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The impact of environmental conditions on water salinity in the area of the city of Inowrocław (north-central Poland)

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Abstract. The article presents the influence of natural and anthropogenic factors on the chemical and physical properties of surface water and groundwater in the area of the city of Inowrocław. It has been shown that the properties of the waters were most strongly affected by the specific geological structure (the city is located within the Zechstein salt dome) as well as the long-term influence of a salt mine and soda plant. The composition of most analysed samples was dominated by Ca^{2+}, Na^{+} and Cl^{-} ions. In places of heavy industrial activity, some water parameters were several time higher than permissible limit values according to Polish standards. It is concluded that, due to the threat to the city's drinking groundwater resources and fertile soils, the surface water and groundwater in the area in question require permanent monitoring.

Key words:
water salinity,
soil salinisation,
salt dome,
salt rock mining,
soda industry

Introduction

Salinity, as a measure of total concentration of dissolved inorganic ions, is a characteristic held by all natural waters, including soil solutions (Williams and Sherwood 1994). Primary salinisation, associated with salts originating from natural sources, is caused mainly by seawater intrusions mixing with paleo-seawater and brines, water–rock interaction (direct dissolution of evaporites by fresh groundwater), infiltration of saline surface water, or concentration of groundwater caused by arid water regime, high evaporation rate (e.g. Szabolcs 1991). However, natural mechanisms can be started and/or accelerated by human activity e.g. over-pumping (Kloppmann et al. 2013). Secondary salinisation is mainly induced by industrial liquid or solid waste, salt mining, the use of salts as road de-icing agents, or intensive fertilisation and irrigation (Williams et al. 2000; Ziemann et al. 2000; Hulisz 2007; Cañedo-Argüelles et al. 2013). The salinisation of groundwater is identified as one of the major factors in the degradation of global water resources (Kloppmann et al. 2013), while the salinisation of surface waters is mentioned as one of the main threats to freshwater ecosystems (Millennium Ecosystem Assessment 2005; Cañedo-Argüelles et al. 2013).

One of the most important factors in the development of the city of Inowrocław in north-central Poland is undoubtedly the presence of the Zechstein rock salt deposits, as a result of which, towards the end of the 19th century it was a major centre of the mining and chemical industry, and a spa town. The extraction of this raw material became a real threat to the city, however, with the appearance of sinkholes leading to the closure of the salt mine in 1991 (Poborska-Młynarska 1984; Szczerbowski 2007). Long-term mining and the heavy development of the soda industry has also contributed to the deterioration of groundwater resources (Krawiec 2005; Górski and Rasała 2008) and to the salinisation of surface water and groundwater (Latour et al. 1966; Niklewska et al. 2000), and soils (Wilkoń-Michalska 1963; Cieśla et al. 1981; Piernik et al. 2015).

The objective of this work was to identify the impact of environmental factors on the salinisation of surface water and groundwater in the Inowrocław area. The analysis also takes into account natural and anthropogenic factors. Such a comprehensive research approach has not been presented to date.

Study area

Inowrocław is a city in Kujavia on the Inowrocław Plain (mesoregion 315.55; Kondracki 2002), in the Kujawsko-Pomorskie voivodeship (52° 40' N; 18° 16' E) – Figure 1. It is a flat plain with an average elevation of 85–90 m a.s.l., made of tills, sands and gravels. It also contains the culmination of the Zechstein salt dome (109 m a.s.l.), on which the town centre is located. The salt tectonics began towards the end of the Late Triassic (the Keuper) and lasted through the Quaternary (Dadlez 1998). The Inowrocław diapir is an irregular ovoid of about 3.5 km long and 2.0 km wide. The salt deposits (untreated) of over 1,100 m thick occur under a clay-gypsum cap (40–130 m thick) and are overlain by a series of Neogene–Quaternary sediments (about 17–50 m thick). The salt dome cover is of steeply deposited Jurassic sediments (Fig. 2).

