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Hydrochemical conditions of three lakes located in the West Pomeranian region in the annual cycle

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Abstract: The objective of the study was to trace the variability of the hydrochemical conditions in three lakes of the West Pomeranian Voivodeship (Poland) – Starzyca, Maszewskie and Nowogardzkie in the annual cycle. The research was done in 2018–2019, and samples for analysis were collected 4 times a year. All analyses were performed applying standard methods. Such hydrochemical indices were determined as dissolved oxygen, chemical oxygen demand, content of orthophosphates, total phosphorus, nitrite, nitrate, ammonium, chlorophyll *a* and iron. The study showed that all lakes in the research cycle were characterised by a polymictic type of water mixing, and the trophic level, based on the adopted criteria, indicated advanced eutrophy, which may also be caused by anthropogenic pressure. Oxygen conditions characterised by deoxidation of the waters in the bottom layer in the spring and summer seasons, and clear oxygenation in the surface water layer (in Lake Maszewskie reaching even 188.5% in the spring) confirm the significant advancement of the eutrophication process. The supply of phosphorus and nitrogen in spring from pelagic waters in the waters of the examined lakes influences concentrations of chlorophyll *a* in the summer. The influence of "internal supply" (bottom waters and bottom sediments) on the amount of nutrients available for autotrophs is clearly visible in the analysed lakes – an increase in nitrogen and mineral phosphorus concentrations in relation to surface waters was observed in the bottom layer.

Keywords: eutrophication, nitrogen, nutrients, phosphorus

INTRODUCTION

Contamination of aquatic ecosystems in urbanised areas results from intense anthropogenic impact from industrial and infrastructural facilities and the local population using lakes and rivers for economic and recreational purposes [Guzeva *et al.* 2021; Pathak, Pathak 2012; Smith, Schindler 2009].

Anthropopression significantly contributes to the eutrophication of waters and elevated concentrations of phosphorus and nitrogen in ageing aquatic ecosystems, which in normal conditions take thousands of years. This process can be greatly accelerated by an excess supply of nutrients associated with human activity, resulting in so-called "cultural eutrophication" [Jekatierynczuk-Rudczyk *et al.* 2014].

The basic physical processes of water mixing that occur within the lake basin throughout the year contribute to the circulation of nutrients and consequently shape the extent of primary production in the lake. Additional nutrient loading from the surrounding catchment areas usually contributes to the trophic deterioration of lake waters, combined with an increase in the intensity of phytoplankton blooms, which in turn leads to a deterioration in water quality, hypolimnetic oxygen deficits, and changes in species biodiversity. The circulation of nutrients within the lake basin (subject to change in the different seasons) and the inflow of nutrients from direct and indirect catchments determine the condition of the lake waters [Chapra *et al.* 2012; Kaiserli *et al.* 2002; Seip 1994; Taylor, Lean 2018; Torres *et al.* 2014].

The lakes most exposed to rapid eutrophication and degradation processes caused by anthropopressure are those situated next to urban areas. Although there are many reports on the impact of anthropopressure on lake waters [e.g. Jekatierynczuk-Rudczyk *et al.* 2014; Grochowska *et al.* 2019; Grochowska, Tandyrak 2021; Tandyrak 2017], small lakes are usually omitted by researchers in their analyses. Their hydrochemical conditions are interesting due to the high dynamics of water mixing and thus high dynamics of biochemical processes. In addition, these lakes, despite their small size, are important for local communities as sites of recreation and sources of food; the fish caught may be an important part of the diet for at least some of the local residents [Nędzarek *et al.* 2021]. An example of a lake with a small area (from 5.57 to 8 ha, depending on the citation source), for which both the dynamics of water masses and hydrochemical conditions are known very well, situated in the urban space (the city of Olsztyn in the Warmian-Masurian Voivodeship) is the Starodworskie Lake. However, it is a unique facility in the world due to the well-documented, several-decades-long history of systematic limnology research [Tandyrak 2017]. Small lakes situated in the urban space in the area of the West Pomeranian Voivodeship have not been subject to systematic limnological studies over many years [Nędzarek *et al.* 2021].

Taking the above into account, the study investigated the variability of selected hydrochemical parameters during one limnological season in the waters of three lakes of different surface areas: Starzyca, Maszewskie and Nowogardzkie, located in the urban space. In order to achieve the assumed objective, the variability of selected hydrochemical parameters in the surface and bottom layers was investigated.

MATERIALS AND METHODS

STUDY AREA

The three lakes included in this study, i.e. Maszewskie, Starzyca and Nowogardzkie, are located in the West Pomeranian Voivodeship, in north-western Poland (Fig. 1). Detailed morphometric and drainage data are presented in Table 1 and Table 2, respectively.

Lake Maszewskie (53°30'40" N, 15°03'04" E) has an area of 13.2 ha and an average depth of 2 m (Tab. 1) and is located in a large, elongated depression with a meridian course. The Leśnica River flows into the lake from the north. The town of Maszewo, with an area of 5.56 km^2 and a population of 3073 as of 2006, lies on the southern part of the lake, while the northern part is surrounded by alder and oak forests. Arable land and forests constitute more than 30% of its catchment area (39 and 32%, respectively) (Tab. 2). Lake Maszewskie is classified as a eutrophic lake with frequent water blooms in spring and summer [Brysiewicz 2018]. The risk of pollution is raised due to villages situated in the direct catchment and rainwater discharged from a nearby road Maszewo–Goleniów which may contain the fertilisers, illegal sewage and salt used on the roads in winter [Brysiewicz 2018]. Intensive fish farming (especially carp) may be an additional polluting factor from 7 fish farms (ponds with a combined surface area of 39.65 ha) connected to the Leśnica River which flows into the lake. In the south of the lake, in the town of Maszewo, there is a recreational beach.

Lake Starzyca (also known as Starzyc or Chociwel Lake) (53°27'39" N, 15°20'43" E) has an area of 59.2 ha and an average depth of 2.6 m and is a flow-through lake (the Krąpiel River flows through the lake). It is kidney-shaped and with a mostly undeveloped shoreline. It is located on the eastern side of

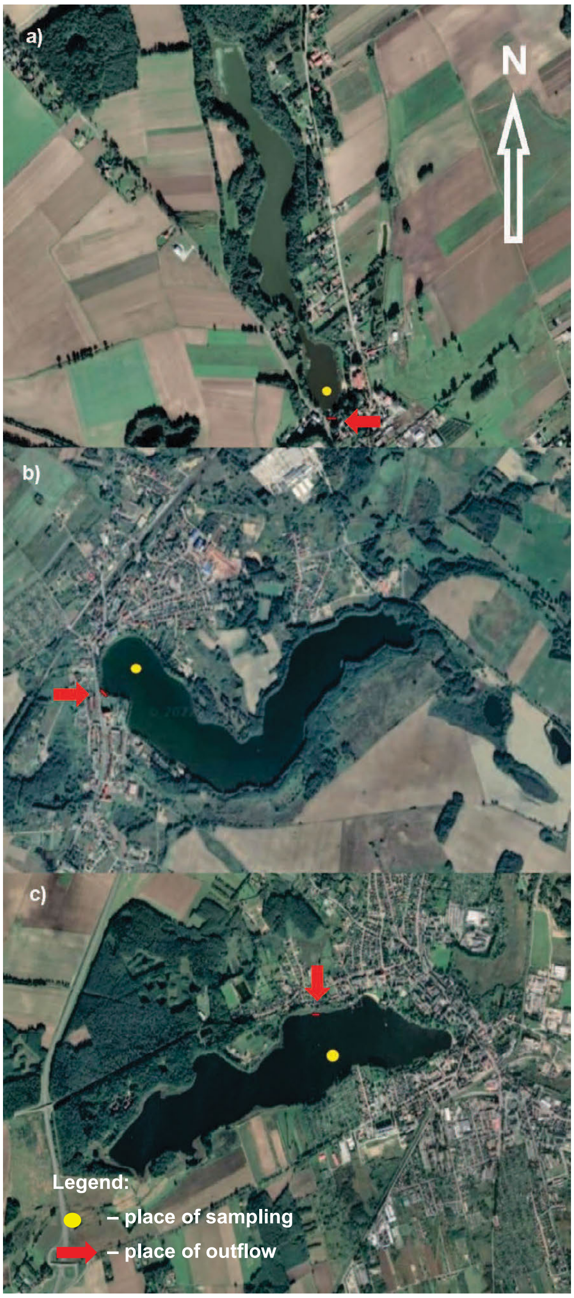

Fig. 1. Study area with marked places of sampling and outflows from the: a) Lake Maszewskie, b) Lake Starzyca, c) Lake Nowogardzkie; source: own elaboration

Table 1. Basic morphometric parameters of the studied lakes

Parameter	Lake		
	Maszewskie	Starzyca	Nowogardzkie
Area (ha)	13.2	59.2	98.3
Lake basin volume (10^3 m^3)	264.0	1575.8	5087.3
Maximum depth (m)	3.0	6.1	10.9
Mean depth (m)	2.0	2.6	5.2
Length (m)	1430	1960	2410
Width (m)	150	370.0	600
Length of shoreline (m)	3180	5175	5700

Source: own elaboration acc. to Jańczak [1996; 1997].

