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ISOTOPIC EFFECTS OF SUSPENDED ORGANIC MATTER FLUXES IN THE SOLINA RESERVOIR (SE POLAND)

The aim of the study was to describe the source and fate of lacustrine suspended organic matter on the basis of nitrogen and carbon isotope effects. During complete depletion of dissolved silica in epilimnion, the differences in nitrogen isotope between substrates and products show that a primary production of organic matter (OM) in the euphotic zone of the reservoir is stimulated by nitrates. Additionally, in the hypolimnion, the decomposition of OM occurs, which in the case of a high primary production may lead to oxygen depletion.

1. INTRODUCTION

Deposition of organic matter (OM) in the whole bottom sediments of the Solina Reservoir results from two reasons: loading with terrestrial organic matter (OM) and primary production. Backwater sediments are mainly of terrestrial origin (~75%), therefore lacustrine sediment is formed due to plankton production (~70%) [9]. The aim of the study was to describe the source and fate of lacustrine suspended organic matter on the basis of nitrogen and carbon isotope effects. This information will be useful for the calculations of permissible discharges of biogens from the catchment area [15] and delays possible expensive restoration [21].

The source of suspended OM and OM fate in lentic ecosystems are described based on stable isotope fractionation from substrates ($N\text{-}NO_3^-$) to products (particulate organic nitrogen – PON). The uptake of nitrogen by plankton leads to the depletion of light isotope ^{14}N, therefore OM is isotopically lighter than NO_3^-. The values of the $\delta^{15}N\text{-}NO_3^-$ becomes higher than those of $\delta^{15}N\text{-}PON$; moreover, a concentration of the $N\text{-}NO_3^-$ in superficial water decreases simultaneously with the growth of PON [6], [12], [17]. Nevertheless, the described isotope effect is unequivocal, provided that

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a primary production is the primary source of OM (e.g. in marine waters) [1], [6]. That effect may be blurred due to higher loads found in a substantial majority of the lakes, estuaries and reservoirs with terrestrial OM and biogens from different sources (e.g. manure, sludge, etc.) [2], [8], [13], [20]. In this situation, $\delta^{15}N\text{-}NO_3^-$ is lesser than $\delta^{15}N$-PON [15]. Additionally a microbial decomposition of seston is connected with the depletion of nitrogen lighter isotope and with $\delta^{15}N$-PON decreasing. Finally, the $\delta^{15}N$-PON can be altered by zooplankton grazing, microbial decomposition processes carried out by microorganisms, protein hydrolysis [12] and the results of the balance between nutrient uptake and OM decaying isotope effects. Additionally the nitrogen isotope effect may be supported by carbon isotope. The uptake of lighter ^{12}C isotope is observed during photosynthesis [6], so residual CO_2 is richer in heavier ^{13}C isotope [3], [6].

2. MATERIAL AND METHODS

The Solina reservoir is the biggest man-made lake in the Vistula basin and accounts for about 15% of total water storage capacity in Poland. Morphometry of the reservoir is shown in figure 1, and other parameters are in detail described in former papers [9], [10].

