

**SEASONAL VARIABILITY OF CARBON FORMS
IN WATER AND BOTTOM SEDIMENT IN LAKES WITH
A DIFFERENT TYPE OF MIXING***

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Key words: TOC, DOC, IC, bottom sediments, urban lakes.

Abstract

The aim of this study was to determine seasonal changes in the occurrence of carbon forms in water and bottom sediment in lakes with a different type of mixing. The study was conducted in five urban lakes located in Olsztyn: Track, Sukiel, Podkówka, Redykajny and Tyrsko. The research was carried out in March, April, August and November. We analyzed TOC, DOC and IC in samples of water collected near the surface and near the bottom, as well as in the overlying and interstitial layer of 0–5 cm and 5–10 cm of sediment. The dominant form of carbon in urban lakes is organic carbon, whose share in the surface water layer in the lakes analyzed in the present study was from 29.3 to 58.4% of the total pool of carbon, and the near-bottom layer was characterized by values ranging from 28.2 to 66%, while the layer of overlying water contained from 34.2 to 63.6% of the total amount of carbon. In the interstitial water, the percentage of organic carbon in the total pool was from 40.1 to 94% within the 0–5 cm layer of sediment and from 56.4 to 88.1% in the layer of sediment at the depth of 5–10 cm. The percentage of inorganic carbon forms ranged from 2.94% to 71.79% of the total amount of carbon. The carbon cycle in lake water depends not only on the inflow of this element from the catchment, but also on its release from the bottom sediment, which can be a large reservoir of organic carbon in lakes.

**SEZONOWA ZMIENNOŚĆ FORM WĘGLA W WODZIE I OSADACH
DENNYCH JEZIOR O ZRÓŻNICOWANYM TYPIE MIESZANIA**

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Słowa kluczowe: TOC, DOC, IC, jeziora miejskie, osady dennie.

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Abstrakt

Celem pracy było określenie sezonowych zmian zawartości węgla w wodzie i osadach dennych w jeziorach o zróżnicowanym typie mieszania. Badania przeprowadzono w pięciu jeziorach miejskich Olsztyna: Track, Sukiel, Podkówka, Redykajny, Tyrsko w marcu, kwietniu, sierpniu i w listopadzie. W pobranych próbkach wody zbadano zawartość TOC, DOC oraz IC. Wodę do badań pobierano z warstwy powierzchniowej, naddennej, nadosadowej oraz interstycjalnej (0–5 i 5–10 cm). Dominującą formą węgla w jeziorach miejskich był węgiel organiczny, którego udział w całkowitej puli węgla wynosił od 29,3% do 58,4% w wodzie powierzchniowej, a w wodzie naddennej od 28,2% do 66%, natomiast w wodzie nadosadowej od 34,2% do 63,6%. W wodzie interstycjalnej procentowa zawartość węgla organicznego wynosiła od 40,1% do 94% w warstwie 0–5 cm osadów, a w warstwie 5–10 cm od 56,4% do 88,1%. Zawartość procentowa węgla nieorganicznego wynosiła od 2,94% do 71,29% całkowitej puli węgla. Uzyskane wyniki wskazują, że obieg węgla w wodzie jeziorowej będzie zależał nie tylko od jego dopływu ze zlewni, ale również od uwalniania tego składnika z osadów dennych, które mogą być dużym rezerwuarem węgla organicznego w jeziorze.

Introduction

In surface waters, carbon appears in the form of total organic carbon (TOC) and inorganic carbon (IC). Total organic carbon consists of dissolved organic carbon (DOC), particulate organic carbon (POC) and volatile organic compounds (VOCs). Inorganic carbon, which dominates in water, comes in three forms: CO_3^{2-} , HCO^- , CO_2 (DUNALSKA 2009). Dissolved organic carbon (DOC) is a key component of all aquatic ecosystems. The pool of DOC in a lake consists of both autochthonous organic matter, produced in the lake, and allochthonous matter, delivered from the catchment. Dissolved organic carbon is an important production regulator in aquatic ecosystems. With its absorption properties, DOC may inhibit the process of photosynthesis (JONES 1998); on the other hand, it provides substrate for heterotrophic bacteria (TRANVIK and DOWNING 2009). DOC originating from the catchment is less readily transformed than that derived from the production in the lake, because the former, before entering the lake, already undergoes a series of changes in soil (SCHIFF et al. 1997). Total DOC contained in the water of a lake is subject to numerous processes which modify its concentration. The impact on these processes depends primarily on the catchment characteristics, such as the nature of the catchment, its runoff coefficient and land use. An external supply of organic carbon in lakes often dominates the amount of carbon produced within these water bodies (CARACO, COLE 2004). In addition, DOC can affect the fate of other dissolved substances such as heavy metals and other organic pollutants (HAITZER et al. 1998). DOC may also perform a protective function towards ultraviolet for flora and fauna inhabiting the ecosystem of a lake (MOLOT et al. 2004).