Table 2. Catchment structure of the studied lakes

Lake		Maszewskie	Starzyca	Nowogar-dzkie
Total catchment area (km^2)		2.32	1.75	6.33
Including	arable land (%)	39	49	51
	forests (%)	32	21	17
	urban buildings (%)	17	20	23
	fields (%)	12	10	9

Source: own study based on data from the State Water Management of Polish Waters, Szczecin.

Chociwel, a town of 3.67 km^2 and a population of 3167 as of 2016. Approximately 50% of the total catchment area of the lake is agricultural land (Tab. 2). It is classified as a eutrophic lake with high content of dissolved mineral salts and nutrients [Wesołowski *et al.* 2011; Wesołowski, Brysiewicz 2015]. Until 1997, domestic and industrial sewage was discharged directly into the lake due to the lack of an efficient sewage system and treatment plant. There is a designated recreational trail around the lake, with a recreational beach and tennis courts located on the southern shore. Rehabilitation of the lake using a wind-driven pulveriser aerator began in 2003 [Konieczny, Pieczyński 2006]. Investigations in 2005–2009 and 2008–2010 showed that the operation of the aerator on Lake Starzyca did not improve the oxygenation of bottom waters; the concentrations of ammonium and nitrate nitrogen (V) and dissolved oxygen near the aerator did not differ from points distant from the aerator. The documented improvements in water quality in the lake were due to the elimination of pollutants flowing into the lake [Wesołowski *et al.* 2011; Wesołowski, Brysiewicz 2015]. Those measurements in 2008 and 2010 showed greater dissolved oxygen content in the water and lower nitrate nitrogen (V) concentrations compared to 2005 [Wesołowski, Brysiewicz 2015].

Lake Nowogardzkie (also known as Lake Nowogardno) (53°40'04.0" N, 15°06'14" E) is the largest of the studied lakes with an area of 98.3 ha and an average depth of 5.9 m (Tab. 1). The lake is located in the centre of the town of Nowogard and is surrounded by a park and historic defensive walls that separate it from the town. The town of Nowogard covers 12.46 km^2 with a population of 16,745 as of 2006. Lake Nowogardzkie is a postglacial reservoir, formed on the plains of a ground moraine. The lake has an ellipsoidal shape and a poorly developed shoreline. There is a beach in the eastern part of the lake. Two small surface streams flow into the lake, while the Dąbrzyca River flows out of the lake. The lake's catchment area is 6.33 km^2 comprising mainly arable land (51%) and urbanised areas (23%) (Tab. 2). The main pollutants are biogens in waters flowing through drainage ditches from agricultural areas.

In 2009, the water quality of Lake Nowogardzkie was examined and its ecological status was assessed as moderate (class III) with a chemical status of "below good" [WIOŚ 2009]. In 2013, rehabilitation of Lake Nowogardzkie was initiated; in the summer months, five surface treatments to precipitate phosphorus compounds were performed over the entire lake using PIX®113 (aqueous solution of iron (III) sulphate (VI) – $Fe_2(SO_4)_3$). In September 2013, a wind-driven pulverising aerator was put into operation to systematically expand the high-oxygenation zone, the so-called "life zone". In October, the lake was stocked with pike (*Esox lucius* L.) to improve the food chain in the lake ecosystem [Podsiadłowski *et al.* 2018].

Based on the trophy indicators according to Carlson [1977], all lakes were classified as eutrophic [Tórz *et al.* 2020]. Resistance of the studied lakes to the influence of the catchment area on the basis of the method proposed by Bajkiewicz-Grabowska [2010] is as follows: Lake Maszewskie is a non-resistant lake, strongly exposed to the influence of the catchment area (category IV), Lake Starzyca shows low resistance to the influence of the catchment area (category III), and Lake Nowogardzkie has the average resistance to the impact from the catchment area (category II) [Tórz *et al.* 2020].

STUDY METHODS

The study was conducted from May 2018 to February 2019 (in May, July, November and February). Water samples were collected from the surface and bottom layers using a Ruttner type bathymeter (3 dm^3 capacity). Directly during water sampling, temperature and water pH were measured (Elmetron CP–103, Poland). In Lake Nowogardzkie, bottom water samples were taken at a depth of 8 m, in Lake Starzyca – 5.0 m, and in Lake Maszewskie – 3.8 m. All samples were collected in the deepest places in the reservoir (Fig. 1). In Lake Maszewskie, due to the possibility of damming the water at the outflow, the maximum depth of 4.1 m was recorded during the research, although the source materials indicate the maximum depth of the lake as 3.0 m [Jańczak 1997]. Water transparency was recorded using a 30 cm diameter Secchi disk. Hydrochemical indices were determined using standard methods as recommended by APHA [1999]. The dissolved oxygen content was determined in the collected water samples – mg $O_2 \cdot dm^{-3}$ (Winkler method), as well as the content of organic matter (through the chemical oxygen demand using the permanganate method – mg $O_2 \cdot dm^{-3}$). The content of orthophosphates (reacting dissolved phosphorus) and total phosphorus (after mineralisation in an acidic potassium persulfate) in the unsaturated samples was also determined, colourimetrically using the molybdenum method (ascorbic acid reducer, λ = 882 nm, mg $P \cdot dm^{-3}$). The concentrations of individual forms of mineral nitrogen were also determined colourimetrically using the following methods: nitrite form with sulfanilamide (λ = 554 nm, mg $N\text{-}NO_2 \cdot dm^{-3}$), ammonium form with indophenol blue (λ = 663 nm, mg $N\text{-}NH_4 \cdot dm^{-3}$) and nitrate after reduction for nitrites on a copper-cadmium column – mg $N\text{-}NO_3 \cdot dm^{-3}$. The amount of chlorophyll *a* was determined colourimetrically after acetone extraction (λ = 663 nm, µg of chlorophyll *a* per dm^3). A Hitachi U-2900 UV-VIS Double Beam Spectrophotometer was used for colourimetric methods. Iron (mg$\cdot$dm^{-3}) was determined using a Hitachi Polarized Zeeman Atomic Absorption Spectrometer ZA3000 Series. Iron was measured using flameless graphite furnace atomic absorption spectrometry (GFAAS). Palladium in 5% HNO_3 was used as a matrix modifier. Calibration curves for Fe were made using certified standard solutions (1000 ppm). All analyses were triplicated. The results were statistically analysed with Statistica 13.3 software using variance analysis (ANOVA, $p < 0.05$) and Tukey's post hoc test ($p < 0.05$) to determine statistically significant differences between the water quality indicators of the studied lakes.

RESULTS

SEASONAL VARIABILITY OF THE ANALYSED HYDROCHEMICAL PARAMETERS

The highest temperature was recorded in the surface layer of Lake Starzyca in spring (21.1°C), while the lowest (3.4°C) was recorded in winter in the surface waters of Lake Nowogardzkie (Fig. 2). The difference in water temperature between the surface zone and the bottom zone in spring and summer seasons were, respectively, 9.1 and 2.2°C (Lake Starzyca), 9.4 and 5.1°C (Lake Maszewskie), and 5.9 and 7.3°C (Lake Nowogardzkie). However, in autumn and winter no significant differences in water temperature between the surface and bottom layers were recorded (Fig. 2).

