Influence of natural and anthropogenic factors on the chemical composition of shallow groundwater in the city of Wrocław, south-west Poland

Marta Trałka*, Marek Błachowicz, Sebastian Buczyński

University of Wrocław, Institute of Geological Sciences, Department of General Hydrogeology, Cybulskiego Street 32, 50-205 Wrocław, Poland
* corresponding author; e-mail address: marta.tralka@uwr.edu.pl

Abstract

Seen in the light of increasing anthropogenic impacts on the environment and a growing demand for potable water, pollution of groundwater is a very important issue, especially in large city areas. The present research includes analyses of the chemical composition at 109 measuring points in the Wrocław area, and of the spatial distribution of groundwater components with regard to land use, geological structure and hydrogeological conditions. Based on spatial analyses, it has been noted that changes depend mainly on land use and the kind of activity carried out in close proximity of water intake. Shallow groundwater in Wrocław is characterised by a great variability of main components. Factor analysis has made it possible to distinguish these components and determine the degree of their influence on the chemical composition of shallow groundwater in the entire study area. The current research demonstrates the high sensitivity of aquifers to pollution and emphasises the role of human activity in levels of groundwater pollution in urban areas.

Key words: groundwater pollution, groundwater chemical composition changes, factor analysis, urban areas

1. Introduction

Currently, over 72 per cent of people across the globe live in urban areas; predictions hold that already by 2050, this will have exceeded 80 per cent. Indeed, despite available data and forecasts indicating a decrease of populations in the majority of European countries, urban and suburban areas have been observed to be spreading (i.e., urban sprawl) (Eurostat, 2016; EEA, 2017). Such urbanisation processes lead to changes in the natural environment, which may greatly impact the quality of groundwater, amongst other things. Deterioration of groundwater quality in urban areas was observed as early as the 1960s and 1970s (Johnson, 1975). The scale of this phenomenon is particularly visible in shallow first aquifer, which is most exposed to contamination as a result of the weakest isolation and of direct connection with surface waters (e.g., Foster, 2020).

In papers dealing with the quality of shallow groundwater in urban areas, the emphasis is mainly on temporal and spatial changes in chemical composition and on factors inducing such changes. For instance, this topic was discussed by Vázquez-Suñé (2003) and Criollo et al. (2018), who minutely described variations in chemical composition of groundwater in Barcelona. For the German city of Dresden, Grischek et al. (1996) produced a valuable paper, while similar research was carried out in the Gdańsk metropolitan area (Lidzbarski et al., 2016) and other cities in Poland, for the creation of Hy-

drogeological Maps of Poland, First Aquifer with a scale 1:50 000. As far as non-European countries are concerned, research on the quality of groundwater in urban areas is being done in China (e.g., Shi et al., 2018), India (Ali et al., 2015) and Iran (Nasrabadi & Abbasi Maedeh, 2014), where, due to climate conditions, geological structure, increase in population and rapid development of cities, the quality of shallow groundwater is deteriorating (Foster, 2020).

Such studies have demonstrated that recognition of the chemical composition of groundwater and the impact of human activity on its variations is critical for any assessment of the condition of the natural environment. Research like this provides data which allow to take the necessary action aimed at minimising negative effects of urbanisation and encouraging a sustainable development of urban areas. Unfortunately, in the Wrocław area, despite rapid expansion, changes in land use and optimistic development forecasts as well as classification of the city in the Gamma group (i.e., cities connecting smaller economic regions into world economy) in GaWC ranking (based on economic factor) (The World According to GaWC, 2020), results of research to this date on the chemical composition of groundwater have been insufficient.

Due to the rapid development of the city of Wrocław, the aim of research carried out in 2021 was to establish the chemical composition of groundwater and distribution of concentration of chosen ions. On the basis of data obtained, a spatial and statistical analysis of the components of groundwater was performed and an attempt was made to determine the origins of pollutants (and factors shaping the chemical composition of water).

2. Material

Wrocław covers an area of 292.8 km^2 and is the fourth largest city in Poland, with a population of 635,800 inhabitants (Statistical Yearbook, 2020). Situated in the south-western part of the country (Fig. 1), this city constitutes the region's main economic, cultural and administrative centre (Dorociak-Tokarczyk et al., 2018). The centre is dominated by areas used for residential premises and commercial or economic activity, occupying 31 per cent of the area. Green spaces (parks, squares) are also located in the direct neighbourhood of the city centre. Together with agricultural areas (mainly in suburbs), they constitute 57 per cent of the city's total area. The remaining 12 per cent pertain to communication and associated areas and those without specific use (Fig. 2). The area analysed is situated


Fig. 1. Location of study area, the city of Wrocław.

in a temperate climate zone (Dubicki et al., 2002), of average temperatures of 10.3°C and average multiannual precipitation of 559 mm, as in the period 2010–2020. Air temperature and precipitation rate in the research period did not vary from the average multiannual value for 2010–2020 (based on data from IMWM-NRI, 2021).

The structure of the geological substratum of Wrocław is characterised by great variability (Fig. 3). Quaternary deposits consists mostly of sands and gravels, as well as Holocene clays and silts, exposed superficially in the northern, eastern and south-eastern part of the city, as well as in river valleys. In the city centre, the subsurface soils are covered by anthropogenic embankments, often of considerable thickness (>2 m). Among Pleistocene formations, sands and gravels, as well as glacial tills from central and northern Poland, prevail in the western, southern and north-western part of the city. In turn, Neogene formations (clays and clayey silts, plus sands and gravels) outcrop locally, mostly in the west of the study area. The thickness of Quaternary formations averages 40–50 m, being usually lesser in the west of Wrocław (<10 m) (Winnicka, 1985).