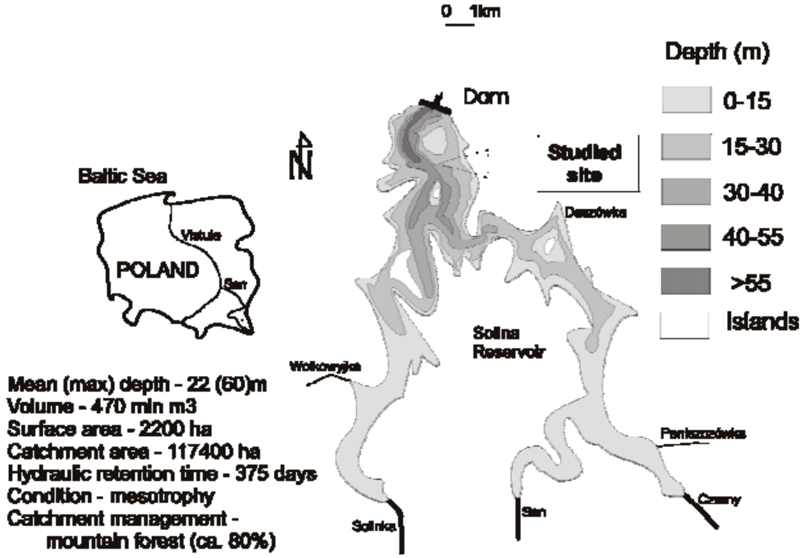

Fig. 1. Bathymetric chart and parameters of the sampling site

Water samples were collected from the site located in the lacustrine zone of the reservoir using a 5-dm^3 Ruttner sampler. Former studies [9] showed this site as the place where primary production is the main source of organic matter. The studies were conducted during summer stagnation and when photosynthetic conditions were good (14th August of 2007, 1:00 p.m., air temperature of 27 °C, strong sun). 9 samples were taken every 5 meters from the surface to the bottom sediment. Dissolved oxygen (DO) concentration and temperature were measured in situ, using ProfiLine Oxi 1970i (WTW, Germany). Aliquot of 100 cm^3 was stored in a glass bottle for total organic carbon (TOC), inorganic carbon ($C\text{-}CO_2$) and chlorophyll *a* (chl *a*) analyses, and the remainder was filtered through a precombusted Whatmann GF/C filter. Filtrate was measured for nitrate nitrogen ($N\text{-}NO_3^-$), ammonia nitrogen ($N\text{-}NH_4^+$) and dissolved silica (DSi) concentrations, using standard colorimetric methods (described in detail in [9]). Total carbon forms and dissolved organic carbon (DOC) were identified in raw and filtered samples, respectively, using an automatic $TOC\text{-}V_{CPN}$ analyser (Shimadzu, Japan). Particulate organic carbon (POC) was calculated as the TOC – DOC difference. Filters were dried at 50 °C and before the analysis of the organic carbon indicators exposed to fuming concentrated HCl for 72 h in an exicator for the purpose of removing carbonates. Filters were also analysed for particulate organic nitrogen (PON) using an elemental analyser (Flask 1112, ThermoQuest, Italy). The ^{15}N:^{14}N and ^{13}C:^{12}C ratios of isotopes shown as $\delta^{15}N$-POC and $\delta^{13}C$-POC were measured, using a DELTA^{Plus} isotopic ratio mass spectrometer (Finnigan Mat, Germany) coupled with the elemental analyser. Isotope composition of inorganic nitrogen ($\delta^{15}N\text{-}NO_3^-$) and carbon ($\delta^{13}C\text{-}CO_2$) was analysed in filtrate according to the methods described by SILVA et al. [19] and MIYAJIMA et al. [14], respectively. Isotopic values were expressed in per mille (‰) versus air and PDB standards, respectively, as follows:

$$\delta^{15}N \quad \text{or} \quad \delta^{13}C = (R_{\text{sample}}/R_{\text{standard}} - 1) \cdot 1000,$$

where R denotes ^{15}N:^{14}N and ^{13}C:^{12}C. The methods were calibrated using IAEA-N standards for $\delta^{15}N$ and the NBS22 standard for $\delta^{13}C$. The standard deviations of the isotopic analyses were less than 0.4 and 0.1‰, respectively ($n = 10$).

3. RESULTS

Superficial waters of the Solina reservoir were well oxygenated (figure 2A). Thermocline and oxycline were present at the depth of 10–15 m. DO concentration decreased from 9.5 g O_2 m^{-3} in epilimnion to 5–6 g O_2 m^{-3} in hypolimnion. In near-bottom waters the oxygen depletion occurred (< 2 g O_2 m^{-3}). The temperature in epilimnion and hypolimnion averaged 23 °C and 10 °C, respectively (figure 2A). Far-reaching depletion of dissolved silica (DSi) was observed in the epilimnion, where concentrations of DSi reached < 1 g Si m^{-3}, while in hypolimnion it was >3 g Si m^{-3} (figure 2B). Chlorophyll *a* was found mainly in the euphotic zone and ranged to 3.3 mg m^{-3} (figure 2B). At the depth of 10 m the water was found to contain traces of chlorophyll *a* from OM sedimentation and water mixing.