Contemporary uplift and settlement processes in the town are associated with the specific geological

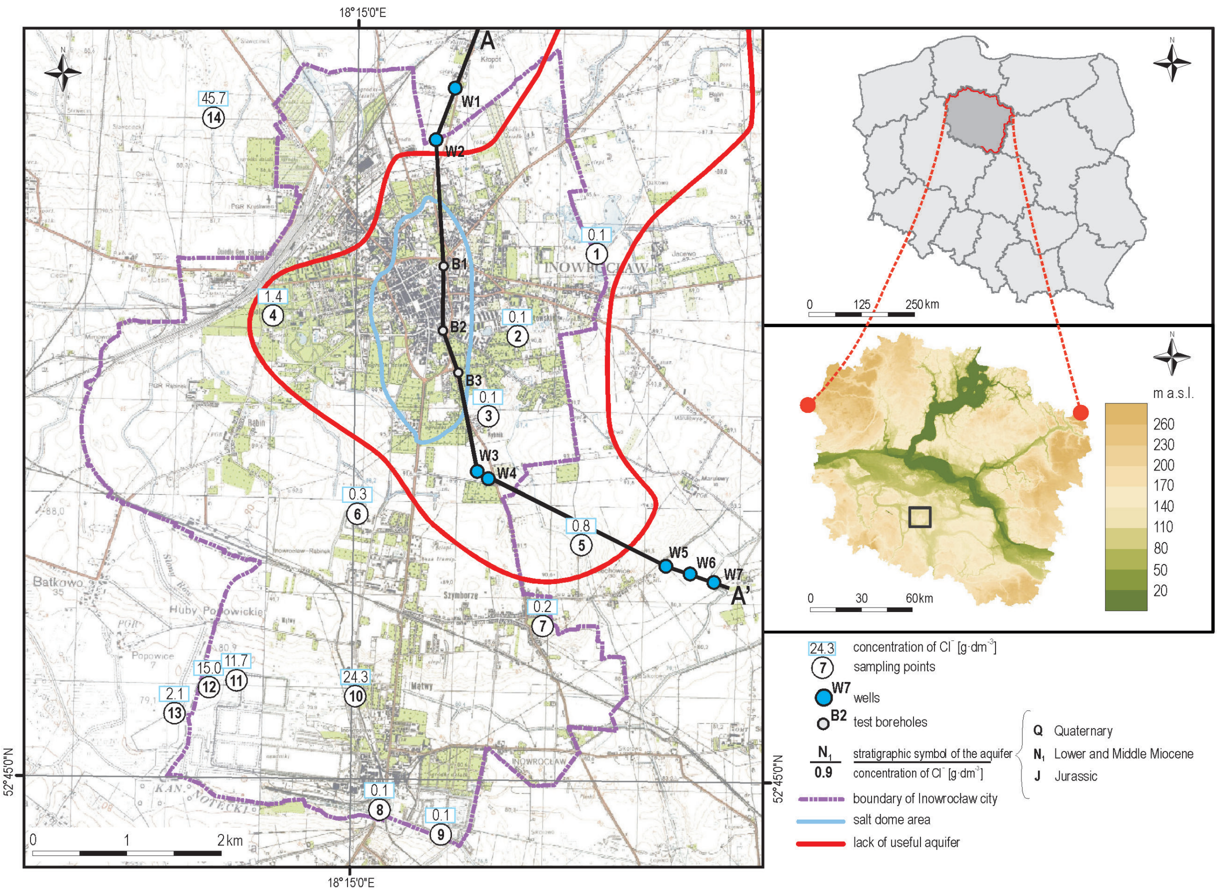

Fig. 1. Location of sampling points, wells and test boreholes

properties of the salt dome, which include changes in groundwater levels and associated changes in the plasticity of the gypsum cap, changes in stress associated with former mining excavations, the load of overlying material and heavy folding of the dome. Halokinesis – the process of uplifting – can contribute to the natural salinisation of groundwater by salt leaching into aquifers, where salts entering through cracks are dissolved (Kortas 2008).

In contrast to the neighbouring lake district, the Inowrocław Plain is almost entirely devoid of lakes. The landscape is scattered with wide, gently-shaped river and marginal valleys, and subglacial valleys and channels. One such form is the Noteć valley on the southern border of Inowrocław (77–78 m a.s.l.), cutting about 10–11 m into the till plain. This valley was filled with Weichselian sediments and sandy deposits, silts and Holocene peats in a combined thickness of 4 to 14 m. The Noteć river which flows through the district of Mątwy is part of the former waterway called the Noteć Canal. The Inowrocław Plain lies in the rain shadow of the upland lake district to the north-west of the hills and has the lowest annual precipitation in Poland, at about 500 mm and less (Kondracki 2002).