Inorganic carbon (IC) is an important constituent of lake systems. The dominant form of inorganic carbon is largely dependent on the water pH.

In typically hard water lakes, pH values may be above 8 and HCO_3^- is usually a dominant species in solution (WETZEL 2001). The amount of IC in lake water depends on a variety of processes, including the equilibrium state with atmospheric CO_2 , bicarbonate-carbonate balance, external loadings, contributions from metabolic respiration, consumption via photosynthesis, temperature and redox reactions including microbial methane fermentation, nitrification, sulfide oxidation, sulfate reduction, Fe and Mn oxide reduction and denitrification (LAMPERT, SOMMER 2007).

The aim of this study was to determine seasonal changes in the occurrence of carbons in different components of a lake ecosystem, including surface water, bottom water, overlying water and interstitial water in lakes with a different type of mixing.

Material and Methods

Study site

The study was conducted in five urban lakes located in Olsztyn: Track, Sukiel, Podkówka, Redykajny and Tyrsko (Figure 1), which belong to the Masurian Lake District. The morphometric, mictic characteristics and present trophic status of studied lakes are shown in Table 1.

Table 1
Morphometric, mictic characteristics and present trophic status of studied lakes

Lake	Area [ha]	Catchment area [ha]	Depth max [m]	Type of mixing	TSI (Chl)	TSI (TP)	TSI (TOC)	TSI (SD)
Tyrsko	18.6	68.2	30.4	di-	45.74	65.23	54.11	41.92
Redykajny	29.9	187.4	20.6	di-	56.04	82.22	62.16	44.15
Podkowka	6.9	25.6	6.0	poly-	66.34	92.60	59.20	46.22
Sukiel	20.8	26.1	25	di-	42.44	55.44	61.38	48.62
Track	52.8	387.1	3.8	poly-	77.65	80.07	66.33	61.52

Track Lake is located on the north-eastern outskirts of Olsztyn. The lakeshores are generally flat or slightly sloping.

Sukiel Lake is located in the western part of Olsztyn. The lake has no outlet. The shores of the lake are gently elevated.

Podkówka Lake is located in the north-western part of Olsztyn. The shores of the lake are distinctly raised and mostly overgrown with trees.

Redykajny Lake is located in the northern part of Olsztyn. The basin is physiographically varied and the shores comprise long elevated sections.

Tyrsko Lake is located in the north-western part of Olsztyn.