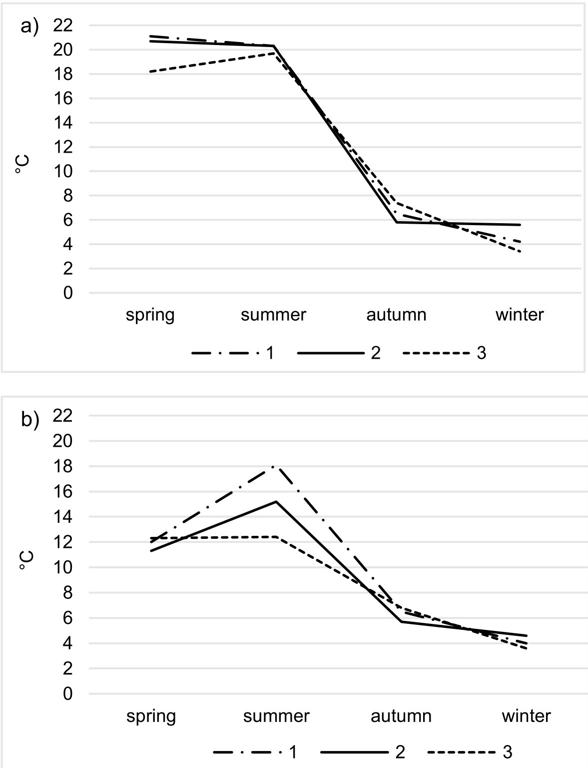

Fig. 2. Temperature variability of lakes during the year: a) in the surface layer, b) in the bottom layer; 1) Lake Starzyca, 2) Lake Maszewskie, 3) Lake Nowogardzkie; source: own study

Dissolved oxygen (DO) in the water differentiated the lakes and was characterised by high seasonal variability. Generally, higher values were recorded in Lake Nowogardzkie. In Starzyca and Nowogardzkie lakes, the highest DO values, both in the surface and bottom layers, were recorded in winter (Fig. 3). In Lake Maszewskie a similar oxygenation of the surface and bottom layers was observed in autumn. The spring and summer seasons were characterised by significant deoxygenation of bottom waters in all lakes. The difference in dissolved oxygen concentrations between the surface and bottom layers for these seasons was, respectively, 11.5 and 11.3 mg·dm^{-3} in Lake Starzyca, 16.9 and 8.1 mg·dm^{-3} in Lake Maszewskie, and 11.5 and 8.2 mg·dm^{-3} in Lake Nowogardzkie in spring (Fig. 3).

Water pH in all the studied lakes was slightly higher in spring and summer than in autumn and winter seasons, being highest in summer (Fig. 4). In Lake Nowogardzkie, the water pH

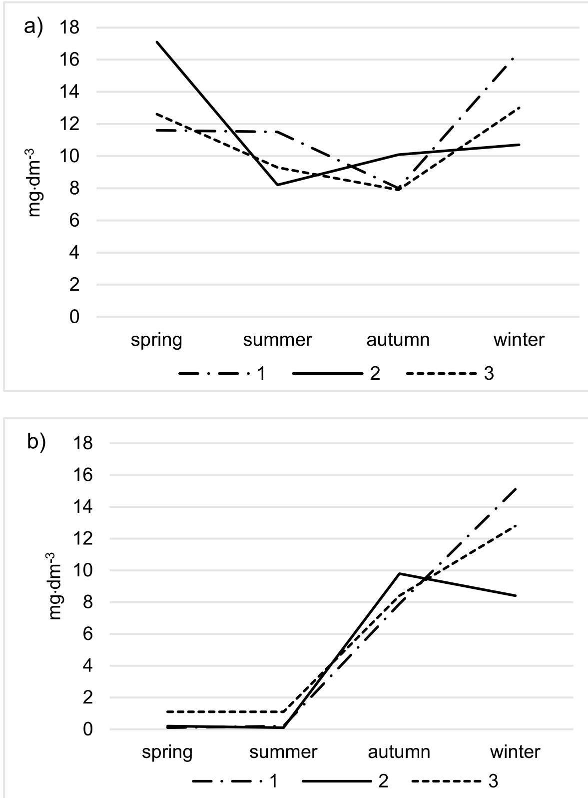

Fig. 3. Dissolved oxygen contents in lakes during the year: a) in the surface layer, b) in the bottom layer; 1) Lake Starzyca, 2) Lake Maszewskie, 3) Lake Nowogardzkie; source: own study

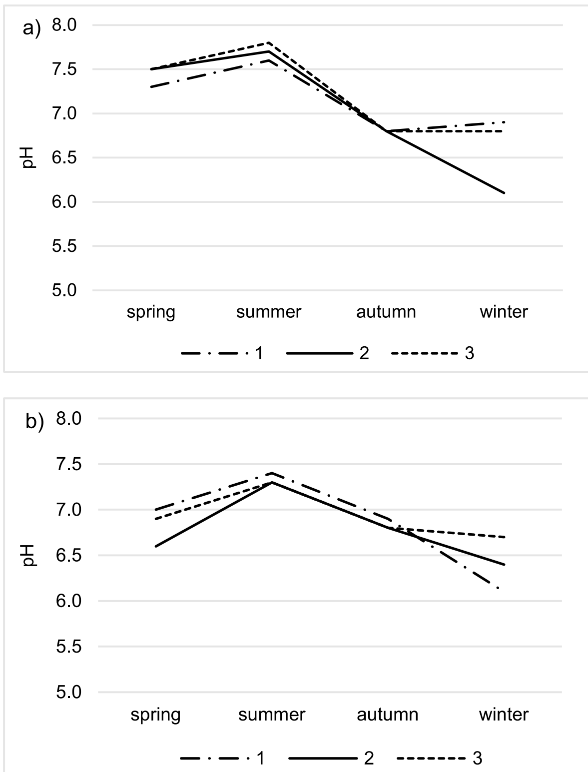

Fig. 4. Variability of pH in lakes during the year: a) in the surface layer, b) in the bottom layer; 1) Lake Starzyca, 2) Lake Maszewskie, 3) Lake Nowogardzkie; source: own study

was higher in the surface layer than in the bottom layer in all seasons. In Lake Starzyca in autumn, the water pH was slightly lower in the surface layer than in the bottom layer. In Lake Maszewskie a lower water pH of the surface layer was observed in winter (Fig. 4).

The seasonal variability of total reactive phosphorus (TRP) concentrations differed between the surface and bottom layers. In the surface layer of the lakes, similar TRP concentrations (ranging from 0.020 to 0.031 mg·dm^{-3}) were recorded in spring. In summer, TRP concentrations decreased slightly in this layer in Starzyca and Maszewskie lakes, while in Lake Nowogardzkie – slightly increased. In autumn, TRP concentrations increased significantly in the surface layer (to a maximum of 0.159 mg·dm^{-3} in Lake Nowogardzkie) and decreased to 0.095 mg·dm^{-3} in the winter (Fig. 5a). The lowest TRP concentrations were observed in the spring in the bottom waters of Starzyca and Nowogardzkie lakes, and the highest concentrations – in the bottom waters of Lake Maszewskie. In the summer, TRP concentrations increased in the bottom waters of Starzyca and Nowogardzkie lakes, with a maximum TRP concentration of 0.565 mg·dm^{-3} in Lake Nowogardzkie, while in the waters of Lake Maszewskie TRP concentrations decreased compared to the spring. In subsequent seasons, TRP concentrations were lower in the bottom waters of all lakes (Fig. 5b).

The seasonal variability of total phosphorus (TP) concentrations had yet another character. The highest TP concentrations were found in the surface layer in winter, while in the bottom layer the highest TP concentrations were recorded in summer (Fig. 6). In the surface layer of Starzyca and Maszewskie lakes an increase in TP concentrations was observed in the summer season, then TP concentrations decreased in autumn, and

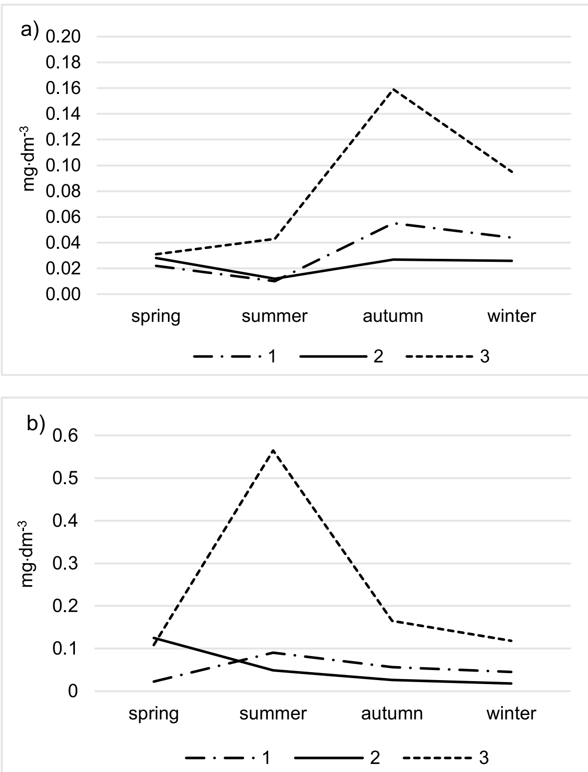

Fig. 5. Variability of total reactive phosphorus (TRP) concentrations in lakes during the year: a) in the surface layer, b) in the bottom layer; 1) Lake Starzyca, 2) Lake Maszewskie, 3) Lake Nowogardzkie; source: own study

increased to the maximum concentrations in the winter season. In Lake Nowogardzkie, TP in the surface layer showed an increasing trend from spring to winter (Fig. 6a). In the bottom waters of all the lakes, TP concentrations reached a maximum in the summer, then decreased in the autumn and increased in winter (Fig. 6b).

