Using Macroelement Content to Characterize Surficial Water Quality of Artificial Reservoirs

Agnieszka Cygan · Andrzej Kłos ·
Piotr Wieczorek

Received: 7 March 2021 / Accepted: 10 September 2021 / Published online: 29 September 2021
© The Author(s) 2021

Abstract The quality of surface waters in the territory of Poland, despite the implemented remedial measures, is mostly classified as bad. This article presents the results of research on the composition of water macroelements in 24 artificial reservoirs located in Opole province (southern Poland), searching for the reasons behind their pollution. Concentrations of the anions F^- , Cl^- , Br^- , NO_2^- , NO_3^- , PO_4^{3-} and SO_4^{2-} and cations Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} were taken into account. An analysis of seasonal changes was carried out and, on the example of a dam reservoir (Turawa Big Reservoir), a multi-point analysis of the distribution of ion concentrations in water at the reservoir surface was also carried out. It was shown that retention and flow-through reservoirs, where the main source of pollution is the

water feeding the reservoirs, are the most vulnerable to pollution. The second group consists of *closed* reservoirs located in industrial and agricultural areas, which are exposed to pollution from rainwater run-off and field leachate. In the case of reservoirs created in marl mining areas, a significant effect was also indicated from the chemical composition of the substrate on the formation of ionic equilibria in waters filling the excavations. The research shows that there are no hard and fast rules regarding the seasonal variability of ion concentrations during the growing season, indicating that eutrophic reservoirs show greater variability of ion concentration.

Keywords Surface waters · Artificial water reservoirs · Pollution · Macroelements · Eutrophication

A. Cygan (✉)
Lukasiewicz - Institute of Ceramics and Building
Materials, Environmental Engineering Division in Opole,
Oświęcimska 21, 45-651 Opole, Poland
e-mail: a.cygan@icimb.pl

A. Cygan · P. Wieczorek
Faculty of Chemistry, Department of Analytical
Chemistry, Opole University, Oleska 48, 45-052 Opole,
Poland
e-mail: pwiecz@uni.opole.pl

A. Kłos
Institute of Environmental Engineering and Biotechnology,
University of Opole, Kard. B. Kominka 6a, 45-032 Opole,
Poland
e-mail: aklos@uni.opole.pl

1 Introduction

Water pollution is one of the consequences of civilization development and one of the most difficult problems we face today. Water quality, necessary for the proper functioning of all living organisms, is often so bad that it makes it unusable for utility purposes (Smith, 2003). Exploitation of natural resources, population growth, and increased consumption generate ever greater amounts of waste. It is estimated that such activities have radically altered about one third of the Earth's surface (Vitousek et al., 1997).

Aquatic ecosystems cover more than two-thirds of the Earth's surface and play a key role in stabilizing the global climate, as well as providing a wide range of services to the rapidly growing human population (Lotze et al., 2006). However, anthropogenic activities are increasingly having detrimental effects on aquatic ecosystems. Five sources of anthropogenic pollution that affect freshwater and sea ecosystems can be identified: wastewater, often containing biogenic substances (nutrients), mining of sedimentary rocks, crude oil and petroleum products, heavy metals and plastics (Häder et al., 2020).

Currently, the problem of eutrophication affects all types of surface waters, from small watercourses, through closed reservoirs and lakes, to rivers and sea waters (Golterman & de Oude, 1991). In European countries, apart from unintentional discharges of pollutants occurring as a result of accidents or disasters, the greatest problem is posed by biogenic substances, which significantly accelerate the natural eutrophication processes of surface waters. The main sources of these substances are agricultural areas and untreated, or poorly treated, municipal sewage. In addition to biogenic substances, along with the leachate from fields and farms, other chemical agents also enter surface and ground waters, e.g. pesticides (Hérivaux et al., 2013). In 1991, the Nitrates Directive (Council Directive 91/676/EEC) was introduced across the European Union to protect waters against pollution by nitrates of agricultural origin, including by promoting the implementation of good agricultural practices.

Various methods have been proposed for assessing the level of eutrophication of reservoirs, e.g. the Trophic State Index (Carlson, 1975), the Organic Carbon Index (Nixon, 1995), the TRIX Trophic State (Vollenwider et al., 1998) or the Eutrophication Index (Primpas et al., 2010).

Scientific studies on the assessment of the ionic composition of surface waters often consider mainly the biogenic element ions, nitrogen and phosphorus (Chang, 1982; Rixon et al., 2020), and the heavy metal cations found in bottom sediments and in organisms inhabiting the ecosystem (Arain et al., 2008; Ikem & Adisa, 2011). Among the studies conducted on macroelement concentrations of surface waters, are those performed in reservoirs formed after lignite mining (Geller, 2013),

In Poland, studies on the quality of surface waters result from the provisions of national law, in

accordance with the requirements of Water Framework Directive (Directive 2000/60/EC). Of the 24 artificial reservoirs discussed in this article, only the dam reservoirs (Turawski Reservoir, Nysa Reservoir and Otmuchowski Reservoir) are subject to assessment under the State Environmental Monitoring, while some of the other reservoirs, which have recreational functions, are only subject to microbiological assessment in terms of suitability for bathing.

The aim of the study was to compare the concentrations of macroelements (macro-ions) in waters of artificial reservoirs of different types according to their genesis. The thesis was put forward that *main factors* shaping the composition of macro-ions in artificial reservoirs is the chemical composition of the waters feeding the reservoirs (which mainly concerns retention and flow-through reservoirs), the chemical composition of soils surrounding the lake (from which chemical substances leak into the reservoir waters due to elution with rainwater and snowmelt, e.g. through small watercourses), and the chemical composition of the bottom of reservoirs. A secondary mechanism regulating the ionic composition are the biochemical processes taking place in the bottom sediments and reservoir waters.

2 Materials and methods

The research was conducted in Opole province. The area is characterized by a lack of natural water reservoirs. Mostly these reservoirs are created after the extraction of sand, gravel and, characteristically for this region, marl. In the nineteenth and twentieth centuries, the cement and lime industries developed rapidly here. Even today, it is an important part of the region's economy. There are also dam and flow reservoirs located in the province, whose main function is flood protection.