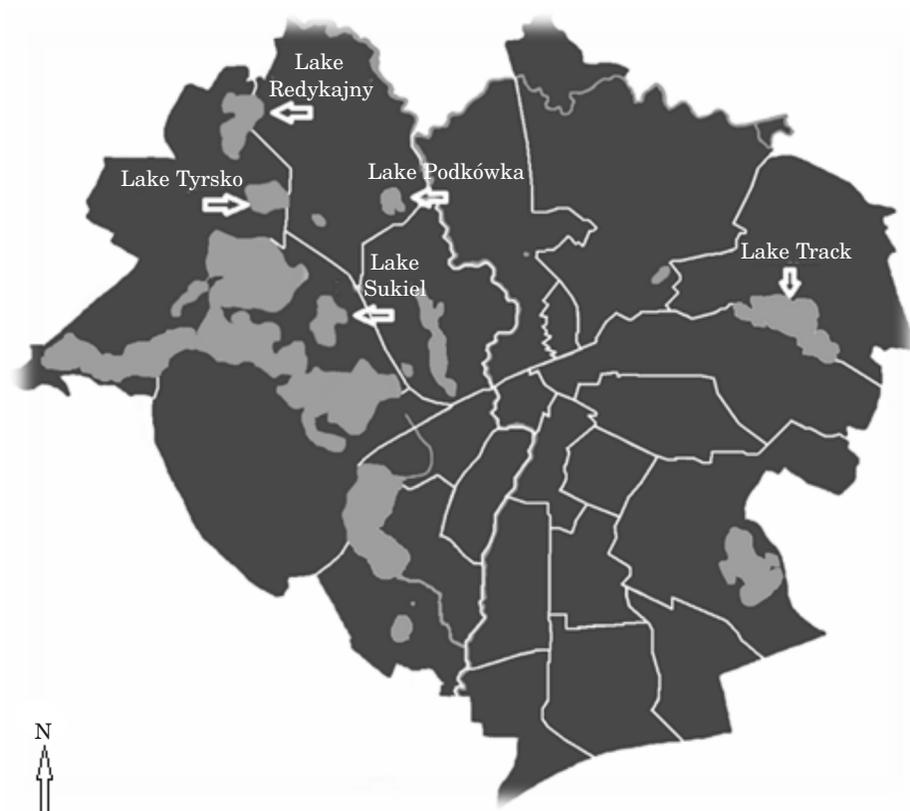


Fig. 1. Location of the lakes in Olsztyn

Water sample collection

The research was carried out in March, April, August and November. We analyzed samples of water collected near the surface and near the bottom, as well as in the overlying and interstitial layer of 0–5 cm and 5–10 cm of sediment. Bottom sediments were collected in the deepest place in each lake. Water and bottom sediment samples were collected using the Ruttner water sampler and Kajak sediment sampler, respectively. Interstitial water was collected by centrifugation in a centrifuge at a speed 2500 rpm.

Carbon determination and chemical analyze

Each water sample was divided into two parts. One was filtered through a Millipore filter with a pore diameter of 0.45 μm , in order to isolate the

fraction of dissolved organic carbon (DOC) (DUNALSKA et al. 2012). The other one was not filtered and used for the determination of total carbon (TC) and inorganic carbon (IC) via high-temperature combustion (HTC) using a IL 550 TOC-TN HACH analyzer. TOC was calculated from the results of TC and IC.

Total phosphorus was determined according to the Standard Methods (1999). Chlorophyll was determined by the spectrophotometric method with the correction for phaeopigments (PN-86/C-05560/02). Water transparency was assayed with the Secchi disc.

Statistical analysis

In order to verify whether the content of carbons depends on the season, the results were submitted to statistical analysis, including tests of normality of the distribution and homogeneity of variance. Normality was checked with the Shapiro-Wilk's test, while homogeneity was assessed with the Levene's test. When both conditions were met, an analysis of variance was performed by ANOVA. ANOVA procedure was used to compare TOC, DOC and IC between different components of a lake ecosystem. In case of given factor, *post hoc* tests were performed by Tukey test.

Results

Total Organic Carbon

The content of TOC in the surface water of the lakes ranged from 7.33 mg C dm⁻³ (Tyrsko Lake in summer) to 18.39 mg C dm⁻³ (Track Lake in spring). In the near-bottom water layer, the highest amount of TOC was observed in Podkówka Lake, and the lowest one in Tyrsko Lake (23.51 mg C dm⁻³ and 6.77 mg C dm⁻³, respectively). The highest and lowest values were obtained in spring. The overlying water in the lakes was characterized by much higher organic carbon content (7.32 mg C dm⁻³ – 522.80 mg C dm⁻³) than in surface and bottom layers (Figure 2). The smallest value was recorded in Tyrsko in summer, and the highest one occurred in Redykajny in spring. The amount of TOC in the interstitial water within the 0–5 cm layer of sediments was of similar magnitude as in overlying water and ranged from 14.41 mg C dm⁻³ in Podkówka Lake in summer to 516.50 mg C dm⁻³ in Redykajny Lake in spring. The concentration of organic carbon in the interstitial water within the 6–10 cm layer of sediments was in the range of 36.82 mg C dm⁻³ in Podkówka Lake in summer to 320.30 mg C dm⁻³ in Sukiel Lake in winter.