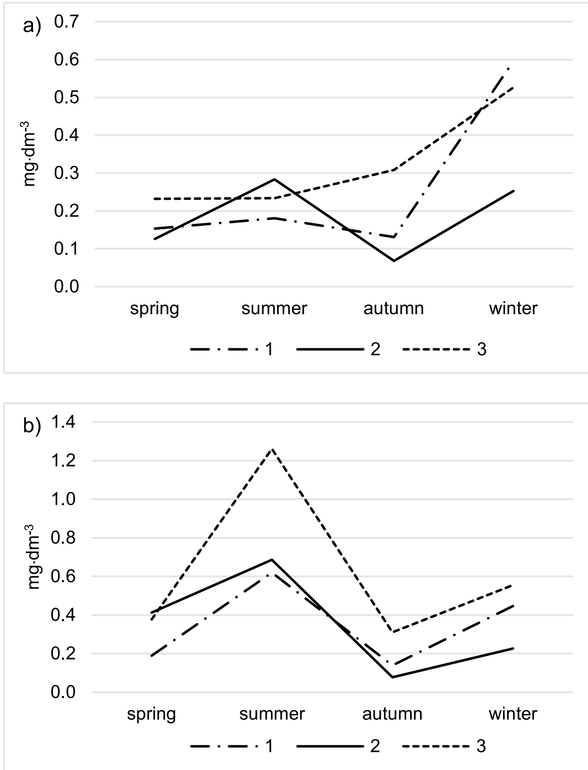

Fig. 6. Variability of total phosphorus (TP) concentrations in lakes during the year: a) in the surface layer, b) in the bottom layer; 1) Lake Starzyca, 2) Lake Maszewskie, 3) Lake Nowogardzkie; source: own study

In the surface layer, the lowest concentrations of nitrate nitrogen (III) (Fig. 7) were observed in Starzyca and Nowogardzkie lakes, while high concentrations were found in Lake Maszewskie, decreasing in summer (Fig. 7a). In autumn there was an increase in nitrite nitrogen concentrations (NO_2-N), and in winter a further increase occurred in Lake Maszewskie, while in Starzyca and Nowogardzkie lakes the concentrations decreased (Fig. 7a). In the bottom waters of Starzyca and Nowogardzkie lakes, nitrate nitrogen (III) concentrations showed insignificant seasonal variability (Fig. 7b). In the bottom waters of Lake Maszewskie the maximum NO_2-N concentration (0.158 mg·dm^{-3}) was recorded in spring, then in the summer the lowest value was recorded, and in subsequent seasons there was a slow increase in its concentration (Fig. 7b).

In both the surface and bottom waters of Lake Maszewskie, the highest concentrations of nitrate nitrogen (V) were recorded in the spring (Fig. 8). In the surface waters of Maszewskie and Nowogardzkie lakes a decrease in NO_3-N concentrations to minimum values was recorded in the summer, while in the waters of Lake Starzyca an increase in the concentration of this parameter was noted. An increase in nitrate nitrogen (V) concentrations was observed in the surface waters of the lakes in the autumn and winter seasons (Fig. 8a). A slight increase in

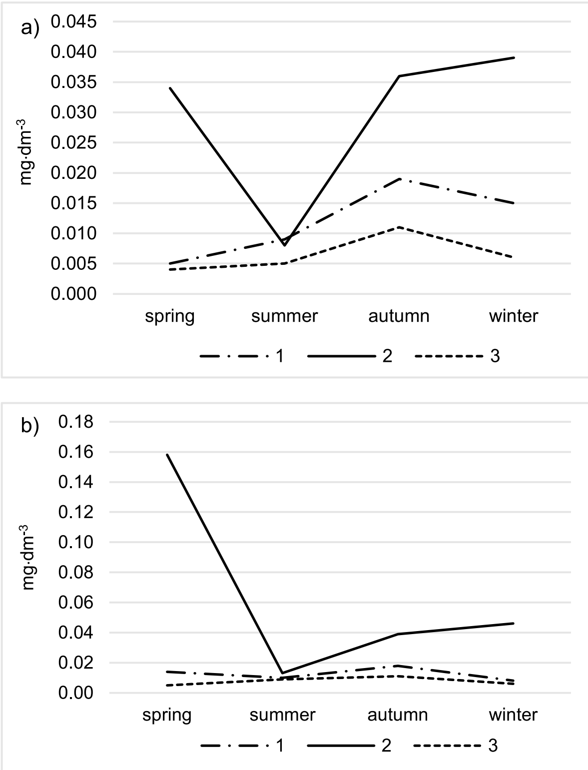

Fig. 7. Variability of nitrate nitrogen (III) concentrations in lakes during the year: a) in the surface layer, b) in the bottom layer; 1) Lake Starzyca, 2) Lake Maszewskie, 3) Lake Nowogardzkie; source: own study

nitrate nitrogen concentrations was observed in the bottom waters of Starzyca and Nowogardzkie lakes during the summer season, while a considerable decrease was observed in the bottom waters of Lake Maszewskie. In autumn all the lakes showed a decrease in NO_3-N concentrations, and in winter – an increase (Fig. 8b).

The seasonal variability of ammonium nitrogen (NH_4-N) concentration in the surface layer was as follows: in all the lakes studied there was a decrease in the summer, an increase in the autumn, a decrease in the winter in the waters of Starzyca and Nowogardzkie lakes and a further increase in Lake Maszewskie to a maximum of 1.814 mg·dm^{-3} (Fig. 9a). In the bottom waters of Starzyca and Nowogardzkie lakes an increase in ammonium nitrogen concentrations was observed in summer, in Lake Nowogardzkie the concentrations decreased in the autumn season, while in Lake Starzyca – increased. In both lakes, a decrease in ammonium nitrogen concentrations was observed in the winter season. In the bottom waters of Lake Maszewskie, a decrease in ammonium nitrogen concentrations was observed from spring to autumn, while in winter there was a sharp increase in the concentration of this parameter to 1.808 mg·dm^{-3} (Fig. 9b).

The surface and bottom waters of Starzyca and Nowogardzkie lakes showed insignificant annual fluctuations in organic matter (Fig. 10); however, the surface and bottom waters of Lake Maszewskie were characterised by the highest organic matter in all seasons. Seasonal variability in organic matter in the surface and bottom waters of this lake was similar. Lower organic matter was more observed in summer than in spring, while the highest

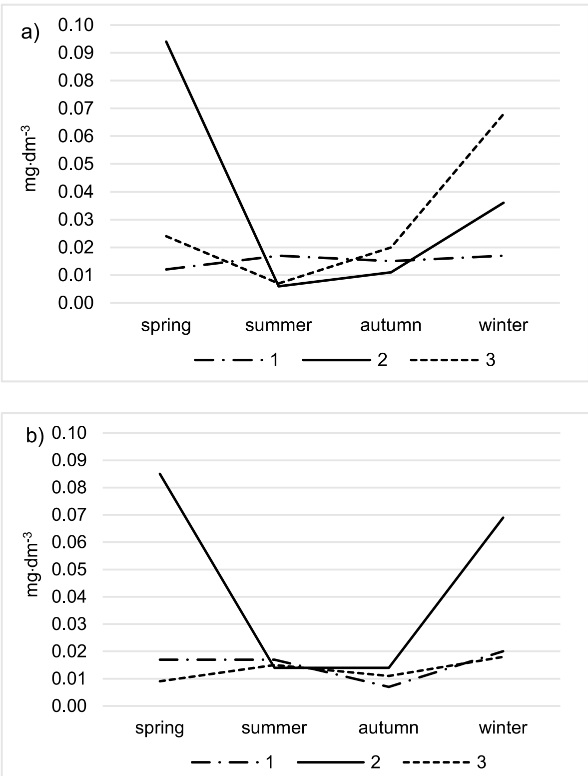

Fig. 8. Variability of nitrate nitrogen (V) concentrations in lakes during the year: a) in the surface layer, b) in the bottom layer; 1) Lake Starzyca, 2) Lake Maszewskie, 3) Lake Nowogardzkie; source: own study

