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SEASONAL CHANGES OF HYDROCHEMICAL CONDITIONS IN SELECTED LAKES OF THE DRAWA NATIONAL PARK (POLAND)

SEZONOWE ZMIANY WARUNKÓW HYDROCHEMICZNYCH WYBRANYCH JEZIOR DRAWIEŃSKIEGO PARKU NARODOWEGO

Abstract: The aim of this study was to determine seasonal changes of hydrochemical conditions in subsurface and near-bottom water in lakes Marta and Sitno located in the Drawa National Park (Poland). Hydrochemical monitoring was conducted in years 2005–2007 and comprised determination of temperature, dissolved oxygen, pH, phosphates, nitrates(III), nitrates(V), iron(II) and total iron. The study revealed that in both lakes oxygen saturation of subsurface and near-bottom water within the littoral zone reached maximum values in spring and minimum values in autumn. In deeper layers, hypoxia occurred in near-bottom water throughout the whole study period. Average temperature of both subsurface and near-bottom water was significantly higher in lake Marta. Concentrations of nitrates (III and V) were higher in lake Sitno, and the difference was statistically significant for near-bottom layer. Elevated concentrations of nutrients observed in both lakes indicate their eutrophic character. Lower nitrate(III) concentrations in lake Marta may evidence occurrence of denitrification processes.

Keywords: hydrochemical conditions, lakes, the Drawa National Park

Water chemistry in lakes and reservoirs is determined by numerous factors of non-monotonous dynamics of changes. Local water chemistry depends on factors such as climate, hydrology, hydrogeology and soil conditions within the catchment area, that can decrease or increase the rate of matter delivery to the lake [1]. Morphometrical and hydrological features of the lake also affect its natural susceptibility to degradation [2], therefore each water body has individual features which differentiate and model its hydrochemical conditions [3]. However, the dynamics of hydrochemical changes in lakes are influenced most significantly by human economic activity, resulting not only in transformation but also often in degradation of the aquatic environment. Human pressure, transforming primary landscape into agricultural one, contributes to disturb-

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ances in water conditions and makes local water cycles shorter. Due to insufficient infiltration of water from precipitation, surface runoff enriches surface waters with chemical elements inflowing from the catchment basin [4], increasing their trophy. Reduction of lake eutrophication rate depends on many factors that affect complicated biogeochemical cycles and determine cycling between biotic and abiotic elements of aquatic systems [5]. These relationships are also conditioned by the dynamics of water masses divided into separate layers of totally different properties [6]. Processes running in particular layers depend on the season of the year. Knowledge on seasonal changes of hydrochemical conditions is especially important in regard to lakes located in protected areas. For such lakes, long-term analysis of physicochemical factors enables detection of possible threats to their homeostasis, which is important for controlled fishery exploitation.

Therefore, the aim of this study was to determine seasonal changes of hydrochemical conditions in two lakes of different kind in the Drawa National Park (Poland). Both lakes have been monitored for the number and health condition of economically valuable fish: whitefish (*Coregonus lavaretus*) and vendace (*Coregonus albula*) in Lake Marta, and lake trout (*Salmo trutta* m. *lacustris*) in Lake Sitno.

Material and methods

Study area

Water bodies (≥ 1 ha) in north-western Poland amount to 1575 lakes of which 21 (total area 937 ha) are located in the Drawa National Park [7]. This study comprised two lakes of similar area situated in the Drawa National Park. The first one – Lake Marta – is a non flow-through, mesotrophic, dimictic lake with a maximum depth of 25 m, average depth of 7.7 m and area of 66.1 ha, inhabited by *Chara spp*. The second one – Lake Sitno – is a flow-through, eutrophic, polymictic lake with a maximum depth of 7 m, average depth of 4 m and area of 67.2 ha. Regarding susceptibility to degradation, these lakes have been classified into categories 2nd and 3rd, respectively [8]. Hydrochemical monitoring of these lakes was conducted in years 2005–2007, in four seasons, in subsurface and near-bottom water layers. Sampling sites were selected within the littoral zone and in the deepest places of the lakes, their location being identified by GPS. Seven sampling sites were located in Lake Marta, while six sites in Lake Sitno. To examine hydrochemical conditions of the flow-through Lake Sitno, water samples were collected in places of inflow and outflow of the Plociczna River.

Spring samples were collected in April or May, summer samples were collected in July or August, autumn samples were collected in September or October, while winter samples were collected in December. The samples were collected with standard hydrochemical methods. Temperature, dissolved oxygen and pH were measured *in situ*, while concentrations of phosphates, nitrates(III), nitrates(V), iron(II) and total iron were determined in the laboratory. Laboratory measurements were based on colorimetric methods and conducted with a HACH DR 890 spectrophotometer.