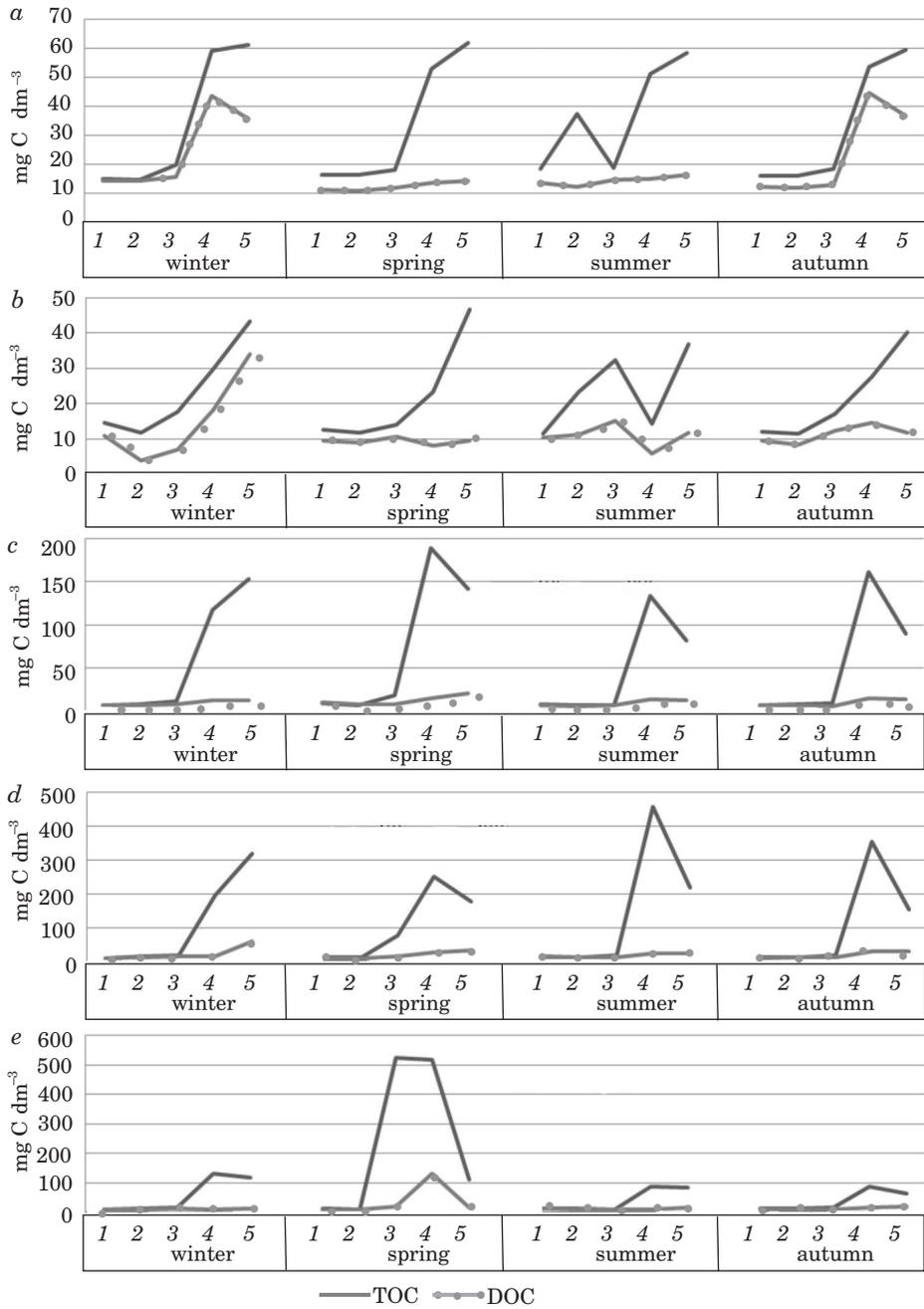


Fig. 2. Organic carbon content and dissolved organic carbon content in water of the analyzed lakes: *a* – Lake Track, *b* – Lake Podkówka, *c* – Lake Tyrsko, *d* – Lake Sukiel, *e* – Lake Redykajny; (1 – surface water, 2 – bottom water, 3 – overlying water, 4 – interstitial water, 0–5 cm, 5 – interstitial water, 5–10 cm)

