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Distribution of metals and extent of contamination in sediments from the south-eastern Baltic Sea (Lithuanian zone)

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Summary The distribution of metals (Pb, Cu, Cd, Ni, Cr, Zn) in surface sediments and the potential pollution sources in the south-eastern part (SE) of the Baltic Sea (Lithuanian zone) were investigated in relation to the environmental characteristics (amount of fine-grained particles, TOC content in sediments, origin of sedimentary organic matter, salinity, water depth) in 2011–2014. The higher metal concentrations were measured in sediments of the Curonian Lagoon and in the open waters. An approach using various environmental indices (enrichment factor EF, geoaccumulation index I_{geo} and contamination factor CF) was used to quantitatively assess a contamination degree. The principal component analysis (PCA) was applied in order to further scrutinize pollution from metal sources. The values of the contamination with Cu, Zn and Pb and moderate—considerable pollution with Cd. The strong relationships among metals suggested their similar distribution pattern and a combination of natural and anthropogenic sources. The higher metal concentrations coincided with an increasing amount of fine-grained fraction and organic carbon. In the territorial waters, the distribution of elements was related to the water

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depth. In addition, the binding of metals with insoluble iron sulphides might explain their high concentrations at the most remote and deepest stations.

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1. Introduction

The intense development of anthropogenic activities since the late 19th century has resulted in enhanced loads of pollutants (e.g., nutrients, metals) from a large densely populated catchment area to the Baltic Sea (HELCOM, 2010). For example, a nearly threefold increase in Cu and Zn accumulation rates was observed in the Gulf of Finland from the period of 1850-1900 to 1975-1998 (Vaalgamaa and Conley, 2008). Metals enter the Baltic Sea either adsorbed onto suspended particles or in dissolved forms mostly through the rivers discharge (Leivuori et al., 2000; Yurkovskis and Poikane, 2008). The significant input of cadmium, lead and mercury via atmospheric deposition was also reported by HELCOM (2010). For instance, 47.5 tonnes of cadmium and 274.2 tonnes of lead entered the Baltic Sea as waterborne pollutants, while the atmospheric deposition accounted for 7.1 tonnes of cadmium and 234 tonnes of lead (HELCOM, 2010). In water systems metals tend to accumulate in sediments in association with organic matter, fine-grained sediments, sulphides and iron-manganese hydroxides and they may be released with changing conditions in sediments, such as changes in pH, dissolved oxygen or temperature (Dang et al., 2015; Leivuori et al., 2000). Several elements, such as Zn and Cu, are known to be essential elements for life, while others, such as Pb and Cd, do not play any physiological role and are highly toxic to all organisms even at low concentration (Jakimska et al., 2011). Therefore, among the metals, particular attention is paid to mercury, cadmium, lead and nickel which are identified as priority and priority hazardous substances by European Commision (Directive 2013/39/EU). To maintain marine ecosystems, management plans considering the human-induced contamination have to be established, where pollutant distribution and transport pattern, sources of contamination and behaviour in ecosystems need to be identified. Since metals originating from natural (e.g., erosion) and anthropogenic sources accumulate together in sediments, it is important (while not an easy task) to determine the ratio between the natural and artificial constituents of sediments (García et al., 2008; Ho et al., 2012).

A common approach to estimate an anthropogenic impact on sediments is to calculate the contamination factors for metal concentrations above uncontaminated background levels. For this purpose, many different enrichment calculation methods (e.g., enrichment factor, geoaccumulation index and contamination factor) have been used in various studies (e.g., Bonnail et al., 2016; Costa et al., 2015; Zalewska et al., 2015). In spite of many geochemical studies (e.g., Emelyanov et al., 2001, 2014, 2015; Mažeika et al., 2004; Pustelnikovas et al., 2007) in the SE Baltic Sea area, the results which concern the extent of the sediment pollution with heavy metals are lacking. The reported bulk metal concentrations may show the natural geochemical peculiarities in the region, however, they do not reflect the ratio between the natural and human-induced pollution of sediments. Moreover, due to the different methodologies (in particular, leaching methods) used by the scientists, it is difficult to compare and estimate the degree of the sediment pollution with heavy metals.

The main tasks of the present study were: (i) to evaluate the distribution of metals in bottom sediments of the SE Baltic Sea (Lithuanian zone) and to define the most polluted sites; (ii) to clarify the influence of the environmental factors (mineral and organic constituents of sediments, origin of organic matter, water depth and salinity) on the accumulation of metals; (iii) to identify the possible sources of contamination and the main driving factors in the Curonian Lagoon, Klaipeda Strait, coastal waters and offshore area. In order to assess a degree of contamination of the SE Baltic Sea, the enrichment factor (EF), the geoaccumulation index (I_{geo}) and the contamination factor (CF) were calculated. Results might be used in preparing the management plans and strategies for the initial assessment of the human-induced contamination in the SE Baltic Sea.

2. Methods

2.1. Study area

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

The Curonian Lagoon is a shallow semi-enclosed transitory brackish-to-fresh water body separated from the SE Baltic Sea by a narrow Curonian Spit (Fig. 1). The southern and central parts of the lagoon are freshwater (<0.5%), while the northern part is oligohaline with irregular salinity (from 0 to 8‰) fluctuations (Remeikaitė-Nikienė et al., 2012). The mean depth of the lagoon is 3.8 m. The lithological composition of the bottom sediments in the Curonian Lagoon is heterogeneous of the main 4 types — medium sand, fine sand, coarse silt and fine silty mud (Trimonis et al., 2003).

The lagoon is connected to the Baltic Sea through the narrow Klaipėda Strait where the Klaipėda town and the Klaipėda Port are located. This is the area where the intensive transfer and settling of sedimentary matter, provided by the Nemunas River and saline water, take place. The Nemunas River mostly supplies silty (0.01-0.1 mm) and clayey (<0.01 mm) particles into the lagoon, while saline water

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