The Inowrocław Plain is a part of what is known as “Czarne Kujawy” (Black Kuyavia), where mainly black earths occur (Mollic Gleysols and Gleyic Phaeozems), generally falling into soil quality classes II and III and the second Polish land capability unit (wheat good soil complex). The high utility value of these soils has resulted in the region being excellent for agriculture (Cieśla 1961).

The greatest natural environmental curiosities of Inowrocław are the natural occurrence of halophytes *Salicornia europaea*, *Glaux maritima*, *Aster tripolium*, *Puccinellia distans*, *Triglochin maritima*. They grow in highly saline areas, mainly close to the man-made waste ponds of soda plants in the district of Mątwy and on the banks of the Noteć Canal (Wilkoń-Michalska 1963; Piernik 2003; Piernik et al. 2015).

Methods

In 2014 studies were carried out within the administrative borders of the city of Inowrocław and neighbouring areas. Surface water samples were taken at 14 sampling points in the following locations: ponds (1–4, 6, 7), ditches (5, 9–13), the Noteć River (8) and stagnant water at the site of a brine pipeline leak (14) – Figure 1. Measurements of pH (by the potentiometric method) and conductivity (EC; by the conductometric method) were taken

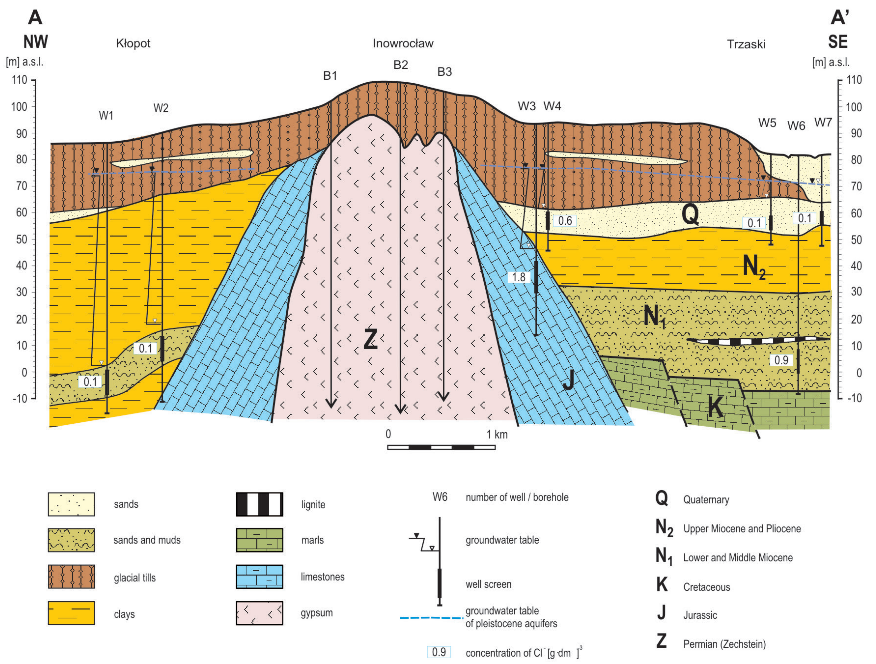

Fig. 2. Geological cross-section through the Inowrocław salt dome with location of wells and boreholes (own work developed from: Nowakowski and Węgrzyn 2002; Molewski 2013; Jamorska et al. 2016)

during field work. Then, after standard preparation, the chloride ion content was determined by argentometric titration, sodium and potassium ions by atomic emission spectroscopy (AES), calcium and magnesium ions by atomic adsorption spectroscopy (AAS) and total dissolved solids content (TDS) by the gravimetric method (Pokojska 1999). Multivariate characterisation (principal component analysis – PCA) was performed using surface water data (14 samples) to analyse the relationships between the observed variables (using MVSP Software). The salinity assessment was conducted according to the FAO classification (Rhoades et al. 1992).

Groundwater samples from wells of the Jurassic (W3; 30-40 m a.s.l.) and Quaternary (W4, W5 and W7; 50-60 m a.s.l.) aquifiers were taken in 2015. The sampling points were located at different distance from the salt dome (Fig. 2). The laboratory analyses were made using the methods described above. The publication also applies archival data (wells of Miocene aquifier: W1 and W2, W6; 0-10 m a.s.l.; Nowakowski and Węgrzyn 2002).