Dissolved Organic Carbon

The concentration of DOC in the surface water of the lakes ranged from 6.35 mg C dm⁻³ in Tyrsko Lake in autumn to 14.26 mg C dm⁻³ in Track Lake in winter. The content of DOC in the near-bottom water was on the level of 3.82 mg C dm⁻³ in Podkówka Lake to 14.50 mg C dm⁻³ Track Lake, both in winter. The highest content of DOC in the overlying lake water appeared in Track Lake in winter (15.76 mg C dm⁻³), and the lowest one – in Tyrsko Lake in autumn (5.61 mg C dm⁻³). The DOC in the interstitial water within the 0–5 cm layer of sediment ranged from 5.82 mg C dm⁻³ in Podkówka Lake in summer to 131.00 mg C dm⁻³ in Redykajny Lake in spring. The 6–10 cm layer of sediment was characterized by the content of DOC in the interstitial water ranging from 9.64 mg C dm⁻³ in Podkówka Lake in spring to 59.27 mg C dm⁻³ in Track Lake in spring (Figure 2).

Inorganic Carbon

The surface water of the examined lakes were characterized by the inorganic carbon content ranging from 7.90 mg C dm⁻³ to 36.33 mg C dm⁻³. In the near-bottom water, the IC content was within the range of 8.14 mg C dm⁻³ to 37.16 mg C dm⁻³, while in the overlying waters it varied from 6.57 mg C dm⁻³ to 37.91 mg C dm⁻³ (Figure 3). In the surface, near bottom and overlying water, the minimum and maximum values were found at the same sampling sites: in Tyrsko Lake in spring and in Track Lake in winter, respectively. The concentration of IC in the interstitial waters of the 0–5 cm layer of bottom sediment ranged from 11.57 mg C dm⁻³ to 48.21 mg C dm⁻³, in Tyrsko Lake in winter (the lowest value) and in Sukiel Lake in autumn (the highest value). The lowest content of IC in the interstitial water of the 6–10 cm layer of sediment was determined in Podkówka Lake in spring (13.74 mg C dm⁻³), and the highest one was in Sukiel Lake in autumn (and 54.98 mg C dm⁻³).

Discussion

Seasonal changes of carbon content in lakes ecosystem

Many studies focus on examining the content of organic carbon in lake sediment (MOLOT, DILLON 1996, STALLARD 1998, EINSELE et al. 2001, KORTELAINEN et al. 2004, ANDERSON et al. 2009, KASTOWSKI et al. 2011), and the results provide information on the carbon budget in lakes and its role in the