In the first stage of the study (August–September 2013), 24 reservoirs of different types were selected with different levels of eutrophication. The eutrophic reservoirs include Turawa Big Reservoir (due to the content of TOC (total organic carbon), phytobenthos and phytoplankton), Otmuchowski Reservoir and Nyski Reservoir — due to the content of TOC, phytobenthos and phosphates (based on data for 2011 and 2012, published by the Regional Inspector of Environmental Protection in Opole (Internet 1). and the

Staw na Bolko, Balaton, Januszkowice Duże, Januszkowice Linowy, Staropolanka, Biskupice-Brzózki and Złoty Potok reservoirs (based on organoleptic assessment; assessment of colour, transparency, and smell during sampling). The small Złoty Potok floodplain is fed by the Złoty Potok River, whose waters were found to be eutrophic in terms of their high BOD (Biochemical Oxygen Demand) values and high phosphate content (Internet 1). The location of the reservoirs and water sampling sites in the Turawa Big Reservoir are shown in Fig. 1. Their brief characteristics are summarized in Table 1.

In the next stage of the study, the temporal changes in the concentration of the tested ions in the waters of four eutrophic reservoirs (Nos. 1, 2, 3 and 7) and four non-eutrophic reservoirs (Nos. 10, 20, 22 and 23) were assessed. The samples were taken from January to August in 2014 and July 2015. Data obtained during the first stage in 2013 were also taken into account.

The last stage of the study concerned the assessment of the distribution of the studied ion concentrations in the waters of the Turawa Big Reservoir (No 1). For this purpose, 17 points were selected in the littoral zone of the lake and four points in the lake basin (Fig. 1). The retention reservoir fed by the Mała

Panew River, is characterized by an excessive cyanobacterial bloom, which has been observed for more than two decades. The research was conducted in September 2019 and February 2020.

2.1 Quality assurance

Water samples were collected in accordance with the standard: (PN-EN ISO 5667-4:2003). A Metrohm 850 Professional IC ion chromatograph was used for the examination. The following anions were assessed in the water: F^- , Cl^- , Br^- , NO_2^- , NO_3^- , PO_4^{3-} and SO_4^{2-} as well as the cations: Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} . The ions were determined in accordance with the standard for determinations performed using the ion chromatography technique: (PN-EN ISO 10304-1:2009/AC:2012) and (PN-EN ISO 14911:2002). Ion concentrations are presented as the mean value of 3 replications. Table 2 summarizes the data on the detection and determination limits of the apparatus as well as the uncertainty of the measurement results of the method, expressed by the standard deviation s_M .

Solution conductivity was measured by a CC-551 conductometer whose absolute reading error was $\Delta K = 0.1 \mu S/cm$. A CP551 pH meter was used; its

Fig. 1 Location of the tested water reservoirs and water sampling sites in the Turawa Big Reservoir

Table 1 Characterization of the examined reservoirs and extraction pits

No	Common name	Locality	Type of reservoir ¹⁾
1	Turawa Big Reservoir	Turawa	Dam—E
2	Nyskie	Nysa	Dam—E
3	Otmuchowskie	Otmuchów	Dam—E
4	Złoty Potok	Pokrzywna	Flow-through—E
5	Brzózki	Biskupice	Flow-through—E
6	Zalew Kluczborski	Kluczbork	Flow-through
7	Staw na Bolko	Opole	Extraction pit S/G—E
8	Balaton	Dobrzeń Wielki	Extraction pit S/G
9	Jezioro Srebrne	Osowiec	Extraction pit S/G
10	Turawa Small Reservoir	Turawa	Extraction pit S/G
11	Turawa Medium Reservoir	Turawa	Extraction pit S/G
12	Dębina	Dębina	Extraction pit S/G
13	Babi Loch	Brzeg	Extraction pit S/G
14	Dębowa	Kędzierzyn-Koźle	Extraction pit S/G
15	Jezioro Srebrne	Januszkowice	Extraction pit S/G
16	Januszkowice Duże	Januszkowice	Extraction pit S/G—E
17	Januszkowice Linowy	Januszkowice	Extraction pit S/G—E
18	Staropolanka	Wielmierzowice	Extraction pit S/G—E
19	Czaple Wolne	Kluczbork	Extraction pit S/G
20	Malina	Opole	Extraction pit M
21	Piast	Opole	Extraction pit M
22	Silesia	Opole	Extraction pit M
23	Bolko	Opole	Extraction pit M
24	Krzanowice	Opole	Extraction pit M

¹⁾ S/G, sand/gravel; M; marl; E, eutrophic waters

absolute reading error was $\Delta\text{pH}=0.02$. Both meters were made by Elmetron (Zabrze, PL).

Table 2 Limits of detection (IDL) and quantification (IQL) and measurement uncertainty expressed in standard deviation s_M characterizing the Metrohm 850 Professional IC ion chromatograph

Ion	IDL (mg/dm ³)	IQL (mg/dm ³)	s_M (%)
F ⁻	0.005	0.05	12
Cl ⁻	0.05	0.50	5
NO ₂ ⁻	0.003	0.030	23
Br ⁻	0.005	0.010	25
NO ₃ ⁻	0.02	0.10	16
PO ₄ ³⁻	0.013	0.050	26
SO ₄ ²⁻	0.05	0.50	22
Na ⁺	0.05	0.50	7
NH ₄ ⁺	0.005	0.050	9
K ⁺	0.05	0.50	19
Ca ²⁺	0.1	1.0	9
Mg ²⁺	0.1	1.0	11

2.2 How to interpret the results

Ion concentrations are expressed in gram equivalents. In order to keep the units compatible with the SI system, the normal concentrations N (val/dm³) were replaced with the following concentrations:

$$c^* = c \cdot z \quad (1)$$

where: c — concentration expressed in mol/dm³, z — valence of the ion (dimensionless unit).