Confidence semi-intervals for the parameters examined (average values for the whole study period and for particulate seasons) were calculated with the non-parametric

Mann-Whitney U test at the significance level $p < 0.05$. The calculations were made with the aid of the StatSoft Statistica 7.1 software.

Results and discussion

In every season during the study period, water in both subsurface and near-bottom layers of lakes Marta and Sitno had slightly alkaline reaction. In Lake Marta pH varied from 7.73 (near-bottom layer, spring) to 8.31 (subsurface layer, autumn), while in Lake Sitno pH ranged from 7.73 (near-bottom layer, spring) to 8.08 (subsurface layer, winter) (Table 1). Statistical analysis revealed that water pH was significantly higher in Lake Marta during the whole study period (Table 2). In both lakes subsurface pH values were slightly higher than near-bottom ones during the whole study period, except for autumn in Lake Sitno. The detected values of water pH were advantageous, as such conditions favour intensification of nitrate(III) reduction [9]. This process occurs mainly in the near-bottom layer containing anaerobic zones where heterotrophic and autotrophic strains of bacteria contribute to denitrification and reduction of nitrate(III) to gaseous nitrogen [10].

The average water temperature in both subsurface and near-bottom layer was significantly higher in Lake Marta (Table 2), despite the lake being deeper than Lake Sitno. This illustrates a significant cooling influence of the Plociczna River on Lake Sitno. Moreover, polymictic character of Lake Sitno contributes to constant mixing of warmer epilimnetic and cooler hypolimnetic water, as evidenced by lower, than in Lake Marta, differences between average temperatures of subsurface and near-bottom layers. Morphometric features of Lake Marta (especially high depth, shape of the lake's basin, clearly distinguished epi- and hypolimnion) create optimal conditions for salmonid fish [11]. On the contrary, a flow-through character of Lake Sitno combined with intensified primary production creates optimal conditions for cyprinid fish.

Another factor crucial for fish is dissolved oxygen. In the summer and autumn periods, values of this parameter were similar for both lakes (Table 2), while in the winter and spring periods water in Lake Sitno contained significantly more dissolved oxygen than water in Lake Marta. Low dissolved oxygen content occurred in Lake Sitno, however it has never been totally depleted [12]. In both lakes, maximum dissolved oxygen in subsurface and near-bottom waters was detected in spring, and minimum – in autumn (Table 1). This tendency might have originated from vegetation zone developed around the lakeshore. In a consequence of an extended littoral zone, organic matter accumulated in autumn after vegetation period and its decomposition temporarily diminished dissolved oxygen content. Higher oxygen saturation of subsurface water might increase pH in the epilimnion [13]. Favourable conditions for brood-stocks of vendace (*Coregonus albula*) and whitefish (*Coregonus lavaretus*) in Lake Marta and lake trout (*Salmo trutta* m. *lacustris*) in Lake Sitno occurre in spring, when the lakes are the richest in dissolved oxygen. Near-bottom water in Lake Marta has the most stable oxygen conditions whole year round, and this favours occurrence of salmonids, however, autumnal hypoxia in the littoral zone may impair reproduction in the fish, as they spawn at that time [14]. This has been reflected by a decrease in

Table 1

Ranges and average values of hydrochemical parameters for 6 sampling sites in Lake Marta and 7 sampling sites in Lake Sitno for years 2005–2007