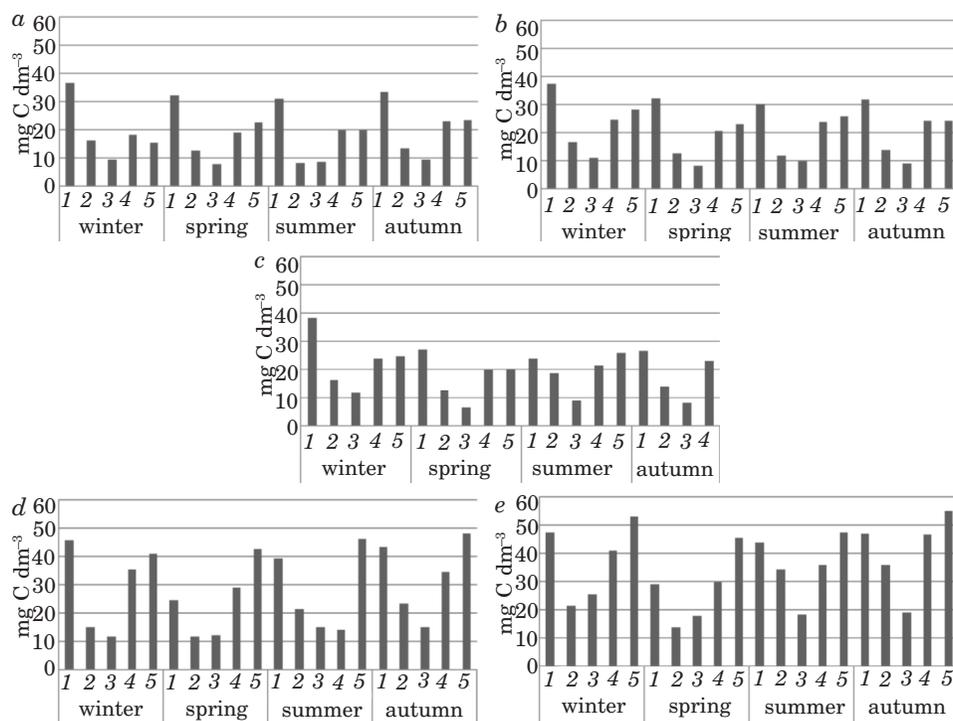


Fig. 3. Inorganic carbon content in water of the analyzed lakes: *a* – surface water, *b* – bottom water, *c* – overlying water, *d* – interstitial water (0–5), *e* – interstitial water (5–10); 1 – Track Lake, 2 – Podkówka Lake, 3 – Tyrsko Lake, 4 – Sukiel Lake, 5 – Redykajny Lake

global cycling. Climate change, hydrology and geochemical processes are different in different parts of the world, hence the carbon cycle will differ in particular regions.

The dominant form of carbon in studied urban lakes is organic carbon, whose share in the surface water was from 29.3 to 58.4% of the total pool of carbon, and the near-bottom layer was characterized by values ranging from 28.2 to 66%, and in the layer of overlying water contained from 34.2 to 63.6% of the total amount of carbon. The lowest values of concentration were recorded in polymictic Track Lake, which was due to the ongoing process of intensive mineralization of organic carbon. The highest values of concentration were observed in Podkówka Lake. The high percentage of TOC in the waters of this lake results probably from the nature of the catchment, dominated by forests. In spring, rainfall imports hardly decomposable organic matter to the lakes. In the interstitial water, the percentage of organic carbon in the total pool was from 40.1 to 94% within the 0–5 cm layer of sediment and from 56.4 to 88.1% in the layer of sediment at the depth of 5–10 cm. Such a significant share

of organic carbon in interstitial water can be associated with the sedimentation of dead phytoplankton (CARMOUZE et al. 1998).

Sediment can play a very important role in the eutrophication process by retaining nutrients, including carbon, and undergoing possible evolution. Until now, many authors have drawn attention to the release of nitrogen and phosphorus from sediments, but too little interest has been paid to the internal loading in carbon, whose availability may significantly affect the ecological status of water bodies.

The current study has demonstrated seasonal changes in the forms of carbon in different parts of the analyzed lake ecosystems. The largest seasonal variation was observed in interstitial water, both in the 0–5 cm and 5–10 cm layer. This can be attributed to sedimentation of dying phytoplankton and organic matter decomposition in sediment, as demonstrated by numerous authors (YACOBI, OSTROVSKY 2012).

The abundance of the particular carbon forms was rather stable ($F_{(4,13)} = 9.72$; $p < 0,0001$). The increase in TOC and DOC in spring was most likely related to the inflow of organic matter along with the spring thaw washed out from soils and forest litter. In summer, the increase in TOC and DOC corresponds to the primary production in a lake basin, which is stimulated by more insolation, higher temperatures as well as an ample supply of nutrients (unpublished data), which all contribute to the enhanced primary production (COLE et al. 2000, GIORGIO del, PETERS 1993).

Reducing the impact of bottom sediment on water is of great importance, especially in urban lakes, which used to receive polluted discharge for many years but now are often used for recreational purposes. An additional supply of nutrients from the bottom sediment, which in some cases may exceed the supply of nutrients from allochthonous sources, can lead to an avalanche of degradation events in a lake and prohibit its use by people.

Carbon cycling and the mixing type

Interstitial water and the overlying are a rich reservoir of organic carbon in the analyzed lakes, so that under favorable conditions during periods of circulation they can supply the water column with organic carbon, thus stimulating metabolic processes in a lake. Carbon trapped in the solid phase of sediments is first released to the interstitial water and then migrates to the overlying water, depending on the concentration gradient. It can be assumed that the actual dynamics of organic carbon in sediment of polymictic lakes (e.g. Track, Podkówka) is higher due to the frequent mixing of water masses and accelerated mineralization, organic carbon is released to the atmosphere as