Then the c^* concentration is equal to the normal concentration, but can be expressed in mol/dm³. Concentrations expressed in this way allow the validity of the results to be estimated by comparing the concentrations of anions and cations. Taking into account the fact that the concentration of the most abundant ions in the aquatic environment is being analyzed, it can be assumed that the sum of the cations should be equal to the sum of the anions: $c^*_{\text{Ct}} = c^*_{\text{A}}$, and the reason for any deviations is mainly the uncertainty of measurements and, with

favorable acidity, the formation of organic anions (Moiseenko et al., 2013). The method for estimating the correctness of the results is based on the determination of PD coefficients, by comparing the absolute values of the difference in the sum of the concentrations of the cations and anions, $c_{\text{Cl}}^* - c_{\text{A}}^*$, to the average concentration of the cations and anions, $0.5 \cdot (c_{\text{Cl}}^* + c_{\text{A}}^*)$. It was assumed that the coefficients (PD%), expressed as percentages, for $c^* \geq 0.5 \text{ mmol/dm}^{-3}$, in the range of $\text{PD} < 10\%$, indicate very good quality analyses, in the range of $10\% > \text{PD} < 20\%$ — good quality, while in the range of $\text{PD} > 20\%$ — unsatisfactory quality of results (Moiseenko et al., 2013).

The results were interpreted by comparing the relative concentration values of x^* ions, determined in the number of n tested reservoirs, in the number of n repetitions or in the number of n sampled sites, according to the relationship:

$$x_i^* = c_i^* / \sum_{i=1}^n c_i^* \quad (2)$$

This way of presenting the results, similar to the case of molar fractions, facilitates graphical interpretation of the results, since the range of variability of concentrations is contained within the limits of $\langle 0, 1$ and not, as in the case of absolute concentrations, in the limits of $\langle 0, \infty \rangle$. On the basis of such interpreted concentrations, it is possible to indicate anomalies and to quantify their share in the whole set consisting of n measurements. In all cases, the

absolute results of the pH and water conductivity measurements were analyzed.

For comparisons, only those ions were selected for which the value of standard deviation s from the mean value determined for the set under consideration was greater than $2 \cdot s_M$ — where s_M is uncertainty of measurements of the method (Table 1). It was assumed that for $s \leq 2 \cdot s_M$ concentration differences may be of random nature.

Concentration values below the IQL quantification limit were used for the calculations as $0.5 \cdot IQL$.

3 Results and discussion

Data on the results of absolute measurements of values of c^* ion concentrations (Eq. (1)) in water sampled for testing in three successive stages are summarized in Tables 3, 4, 5.

Table 3 presents data on concentrations of c^* ions (mmol/dm^3), pH index and conductivity in water sampled for studies in 24 reservoirs situated in the Opole region.

The data in Table 3 show that the condition $s \leq 2 \cdot s_M$ was fulfilled only in the case of potassium, which, as mentioned, may indicate random (within the limits of measurement uncertainty) differences in concentrations of this ion, difficult to interpret. In this series of measurements, $c_{\text{A}}^* = 1.03 \cdot c_{\text{Cl}}^*$, with the set value of the free expression $b=0$ and the correlation coefficient $R^2=0.951$. PD coefficients indicate very good and good quality of analyses, with the exception of the data concerning the highly saline reservoirs

Table 3 Data on the results of measurements of c^* ion concentration (mmol/dm^3), pH index and conductivity in water sampled for studies in 24 reservoirs

Parameter	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
Mean	0.016	3.35	0.00063	0.0288	0.0286	0.0019	1.83
Median	0.013	1.69	0.00033	0.0006	0.0060	0.0008	1.72
s (%) ¹⁾	66	128	95	214	122	108	68
Min	0.003	0.33	0.00027	0.0001	0.0006	0.0008	0.28
Max	0.050	15.41	0.00261	0.2324	0.1290	0.0073	5.65
Parameter	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	pH (-)	κ ($\mu\text{S/cm}$)
Mean	0.89	0.009	0.14	2.81	1.03	7.85	795
Median	0.41	0.002	0.12	2.15	0.82	7.82	491
s (%) ¹⁾	157	160	31	69	80	7	103
Min	0.08	0.001	0.11	0.70	0.23	7.05	147
Max	5.80	0.056	0.23	7.31	3.83	10.01	3240

¹⁾ s , standard deviation from mean value of ion concentration determined for all reservoirs

Table 4 Identification of studied water reservoirs with relatively high seasonal variability of the tested ions concentrations; X indicates that condition: $s > 2 \cdot s_M$ is fulfilled

Ion	Reservoir number							
	1	2	3	7	10	20	22	23
F ⁻	X		X	X				
Cl ⁻	X		X	X	X			
NO ₂ ⁻	X	X	X					
Br ⁻		X	X		X	X	X	X
NO ₃ ⁻	X			X	X			
PO ₄ ³⁻	X	X	X	X				
NH ₄ ⁺	X	X	X	X	X	X	X	X

Table 5 Data on the results of measurements of c^* (mmol/dm³) ion concentration in water collected for testing in the Turawa Big Reservoir

Parameter	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
Mean	0.015	1.38	0.0009	0.022	0.20	0.0009	1.50
Median	0.015	1.31	0.0004	0.020	0.13	0.0008	1.52
s (%) ¹⁾	26	23	150	55	79	56	13
Min	0.005	0.53	0.0003	0.001	0.12	0.0008	1.19
Max	0.028	2.20	0.0064	0.056	0.79	0.0035	1.95

Parameter	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	pH (-)	κ (μ S/cm)
Mean	1.00	0.0015	0.206	1.60	0.51	9.3	561
Median	1.00	0.0014	0.211	1.46	0.53	9.6	543
s (%) ¹⁾	14	22	14	25	13	17	6
Min	0.55	0.0014	0.099	1.15	0.40	7.8	444
Max	1.40	0.0029	0.259	3.02	0.66	9.8	880

¹⁾ s , standard deviation from the mean value of the ion concentration determined for all measurement sites in the two study periods

Januszkowice Duże (No. 16; $\kappa=3240 \mu\text{S/cm}$) and Januszkowice Linowy (No. 17; $\kappa=2650 \mu\text{S/cm}$). Repeated measurements of the water in those reservoirs show the relation: $c_A^* \approx 1.4 \cdot c_{Cl}^*$, $PD > 30$. At the present stage of the research, the observed anomalies are difficult to explain. It may be assumed that, with high salinity and simultaneously a high content of organic matter, resulting from advanced eutrophication, the metal cations may be complexed by organic compounds and therefore are not identified by the applied measurement method.