Results and discussion

The impact of environmental factors on tested water properties

The salinisation of surface waters in the Inowrocław area is caused by the complex interaction of several environmental factors. The first of these is the natural degradation of the salt dome in Inowrocław, which, through underground karst phenomena, i.e. the dissolution of the gypsum rock cap and the upper part of the salt deposit, leads to salinisation of the waters (Poborska-Młynarska 1984; Górski and Rasała 2008; Jamorska et al. 2016). There are other more complex factors related to human activities. These result from more than 100 years of mining activity using various methods of salt extraction, including uncontrolled borehole mining in the roof part of the dome, unsustainable exploitation of a flooded mine, exploitation with deep boreholes and wet underground exploitation using a pillar-chamber system (Hus et al. 1996; Szczerbowski 2005). As a result, over the surface of the land above the dome, sinkholes and subsidence troughs can occur (Budryk 1933; Poborska-Młynarska 1984; Szczerbowski 2010).

As Table 1 shows, in the area of the Inowrocław salt dome, groundwater has relatively high concentrations of chloride (0.1-1.76 g·dm^{-3}), sulphate (0.09-1.0 g·dm^{-3}) and sodium (0.07-0.62 g·dm^{-3}) ions. The occurrence of saline groundwater was found here in Jurassic, Cretaceous and Neogenic deposits and in parts of the Quaternary layers. The halo of waters of higher Cl^- ion concentrations covers a significant part of the Inowrocław area (Figs 1 and 2). Hence, there are problems in sourcing fresh (drinking) water in the area of the city (Jamorska et al. 2016). Chloride concentrations gradually decrease with distance from the city centre and salt dome (Fig. 2). The largest drinking groundwater intake from Quaternary aquifer is to the south-east of the city (outside of the salt dome), around the village of Trzaski. The aquifer occurs in sandy and sandy-gravel deposits under the till layer at the depth of 20-40 m (Fig. 2; W5 and W7, Table 1). The efficiency of the wells is usually from 20 to 50 m^3·h^{-1}. The Miocene aquiferous layer (W6) is located at depth of over 50 m. Due to the inflow of mineralised waters rich in chlorides it is currently out of operation.

In the surface waters analyzed within or around the halo of contamination (points 1–7; Fig. 1) the clear influence of saline groundwater was observed. This is attested by the following physico-chemical and chemical parameters: pH 7.7–8.6, EC 0.7–4.5 dS·m^{-1}, Na^+ 0.01–0.75 g·dm^{-3}, K^+ 0.01–0.03 g·dm^{-3}, Ca^{2+} 0.03–0.09 g·dm^{-3}, Cl^- 0.09–1.40 g·dm^{-3} and TDS 0.51–2.88 g·dm^{-3} (Table 2). It should be emphasised that results in the above ranges for the waters of ponds to the north-east of the city, i.e. near the villages of Jacewo and Dalkowo, have previously been reported (Cl^- 0.29 g·dm^{-3}, TDS 1.5 g·dm^{-3}, Latour et al. 1966), in ditches around the villages of Komaszyce and Turzany (0.11–0.49 g·dm^{-3}, Wilkoń-Michalska 1963), and also in the village of Słońsk (EC 0.9–1.4 dS·m^{-1}, Cl^- 0.06–0.12 g·dm^{-3}, TDS 0.74–1.10 g·dm^{-3}, Czerwiński 1996). For comparison, there was much higher salinity (Cl^- 5–16 g·dm^{-3}) in the waters of no-longer-existant sinkhole ponds in Inowrocław (Wilkoń-Michalska 1963; Latour et al. 1966). It can be assumed that the properties of the examined waters may be influenced by the ascent highly mineralised groundwater (Górski and Rasała 2008; Jamorska et al. 2016). With a shallow overlying gypsum cap (as in Inowrocław) it is impossible to exclude the impact of salt domes on the waters in quaternary deposits (Prochazka 1970). However, taking into account the heavy exploitation of salt deposits in the past, it is hard to assume that only geogenic factors are in effect. Similar properties were also recorded in the waters of the Noteć River and a nearby drainage ditch (samples 8–9).

