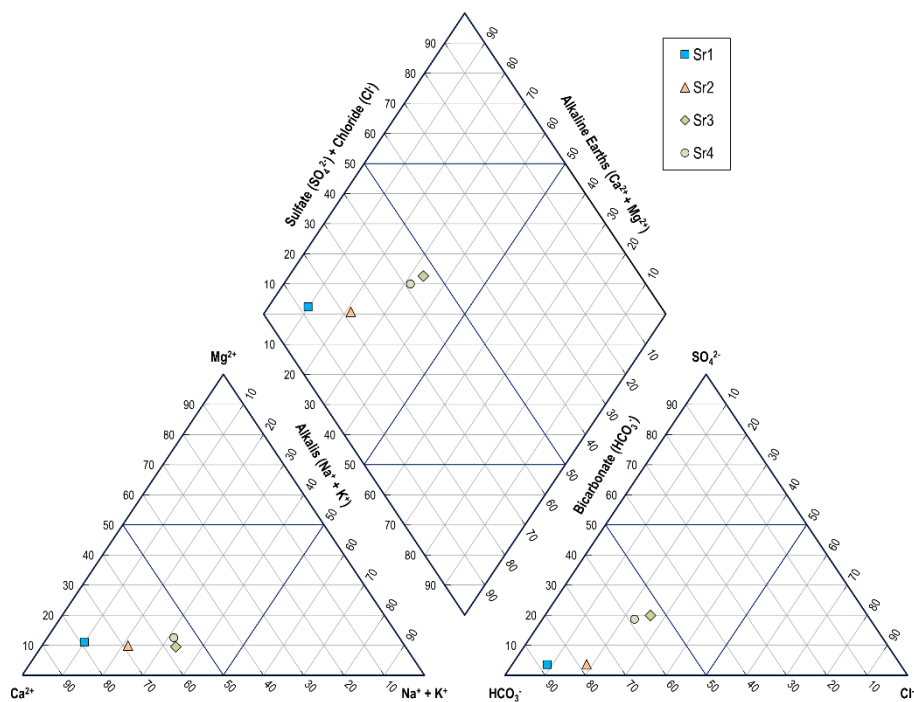


Fig. 3. Piper's diagram showing results for macro elements (ME) depending on piezometer level

Table 1

Results for basic physico-chemical parameters and macro elements (MEs) for a multilevel piezometer in Šrem and for waters of the Miocene aquifer in the Šrem area (Górski *et al.* 2014; Drobnik, Latour 2016)

Parameter	Unit	Multilevel piezometer				Miocene aquifer waters in Šrem area	
		Sr1	Sr2	Sr3	Sr4	Drobnik, Latour (2016)	Górski <i>et al.</i> (2014)
Temperature	°C	10.2	11.1	11.1	11.1	–	–
pH	–	6.91	7.02	7.17	7.03	6.90	7.15
Electrolytic conductivity	μS/cm	269	558	748	871	739.5	718
COD	mgO ₂ /l	8.50	13.3	8.00	7.25	–	70
NH ₄ ⁺	mg/l	0.102	0.495	1.03	1.24	–	<0.05
NO ₂ ⁻		0.002	0.004	0.008	0.011	–	<0.02
NO ₃ ⁻		3.40	1.08	0.928	0.418	–	1.6
Cl ⁻		9.13	38.6	72.7	77.9	84.4	88.6
HCO ₃ ⁻		158.6	280.6	256.2	341.6	360.3	397.3
PO ₄ ³⁻		0.12	0.10	0.08	0.08	–	–
SO ₄ ²⁻		5.07	10.3	74.7	85.3	–	<1.0
Ca ²⁺		46.9	79.9	88.6	105.4	25.6	27.1
Mg ²⁺		3.98	6.97	8.88	14.2	–	12.8
Na ⁺		5.98	27.3	57.8	66.3	142.8	150.0
K ⁺		1.33	1.98	2.84	2.99	–	6.82