Inorganic and organic carbon identified in epilimnion and hypolimnion showed unequal distributions. Inorganic carbon (bounded and free CO_2) concentration decreased from 21.8 g C m^{-3} near to air/water interface to ca. 23 g C m^{-3} in hypolimnion (figure 2C), while in the case of TOC, C depletion ranged from 4 g C m^{-3} to 2 g C m^{-3} going down the profile (figure 2D). These TOC concentrations were limited by POC, not by more homogeneous DOC (figure 2D). Simultaneously with a C-CO_2 decrease observed down the water column, ^{13}C depletion expressed as δ^{13}C-CO_2 decreased from –6‰ to –11‰ (figure 2E). Moreover, a significant linear correlation between C-CO_2 depletion and δ^{13}C-CO_2 value was indentified (n = 9; R = –0.9115; R^2 = 0.8308; $p < 0.001$). A significant influence of C-CO_2 concentration on δ^{13}C was also identified in the case of organic forms. δ^{13}C-POC ranged from –27.21‰ (surface) to –27.61‰ (bottom) (figure 2H) and was significantly correlated with POC (n = 9; R = 0.9277; R^2 = 0.8606; $p < 0.001$).

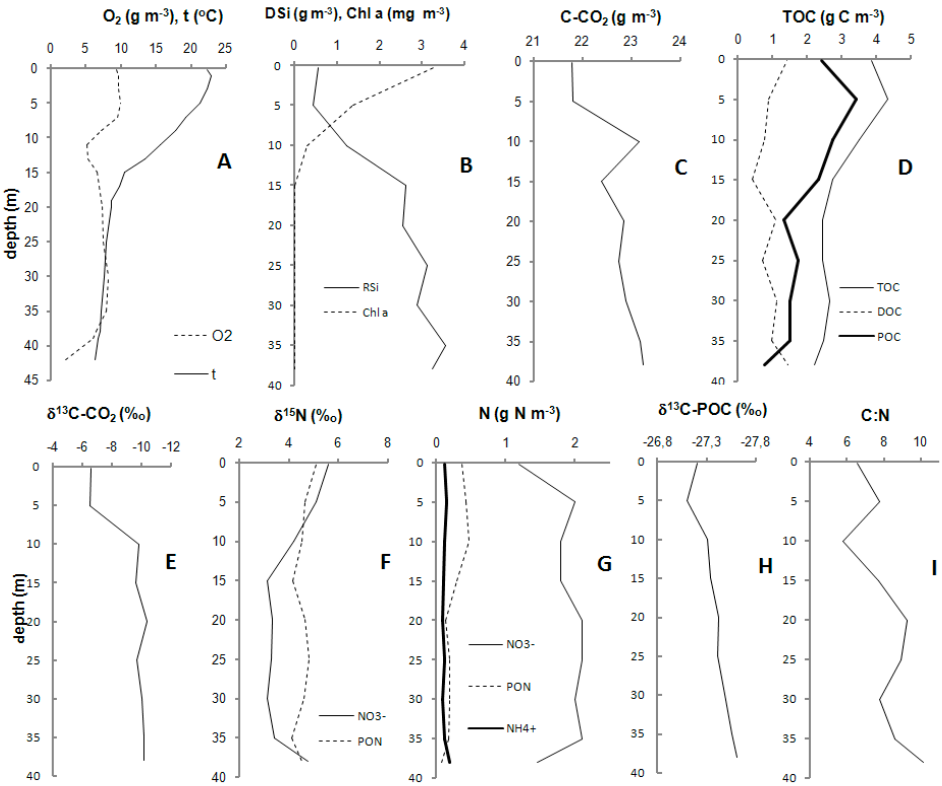

Fig. 2. Vertical distribution of parameters analysed in the lacustrine zone of the Solina reservoir. Denotations as in the text

Concentration of nitrate nitrogen was lower in both surface and near-bottom layer (<1.5 g N m^{-3}). In other waters, nitrate concentration ranged from 1.8 to 2.1 g N m^{-3} (figure 2G). Concentration of the ammonia nitrogen increased with the water depth from 0.12 to 0.19 g N m^{-3} (figure 2G). Epilimniom was richer in particulate organic nitrogen (PON) than hypolimnion (0.3–0.5 g N m^{-3} vs. 0.08–0.2 g N m^{-3}); moreover, a clearly lower PON concentration in the near-bottom layer was noted (figure 2G). The values of δ^{15}N-PON were stable with depth (4.5–5‰); however, δ^{15}N-NO_3^- decreased in epilimnion from its surface (5.6 ‰) to thermocline zone (3.2‰), and further was stable in hypolimnion down the near-bottom waters where ^{15}N isotope reached 4.8‰ (figure 2F). Contrary to the deeper parts of the Solina reservoir water, in the euphotic zone nitrates were generally richer in ^{15}N than in PON (figure 2F). C:N ratio increased from 6.5:1 to 10:1 down the water profile (figure 2I).