Another important factor influencing the salinisation of Inowrocław's surface waters is the soda industry in the southern part of the city (the Mątwy district). This industry is an anthropogenic producer of saline waters containing significant quantities of Cl^- and SO_4^{2-} anions, normally associated with Ca^{2+}, Mg^{2+} and Na^+ (Kamiński 1973). CIECH Soda Polska S.A.'s main product is soda ash. The soda production process by the Solvay method is burdensome on the environment. It consumes very large quantities of water and consequently leads to large amounts of wastewater being discharged by pipeline into the Vistula river. According to Cyms-Chmielewska (1994), the production of 1 Mg of soda also produces 1 Mg of saline solid waste and 20 m^3 of production effluent containing 42 $g·dm^{-3}$ of chloride ions. Solid and semi-liquid solid industrial waste has been deposited in waste ponds for years without the appropriate safety measures, resulting in readily soluble salts (mainly $CaCl_2$ and NaCl) penetrating to shallow ground-water and arable soils in neighbouring areas (Cieśla et al. 1981; Pokojska et al. 1998; Hulisz and Piernik 2013). The process of waste accumulation has for now been stopped and waste ponds are being reclaimed. The conductivity values and other salinity parameters for surface waters (samples 10–13) were very high (pH 6.9–7.9, EC 6.8–56.2 $dS·m^{-1}$, Na^+ 0.46–3.97 $g·dm^{-3}$, K^+ 0.10–0.20 $g·dm^{-3}$, Ca^{2+} 0.74–8.40 $g·dm^{-3}$, Cl^- 2.12–24.3 $g·dm^{-3}$, TDS 4.35–36.0 $g·dm^{-3}$) – Table 2. This has confirmed what has undoubtedly been for many years a very high level of salinity, which is also observed in shallow groundwater and soils (Wilkoń-Michalska 1963; Cieśla et al. 1981; Hulisz et al. 2010; Piernik et al. 2015). Because of their saturation in highly saline waters, the highest electrical conductivity values (up to 150 $dS·m^{-1}$) were generally recorded in soil and groundwater (Niklewska et al. 2000; Table 3). Some authors (Strzelecka et al. 2011) suggest that, despite excluding soda waste ponds from the production process, the acreage of saline soils is still increasing, as confirmed by botanical observations. The main reasons for this state of affairs probably include the large quantity of accumulated waste and the environmentally disadvantageous location of the soda plants in the Noteć valley (above all, the shallow groundwaters). However, given the location of the

Table 1. Selected properties of groundwater samples

Sample No.	Stratigraphy	pH	EC	Cl^-	Mg^{2+}	$SO4^{2-}$	Na^+	Ca^{2+}	TDS
			[$dS·m^{-1}$]	[$g·dm^{-3}$]					
W1*	N1	7.4	n.d.	0.11	n.d.	0.09	n.d.	n.d.	n.d.
W2*	N1	7.1	n.d.	0.12	n.d.	1.00	n.d.	n.d.	n.d.
W3	J	7.1	5.63	1.76	0.11	0.24	0.62	0.33	2.90
W4	Q	7.2	4.08	0.63	0.06	0.43	0.27	0.14	1.65
W5	Q	8.1	1.19	0.10	0.05	0.31	0.07	0.19	n.d.
W6*	N1	7.1	n.d.	0.89	0.04	0.62	n.d.	0.21	1.62
W7	Q	7.0	1.26	0.09	0.04	0.25	0.03	0.18	0.95
DWL**	-	6.5-9.5	2.50	0.25	0.03-0.125	0.25	0.20	-	-
HB***	-	6.5-8.5	0.20-0.70	0.002-0.06	0.001-0.03	0.005-0.06	0.001-0.06	0.002-0.02	-

* archive data (Nowakowski and Węgrzyn 2002)
** drinking water limits (Journal of Laws, item 1989, 2015)
*** hydrochemical background (Journal of Laws, item 85, 2015)
n.d. – no data

Table 2. Selected properties of surface water samples

Sample No.	pH	EC	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	TDS
		[dS·m^{-1}]	[g·dm^{-3}]					
1	7.7	1.1	0.09	0.05	0.01	0.01	0.10	0.70
2	8.1	1.1	0.09	0.04	0.01	0.02	0.12	0.70
3	8.2	0.9	0.08	0.02	0.01	0.01	0.09	0.58
4	8.4	4.5	0.05	0.03	0.75	0.03	1.40	2.88
5	8.5	3.2	0.03	0.04	0.12	0.03	0.75	2.05
6	8.5	2.4	0.06	0.02	0.14	0.02	0.34	1.54
7	8.6	0.8	0.05	0.03	0.03	0.01	0.22	0.51
8	8.0	0.8	0.05	0.02	0.02	0.01	0.11	0.45
9	8.0	0.7	0.05	0.02	0.02	0.01	0.08	0.45
10	7.7	56.2	8.40	0.04	2.88	0.13	24.3	36.0
11	7.9	45.3	6.58	0.02	3.97	0.20	17.4	29.0
12	6.9	36.6	4.71	0.01	1.62	0.10	15.0	23.4
13	7.8	6.8	0.74	0.04	0.46	0.12	2.12	4.35
14	8.4	85.2	15.8	0.15	6.93	0.39	32.7	54.5