We here use the term "shallow groundwater" for the subsurface aquifer where recognised first groundwater and deeper aquifers are strongly connected with the subsurface groundwater flow system. Shallow aquifers in the study area are mostly included in Quaternary formations, which can be divided into Pleistocene and Holocene aquifers system. The Pleistocene aquifers are often recognised as sandy-gravel systems, of several metres in thicknes (mostly of a fluvioglatial origin), divided by impermeable glacial soils such as glacial tills
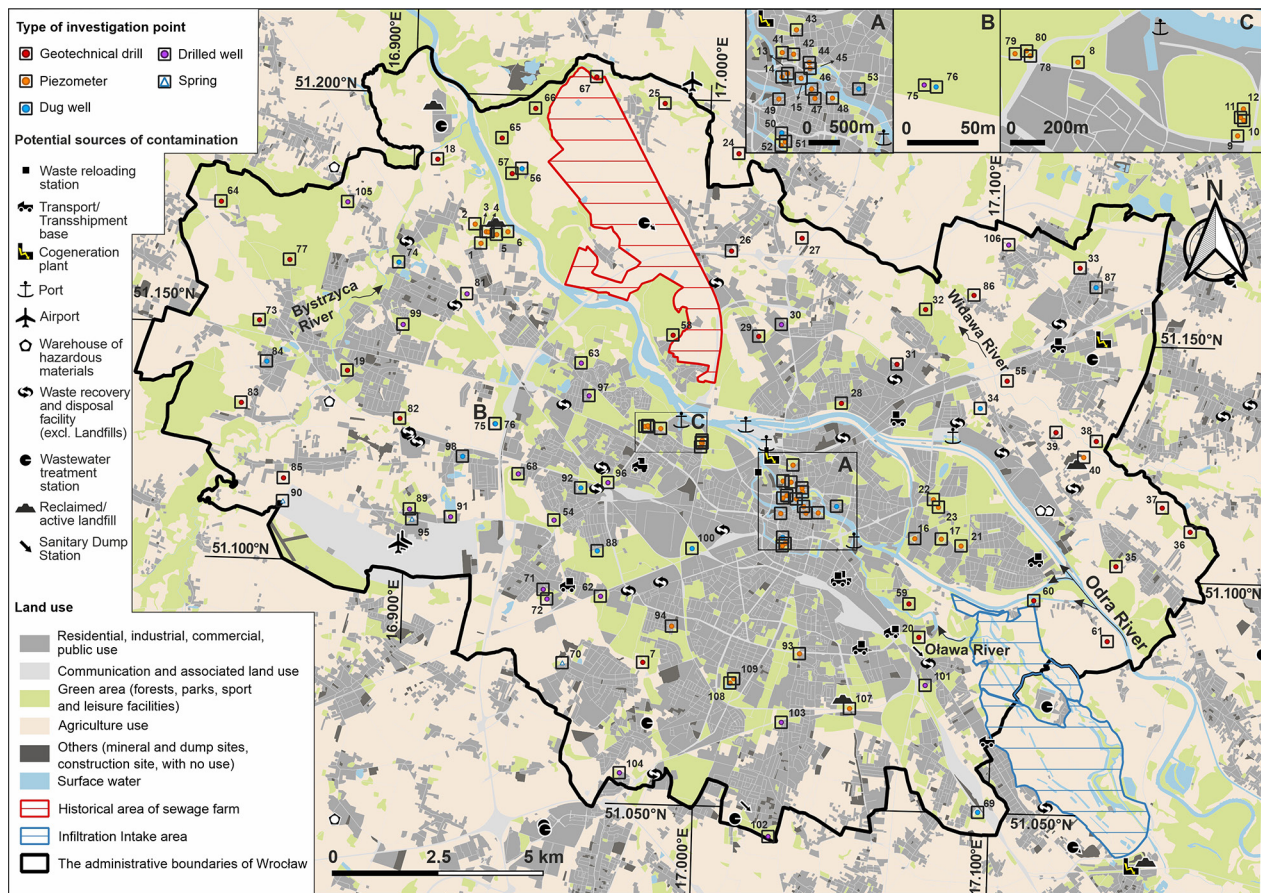
Fig. 2. Location of measurement points on the background of land use in the city of Wrocław (from Trałka et al., 2021; based on European Commission, 2018). Potential sources of contamination are modified from Różański & Gawlikowska (2015a, b, c, d).

(Mroczkowska & Michniewicz, 1976). In the Odra River valley and its tributaries, shallow aquifers are known as sandy-gravel with well-permeable deposits (5 to 30 metres in thickness) of fluvial origin and recognised as a single, continuous aquifer system. The shallow aquifers in most cases are known as unconfined aquifers, but in the city centre, the urban embankments can locally change into the confined type. In the western part of Wrocław, where Miocene and Pliocene strata outcrop (see Fig. 3), the Quaternary aquifer system is replaced by shallow Miocene and Pliocene sediments (mostly as confined aquifer) which are isolated from deeper-lying aquifers of Neogene age by several dozens of metres thick clays and muds (Żuk, 2000, Kień, 1997; Kiełczawa et al., 1997; Wojciechowska, 1997).

Hydrogeological and hydrochemical conditions in the city vary, mainly due to different sensitivity of the shallowest aquifer to contamination, resulting from increasing anthropogenic impact on the environment. On average, the groundwater level in the measuring period was at 0.4–0.7 m b.g.l., and in the very centre of the city it was at a depth of 3.22 –6.22

m b.g.l. The Odra River constitutes the main drainage axis for the Quaternary aquifers. Subordinately, the same role is fulfilled by its main inflows, e.g., the Bystrzyca and Ślęza in the south-western part of Wrocław, and Widawa and Dobra in the northern and north-eastern part of the city. This image is complicated by the presence of dams and channels of the Wrocław Floodway System and Hydroelectric Power Plant, due to which groundwater levels and flow directions (especially in the centre and areas surrounding it) are determined mainly by the volume of surface water damming, which is confirmed by results of observations carried out by others (Worsa Kozak et al., 2008; Worsa-Kozak & Kotowski, 2009). The main direction of groundwater flow and various hydrogeological conditions of the shallow aquifer system are presented in Figure 4.

