


# IDENTIFICATION OF RIVER VALLEY AREAS THREATENING THE CHEMICAL STATUS OF GROUNDWATER, IN THE EXAMPLE OF THE UPPER COURSE OF THE NER RIVER BASIN, CENTRAL POLAND

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Manuscript received: July 19, 2023

Revised version: January 24, 2024

KROGULEC E., MAŁECKI J.J., SZOSTAKIEWICZ-HOŁOWNIA M., TRZECIAK J., ZABŁOCKI S., ZIUŁKIEWICZ M., 2024. Identification of river valley areas threatening the chemical status of groundwater, in the example of the upper course of the Ner River basin, central Poland. *Quaestiones Geographicae* 43(3), Bogucki Wydawnictwo Naukowe, Poznań, pp. 21–45. 13 figs, 7 tables.

**ABSTRACT:** The planning and management of water in the river basins require the identification of places where the quality of groundwater is being threatened. The risk of launching the accumulated pollutants present in the solid phase of the soil may be caused by both the changes in the pressure gradients in the aquifers and the changes in the hydrogeochemical balances. In the example of the Ner river valley, into which wastewater from the Łódź agglomeration has been discharged, the factors threatening the chemical status of groundwater were determined. This assessment was carried out based on the results of the determination of the hydrodynamic balance disturbances in the Upper Cretaceous formations, model studies of groundwater flow and hydrogeochemical studies conducted on the sorption complex of the Ner alluvium as well as the chemistry of the river water, alluvial water and groundwater. The results showed that the river water is heavily anthropogenically transformed. Model studies have shown that when the Ignacew -intake wells are pumped collectively, the inflow takes place through the Ner valley, where the hydrogeological window between the Quaternary and the Upper Cretaceous aquifers is found. The withdrawal by the Ignacew intakes may result in the reversal of piezometric pressures in the valley, which creates the possibility of the infiltration of polluted surface water into groundwater. Observations indicate the need to take into account the zones where surface water and water from the river alluvium are a real threat to the chemical status of the aquifers. These aspects are important when determining the protection zones and in renewable and disposal resource assessments of the Main Groundwater Reservoirs.

**KEYWORDS:** Ner river valley, changes in hydrodynamic balance, chemistry of river water, chemistry of alluvial water and groundwater, active wells

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## Introduction

The designation of the protection areas of the Main Groundwater Reservoirs for the purposes

of planning and water management in the river basins requires identifying areas that threaten the quality of the groundwater. Essential conditions for groundwater management include the

assessment of the possibility of the migration of pollutants in the filtration stream and the definition of factors ensuring a balance between the pollutants accumulated in the solid phase of the soil and groundwater. The risk of launching the accumulated pollutants in the solid phase of the soil may be caused by both the changes of the pressure gradients in the aquifers and the hydrogeochemical balances in the examined system.

The results of the authors' research and the literature on the subject (Małecki 1998, Wildi et al. 2004, Gruszczyński, Małecki 2010, Małecki et al. 2017, Postma et al. 2017, Małecki, Ziułkiewicz 2019) indicate that such threats occur in river valley zones, which have been the places of discharge of sewage from large urban agglomerations for decades. It is necessary to recognise the geological structure and the hydrogeological conditions, with particular emphasis on the assessment of the occurrence of aquifers and aquitards, including their nature and hydrogeological features. The hydraulic relationships between the surface water and groundwater and the relationships between aquifers are basic elements determining the sensitivity of the hydrogeological system to pollution, especially in river valley zones exposed to strong anthropopressure (Wu et al. 2007). This type of assessment requires extended (dedicated) hydrogeological and hydrogeochemical studies. The current paper focuses on the scope of the research assessing the pollution risk of the aquifer, namely, the aquifer of the Upper Cretaceous. According to the authors, a good testing field for this type of assessment is the Ner river valley, located near the large urban agglomeration of Łódź (central Poland) within the limits of the Main Groundwater Reservoirs No. 401 – Łódź basin.

## Materials and methods

### Characteristics of the research area

The Ner is a right tributary of the Warta River, flowing from the Łódź Hills through the Laska Upland and the Kolska Valley, flowing out at an altitude of about 208 m a.s.l. to the south-east from Łódź (Penczak et al. 2010). The average width of the river bed in its upper course is 12 m with the width of the valley from 300 m to 900 m (Fig. 1).

The average annual flow of the Ner in the lower course (Dąbie section) according to (IMGW 2023) for the period 2010–2021 is  $8.0 \text{ m}^3 \cdot \text{s}^{-1}$ .

In the upper part of the Ner River near Konstancynów Łódzki, a sewage treatment plant has been operating since 1930. For decades, heavily polluted wastewater from the industrial agglomeration of Łódź (textile industry and related dyeing plants) has been discharged. This wastewater, which is only mechanically treated, has deteriorated the water quality of the Ner River and also that of the Warta River that flows at the estuary of the Ner River. This wastewater has also caused the accumulation of pollutants in the alluvial valley formations (Lis, Pasieczna 1998). Wastewater has been subjected to more effective treatment, including biological treatment, since 1997. Currently, the Group Wastewater Treatment Plant in Konstancynów Łódzki treats 51% of all the wastewater from the Łódź Voivodeship, which is approximately  $210,000 \text{ m}^3 \cdot \text{day}^{-1}$  on average (ZWiK 2022). Using the slope of the terrain, the sewage system gravitationally transports municipal sewage from the Łódź agglomeration, including storm sewage, from the city towards the Ner river basin. In addition, during periods of torrential rains, accumulated pollutants in the form of suspensions are washed off the city surface. This leads to an increase in pollutant loads in the mixture of household and precipitation sewage. This unfavourable phenomenon is intensified by the combined sewage system in the downtown part of the city.

For decades, rainwater from the city was also used to irrigate the grasslands of the Ner valley. Irrigation resulted in the accumulation of pollutants in the soil profile of meadow complexes, which potentially threaten the quality of groundwater of the Quaternary (Q) and the Upper Cretaceous ( $\text{Cr}_3$ ) aquifers within the boundaries of the Main Groundwater Reservoir No. 401 – Łódź Basin.

The study area is located in the Ner river valley in the western foreground of the Łódź Hills, in the mesoregion of the Łaska Upland, belonging to the macroregion of the South Wielkopolska Lowland (Solon et al. 2018). The Upper Ner Valley is located within the large geological structure of the Mogilno – Łódź Basin, on the eastern side of the Lutomiensk Anticline near Konstancynów Łódzki, which belongs to the Łódź

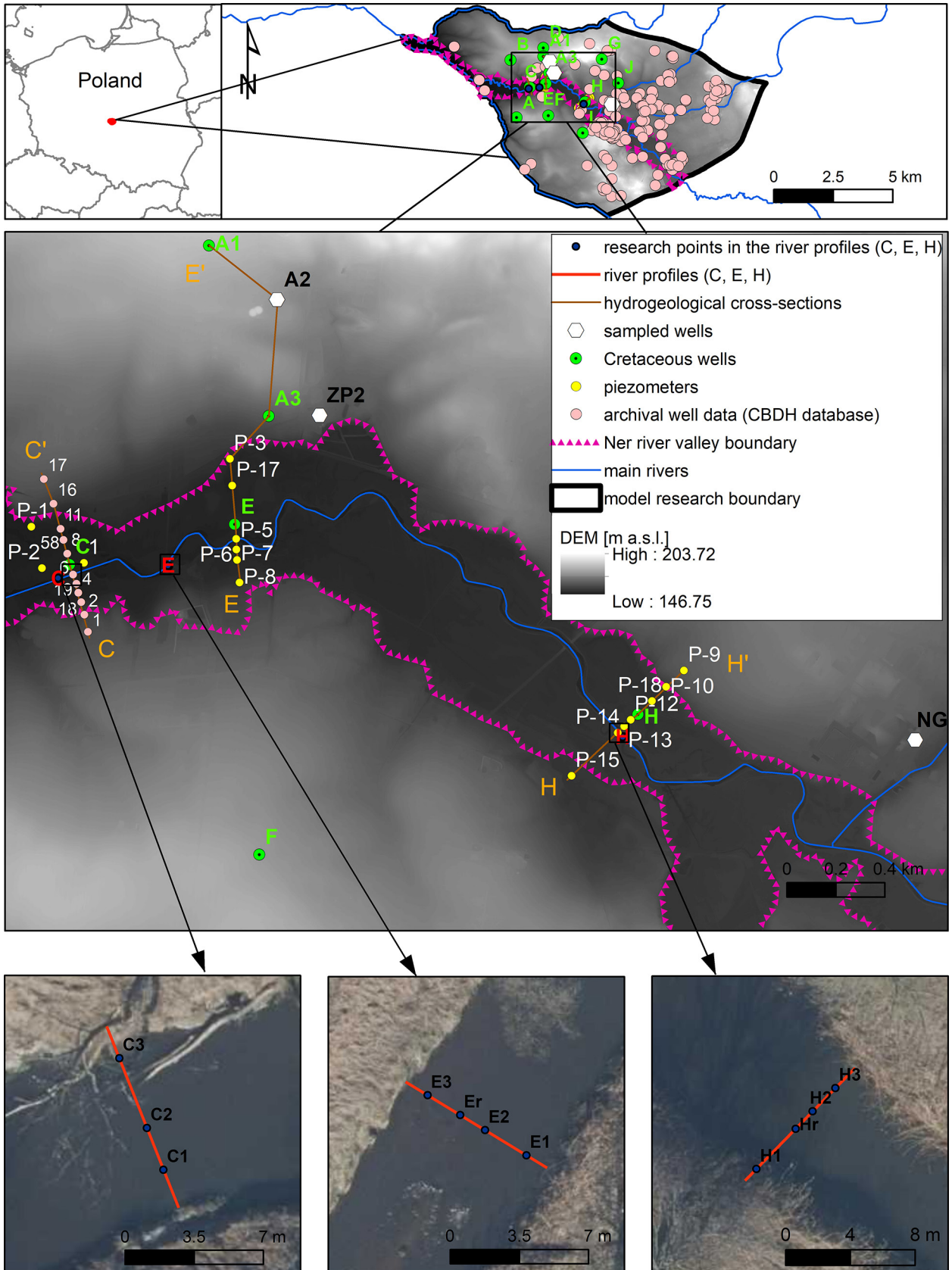


Fig. 1. Documentation map of the research area.

agglomeration. Both peripheries of this anticline are strongly dislocated. In the Mesozoic formations, height differences reaching 600–700 m are noticeable (Baliński 1992, Ziulkiewicz 2003). The Lutomiersk Anticline marks the western border of the Main Groundwater Reservoir No. 401, created to protect groundwater resources in the limestone formations of the Łódź Basin.

In the area of Konstaktyńów Łódzki, the main usable aquifer is the Upper Cretaceous, composed of varied limestone and marls. Numerous tectonic structures and lithological diversity of the Upper Cretaceous aquifer result in significant diversification of its hydrogeological parameters, as indicated by the values of its transmissivity, from below  $100 \text{ m}^2 \cdot \text{day}^{-1}$  to over  $1000 \text{ m}^2 \cdot \text{day}^{-1}$  (Fabianowski 2002).

The Cenozoic formations of the moraine plateau, within which the test site is located, are dominated by Quaternary glacial tills with local interbeddings of sands and gravels. Conditions for the occurrence of groundwater in the Cenozoic formations can be considered good only in the river valley where erosion reached to the ceiling of the Mesozoic formations (Fig. 2). Water reservoir conditions are created there in thicker clastic formations. The contemporary

bottom of the Ner valley is built of deposits from the Late Vistulian and Holocene. These are various-grained and fine-grained sands of river origin, sometimes underlain by fluvio-glacial sands and, to a lesser extent, hardly permeable stagnant formations (Balwierz, Piwowarski 2008, Kittel 2012, Brzeziński, Gałazka 2013). Within the valley, there is one Quaternary aquifer present in the alluvial formations drained by the river.

The range of the Neogene aquifer is very limited. It occurs within the local depressions of the Upper Cretaceous top or the forms of glacetectonic 'extrusion' (Bierkowska et al. 1990).

The Ner river valley is a regional drainage base for Cenozoic and Upper Cretaceous aquifers. The lateral inflow of groundwater is mainly from the south, as it is limited from the north-east by the watershed between the Warta and the Vistula. The watershed in the upper part of the Ner catchment is also the western border of the Upper Cretaceous regional depression cone of the Łódź agglomeration. The development of the depression cone in the Quaternary formations began to move towards the Ner river valley, covering the north-eastern part of the city of Konstaktyńów Łódzki (Fig. 3).