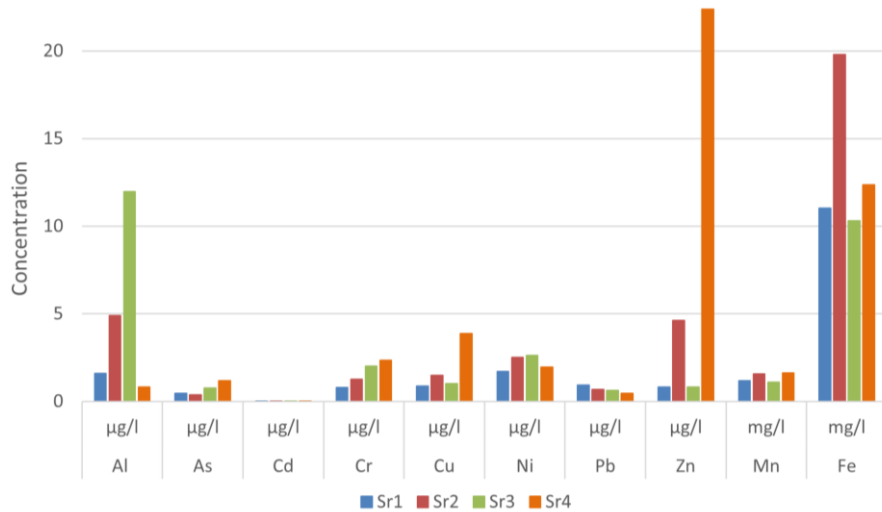


Fig. 4. Trace element (TE) concentrations in samples collected from a multilevel piezometer

the waters of the multilevel piezometer in Śrem are presented in Table 1.

Among the analysed TEs, the highest concentrations were observed for Fe and Mn, with values ranging from 10.3 to 19.8 mg/L for Fe and 1.1 to 1.63 mg/L for Mn. However, their distribution in the vertical profile was irregular. Zn also showed relatively high concentrations at the deepest level, significantly deviating from the other levels (Fig. 4).

The concentrations of Al and Ni increased from Sr1 to point Sr3, reaching 12.0 µg/L and 2.63 µg/L, respectively, but then decreased to 0.83 µg/L and 1.94 µg/L at point Sr4. Cu and As did not show a specific trend, though both reached their highest values at the deepest level, at 3.87 µg/L and 1.18 µg/L, respectively. Cd and Pb had their highest concentrations at point Sr1 and

gradually decreased with depth. Notably, the concentrations of both were low, ranging from 0.002 to 0.004 µg/L for Cd and from 0.46 to 0.92 µg/L for Pb. The only TE that showed a consistent increase with depth was Cr, which rose from 0.80 µg/L at point Sr1 to 2.33 µg/L at point Sr4.

Water quality assessment

The analysis conducted using the WQI indicates that, for the parameters potentially influenced by the upward flow of Miocene aquifer waters, the waters of the Warsaw–Berlin ice-marginal valley exhibited excellent water quality. However, a slight decrease in water quality is noticeable with increasing depth. The calculated WQI values range from 2 at point Sr1 to 11 at point Sr4 (Tab. 2).

Table 2

Water quality index (WQI) results with depth

Sample name	WQI value	Water quality
Sr1	2	Excellent
Sr2	5	Excellent
Sr3	10	Excellent
Sr4	11	Excellent

Discussion

The upward flow of waters with poorer chemical parameters into usable aquifer levels is a significant research topic, and its importance is growing, particularly in areas potentially threatened by water shortages. Groundwater contamination in such areas can especially hinder the achievement of United Nations Sustainable Development Goal 6 (United Nation 2015). Water shortages and the impact of drought on available water resources are increasingly affecting a growing number of countries (Jasechko *et al.* 2024), including Poland (Kubiak-Wójcicka, Machula 2020; Kaznowska *et al.* 2024). This amplifies the need to identify potential threats to water quality from various sources. Śrem is not currently significantly at risk of water shortages; however, conducting research in this area allows for a better understanding of certain upward flow mechanisms. Identifying potential threats posed by water upward flow and the method for its detection requires a detailed understanding of local water circulation conditions. A comprehensive description of these conditions in the Śrem area, including the recharge and drainage zones of the Miocene aquifer, was provided by Górski (1989; Fig. 5). The research conducted in the Śrem area allows conclusions to be drawn that are largely similar to, and expand upon, those found in earlier studies (Górski 1989; Dragon *et al.* 2005; Dąbrowski *et al.* 2011).