The second stage of the study consisted in the evaluation of temporal changes in ion concentrations in 8 selected reservoirs (Table 1; Nos. 1, 2, 3, 7 and 10, 20, 22, 23). Table 4 indicates the reservoirs where, expressed by standard deviation, the variability of ion determinations in water samples collected for testing in August 2013 in monthly intervals from January to August 2014 and in July 2015, met the condition $s > 2 \cdot s_M$. The SO_4^{2-} , Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions,

for which the condition $s > 2 \cdot s_M$ was not met, were not included in Table 4.

As can be seen from the table, the greatest variability in concentrations of the analyzed ions is observed in eutrophic, dam reservoirs (Nos. 1 and 3), while the smallest variability is observed in the reservoirs formed in the marl mining areas (Nos. 20, 22 and 23). None of the reservoirs showed significant changes in concentrations of SO_4^{2-} , Na^+ , K^+ , Ca^{2+} and Mg^{2+} . The sampling site in the Turawa Big Reservoir (No. 1) is marked in Fig. 1 with the number 17. In this series of measurements $c_A^* = 1.06 \cdot c_{Cl}^*$, with the set value of free expression $b=0$ and the correlation coefficient $R^2=0.924$. The PD coefficients indicate good quality of analyses.

Table 5 collects data on the results of measurements of c^* (mmol/dm³) ion concentration, pH index and conductivity κ in water collected for testing in 21 locations in the Turawa Big Reservoir (Table 1; No: 1), in the months of September 2019 and in February 2020.

The condition of $s \leq 2 \cdot s_M$ was met for sulphate anions and Na^+ , K^+ i Mg^{2+} cations, indicating comparable concentrations of these ions in all places from which samples were taken.

In this series of measurements $c_A^* = 0.943 \cdot c_{Ct}^*$, with the free expression value $b=0$ and correlation coefficient $R^2=0.912$. The PD coefficients indicate very good and good quality of analyses.

Figure 2 shows the results of the relative values of concentrations x^* as well as the absolute values of conductivity and pH determined in waters sampled from the tested 24 reservoirs. The figures for the absolute values are summarized in Table 3.

Differences in the ionic composition of waters in the studied reservoirs shown in Fig. 2 indicate certain regularities related to the level of eutrophication, type of reservoir and substrate—the chemical composition of the bottom.

Dam and flow-through reservoirs (Nos. 1–6) are characterized by an increased content of biogenic compounds, mainly nitrate anions, nitrite anions and phosphate(V) anions. The reservoirs (Nos. 1–5), considered as eutrophic, were constructed at least 25 years ago. The contamination with biogenic compounds [nutrients] of this type of reservoir is reported by many authors, e.g. (Koronkevich et al., 2019; Kuriata-Potasznik, 2018). The source of the nutrients is mainly the water supplying the reservoirs, in which organic suspended solids are also transported to the reservoirs, supporting the formation of the sapropelic bottom sediments, another source of nutrients (Deng et al., 2020; Kuriata-Potasznik et al., 2020). An exception is the Zalew Kluczborski (No. 6). This reservoir, fed with the waters of the Stobrawa River, was constructed between 2009 and 2013 and so came into operation in the year in which the water samples were taken. Relatively high concentrations of nitrate(III) and nitrate(V) anions, but also ammonia nitrogen, were found in its waters. Main source of contamination of the newly-created reservoir is the water of the Stobrawa River flowing through agricultural areas. As evidenced by prognostic studies conducted before the construction of the reservoir in 2005–2008, which indicated the poor quality of the Stobrawa water in terms of nutrient content (Wiatkowski, 2009).

The next type of reservoir are those regarded as eutrophic with sand/gravel substrate (Nos. 7 and 16, 17 and 18). These reservoirs are characterized by relatively high concentrations of sulphates and halides,

mainly sodium, calcium and magnesium. Reservoir 7 is a small, shallow reservoir with an area of approx. 0.2 km^2 , located in a park and recreation area in the city of Opole. The significant salinity of this reservoir is a result of long-term (the park was created in the first decades of the twentieth century) soil elution from rainwater flowing into the reservoir, which is observed in this type of water reservoir (Luo et al., 2011). Reservoir nos. 16–18 are considered the most polluted water reservoirs in Opole Province. They are situated close to the industrial town of Zdzeszowice, where the largest coking production plant in Poland has been located since the 1930s. The reservoirs in question, Januszkowice Duże (16), Januszkowice Linowy (17) and Staropolanka (18), are situated close to each other, in an area of about 4 km^2 . The waters of these reservoirs, apart from their relatively high salinity, are characterized by the high concentrations of nitrates(V) and phosphates(V) determined in reservoirs Nos. 16 and 17 and the highest relative concentration of ammonium ions in reservoir No. 18. Such a high salinity and accumulation of biogenic ions is probably the result of many years' accumulation of leachate from agricultural areas, e.g. by the Potok Padół (Cedruń), a stream flowing near the reservoirs and forming floodplains during thawing and intensive rainfall. The impact of agricultural management on surface water pollution has been addressed in many publications, e.g. (Racchetti et al., 2019; Tong & Chen, 2002). Dry and wet deposition is not insignificant for the pollution of water bodies (Luo et al., 2007). A similarly high level of salinity, but with low concentrations of biogenic ions, was recorded in Czaple Wolne reservoir (19), located near agricultural fields. The reason for the low nutrient content may be a strip of wasteland around the lake that separates it from the agricultural fields.