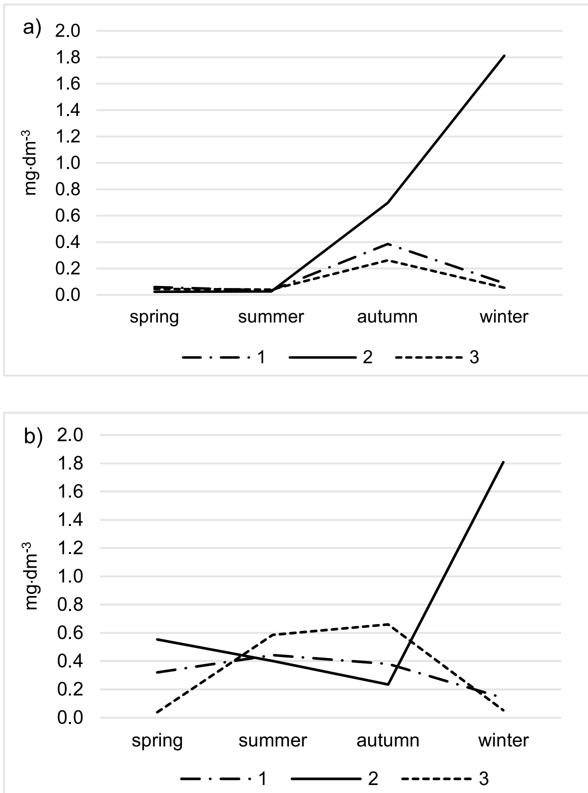

Fig. 9. Variability of ammonium nitrogen concentrations in lakes during the year: a) in the surface layer, b) in the bottom layer; 1) Lake Starzyca, 2) Lake Maszewskie, 3) Lake Nowogardzkie; source: own study

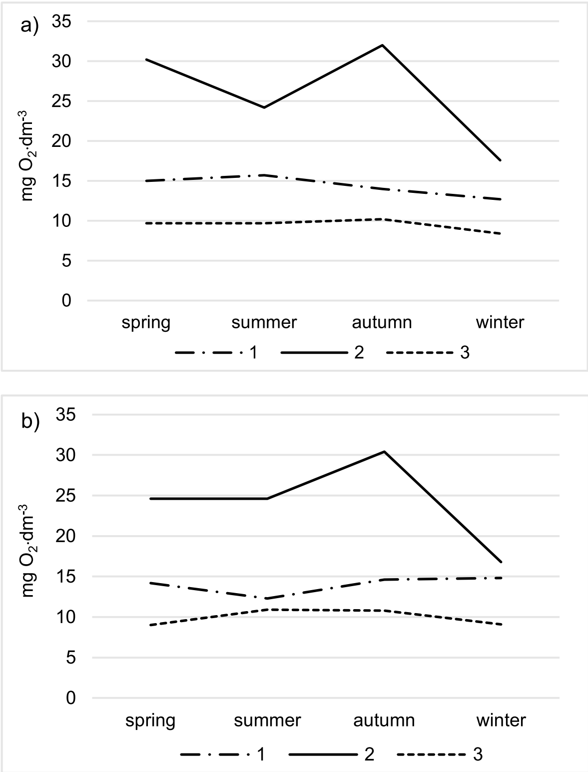

Fig. 10. Organic matter load (COD) in lakes during the year: a) in the surface layer, b) in the bottom layer; 1) Lake Starzyca, 2) Lake Maszewskie, 3) Lake Nowogardzkie; source: own study

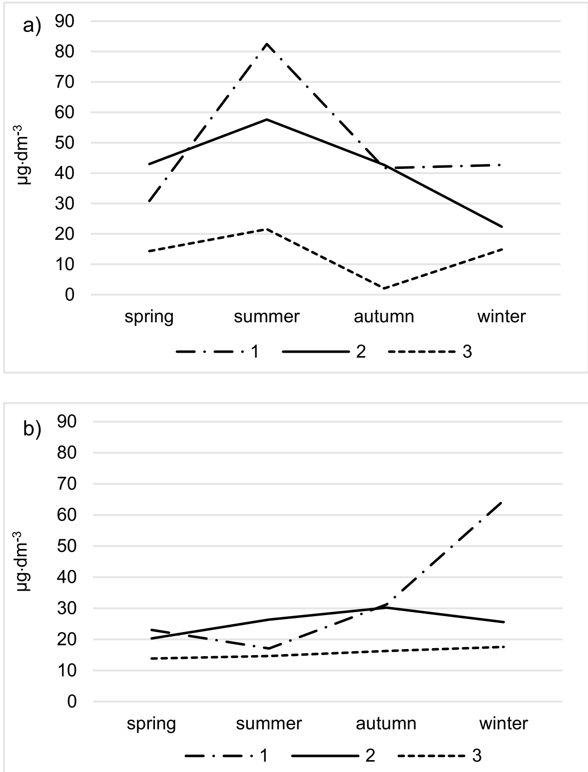

Fig. 11. Variability of chlorophyll *a* concentrations in lakes during the year: a) in the surface layer, b) in the bottom layer; 1) Lake Starzyca, 2) Lake Maszewskie, 3) Lake Nowogardzkie; source: own study

organic matter was found in autumn, decreasing in winter (Fig. 10).

The highest concentrations of chlorophyll *a* in the surface waters of the studied lakes were recorded during the summer season. In autumn, chlorophyll *a* concentrations decreased, while in winter in the surface waters of Lake Starzyca they remained at similar levels as in the autumn season, in the waters of Lake Maszewskie the concentrations decreased compared to the autumn season, while in the waters of Lake Nowogardzkie they increased (Fig. 11a). In the bottom waters of Maszewskie and Nowogardzkie lakes, chlorophyll *a* concentrations remained at a lower level than in the surface waters, changing slightly during the annual cycle (Fig. 11b). In the waters of Lake Starzyca, an increase in chlorophyll *a* concentrations was observed from summer to winter – 64.6 μg·dm^{-3} was recorded (Fig. 11b).

Iron content in the waters of the studied lakes showed seasonal variability. Clearly higher iron concentrations were recorded in the bottom waters (Fig. 12). In the surface waters of Lake Starzyca, a higher iron concentration was observed in the summer season, followed by a decrease in autumn and a slight increase in the winter season. In the waters of Lake Nowogardzkie, a slight downward trend in iron content was observed from spring to winter. The variability of iron concentrations in the surface waters of Lake Maszewskie was even more different. From spring to autumn, iron concentrations remained at similar levels, and in winter there was a sharp, almost threefold increase in concentrations to 0.279 mg·dm^{-3} (Fig. 12a). In the bottom waters of all the lakes, an increase in iron concentrations was observed in summer with the highest recorded concentration of 0.301 mg·dm^{-3} in Lake Starzyca. On the other hand, in autumn there was a decrease in iron content, with a significant decrease in