In terms of chemical composition, shallow groundwater is characterised by variability in chemical composition and high concentrations, e.g., sulphate, nitrite, nitrate, ammonium and potassium ions (Konieczyńska, 1998). Due to frequent occurring poor isolation, the aquifer is exposed to
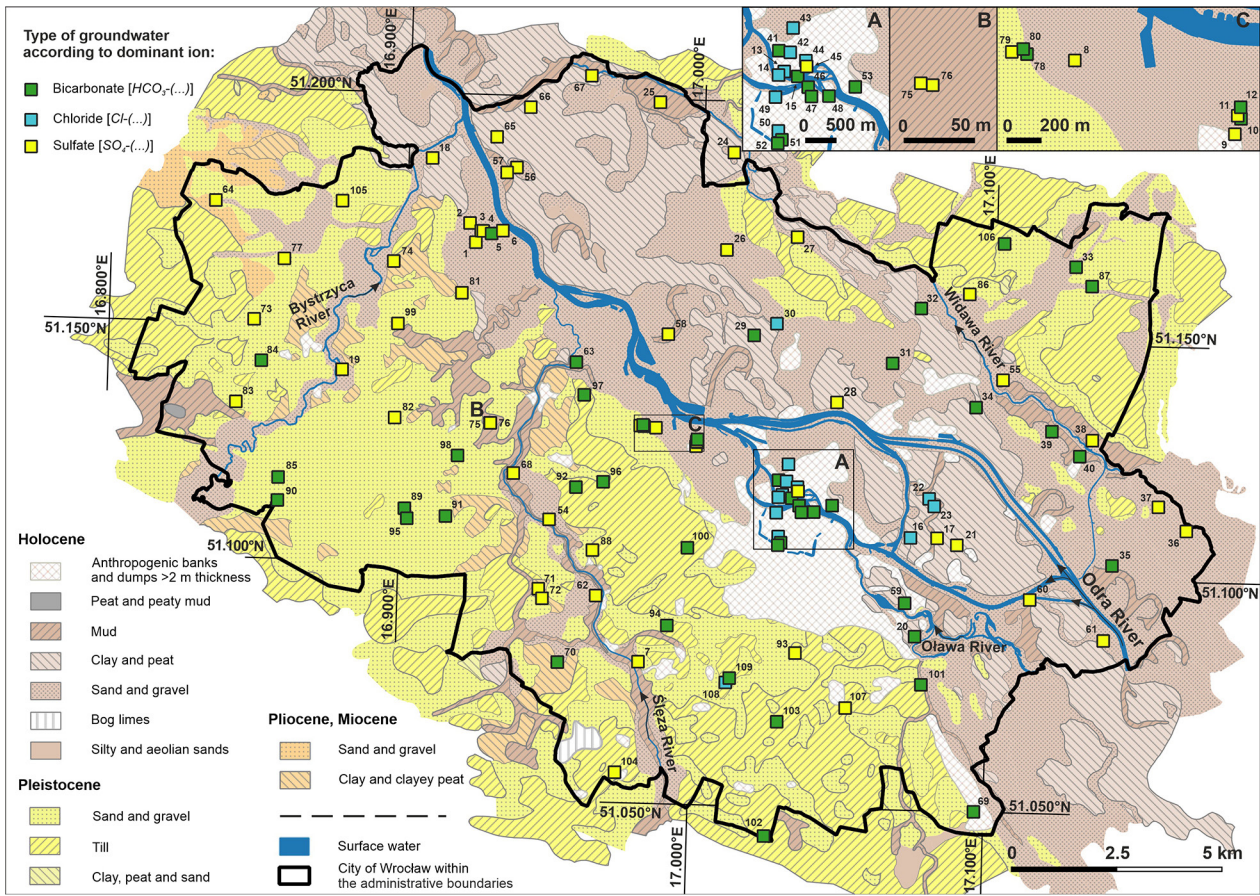
Fig. 3. Type of shallow groundwater in Wrocław on the background of simplified geological settings of cover deposits (from Trałka et al., 2021; based on and modified from Gizler, 1982; Łabno, 1986; Winnicka, 1985; Winnicki, 1985).
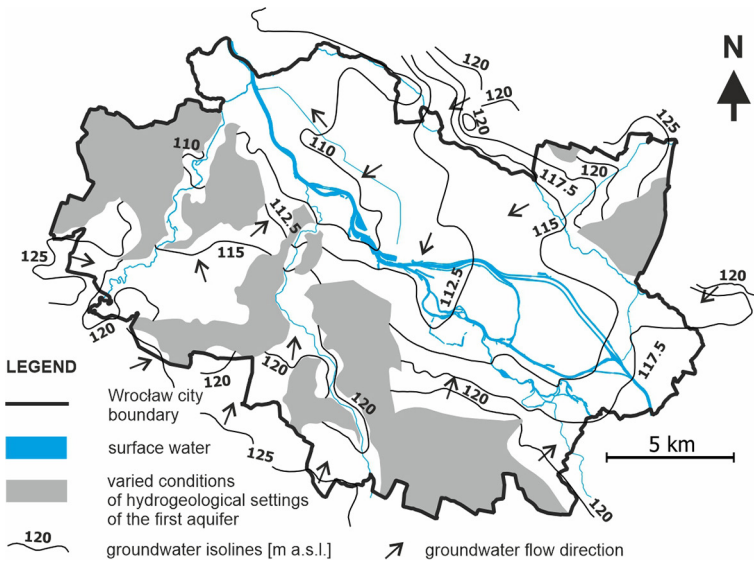

Fig. 4. Hydrodynamics of top aquifer system in Wrocław according to Zawistowski & Wojtkowiak (2006), Czerski & Ihnatowicz (2006), Chudzik & Wojtkowiak (2006), Kiełczawa (2006) modified.

contamination encouraged by large- and small-area sources of pollution, e.g., petrol stations, old municipal landfills, cemeteries, transportation hubs or the area of sewage farms (Fig. 2) not exploited since 2013 (Różański & Gawlikowska, 2015).

3. Methods

Field research carried out between March and May 2021 included sampling from 109 measuring points. The measurement grid was designed primarily with

an even distribution of points throughout the city and with a varied geological structure in mind (Fig. 3). Shallow geotechnical boreholes were drilled in areas where well or piezometer coverage was insufficient. The measurement grid with a density of 2.7 points per km² consists of 39 piezometers, 34 manual geotechnical boreholes, 20 drilled wells, 13 dug wells and 3 springs (Fig. 2). The majority of these points are located in green areas (63 per cent). The remainder is located in areas with commercial and residential premises, industrial and economic activity areas (19 per cent), agricultural land (17 per cent) or wasteland (1 per cent). The distribution of measurement points in terms of land use and their type shows diversity – piezometers are located mainly in the city centre and its immediate surroundings, whereas geotechnical boreholes were drilled mainly in the outskirts of the study area (Fig. 2). Shallow test holes were drilled with a 75-mm-diameter hand drill. A 14-mm-diameter mini-piezometer was then placed in these, driven a few tens of centimetres below the drilled groundwater table/bottom of the borehole. The depths of the geotechnical boreholes ranged from 1.30 m to 4.60 m b.g.l., to a maximum of 12.6 m b.g.l. for the remaining permanent test points (excluding springs).

Temperature, pH and electrolytical conductivity of groundwater samples were measured in the field using a multi-parameter measuring device ELMETRON CX-461. The determination of total alkalinity [mval/L] and HCO_3^- ion content [mg/L] in the samples was performed by instrumental titration. For the determination of other groundwater

components (SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+), the samples were diluted and filtered through a 0.45 μm PTFE membrane filter and injected into ampoules (approx. 2 ml) and then performed with a high-pressure liquid chromatograph HPLC Waters Alliance 2695, with a conductometric detector Waters 432. Mineralisation as the sum of all components was also calculated.

Factor analysis was performed using principal components analysis, after prior standardisation of the data. By means of the graphical "landfill" method (Cattell, 1966), the main factors were distinguished and, in order to obtain a clear structure of the loads, the data were biquartimax rotated. After sample analyses, it was decided to remove ammonium ion from the analysis as it would hinder the selection of factor quantities and their interpretation, due to low concentration variability.

4. Results

4.1. Spatial distribution of groundwater components

The results of chemical analyses show a spatial variation (Figs 3, 5). Shallow groundwaters at Wrocław are characterised by a variable pH (4.34–9.05) and are dominated by the following ions: Na^+, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, which at individual measurement points located in green areas (parks, forests) reach values strongly deviating from the mean (Table 1;

Table 1. Basic statistical parameters of chemical constituents in the groundwater samples analysed.