Parameters	Subsurface layer				Near-bottom layer			
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
	Lake Marta							
pH	7.76 (7.67–7.87)	8.06 (7.62–8.5)	8.31 (8.15–8.56)	8.03 (8.00–8.05)	7.73 (7.61–7.80)	7.94 (7.42–8.51)	8.14 (8.01–8.36)	7.94 (7.92–7.96)
Temperature [°C]	14.6 (13.8–15.6)	22.2 (19.9–26.4)	15.8 (10.2–19.1)	5.1 (4.0–6.5)	14.0 (12.4–15.3)	20.1 (17.1–23.0)	14.1 (9.5–17.1)	5.0 (4.0–6.4)
O_2 [$mg \cdot dm^{-3}$]	11.1 (10.5–11.9)	9.1 (8.3–10.5)	9.3 (7.8–10.5)	9.9 (9.5–10.1)	10.5 (10.3–10.8)	8.3 (7.0–10.4)	8.4 (6.9–10.2)	8.4 (8.1–8.7)
NO_2-N [$mg \cdot dm^{-3}$]	0.011 (0.010–0.012)	0.011 (0.008–0.014)	0.017 (0.012–0.023)	0.011 (0.010–0.013)	0.010 (0.010–0.011)	0.008 (0.005–0.010)	0.017 (0.014–0.018)	0.013 (0.012–0.013)
NO_3-N [$mg \cdot dm^{-3}$]	8.6 (8.5–8.8)	6.7 (5.3–10.6)	8.6 (6.2–10.6)	7.2 (5.0–8.9)	8.8 (8.8–8.9)	6.1 (5.4–7.0)	6.4 (5.9–6.9)	6.7 (4.6–8.9)
PO_4^{-3} [$mg \cdot dm^{-3}$]	0.43 (0.25–0.65)	1.26 (0.40–2.60)	0.95 (0.15–2.21)	3.24 (2.69–3.97)	0.44 (0.22–0.65)	0.51 (0.36–0.79)	1.02 (0.16–2.41)	0.77 (0.64–0.99)
Fe^{2+} [$mg \cdot dm^{-3}$]	0.02 (0.01–0.04)	0.02 (0.01–0.02)	0.02 (0.01–0.02)	0.03 (0.02–0.04)	0.03 (0.01–0.04)	0.01 (0.01–0.02)	0.04 (0.01–0.06)	0.02 (0.01–0.03)
Total Fe [$mg \cdot dm^{-3}$]	0.09 (0.02–0.22)	0.02 (0.01–0.03)	0.04 (0.03–0.04)	0.05 (0.03–0.06)	0.03 (0.02–0.03)	0.03 (0.02–0.03)	0.06 (0.03–0.09)	0.04 (0.02–0.06)

Table 1 contd.

Parameters	Subsurface layer				Near-bottom layer			
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Lake Sitno								
pH	7.75 (7.50–7.90)	8.00 (7.16–8.86)	7.97 (7.78–8.10)	8.08 (8.03–8.13)	7.73 (7.48–7.89)	7.94 (7.38–8.62)	8.00 (7.95–8.07)	7.97 (7.82–8.09)
Temperature [^{o}C]	13.9 (12.7–14.6)	20.8 (17.6–25.5)	12.1 (8.4–18.1)	4.8 (2.8–6.4)	13.1 (11.9–13.8)	19.7 (17.2–23.1)	11.3 (8.6–16.5)	4.5 (2.4–6.4)
O_2 [mg · dm^{-3}]	12.9 (12.4–13.5)	11.0 (8.6–15.5)	7.6 (6.0–8.7)	10.4 (9.9–11.4)	11.9 (11.5–12.6)	10.0 (7.0–14.5)	7.6 (7.3–8.0)	9.7 (8.0–11.1)
NO_2-N [mg · dm^{-3}]	0.028 (0.024–0.035)	0.019 (0.014–0.024)	0.050 (0.032–0.063)	0.030 (0.022–0.035)	0.031 (0.025–0.039)	0.019 (0.009–0.035)	0.060 (0.032–0.079)	0.024 (0.011–0.044)
NO_3-N [mg · dm^{-3}]	9.6 (7.6–12.0)	8.1 (1.4–11.9)	6.8 (5.4–8.5)	8.1 (4.7–10.6)	9.6 (7.2–12.0)	8.1 (1.4–8.5)	6.4 (5.3–7.2)	8.7 (5.5–10.6)
PO_4^{-3} [mg · dm^{-3}]	0.64 (0.37–1.18)	1.25 (0.52–2.41)	0.40 (0.32–0.44)	0.53 (0.15–0.80)	0.63 (0.33–1.18)	0.88 (0.62–1.16)	0.34 (0.28–0.43)	0.99 (0.76–1.30)
Fe^{2+} [mg · dm^{-3}]	0.06 (0.04–0.08)	0.05 (0.02–0.08)	0.06 (0.03–0.09)	0.06 (0.03–0.09)	0.05 (0.04–0.05)	0.06 (0.04–0.08)	0.05 (0.02–0.08)	0.06 (0.02–0.08)
Total Fe [mg · dm^{-3}]	0.19 (0.06–0.40)	0.08 (0.06–0.09)	0.09 (0.05–0.12)	0.08 (0.04–0.13)	0.14 (0.06–0.25)	0.06 (0.04–0.09)	0.08 (0.06–0.10)	0.07 (0.04–0.10)

populations of vendace and whitefish in Lake Marta and lake trout in Lake Sitno [oral information from the Drawa National Park]. Additionally, reproduction of these fish species may have been reduced by progressing eutrophication [15].