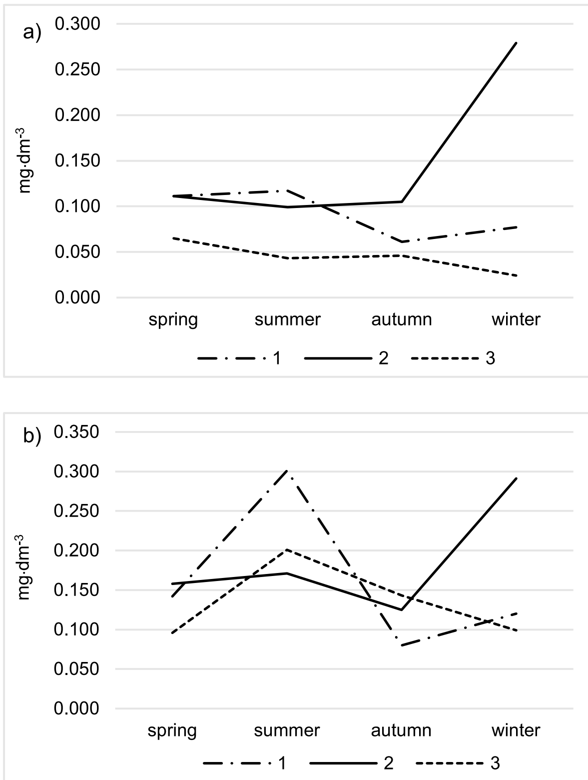

Fig. 12. Variability of iron concentrations in lakes during the year: a) in the surface layer, b) in the bottom layer; 1) Lake Starzyca, 2) Lake Maszewskie, 3) Lake Nowogardzkie; source: own study

iron concentration to 0.080 mg·dm^{-3} in Lake Starzyca (Fig. 12b). During the winter there was an increase in concentrations in the bottom waters of lakes Starzyca and Maszewskie, with a significant increase of 0.291 mg·dm^{-3} in Lake Maszewskie. In turn, a further decrease in iron content was observed in Lake Nowogardzkie (Fig. 12b).

Lake Nowogardzkie was characterised by the highest Secchi disc visibility during the tests with the highest visibility recorded in the autumn season, amounting to 2.0 m, and the lowest visibility in the summer season, amounting to 1.2 m. In turn, the lowest visibility of the Secchi disc was observed in the Lake Maszewskie, in summer it was 0.9 m, and in winter 1.3 m. In Lake Starzyca, the lowest visibility was also observed in the summer season – 1.0 m, and the highest, in the spring and autumn seasons – 1.5 m (Fig. 13).

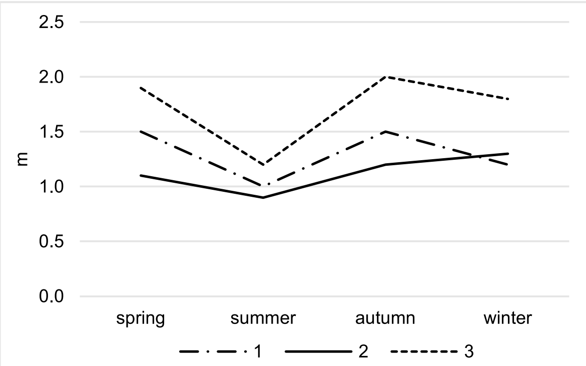

Fig. 13. Secchi disc visibility in lakes during the year: 1) Lake Starzyca, 2) Lake Maszewskie, 3) Lake Nowogardzkie; source: own study

AVERAGE VALUES OBTAINED FROM THE RESULTS OF MEASUREMENTS IN FOUR LIMNOLOGICAL SEASONS IN THE SURFACE WATERS OF THE ANALYSED LAKES

The average value of the Secchi disc visibility obtained from the results of measurements in four limnological seasons is presented in Fig. 14. The study showed that the highest mean Secchi disc visibility is in Lake Nowogardzkie and the lowest in Lake Maszewskie (Fig. 13). The surface waters of the studied lakes were characterised by similar thermal, oxygen and pH conditions (no statistically significant differences, $p > 0.05$) (Tab. 3). The mean water temperature in the studied lakes ranged between 12.1 and 13.1°C. The mean dissolved oxygen content in water was 10.7 mg·dm^{-3} in Lake Nowogardzkie, 11.5 mg·dm^{-3} in Lake Maszewskie, and 11.9 mg·dm^{-3} in Lake Starzyca (Tab. 3).

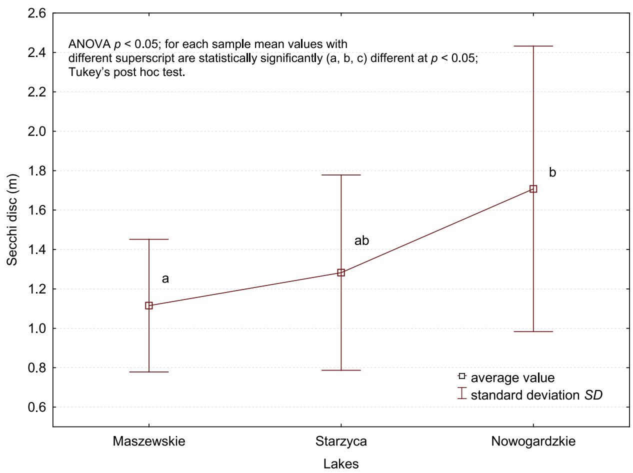

Fig. 14. Annual mean values of Secchi disc visibility of the researched lakes; source: own study

Maszewskie, Starzyca, and Nowogardzkie lakes did not differ significantly ($p > 0.05$) in mean TP, NO_3-N, and NH_4-N levels. Significant differences ($p < 0.05$) were noted for TRP and N-NO_2^-. In the waters of Lake Nowogardzkie, the concentration of TPR was more than three times higher (0.082 mg·dm^{-3}) than in Lake Maszewskie (0.023 mg·dm^{-3}) (Tab. 4). The opposite was true for NO_2-N concentration – in Lake Nowogardzkie the mean nitrite was 4 times lower at 0.007 mg·dm^{-3} than in Lake Maszewskie (0.029 mg·dm^{-3}) (Tab. 3).

Significant differences ($p < 0.05$) were also noted for chlorophyll *a* concentrations and organic matter (COD_{Mn}) with the lowest mean values recorded in Lake Nowogardzkie. The highest chlorophyll *a* values were recorded for Lake Starzyca (49.5 mg·m^{-3}), and the highest COD_{Mn} in the waters of Lake Maszewskie (26.6 mgO_2·dm^{-3}) (Tab. 3).

Iron concentration in surface waters reached the highest levels in Lake Maszewskie where it was over three times higher than in Lake Nowogardzkie (statistically significant difference, $p < 0.05$) (Tab. 3).

AVERAGE VALUES OBTAINED FROM THE RESULTS OF MEASUREMENTS IN FOUR LIMNOLOGICAL SEASONS IN THE BOTTOM WATERS OF THE ANALYSED LAKES

The bottom layer waters of the three studied lakes had similar thermal, oxygen and pH conditions (no statistically significant differences) (Tab. 4).

Considering biogenic indicators, the waters of the studied lakes did not differ significantly in mean TP, NO_3-N or NH_4-N levels. The concentration of TPR in Lake Nowogardzkie was more than double (0.125 mg·dm^{-3}) than in Lake Maszewskie (0.055 mg·dm^{-3}) (Tab. 4). However, the mean nitrite value for Lake Maszewskie was eight times higher (0.064 mg·dm^{-3}) than in Lake Nowogardzkie (0.008 mg·dm^{-3}) (Tab. 4).

Similarly to the surface waters, statistically significant differences were noted for chlorophyll *a* concentrations and organic matter (COD) in the bottom layers with the lowest average annual values in Lake Nowogardzkie (Tab. 4).

The iron levels in the bottom waters of the studied lakes were more than two times higher than in the surface waters – 0.149 mg·dm^{-3} in Lake Maszewskie, 0.161 mg·dm^{-3} in Lake Starzyca, and 0.135 mg·dm^{-3} in Lake Nowogardzkie (Tab. 4). The bottom waters of the studied lakes did not significantly differ statistically in terms of Fe levels (Tab. 4).