The conducted hydrogeochemistry research confirms the continuous occurrence of Miocene aquifer water upward flow in the Śrem area, despite the large-scale decline in the Miocene water levels across Wielkopolska between 1975 and 1993, as demonstrated by Dąbrowski (1995), which resulted from increased groundwater exploitation. However, monitoring studies conducted by the Polish Hydrogeological Survey did not show a declining trend in Miocene water levels in the Śrem area from 2003 to 2011, with an average level of 67.46 meters above sea level (Fig. 6). This level has not changed significantly compared to the analysis conducted by Górski (1989) for the years 1955–1985, when it fluctuated between approximately 67 and 68 meters a.s.l. Similarly, the monitoring conducted by the Polish Hydrogeological Survey did not reveal a decline in Quaternary water levels between 2004 and 2014 (Fig. 6), with recorded results similar to data from previous studies and reports (Górski *et al.* 1998; Dąbrowski *et al.* 2005, 2011). Therefore, it can be assumed with high probability that the hydrogeological conditions in the Śrem area have not changed in

recent years, and the conclusions drawn by Górski (1989), Dragon *et al.* (2005) and Dąbrowski *et al.* (2011) remain valid (Fig. 5). According to Górski (1989), the upward flow in the Śrem area likely occurs along a hydraulically active tectonic fault. This structure is evident within the Jurassic substratum; however, it has not yet been mapped in the Neogene sediments (Fig. 5).

The conducted studies indicate that Na^+ , K^+ , and Cl^- are particularly associated with the upward flow of Miocene waters in the Śrem region, which is consistent with conclusions drawn by other authors, who primarily emphasised the association of upward flow with increasing concentrations of Cl^- and Na^+ in the waters of the Warsaw–Berlin ice-marginal valley aquifer (Górski 1989; Dragon *et al.* 2005). This is confirmed by the comparison of the results obtained with the chemistry of Miocene aquifer waters in Śrem (Tab. 2). The increase in SO_4^{2-} and HCO_3^- with depth should not be linked to the occurrence of upward flow in this area, as it is a typical phenomenon for Quaternary groundwater in temperate zones, resulting from other processes, such as carbonate dissolution and sulphate oxidation from organic matter (Macioszczyk, Dobrzyński 2007; Górski 2022). Additionally, NO_3^- , NO_2^- , and NH_4^+ likely originate from both anthropogenic sources and geogenic processes occurring in the Quaternary deposits of the glacial marginal valley (Żurek 2002; Macioszczyk, Dobrzyński 2007).

The analysis of TEs suggests that the upward flow of waters from the Miocene aquifer in the studied area is likely related to As, Cr, Cu and Zn. Siepak (2005) has observed that As concentrations in the multilevel piezometer in Śrem reached the highest values at point Sr4. The association of As with the occurrence of upward flow was later confirmed by studies conducted by Siepak *et al.* (2010), which demonstrated that As, Cr, Cu and Zn concentrations in the Miocene aquifer in this region were among the highest recorded. Nevertheless, detailed published data on TEs concentrations in the waters of the Miocene aquifer in this area remain limited. Thus, it is recommended to expand future research to determine the exact concentrations of a broader range of TEs, which would enable a better understanding of the upward flow phenomenon in the Śrem region.

