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Distribution and sources of organic matter in sediments of the south-eastern Baltic Sea

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ABSTRACT

Temporal and spatial distribution of sedimentary organic matter (SOM) as well as its sources in the south-eastern Baltic Sea were investigated. Organic matter was characterized by the organic carbon content, $\delta^{13}C$ and $\delta^{15}N$ signatures and C/N ratios. The sampling was performed in the coastal, offshore areas and in the Curonian Lagoon in the period from May 2012 to September 2014. The average elemental (C/N ~ 6.4) and isotopic composition ($\delta^{13}C$ from −29.6‰ to −24.9‰) of SOM suggested that during most of the year it was composed of both freshwater and marine phytoplanktonic material. Elevated $\delta^{15}N$ values (average ranging from 5.6‰ to 6.7‰) were detected in SOM from the Curonian Lagoon. This most likely reflected the increased isotopic signal of the Nemunas River ($\delta^{15}N$ ~ 8‰) derived from the anthropogenic input in the basin area. At the Baltic Sea offshore sites, SOM had lower $\delta^{15}N$ values ($\delta^{15}N$ ~ 3.5‰ on average), indicating phytoplankton blooms.

A two-end member mixing model based on the carbon stable isotopic composition showed that a large proportion (~90%) of SOM in the northern part of the Curonian Lagoon was of the freshwater origin. The allochthonous organic matter accounted for about 47% of SOM in the studied Baltic Sea area with the highest contribution (about 75%) within the Curonian Lagoon plume zone in the coastal waters.

1. Introduction

Particulate and sedimentary organic matter in marine waters originates from different allochthonous (e.g., terrestrial vegetation detritus, riverine plankton) and autochthonous sources (e.g., primary production within the coastal area). However, it is often difficult to distinguish their individual contribution (Maksymowska et al., 2000; Bănaru et al., 2007). The intense supply of organic matter to the upper sediment layer and its mineralization lead to the enhanced release of nitrogen and phosphorus from the sediments. This has been extensively reported for the central part of the Baltic Proper and the eutrophic estuarine ecosystems where formation of anoxic conditions in near-bottom water and sediments is regularly observed (e.g., Löffler et al., 2011; Zilius et al., 2015). Although an increase of the continental nutrient inputs has not been reported for the past 10–20 years, eutrophication and its consequences are still considered a major threat to the Baltic Sea ecosystem (HELCOM, 2011). Therefore, characterization of organic matter sources and its fate in the ecosystem is important for the efficient ecosystem management and establishment of appropriate environmental policies aimed at achievement of the good environmental status.

Stable carbon and nitrogen isotope ratios ($^{13}C/^{12}C$, $^{15}N/^{14}N$, or $\delta^{13}C$ and $\delta^{15}N$) are considered as good tracers for studying the origin and fate of organic matter (Maksymowska et al., 2000; Voss et al., 2005; Szczepańska et al., 2012). The concept is based on differences in the isotopic composition between terrestrial and marine materials. In C_3 terrestrial plants, the $\delta^{15}N$ and $\delta^{13}C$ signatures are low (~3‰ and ~ −28‰, respectively), and marine plankton is enriched in heavy isotopes of N and C (4‰–6‰ and −22‰, respectively). Freshwater algae in C_3-dominated environments tend to have $\delta^{13}C$ values ranging from −35‰ to −25‰ and $\delta^{15}N$ around 5‰ (Voss et al., 2005; Lamb et al., 2006; Bănaru et al., 2007 and references therein). These differences in $\delta^{13}C$ signals are mainly a result of differences in $\delta^{13}C$ values of the dissolved inorganic carbon (DIC) utilized by the phytoplankton and terrestrial vegetation. Organic matter produced by terrestrial plants and freshwater algae from atmospheric and dissolved CO_2 ($\delta^{13}C$ ~ −8‰)

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consequently has lower $\delta^{13}C$ signals. Marine phytoplankton utilizes predominantly dissolved bicarbonates HCO^{3-} with the $\delta^{13}C$ value of ~0‰ (Lamb et al., 2006 and references therein). Since $\delta^{13}C$ values are lower in terrestrial DIC compared to marine one, the decreasing terrestrial influence is reflected by increasing $\delta^{13}C$ values in phytoplankton towards the open Baltic Sea.