Noteworthy are the ion concentrations in reservoirs formed in the marl extraction pits (Nos. 20–24). A characteristic feature of these reservoirs is the comparable concentrations of all ions as well as the comparable conductivity and pH of the water. This indicates a significant influence of limestone on shaping the chemistry of the aquatic environment; particularly on the concentrations of phosphate(V) and fluoride ions, which form barely soluble salts with calcium ions, the solubility products of which are respectively: $1.3 \cdot 10^{-32}$ and $1.7 \cdot 10^{-14}$. For comparison, the solubility product of calcium carbonate is $4.7 \cdot$

◀ **Fig. 2** Relative concentrations x^* of ions, absolute values of conductivity and pH of water in the tested reservoirs; D — dam reservoirs, F — flow reservoirs, S/G — sand/gravel pits, M — marl pits

10^{-9} (Table of Solubility, 2017), which in turn indicates that, at equilibrium, with a significant excess of solid CaCO_3 , calcium ions reach concentrations of the order of 10^{-4} mol/dm³. At such a concentration of calcium ions, the concentrations of phosphate(V) and fluoride ions do not exceed the order of 10^{-10} and 10^{-5} mol/dm³. For comparison, in water samples collected from reservoirs Nos. 20–24, the concentrations of phosphate(V) ions were below the quantification limit ($< 6 \cdot 10^{-6}$ mol/dm³) and the average concentration of fluoride ions was $2.2 \cdot 10^{-5}$. The influence of the substrate on the ionic composition of water is also reported by other authors (Geller, 2013).

Good water quality status is indicated by concentrations of ions determined in reservoirs Nos. 8–15. A slight increase in nitrate(III) and nitrate(V) concentrations was determined in the Turawa Small Reservoir (No. 10). In all reservoirs, the pH value oscillated around 8.

From the point of view of the preliminary assessment of water quality, conductivity measurements, indicating the general state of salinity, seem to be important. A linear relationship was established between the mean value of c^* concentrations of the determined ions in individual reservoirs (excluding anomalous concentrations in reservoirs 16 and 17; $\text{PD} > 30$) and the determined conductivity: $\kappa = 166.2 \cdot c^* - 60$ (correlation coefficient $R^2 = 0.946$). However, this is not a meaningful quantitative assessment. Studies have shown that in the range of linear relationships $\kappa = f(c^*)$ the directional coefficient is close to the value $115 \text{ (S/cm)} \cdot (\text{mmol/dm}^3)$, while the free expression to the conductivity of perfectly pure water is: $0.0547 \mu\text{S/cm}$ (Kłos & Wierzbą, 2019). However, inexpensive water conductivity tests, which require no special training, can reveal significant changes occurring in the ecosystem.

Figure 3 shows the seasonal changes in concentrations of the ions highlighted in Table 4, determined in water samples collected for study in August 2013, at monthly intervals from January to August 2014 and in July 2015 from four eutrophic reservoirs (Nos. 1, 2, 3 and 7) and four non-eutrophic reservoirs (Nos. 10, 20, 22 and 23), three of which are dam type reservoirs

(Nos. 1, 2 and 3), two were formed in sand extraction sites (Nos. 7 and 10), and three were formed by marl extraction sites (Nos. 20, 22 and 23). As a reminder, only ions showing significant temporal variations in concentration and meeting the condition $s > 2 \cdot s_M$ were taken into account.

The results presented in Fig. 3 indicate that the seasonal changes in concentrations depend on the type of ion and the type of reservoir. Fluoride anions showed significant concentration changes only in three reservoirs considered eutrophic. Their highest concentrations were recorded in the spring. Fluorine compounds occur in nature in the form of poorly soluble salts, e.g.: CaF_2 (fluorite) and $\text{Na}_3[\text{AlF}_6]$ (cryolite). Their presence in surface waters is believed to be associated with industrial production (Mohapatra et al., 2009). Chloride anions showed significant changes in concentrations in four reservoirs: two of dam type and two formed in sand pits. Three of them are eutrophic reservoirs. Variation in the concentrations of chloride anions in dammed reservoirs probably results from the quality of water feeding the reservoir, while a similar trend as for fluoride anions can be observed in reservoir No. 3 and reservoirs 7 and 10. Sources of chloride anions are most commonly reservoir feed waters and, in the case of closed reservoirs, rainwater and groundwater (Kelly et al., 2008).

Significant variability of nitrate(III) anion concentrations was recorded in three eutrophic dam reservoirs (No. 1–3). Nitrate(III) is an intermediate product in the nitrification or denitrification process (Bertrand et al., 2015), which depends, among other things, on the chemical composition of the water, including the pH index and degree of oxygenation, and on the chemical composition of the bottom sediments.

Bromide anions are a natural component of surface waters. Their c^* concentration in freshwater reservoirs ranges from approx. 0.0001 to over 0.125 mmol/dm³ (Heeb et al., 2014). For surface waters in Poland this ranges from $c^* = 0.0050$ to 0.0088 mmol/dm³ (Magazinovic et al., 2004); in this work, c^* : 0.0001–0.2324 mmol/dm³ (Table. 3). Seasonal changes of bromide anions were recorded in seven reservoirs: two dam type (Nos. 1 and 3), one reservoir formed after sand extraction (No. 10) and three reservoirs formed after marl extraction (Nos. 20, 22 and 23). The data presented in the Fig. 3 indicate that their concentrations in the studied waters increase during the summer months.

◀ **Fig. 3** Seasonal variations in the relative x^* concentrations of ions in 8 selected reservoirs: eutrophic (No. 1, 2, 3 and 7) and non-eutrophic (No. 10, 20, 22 and 23)

Seasonal variability of nitrate(V) anion concentrations was demonstrated in three reservoirs, two eutrophic dam reservoirs (Nos. 1 and 2) and in a closed reservoir, No. 10. In dam reservoirs, the highest concentrations of nitrates(V) were recorded in winter, with a downward tendency from January to July. Nitrate nitrogen(V) is introduced into surface waters mainly through leachate from agricultural land, especially from animal husbandry areas (Adelana et al., 2020). The correlation between the area of agricultural land and the nitrates content in surface waters is indicated by studies conducted in the Czech Republic in 1986–2005 (Kvítek et al., 2009). The catchments of waters of the Mała Panew River, feeding reservoir No. 1, and the waters of the Nysa Kłodzka River, feeding reservoir No. 2, are located mostly in agricultural areas. No significant seasonal changes in nitrate(V) concentrations were recorded in reservoir No. 3, also fed by the waters of the Nysa Kłodzka River and situated upstream of reservoir No. 2. In reservoir No. 10, formed after sand extraction, unlike in the case of the dam reservoirs discussed above, the highest nitrate(V) concentrations were recorded in April, which indicates the multidimensional character of factors affecting the ionic composition of waters.