4. DISCUSSION

The analysis of vertical distribution of the parameters analysed testifies to the significance of the primary production of OM in lentic zone of the Solina reservoir. Significant linear and inversely proportional relationships exist between DSi and chlorophyll *a* ($n = 9$, $R = -0.7844$, $R = 0.6152$, p = 0.012), which means that the summer depletion of silica encourages the growth of phytoplankton, especially non-siliceous organisms [4], [18]. Additionally, the significant influence of DSi on TOC and POC ($n = 9$, $R = -0.9614$, $R^2 = 0.9242$, $p < 0.001$ and $n = 9$, $R = -0.8373$, $R^2 = 0.0.7011$, $p < 0.01$, respectively) confirms that DSi is the limiting nutrient and that primary production depends on N:P ratio. In the Solina reservoir, primary production isotope effect was clearly visible in the euphotic zone of lacustrine waters. At the depth of 5–7 m under the water surface δ^{15}N-NO_3^- was greater than δ^{15}N-PON by 0.5‰. Moreover, the surface water was poorer in nitrates than the depths. Despite the fact that highly eutrophic ecosystems are characterized by a clearer isotope effect and nitrate depletion (>3‰ and >1 g N m^{-3}, respectively [12], [17]), in the site analysed nitrates are most essential for OM production. These facts are confirmed by a significant correlation between N-NO_3^- and δ^{15}N-NO_3^- ($n = 9$, $R = -0.7279$, $R^2 = 0.5298$, $p < 0.05$) [1]. The above mentioned effect of blurring a primary production by nitrates of external (terrestrial) origin is improbable because δ^{15}N-NO_3^- in nitrates supplied to the reservoir was on average 3.5‰ [9], i.e., by 2‰ less than in superficial waters. This interpretation is confirmed by the carbon isotope effect. The uptake of lighter ^{12}C isotope is observed during photosynthesis [6], so residual CO_2 is richer in heavier ^{13}C isotope [3], [6]. In the case analysed, a decrease in δ^{13}C-CO_2 from –6‰ to –11‰ is in line with a decrease in C-CO_2, therefore ^{12}C depletion may be a consequence of photosynthesis.

In the hypolimnion of the lacustrine zone of the Solina reservoir, OM is decomposed, especially in the presence of oxygen (~5 g O_2 m^{-3}). Because this decomposition is effective, OWO, POC and PON in depths occur in low concentrations. This is confirmed by a significant correlation between δ^{13}C-POC and C:N ratio ($n = 7$, $R = -0.7207$, $R^2 = 0.5194$, $p < 0.05$). A similar phenomenon was described by de JUNET et al. [7], who found an inverse proportional influence of ^{12}C depletion on C:N ratio and interpreted it as OM decaying down the reservoir waters column. It can be stressed that the enrichment of near-bottom waters with ^{15}N may be connected with denitrification. The isotope effect during denitrification is associated with an increase in δ^{15}N value of residual nitrates [5], [13]. In eutrophic Lake Lugano [11], there is reported an enrichment of residual nitrate by 10‰, and in the Solina reservoir profundal denitrification rates are relatively slow (about 1.5 mmol N_2 m^2 day^{-1}, limiting the role of temperature [10]) and the diversification observed may correspond to this phenomenon.

5. CONCLUSIONS

1. Organic matter primary production in the lacustrine zone of the Solina reservoir during summer stratification is limited by dissolved silica.

2. During a complete depletion of DSi the nitrogen isotope effect of the substrates on the products in the euphotic zone of the reservoir proves that OM primary production is controlled by nitrate concentrations.

3. In hypolimnion, there is observed OM decomposition, which in the case of intensification of primary production may lead to oxygen depletion.

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