Additionally, the high values obtained for Fe and Mn are likely of geogenic origin, being associated with the decomposition of organic matter present in the sediments of the Warsaw–Berlin ice-marginal valley. This is confirmed by documentation for this area (Górski *et al.* 1998; Dąb-

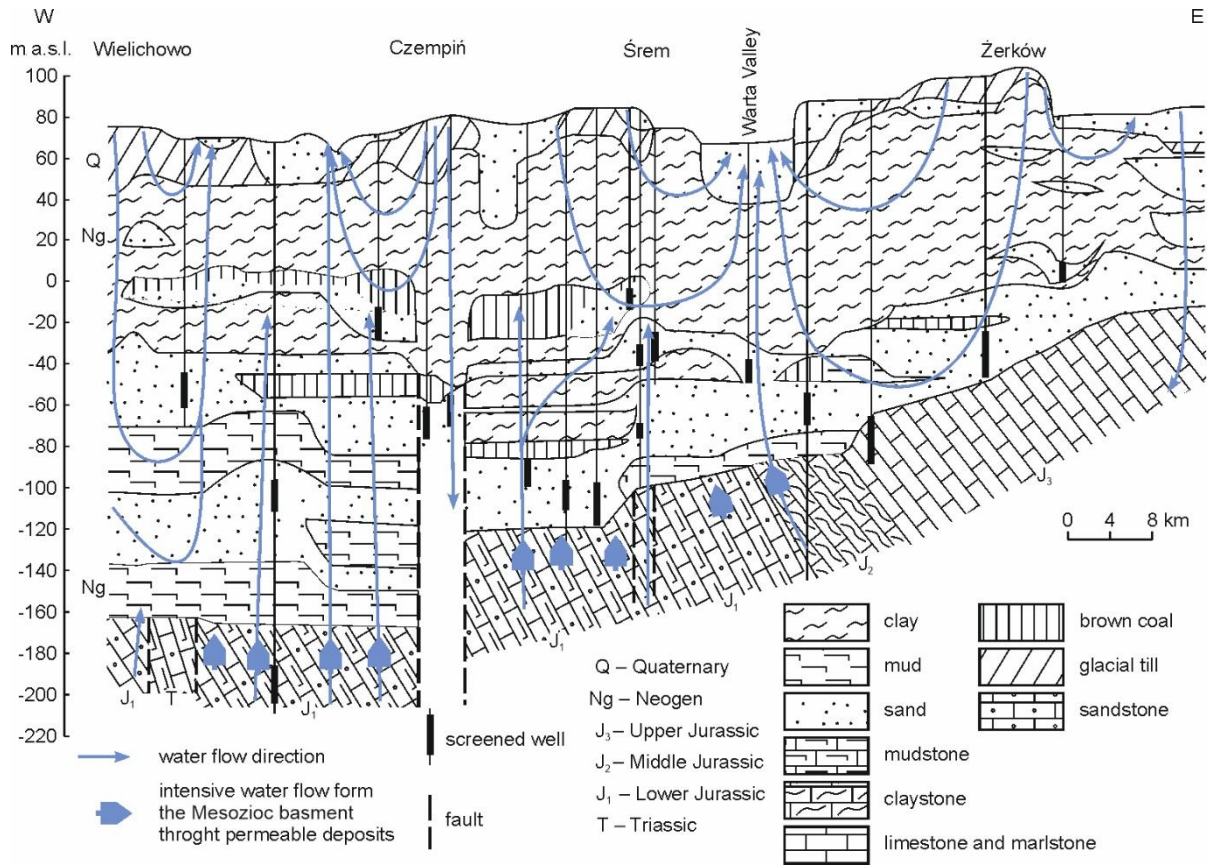


Fig. 5. Hydrogeological cross-section showing the approximate water flow paths in the Śrem region (Górski 1989, modified and simplified)