Table 2

Average values of physiochemical parameters for lakes Marta and Sitno
for the whole 2005–2007 period and for individual seasons (spring, summer, autumn, winter)

Parameters	Lake Marta	Lake Sitno	U*	Z	p-value	Z corrected
2005–2007 period						
pH	7.99	7.93	8169.5	2.88	0.004	2.88
Temperature [^oC]	13.9	12.5	8552.5	2.43	0.015	2.43
NO_2^--N [$mg \cdot dm^{-3}$]	0.012	0.033	264.5	–7.54	0.000	–7.55
Fe^{2+} [$mg \cdot dm^{-3}$]	0.02	0.06	454.5	–6.60	0.000	–6.68
Total Fe [$mg \cdot dm^{-3}$]	0.05	0.11	415.0	–6.82	0.000	–6.86
Spring						
Temp.[°C]	14.3	13.5	435.5	2.90	0.004	2.91
O_2 [$mg \cdot dm^{-3}$]	10.8	12.4	322.5	–3.81	0.000	–3.81
NO_2^--N [$mg \cdot dm^{-3}$]	0.011	0.030	8.0	–4.13	0.000	–4.14
Fe^{2+} [$mg \cdot dm^{-3}$]	0.03	0.06	12.5	–4.13	0.000	–4.23
Total Fe [$mg \cdot dm^{-3}$]	0.06	0.17	49.5	–2.59	0.009	–2.61
Summer						
pH	8.00	7.97	1247.5	2.04	0.041	2.04
Temperature [^oC]	21.1	20.2	1190.0	2.37	0.018	2.37
NO_2^--N [$mg \cdot dm^{-3}$]	0.010	0.019	61.5	–4.52	0.000	–4.54
Fe^{2+} [$mg \cdot dm^{-3}$]	0.02	0.06	89.5	–3.92	0.000	–3.98
Total Fe [$mg \cdot dm^{-3}$]	0.03	0.08	76.0	–4.21	0.000	–4.24
Autumn						
pH	8.22	8.00	744.0	2.88	0.004	2.88
Temperature [^oC]	15.0	11.7	872.0	2.09	0.036	2.10
NO_2^--N [$mg \cdot dm^{-3}$]	0.017	0.055	10.5	–4.82	0.000	–4.84
Fe^{2+} [$mg \cdot dm^{-3}$]	0.03	0.06	60.0	–3.31	0.001	–3.34
Total Fe [$mg \cdot dm^{-3}$]	0.05	0.09	32.5	–4.15	0.000	–4.18
Winter						
pH	7.99	8.03	193.5	–3.25	0.001	–3.26
O_2 [$mg \cdot dm^{-3}$]	9.1	10.1	268.5	–2.84	0.005	–2.84
NO_2^--N [$mg \cdot dm^{-3}$]	0.012	0.027	12.0	–2.54	0.011	–2.56
PO_4^{-3} [$mg \cdot dm^{-3}$]	2.00	0.76	8.0	2.87	0.004	2.87
Fe^{2+} [$mg \cdot dm^{-3}$]	0.03	0.06	10.5	–2.66	0.008	–2.71
Total Fe [$mg \cdot dm^{-3}$]	0.05	0.08	1.0	–3.46	0.001	–3.48

* Confidence semi-intervals calculated with the non-parametric Mann-Whitney U test: U – the Mann-Whitney U test; Z – standardized value of variable at normal distribution; Z corrected – correction due to tied ranks; p-value – significance level, $p < 0.05$.

