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Original Research

An isotopic model for the origin of autochthonous organic matter contained in the bottom sediments of a reservoir

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ABSTRACT

Geochemical analysis of surface sediment samples collected in 2005 and 2006 was used to evaluate the potential sources of the organic matter present in sediments of southeast Poland's Solina Reservoir. Statistical analysis of sediment variables (carbon to nitrogen ratio, and the carbon 13 and nitrogen 15 isotope ratios) determined for the organic fraction indicated significant spatial variability with respect to sources of organic matter. A binary mixing model was developed from literature sources to predict the relative contributions of allochthonous and autochthonous production to sediment organic matter. Autochthonous production was shown to account for 60–75% of bulk sedimentation in the lacustrine parts of the reservoir, near the dam. In contrast, autochthonous production accounted for only 25% of sedimentation in the riverine zone receiving stream inputs. Statistical analysis identified the δ^{15}N of organic matter as the best predictor of the source of organic matter. Multiple regression analysis indicated that two water-quality variables (nitrate and dissolved silica) were significantly related to the δ^{15}N signature of organic matter. This led to a conclusion that limnetic nitrate and dissolved silica concentrations were regulating organic matter production in the Solina Reservoir.

1. Introduction

Identification of the sources, directions of transport, and fate of organic matter (OM) in aquatic ecosystems currently represents one of the main courses of research development of limnology and oceanography (Alin & Johnson, 2007; Kruger et al., 2016; Smal et al., 2015). The formation of bottom sediments, as inseparably linked with a reservoir's accumulation of matter from its drainage basin, is related to the sedimentation and simultaneous early diagenesis (Patience et al., 1995) of OM containing biogenic elements. Quantitative estimation of the permanent accumulation of carbon or nitrogen in bottom sediments is vital in determining the global balance of these elements (Chen et al., 2015; Lehmann et al., 2002), especially where immobilization of nitrogen or phosphorus in bottom sediments represents a key mechanism curbing eutrophication (Gołdyn et al., 2003; Grochowska et al., 2015).

Sources of OM in aquatic ecosystems are typically classed as either allochthonous (terrigenous) or autochthonous (planktonic). Given the abundance of biogenic compounds, OM deriving from ecosystem production can exert a vital influence on the amount of bottom sediment present in stagnant water in reservoirs. Various studies show that up to 35% of the OM produced in the euphotic layer of a reservoir goes on to enrich the surface layer of bottom sediment (de Junet et al., 2005; Lehmann et al., 2002; O'Beirne et al., 2015; Wiatkowski, 2010). On a global scale, the mineralization-related formation of sediments leads to the permanent accumulation of only 0.1% of the net primary production (Lehmann et al., 2002). However, paleolimnological studies show that the process of aggradation of bottom sediments is directly proportional to an increase in primary production (Tadonléké et al., 2000; Tyson, 2001).

Thus far, the most common method to identify the origin of organic matter in bottom sediments has been analysis of changes in the content of organic carbon (TOC) relative to nitrogen (TN) (the C/N ratio). A high C/N ratio is characteristic of organic matter originating from the sedimentation of terrigenous substances; this is the same as for cellulose, as a component of land plants. Autochthonous (planktonic) matter is characterized by lower values for this ratio (approximately 6/1), as algal debris contains more nitrogen than matter originating on land (Calvert, 2004, de Junet et al., 2005; Gu et al., 1999; Koszelnik, 2009). Analysis of the stable-isotope ratios of carbon and nitrogen has become increasingly popular as a method by which to evaluate the origins of bottom sediments (e.g., Hou et al., 2013; Koszelnik et al., 2008;

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Murase & Sakamoto, 2000; Zigah et al., 2012). Such methodologies are based on the rationale that the deposition of organic matter in bottom sediments represents the final stage in a series of transformations of carbon and nitrogen compounds within the land and water column that affect the relative abundance of isotopes. This deposition results in a difference in content with respect to the $^{15}N/^{14}N$ and $^{13}C/^{12}C$ isotopic ratios, in bottom sediments of different origins.

While the isotopic ratios of carbon or nitrogen, expressed as $\delta^{13}C$ or $\delta^{15}N$, often serve as tools in the identification of OM origins in bottom sediments, they have been used only rarely in the quantitative analysis of sediment deposition (Hou et al., 2013; Koszelnik et al., 2008; Zhang et al., 2017). Considering the possibilities for isotopic analysis to serve this kind of purpose was, thus, the main aim of the work described in this paper, which considered a large piedmont dam reservoir of mesotrophic character. The highlights of the study described concern ways in which stable-isotope datasets from reservoir surface sediments can complement site-specific studies of isotope processes, helping identify key processes controlling the accumulation and degradation or reservoir sediment. Solina Reservoir's close similarity to many others ensured its status as a perfect testing ground for interpretation of the foregoing kind of analysis.