Parameter		N	Mean	Median	Min	Max	First quartile Q_1 (25%)	Third quartile Q_3 (75%)	St. dev. SD
pH	[–]	109	7.18	7.15	4.34	9.05	6.7	7.8	0.8
EC	[μScm⁻¹]	109	1140.33	1043.00	141.60	5660.0	736.4	1360.0	662.6
Ca^{2+}		109	107.06	89.52	13.52	379.3	64.9	124.3	67.9
Mg^{2+}		109	15.26	12.42	1.79	61.26	8.8	18.9	10.1
K^+		109	12.30	6.95	0.01	110.43	4.1	15.6	15.5
Na^+		109	79.50	50.15	1.48	1056.90	26.2	89.7	112.4
NH_4^+		109	0.48	0.01	0.01	25.81	0.01	0.01	2.8
HCO_3^-	[mgL⁻¹]	109	286.22	305.10	0.00	854.28	164.8	396.6	177.3
SO_4^{2-}		109	178.01	119.34	0.00	926.83	72.2	219.7	166.5
Cl^-		109	96.99	64.90	3.26	1276.25	29.9	110.2	141.8
NO_3^-		109	18.05	7.81	0.00	184.63	3.3	16.7	30.8
NO_2^-		109	2.37	0.43	0.00	20.54	0.1	3.6	3.8
PO_4^{3-}		109	0.95	0.39	0.00	17.78	0.0	0.8	2.1
Mineralization		109	797.18	727.89	88.04	3406.19	519.8	955.2	462.0

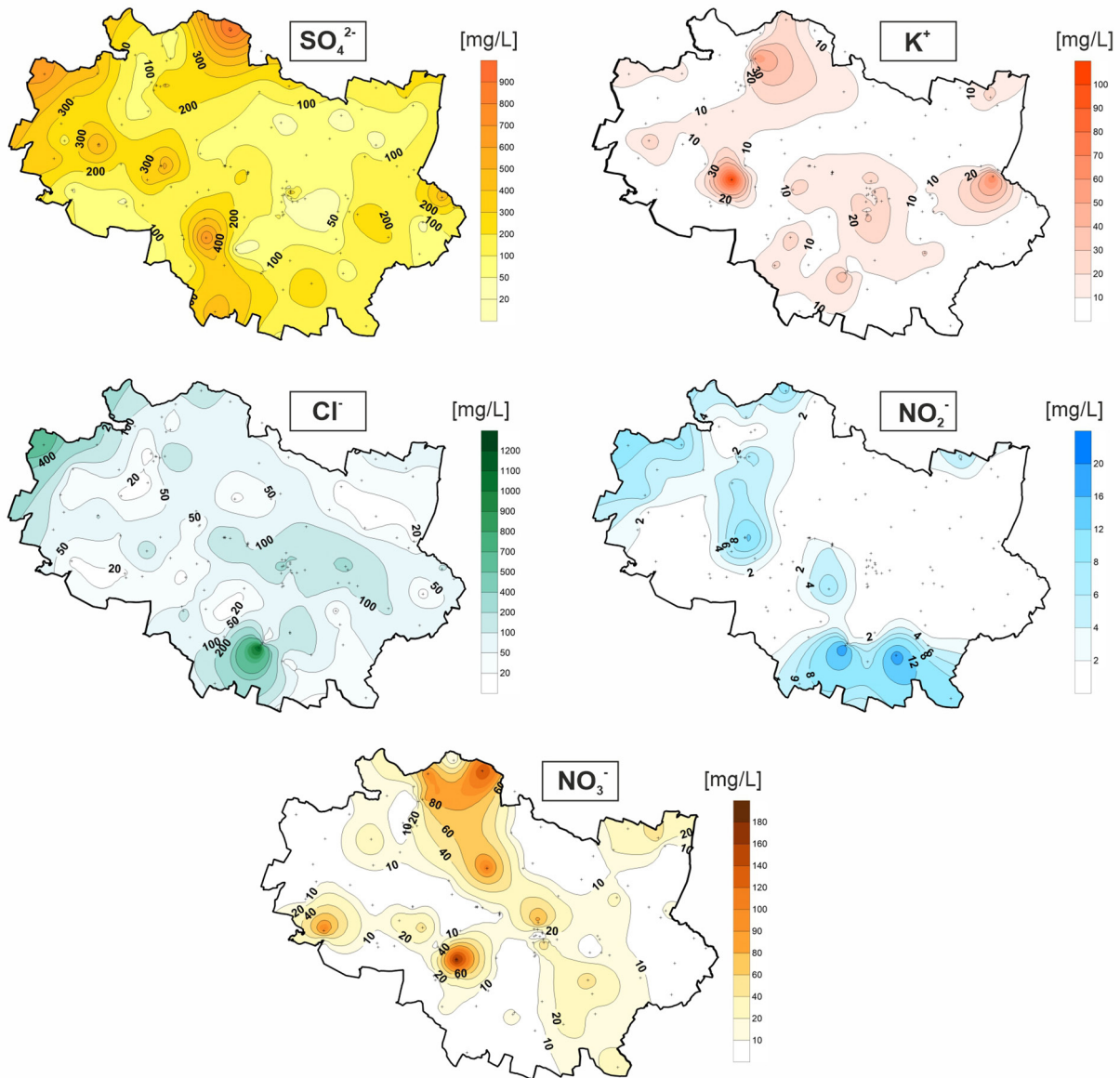Explanation: EC – electrolytic conductivity.

Fig. 5. Distribution of selected chemical component concentrations in the study area

Fig. 3). This also applies to the specific electrolytic conductivity (EC), which was as high as 5660 μS/cm in the south of Wrocław (Fig. 3; point 108). The mineralisation of samples collected ranged from 88.04 mg/L – 3406.19 mg/L (Table 1). These values do not show spatial dependence; however, it is worth noting that the majority of samples with a mineralisation > 1 g/L were taken from piezometers, dug and drilled wells. Less frequently, such high concentrations occurred in waters taken from temporary geotechnical holes. Samples taken from the springs show mineralisation in the range of 423 mg/L – 1087 mg/L and a neutral pH (6.63 – 7.60). Nitrate, nitrite, potassium and chloride ions, considered as indicators of pollution, show local concentration and locally coincide with each other in

the study area (Fig. 5). Excess amounts of potassium ion and nitrogen compounds are concentrated mainly at measurement points located in allotment gardens. High concentrations of chlorides and sulphates occur mainly in the south and south-west of the city (Fig. 5).

During analyses of the distribution of groundwater component concentrations in the city, natural and anthropogenic factors that can significantly affect the final image of the chemical composition should be considered. Therefore, when analysing the results, the impact of the sampling site (land development), the type of the youngest geological formations, the type of measurement point and the character of the groundwater table were taken into account. However, concentrations of individual

ions also demonstrated dependence on sampling location (Fig. 5). In the green areas (forests, parks, squares), increased concentrations of all ions and pH values can be noted, while areas of agricultural activity are characterised by increased concentrations of phosphates, nitrates and nitrite ions. In the case of areas developed for housing and services (residential and commercial areas), as well as economic and industrial activities, a certain stability in the chemical composition of all ions analysed can be observed, with single exceptions of increased values of PO_4^{3-}, NO_3^- and NO_2^-. When considering the contents of individual components of waters analysed in relation to the geological formations from which they were sampled, it was found that, only for sulphate ion and nitrite ion, outliers were recorded at several points (Appendix). Pleistocene and Holocene formations were characterised by a very high variability of concentrations of all components in groundwater samples, irrespective of lithology.