Monitoring of nutrients revealed that in years 2005–2007, nitrate(V) content in subsurface water of Lake Marta was the lowest in summer (on average 6.7 mg · dm^{-3}), and the highest in spring and autumn (on average 8.6 mg · dm^{-3}) (Table 1). A regularity was observed that concentrations of mineral nitrogen compounds for subsurface water were higher than for near-bottom one (except for spring). Differently in Lake Sitno, nitrate(V) concentrations in each season were similar for both water layers. Near--bottom nitrate(V) concentrations for spring were higher than for the other seasons. For the 2005–2007 period, average nitrate(V) concentrations in subsurface and near-bottom waters were higher for Lake Sitno than for Lake Marta in spring, summer and winter seasons, however the differences have not been statistically confirmed (Table 2). At the same time, average nitrate(III) concentrations in Lake Marta ranged from 0.008 mg · dm^{-3} for summer to 0.017 mg · dm^{-3} for autumn, while in Lake Sitno nitrate(III) levels were higher and varied from 0.019 mg · dm^{-3} for summer to 0.060 mg · dm^{-3} for autumn (Table 1), and this difference between lakes was statistically significant. The relationships observed might have resulted from different sediment ability to retain chemicals, including nitrates(III) and (V). As nitrates(III) and (V) poorly adhere to organic particles in sediments, they may be easily released from the substratum. Nitrate content is also modified by denitrification intensity. The results obtained indicate that denitrification is more intensive at higher temperature, as evidenced by the fact that the lowest nitrate content occurred in summer in near-bottom water of both lakes [16]. A detailed study revealed that average level of nitrate removed from Lake Sitno by the Plociczna River was higher than average level delivered [12]. The source of the river, located at an agricultural area, may contribute to nutrient inflow. According to Lossow [17], agricultural fertilizers may be responsible for 10–20 % of nitrogen and 5 % of phosphorus delivered to freshwaters. Phosphate levels in Lake Marta tended to be the highest in winter in the subsurface layer and the lowest in spring in both layers (Table 1). Significantly higher winter concentrations of phosphates in Lake Marta may have resulted from occurrence of free phosphorus form, not built in animal or plant tissues. A considerable amount of nutrients is accumulated in the sediments and invertebrates [8]. Release of phosphorus from sediments may be intensified by mixing of near-bottom water with water from the above layers [4]. This took place in Lake Sitno where, in wintertime, near-bottom water contained more phosphorus than subsurface one (Table 1). Lake Sitno, therefore, being a shallow lake with high dynamics of water masses, is more susceptible to eutrophication. Similar regularities were reported by Kubiak [18]. A significant role in the processes of phosphorus sorption and binding to sediments is played by iron hydroxides and calcium carbonate, while sediment bacteria have a significant role in anaerobic release of iron-bound phosphorus [19]. Concentrations of Fe^{2+} in Lake Marta were nearly constant (from 0.01 to 0.06 mg · dm^{-3}) during the whole study period (Table 1). The highest concentration of total iron occurred in spring, while in the other periods its levels ranged from 0.01 to 0.09 mg · dm^{-3} (Table 1). Fe^{2+} concentrations in Lake Sitno were significantly higher than in Lake Marta (Table 2). In both lakes, total iron levels were the highest in spring.

The results of this study indicate that the examined lakes were characterized by high nutrient concentrations and temporary near-bottom hypoxia, while the dynamics of nutrient accumulation and bioaccumulation ensured maintenance of balance.

Conclusions

1. Marta and Sitno lakes were characterized by high nutrients concentrations and near-bottom hypoxia.

2. The observed dynamics of nutrient concentrations may reflect the compounds accumulation and bioaccumulation in sediments as well as their dynamic mobilization, confirmed by balanced concentrations in the whole water body.

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SEZONOWE ZMIANY WARUNKÓW HYDROCHEMICZNYCH WYBRANYCH JEZIOR DRAWIEŃSKIEGO PARKU NARODOWEGO

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Abstrakt: Celem pracy było określenie sezonowych zmian warunków hydrochemicznych w warstwie powierzchniowej i przydennej jezior Marta i Sitno w DPN. Badania hydrochemiczne przeprowadzono w latach 2005–2007, podczas których mierzono pH, temperaturę, zawartość tlenu, azotanów(III i V), fosforanów, żelaza dwuwartościowe i ogólną zawartość żelaza.

Pomiary zawartości O_2 wykazały, że warstwy powierzchniowe i przydenne w litoralu obydwóch jezior były maksymalnie wysycone tlenem wiosną, a minimalnie jesienią. W całym okresie badań stwierdzono niedotlenienie warstw przydennych w obydwóch jeziorach. Kontrola warunków termicznych wykazała, że średnia temperatura wody w obu warstwach w jeziorze Marta jest znacznie wyższa aniżeli w jeziorze Sitno. Analiza stężeń azotanów(III i V) wykazała większą ich zawartość w obu warstwach w jeziorze Sitno, aniżeli w jeziorze Marta. Różnice te udowodniono statystycznie dla warstwy przydennej. Wykazana w obydwóch zbiornikach podwyższona zawartość pierwiastków biogennych klasyfikuje je jako eutroficzne. Mniejsze stężenie azotanów(III) w jeziorze Marta może świadczyć o zachodzącym w nim procesie denitryfikacji.

Słowa kluczowe: właściwości hydrochemiczne, jeziora, Drawieński Park Narodowy