DISCUSSION

The role and location of lakes in the hydrosphere are shaped by environmental conditions. The ageing of lakes depends on climatic conditions in conjunction with the geological structure of the catchment and the morphology of the reservoir, as well as

Table 3. Comparison of the average annual values of the researched parameters of surface water in the following lakes: Maszewskie, Starzyca and Nowogardzkie

Lake	Parameter											
	T (°C)	pH	DO	COD_{Mn}	Fe (ppm)	TSS	TP	TRP	NO_2-N	NO_3-N	NH_4-N	Chlorophyll *a* ($mg \cdot m^{-3}$)
			mg $O_2 \cdot dm^{-3}$			$mg \cdot dm^{-3}$						
Maszewskie	12.7 ±7.7^{a}	7.0 ±0.7^{a}	11.5 ±3.9^{a}	26.0 ±6.5^{b}	0.149 ±0.087^{b}	87.3 ±28.5^{b}	0.060 ±0.033^{a}	0.023 ±0.008^{a}	0.029 ±0.014^{b}	0.037 ±0.040^{a}	0.641 ±0.844^{a}	41.5 ±14.5^{b}
Starzyca	13.1 ±8.3^{a}	7.2 ±0.4^{a}	11.9 ±3.5^{a}	14.4 ±1.3^{ab}	0.092 ±0.019^{b}	90.0 ±27.5^{b}	0.086 ±0.072^{a}	0.033 ±0.020^{ab}	0.012 ±0.006^{ab}	0.015 ±0.002^{a}	0.142 ±0.164^{a}	49.5 ±22.7^{b}
Nowogardzkie	12.1 ±7.4^{a}	7.2 ±0.5^{a}	10.7 ±2.5^{a}	9.5 ±0.8^{a}	0.045 ±0.017^{a}	42.5 ±23.9^{a}	0.106 ±0.045^{a}	0.082 ±0.058^{b}	0.007 ±0.003^{a}	0.030 ±0.027^{a}	0.101 ±0.107^{a}	17.5 ±3.1^{a}

Explanations: TSS = total suspended solids, DO = dissolved oxygen, COD_{Mn} = chemical oxygen demand, TP = total phosphorus, TRP = total reactive phosphorus, for each sample mean values in rows marked with different superscript (a, b, c) are statistically significantly different at $p < 0.05$.
Source: own study.

Table 4. Comparison of the average annual values of the researched parameters of bottom water in the following lakes: Maszewskie, Starzyca and Nowogardzkie

Lake	Parameter											
	T (°C)	pH	DO	COD_{Mn}	Fe (ppm)	TSS	TP	TRP	NO_2-N	NO_3-N	NH_4-N	Chlorophyll *a* ($mg \cdot m^{-3}$)
			mg $O_2 \cdot dm^{-3}$			$mg \cdot dm^{-3}$						
Maszewskie	9.2 ±5.0^{a}	6.8 ±0.4^{a}	4.6 ±5.2^{a}	24.1 ±5.6^{b}	0.186 ±0.072^{a}	113.5 ±57.3^{b}	0.114 ±0.086^{a}	0.055 ±0.049^{a}	0.064 ±0.064^{b}	0.046 ±0.037^{a}	0.750 ±0.718^{a}	25.6 ±4.1^{b}
Starzyca	10.2 ±6.3^{a}	6.9 ±0.5^{a}	5.8 ±7.2^{a}	14.0 ±1.1^{ab}	0.161 ±0.097^{a}	115.3 ±52.7^{b}	0.114 ±0.076^{a}	0.053 ±0.028^{a}	0.013 ±0.004^{ab}	0.015 ±0.006^{a}	0.321 ±0.131^{a}	34.0 ±21.2^{b}
Nowogardzkie	8.8 ±4.3^{a}	6.9 ±0.3^{a}	5.9 ±5.8^{a}	10.0 ±1.0^{a}	0.135 ±0.049^{a}	52.8 ±28.7^{a}	0.139 ±0.035^{a}	0.125 ±0.027^{b}	0.008 ±0.003^{a}	0.013 ±0.004^{a}	0.334 ±0.335^{a}	11.4 ±1.7^{a}

Explanations: TSS, DO, COD_{Mn}, TP, TRP, (a, b, c) in superscript as in Tab. 3.
Source: own study.

the vegetation cover and human activity [Jekatierynczuk-Rudczyk *et al.* 2014].

Lakes located in a temperate climate show seasonal variability in surface water temperatures, which produces a rhythmic occurrence in mechanisms and processes. The thermal conditions of lake waters are shaped by meteorological factors (such as the wind) that depend on the morphological features of the area of the lake. Water temperature affects the rate of matter circulation in reservoirs (determines the intensity of water masses mixing) hence it is an important parameter in assessing the trophic formation of individual reservoirs [Skowron 2011; Choiński *et al.* 2014].

The difference in water temperature between the surface zone and the bottom zone in the studied lakes could indicate their polymictic character. The high dynamics of water masses also caused temperature equalisation between the surface and bottom layers of the studied lakes in the autumn and winter seasons (Fig. 2). The occurring thermal systems indicated a high susceptibility of the studied lakes to climatic factors. Favourable conditions for the intensive mixing of waters in these lakes resulted primarily from their shallow maximum depths [Skowron 2011; Tandyrak 2017].

Oxygen conditions, being the main indicator of the intensity of metabolism in the lakes, are an important element in the assessment of their trophic levels. Oxygen systems determine the nature, extent and intensity of the basic processes forming the biocenosis, mainly in the bottom waters, and change depending on the seasons or the extent of vertical mixing of the waters [Wetzel 2001]. The oxygen conditions in the lakes studied, characterised by the deoxygenation of waters in the bottom water layer in spring and summer seasons and simultaneously marked over-oxygenation in the surface water layer (in Lake Maszewskie even reaching 188.5% in spring), indicate that the eutrophication process is advanced. The advanced trophic level is also indicated by oxygen deficits observed during the autumn mixing in the whole mass of the examined waters (in Lake Starzyca oxygenation was at the level of 64.5%, in Lake Maszewskie 79.2%, and in Lake Nowogardzkie 66.5%). The eutrophic nature of the waters of these lakes was also demonstrated in the study by Tórz *et al.* [2020], who assessed their trophic status according to Carlson [1977]. This analysis showed the definitely eutrophic character of their waters, and according to other trophic indices, Starzyca and Maszewskie lakes are even eutrophic-hypertrophic lakes [Tórz *et al.* 2020]. The high mean annual oxygen content recorded in Lakes Starzyca and Nowogardzkie may be partly due to the operation of wind-driven pulverising aerators [Wesołowski *et al.* 2011; Wesołowski, Brysiewicz 2015]. The operation of a pulverising aerator sucks deoxygenated water from the bottom zone then pulverises it, allowing for prominent gas diffusion, and discharges the oxygenated water into the surface [Podsiadłowski *et al.* 2018].

In eutrophic lakes, "internal loading" is a significant source of nutrient supply to surface waters. The formation of summer stratification (thermal and aerobic) contributes to the periodic accumulation of nutrients in the interstitial layer and ultimately in bottom sediments [Noe *et al.* 2001]. During the whole research cycle, during the individual seasons in the bottom layer of the studied lakes elevated concentrations of the analysed phosphorus forms were observed in comparison to the surface layer (Figs. 5, 6). In the autumn and winter seasons, good oxygen conditions found in the bottom layers of the studied lakes could have contributed to the deposition of nutrients, especially phosphorus, in bottom sediments. In turn, in the summer season, deoxidation of the waters of the bottom layer occurred, most probably due to the consumption of oxygen for the biochemical decomposition of indigenous organic matter. Such oxygen conditions favoured the "internal loading" of the waters of the tested lakes with nutrients, which was confirmed by the increase in TPR concentrations in the waters of the bottom layer, while in these waters of Lake Nowogardzkie, the increase in TPR concentrations in the summer season was exceptionally rapid (Fig. 5). It is these two processes, on the one hand, the accumulation of nutrients in bottom sediments (under good oxygen conditions), and on the other hand, the release of nutrients into the water (under unfavourable oxygen conditions), that may have shaped the higher load of phosphorus compounds in the bottom waters of the studied lakes over the entire study cycle [Tórz, Nędzarek 2009].

Organic matter in the studied lakes is of both allochthonous and autochthonous origin. The allochthonous substances come primarily from surface runoff from the catchment area of these lakes, such as from urban and farming areas, and largely indicate anthropogenic pressure. The significant amount of organic matter (autochthonous and allochthonous) present in the waters of the studied lakes intensifies the eutrophication [Kortelainen 1993; Nędzarek *et al.* 2007]. The obtained mean annual values of total suspended solids in the waters of the studied lakes indicate that it is over two times higher in lakes Starzyca and Maszewskie. In the case of Lake Maszewskie, in addition to inflow from the catchment, this may also be due to the fact that the Leśnica River, where fish farming is carried out, inflows into this water body. An increased amount of total suspended solids in the water is dangerous, especially during the spawning season of fish and during their embryonic development [Bonisławska *et al.* 2011; Schubel *et al.* 1974].