The variability in phosphate (V) anion concentrations was recorded in four eutrophic reservoirs — three of them of dam type (Nos. 1–3) — and in eutrophic reservoir No. 7, located in the city park. The lowest concentrations were recorded in the winter-spring months (January–April) with an upward trend in May–August, contrary to the results of the Volga River water study (Seleznev et al., (2018) where the lowest phosphate concentrations were recorded in the summer months (June–August). This type of anomaly can be explained by the increased proportion of phosphate fertilizers in the leachate from arable land. The equilibrium between the phosphate content in water and in bottom sediments also plays a role here, which is influenced by many physicochemical factors, e.g. oxygenation, carbon dioxide content, phosphorus/iron ratio, which has not been fully recognized (van Dael et al., 2020).

The variability of the ammonium cation concentrations is difficult to interpret. The data shown in the graph indicate that in the studied reservoirs the greatest similarities in concentrations occur in January to March. In other months the ammonium cation concentrations vary considerably, even among groups of the same types of reservoirs. The presence of ammonium cations is often anthropogenic in nature (Venitsianov & Kirpichnikova, 2020), but they can also be formed as a result of biochemical reactions f.e. ammonification (the formation of ammonia or its compounds from nitrogenous compounds, especially as a result of bacterial decomposition. (Bertrand et al., 2015).

Figure 4 shows the results of the research carried out in September 2019 and repeated in February 2020 in the Turawa Big Reservoir (Table 5). The figure shows the relative values of the mean concentrations of x^* ions from the two measurement series and the absolute mean values of the water conductivity κ and pH measurements. In this case, the average values better illustrate the surface distribution of the concentrations of the tested ions and reduce the effect of seasonal changes. Only ions showing significant concentration differences, meeting the condition: $s > 2 \cdot s_M$, were taken into account. This condition was not met in case of the sulphate(VI) anion and cations Na^+ , K^+ and Mg^{2+} .

The results presented in Fig. 4 indicate a significant increase in the concentration of ions in water samples collected for testing at sites 9 to 11. Water samples collected from these sites also show higher conductivity values and lower pH values than water collected from the other designated sites. These sites, shown on the map (Fig. 1), are situated near the inflow of the Mała Panew river to the reservoir. Significant increases in the concentrations of the tested ions were not observed at point D, located in the lake basin, outside the littoral zone, distant from points 9 and 10 by 300 m. This effect may be the result of mixing of flowing waters with the waters of the reservoir. This indicates the source of origin of the ions. In 2017, the water quality status of the Mała Panew river above the Turawa Big Reservoir was classified as bad (Voivodship Inspector of Environmental Protection in Opole). The ionic composition of the reservoir's waters is also shaped by the accumulation of large quantities of bottom sediments, particularly sapropelic muds,

Fig. 4 Relative concentrations of x^* ions and absolute values of conductivity and pH measurements of water in Turawa Big Reservoir

which accumulate pollutants e.g. heavy metals (Simeonov et al., 2007). Studies of the bottom sediments of the Turawa Big Reservoir carried out in 2008 revealed high concentrations of phosphate(V) both in the sediments (0.86–3.25 mg/g) and in pore water (0.045–0.839 mg/dm³) (Trojanowska & Jezierski, 2011). Relatively high concentrations of ammonium ions were recorded at sites 12 and 17. These are sites overgrown with marsh vegetation. As mentioned, ammonium ions are released, among other ions, due to the biochemical decomposition of organic and animal compounds.

The Turawa Big Reservoir is characterized by relatively high water pH values. At the end of the growing season pH values are close to 10 (Fig. 2). The lowest pH values were recorded at sites 9–11, at the

inflow of the Mała Panew river into the reservoir. This is also confirmed by other studies (Wiatkowski & Wiatkowska, 2019).

Summing up, the results presented in Fig. 4 indicate that the pollution of the Turawa Big Reservoir with ionic substances, e.g. nitrate(III) and (V) and phosphate(V) anions is the result of contamination of the Mała Panew river feeding the reservoir.

4 Conclusions

The study indicates that the concentration of macrolelements in water reservoirs, even those of similar origin, is an individual matter dependent on external factors: both distant, such as the chemical composition

of inflowing waters, and local, in which the main contribution is the chemical composition of the rain-water and snowmelt flowing into the reservoir. It can also be, as in the case of flooded marl pits, shaped and buffered by the chemical composition of the substrate. The ionic composition of waters, also in terms of seasonal changes, is also shaped by the biochemical processes occurring in the reservoir waters. Their intensity increases with increasing levels of eutrophication. The conducted research shows that activities related to the improvement of water quality cannot be limited to systemic solutions, financed under the European Union programs for the expansion of the sewage network and sewage treatment plant. Local measures limiting the inflow of pollutants from nearby sources should contribute significantly to the improvement of the water quality of such reservoirs, which can often perform recreational functions.

Funding Financial support for this work was provided by the National Centre for Research and Development, programme BIOSTRATEG (ZBIORTUR, project 3/343733/15/NCBR/2018).