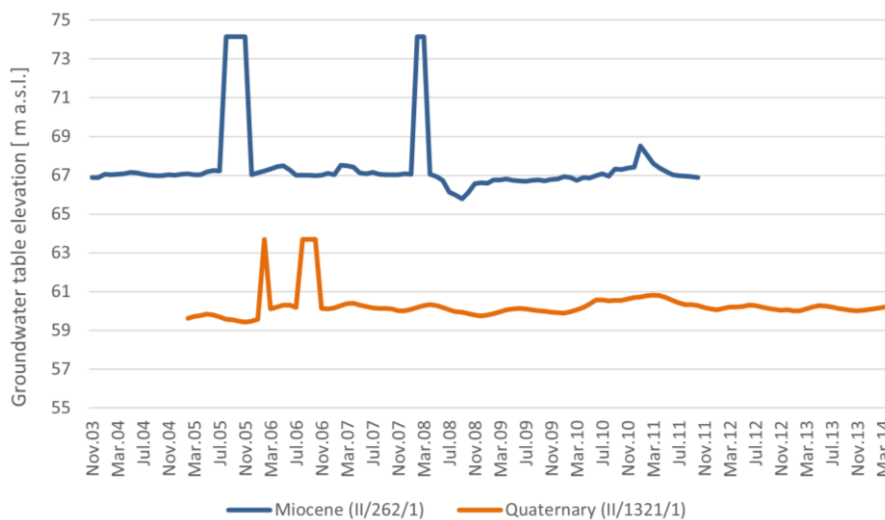


Fig. 6. Groundwater table elevation for the Miocene and Quaternary aquifers in the Śrem area during the monitoring period (2003–2014) by the Polish Hydrogeological Survey (Kazimierski 2005–2014; Sadurski 2015)

rowski *et al.* 2005) and by the conclusions of scientific publications (Górski 1989; Dragon *et al.* 2005). The genesis of Al and Ni is likely also associated with geogenic processes, and their uneven vertical distribution suggests a possible link to the erosion of sulphides and organic matter contained within the sediments (Górski 1989). Pb and Cd did not reach high concentrations, and their decrease with depth may suggest an anthropogenic influence. However, their concentrations are sufficiently low so that it is not possible to identify a specific source.

The water quality assessment using the WQI for elements associated with Miocene aquifer water upward flow (Na^+ and Cl^- , As, Cr, Cu) indicated a slight decrease in water quality with depth. However, the water at all depths maintained an excellent class of quality in terms of the listed components. Therefore, it can be concluded that the upward flow of Miocene aquifer waters in the Śrem region does not significantly affect the usability of the supplied aquifer as a source of drinking water (according to the Ministry of Health Regulation 2017). It should be noted, however, that the upward flow of Miocene waters into Quaternary aquifers in Wielkopolska (especially in areas where the waters are heavily coloured) may limit their use due to a drastic reduction in organoleptic qualities. This is confirmed by the studies conducted by Dragon *et al.* (2007) at the Joanka groundwater intake near Poznań, where upward flow occurs through an improperly constructed well and significantly affects the quality of the Wielkopolska Buried Valley aquifer.

Conclusion

The analysis conducted, involving the determination of MEs and TEs in water collected from the multilevel piezometer located in the area of the Warsaw–Berlin ice-marginal valley in Śrem, revealed the following:

- the upward flow of Miocene aquifer waters into the Quaternary aquifer in Śrem area continues to occur, as confirmed by the analysis of MEs, and the conclusions drawn from earlier studies regarding local water conditions remain valid;
- with increasing depth, there is a marked increase in Cl^- , Na^+ , and K^+ concentrations, associated with the upward flow;
- the upward flow of Miocene waters is not significantly reducing water quality in terms

of the parameters associated with the upward flow, as confirmed by the WQI assessment;

- the upward flow of Miocene aquifer waters may increase the concentrations of certain TEs (As, Cr, Cu, and Zn) in the waters of the Warsaw–Berlin ice-marginal valley aquifer.