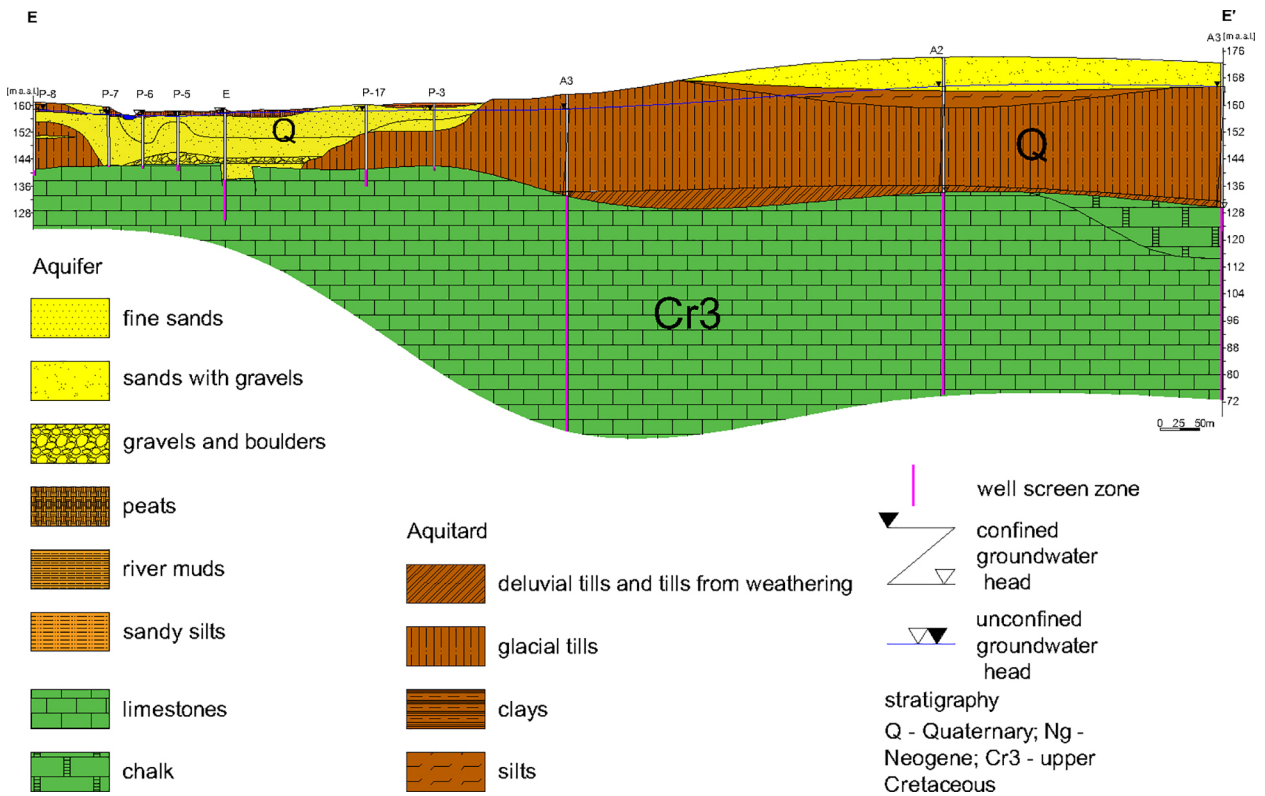


Fig. 2. Hydrogeological cross-section (line of cross-sections shown in Fig. 1).



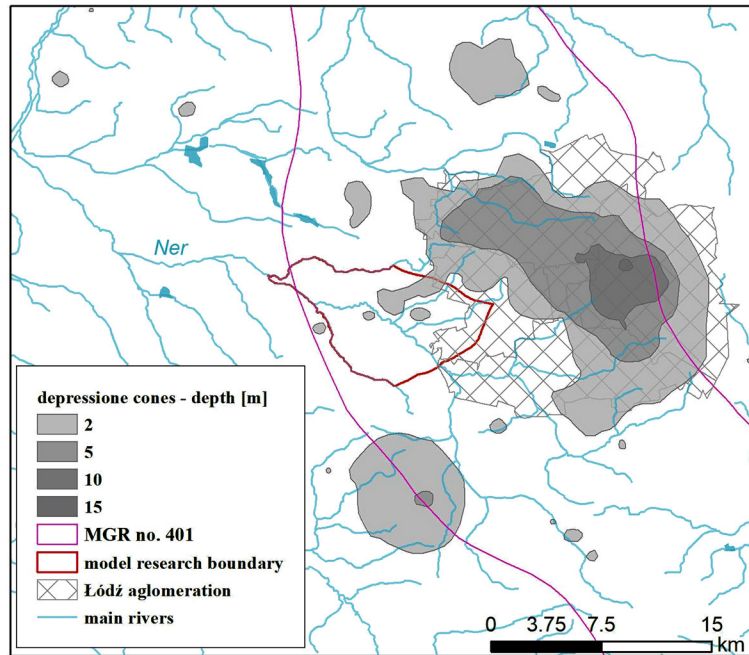


Fig. 3. The extent of the depression cone in the Quaternary aquifers of the Łódź agglomeration as a part of Main Groundwater Reservoir No. 401 (Rodzoch et al. 2013).

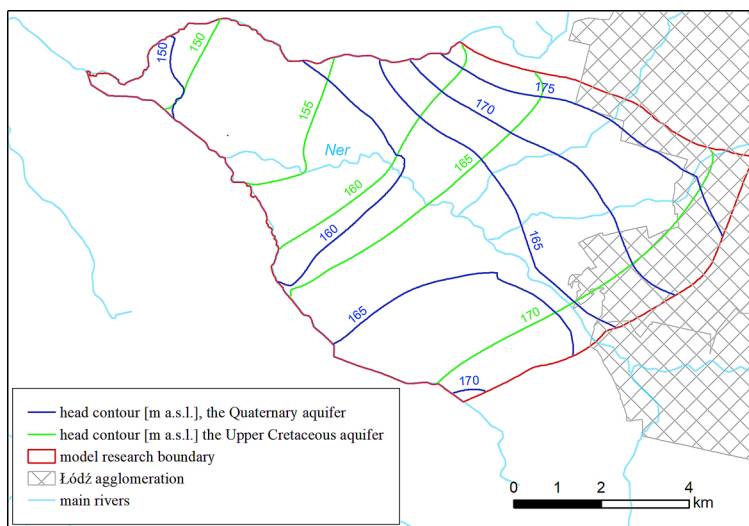


Fig. 4. Groundwater table of the Quaternary and Upper Cretaceous aquifers in the area of modelling studies.

The analysis of the head contours of the Upper Cretaceous and Quaternary aquifers shows their hydraulic connection in zones where there are no impermeable formations (Fig. 4).

### Scope and results of archival research

In the 1980s, work was carried out on the design construction of the 'Lutomiersk' purified water reservoir in the Ner river valley. The main objective of the archival research was to determine

the impact of the reservoir water on the groundwater of the usable Cretaceous aquifer. This impact was assessed on the basis of hydraulic relationships between surface water and groundwater and relationships between the Quaternary and Cretaceous aquifers, with the indication of zones of possible leakage from the Quaternary into the Upper Cretaceous. When assessing the threat to usable aquifers in the Ner river valley today, the above-mentioned archival research results were taken into account, especially the

research of the hydrodynamic balance changes in the Upper Cretaceous formations (Murzynowski, Małeckı 1982).

As part of the mentioned work in the Ner river valley, C, E and H pumping wells with observation wells were tested (Fig. 1). The E well is located in the zone of full contact between the Quaternary aquifer and the Cretaceous aquifer (Fig. 2). The C well is located in an area where the contact between the Quaternary and the Cretaceous aquifers could be limited by a layer of weathering, about half a meter thick, and the H well is in the zone with the contact between the Neogene and Cretaceous aquifers limited by a two-meter layer of limestone weathering. The contact between the subsurface Quaternary aquifer and the Neogene aquifer is strongly limited by 25–30 m thick Pliocene clays and silts (Fig. 5).

In the C well, a stabilised self-outflow was obtained at the level of 1.5 m a.g.l., which corresponds to 157.0 m a.s.l., and in piezometers, the water table in Quaternary sands and gravels was 0.9 m b.g.l., which corresponds to 154.6 m a.s.l. In the C location, piezometric pressure differences between Cr3 and Q amounted to about 2.4 m. No aquitards were found in the E location. The unconfined head stabilised at a depth of 0.86 m b.g.l., and the pressures in the Cretaceous and Quaternary aquifers were at the same level. In the H location, below a series of Quaternary formations, significant thicknesses of the Neogene clay formation with brown coal inserts and clayey weathered limestone were found; these formations constituted the aquitards above the Cretaceous aquifer. In the H well, self-outflow was obtained, stabilising at

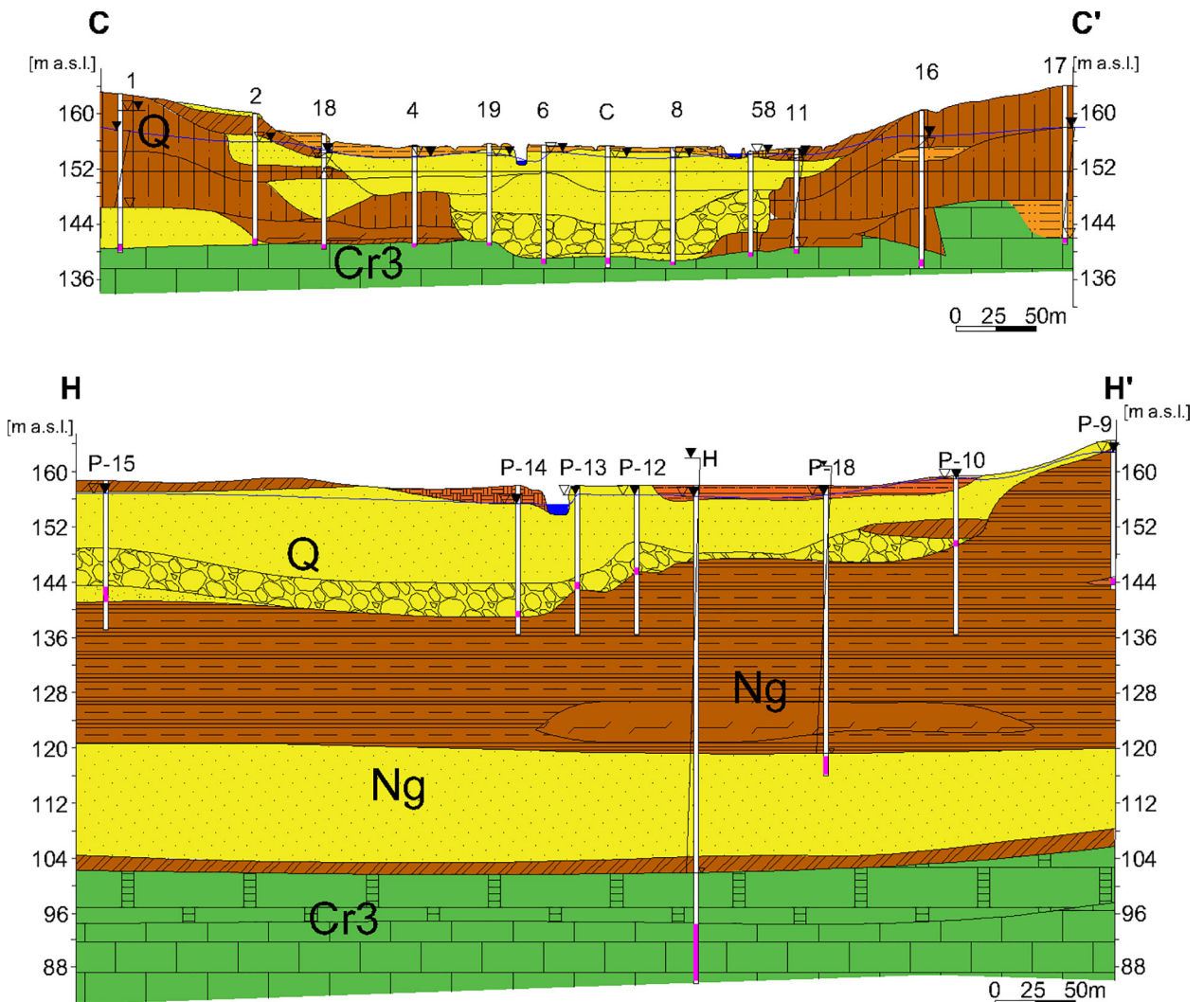


Fig. 5. Hydrogeological cross-sections (lines of cross-sections shown in Fig. 1, explanations to cross-sections shown in Fig. 2).

Table 1. Basic information about C, E and H pumping wells and observation wells.

Pumping and observation wells	Well name	Well depth	Aquifer stratigraphy	Aquifer lithology	Piezometric water table	Water table
		[m]			[m b.g.l.]	
C	C pumping well	30	Cr <sub>3</sub>	limestones	-1.50	13.50
	P-1 observation well	nd	Q	nd	0.59	0.59
	1 observation well	14	Q	sands and gravels	0.90	0.90
	P-2 observation well	nd	Q	nd	0.95	0.95
E	E pumping well	35	Cr <sub>3</sub>	limestones	0.86	0.86
	P-5 observation well	17	Q	sands of different granulation	1.46	1.46
	P-6 observation well	18	Q	sands of different granulation	0.91	0.91
	P-7 observation well	18	Q	sands of different granulation	2.30	2.30
H	H pumping well	70	Cr <sub>3</sub>	limestones	-4.00	53.50
	P-10 observation well	22	Q	sands and gravels	0.40	0.40
	P-11 observation well	12	Q	sands and gravels	1.00	1.00
	P-15 observation well	18	Q	sands and gravels	1.80	1.80

nd - no data.

about 4 m a.g.l., which corresponds to 162 m a.s.l. The unconfined Quaternary groundwater table in the piezometers was at a depth of 0.9 m b.g.l. The pressure difference between Cr<sub>3</sub> and Q in this location was 4.9 m (Table 1).