Data and materials availability All data are available from the authors upon reasonable request.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Adelana, S. M., Heaven, M. W., Dresel, P. E., Giri, K., Holmberg, M., Croatto, G., & Webb, J. (2020). Controls on species distribution and biogeochemical cycling in nitrate-contaminated groundwater and surface water, southeastern Australia. *Science of the Total Environment*, 726, 138426. <https://doi.org/10.1016/j.scitotenv.2020.138426>.
- Araín, M. B., Kazi, T. G., Jamali, M. K., Jalbani, N., Afridi, H. I., & Shah, A. (2008). Total dissolved and bioavailable elements in water and sediment samples and their accumulation in *Oreochromis mossambicus* of polluted Manchar Lake. *Chemosphere*, 70(10), 1845–1856. <https://doi.org/10.1016/j.chemosphere.2007.08.005>.
- Bertrand, J. C., et al. (2015). Biogeochemical cycles. In: J. C. Bertrand, P. Caumette, P. Lebaron, R. Matheron, P. Normand, T. Sime-Ngando (Eds.) *Environmental microbiology: Fundamentals and applications*. Springer. https://doi.org/10.1007/978-94-017-9118-2_14.
- Carlson, R. E. (1975). A trophic state index for lakes. *Limnology and Oceanography*, 2(22), 361–369. <https://doi.org/10.4319/lo.1977.22.2.0361>.
- Chang, W. Y. B. (1982). Primary productivity and nutrients in the sediment retention basin of Lake Monroe. *Hydrobiologia*, 87, 193–200. <https://doi.org/10.1007/BF00007227>.
- Council Directive 91/676/EEC of 12 December 1991: Current consolidated version: 11/12/2008, ELI: data.europa.eu/eli/dir/1991/676/oj.
- Deng, M., Hou, J., Song, K., Chen, J., Gou, J., Li, D., & He, X. (2020). Community metagenomic assembly reveals microbes that contribute to the vertical stratification of nitrogen cycling in an aquaculture pond. *Aquaculture*, 520, 734911. <https://doi.org/10.1016/j.aquaculture.2019.734911>.
- Geller, W. (2013). Case Studies and Regional Surveys. In: Geller, W., Schultze, M., Kleinmann, R., Wolkersdorfer, C. (Eds.) *Acidic Pit Lakes. Environmental Science and Engineering (Environmental Engineering)*. Springer. https://doi.org/10.1007/978-3-642-29384-9_5.
- Golterman, H. L., de Oude, N. T. (1991). Eutrophication of Lakes, Rivers and Coastal Seas. In: B. Allard, G. F. Craun, N. T. de Oude, M. Falkenmark, H. L. Golterman, T. Lindstrom, W. T. Piver, *Water Pollution*. 5/5A, 79–124. Springer. https://doi.org/10.1007/978-3-540-46685-7_3.
- Häder, D.-P., Banaszak, A. T., Villafañe, V. E., Narvarte, M. A., González, R. A., & Helbling, E. W. (2020). Anthropogenic pollution of aquatic ecosystems: Emerging problems with global implications. *Science of the Total Environment*, 713, 136586. <https://doi.org/10.1016/j.scitotenv.2020.136586>.
- Heeb, M. B., Criquet, J., Zimmermann-Steffens, S. G., & von Gunten, U. (2014). Oxidative treatment of bromide-containing waters: Formation of bromine and its reactions with inorganic and organic compounds — A critical review. *Water Research*, 48, 15–42. <https://doi.org/10.1016/j.watres.2013.08.030>.
- Hérivaux, C., Orban, P., & Brouyère, S. (2013). Is it worth protecting groundwater from diffuse pollution with agri-environmental schemes? A hydro-economic modeling approach. *Journal of Environmental Management*, 128, 62–74. <https://doi.org/10.1016/j.jenvman.2013.04.058>.
- Ikem, A., & Adisa, S. (2011). Runoff effect on eutrophic lake water quality and heavy metal distribution in recent littoral sediment. *Chemosphere*, 82(2), 259–267. <https://doi.org/10.1016/j.chemosphere.2010.09.048>.
- Internet 1 – Provincial Inspectorate for Environmental Protection in Opole (Engl. transl.). undated. <http://opole.pios.gov.pl/index.php>.