waste ponds near the salt dome, which was heavily exploited in the past, and the dome's associated faults (Budryk 1933; Szczerbowski 2005) it is also impossible to exclude a natural source of salinisation having an influence at the same time. This issue requires further research in order to be clarified.

The last factor contributing to the salinisation of waters in the area of Inowrocław is failures in pipelines carrying away waste water and brine, which lead to local pollution of waters and soils. According to Rytelewski et al. (1993) the total length of brine pipelines in the Kujavian region was 140 km. Rock salt is extracted by underground mining in Góra near Inowrocław and in Przyjma near Mogilno. Brine with an average NaCl concentration of 310 g·dm^{-3} is piped from mines to chemical plants in Inowrocław, Janikowo and Włocławek. Uncontrolled leaks of highly saline waste water and brine are mainly the result of the use of construction materials prone to electrolytic corrosion. In the past there were numerous failures. For example, on a 10-km section of the Góra–Mątwy pipe-line carrying brine to IZCH there were as many as 50 failures in the period 1993–2000 (Hulisz et al. 2001). At present, the situation has improved due to the comprehensive replacement of infrastructure (including the use of pipes from synthetic materials). Another important element of the pipeline system is the 40-km-long sump collector, which carries away extremely saline (EC = 131 dS·m^{-1}) and strongly alkaline (pH = 11.7) waste water from chemical plants in Inowrocław and Janikowo to the Vistula. At the outlet of this pipeline in Dybowo, near Toruń, its impact on the chemistry of river waters and surrounding soils is noticeable (Hulisz and Skalska 2004).

Sample 14 was taken from the site in Sławęcinek where there was the failure of a currently out-of-use pipeline which transported brine to the Zachem chemical plant in Bydgoszcz. In a small depression there, there are extremely saline stagnant waters (pH 8.4; EC 85.2 dS·m^{-1}; Na+ 6.93 g·dm^{-3}; K+ 0.39 g·dm^{-3}; Ca^{2+} 15.8 g·dm^{-3}; Cl- 32.7 g·dm^{-3}; TDS 54.5 g·dm^{-3} – Table 2), despite the accident having occurred in the 1990s. The area is overgrown with the halophyte *Salicornia europaea*, which is an ecological indicator of a stable high salinity level (Piernik 2003).

Table 3. Salinity of soil and groundwaters in the area adjacent to soda waste ponds in Inowrocław-Mątwy (Niklewska et al. 2000)

Parameter	Soil*	Groundwater
pH	6.4 – 7.5	6.0 – 6.5
EC [dS·m^{-1}]	36.5 – 147	61.0 – 150
Cl^{-} [g·dm^{-3}]	3.24 – 62.1	19.9 – 62.8
Ca^{2+} [g·dm^{-3}]	4.63 – 19.2	6.68 – 18.7
Na^{+} [g·dm^{-3}]	2.11 – 17.8	5.76 – 17.9
Mg^{2+} [g·dm^{-3}]	0.01 – 0.47	0.01 – 0.30

*saturated paste extract

Types of salinisation of surface waters

Samples 1–3 and 7–9 were classified as slightly saline (EC 0.7–2 dS·m^{-1}), samples 4–6 and 13 as moderately saline (2–10 dS·m^{-1}), sample 12 as very highly saline (25–45 dS·m^{-1}) and samples 10, 11 and 14 as brines (EC > 45 dS·m^{-1}).

The share of the individual cations as a percentage of the total (% mmol$_c$·dm^{-3}) in the analyzed surface water samples are shown in the ternary plot (Fig. 3). Based on this, four groups of waters were identified, of the following hydrochemical types:

I: $Na^+ + K^+ >> Ca^{2+} > Mg^{2+}$ (samples 4–6),

II: $Ca^{2+} > Na^+ + K^+ > Mg^{2+}$ (samples 7–9),

III: $Ca^{2+} >> Na^+ + K^+ > Mg^{2+}$ (samples 10–14),

IV: $Ca^{2+} >> Mg^{2+} > Na^+ + K^+$ (samples 1–3).