Even though the application of stable carbon and nitrogen isotopes is one of the techniques most commonly used for tracing terrestrial matter, the distinguishing of sources is not straightforward since the isotopic composition is often overlapping (Schoeninger and DeNiro, 1984). For this reason, an additional tracer such as the elemental C/N ratio is used with the C/N values of below 10 and significantly above 12 for distinguishing between organic matter of the planktonic and terrestrial origin, respectively (Müller and Mathesius, 1999; Szczepańska et al., 2012).

Although some studies based on the isotopic and elemental composition of organic matter report the terrestrial and riverine contribution to marine particulate and sedimentary material in the Baltic Sea (e.g., Müller and Mathesius, 1999; Maksymowska et al., 2000; Voss et al., 2000, 2005; Lesutienė et al., 2008, 2014; Szczepańska et al., 2012), the assessment for the south-eastern part of the Baltic Sea is still missing.

The previously published data on the isotopic composition of particulate (POM) and sedimentary (SOM) organic matter from the studied area (Voss et al., 2000; Lesutienė et al., 2008, 2014; Remeikaitė-Nikienė et al., 2012; Lujanienė et al., 2013) have shown a wide range of $\delta^{13}C$ (between −35.9‰ and −21.7‰) and $\delta^{15}N$ (between 0.9‰ and 10.7‰) values. However, those studies mainly focused on the POM distribution in the Curonian Lagoon and only a few samples were taken from the Baltic Sea coastal stations (and none of the samples were collected from the open waters).

Galkus and Jokšas (1997) investigated the composition of particulate and sedimentary material in the Curonian Lagoon by using the polarising microscope analysis. Their results showed that the most important source of organic matter in the Curonian Lagoon (south-eastern Baltic Sea) was the autochthonous phytoplanktonic primary production, the annual contribution of which to particulate organic matter ranged from 37% to 80% (depending on the season). About 19%–29.5% of biogenic matter was annually transported to the lagoon with the river runoff (mainly with the Nemunas River, which is the third largest one in the catchment basin of the Baltic Sea). The riverine phytoplankton dominated during the vegetation season and the allochthonous organic matter input increased in winter (Galkus and Jokšas, 1997; Pustelnikovas, 1998). Tomczak et al. (2009) estimated the primary production in the Curonian Lagoon (1516 g C m^{-2} $year^{-1}$) and the Lithuanian Baltic Sea coastal waters (385 g C m^{-2} $year^{-1}$) using the ECOPATH approach and also stated that the largest proportion of the primary production was comprised of phytoplankton. Lesutienė et al. (2008, 2014) used the stable carbon and nitrogen isotope approach to study the transfer of organic matter across the Curonian Lagoon food web. The authors concluded that most of the particulate organic matter (POM) was derived from the phytoplanktonic primary production and the allochthonous detritus was not expected to substantially contribute to the general pool of POM. Macrophytes might be considered as an important source of sedimentary organic matter in the littoral zone of the Curonian Lagoon with the average contribution of 50%–80% in August–October (Lesutienė et al., 2008).

The main aim of this study was to describe the spatial and temporal variations of sedimentary organic matter (SOM) and assess the sources and fate of SOM via its isotopic ($\delta^{13}C$, $\delta^{15}N$) and elemental (C/N) ratios. Characterization of organic matter may be used in the further assessment of organic carbon transfer in the trophic web or provide a background information for the management decisions on the coastal Baltic ecosystems.

2. Methods

2.1. Study area

The area of this study includes the Lithuanian part of the Curonian Lagoon and the Baltic Sea (Fig. 1).