- Kelly, V. R., Lovett, G. M., Weathers, K. C., Findlay, S. E. G., Strayer, D. L., Burns, D. J., & Likens, G. E. (2008). Long-term sodium chloride retention in a rural watershed: Legacy effects of road salt on streamwater concentration. *Environmental Science and Technology*, 42(2), 410–415. <https://doi.org/10.1021/es0713911>.
- Kłos, A., & Wierzbna, S. (2019). Application of conductometric and pH metric measurements in determining the kinetics and equilibrium parameters of the heterophasic ion exchange: Metal cation-proton. *Electrochemistry Communications*, 102, 5–12. <https://doi.org/10.1016/j.elecom.2019.03.011>.
- Koronkevich, N. I., Dolgov, S. V., Kashutina, E. A., et al. (2019). Specific features of the formation of water flow and pollution export from agricultural, forest, and urbanized landscapes. *Water Resources*, 46, S137–S144. <https://doi.org/10.1134/S0097807819070121>.
- Kuriata-Potasznik, A. (2018). The functioning of a water body within a fluvio-lacustrine system as an effect of excessive nitrogen loading — The case of Lake Symsar and its drainage area (Northeastern Poland). *Water*, 10, 1163. <https://doi.org/10.3390/w10091163>.
- Kuriata-Potasznik, A., Szymczyk, S., & Skwierawski, A. (2020). Influence of cascading river—Lake systems on the dynamics of nutrient circulation in catchment areas. *Water*, 12, 1144. <https://doi.org/10.3390/w12041144>.
- Kvítek, T., Žlábek, P., Bystřický, V., Fučík, P., Lexa, M., Gergel, J., Novák, P., & Ondr, P. (2009). Changes of nitrate concentrations in surface waters influenced by land use in the crystalline complex of the Czech Republic. *Physics and Chemistry of the Earth Parts A/B/C*, 34(8–9), 541–551. <https://doi.org/10.1016/j.pce.2008.07.003>.
- Lotze, H. K., Lenihan, H. S., Bourque, B. J., Bradbury, R. H., Cooke, R. G., Kay, M. C., Kidwell, S. M., Kirby, M. X., Peterson, C. H., & Jackson, J. B. C. (2006). Depletion, degradation, and recovery potential of estuaries and coastal seas. *Science*, 312(5781), 1806–1809. <https://doi.org/10.1126/science.1128035>.
- Luo, L., Qin, B., Yang, L., et al. (2007). Total inputs of phosphorus and nitrogen by wet deposition into Lake Taihu, China. *Hydrobiologia*, 581, 63–70. <https://doi.org/10.1007/s10750-006-0515-3>.
- Luo, J., Wang, X., Yang, H., Zhen Yu, J., Yang, L., & Qin, B. (2011). Atmospheric phosphorus in the northern part of Lake Taihu, China. *Chemosphere*, 84(6), 785–791. <https://doi.org/10.1016/j.chemosphere.2011.01.043>.
- Magazinovic, R. S., Nicholson, B. C., Mulcahy, D. E., & Davey, D. E. (2004). Bromide levels in natural waters: Its relationship to levels of both chloride and total dissolved solids and the implications for water treatment. *Chemosphere*, 57(4), 329–335. <https://doi.org/10.1016/j.chemosphere.2004.04.056>.
- Mohapatra, M., Anand, S., Mishra, B. K., Giles, D. E., & Singh, P. (2009). Review of fluoride removal from drinking water. *Journal of Environmental Management*, 91(1), 67–77. <https://doi.org/10.1016/j.jenvman.2009.08.015>.
- Moiseenko, T. I., Gashkina, N. A., Dinu, M. I., Kremleva, T. A., & Khoroshavin, VYu. (2013). Aquatic geochemistry of small lakes: Effects of environment changes. *Geochemistry International*, 51(13), 1031–1148. <https://doi.org/10.1134/S0016702913130028>.
- Nixon, S. (1995). Coastal marine eutrophication: A definition, social causes and future concerns. *Ophelia*, 41, 199–219. <https://doi.org/10.1080/00785236.1995.10422044>.
- PN-EN ISO 14911:2002 Water quality - determination of dissolved Li^+ , Na^+ , NH_4^+ , K^+ , Mn^{2+} , Ca^{2+} , Mg^{2+} , Sr^{2+} and Ba^{2+} using ion chromatography - method for water and waste water.
- PN-ISO 10304-1:2009/AC:2012 Water quality - determination of dissolved anions by liquid chromatography of ions.
- PN-ISO 5667-4:2017-10:2003 Water quality - Sampling - Part 4: Guidelines for sampling of natural lakes and artificial dammed reservoirs.
- Primpas, I., Tsirtsis, G., Karydis, M., & Kokkoris, G. D. (2010). Principal component analysis: Development of a multivariate index for assessing eutrophication according to the European water framework directive. *Ecological Indicators*, 10, 178–183. <https://doi.org/10.1016/j.ecolind.2009.04.007>.
- Racchetti, E., Salmaso, F., Pinardi, M., Quadroni, S., Soana, E., Sacchi, E., Severini, E., Celico, F., Viaroli, P., & Bartoli, M. (2019). Is flood irrigation a potential driver of river-groundwater interactions and diffuse nitrate pollution in agricultural watersheds. *Water*, 11, 2304. <https://doi.org/10.3390/w11112304>.
- Rixon, S., Levison, J., Binns, A., & Persaud, E. (2020). Spatiotemporal variations of nitrogen and phosphorus in a clay plain hydrological system in the Great Lakes Basin. *Science of the Total Environment*, 714, 136328. <https://doi.org/10.1016/j.scitotenv.2019.136328>.
- Seleznev, V. A., Bespalova, V. K., & Selezneva, A. V. (2018). Seasonal variability of phosphate content in the Volga water under conditions of anthropogenic eutrophication of reservoirs. *Journal of Water Chemistry and Technology*, 40(5), 307–311. <https://doi.org/10.3103/S1063455X18050107>.
- Simeonov, V., Wolska, L., Kuczyńska, A., Gurwin, J., Tsakovski, S., Protasowicki, M., & Namieśnik, J. (2007). Sediment-quality assessment by intelligent data analysis. *Trends in Analytical Chemistry*, 26(4), 323–331. <https://doi.org/10.1016/j.trac.2006.12.004>.
- Smith, V. H. (2003). Eutrophication of freshwater and coastal marine ecosystems a global problem. *Environmental Science and Pollution Research*, 10, 126–139. <https://doi.org/10.1065/espr2002.12.142>.
- Tong, S. T. Y., & Chen, W. (2002). Modeling the relationship between land use and surface water quality. *Journal of Environmental Management*, 66(4), 377–393. <https://doi.org/10.1006/jema.2002.0593>.
- Trojanowska, A., & Jezierski, P. (2011). Phosphorus in sediments and pore waters of selected Polish dam reservoirs. *Oceanological and Hydrobiological Studies*, 40(2), 72–85. <https://doi.org/10.2478/s13545-011-0018-3>.
- Van Dael, T., De Cooman, T., Verbeeck, M., & Smolders, E. (2020). Sediment respiration contributes to phosphate release in lowland surface waters. *Water Research*, 168, 115168. <https://doi.org/10.1016/j.watres.2019.115168>.
- Venitsianov, E. V., & Kirpichnikova, N. V. (2020). Assessment of water quality in the system of reservoirs—Sources of water supply in Moscow based on long-term dynamics of hydrochemical parameters. *Russian Meteorology*

- and *Hydrology*, 45(8), 571–578. <https://doi.org/10.3103/S1068373920080087>.
- Vitousek, P. M., Mooney, H. A., Lubchenco, J., & Melillo, J. M. (1997). Human domination of earth's ecosystems. *Science*, 277(5325), 494–499. https://doi.org/10.1007/978-0-387-73412-5_1.
- Vollenwider, R., Giovanardi, F., Montanai, G., & Rinaldi, A. (1998). Characterization of the trophic conditions of marine coastal waters with special reference to the NW Adriatic Sea: Proposal for a trophic scale, turbidity and generalized water quality index. *Environmetrics*, 9, 329–357. [https://doi.org/10.1002/\(SICI\)1099-095X\(199805/06\)9:3%3c329::AID-ENV308%3e3.0.CO;2-9](https://doi.org/10.1002/(SICI)1099-095X(199805/06)9:3%3c329::AID-ENV308%3e3.0.CO;2-9).
- Water Framework Directive - Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000.
- Wiatkowski, M. (2009). Hydrochemical conditions for localization of small water reservoirs on the example of Kluczbork reservoir. *Archives of Environmental Protection*, 35(4), 129–144. <https://bwmeta1.element.baztech-article-BUS8-0002-0011>.
- Wiatkowski, M., & Wiatkowska, B. (2019). Changes in the flow and quality of water in the dam reservoir of the Mała Panew catchment (South Poland) characterized by multi-dimensional data analysis. *Archives of Environmental Protection*, 45(1), 26–41. <https://doi.org/10.24425/aep.2019.126339>.

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.