Shallow groundwater was collected from 76 boreholes characterised by an unconfined groundwater table, while in the remaining boreholes a confined character of groundwater surface was recorded. In unconfined aquifers, the mineralisation varied in the range 163.30 mg/L to 3406.19 mg/L, while confined aquifers were characterised by a range of values between 88.04 mg/L and 1502.79 mg/L. No relationship was noted between the magnitude of mineralisation and the depth to the groundwater table. This may be due to the fact that the maximum depth to the groundwater table was 6.65 m b.g.l., suggesting that the trend of increasing mineralisation with depth in such shallow aquifers is not marked and that total mineralisation values are also anomalously low (88.04 mg/L, depth to water table 1.02 m b.g.l.) and high (3406.19 mg/L, depth to water table 1.27 m b.g.l.)

4.2. Effects of factor analysis

On the basis of factor analysis, three factors were identified, together explaining 85.8 per cent of the variation (Table 2). The first factor characterises the variability of water chemical composition to the greatest extent (36.2 per cent of explained variance). Electrolytic conductivity, namely ion Na^+, Cl^-, PO_4^{3-}, has the strongest factor charges, with ion NO_2^- being of a slightly weaker charge. The second factor, explaining 33 per cent of the variation in water chemical composition, concentrates ions Ca^{2+}, Mg^{2+}, SO_4^{2-}. The third factor accounts for the smallest percentage of variation in chemical com-

Table 2. Factor loadings (after biquartimax rotation).

Parameter		Factor 1	Factor 2	Factor 3
Depth to water [m]	[m]	0.20	−0.33	**0.55**
pH	[–]	−0.06	−0.32	0.32
EC	[µScm⁻¹]	**0.78**	0.53	0.23
Ca^{2+}		0.26	**0.90**	0.15
Mg^{2+}		0.22	**0.88**	0.26
K^+		0.25	0.18	**0.55**
Na^+		**0.95**	0.07	0.09
HCO_3^-	[mgL⁻¹]	0.07	0.34	**0.82**
SO_4^{2-}		0.03	**0.91**	−0.16
Cl^-		**0.94**	0.14	0.04
NO_3^-		−0.16	0.27	−0.15
NO_2^-		**0.59**	0.41	−0.26
PO_4^{3-}		**0.80**	0.01	−0.07
Part of diversity	[%]	36.2	33.0	16.6

Explanations: EC – electrolytic conductivity; factor loadings >0.55 marked as bold font.

position (16.6 per cent) and contains the bicarbonate ion of the strongest charge. Subordinately, it has a moderate to strong relationship with the potassium ion and depth to the groundwater table (positive correlation).

4.3. Hydrochemical types of groundwater

Shallow groundwaters in the Wrocław area are characterised by three- and four-ion types predominance. Groundwater mainly represents the SO_4-Cl-Ca-Mg type (53 samples), which dominate in the green and agricultrural areas, a high number of samples were of HCO_3-Mg-Ca type (37 samples) and HCO_3-Na type (7). In the study area, the Cl-HCO_3-Na and Cl-Na types were also distinguished (a total of 12 samples) (Fig. 6).

In terms of spatial differentiation, the sulphate type of water, together with bicarbonate water, occurs throughout the study area, dominating in its north-western part and in the valley the Ślęza River (Fig. 3). However, it is worth noting that in the very centre of the city, an area covered by anthropogenic embankments (Fig. 3; area A), and in the immediate downtown area (east of the centre), the chloride type is concentrated. It is important for classification that the zone where samples are located on the borderline between two types HCO_3-Mg-Ca and SO_4-Cl-Ca-Mg is clearly marked. Therefore, it can be concluded that the chemical composition of shallow groundwater within the city is undergoing a
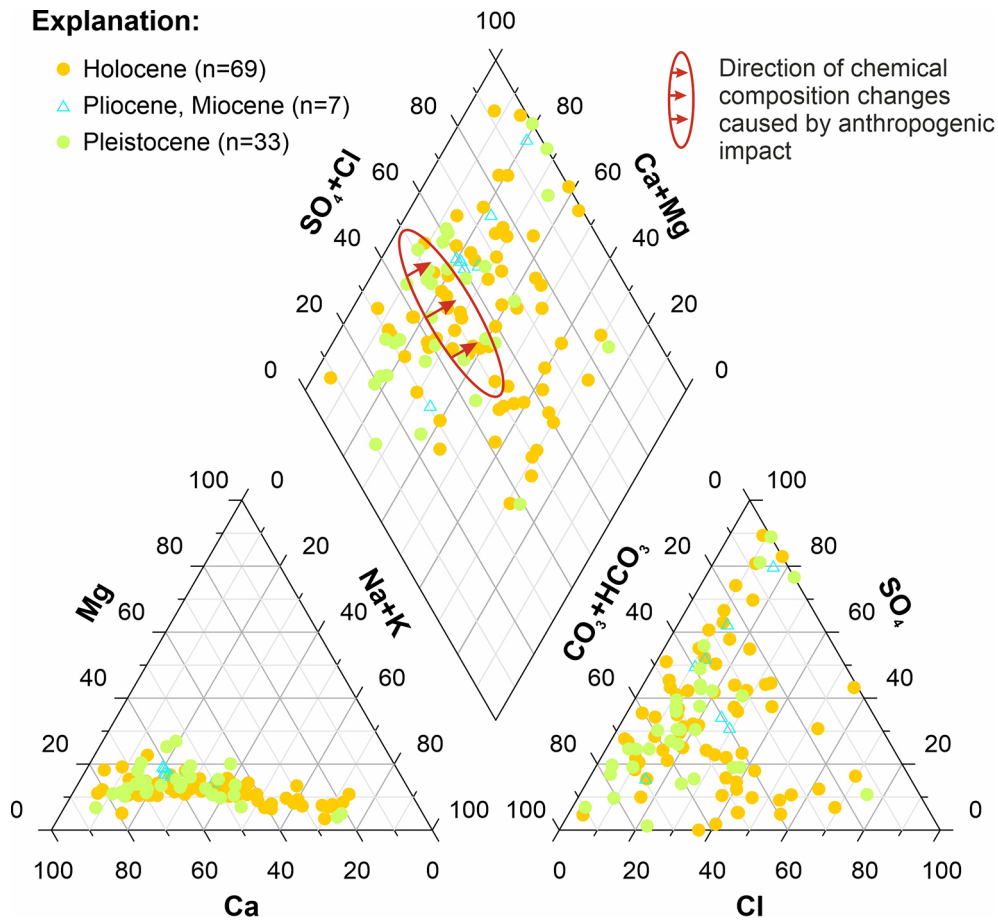
Fig. 6. Piper diagram for chemical composition of water.

gradual zonal transformation. Waters drawn from areas in which Neogene (Pliocene and Miocene) formations are present at the surface are of the sulphate type (Fig. 6).