To confirm the existence of contact zones between the Upper Cretaceous and Quaternary aquifers, the hydrodynamic balance in the Cretaceous formations in the C, E and H locations was disturbed, which was only possible when the maximum discharge rate of the well was exceeded (Murzynowski, Małeckı 1982). In the H location, during pumping, no correlation was found between the lowered pressure of the Cretaceous groundwater table and the Quaternary groundwater table level. A different dependence was found in the E location. Observation piezometers showed a straight reaction to changes confirmed

in the depression in both aquifers. The analysis of pressures indicates that in this zone, there is leakage of the Cretaceous aquifer to the Quaternary aquifer. The C location showed less interdependence between the Cretaceous and Quaternary groundwater tables during pumping (Fig. 6).

Changes in the hydrodynamic balance of the Cretaceous aquifer have shown that despite the existence of significant pressure values in the Cretaceous (well H - 39.22 kPa, the C well - 14.71 kPa), there are zones (the E well) where pressure reduction in the Upper Cretaceous aquifer will be led to the drainage of Quaternary groundwater and the occurrence of potential hazards to the chemical status of groundwater of the Cretaceous aquifer.

The pumping of the E, H and C wells also allowed determining the filtration parameters

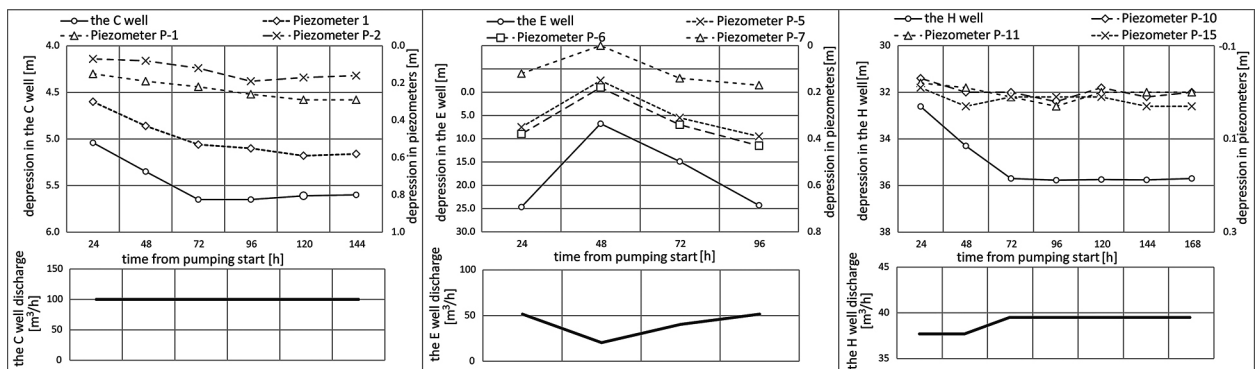


Fig. 6. Observations of the groundwater table level during pumping in the C, E and H wells.

Table 2. Results of calculations of the filtration parameters of the Upper Cretaceous aquifer based on pumping of the H, C and E wells.

Well	Pumping type	Pumping stage	Discharge rate Q	Stabilized depression s	Conductivity k	Average conductivity k	Depression cone radius during pumping test	Permissible discharge rate Q max
			[m <sup>3</sup> · h <sup>-1</sup> ]	[m]	[m · s <sup>-1</sup> ]	[m · s <sup>-1</sup> ]	[m]	[m <sup>3</sup> · h <sup>-1</sup> ]
H	one stage	1	39.5	35.73		1.19 · 10 <sup>-5</sup>	370.1	7
C	one stage	1	100.0	5.63		3.58 · 10 <sup>-4</sup>	320.0	41
E	three stages	1	24.7	6.80	8.16 · 10 <sup>-5</sup>	5.53 · 10 <sup>-5</sup>	168.0	11
		2	40.4	14.90	5.05 · 10 <sup>-5</sup>		376.0	
		3	51.6	24.30	3.37 · 10 <sup>-5</sup>		612.0	

of the Cretaceous complex. Calculations of the conductivity were made in accordance with the methodology provided in the guidebook by Dąbrowski and Przybyłek (2005) (Table 2).

The obtained values of the conductivities were helpful in creating a hydrodynamic groundwater model enabling the assessment of the relationship between the water of the Quaternary and Cretaceous aquifers.

## Research methodology

### The hydrodynamic model of groundwater flow

Model tests were carried out in the Visual ModFlow Flex 7.0, Waterloo Hydrogeologic program, based on an algorithm using the finite difference method (McDonald, Harbaugh 1988). The model was made for the steady-state conditions, defined as the average annual hydrodynamic state representing the period of 1976–2021. The aim of the modelling studies was to determine the possibility of infiltration of surface water in the Ner river valley and leakage of Quaternary aquifer groundwater as a result of the decrease in piezometric pressures in the Upper Cretaceous aquifers caused by water withdrawal in Ignacew, by the Municipal Company of Konstantynów Łódzki Spółka z o.o.

The conceptual model was based on the separation of a fragment of the aquifer system of the Konstantynów Łódzki region, with the assumption that with such a large area there would be no direct impact of the boundary conditions on the area of water inflow to the Ignacew wells. The conceptual model was constructed based on the recognition of the hydrogeological conditions of the area. Water circulation in this hydrogeological

system occurs in the Quaternary, locally Neogene aquifer and main usable aquifer in the Upper Cretaceous formations.

The model included an area of 71.85 km<sup>2</sup> within the range of occurrence of hydrogeological units 1Q/baCr3II and 2bCr3II according to the Hydrogeological Map of Poland, scale 1:50,000, Łódź Zachód sheet (Fabianowski 2002). The side boundaries were drawn as follows:

- northern border: along the course of the Lubczyna River,
- western border: along the course of the Zalewka River, then along the course of the Ner River,
- southern border: along the head contour of 170 m a.s.l. in the Upper Cretaceous aquifer (Rodzoch et al. 2013), and
- eastern border: along the head contour of 180 m a.s.l. in the Quaternary aquifer (Rodzoch et al. 2013).

The upper surface of the model research object is the groundwater table of the subsurface aquifer occurring in the Quaternary formations. For most of the area, it remains unconfined. The bottom model surface was assumed as the bottom of the Upper Cretaceous formations. This surface is characterised by small denivelations of 360 m from -152 m a.s.l. to -410 m a.s.l., which corresponds to depths from 312 m b.g.l. to 589 m b.g.l. It is inclined towards the south-east.

Exchange of water with the environment of the system takes place as a result of:

- infiltration and evaporation from the surface of the shallow groundwater occurrence, in the river valleys;
- groundwater inflow from the south and east outside the mapped system (lateral inflow to aquifers);
- direct drainage through larger rivers: Ner, Lubczyna, Zalewka and their tributaries, in-



cluding drainage ditches; indirect drainage in river valleys through erosive hydrogeological windows; and

- lateral outflow of groundwater to the north-west, according to the Fabianowski (2002).

The area was divided into square cells of size  $x = 50$  m,  $y = 50$  m, 175 rows and 304 columns; the number of active cells was 28,740.

The discretisation of the area in the vertical direction covered the distinction of seven layers described in order from the top:

- first: subsurface aquifer (Q1),
- second: glacial tills constituting an aquitard, locally discontinuous in river valleys (Q1-Q2),
- third: Quaternary usable aquifer, according to the record of the hydrogeological unit, locally the Neogene aquifer (Q2 -Ng),
- fourth: glacial tills or silts and clays constituting an aquitard, locally discontinuous in river valleys (Q2-Ng-Cr),
- fifth: top part of the Upper Cretaceous aquifer, at a depth of 12 m in the Ner valley to 91 m in the eastern part of the area (marked as Cr<sub>3\_1</sub>),
- sixth: the middle part of the Upper Cretaceous aquifer, characterised by weaker filtration parameters due to the smaller share of fracturing, at a depth of 62 m in the Ner valley to 143 m (marked as Cr<sub>3\_2</sub>), and
- seventh: the lower part of the Upper Cretaceous aquifer, characterised by the weakest filtration parameters, at a depth of 228 m in the north to 313 m in the south-eastern part (marked as Cr<sub>3\_3</sub>).

The thicknesses of the individual layers were determined on the basis of the borehole profile cards, in accordance with the Central Hydrogeological Data Bank (CBDH). For the model, it was assumed that the minimum thickness of the layer is 5 m to maintain the stability of the calculations in places where the aquitards were discontinuous.

### Hydrogeochemical studies

Research work in the Ner river bed was carried out in October 2022, in three profiles (H, E and C), at a distance of approximately 5 km below the point of discharge of sewage from the Group Sewage Treatment Plant, on the day when  $1.71 \text{ m}^3 \cdot \text{s}^{-1}$  of post-treatment water was discharged into the river, i.e. slightly below average

for October 2022 ( $1.83 \text{ m}^3 \cdot \text{s}^{-1}$ ). Approximately  $1.69 \text{ m}^3 \cdot \text{s}^{-1}$  of water flowed down the river bed, which almost corresponded to the amount of water discharged from the Group Sewage Treatment Plant.

### Analyses of the content of chemical elements in river sediments

Samples of river sediments in the E, C and H profiles were collected from the river bed using a sludge pipe. Sampling sites were selected on the basis of earlier gradientmeter measurements of water flow directions in river alluvium. Places representing zones of river water infiltration into the bottom of the channel, as well as places of its drainage after mixing with groundwater, were selected (Fig. 1). Determination of chemical elements in river sediments was carried out using the aqua regia extraction method. The content of elements in the obtained filtrate was determined by the ISO 11885/ISO 17294-2 method in the Wessling laboratory and by ICP-OES emission spectrometry using a Perkin-Elmer device in the Laboratory of Geomicrobiology and Environmental Geochemistry of the Faculty of Geology, University of Warsaw.

### Analyses of the sorption complex

Cation exchange capacity (CEC) was also determined in the sediments collected from the Ner river bed. The CEC value was estimated by the Breeuwsma formula (Appelo, Postma 1993), based on the percentage of particles <2 m and the percentage of organic matter. The percentage content of particles <2 m was determined based on the analysis of the granulometric composition of the samples, while the content of organic matter was determined using the loss on ignition method. In addition, in all samples, the CEC was determined by the Kappen method. The research was carried out in the Applied Geology Laboratory of the Faculty of Geology, University of Warsaw.

### Analyses of water chemistry

Groundwater samples from the Quaternary, Neogene and Cretaceous aquifers were collected directly from the wells. Water samples in the alluvium were collected from the Ner river bed, 20 cm below the bottom of the river, using

a gradientmeter, and river water samples were taken directly from the main stream (Hr and Er points). The location of the documentation points is marked in Figure 1.

In each of the water samples in the field, the following measurements were made: water temperature, pH and electrolytic conductivity with a multifunctional Eijkelkamp device. Measurements of the red-ox potential and the content of dissolved oxygen were performed with a multifunctional device CX-401 by Elmetron. Samples for chemical analysis were collected in bottles made of HDPE plastic, which is inert towards water. Whatman filters of 0.45 m were used for sample filtration. Samples for testing by emission spectrometry were fixed directly in the field with concentrated 65% pure nitric acid. The analyses were carried out in accordance with the recommendations of Witczak et al. (2013). Anion content was determined by the colorimetric or spectrophotometric method in the Applied Geology Laboratory of the Faculty of Geology, University of Warsaw, while Ag, Al, As, Ba, Be, Bi, Br, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Sr, Ti, V, W and Zn by the ISO 11885/ISO 17294-2 method in the

Wessling laboratory and by ICP-OES emission spectrometry with a Perkin-Elmer device in the Geomicrobiology and Geochemistry Laboratory Environment at the Faculty of Geology of the University of Warsaw.

To more fully characterise the chemistry of the tested water, models of the solution state were made. The models were made in the Geochemist's Workbench (2023) program with the thermo.tdat thermodynamic database, supplemented with forms of bismuth and cadmium. The selected thermodynamic database allows for the full range of water components to be included in the calculations. If the contents of individual components were lower than the limit of their detection (DL), half of the DL was adopted for model calculations.

## Results

### Hydrodynamic model of groundwater flow

#### Layer properties and boundary conditions

The conductivities of the individual layers were subject to changes at the calibration stage.

