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title: **Variability of chemical composition of groundwater at the Miocene aquifer in the Poznań-Gostyń fault graben region (Poland)**

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INTRODUCTION

The water supply system in the Region of Wielkopolska (Poland) is to a large extent based on the Miocene aquifer. However, the use of water from this aquifer is difficult due to a significant variability of chemical composition of water related to the occurrence of dispersed organic matter within the sand water-bearing formations as well as to the present and paleohydrogeological conditions of water circulation systems (Górski, 1989). One of the main hydrogeochemical anomalies is connected with the Poznań-Gostyń fault graben, developed longitudinally in the Mesozoic basement of the Miocene aquifer. The fault graben region is marked by the occurrence of active hydraulic tectonic faults, with deep circulating water ascending from the Mesozoic basement which consists mainly of weakly permeable carbonate and mud formations of the Jurassic and Cretaceous periods. The ascent of water is also noticeable in the outcrop belt of the Lower Jurassic deposits consisting of sand and mud.

The problems of variable water chemistry in the Miocene formations in the Wielkopolska Region and the relations of water chemistry to the current and paleohydrogeological conditions of water circulation were discussed in papers by Błaszyk (1966), Pawuła (1975), Przybyłek (1986), Górski (1989), Górski, Przybyłek (1996), Przybyłek et al. (2000), Dąbrowski et al. (2000). The above mentioned papers were mainly based on archive hydrochemical data and they did not concern the analysis of microcomponents. This paper is based on current analyses comprising the microcomponents which have not been analysed so far, or which have been studied only in the region of Poznań (Siepak et al., 2006; Siepak et al., 2007).

The aim of this study was: (1) the determination of the current state of water chemistry of the Miocene aquifer, with emphasis on microcomponents; (2) the characteristics of hydrochemical zones against the background of groundwater flow and geological structure; (3) the use of the results of physicochemical parameters determinations of the studied water, and especially of the microcomponents, in the identification of groundwater ascent from the Mesozoic to the Miocene aquifer in the zone of the Poznań-Gostyń fault graben.

MATERIALS AND METHODS

Study area

A part of the groundwater Miocene aquifer in the area of the Poznań-Gostyń fault graben (Wielkopolska, Poland) was selected for the study. In the north, the study area is limited by the parallel length of the Warta River, and its southern borderline is the Barycz Old Valley. The western and eastern borderlines were defined arbitrarily and they have no structural reference. The western borderline runs 10 km west from Leszno, while the eastern borderline runs 20 km east from Gostyń (Figure 1).

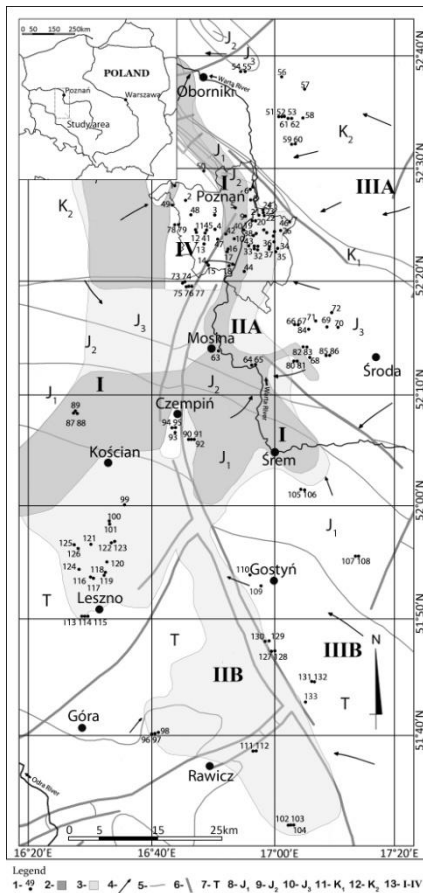


Figure 1. The occurrence of zones of anomalous salinity and colour of water at the Miocene aquifer against the background of the main structural elements of the Mesozoic basement. 1 — sample collection points; 2 — the zone of water colour >80 mg Pt/L; 3 — the zone of chloride content >20 mg/L; 4 — the main directions of the Miocene aquifer groundwater flow; 5 — stratigraphic borders; 6 — faults; 7 — Triassic; 8 — Lower Jurassic; 9 — Middle Jurassic; 10 — Upper Jurassic; 11 — Lower Cretaceous; 12 — Upper Cretaceous; 13 — hydrochemical zones (see the text for description).