Groups II–IV were characterised by a predominance of calcium (41–73%). The properties of the samples taken from the ditches in Inowrocław–Mątwy (samples 10–13, group III) reflected the chemistry of soda-industry waste. The very high proportion of calcium in the stagnant water at the site of the brine pipeline failure (sample 14, group III) may, however, have been caused by the restoration of soils using phosphogypsum or other calcium-based fertilisers (Przedwojski et al. 1993). The share of cations in groups II and IV, meanwhile, was similar to that commonly observed in freshwater. In the case of samples 4–6 (group I), which had the highest EC values among waters within the halo of salt contamination, the cation composition was dominated by sodium and potassium (67–90%).

Principal component analysis (PCA) indicated that most of the variance in the analyzed data set was accounted for by the main component, PC1 (78.2%), which is explained by the EC and contents of Cl^-, Na^+, K^+ and Ca^{2+}. Meanwhile, only 16% of the variance was related to pH (PC2). Figure 4 showed a distinct separation between the three groups of surface water samples. This was mostly linked to the kind of salinity source. The first (sample 14) had the highest values of all salinity parameters (brines) except pH. At the other end of the spectrum was the largest group of samples (1–9 and 13; from slightly to moderately saline waters) with the lowest salinity and the highest pH values. The middle ground was occupied by the final group (samples 10–12) which included highly saline waters and brines but with lower pH values than the first and second groups.

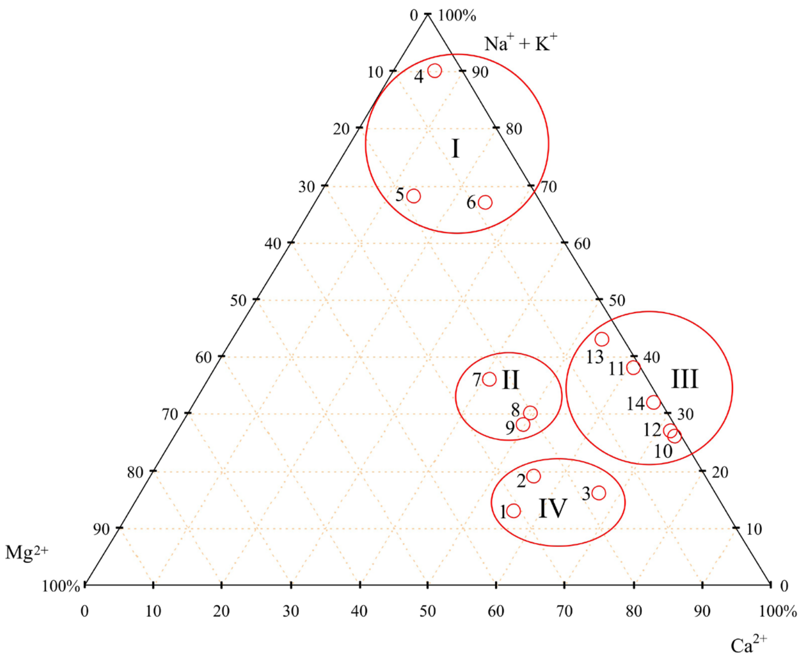

Fig. 3. Ternary plot of magnesium, calcium and sodium plus potassium of surface water (in %mmol$_c$·dm^{-3}) in the area of Inowrocław. I–IV: groups of samples