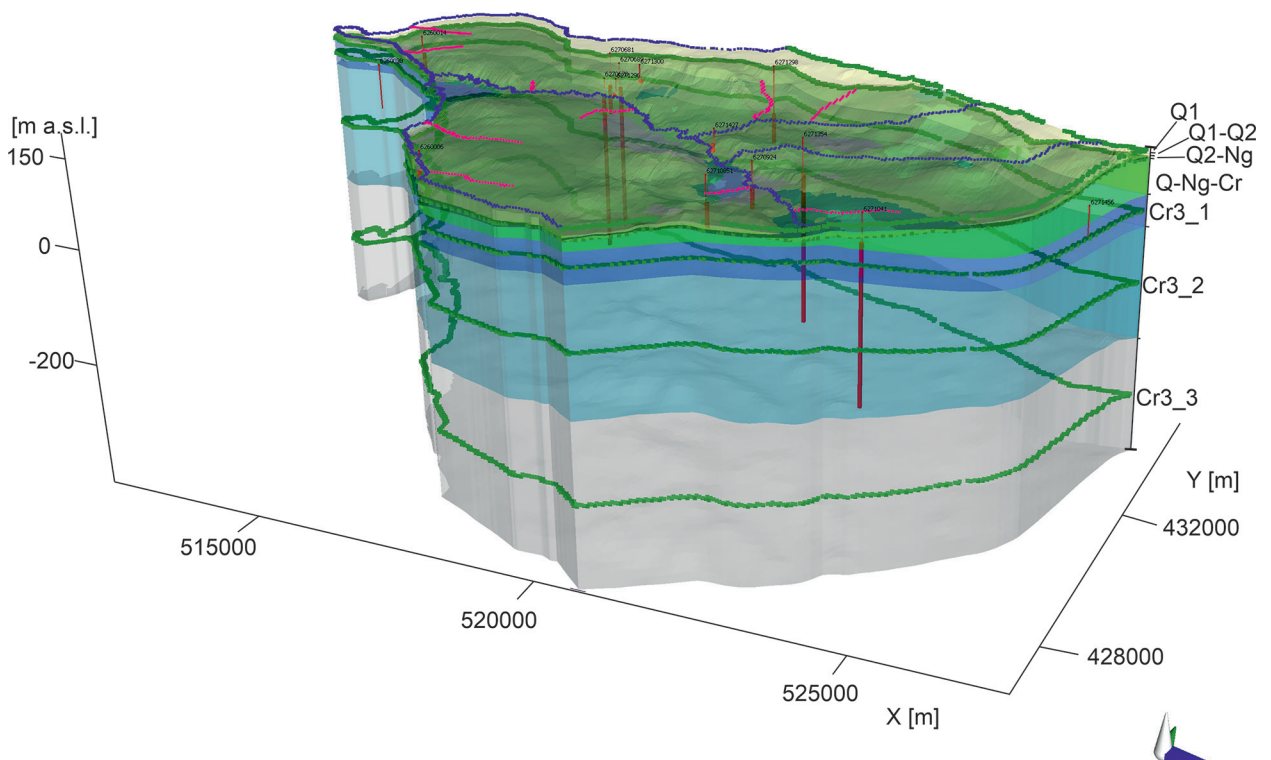


Fig. 7. Model structure and boundary conditions: RIVER (blue), WELL (brown), DRAIN (purple), general head boundary (green), 3D view from the south, exaggeration of the vertical scale  $\cdot 10$ .

The initial values were adopted on the basis of own calculations from test pumpings, data from borehole charts (CBDH) and result maps of the modelled Main Groundwater Reservoir No. 401 on a regional scale (Rodzoch et al. 2013). The isotropy of the medium in the directions ( $x$  and  $y$ ) was assumed; for the direction ( $z$ ), the values were one order lower.

The values of infiltration recharge were mapped using the II type boundary condition ( $Q = \text{const.}$ ). The amount of recharge in the range from  $0 \text{ mm} \cdot \text{year}^{-1}$  in the drainage zones to  $120 \text{ mm} \cdot \text{year}^{-1}$  was assumed. With a shallow groundwater table, mainly in the drainage zones, the amount of groundwater evaporation was also determined. The maximum annual values were assumed to be  $50 \text{ mm} \cdot \text{year}^{-1}$  in the case of the presence of a groundwater table on the ground surface, and the so-called depth of extinction of the impact of this process at 1.0 m (Dowgiałło et al. 2002).

In the study area, the groundwater withdrawal was mapped as a type II point condition with known outflow rate, adopted on the basis of data obtained from the POBORY database, Polish Geological Institute-National Research Institute (average value over many years).

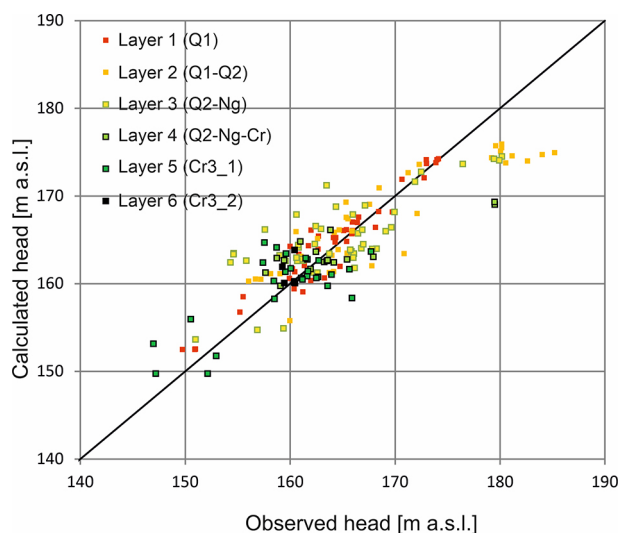
The III type boundary condition represented drainage through watercourses and the lateral inflow through the model boundaries (Fig. 7). The III type RIVER condition was set for model cells simulating rivers characterised both as boundaries of the model and within the model. For this condition, the width of the watercourses was introduced, the layer of water in the watercourses was adopted on the basis of field observations, supplemented with data from the Map of the Hydrographic Division of Poland in the scale of 1:200,000 (Czarnecka 2006). The DRAIN condition was set at the drainage ditch courses visible in the image of the WMS orthophotomap service (GUGiK 2023).

The condition of the III type - General Head Boundary (GHB) - was used to map the vertical boundaries of the model along a separate fragment of the system. After the hydrogeological analysis, it was found that the boundaries of the modelled system are open to water exchange with the surroundings from the south and east for the first layer and from all sides for deeper layers.

## Model calibration

The calibration process consisted in finding a solution to the inverse problem by the method of successive approximations. The solution found for the condition of the aquifer system was confirmed by calibrating the heads at 180 points, including aquifers marked as Q1, Q2-Ng, Cr3\_1 and Cr3\_2. In the calibration process, the properties of the filtration field were refined by increasing or decreasing the conductivity. The obtained range of values was slightly lower than the initial values: from  $0.8 \text{ m} \cdot \text{day}^{-1}$  to  $5 \text{ m} \cdot \text{day}^{-1}$  for the subsurface aquifer (model layer no. 1) and  $5\text{--}10 \text{ m} \cdot \text{day}^{-1}$  for the Quaternary aquifer (model layer no. 3). The conductivity of the top part of the Upper Cretaceous was determined at  $4\text{--}7 \text{ m} \cdot \text{day}^{-1}$ , the middle part at  $3 \text{ m} \cdot \text{day}^{-1}$  and the bottom part at  $1 \text{ m} \cdot \text{day}^{-1}$ . The conductivity of aquitard formations was set to the value of water permeability in the range of  $0.00005\text{--}0.05 \text{ m} \cdot \text{day}^{-1}$ .

As a result of the calibration, errors characterising the compliance of the model calculation results with the input data at the calibration points were determined (Fig. 8). The maximum difference between the measured and calculated heads was  $-11 \text{ m}$ ; the absolute mean was  $2.81 \text{ m}$ . The



Number of Data Points: 180  
 Min.Residual: 0.073 (m) at 6270998/1  
 Max.Residual: -11 (m) at 6271388/1  
 Residual Mean: -0.29 (m)  
 Abs.Residual Mean: 2.81 (m)  
 Standard Error of the Estimate: 0.27 (m)  
 Root Mean Squared: 3.68 (m)  
 Normalized RMS: 9.62 (%)  
 Correlation Coefficient: 0.87

Fig. 8. Model calibration chart.



estimation error of 0.27 m and the absolute mean error of 3.68 m were considered low enough to complete the calibration process and to recognise the credibility of the obtained model. During the calibration, special attention was paid to adjusting the modelling results to the groundwater levels at the Ignacew wells, assuming the position of the dynamic water table caused by the withdrawal (concordance approx. 1 m).

### Model of the groundwater withdrawal in Ignacew

The Ignacew wells' (A1, A2, A3) work was mapped by assigning appropriate discharge rate. During field works, it was found that the actual value of withdrawal is similar to the value approved in the water law permit and amounts to approximately 90% (Table 3). To assess the impact on the Quaternary aquifer and the surface water of the Ner River, remaining in hydraulic contact with the Upper Cretaceous aquifer, the heads of all aquifers were determined in quasi-natural conditions with inactive wells' simulation and in the conditions of the active wells.

The numerical model of the filtration field made it possible to determine the 25-year time ( $t = 9125$  days) of the lateral inflow to the Ignacew wells (A1, A2, A3), owing to the recognition of the directions and filtration velocity. For this purpose, the MODPATH module included with Visual Modflow Flex 7.0 was used. This module enables 'tracking' of water particles flowing in the three-dimensional space of the model.

Model tests have shown that when pumping the Ignacew well with the assumed actual rate, the water inflow comes from different directions: for the A1 well, from the north and south; for the A2 well, from the east and south and for the A3 well, from the south and south-east (Fig. 9). The inflow to all wells is through the Ner river valley in the area of C and E research profiles and hydrogeological sections, where the presence of hydrogeological windows between the Quaternary and Cretaceous aquifers was found. The range of influence of the well on the river valley is the smallest for the A2 well and the largest for the A3 well. The inflow time ranges from 1 year to 25 years, and at the intersection with the Ner river

Table 3. Discharge rate and the depression size for the Ignacew-intake wells.

Well no./ No. According to the Central Hydrogeological Database	Aquifer and its screened part	Exploitable / actual discharge rate	Depression size
		[ $\text{m}^3 \cdot \text{d}^{-1}$ ]	[m]
A1 / 6270670	Cr <sub>3</sub> _1 (upper part)	3871.2 / 3360.0	20.1
A2 / 6270689	Cr <sub>3</sub> _1, Cr <sub>3</sub> _2 (upper and central part)	3508.8 / 3120.0	21.4
A3 / 6270681	Cr <sub>3</sub> _1, Cr <sub>3</sub> _2 (upper and central part)	2805.6 / 2520.0	20.7

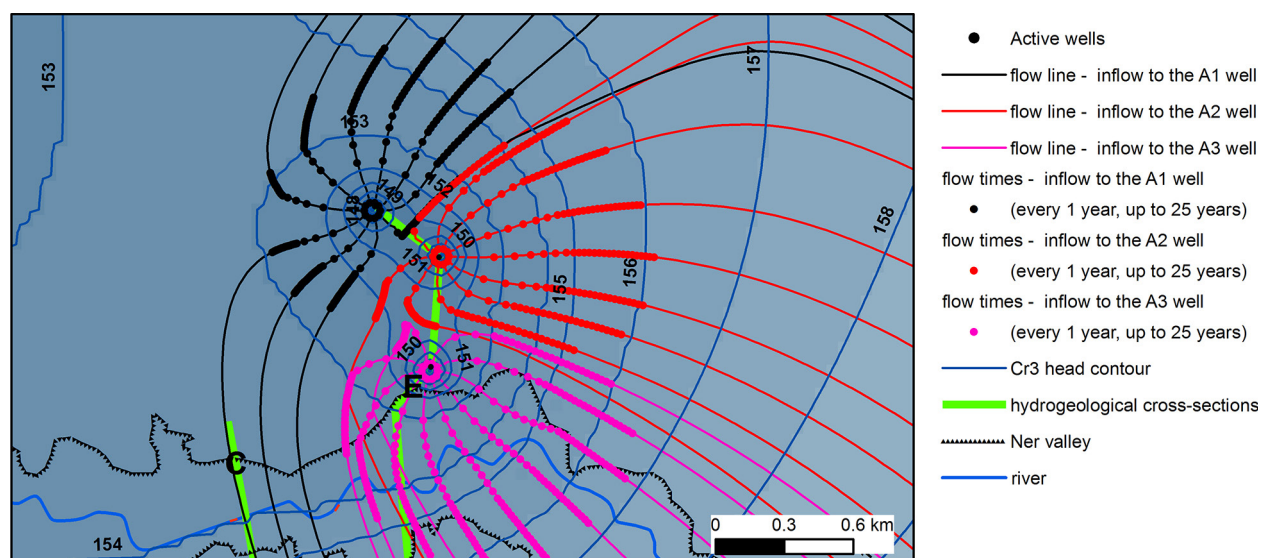


Fig. 9. Layout of the stream line on the way of water inflow to the Ignacew-intake wells as a result of model research.



bed, it is from 6 years to 15 years. The work of A1, A2 and A3 wells with assumed rate causes a local reversal of piezometric pressures (Fig. 10). In the Ner valley, the Upper Cretaceous aquifer groundwater table is lower than the Quaternary aquifer, which makes it possible for surface water to infiltrate to the main usable aquifer. This depression ranges from 0.04 m to 1.99 m (the largest on the northern border of the valley), while in natural conditions, the level of the Upper Cretaceous table was higher than the Quaternary with a value of 0.01–0.39 m.

Since the previous studies, including model studies, showed the possibility of seepage of water from the vadose zone and leakage of water from the overlying layers to the Upper Cretaceous aquifer, the next stage of work was to determine the potential migration risk of

pollutants accumulated in the overlying layers. For this purpose, sorption parameters of river sediments, accumulated pollutants in them and the chemical composition of surface water and groundwater were determined.