2. Materials and methods

2.1. Study site

The research detailed here was done in the dimictic, mesotrophic Solina Reservoir (Fig. 1), a part of Poland's Vistula-San river system, situated in the upper part of the catchment area (at c. 450 m above sea level). The reservoir accounts for approximately 15% of the overall water storage in Poland, having a volume of c. 470 M m^3, and a surface area of 22 km^2. The hydraulic retention time (HRT) is on the order of 150–350 days, while mean depth is 22 m (maximum 60 m). The fluctuation in water levels is up to 10 m, leading to a reduction of the littoral zone. The reservoir came into existence in 1968. Its (1175 km^2) catchment area comprises the Bieszczady Mountains, which are dominated by forests and mountain pastures. Farmland and settlements are mainly located at the mouths of the tributary valleys. The reservoir supplies a hydroelectric power plant, but also serves for flood control, recreation and the water supply.

2.2. Sampling strategy

Bottom sediment cores were collected using a gravity sampler in the March-November periods of 2005 and 2006 (on 18 occasions), at four sampling sites (S1-S4) located along the studied reservoir's longitudinal axis (Fig. 1). The shallower (~15 m-deep) Sites S1 and S2 were located in upstream areas of the reservoir (Fig. 1), and were characterized by an OM sedimentation rate of ~3000 t yr^{-1} (Bartoszek & Koszelnik, 2016). The downstream Sites S3 and S4 were in turn at greater (respectively 45, and 55 m) depths, and their OM sedimentation rates were lower (at ~1400 t yr^{-1}; Bartoszek & Koszelnik, 2016). Reservoir water was sampled at the aforementioned stations on the same occasions as bottom sediment was collected.

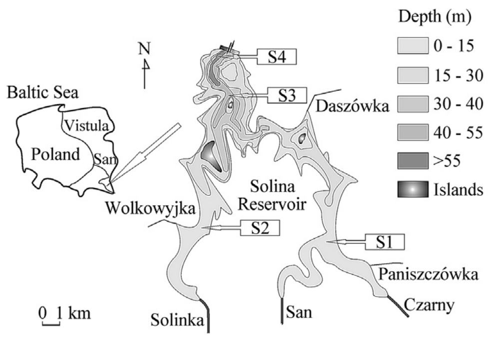

Fig. 1. Bathymetric chart of the Solina Reservoir showing the locations of the sampling sites (S1-S4).

2.3. Laboratory analysis

Each analysis related to a thin (2 cm) upper layer of sediment, which was dried at 60 °C, milled, and subjected to the removal of the carbonate fraction via 72-h contact with the vapour of 30% hydrochloric acid in a desiccator. The content of OM was analyzed using the loss ignition method, at 550 °C for 4 h. The contents of TOC and TN were measured using an elemental analyzer (Flask 1112, ThermoQuest), with a standard deviation less than 0.05 and 0.01%, respectively. Biogenic silica (BSi) was analyzed after Teodoru et al. (2006), to a precision of 10%. All parameters were expressed as percentage of dry mass (%). The N and C isotopic compositions were detected using a DELTA^{Plus} isotopic ratio mass spectrometer (Finnigan Mat), as coupled with an elemental analyzer. $\delta^{15}N$ and $\delta^{13}C$ values were expressed in permil (‰), as set against the respective Air and Pee Dee Belemnite (PDB) standards as follows:

$$\delta^{15}\mathrm{N\ ord}\ ^{13}\mathrm{C} = (R_{sample}/R_{standard} - 1) \times 1000 \tag{1}$$

where R denotes ^{15}N:^{14}N and ^{13}C:^{12}C. The methods were calibrated using International Atomic Energy Agency-N (IAEA-N) standards for $\delta^{15}N$ and the National Bureau of Standards 22 (NBS22) standard for $\delta^{13}C$. The standard deviations of the isotopic analysis standards were $<$ 0.4‰ and $<$ 0.1‰, respectively ($n = 10$).

Waters collected were analyzed for nitrogen (total nitrogen - TN_{water}, and inorganic nitrogen – IN as the sum of nitrate, nitrite (NO_3^-) and ammonia nitrogen) and phosphate (PO_4^{3-}), dissolved silicon (DSi), chlorophyll *a* (Chl *a*) and dissolved oxygen content. Well–known, standard colorimetric methods were used in these determinations (Rand et al., 1976).

2.4. Calculations and statistical analysis

The fractional contributions of autochthonous OM to the thin (0–2 cm) upper layer of bottom sediment were estimated by reference to the binary mixing model (Murase & Sakamoto, 2000; Thornton & McManus, 1994). Relevant analysis concerned suspended matter collected at a depth of *ca.* 0.7 m from Sites S3 and S4 in July and August, and from Sites S1 and S2 in April. Determinations involved C/N, $\delta^{15}N$, and $\delta^{13}C$, with values obtained serving as end-member values of autochthonous and terrigenous OM.

The binary mixing model is:

$$Y_s = Y_a \cdot u_a + Y_t \cdot u_t \tag{2}$$

$$u_a = \frac{Y_t - Y_s}{Y_a - Y_t} \tag{3}$$

where:

Y_p is the value of C/N, $\delta^{15}N$, or $\delta^{13}C$ in the bottom sediment,
Y_a is the value of the C/N, $\delta^{15}N$, or $\delta^{13}C$ autochthonous end-member,
Y_t is the value of the C/N, $\delta^{15}N$, or $\delta^{13}C$ terrigenous end-member,
u_a is the share accounted for by autochthonous OM sources,
u_t is the share accounted for by terrigenous OM sources.

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