5. Discussion

The diversity of research results obtained in the city area is related to both natural and anthropogenic factors that have an influence on the formation of the chemical composition of shallow groundwater, of which mainly the share of land development at the sampling site and type of measurement point are distinguished. Due to numerous transformations of city development and constantly growing anthropopressure, shallow groundwater is characterised by a high changeability of chemical composition and is exposed to the risk of pollution migration from rainwater infiltration, pollution from agricultural and industrial activities and, consequently, a change in natural conditions.

With regard to the source of changes in water chemistry, it is often very difficult or impossible to indicate the specific share of each of these (e.g. Dragon, 2006). On the basis of the factor analysis performed, three groups of components were distinguished. Two of these can be interpreted as anthropogenic factors that are most responsible for these changes. The first one, containing the strongest charges of electrolytic conductivity (EC), sodium, chloride, phosphate and, to a lesser extent, nitrite ions, dominates in green areas and less so in the city centre and sub-agricultural areas. The high proportion of PO_4^{3-} ions is associated mainly with the inflow of pollutants, e.g., municipal, farm or industrial sewage, which is additionally emphasised by the correlation with the sodium ion. Chloride ions in such shallow groundwater may result from contact with infiltration (rainfall) waters, which can be polluted by industrial emissions. Importantly, high concentrations of chlorides at insignificant depths are almost always an indicator of pollution that can be associated with various human activities in the agglomeration area, as in the case of PO_4^{3-} ions. These ions in green areas are most likely linked to the use of plant-keeping substances. In areas of predominance of the first factor, water was collected

mainly from piezometers, dug and drilled wells, which suggests the impact of the construction and use of boreholes (measurement points are mainly not in active groundwater monitoring network) on the quality of water abstracted and the increase in selected water components (Davies et al., 2010).

The second factor, containing strong loads of Ca^{2+}, Mg^{2+}, SO_4^{2-} ions, predominates primarily in agricultural areas, which indicates anthropogenic transformations of both soil and water environment. It also contains a low negative correlation with depth to water, which may mean a near-surface contamination. The presence of sulphates in the waters is due to, inter alia, infiltration of atmospheric precipitation, enriched with sulphur compounds, from anthropogenic emissions, directly from industrial and domestic wastewater and from natural fertilisers used in agriculture (Macioszczyk & Dobrzyński, 2002, Khatri & Tyagi, 2015). A calcium and magesium ion content mostly comes from fertiliser use in this area type. The third factor with a high factor load of only one ion (HCO_3^-) and moderate correlation of potassium ion and depth to water, can represent a natural factor which indicates high ion exchange. On the other hand, concentration of bicarbonate ion is positively correlated with depth to water which may mean some sort of anthropogenic source for this ion in shallow groundwater. This factor has the greatest share in residential areas and wastelands. In the area of the city centre, it is dominant in places away from the river, containing insulation from the ground surface in the form of non-construction embankments that prevent direct infiltration of rainwater. An area of chloride waters was here observed, which may be related to historical pollution, a dense water and sewage network or the close vicinity of the Odra River, which, due to forced damming on weirs of hydroelectric power plants, uniquely supplies nearby aquifers in this area (area A in Figures 2 and 3). Mainly piezometers were located there, in which the depth of the groundwater table was in the range of 4.31 m b.s.l. – 6.65 m b.s.l. Archive studies carried out at this point in 2019 also showed an increased content of this element (313 mg/L).

The anthropogenic processes determining changes in chemical composition are also indicated by the hydrochemical index $r\dfrac{Ca^{2+}}{Mg^{2+}}$, which can be used to determine whether high values of these ions concentration at points are related to the pollution of low-mineralised groundwater, derivatives of calcium and magnesium fertilisers (Macioszczyk, 1987; Khatri & Tyagi, 2015). It was exceeded

at 19 points located in agricultural and green areas, mainly in the shallowest geotechnical exploratory boreholes and in wells drilled in allotments, and indicates an anthropogenic source of the inflow of pollutants (agricultural activities – application of fertilisers). Minor (at two measuring points), it was exceeded in piezometers located in the very centre. These points were mainly related to the Holocene formations (sand and gravel) in places where there is no insulation of the shallowest aquifers. The analysis of the $r\dfrac{Na^+ + K^+ + Mg^{2+}}{Cl^-}$ index, which in almost all cases (in 107 measurement points was > 1), showed the possibility of contact of groundwater with rainwater, which in areas with a shallow surface of the mirror affects the determination of this composition, especially in the outskirts of the city, where the sum of effective infiltration reaches 100–150 mm/year (17–28 per cent of precipitation), while the average in the entire city area is 16.5 mm (3 per cent of precipitation) (Szkudlarek-Kajewska et al., 2018). In the areas of large cities, the variability of precipitation chemistry caused by human activities (mainly economic and residential) is increasingly more often noticeable (e.g., Ciężka et al., 2016). In the case of the centre (area A in Figures 2 and 3), it most likely has a subordinate role for reasons mentioned above. In addition, chemically altered rainfall in contact with concrete or metal structures may cause chemical changes that will intensify the increase in the degree of degradation of shallow groundwater (Davies et al., 2010).

The problem of high susceptibility of shallow aquifers to pollution has been highlighted for many years. Already in 1998, on the basis of research carried out for Wrocław and the surrounding area (Konieczyńska, 1998), the chemistry of shallow groundwater was characterised by a high variability, multi-ionic, concentration excesses of many components (including SO_4^{2-}, K^+, NO_3^-, NO_2^-) and high variability of EC, pH or HCO_3^- ions. A significant change in the results of the current research is the marking of the zone of chloride waters (Fig. 3) much higher values of the Cl^- ion concentrations compared to the 1998 analyses. Based on analyses carried out in 2007–2009 (Zawistowski & Wojtkowiak, 2007; Horbowy et al., 2010; Kiełczawa, 2007; Serafin et al., 2010) for the first aquifer in Wrocław, it can be stated that the excess values of nitrate and sulfate ions and EC values, occur in the same locations as the current test wells, namely in the immediate vicinity of point 92. This is indicated by the constantly existing point conditions facilitating the migration of pollutants. Similar trends were record-

Table 3. Present-day hydrogeochemical background determined for the study area.