The Curonian Lagoon is the largest coastal lagoon in the Baltic Sea (total area of 1584 km^2, mean depth 3.8 m, maximum depth 5 m) connected to the Baltic Sea by the narrow (width 400–600 m) and artificially deepened Klaipėda Strait (Trimonis et al., 2003). The lagoon is mainly freshwater due to the high input of the Nemunas River (98% of the total freshwater input, mean annual runoff 632 m^3 s^{-1}), and only in the northern part of the lagoon is the salinity gradient approximately less than 0.5 to nearly 8. The average water residence time in the lagoon is about 80 days, but it varies spatially and depends on changes in river discharge conditions (Ferrarin et al., 2008). The Curonian Lagoon is a hypereutrophic system with values of chlorophyll a concentrations up to 400 μg l^{-1}, and recurring summer blooms of cyanobacteria, including the nitrogen fixer *Aphanizomenon flos-aquae* (Zilius et al., 2015 and references therein). The concentration of total suspended matter in the lagoon area (20.19 ± 22.48 g m^{-3}) is about 3 times higher compared to those in the Baltic Sea (Remeikaitė-Nikienė et al., 2012).

The main bottom sediment types in the lagoon area are sand, silt and shell deposits, with the dominance of sand fractions in the surface sediments (Trimonis et al., 2003). The shallow Curonian Lagoon is well mixed and sediment resuspension occurs in most of the lagoon area (Emelyanov, 2001).

Based on the HELCOM (2011) assessment, the total waterborne nitrogen and phosphorus input to the Baltic Sea from Lithuania is about 28,000 t and 1240 t per year, respectively (HELCOM, 2011). The figures do not reflect the real contamination since the assessment was made based on the nutrient concentrations in the Nemunas River flow. The actual loads through the Klaipėda Strait into the Baltic Sea have not been calculated so far due to the lack of information on changes of the nutrient balance in the Curonian Lagoon. The freshwater runoff from the Curonian Lagoon to the Baltic Sea through the Klaipėda Strait is approximately 27.7 km^3 $year^{-1}$ (Jakimavičius and Kovalenkovienė, 2010). According to the long-term observations and modelling results, this water moves in the Baltic Sea mostly along the Lithuanian coast northwards (Davulienė and Trinkūnas, 2004). As a consequence, the plume of the Curonian Lagoon waters in the Baltic Sea is characterized by a high variability in salinity, chlorophyll *a* and nutrient concentrations. The Baltic Sea area affected by the Curonian Lagoon plume ranges from about 112.98 km^2 up to 630 km^2 based on the satellite images (Remeikaitė-Nikienė et al., 2012; Vaičiūtė, 2012). The water salinity within the area is sometimes less than 1 as a result of the mixing of fresh lagoon water and seawater, meanwhile the water salinity is 7–8 some nautical miles away. Within the plume, the concentrations of phosphorus and nitrogen are up to 3–5 times higher than in the ambient sea water (Remeikaitė-Nikienė et al., 2012). As a consequence, concentrations of chlorophyll *a* are also elevated in this zone. For instance, in 2010–2011, chlorophyll *a* concentrations within the plume varied between 4.70 and 156.18 μg l^{-1}, while lower concentrations (2.23–20.16 μg l^{-1}) were measured outside the plume area. The measured average concentration of total suspended matter in the area affected by the outflow of the Curonian Lagoon was 12.79 ± 7.48 g m^{-3}, while about a threefold lower concentration (3.84 ± 1.59 g m^{-3}) was measured in the adjacent coastal waters (Vaičiūtė, 2012). In 2012–2013, the average concentration of DIN within the plume area was similar to that measured in the Curonian Lagoon (26.97 ± 33.99 μmol l^{-1} and 32.19 ± 40.17 μmol l^{-1}, respectively; Remeikaitė-Nikienė, unpublished data). It is estimated that around 50% of total sedimentary material is carried from the Curonian Lagoon to the sea (Pustelnikovas, 1998).

Sand and gravel are the typical sediments in the shallow and exposed Baltic Sea coastal waters, while aleurites and pelitic muds accumulate in a deeper area (Emelyanov, 2001; Bitinas et al., 2005). Active