Hydrogeology

Three water-bearing layers (lower, middle and upper) can be distinguished within the Miocene. The layers combine to create one aquifer to the west from Poznań (Dąbrowski et al., 2007). The lower layer consists of the lower Miocene sands with the thickness of approximately 30–40 metres. Between the lower and upper water-bearing layer there is a carbonate series with silts, in which the middle water-bearing layer occurs. It consists of fine, dusty, locally middle-grained and coarse sands with the thickness of 1 to 50 metres. The upper water-bearing layer consists of fine-grained and dusty sands of the middle and upper Miocene (so called adamowskie layers sands). Their thickness amounts to approximately 20–40 m (maximum up to 80 m) (Dąbrowski et al., 2007).

The recharge of the Miocene aquifer results from the process of percolation of water from the Quaternary aquifers. The process occurs especially in the places of decreased thickness of isolation layers, also where the layers of Poznań silts were glaciotectionally disturbed and locally, in the places of hydraulic contact through hydrogeological windows, which were formed as a result of erosive cuts in Poznań silts in the areas of buried valleys (Przybyłek et al., 2000; Dąbrowski et al., 2007). The ascent flow of water from the lower basement occurs in the deepest parts of Miocene formations, where basement deposits of good permeability occur and along some hydraulically-active tectonic faults. The natural regional discharge zone of the discussed groundwater is the Warsaw-Berlin Old Valley, the Barycz Old Valley and the Warta Valley.

Sample collection

The groundwater samples from the Miocene aquifer were collected for physicochemical analysis from 133 wells. The measurements of water temperature, pH reaction, redox potential, electrical conductivity and dissolved oxygen were taken directly on the research site. The measurements were taken using the *MULTI 1971* (WTW, Weilheim, Germany). The colour and alkalinity were also determined on the research site. The water samples were collected in Nalgene® (Rochester, USA) polyethylene bottles (LDPE). Depending on the determined water quality indicators, the samples were fixed with HNO₃ or CHCl₃ (Merck, Darmstadt, Germany). After the collection, the samples were stored at 4°C.

Chemical analysis

In order to determine the anions (Cl⁻, SO₄²⁻, F⁻, PO₄³⁻, NO₃⁻) and the cations (NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺), Dionex DX-120 ion chromatograph (IC) (Dionex, USA) was used. The determinations of Fe, Mn, Cr, Cd, Cu, Zn, Pb and Ni were performed by atomic absorption spectrometry with flame atomization (F-AAS) using an Analyst 300 apparatus produced by Perkin Elmer (Perkin Elmer, Norwalk, CT, USA). As, Sb and Se were determined by atomic absorption spectrometry combined with the hydride generation technique (HG-AAS) using a Varian apparatus (Spectra 280FS, Varian, Australia). Be, V and Mo were determined by the technique of inductively coupled plasma with atomic emission detection (ICP-AES); the system consisted of the spectrometer Jobin-Yvon Model 170 Ultrace (Jobin-Yvon, Longjumeau, France). Ag, Al, Ba, Li, Tl, Ce, Cs, La, Nd, Pr and Sm determinations were performed using the technique of inductively coupled plasma with mass spectrometry detection (ICP-MS), using a 7500ce apparatus produced by Agilent (Agilent Technologies, Inc. Headquarters, USA). Hg content was determined by cold vapour atomic fluorescence spectroscopy (CV-AFS) using Millennium Merlin Analyzer 10.025 (PSAnalytical, England).

The determinations of total alkalinity were performed by the titration of the 0.1 mol/L HCl water sample against methyl orange as an indicator. The obtained results were verified based on the ion balance. The difference between the sum of cations and anions did not exceed ± 5%.

RESULTS AND DISCUSSION

The general characteristics of groundwater chemistry at the Miocene aquifer

The groundwater of the Wielkopolska Miocene aquifer is marked by weakly acidic to weakly alkaline pH reaction (from 6.20 to 8.08). Electrolytic conductivity ranges from 387 μS/cm to

2140 $\mu\text{S}/\text{cm}$, and TDS from 193 to 1049 mg/L. A characteristic feature of the groundwater at the Miocene aquifer is its variability in terms of colour intensity and chloride concentrations (Figure 2A). The regions of very high colour intensity are noticeable (>80 mg Pt/L, and even as large as several thousand mg Pt/L), as well as those marked by very low colour intensity (<20 mg Pt/L) — Figure 1. The water marked by high colour intensity and increased salinity occurs zonally, and its origin is related to the flow of the deep circulation water from the Mesozoic basement through tectonic faults and/or formations with increased permeability in the basement (Lower Jurassic formations). High colour intensity occurs in these parts of the discharge zones where the water from the Mesozoic basement had difficulties flowing to the surface discharge zones. On the other hand, the low concentrations of colour are characteristic for the regions where the conditions for intensive water exchange existed. The zones of water colour intensity overlap with the salinity zones (Figure 1). The water hardness, from 1.14 to 12.9 mval/L, is marked by clearly regional variability. The lowest hardness is observed in the zones of water ascent from the Mesozoic basement, and the highest – in the areas of recharge from Quaternary aquifers and the zones where water flows to the discharge zones (transit zones). Significant variability of macrocomponents concentrations in terms of Na^+ , Ca^{2+} , Mg^{2+} , Fe and SO_4^{2-} was observed (Figure 2A), while in the case of microcomponents, clear variability of concentrations for F, Al, Ni, Pb, Cu, Cr, Ba, Hg, Mo, Li and Se was stated (Figure 2B). Such clear differences were not observed for V, Cd, Be, Ag, Tl or Cs.