Parameter		10-90 percentile 16-84 percentile*	Hydrogeochemical background of typical natural groundwater in Poland (Witczak et al., 2013)
pH	[–]	6.37–8.17	6.5–9.5
EC	[μScm⁻¹]	556–1840	200–700
Ca^{2+}		43–187	2–200
Mg^{2+}		6–28	0.5–30
K^+		2–28	0.5–10
Na^+		13–164	1–60
HCO_3^-		49–513	60–360
SO_4^{2-}	[mgL⁻¹]	30–402	5–60
Cl^-		13–197	2–60
NO_3^-		0.62–50	0–5
NO_2^-		0.06–4*	0–0.01
Mineralization		343–1329	–

Explanation: EC – electrolytic conductivity.

ed in Berlin in 1991 and 2000 (SenStadt, 1993, 2006), where human activity has become increasingly more pronounced in the participation of chemical transformations and exceeding mainly SO_4^{2-}, NO_3^- and Cl^- ions.

The above-mentioned relationships affect changes in the hydrochemical background, which is strongly transformed in the study area and deviates from the naturally occurring values of individual components determined (Table 3).

Noteworthy is the background range of nitrates, nitrites and potassium, which differs significantly from the normal concentrations of this element in waters. Increased concentrations of these compounds occurred in allotments, which are the focus of contamination resulting from fertilisation of crops.

6. Conclusions

The chemical composition of Wrocław's shallow groundwater is characterised by high spatial variability. Due to the high susceptibility of waters to pollution, data interpretation requires taking into account a number of anthropogenic and natural components. The way of land development has a special effect on the chemistry of shallow groundwater, which is reflected in the results obtained. Areas that should be especially noted are allotments

and landfills. The analyses also highlight the possible role of type of test borehole on results obtained and the anthropogenic impact on the quality of precipitation infiltrating shallow aquifers. The geology of the subsurface formations showed a possible relationship between groundwater chemical composition and thickness of poorly permeable overburden, also in the centre of the city. Due to factor analysis three of the most important factors were distinguished and interpreted as two anthropogenic factors and one natural with some tendency to change into anthropogenic. The most important sources, which complement the effects caused by these factors, are human activity connected with industry, economy and maintenance of green areas. The natural factors of changes in chemical composition in Wrocław are *inter alia* geology, climate and hydrology, but also in these factors an increased human influence is observed. On the basis of archive data, increased ranges of hydrochemical background of many components and the persistently poor quality of groundwater at selected present points were noted.

The present research emphasises the importance of this topic in the light of growing changes in the natural environment caused by human activity and shows the specificity of the issue, which illustrates the necessity of multidirectional interpretations.

Appendix is available in digital version of the article: http://www.geologos.com.pl/

References

Ali, J., Kumar, M., Saraf, S. & Jain, T., 2015. Study of water quality of shallow groundwater. *Advances in Applied Science Research* 6, 78–87.

Cattell, R.B., 1966. The scree test for the number of factors. *Multivariate behavioral research* 1(2), 245–276.

Chudzik, L. & Wojtkowiak, A., 2006. *Hydrogeological Map of Poland, scale 1:50,000, Top aquifer – hydrodynamics and occurence, sheet 764 Wrocław*. Polish Geological Institute – National Research Institute, Warszawa.

Ciężka, M., Modelska, M., Górka, M., Trojanowska-Olichwer, A. & Widory, D., 2016. Chemical and isotopic interpretation of major ion compositions from pre-

cipitation: a one-year temporal monitoring study in Wrocław, SW Poland, *Journal of Atmospheric Chemistry* 73, 61–80.

Criollo, R., Vázquez-Suñé, E., Burdons, S., Enrich, M. & Chesa, M.J., 2018. *Urban groundwater quality. Update of the Barcelona city.* [In:] EGU General Assembly Conference Abstracts, p. 18937.

Czerski, M. & Ihnatowicz, A., 2006. *Hydrogeological Map of Poland, scale 1:50,000, Top aquifer – hydrodynamics and occurence, sheet 727 Trzebnica.* Polish Geological Institute – National Research Institute, Warszawa.

Davies, P.J., Wright, I.A., Jonasson, O.J. & Findlay, S.J., 2010. Impact of concrete and PVC pipes on urban water chemistry. *Urban Water Journal* 7, 233–241.

Dorociak-Tokarczyk, K., Kazak, J. & Szewrański, S., 2018. The impact of a large city on land use in Suburban area – the case of Wrocław (Poland). *Journal of Ecological Engineering* 19, 89–98.

Dragon, K., 2006. Application of factor analysis to study contamination of a semi-confined aquifer (Wielkopolska Buried Valley aquifer, Poland). *Journal of Hydrology* 331, 272–279.

Dubicki, A., Dubicka, M. & Szymanowski, M., 2002. *Klimat Wrocławia* [*Climate of Wroclaw*]. [In:] Smolnicki, K. & Szykasiuk, M. (Eds), Środowisko Wrocławia – Informator [Environment of Wroclaw]. Dolnośląska Fundacja Ekorozwoju, Wrocław, p. 9–20 (in Polish).

EEA report | No 10/2017 *Landscapes in transition – An account of 25 years of land cover change in Europe.* https://www.eea.europa.eu/publications/landscapes-in-transition (access 20 January 2022).

European Commission, 2018. *Urban Atlas 2018.* FUA Delivery Report. https://land.copernicus.eu/local/urban-atlas/urban-atlas-2018 (access 9 September 2021).

European Commision, Eurostat, 2016. *Urban Europe – statistics on cities, towns and suburbs.* Publications Office, https://doi.org/10.2785/594675.

Foster, S., 2020. Global overview of groundwater in urban development – A tale of 10 cities. *Water* 12, 456, 1–8.

Gizler, H., 1982. *Detailed Geological Map of Poland, 1:50,000, sheet 726 Oborniki Śląskie.* Polish Geological Institute – National Research Institute, Warszawa.

Grischek, T., Nestler, W., Piechniczek, D. & Fischer, T., 1996. Urban groundwater in Dresden, Germany. *Hydrogeology Journal* 4, 48–63.

Horbowy, K., Krawczyk, A. & Krawczyk, J., 2010, *Hydrogeological Map of Poland, scale 1:50,000, Top aquifer – quality, sheet 727 Trzebnica.* Polish Geological Institute – National Research Institute, Warszawa.

IMWM-NRI (The Polish Institute of Meteorology and Water Management – National Research Institute), 2021. https://danepubliczne.imgw.pl/datastore (access 20 January 2022).

Johnson, A.I., 1975. Report on the activities of the international commission on subsurface water for the period 1971–1975. *Hydrological Sciences Journal* 20, 413–419.

Khatri, N. & Tyagi, S., 2015. Influences of natural and anthropogenic factors on surface and groundwater quality in rural and urban areas. *Frontiers in Life Science* 8, 23–39.

Kiełczawa, J., 2006. *Hydrogeological Map of Poland, scale 1:50,000, Top aquifer – hydrodynamics and occurence, sheet 763 Leśnica.* Polish Geological Institute – National Research Institute, Warszawa.

Kiełczawa, J., 2007. *Hydrogeological Map of Poland, scale 1:50,000, Top aquifer – quality, sheet 763 Leśnica.* Polish Geological Institute – National Research Institute, Warszawa.