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References

- Alekin O.A. 1956. Podstawy hydrochemii. Wydawnictwa Geologiczne, Warszawa.
- Dąbrowski S. 1995. Lowering of piezometric ground water surface in big area Wielkopolska region. *Współczesne problemy hydrogeologii* 7: 101-108.
- Dąbrowski S., Olejnik Z., Trzeciakowska M. 2005. Annex no. 2 to "Dokumentacji zasobów eksploatacyjnych ujęcia wód podziemnych z utworów czwartorzędowych dla m. Śremu" określający obszar zasobowy ujęcia, przy $Q=577 \text{ m}^3/\text{h}$ oraz obszar wpływu wody i granice strefy ochronnej ujęcia wody, przy eksploatacji z wydatkiem $Q=430 \text{ m}^3/\text{h}$. Archive of the Department of Hydrogeology and Water Protection, Institute of Geology, Adam Mickiewicz University, Poznań.
- Dąbrowski S., Rynarzewski W., Straburzyńska-Janiszewska R., Zachaś J., Pawlak A. 2011. The groundwater resources of hydrogeological system in the eastern Wielkopolska lake region. *Biuletyn Państwowego Instytutu Geologicznego* 445: 75-86.
- Dowgiałło J., Kleczkowski A.S., Macioszczyk T., Rózkowski A. (eds.). 2002. Słownik Hydrogeologiczny. Ministerstwo Środowiska i Państwowy Instytut Geologiczny.
- Dragon K., Górski J. 2003. The influence of ground water ascent from tertiary aquifer on ground water chemistry of the Wielkopolska Buried Valley Aquifer. *Współczesne problemy hydrogeologii* 11(2): 125-130.
- Dragon K., Marciniak M., Górski J. 2003. The recognition of the reasons of brown water occurrence in the Wielkopolska Buried Valley Aquifer on the basis of multilevel