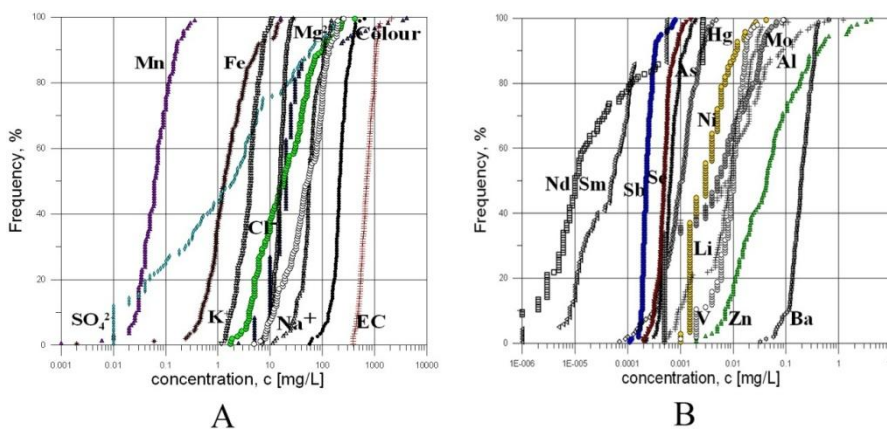


Figure 2. Cumulative frequency curves for selected macro-components (A) and micro-components (B)

Hydrochemical zonality

Based on the spatial distribution of hydrochemical parameters, and especially of colour, Cl⁻, Mn and hardness, taking into consideration the geological structure of the Mesozoic basement and hydrodynamic conditions, four hydrochemical zones marked with the Roman numbers I to IV (Figure 1) were separated in the study area. The variability of water chemistry in the zones was presented on the Piper diagram (Figure 3).

Zone I comprises the area of water with high colour intensity (>80 mg Pt/L). The zone stretches along the Szamotyły structure and the Poznań fault. It also comprises the outcrop belt of Lower Jurassic in the region of Wielichowo-Śrem (Figure 1). It is the area where, due to the hindered exchange conditions of water discharged from the Mesozoic basement, high colour intensity of

water occurs and increased concentration of chlorides (>20 mg/L) as well as the lowest hardness (<4 mval/L) may be observed, and the concentration of manganese amounts (<0.1 mg/L). This zone is clearly marked by microcomponent concentrations higher than in the other zones. These are especially the concentrations of As, Sb, Se, Cu and, less significantly of Pb, Ni and Cr. The concentrations of iron are also higher. The occurrence of increased concentrations of these parameters should be linked to the enrichment of the ground environment and groundwater in humus substances.

Zone II comprises the areas where, similarly to zone I, the water ascent from the Mesozoic basement occurs (Figure 3), but the water colour intensity does not exceed the anomalous limit (>80 mg Pt/L). In some parts of this zone, the discharge of water from the Miocene to the Quaternary aquifer may be observed. The features distinguishing this zone are: the concentration of chlorides >20 mg/L and relatively low hardness, generally <5 mval/L. In terms of micro-components, similarly to zone I, the increased concentrations of Li, Al, Mo, Cr and Hg may be observed. The zone comprises the areas marked by varied conditions of water ascent from the Mesozoic basement. In the northern part (from Poznań to Czempin), the recharge originates mainly in the Lower Jurassic formations. In the southern part (from Czempin to Rawicz), the recharge originates in the Triassic formations. The difference also concerns the conditions of water circulation. In the northern part, the zone of ascent is relatively narrow. The water here flows to the Quaternary in the Warta Valley. In the southern part, the water ascending from the Triassic basement moves south-west to the discharge zone in the Warsaw-Berlin Old Valley. As a result, zone II was divided into IIA and IIB (Figure 1). Certain differences may be observed in the water from these zones in terms of macro- and microcomponents. Lower concentrations of Cl^- in zone IIB are observed, while the concentrations of SO_4^{2-} are slightly higher. In relation to microcomponents, the concentrations of Al, Mo and Hg are much higher in zone IIB than in zone IIA.