Kiełczawa, J., Mroczkowska, B. & Kłonowski, M., 1997. *Hydrogeological Map of Poland, scale 1:50,000, sheet 763 Leśnica (with Explanations).* Polish Geological Institute – National Research Institute, Warszawa.

Kień, D., 1997. *Hydrogeological Map of Poland, scale 1:50,000, sheet 727 Trzebnica (with Explanations).* Polish Geological Institute – National Research Institute, Warszawa.

Konieczyńska, M., 1998. *Geochemical atlas of Wrocław and environs, Part II: groundwater.* Polish Geological Institute – National Research Institute, Warszawa.

Lidzbarski, M., Sokołowski, K. & Warumzer, R., 2016. Factors affecting resources and chemistry of groundwater in the Gdańska agglomeration area. *Przegląd Geologiczny* 64, 389–398 (in Polish with English summary).

Łabno, A., 1986. *Detailed Geological Map of Poland 1:50,000, sheet 763 Leśnica.* Polish Geological Institute – National Research Institute, Warszawa.

Macioszczyk, A., 1987. *Hydrogeochemia* [*Hydrogeochemistry*]. Wydawnictwa Geologiczne, Warszawa (in Polish), 475 pp.

Macioszczyk, A. & Dobrzyński, K., 2002. *Hydrogeochemia strefy aktywnej wymiany wód podziemnych* [*Hydrogeochemistry of active exchange groundwater zone*]. PWN, Warszawa (in Polish), 448 pp.

Mroczkowska, B. & Michniewicz. M., 1976. *Atlas geologiczny Wrocławia, część III – Hydrogeologia [Geological atlas of Wrocław, part III – Hydrogeology]* Wydawnictwa Geologiczne, Warszawa (in Polish).

Nasrabadi, T. & Abbasi Maedeh, P., 2014. Groundwater quality degradation of urban areas (case study: Teheran city, Iran). *International Journal of Environmental Sciences and Technology* 11, 293–302.

Różański, P. & Gawlikowska, E., 2015a. *Geoenvironmental Map of Poland II 1:50,000, B, sheet 726 Oborniki Śląskie.* Polish Geological Institute – National Research Institute, Warszawa.

Różański, P. & Gawlikowska, E., 2015b. *Geoenvironmental Map of Poland II 1:50,000, B, sheet 727 Trzebnica.* Polish Geological Institute – National Research Institute, Warszawa.

Różański, P. & Gawlikowska, E., 2015c. *Geoenvironmental Map of Poland II 1:50,000, B, sheet 763 Leśnica.* Polish Geological Institute – National Research Institute, Warszawa.

Różański, P. & Gawlikowska, E., 2015d. *Geoenvironmental Map of Poland II 1:50,000, B, sheet 764 Wrocław.* Polish Geological Institute – National Research Institute, Warszawa.

Senate Department for Urban Development (SenStadt): Berlin Environmental Atlas: Map Description, 1993. https://www.berlin.de/umweltatlas/en/water/

quality-of-groundwater/1991/map-description (access 12 February 2022).

Senate Department for Urban Development (SenStadt): Berlin Environmental Atlas: Map Description, 2006. https://www.berlin.de/umweltatlas/en/water/quality-of-groundwater/2000/map-description (access 12 February 2022).

Serafin, R., Krawczyk, A. & Chudzik, L., 2010. *Hydrogeological Map of Poland scale 1:50,000, Top aquifer – quality, sheet 764 Wrocław.* Polish Geological Institute – National Research Institute, Warszawa.

Shi, X., Wang, Y., Jiao, J.J., Zhong, J., Wen, H. & Dong, R., 2018. Assessing major factors affecting shallow groundwater geochemical evolution in a highly urbanized coastal area of Shenzhen City, China. *Journal of Geochemical Exploration* 184, 17–27.

Statistical Yearbook of Wrocław City, 2020. https://wroclaw.stat.gov.pl/en/publications/statistical-yearbooks/statistical-yearbook-of-wroclaw-city-2020,4,14.html (access 20 January 2022).

Szkudlarek-Kajewska, J., Kajewski, I. & Otop, I., 2018 Bilans wodny powierzchni ziemi na obszarze Wrocławia na podstawie badań symulacyjnych przy pomocy modelu Wetspass [Earth surface water balance for area of Wrocław based on wetspass model simulations]. *Inżynieria Ekologiczna* 19, 33–41 (in Polish).

The World According To GaWC, 2020. https://www.lboro.ac.uk/gawc/world2020t.html, (accessed 20 January 2022).

Trałka, M., Modelska, M. & Błachowicz, M., 2021. Agresywność chemiczna płytkich wód podziemnych Wrocławia [Chemical aggressiveness of shallow groundwater in Wrocław]. *Przegląd Geologiczny* 69, 901–908 (in Polish with English summary).

Vázquez Suñé, E., 2003. *Urban groundwater. Barcelona City case study.* Universitat Politècnica de Catalunya, 134 pp.

Winnicka, G., 1985. *Detailed Geological Map of Poland 1:50,000, sheet 764 Wrocław.* Polish Geological Institute – National Research Institute, Warszawa.

Winnicki, J., 1985. *Detailed Geological Map of Poland 1:50,000, sheet 727 Trzebnica.* Polish Geological Institute – National Research Institute, Warszawa.

Wojciechowska, R., 1997. *Hydrogeological Map of Poland, scale 1:50,000, sheet 726 Oborniki Śląskie (with Explanations).* Polish Geological Institute – National Research Institute, Warszawa.

Worsa-Kozak, M. & Kotowski, A., 2009. Przykład wykorzystania danych z monitoringu wód podziemnych do oceny wpływu elektrowni wodnych na środowisko [The example of using data form groundwater monitoring to analyse the environmental effects of water-power plants]. *Biuletyn Państwowego Instytutu Geologicznego* 436, 555–562 (in Polish).

Worsa-Kozak, M., Kotowski, A. & Wartalski, A., 2008. Monitoring stanów wód podziemnych w rejonie Śródmiejskiego Węzła Wodnego we Wrocławiu [Groundwater fluctuations monitoring program in Wrocław Downtown Water Floodway System]. *Przegląd Geologiczny* 56, 302–308 (in Polish with English summary).

Zawistowski, K. & Wojtkowiak, A., 2006. *Hydrogeological Map of Poland scale 1:50,000. Top aquifer – hydrodynamics and occurence, sheet 726 Oborniki Śląskie.* Polish Geological Institute – National Research Institute, Warszawa.

Zawistowski, K. & Wojtkowiak, A., 2007. *Hydrogeological Map of Poland scale 1:50,000. Top aquifer – quality, sheet 726 Oborniki Śląskie.* Polish Geological Institute – National Research Institute, Warszawa.

Żuk, U., 2000. *Hydrogeological Map of Poland scale 1:50,000, sheet 764 Wrocław (with Explanations).* Polish Geological Institute – National Research Institute, Warszawa.