The inanimate matter is a very important factor in the nutrient cycle in lake waters. Dissolved forms of phosphorus and nitrogen can be adsorbed by small particles of suspended matter, the sediment of which forms bottom sediments. Sediments generally represent both the largest sink and the largest source of phosphorus and nitrogen [Baldwin *et al.* 1996]. Therefore, information on sediment phosphorus speciation is important in understanding the aquatic biogeochemistry of phosphorus. However, like soils, sediments typically consist of a complex mixture of clay, silt, sand, organic matter, various minerals, micro- and macro-organisms, water, and therefore present a potentially difficult medium for studying phosphorus speciation. The cycling of phosphorus in many aquatic ecosystems is closely associated with the iron cycle [Mitchell, Baldwin 1998; 2005]. Phosphate binds strongly to ferric oxides. Under anaerobic conditions, ferric oxides can be reduced directly by iron-reducing bacteria. Phosphorus associated with the iron surface is released into solution, so the bacterially mediated reductive dissolution of phosphorus is potentially an important process in the biogeochemical cycling of phosphorus. Baldwin *et al.* [1996] showed that organic phosphorus compounds can also bind to iron minerals, and more importantly that the mineral surface facilitates the hydrolysis of the organic phosphorus compound. Under oxic conditions, the resultant free phosphate ion irreversibly binds to the mineral surface. However, microbially mediated reductive dissolution of the mineral surface under anaerobic conditions presents a pathway for recycling the phosphate group. In the studied lakes the reactive phosphorus and iron concentrations showed a similar tendency of variability except for the Lake Maszewskie (Figs. 5, 12). In the summer in the deoxygenated bottom layer of the studied lakes, there was a significant increase in both TRP and iron concentrations, which indicates that in this period also "internal loading" took place (Figs. 4, 5, 12). Analysing the relationships between phosphorus and iron concentrations in the lake waters (high total and reactive phosphorus and iron concentrations in the bottom layer of the lakes in summer and much lower in autumn), it can be concluded that the iron (depending on the oxidation level) could be responsible, on one hand, for phosphorus deposition to the bottom sediments (under favourable oxygen conditions) and, on the other hand, for phosphorus release from the bottom sediments (under unfavourable oxygen conditions) (Figs. 5, 6, 12). Similar relationships were observed by Tórz and Nędzarek [2009], analysing the changes in nitrogen and phosphorus in the waters of Lake Żeglica during the annual cycle.

Nitrification and denitrification processes are also very important processes involved in the dynamics of nitrogen transformations in surface waters. Aerobic conditions play a key role in the transformation of nitrogen compounds. Oxidation of ammonia to nitrates (III) and nitrates (V) depends on the presence of oxygen. In aerobic conditions, ammonium nitrogen is first oxidised by nitrifying bacteria into nitrates (III), followed by nitrates (V), in a well-known nitrification process, which contributes to oxygen consumption in the water [Eck *et al.* 2019; Shoda, Ishikawa 2014]. In the first stage, the process is carried out by bacteria capable of oxidising ammonium nitrogen (*Nitrosomonas*, *Nitrosococcus*, *Nitrospira*, *Nitrosovibrio*). The next stage is conducted by bacteria oxidising nitrate (III) nitrogen (*Nitrobacter*, *Nitrococcus, Nitrospina*). The efficiency of the nitrification process depends on the pH of the water. It is assumed that an optimal pH for the nitrification process is between 7.5 and 8.0. It should also be remembered that plants absorb mineral forms of nitrogen (nitrate (V) and ammonium nitrogen) and this absorption depends on, e.g., the presence of carbon dioxide in the water [Wongkiew *et al.* 2017]. In the waters of the studied lakes, activity in nitrification was observed in the autumn and winter seasons (Figs. 3, 7, 8). In these seasons, good oxygen conditions and an increase in nitrate nitrogen (III) and nitrate nitrogen (V) were observed. In the winter season there was a decrease in nitrate nitrogen (III) and a further increase in nitrate nitrogen (V).

Denitrification leads to the reduction of nitrate nitrogen (V) mainly to molecular nitrogen, with ammonium nitrogen being an intermediate form. For denitrification to occur, anaerobic conditions are required, and such conditions were detected during the study. In the bottom waters of Starzyca and Maszewskie lakes, the lack of dissolved oxygen occurred in the spring and summer seasons (Fig. 3), and in summer nitrate nitrogen (III) and nitrate nitrogen (V) concentrations decreased (Figs. 7, 8). It should be assumed that in the bottom waters of these lakes the denitrification process took place during the summer. Also in Lake Nowogardzkie nitrate nitrogen concentrations decreased in summer, but another process could be taking place in this lake – anammox, which takes place when dissolved oxygen concentrations are strongly reduced, and such conditions were observed in the bottom layer of Lake Nowogardzkie in summer (Fig. 3). Anaerobic ammonia oxidation (anammox) is a microbially-mediated process [Mulder *et al.* 1995] identified in engineered systems as well as in natural environments, and has been applied to wastewater treatment systems. Carried out by bacteria of the order *Planctomycetales*, anammox eliminates nitrogen by combining ammonia and nitrite to produce nitrogen gas [van de Graff *et al.* 1995], thereby providing an alternative approach to nitrogen removal via denitrification.

The biological uptake of mineral phosphorus by algae occurs continuously, even when their organisms have reached a saturated state. Assimilation of phosphorus by animate matter occurs during the growing season within 15–20 days, and then the rate of assimilation decreases. The increase in algal biomass is directly proportional to phosphorus availability in the lake waters, which is observed when the supply of this element from the direct and indirect catchment is higher [Noe *et al.* 2001]. In the waters of the studied lakes, similar trends in the variability of chlorophyll *a* concentrations during the summer stagnation period were observed as a function of mineral nitrogen and mineral phosphorus concentrations during the summer (Figs. 5, 8, 11). In the summer season, when the highest concentrations of chlorophyll *a* were recorded in the surface layer of the studied lakes, the concentrations of total reactive phosphorus and nitrate nitrogen (V) decreased sharply, whereas in autumn total reactive phosphorus and nitrate nitrogen (V) increased sharply while the concentration of chlorophyll *a* decreased. It is reasonable to assume that mineral phosphorus and mineral nitrogen were incorporated into the algal biomass during the summer season, and once this biomass died, the phosphorus and nitrogen were released into the water body.

All of the lakes studied show significant advancement in the eutrophication process. However, when taking into account most of the indices (concentrations of biogenic substances or organic matter load), Lake Maszewskie shows the highest advancement in the eutrophication process. Lake Maszewskie is the shallowest lake and has the smallest surface area of all three lakes analysed. Tórz *et al.* [2020] demonstrated that Lake Maszewskie is an unresilient lake, highly exposed to catchment influences. Therefore, reclamation measures should be undertaken within the basin of this lake to prevent an increase in the already rapid rate of ageing of this lake. Reclamation measures were carried out on Starzyca and Nowogardzkie lakes. In the case of Lake Nowogardzkie (which is the deepest and covers the largest area but has the highest anthropogenic pressure due to its location within the town of Nowogard, which, in turn, has the largest population of the towns on which the studied lakes are situated), the recultivation measures could have resulted in a decrease in oxygen deficits in the bottom layer in spring and summer. Oxygen deficits in this layer are currently at 10%.

CONCLUSIONS

The analysed lakes Starzyca, Maszewskie and Nowogardzkie, despite some common morphological or trophic features, were characterised by different seasonal variability in some of the hydrochemical parameters studied. The dynamics of water masses means that biochemical transformations take place very quickly in lakes of small area, and therefore such lakes should not be overlooked in monitoring studies. The lakes under study were classified as having an advanced trophic level. The thermal systems present in the studied lakes indicated that they were highly susceptible to climatic factors. The oxygen conditions confirm the significant advancement of the eutrophication process, as characterised by the deoxygenation of waters in the bottom layer in spring and summer as well as marked over-oxygenation in the surface water layer (in Lake Maszewskie it reached even 188.5% in spring). The accumulation of nutrients in the bottom sediments (under good oxygen conditions) and the release of nutrients to the water surface (under unfavourable oxygen conditions) resulted in a higher load of phosphorus compounds in the bottom waters of the studied lakes throughout the research cycle. In the studied lakes, organic matter is of both allochthonous and autochthonous origin. In Lakes Starzyca and Nowogardzkie, the concentrations of phosphorus and iron showed a similar trend of variability in the annual cycle. In summer, mineral phosphorus and mineral nitrogen were incorporated into the algal biomass, and after the death of this biomass, phosphorus and nitrogen were released into the water body.

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