- pumping. *Przegląd Geologiczny* 51(2): 151-158.
- Dragon K., Mądrala M., Górski J. 2005. The hydrogeochemical environment of the Warta river valley in the Śrem region and its changes during exploitation. *Współczesne problemy hydrogeologii* 12: 165-172.
- Dragon K., Górski J., Marciniak M., Kasztelan D. 2006. Use of groundwater numerical modeling for the assessment of the "brown" water migration in the Joanka well-field region near Poznan city. *Geologos* 10: 35-46.
- Dragon K., Górski J., Marciniak M., Kasztelan D. 2007. The origin and conditions of brown water migration in the Wielkopolska Buried Valley Aquifer. *Geologos* 12, *Monographiae* 4.
- Dragon K., Górski J., Marciniak M., Kasztelan D. 2009. Use of mathematical modeling to investigate inter-aquifer contamination by organic-rich water through an unplugged well (central Wielkopolska, Poland). *Hydrogeology Journal* 17: 1257-1564.
DOI: 10.1007/s10040-009-0432-4
- Drobnik M., Latour T. 2016. Basic physicochemical and chemical properties and possibility of usage of gradually coagulating brown ground waters from the Miocene aquifer of the Wielkopolska region. *Przegląd Geologiczny* 64(12): 1034-1039.
- Fahimah N., Salami I.R.S., Oginawati K., Muhiarto H. 2024. Appraisal of pollution levels and non-carcinogenic health risks associated with the emergence of heavy metals in Indonesian community water for sanitation, hygiene, and consumption. *Emerging Contaminants* 10(3): 100313.
DOI: 10.1016/j.emcon.2024.100313
- Górski J. 1989. Główne problemy chemizmu wód podziemnych utworów kenozoiku środkowej Wielkopolski. *Zeszyty Naukowe Akademii Górniczo-Hutniczej im. Stanisława Staszica* 45.
- Górski J. 2021. Ułatwiona migracja zanieczyszczeń do użytkowych poziomów wodonośnych w wyniku wad technicznych studni i otworów hydrogeologicznych. In: E. Krogulec (Ed.), *Wybrane zagadnienia hydrogeologiczne oraz różne aspekty związane z eksploatacją wód podziemnych*. Polskie Zrzeszenie Inżynierów i Techników Sanitarnych Oddział Częstochowa: 53-61.
DOI: 10.18778/8220-655-5.05
- Górski J. 2022. Ochrona wód podziemnych w Polsce. Wyd. Naukowe UAM, Poznań.
- Górski J., Przybyłek J., Kasztelan D., Remisz W. 1998. Dokumentacja hydrogeologiczna strefy ochronnej ujęcia wody stanowiąca aneks do "Dokumentacji zasobów ujęcia wód podziemnych z utworów czwartorzędowych dla miasta Śremu". Archive of the Department of Hydrogeology and Water Protection, Institute of Geology, Adam Mickiewicz University, Poznań.
- Górski J., Latour T., Siepak M., Drobnik M., Sziwa D. 2012. Prospects of using brown water from the Miocene aquifer of the Wielkopolska region for physiotherapy. *Biuletyn Państwowego Instytutu Geologicznego* 452: 59-66.
- Górski J., Latour T., Siepak M., Drobnik M., Sziwa D. 2014. Wody zabarwione w utworach miocenu środkowej Wielkopolski występowanie, geneza, możliwość wykorzystania w przyrodolecznictwie. *Studia i Prace z Geografii i Geologii* 40.
- Jasechko S., Seybold H., Perrone D., Fan Y., Shamsudduha M., Taylor R.G., Fallatah O., Kirchner J.W. 2024. Rapid groundwater decline and some cases of recovery in aquifers globally. *Nature* 625: 715-721.
DOI: 10.1038/s41586-023-06879-8
- Kazimierski B. (ed.). 2005–2014. Hydrogeological Annual Report Polish Hydrogeological Survey. Hydrological year 2004–2013. Polish Geological Institute – National Research Institute, Warszawa.
- Kaznowska E., Wasilewicz M., Hejduk L., Krajewski A., Hejduk A. 2024. The Groundwater Resources in the Mazovian Lowland in Central Poland during the Dry Decade of 2011–2020. *Water* 16(2): 201.
DOI: 10.3390/w16020201
- Kotowski T., Kachnic M. 2007. The formation of chemical composition of groundwaters from the Miocene and Pleistocene aquifers within of the buried valley near Wysoka (Krajeńskie Lake District). *Biuletyn Państwowego Instytutu Geologicznego* 427: 47-60.
- Kubiak-Wójcicka K., Machula S. 2020. Influence of Climate Changes on the State of Water Resources in Poland and Their Usage. *Geosciences* 10(8): 312.
DOI: 10.3390/geosciences10080312
- Latour T., Drobnik M., Sziwa D. 2015. Studies to determine whether underground waters in Wielkopolska region (Poland) containing humus substances are suitable for practical purposes. *Roczniki Państwowego Zakładu Higieny* 66(1): 39-44.