Zones IIIA and IIIB comprise the areas of the Miocene recharge from the upper aquifers, as well as of the water transit to the discharge zones. The central parts of the recharge zones are located east- and southwards from the studied area. Thus, in the analysed area, water typical for the transit zones prevails (Figure 3). It is marked by chloride concentration <20 mg/L, hardness higher than 4 mval/L and manganese concentration >0.1 mg/L. The division into zones IIIA and IIIB was made considering the different conditions of water recharge and flow to the north and south of the Warsaw-Berlin Old Valley. In the basement of zone IIIA, the Upper Jurassic and Cretaceous deposits occur, while in zone IIIB the Triassic and lower Jurassic deposits occur (Figure 1). The water chemistry in zones IIIA and IIIB is similar both in relation to macro- and microcomponents. However, the hardness, SO_4^{2-} and Ca^{2+} concentrations are much higher in zone IIIB. In terms of microcomponents, the whole zone III is marked by the higher concentrations of Ba in relation to I and II zones.

Additionally, zone IV was separated in the region westwards from Poznań. The zone is located between the areas of water marked by high colour intensity. It is a small area, where the water chemistry is mainly determined by the direct, limited, recharge from the upper aquifers. The water chemistry in this zone is similar to zones IIIA and IIIB, but a smaller leakage of filtration from upper aquifers is observed here. The water chemistry in this zone to the largest extent reflects the hydrogeochemical conditions of the Miocene deposits environment.

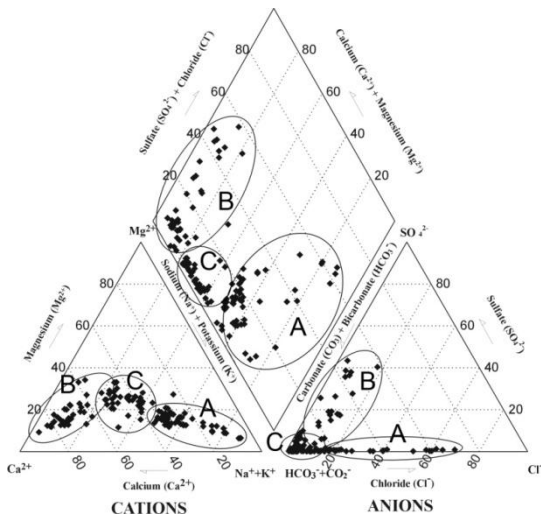


Figure 3. The Piper diagram with the marked points located: A — discharge zones of water ascending from Mesozoic basement (zone I, IIA and IIB), B — zones of recharge from Quaternary aquifers and transit (zone IIIA and IIIB), C — zone of limited recharge from Quaternary aquifers (zone IV).

CONCLUSIONS

Based on the obtained study results, the following conclusions may be drawn:

- The chemical composition of the Miocene aquifer in the Wielkopolska Region in the area of Poznań-Gostyń fault graben and the Szamotuły structure is marked by high variability, especially in terms of colour intensity, chlorides, hardness and manganese.
- The chemistry of water in the studied region is mainly formed as a result of the ascent from the Mesozoic basement and the recharge from the Upper Quaternary aquifers.
- The ascent of water from the Mesozoic basement is mainly observed in the hydraulically-active zones of tectonic faults and in the outcrop zone of the Lower Jurassic formations.
- In the area of ascent recharge from the Mesozoic basement, the water of the Miocene aquifer is marked by the increased concentrations of Cl^- (>20 mg/L), Mn (<0.1 mg/L) and low hardness (mostly lower than 4 mval/L). In terms of microcomponents, the increased concentrations of Al and Li are stated.
- In the area of ascent recharge, the zone marked by anomalously high colour intensity (>80 mgPt/L) may be distinguished. The zone has been formed paleohydrogeologically and occurs in the parts where the transit of water discharged from the Mesozoic basement to the surface discharge zones was hindered. Apart from the increased Cl^- concentrations and low hardness and Mn, the water with high colour intensity is marked by the increased concentrations of Fe, As, Sb and Se and, to a smaller extent, of Pb, Cu, Ni and Cr.
- In the zones where the chemical composition of water at the Miocene aquifer is formed due to the influence of the recharge from the Quaternary aquifers, the water is marked by the low concentrations of Cl^- (<20 mg/L). On the other hand, higher hardness (>4 mval/L), Mn concentrations (>0.1 mg/L) and, locally SO_4^{2-} concentrations may be observed. In terms of microcomponents, the increased concentration of Ba may be stated.

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