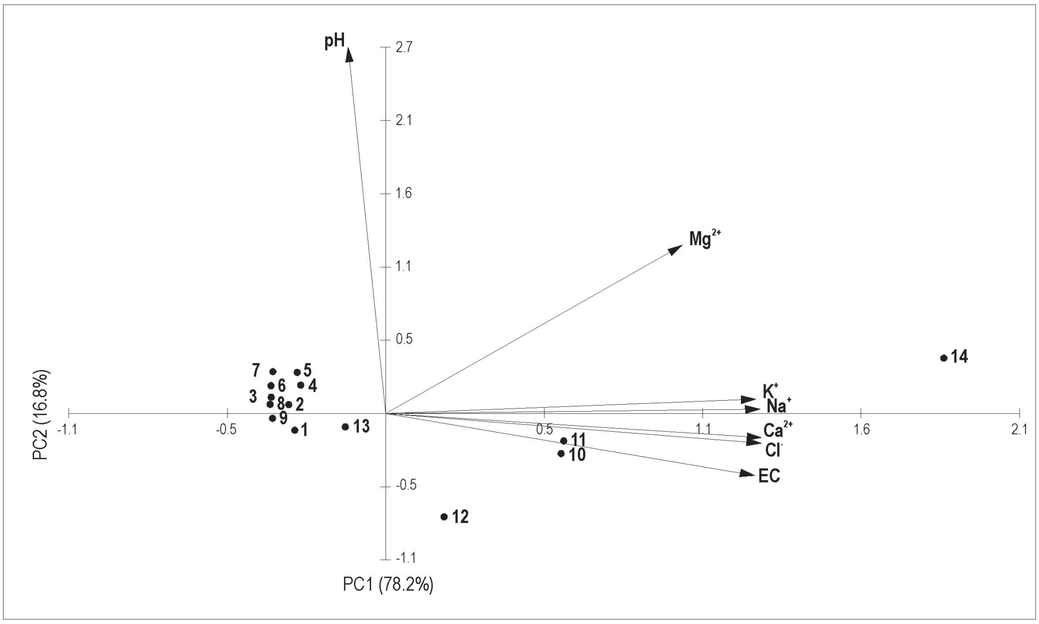

Fig. 4. Principal component analysis (PCA) bi-plot based on surface water properties. Numbers indi-cate sampling points

Assessment of surface water and groundwater quality according to the applicable standards

The Regulation of the Polish Minister of the Environment of 22 October 2014 (Minister Środowiska 2014a) identifies 5 classes of surface water quality. For parameters such as pH, EC, TDS and content of Cl^-, Mg^{2+} and Ca^{2+}, only two classes exist. According to the listed properties, samples 1–3 and 7–9 were in classes I and II, and the remainder (samples 4–6 and 10–14) exceeded threshold values for class II (EC ≤ 1.5 $dS{\cdot}m^{-1}$, TDS ≤ 0.8 $g{\cdot}dm^{-3}$, Ca^{2+} ≤ 0.2 $g{\cdot}dm^{-3}$, Mg^{2+} ≤ 0.1 $g{\cdot}dm^{-3}$ and Cl^- ≤ 0.3 $g{\cdot}dm^{-3}$). It should also be noted that, in accordance with the Regulation of the Ministry of the Environment 2014 of 18 November 2014 (Minister Środowiska 2014b), TDS and concentrations of Cl^- and Na^+ in the surface waters of waste pond sites (samples 10–13) and the location of the brine pipeline failure (sample 14) were many times higher than the highest permissible values of pollution indicators for waste water being conducted into waters and soil (TDS 2.0 $g{\cdot}dm^{-3}$, Cl^- 1.0 $g{\cdot}dm^{-3}$, Na^+ 0.08 $g{\cdot}dm^{-3}$).

The permissible range for chloride ion values in drinking water is Cl^- ≤ 0.25 $g{\cdot}dm^{-3}$ (Minister Zdrowia 2015). This value was exceeded in the groundwater samples W3, W4 and W6 from wells reaching Jurassic, Miocene and Quaternary aquifers located to the south and east of the Inowrocław salt dome (Table 1, Fig. 2). Moreover, chlorides, sulphates and sodium concentration in those samples many times exceeded the geochemical background (Minister Środowiska 2015, Table 2).

Conclusions

1. Water salinity in the area of Inowrocław is influenced by: the salt dome, which was mined heavily in the past; the impact of the soda-industry waste disposal site; and the failure of brine pipelines. The negative impact of human activity and geogenic factors related to the geological structure of the analysed area overlap each other, and are undoubtedly difficult to separate.
2. The conducted research indicated a varied level of salinity in surface water and groundwater. The most saline calcium-, sodium- and chloride-rich waters (often exceeding Polish standards many-fold) were surface waters contaminated with soda-industry waste and industrial brine.
3. Saline inflows are a potential threat to groundwater resources, which are the main source of drinking and industrial water, and also to arable soils (which are often of high utility value). It is therefore necessary to conduct detailed monitor-

ing of these components of the environment. These studies should be conducted systematically, based on a properly prepared research programme.

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