- Macioszczyk A. 1973. Chemizm wód podziemnych występujących w utworach miocenu niżowego Polski. *Biuletyn Państwowego Instytut Geologicznego* 277(3): 293-312.
- Macioszczyk A., Dobrzyński D. 2007. Hydrogeochemia strefy aktywnej wymiany wód podziemnych. Wyd. Naukowe PWN, Warszawa.
- Macioszczyk A., Pich J., Płochniewski Z. 1972. Chemical nature of ground waters in tertiary formations within the area of Poland (except for the Carpatians). *Kwartalnik Geologiczny* 16(2): 428-445.
- Olichwer T., Tarka R. 2015. Impact of climate change on the groundwater run-off in southwest Poland. *Open Geosciences* 7(1): 1-14. DOI: 10.1515/geo-2015-0001
- Piper A.M. 1944. A graphic procedure in the geochemical interpretation of water-analyses. *Eos, Transactions American Geophysical Union* 25(6): 914-928. DOI: 10.1029/TR025i006p00914
- QGIS Development Team 2024. *QGIS Geographic Information System*. Open Source Geospatial Foundation Project.
- Regulation of the Minister of Health (2017) on the quality of water intended for human consumption* (Journal of Laws 2017 item 2294).
- Sadurski A. (ed.) 2015. Hydrogeological Annual Report Polish Hydrogeological Survey. Hydrological year 2014. Polish Geological Institute – National Research Institute, Warszawa.
- Siepak M. 2005. Arsenic, antimony and selenium occurred in ground water of the Warta River valley between Poznań and Śrem. *Geologos* 7, *Monographiae* 1.
- Siepak M., Sojka M. 2017. Application of multivariate statistical approach to identify trace elements sources in surface waters: A case study of Kowalskie and Stare Miasto reservoirs, Poland. *Environmental Monitoring and Assessment* 189: 364. DOI: 10.1007/s10661-017-6089-x
- Siepak M., Lewandowska A., Sojka M. 2023. Variability in the Chemical Composition of Spring Waters in the Postomia River Catchment (Northwest Poland). *Water* 15(1): 157. DOI: 10.3390/w15010157
- Siepak M., Novotný K., Vaculović T., Górski J., Przybyłek J. 2010. Variability of chemical composition of groundwater at the Miocene aquifer in the Poznań-Gostyń fault graben region (Poland). *Biuletyn Państwowego Instytutu Geologicznego* 441: 145-156.
- Solon J., Borzyszkowski J., Bidłasik M., Richling A., Badora K., Balon J., Brzezińska-Wójcik T., Chabudziński Ł., Dobrowolski R., Grzegorzczak I., Jodłowski M., Kis-towski M., Kot R., Krąż P., Lechnio J.R., Macias A., Majchrowska A., Malinowska E., Migoń P., Myga-Piątek U., Nita J., Papińska E., Rodzik J., Strzyż M., Terpiłowski S., Ziaja W. 2018. Physico-geographical mesoregions of Poland: Verification and adjustment of boundaries on the basis of contemporary spatial data. *Geographia Polonica* 91(2): 143-170. DOI: 10.7163/GPol.0115
- Stosch H.G. 2022. Excel template to plot hydrochemical data into a Piper diagram (Version 1.0). *Zenodo*. DOI: 10.5281/zenodo.5994292
- Śniady I., Orzechowska W., Smardz E., Siepak M. 2024a. Trace elements in Turkusowe Lake waters and bottom sediments (Wolin National Park, Poland). *Przegląd Geograficzny* 96(4): 459-471. DOI: 10.7163/PrzG.2024.4.3
- Śniady I., Zięba M., Wojciechowska J., Majewski M., Siepak M. 2024b. Condition of the post-reclamation Przykona reservoir (Turek, Poland): water and sediment chemistry. *Acta Geographica Lodziensia* 114: 19-34. DOI: 10.26485/AGL/2024/114/2
- Tyagi S., Sharma B., Singh P., Rajendra Dobhal R. 2013. Water Quality Assessment in Terms of Water Quality Index. *American Journal of Water Resources* 1(2): 34-38. DOI: 10.12691/ajwr-1-3-3
- United Nations 2015. Sustainable development goal 6: ensure availability and sustainable management of water and sanitation for all. United Nation, New York.
- Walna B., Siepak M. 2012. Heavy metals: Their pathway from the ground, groundwater and springs to Lake Góreckie (Poland). *Environmental Monitoring and Assessment* 184: 3315-3340. DOI: 10.1007/s10661-011-2191-7
- Zakir H.M., Sharminb S., Akter A. Rahman M.S. 2020. Assessment of health risk of heavy metals and water quality indices for irrigation and drinking suitability of waters: a case study of Jamalpur Sadar area, Bangladesh. *Environmental Advances* 2: 100005. DOI: 10.1016/j.envadv.2020.100005
- Ziętkowiak Z. 1988. Chemistry of groundwater and its regional variability, as exemplified by a selected portion of middle Greater Poland. *Badania Fizjograficzne nad Polską Zachodnią, Seria A, Geografia Fizyczna* 40: 75-85.
- Żurek A. 2002. Nitrates in groundwater – an overview. *Biuletyn Państwowego Instytutu Geologicznego* 400: 115-141.