## Hydrogeochemical studies

### Elements in river sediments

The results of laboratory analyses of the element content in the collected samples of the Ner alluvium (Table 4) were compared with the archival data contained in the Hydrogeochemical Atlas of the Łódź agglomeration (Lis, Pasieczna 1998). The contents of most elements in the alluvium are small and definitely lower than the average values determined for the entire agglomeration area. The exceptions are cadmium,

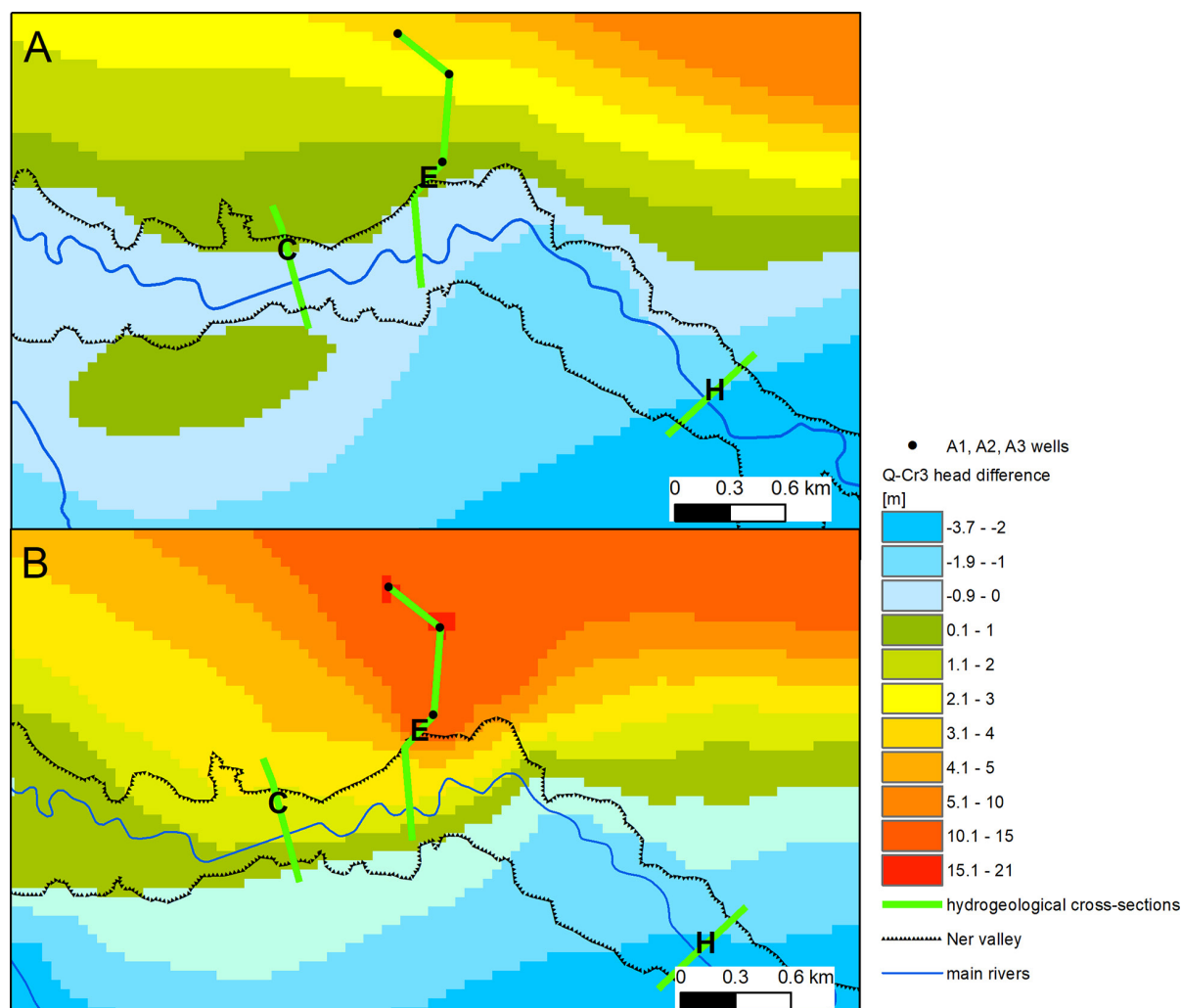


Fig. 10. Head difference between the Quaternary and the Upper Cretaceous aquifers as a result of flow modelling in conditions of: A – average head without withdrawal; B – average head with actual withdrawal from the POBORY database.

chromium, copper, mercury, strontium, silver and zinc. Chromium content higher than average was found in all tested samples. According to Lis and Pasieczna (1998), the main potential source point of contamination with this element are discharges of sewage into the tributaries of the Ner, i.e. the Łódka and Dobrzyńska rivers. The estuary of the Łódka is located 1.8 km from the farthest upstream Ner, the H cross-section (Fig. 5). In 1998, the Łódka alluvial had the highest average chromium content in the entire area of the agglomeration, amounting to 102 ppm. The highest content of chromium in a single measurement (977 ppm) was determined in the Dobrzyńska alluvium, whose estuary to the Ner is located from the H-section at a distance of about 6 km upstream. In the tested samples, the highest concentrations of chromium were found in the H-section (69.60 ppm at H2). The decrease in

the content of this element in individual research profiles follows the direction of the flow of the Ner, up to the value of 18.7 ppm at point C2 located in the most downstream C section (Table 4).

Discharges of municipal and industrial wastewater are also a potential source point of cadmium, copper and zinc contamination of the alluvium of the Ner, with the content of these elements higher than the average for the entire Łódź agglomeration in the H and E profiles (Table 4). Significant mercury content reaching a maximum of 0.74 ppm (point H2) was also found in the H and E profiles, and the origin can be seen mainly in the discharge of sewage into the Olechówka and Dobrzyńska rivers flowing into the Ner (Lis, Pasieczna 1998).

When analysing the elemental composition of Ner alluvium, one should also pay attention to bismuth. The maximum contents of this element

Table 4. Contents of elements in the sediments of the Ner River (values greater than the average are marked in red)\*.

Concentration		Sampling site									Łódź Agglomeration
Element	Unit	H1	H2	H3	E1	E2	E3	C1	C2	C3	max-min (average)**
Ag	ppm	0.38	1.77	0.76	0.48	0.62	0.28	nd	nd	nd	<1-198 (<1)
Al	%	0.02	0.06	0.01	0.02	0.02	0.01	0.01	0.01	0.01	<0.01-3.74 (0.21)
As	ppm	0.66	2.16	1.84	0.77	1.06	0.61	<0.1	<0.1	<0.1	<5-906 (<5)
Ba	ppm	10.08	40.2	8.02	12.96	12.44	5.98	5.92	7.95	7.27	3-484 (42)
Bi	ppm	200	640	76	280	300	66	0.1	<0.1	0.07	nd
Pb	ppm	9.6	40	5.68	11.4	13.26	4.72	2.93	2.12	3.88	<5-10 200 (15)
Br	ppm	56	58	54	66	44	66	<0.1	<0.1	<0.1	nd
Cd	ppm	1.45	1.09	0.64	0.69	1.14	1.19	0.3	0.27	0.42	<0.5-59.6 (0.6)
Ca	%	0.1	0.61	0.05	0.1	0.1	0.06	0.04	0.04	0.04	0.02-16.90 (0.42)
Cr	ppm	27.6	69.6	47.4	32	42.8	36	19.56	18.7	20.2	<1-977 (5)
Co	ppm	0.66	0.68	0.46	0.66	0.72	0.37	0.45	0.29	0.27	<1-46 (2)
Fe	%	0.08	0.22	0.09	0.06	0.08	0.06	0.03	0.07	0.03	0.03-11.80 (0.45)
K	ppm	29	32.4	23	33.2	28.8	18.84	12.51	9.91	12.3	nd
Cu	ppm	10.42	38.6	11.12	14.58	18.68	8.66	5.69	4.62	6.85	<1-1720 (9)
Mg	%	0.01	0.02	<0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01-0.92 (0.06)
Mn	ppm	23.2	40.8	4.84	11.02	7.2	6.58	4.73	69.64	5.58	4-2 896 (129)
Mo	ppm	<0.1	0.12	0.3	0.3	0.23	0.12	0.03	<0.1	0	nd
Na	ppm	33.4	48.4	33.6	62.2	36.2	26.2	16.13	16.99	13.29	nd
Ni	ppm	1.4	2.5	1.83	1.63	2.06	0.68	0.96	0.6	0.55	<1-345 (4)
Hg	ppm	0.25	0.74	0.39	0.4	0.45	0.26	nd	nd	nd	<0.05-20.50 (0.06)
Sr	ppm	2.92	14.78	3.84	2.9	2.72	1.36	1.29	2.78	1.58	<1-269 (13)
Ti	ppm	6.56	13.18	3.36	6.26	6.98	3	1.88	1.3	2.67	4-528 (30)
V	ppm	0.9	2.24	0.9	0.95	1.07	0.75	0.32	0.06	0.41	<1-77 (5)
W	ppm	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	nd
Zn	ppm	58.4	460	89	89.8	132.2	50.2	39.98	34.08	48.57	4-84 900 (64)
Sn	ppm	1.37	6.32	0.8	1.65	1.51	0.54	<0.1	<0.1	<0.1	nd

\* ecotoxicity levels according to McDonald, Ingersoll (2000) and WT-732 2003 are marked with colors: green - level I, yellow - level II, red - level III.

\*\*after Lis and Pasieczna (1998).

reaching as much as 640 ppm were found in the H profile at point H2. This element was not determined during the research on the Geochemical Atlas of the Łódź agglomeration (Lis, Pasieczna 1998). According to Kabata-Pendias and Pendias (1999), in the zone of hypergenesis, bismuth is not very mobile and is part of insoluble compounds retained by iron hydroxides and manganese and organic matter. Bismuth contents in soils reaching several 100 ppm are found near copper smelters and in metal mining areas (Pasieczna 2012). In the case of the Ner alluvium, such high contents of this element can be associated with pollution supplied to the river with sewage discharged by an unidentified metallurgical plant. In the H2 sample, containing the largest amounts of bismuth, the presence of macroscopically visible fragments of easily crumbling sinters was found. Such a focus on pollution may also be indicated by high values of the coefficient of determination describing the dependence of bismuth content in relation to zinc ( $R^2 = 0.83$ ), tin ( $R^2 = 0.92$ ), lead ( $R^2 = 0.93$ ), copper ( $R^2 = 0.93$ ) and titanium ( $R^2 = 0.98$ ).

Contamination of alluvial sediments with metals causes their toxic impact on aquatic organisms. According to the criteria used by the Chief Inspectorate for Environmental Protection (GIOŚ), using the values of Threshold Effect Concentration (TEC), Probable Effect Concentration (PEC) and Midpoint Effects Concentrations (MEC) (MacDonald et al. 2000, WT-732 2003), the content in all the samples of arsenic, iron, manganese and nickel allowed them to be included in the first level, i.e. uncontaminated sediments that do not have a negative impact on aquatic organisms. In the case of silver, lead,

cadmium, chromium, copper and zinc in some samples, and in the case of mercury in all samples in which this element was determined, second level or third was found, indicating sediment contamination, which may have a negative impact on aquatic organisms. The classification was carried out in terms of elements determined as part of the monitoring of river sediments carried out by the Chief Inspectorate of Environmental Protection (Table 4).

### Sorption complex

The results of the determination of the CEC of the alluvium accumulated in the Ner river bed, by the Breeuwsma formula and the Kappen method, are similar and indicate a low capacity of these formations to store absorbed substances. This is related to the lithology of river sediments, among which the occurrence of fine-grained sands and sands without a fraction of less than 2 m and with a low content of organic carbon, reaching a maximum of 1.36%, was found (Table 5). The results of the Kappen method indicate that the sorption complex is saturated with acidic cations (e.g.  $H^+$ ,  $Al^{3+}$ ). The exception is the sample taken at the H2 site, in which the exchange capacity for basic cations (BEC) was two orders of magnitude greater than the electrolytic acidity. It is a sample in which the fragments of easily crumbling sinters were found macroscopically. It is assumed that such a high BEC value in the H2 sample may be the result of dissolution in hydrochloric acid (HCl) of the metals contained in the sediments (e.g. bismuth), and not displacement of basic cations from the sorption complex. It is worth mentioning that due to the lack of the smallest fractions and organic matter, alluvial

Table 5. The cation exchange capacity (CEC) estimated by the Breeuwsma formula and sorption capacity determined by the Kappen method.

Sample no.	TOC content	Particle content below 2 $\mu m$	CEC	Hydrolytic acidity	BEC	Total sorption capacity
H1	0.69	0.00	2.40	0.6	0	0.6
H2	1.30	0.00	4.56	0.68	10	10.68
H3	0.23	0.00	0.81	0.45	0	0.45
E1	1.36	0.00	4.76	1.73	0	1.73
E2	0.72	0.00	2.52	3.23	0	3.23
E3	0.61	0.00	2.13	2.03	0	2.03
C1	0.60	0.00	2.10	0.6	0	0.6
C2	0.19	0.00	0.66	0.45	0	0.45
C3	0.31	0.00	1.09	0.83	0	0.83

sediments do not constitute a typical colmation layer here that would retain pollution from the infiltrating river water as known in other studies (Wang et al. 2007).

### Water chemistry

In terms of the content of macroelements, the Ner water is clearly distinct from both waters taken from river sediments and groundwater (Figs 11 and 12). With their hydrochemical characteristics, the multi-ionic nature of water types ( $\text{HCO}_3\text{-Cl-Ca-Na}$ ,  $\text{Cl-HCO}_3\text{-Na-Ca}$ ), with a significant share or even dominance of chloride and sodium ions is noteworthy, which indicates their strong anthropogenic transformation. The poor quality of the water of the Ner River is also represented by the values of electrolytic conductivity exceeding  $1200 \mu\text{S} \cdot \text{cm}^{-1}$ , low content

of dissolved oxygen (below  $4.04 \text{ mg} \cdot \text{dm}^{-3}$ ) and concentrations of nutrients: nitrate nitrogen (over  $4.93 \text{ mg N-NO}_3 \cdot \text{dm}^{-3}$ ), ammonium nitrogen (above  $1.57 \text{ mg N-NH}_4 \cdot \text{dm}^{-3}$ ) and phosphate phosphorus (above  $0.88 \text{ mg P-PO}_4 \cdot \text{dm}^{-3}$ ). The concentrations of the above-mentioned elements in the Ner significantly exceed the threshold values of good chemical status of surface water set out in the Regulation of the Minister of Infrastructure of 25 June 2021 (Journal of Laws 2021, item 1475).