CO₂. Mineralization of organic matter also promotes the release of phosphorus into the water column and thus contributes to the growth of lake trophy. Regarding the lakes discussed herein, the highest trophic index based on the content of phosphorus was achieved by the two polymictic lakes: Track and Podkówka (TSI (TP) = 80 and 92.6, respectively, Table 1). In the dimictic lakes, the bottom sediment can play a positive role, as they accumulate organic matter and pollutants inflowing from the catchment. This way, sediment may reduce the adverse impact of the catchment by removing a pool of pollutants deposits. This assumption was confirmed by our results, according to which a deep, dimictic lake is characterized by lower rates of the trophy based on a phosphorus content – TSI (TP). In polymictic lakes, organic carbon trapped in bottom sediment, via mineralization, supplies the water column with CO₂ and contributes to the degradation of the lake.

Based on the TOC transfer through all the elements of a lake ecosystem, it can be concluded to depend on the mictic type of a lake. Polymictic lakes (Track, Podkówka) (Figure 4) are characterized by the highest TOC content in the interstitial water within the 5–10 cm layer of sediments. However, in dimictic lakes (Tyrsko, Redykajny, Sukiel) – Figure 5, the interstitial water of shallower sediment (0–5 cm) was the richest in TOC.

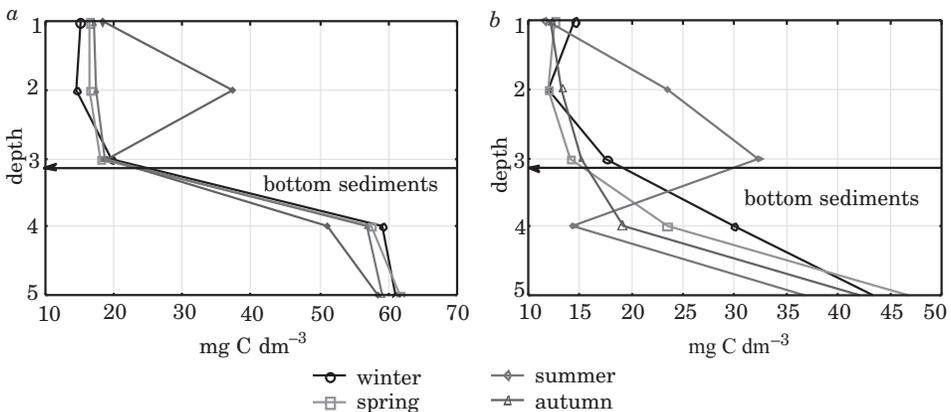


Fig. 4. TOC distribution in particular lake ecosystem elements in polymictic lakes: *a* – Lake Track, *b* – Lake Podkówka; depth: 1 – surface water, 2 – bottom water, 3 – overlying water, 4 – interstitial water (0–5), 5 – interstitial water (5–10)

The shallower, polymictic lakes with higher water temperature in the bottom layer, and additionally frequent mixing water masses accelerate the decomposition of organic matter, then large amounts of sediment-trapped pollutants can be liberated, thus stimulating metabolic processes and deteriorating the ecological status of the water body. In dimictic lakes, an increase