In the alluvium water, among the macroelements, there is a clear dominance of hydrocarbonate and calcium ions. The sulphate, chloride and sodium ions appear as secondary in the water type (Fig. 11, Table 6). The values of the electrolytic conductivity (EC) are lower than those observed in river water and are within a

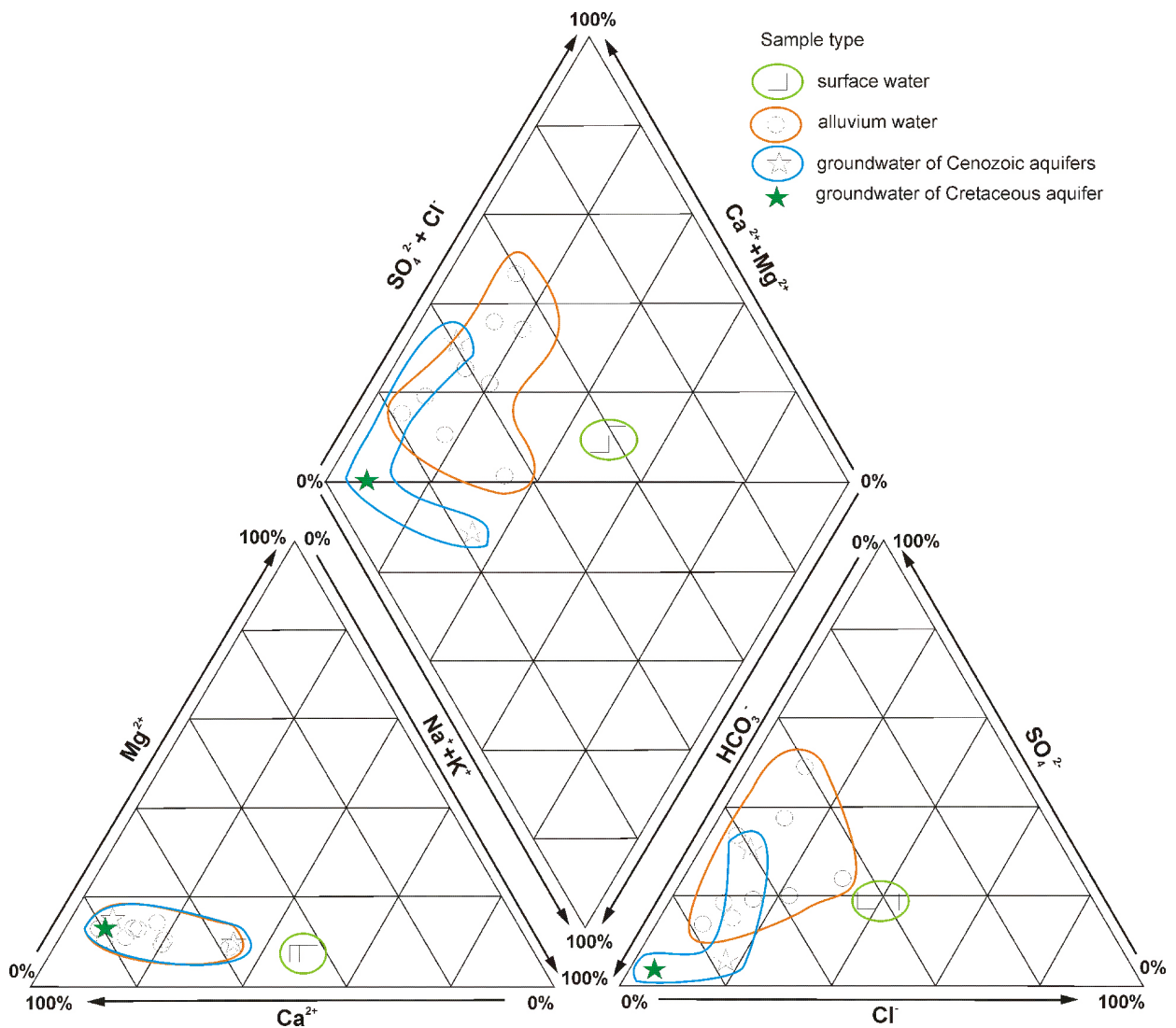


Fig. 11. Chemical composition of the tested water presented on the Piper diagram.



wide range of  $469 - 1070 \mu\text{S} \cdot \text{cm}^{-1}$ . Similarly, in alluvial water, the average content of nutrients is lower than in river water:  $1.71 \text{ mg N-NO}_3 \cdot \text{dm}^{-3}$ ,  $1.26 \text{ mg N-NH}_4 \cdot \text{dm}^{-3}$  and  $0.29 \text{ mg P-PO}_4 \cdot \text{dm}^{-3}$ . River alluviums are an extremely dynamic zone where surface waters mix with groundwater drained by the river. The shares of individual water streams are constantly changing depending on the temporary pressure systems. Changes in the flow of water result in changes in chemistry. The presented research results describe the temporary hydrochemical state of this zone. It can be assumed that the lower values of EC and the content of nutrients are, apart from the activity of living organisms, caused by the mixing of heavily polluted river water with groundwater in the alluvium, which, according to the conducted research, is of better quality. The EC reached a maximum of  $676 \mu\text{S} \cdot \text{cm}^{-1}$ , and the maximum content of nitrate nitrogen  $1.36 \text{ mg N-NO}_3 \cdot \text{dm}^{-3}$ , ammonium nitrogen  $0.67 \text{ mg N-NH}_4 \cdot \text{dm}^{-3}$  and phosphate phosphorus  $0.03 \text{ mg P-PO}_4 \cdot \text{dm}^{-3}$ .

The collected groundwater samples represent the chemical composition of three aquifers (Fig. 11). The water of the Quaternary is characterized by mineralisation ranging from  $100 \text{ mg} \cdot \text{dm}^{-3}$  to  $1237 \text{ mg} \cdot \text{dm}^{-3}$  with the predominance from  $100 \text{ mg} \cdot \text{dm}^{-3}$  to  $400 \text{ mg} \cdot \text{dm}^{-3}$  and domination in the composition of hydrocarbonate, calcium and rarely magnesium ion ( $\text{HCO}_3\text{-Ca}$  and  $\text{HCO}_3\text{-Ca-Mg}$ ) (Fabianowski 2002, Rodzoch, Karwacka 2015, Małecki et al. 2017). At the same time, it should be emphasized that the higher values of water mineralisation (above  $750 \text{ mg} \cdot \text{dm}^{-3}$ ) were documented during pumping tests within the plateau, with the dominating value of about  $500 \text{ mg} \cdot \text{dm}^{-3}$  (Murzynowski, Małecki 1982). The physicochemical properties and ionic composition of the groundwater studied today, covering the Quaternary aquifer, are similar to the results of archival research. A general mineralisation of about  $500 \text{ mg} \cdot \text{dm}^{-3}$  is seen, with a clear dominance of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  ions (Table 6). However, significant concentrations

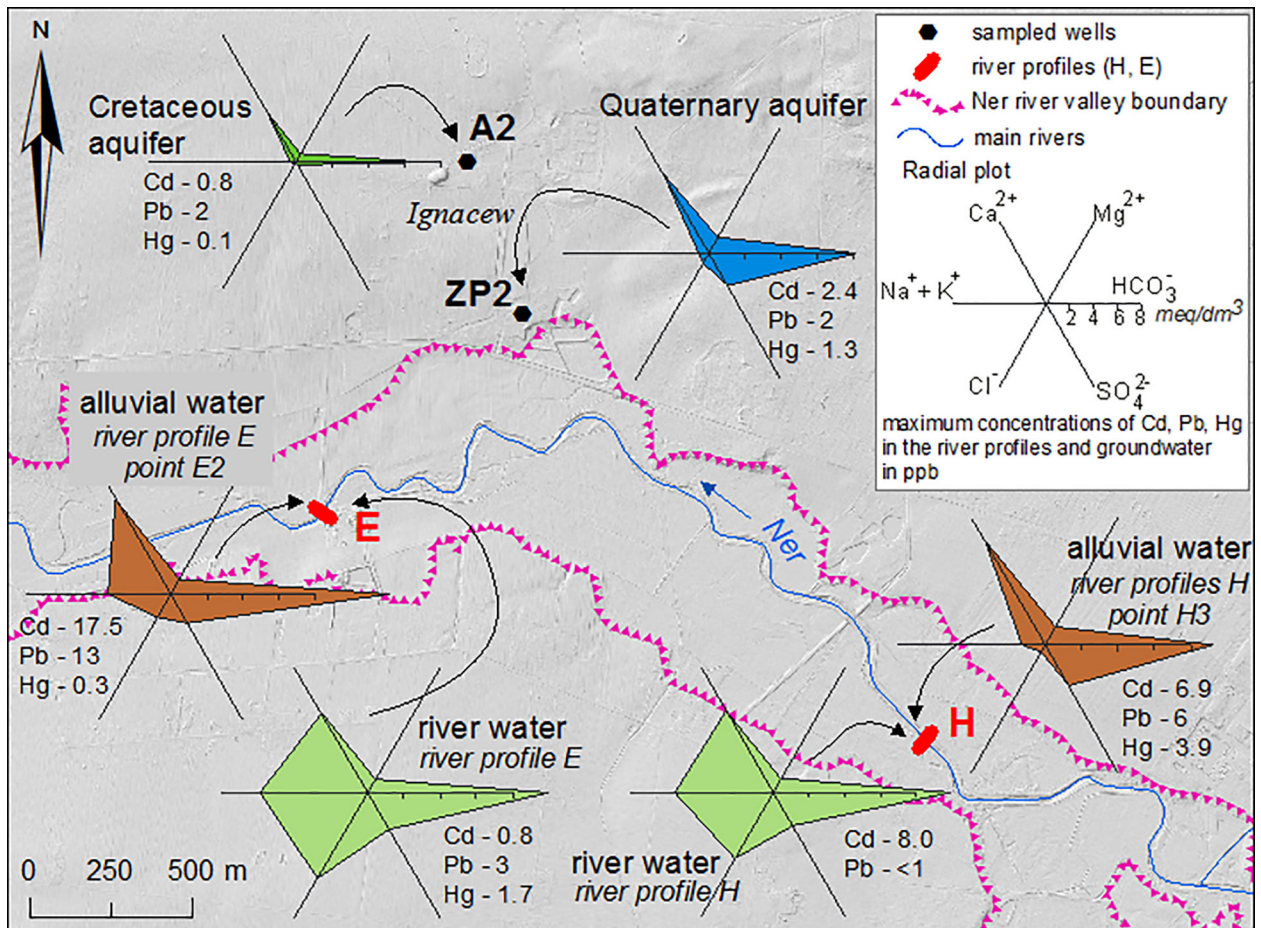


Fig. 12. Chemistry map of groundwater and river and alluvial waters in the H and E profiles (colors consistent with Fig. 11).

Table 6. Physicochemical properties of the tested water.

Parameter	Units	River water		Water from alluvium										Groundwater				Drinking water*
		Hr	Er	H1	H2	H3	C1	C2	C3	E1	E2	E3	Q	Ng	Cr3			
EC	mikroS/cm	1229	1307	479	469	727	681	737	567	745	875	1070	649	676	376	2500		
TDS	mg/dm <sup>3</sup>	836.6	898.9	332.7	351.17	604.7	498.5	548.9	412.3	548.8	740.9	651.2	503.3	524.7	309.8			
Water type		HCO <sub>3</sub> -Cl-Ca-Na	Cl-HCO <sub>3</sub> -Na-Ca	HCO <sub>3</sub> -Cl-SO <sub>4</sub> -Ca	HCO <sub>3</sub> -Ca	HCO <sub>3</sub> -SO <sub>4</sub> -Ca	HCO <sub>3</sub> -SO <sub>4</sub> -Ca	HCO <sub>3</sub> -Ca	HCO <sub>3</sub> -SO <sub>4</sub> -Ca	HCO <sub>3</sub> -Cl-Ca	HCO <sub>3</sub> -Ca-Na	HCO <sub>3</sub> -Ca	HCO <sub>3</sub> -SO <sub>4</sub> -Ca	HCO <sub>3</sub> -Ca-Na	HCO <sub>3</sub> -Ca			
pH		7.3	6.46	6.5	7	6.89	6.73	7.13	6.59	6.93	6.71	7.11	7.32	7.2	7.45	6.5-9.5		
Temp.	st.C	15.1	16.1	15.2	15.6	15.8	16.5	16.9	16.4	15.4	15.4	16.3	15.4	11.3	11.5			
Eh	mV	132	-28	-50.1	-116	-66.8	-7.8	-84	-58.6	-63	-56.5	-55	125	-53.5	-66.7			
O <sub>2</sub>	mg/dm <sup>3</sup>	3.13	4.04	1.6	0.72	1.45	1.71	1.93	1.28	1.85	1.34	1.54	1.44	0.09	0.09			
SO <sub>4</sub> <sup>2-</sup>	mg/dm <sup>3</sup>	105	115	55	40	125	155	50	100	75	90	60	100	19	8	250		
Cl-	mg/dm <sup>3</sup>	152.93	192.85	51.69	16.59	13.83	24.96	33.25	24.74	60.97	51.33	101.39	24.04	40.63	5.25	250		
NO <sub>3</sub> <sup>-</sup>	mg/dm <sup>3</sup>	21.83	26.54	7.7	8.56	4.28	22.68	8.13	4.28	5.14	3.85	3.42	5.99	3.42	3.85	50		
NH <sub>4</sub> <sup>+</sup>	mg/dm <sup>3</sup>	2.02	2.24	2.07	0.97	0.45	0.15	2.6	1.83	0.5	2.2	3.84	0.01	0.86	0.36	0.5		
PO <sub>4</sub> <sup>3-</sup>	mg/dm <sup>3</sup>	2.9	2.75	0.08	0.48	0.1	0.12	5.6	0.52	0.33	0.06	0.88	0.08	0.06	0.08			
Al	mg/dm <sup>3</sup>	0.009	0.051	<0.05	0.074	<0.05	0.022	0.002	0.029	0.003	0.069	0.079	<0.05	<0.001	<0.05	0.2		
As	mg/dm <sup>3</sup>	<0.001	<0.003	0.026	0.006	0.003	<0.001	<0.001	<0.001	0.015	<0.003	<0.003	<0.003	<0.001	<0.003	0.01		
Ba	mg/dm <sup>3</sup>	0.05	0.06	0.05	0.09	0.24	0.12	0.05	0.14	0.03	0.24	0.12	0.04	0.16	0.06			
Be	mg/dm <sup>3</sup>	nd	<0.005	<0.005	<0.005	<0.005	nd	nd	nd	nd	<0.005	<0.005	<0.005	nd	<0.005			
Bi	mg/dm <sup>3</sup>	<0.005	0.09	<0.005	0.1	0.07	<0.005	<0.005	<0.005	<0.005	<0.005	0.04	0.06	<0.005	<0.005			
Pb	mg/dm <sup>3</sup>	<0.001	0.003	0.002	0.006	0.002	<0.001	<0.001	<0.001	0.013	0.003	0.004	0.002	<0.001	0.002	0.01		
Br	mg/dm <sup>3</sup>	nd	<1	<1	<1	<1	nd	nd	nd	nd	<1	<1	<1	nd	<1			
Cd	mg/dm <sup>3</sup>	0.0080	0.0008	0.0017	0.0028	0.0069	0.0013	0.0009	0.0011	0.0175	0.0016	0.0012	0.0024	0.0005	0.0008	0.005		

Ca	mg/dm <sup>3</sup>	104.57	101	56.7	70.3	133	102.44	99.35	83.01	95.23	123	122	100	75.29	62.2
Cr	mg/dm <sup>3</sup>	0.005	<0.005	<0.005	0.01	<0.005	0.005	0.005	0.007	0.006	<0.005	0.005	<0.005	0.002	<0.005
Co	mg/dm <sup>3</sup>	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Fe	mg/dm <sup>3</sup>	0.04	0.36	3.34	5.26	4.17	1.39	3.19	4.54	0.1	0.75	5.14	<0.02	0.67	0.64
K	mg/dm <sup>3</sup>	14.43	17.6	4.75	2.48	9.34	7.16	3.94	3.39	3.76	13.1	3.07	1.32	4.16	2.52
Cu	mg/dm <sup>3</sup>	0.001	<0.005	<0.005	0.005	<0.005	<0.001	<0.001	<0.001	<0.001	<0.005	<0.005	<0.005	<0.001	<0.005
Mg	mg/dm <sup>3</sup>	10.64	10.5	5.3	5.43	14.3	9.18	12.76	8.83	7.9	12	11.7	11.9	7.98	6.24
Mn	mg/dm <sup>3</sup>	0.113	0.122	0.361	0.51	0.296	0.32	0.384	0.542	0.002	0.257	0.749	0.088	0.042	0.036
Mo	mg/dm <sup>3</sup>	<0.001	<0.005	<0.005	<0.005	<0.005	<0.001	<0.001	<0.001	0.01	<0.005	<0.005	<0.005	<0.001	<0.005
Na	mg/dm <sup>3</sup>	119.29	125	16	7.76	23.2	15.23	26.2	15.62	28.76	72.9	9.52	12.1	48.37	4.94
Ni	mg/dm <sup>3</sup>	0.009	0.014	0.006	<0.005	<0.005	0.006	0.001	0.005	0.007	0.006	<0.005	<0.005	<0.001	<0.005
Hg	mg/dm <sup>3</sup>	nd	0.0017	0.0004	0.0039	0.0004	nd	nd	nd	nd	0.0003	0.0002	0.0013	nd	0.0001
Ag	mg/dm <sup>3</sup>	nd	<0.005	<0.005	<0.005	<0.005	nd	nd	nd	nd	<0.005	<0.005	<0.005	nd	<0.005
Si	mg/dm <sup>3</sup>	4.7	7.76	7.46	7.38	5.15	3.43	6.16	6.89	3.39	8.52	6.11	4.51	8.14	12.6
Sr	mg/dm <sup>3</sup>	0.33	0.4	0.22	0.18	0.43	0.36	0.67	0.37	0.17	1.19	0.33	0.18	2.02	1.38
Ti	mg/dm <sup>3</sup>	<0.001	<0.005	<0.005	<0.005	<0.005	<0.001	<0.001	<0.001	<0.001	<0.005	<0.005	<0.005	<0.001	<0.005
V	mg/dm <sup>3</sup>	0.05	<0.004	<0.004	<0.004	<0.004	0.04	0.05	0.04	0.04	<0.004	<0.004	<0.004	0.03	<0.004
W	mg/dm <sup>3</sup>	<0.001	<0.005	<0.005	<0.005	<0.005	<0.001	<0.001	<0.001	0.02	<0.005	<0.005	<0.005	<0.001	<0.005
Zn	mg/dm <sup>3</sup>	0.06	0.09	0.06	0.06	0.06	0.08	0.05	0.03	0.02	0.05	0.06	0.09	<0.001	0.02
Sn	mg/dm <sup>3</sup>	<0.001	<0.005	<0.005	<0.005	<0.005	<0.001	<0.001	<0.001	<0.001	<0.005	<0.005	<0.005	<0.001	<0.005

nd - no data, \* red numbers in the table mean values exceeding the permissible ranges for drinking water, the ranges are given in accordance with the Regulation of the Minister of Health of December 7, 2017 on the quality of water intended for human consumption (Journal of Laws of 2017, item 2294); the color scale applies to the quality classification of groundwater bodies according to the Regulation of the Minister of Maritime Economy and Inland Navigation of October 11, 2019 on the criteria and method of assessing the status of groundwater bodies: quality class I - dark green, quality class II - light green, III quality class - yellow, quality class IV - orange, quality class V - red.

of sulphate ions ( $100 \text{ mg} \cdot \text{dm}^{-3}$ ) are noteworthy, exceeding the background range determined by Fabianowski (2002) for this aquifer and allowing the tested water to be classified as  $\text{HCO}_3\text{-SO}_4\text{-Ca}$ .

The Neogene aquifer is exploited only locally due to variable hydrogeological parameters and significant iron and brown coal dust contents (Fabianowski 2002). For this reason, its hydrochemical recognition is insufficient for full characterisation. Based on the research carried out by the authors, it can be concluded that in terms of EC ( $676 \mu\text{S} \cdot \text{cm}^{-1}$ ) and mineralisation ( $525 \text{ mg} \cdot \text{dm}^{-3}$ ), the tested water is similar to the Quaternary water. Its composition is dominated by hydrocarbonate and calcium ions with a significant share of sodium ions. This is water of the  $\text{HCO}_3\text{-Ca-Na}$  type (Table 6).

The Upper Cretaceous aquifer is the most intensively exploited in the area covered by the study. The water of this aquifer is characterised by low electrolytic conductivity ranging from  $100 \mu\text{S} \cdot \text{cm}^{-1}$  to  $650 \mu\text{S} \cdot \text{cm}^{-1}$  and mineralisation of  $200\text{-}500 \text{ mg} \cdot \text{dm}^{-3}$  (Murzynowski, Małecki 1982). These are simple water types of the  $\text{HCO}_3\text{-Ca}$ . The collected water sample falls within the background ranges determined for the Upper Cretaceous aquifer: EC =  $376 \mu\text{S} \cdot \text{cm}^{-1}$ , TDS =  $309.8 \text{ mg} \cdot \text{dm}^{-3}$  and water type of  $\text{HCO}_3\text{-Ca}$  (Table 6).

It is worth noting that the study by Małecki et al. (2017) and Ziułkiewicz (2003), conducted on the scale of the entire Łódź agglomeration, documented the stability of the chemical composition of the waters of this aquifer during its long-term exploitation. However, on a local scale, a potential inflow of polluted water into the Upper Cretaceous aquifer cannot be omitted, especially in places where hydraulic windows occur between the Quaternary and Cretaceous aquifers.

### Speciation modelling

The impact of anthropopressure on the water chemistry is noticeable not only in their chemical composition, but also in the distribution of speciation of water macroelements. In the case of alkaline elements (Na and K) and alkaline earth metals (e.g. Ca and Mg), the dominance of simple ionic speciation is observed. It is characteristic for water occurring in natural conditions. On the other hand, in surface water, water taken from alluvial water and water of the Quaternary aquifer,

the significant share of sulphate and polyelemental speciation is clearly visible, which proves the anthropogenic transformation of their chemistry. In the water from the Upper Cretaceous aquifer, the assessment of sodium and potassium speciation did not reveal the presence of sulphate, and in the case of calcium and magnesium, these speciation are secondary to hydrocarbonate speciation ( $\text{CaHCO}_3^+$  and  $\text{MgHCO}_3^+$ ) (Table 7). The observed trends in the speciation distribution indicate the high degree of their anthropogenic transformations and are consistent with the results of research conducted by Józwiak and Krogulec (2006) in the area of the Warsaw agglomeration.

### Microelements in the tested sediments and water

The characteristics of the content of microelements in water and sediment are also a sensitive indicator of anthropogenic impacts. Studies of the alluvial deposits of the Ner documented the presence of chromium, zinc, copper, mercury and cadmium and, in individual cases, lead and silver in concentrations considered harmful to living organisms. The next step in such an assessment is to determine whether the above-mentioned elements accumulated in river sediments are activated and are also present in water in concentrations that pose a threat to living organisms.

In the tested water samples, the concentration of silver did not exceed the detection limit of  $0.005 \text{ mg} \cdot \text{dm}^{-3}$  and the limit value for drinking water ( $0.010 \text{ mg} \cdot \text{dm}^{-3}$ ). The same is true for zinc and copper. The maximum contents of Zn ( $0.09 \text{ mg} \cdot \text{dm}^{-3}$ ) and Cu ( $0.005 \text{ mg} \cdot \text{dm}^{-3}$ ) do not exceed the contents that may have a negative impact on living organisms. In the case of copper, they also do not exceed the limit values for drinking water (Table 6).

Concentrations of chromium are considered in surface water as harmful to biological activity with content exceeding  $0.1 \text{ mg} \cdot \text{dm}^{-3}$  (Kabata-Pendias, Pendias 1999), and in drinking water, the content of this element should not exceed  $0.05 \text{ mg} \cdot \text{dm}^{-3}$  (Journal of Laws of 2017, item 2294). In the tested water samples, the chromium content was lower than the limit values given above. The highest concentrations, reaching  $0.010 \text{ mg} \cdot \text{dm}^{-3}$ , were found in the water taken from the alluvium of the Ner River. The results of speciation



modelling indicate that this element occurs mainly in the sixth oxidation state in the form of the easily soluble  $\text{CrO}_4^{2-}$  form (Tables 6 and 7). This is worrying because forms of hexavalent chromium are mobile in the soil and water environment and are subject to intensive bioaccumulation (Kabata-Pendias, Pendias 1999).

The contents of cadmium, mercury, arsenic and lead in water from the alluvium of Ner, in individual samples, exceed the limit

values for drinking water, which are:  $0.005 \text{ mg Cd} \cdot \text{dm}^{-3}$ ,  $0.01 \text{ mg Pb} \cdot \text{dm}^{-3}$ ,  $0.01 \text{ mg As} \cdot \text{dm}^{-3}$  and  $0.001 \text{ mg Hg} \cdot \text{dm}^{-3}$  (Journal of Laws of 2017, item 2294). In addition, mercury concentrations exceed the values allowed for drinking water also in the sample taken from the Quaternary aquifer ( $0.00132 \text{ mg} \cdot \text{dm}^{-3}$ ). It should be emphasised that all forms of mercury are toxic. Mercury easily passes from adsorbed forms to water (Kabata-Pendias, Pendias 1999). Extreme mercury content

Table 7. Percentage contribution of the speciation of selected elements.