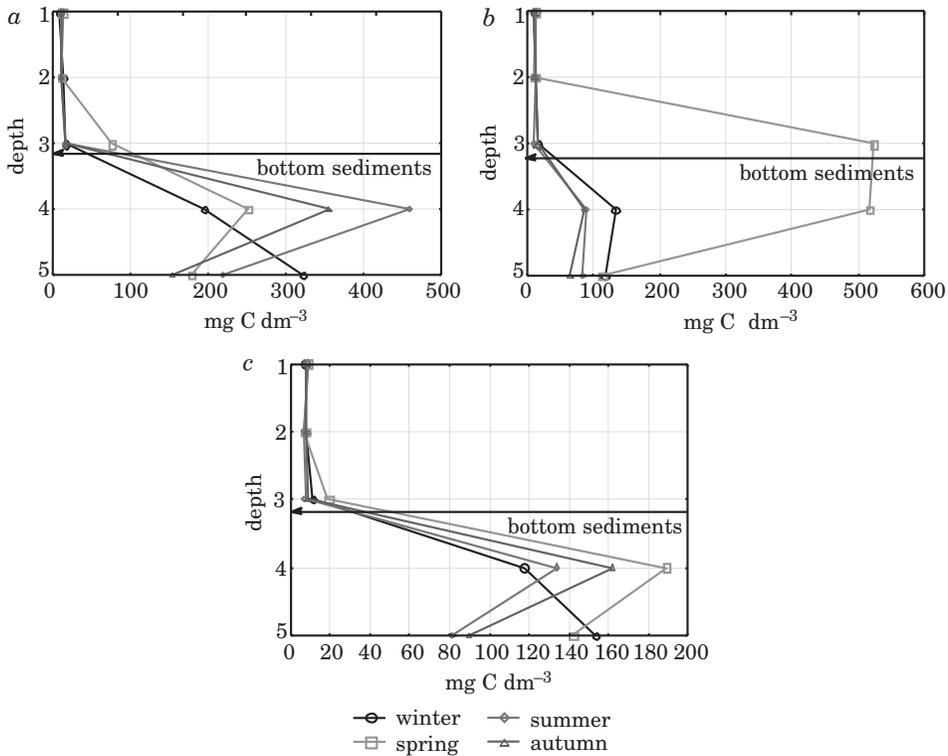


Fig. 5. TOC distribution in particular lake ecosystem elements in dimictic lakes: *a* – Lake Sukiel, *b* – Lake Redykajny, *c* – Lake Tyrsko; depth: 1 – surface water, 2 – bottom water, 3 – overlying water, 4 – interstitial water (0–5), 5 – interstitial water (5–10)

in the carbon content will be different than in polymictic lakes. Organic carbon is accumulated in sediment and therefore sedimentation will limit its impact on the processes of degradation of lakes (XU et al. 2012). In polymictic lakes studied, the amount of organic carbon in sediment was 3- to 4-fold higher than in water, but the analogous difference in dimictic lakes can be up to 45-fold. The analytical results confirm that a dimictic lake may accumulate more carbon in sediment than polymictic one.

The buffering properties of water are closely related to its alkalinity, which is affected by bicarbonates, carbonates and hydroxides. These compounds enable the maintenance of the pH of water by neutralizing pollutants. The percentage of inorganic carbon ranged from 2.94% to 71.79% of the total amount of carbon. The results also indicate a greater share of this form of carbon in the interstitial water of polymictic lakes, probably due to more intensive organic matter mineralization in such lakes.

The content of IC in water varies with depth, which is a consequence of an increased CO₂ solubility in cooler water. In the hard-water eutrophic lakes,

CO₂ becomes especially depleted in the epilimnion due to photosynthesis and precipitation of calcite. An increase in IC found in the hypolimnion corresponds mainly to the dissolution of calcite and decomposition of organic matter (XU et al. 2012). This assumption is supported by the results showing that the content of IC increased with the depth, reaching the highest value in the lower layer of interstitial water. In the analyzed lakes, the highest IC values were recorded in winter, resulting from the prevalent meteorological conditions during that season and IC content was less varied than the TOC content.

Among all the lakes, the highest IC content was found in Track Lake. This was reflected by the trophic index based on chlorophyll *a*. The inorganic form of carbon alongside the high availability of phosphorus in water (a high trophic index based on total phosphorus) promote excessive growth of phytoplankton, adding to the degradation processes of the lake. However, the smallest amount of IC throughout the whole research was determined in Tyrsko Lake. A small amount of IC co-occurring with a high amount of available phosphorus (TSI (TP) = 65.23, Table 1) may indicate limitation of the primary production by IC. However, there is a risk that if larger quantities of IC are delivered from the basin or atmosphere, Tyrsko Lake can undergo rapid eutrophication.

Conclusions

The carbon cycle in lake water depends not only on the influx of this element from the catchment, but also on its release from the bottom sediment, which can be a large reservoir of organic carbon in lakes. Bottom sediment have a dual role. On the one hand, they may lock nutrients from a water body; on the other hand, they can release large amounts of nutrients into water, contributing to the degradation of a lake. The release of carbon into water will depend on the mictic status of a lake. In a polymictic lake, the highest content of organic carbon was in the surface (0–5 cm) layer of bottom sediment, while in dimictic lakes the 5–10 cm layer of sediment contained most organic carbon. Polymictic lakes are shallower and mineralization processes in such lakes are accelerated by more frequent mixing of water masses than in dimictic lakes, so that more organic carbon is released from sediment of polymictic lakes.

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