Speciation	River water*	Water from alluvium*	Quaternary aquifer (ZP2 well)	Upper Cretaceous (A2 well)	Speciation	River water*	Water from alluvium*	Quaternary aquifer (ZP2 well)	Upper Cretaceous (A2 well)
Carbon					Magnesium				
$\text{HCO}_3^-$	71.4	70.1	87.1	89.6	$\text{Mg}^{2+}$	92.9	91.5	91.8	97.0
$\text{CO}_{2(\text{aq})}$	26.5	27.5	10.3	8.5	$\text{MgSO}_4$	4.9	5.6	5.8	0.6
$\text{CaHCO}_3^+$	1.7	1.6	2.0	1.5	$\text{MgHCO}_3^+$	2.0	2.1	2.3	2.3
$\text{MgHCO}_3^+$	0.2	0.2	0.3	0.2	$\text{MgCl}^+$	0.1	0.5	0.1	0.0
$\text{NaHCO}_3$	0.1	0.5	0.1	0.0	$\text{MgHPO}_4$	0.1	0.2	0.0	0.0
$\text{CaCO}_3$	0.0	0.1	0.1	0.1	$\text{MgCO}_3$	0.0	0.1	0.1	0.1
$\text{CO}_3^{2-}$	0.0	0.0	0.1	0.1	Bismuth				
Chlorides					$\text{Bi}(\text{OH})_{3(\text{aq})}$	94.5	93.3	98.3	98.7
$\text{Cl}^-$	99.1	99.1	99.1	99.2	$\text{Bi}(\text{OH})_2^+$	5.5	6.7	1.7	1.3
$\text{CaCl}^+$	0.9	0.9	0.9	0.7	Cadmium				
Sulfur					$\text{Cd}^{2+}$	83.1	70.2	82.5	89.6
$\text{SO}_4^{2-}$	81.1	81.8	80.7	84.8	$\text{CdCl}^+$	5.7	18.4	3.3	0.9
$\text{CaSO}_4$	16.3	14.6	16.4	13.3	$\text{CdSO}_{4(\text{aq})}$	5.2	4.9	6.2	0.7
$\text{MgSO}_4$	2.2	2.1	2.7	1.8	$\text{CdHCO}_3^+$	4.1	3.6	4.7	4.6
$\text{NaSO}_4^-$	0.3	1.3	0.1	0.1	$\text{CdCO}_{3(\text{aq})}$	1.1	1.4	3.1	4.1
$\text{KSO}_4^-$	0.1	0.1	0.0	0.0	$\text{CdHPO}_{4(\text{aq})}$	0.6	1.1	0.1	0.1
$\text{NH}_4\text{SO}_4^-$	0.0	0.1	0.0	0.0	$\text{Cd}(\text{SO}_4)_2^{2-}$	0.1	0.1	0.1	0.0
Sodium					$\text{CdCl}_{2(\text{aq})}$	0.0	0.3	0.0	0.0
$\text{Na}^+$	99.4	99.3	99.3	99.5	$\text{CdNO}_3^+$	0.0	0.1	0.0	0.0
$\text{NaHCO}_3$	0.4	0.4	0.5	0.5	Copper				
$\text{NaSO}_4^-$	0.2	0.3	0.3	0.0	$\text{Cu}^{2+}$	68.0	64.8	44.9	46.2
Potassium					$\text{CuOH}^+$	30.7	32.1	55.0	53.5
$\text{K}^+$	99.7	99.6	99.6	100.0	$\text{CuHPO}_4$	1.0	2.6	0.1	0.1
$\text{KSO}_4^-$	0.3	0.4	0.4	0.0	$\text{CuNH}_3^{2+}$	0.2	0.3	0.0	0.1
Calcium					$\text{CuCl}^+$	0.0	0.1	0.0	0.0
$\text{Ca}^{2+}$	90.6	88.3	89.3	95.5	Chrome				
$\text{CaSO}_4$	5.8	6.5	6.9	0.7	$\text{CrO}_4^{2-}$	73.0	72.7	89.6	91.5
$\text{CaHCO}_3^+$	2.9	3.0	3.3	3.4	$\text{HCrO}_4^-$	27.0	27.3	10.4	8.5
$\text{CaCl}^+$	0.4	1.7	0.3	0.1	Mercury				
$\text{CaCO}_3$	0.1	0.1	0.2	0.3	$\text{HgCl}_2$	85.5	57.3	91.4	97.9
$\text{CaHPO}_4$	0.1	0.2	0.0	0.0	$\text{HgCl}_3^-$	14.5	42.7	8.6	2.1
$\text{CaNO}_3^+$	0.1	0.2	0.0	0.0	Lead				
					$\text{PbCO}_3$	100.0	100.0	100.0	100.0

\*average content.

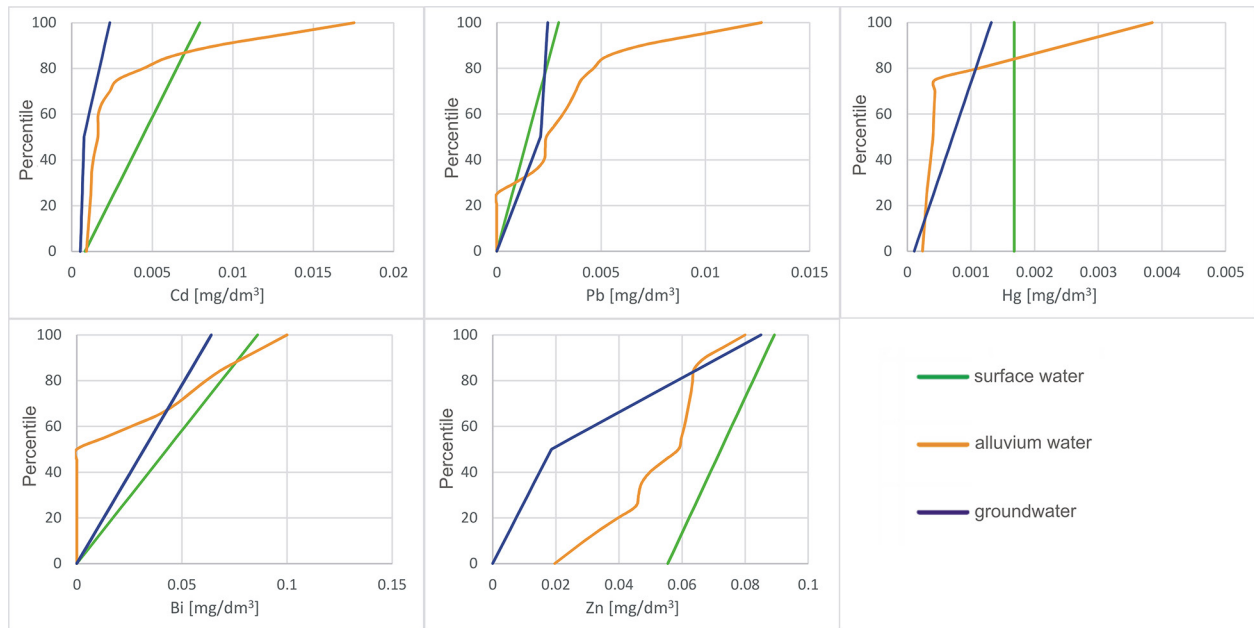


Fig. 13. Cumulative concentration curves of selected microelements in water ( $n = 14$ ).

in the water taken from the Ner alluvium significantly exceeds the Hg content found both in the analysed groundwater and surface water, which may indicate the release of mercury accumulated in the alluvium into the solution. The same trend was observed for cadmium, lead and bismuth, and for zinc, the course of the cumulative curve for surface water and alluvial water is similar, lower values occur in groundwater (Figs 12 and 13).

The analysis of microelements concentrations in the tested waters in the case of their mixing indicates a negative impact of water from alluvial sediments on the chemical status of waters of the Quaternary and Upper Cretaceous horizons.

## Discussion and conclusions

The assessment of hydraulic relationships between surface water and groundwater, and the relationships between aquifers are fundamental elements determining the sensitivity of the hydrogeological system to pollution in river valley zones exposed to strong anthropopressure. The disturbance of the hydrodynamic balance of the Upper Cretaceous aquifer showed that despite the existence of significant pressure values in the Cretaceous (H well 0.4 atm., C well 0.15 atm.), there are zones (E well) where the pressure in the Upper Cretaceous horizon decreased as a result

of groundwater withdrawal. This will lead to the drainage of water from the above aquifers and pose a threat to the chemical status of the water in the Cretaceous aquifer.

To assess this threat, a numerical model of the groundwater system in the Konstanyńów Łódzki region was created, taking into account groundwater withdrawal from the Upper Cretaceous aquifer in Ignacew, located near the Ner river valley. Model tests have shown that when group pumping of the A1, A2 and A3 Ignacew wells with actual discharge rate occurs, the water inflow to all wells takes place through the Ner river valley in the area of the research profiles and hydrogeological cross-sections of C and E, where the occurrence of hydrogeological windows between the Quaternary and Cretaceous aquifers was found.

Hydrochemical characteristics of surface water and groundwater in this region showed that in terms of macroelements content, the waters of the Ner river are clearly different from both water collected from river sediments and groundwater (Fig. 11). River waters are characterised by poly-ionic types ( $\text{HCO}_3\text{-Cl-Ca-Na}$ ,  $\text{Cl-HCO}_3\text{-Na-Ca}$ ) with a significant share or even dominance of chloride and sodium ions, which indicates their strong anthropogenic transformation. The waters of the Quaternary aquifer are characterised by mineralisation ranging from  $100 \text{ mg} \cdot \text{dm}^{-3}$  to  $1237 \text{ mg} \cdot \text{dm}^{-3}$  with the predominance of waters ranging from  $100 \text{ mg} \cdot \text{dm}^{-3}$  to  $400 \text{ mg} \cdot \text{dm}^{-3}$  and

the dominance of the following composition: bicarbonates, calcium ions, and locally magnesium ions (water type of  $\text{HCO}_3\text{-Ca}$  and  $\text{HCO}_3\text{-Ca-Mg}$ ).

Higher values of water mineralisation (above  $750 \text{ mg} \cdot \text{dm}^{-3}$ ) were documented during test pumping in the plateau, and lower values in the Ner river valley, with an average value of approximately  $500 \text{ mg} \cdot \text{dm}^{-3}$ . The groundwater of the Quaternary aquifer is water with a total mineralisation of approximately  $500 \text{ mg} \cdot \text{dm}^{-3}$ , with a clear dominance of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  ions and significant contents of sulphate ions ( $100 \text{ mg} \cdot \text{dm}^{-3}$ ), exceeding the background range of the Quaternary aquifer, classifying tested waters to the type  $\text{HCO}_3\text{-SO}_4\text{-Ca}$ . The Neogene aquifer was characterised by variable hydrochemical parameters and significant contents of iron and lignite dust. The Upper Cretaceous aquifer, which is most intensively exploited in the study area, is characterised by low electrolytic conductivity ranging from  $100 \mu\text{S} \cdot \text{cm}^{-1}$  to  $650 \mu\text{S} \cdot \text{cm}^{-1}$  and mineralisation of  $200\text{-}500 \text{ mg} \cdot \text{dm}^{-3}$ . These are waters of the  $\text{HCO}_3\text{-Ca}$  type. The results of archival and contemporary research indicate the stability of their chemical composition during long-term exploitation.

Anthropogenic changes in water chemistry are noticeable not only in their composition, but also in the share of macroelement speciations. In surface water, water taken from alluvium and water of the Quaternary aquifer, there is a clearly higher share of sulphate forms and multi-element speciation, indicating the anthropogenic transformation of their chemistry. However, in the water of the Upper Cretaceous aquifer, the dominance of simple ionic forms is observed, characteristic of water occurring in natural conditions. Water pollution in the near-surface zone is also documented by the concentration of cadmium, mercury and lead. In the water from the Ner alluvium, in individual samples, they exceed the permissible values for drinking water. Also in a sample taken from the Quaternary aquifer, mercury concentrations exceed the permissible values for drinking water. High mercury content in water collected from the Ner alluvium, significantly exceeded the Hg content found in the analysed groundwater and surface water, indicating the release of mercury accumulated in the alluvium from adsorbed forms to the solution. A similar tendency was observed in the case of cadmium and lead.

The results of the research showed that the accumulated pollutant loads in the near-surface zones of the studied area actually pose a threat to the Upper Cretaceous aquifer. Maintaining good chemical condition of this aquifer is conditional on strict compliance with the current withdrawal. Limiting exploitation by monitoring discharge rates will allow maintaining the current pressure gradients, which will minimise the possibility of releasing accumulated pollutants. These findings should be used in the management of groundwater in the studied region, in documenting groundwater withdrawal in planning and in water-protection issues. At the same time, in the active and monitoring wells located on the plateau and in the Ner valley, monitoring of the chemical state of Quaternary and Upper Cretaceous water should be carried out in accordance with the schedule specified in the Regulation of the Minister of Infrastructure of 13th July 2021, on the forms and methods of monitoring surface water and groundwater bodies (Journal of Laws of 2021, item 1576) every 6 years.

In the regional assessment, in connection with the designation of the protection areas of the Main Groundwater Reservoirs for the purposes of planning and managing water in river basin areas, it is necessary to indicate places of groundwater quality threat, especially of the useful aquifers. Undoubtedly, such threats occur in river valley zones, which for decades have been the site of sewage discharge from large urban agglomerations, an example of which is the Ner river valley.

### Author's contribution

E.K. and J.J.M. – conceptualization; J.J.M and M.Z. – methodology; M.S.H., J.T., S.Z. and M.Z. – field sampling; M.S.H. – hydrochemical software; S.Z. – hydrodynamical software; E.K., J.J.M. and J.T. – validation; J.T. – formal analysis; J.J.M., J.T., M.S.H., S.Z. and M.Z. – writing, review and editing; J.J.M. – project administration; E.K. – funding acquisition.

### Acknowledgements

The authors would like to thank Prof. dr hab. Monika Rzodkiewicz for her help and involvement in preparing the publication and

anonymous Reviewers for providing constructive comments and suggestions that improved the manuscript.

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