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**DISTRIBUTION OF ORGANIC MATTER AND METALS IN THE
SOUTH-EASTERN BALTIC SEA (LITHUANIAN ZONE)**

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**ORGANINĖS MEDŽIAGOS IR METALŲ PASISKIRSTYMAS
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Abbreviations

- BAF – Biota accumulation factor or Bioaccumulation factor
- Chl-*a* – Chlorophyll *a*
- CF – Contamination factor with the individual metal
- C_d – an integrated Contamination degree of the study site
- DOM – Dissolved organic matter
- DIC – Dissolved inorganic carbon
- DIN – Dissolved inorganic nitrogen
- d.w. – dry weight
- EAC - Environmental assessment criterion
- EF – Enrichment factor
- EPA – Environmental Protection Agency
- E_rⁱ – Potential ecological risk index for each metal
- GES – Good environmental status as defined by the MSFD
- GGI of NRC – Geology and Geography Institute of the Nature Research Centre
- HELCOM – Helsinki convention
- I_{geo} - Geoaccumulation index
- KU MSTC – Klaipėda University Marine Science and Technology Centre
- LHS – Lithuanian Hydrometeorological Service under the Ministry of Environment
- MRD – Marine Research Department
- MSFD – Marine Strategy Framework Directive (2008/56/EC)
- OM – Organic matter
- PEL – the Probable effect level
- POM – Particulate organic matter
- PCA – Principal component analysis
- RI – an integrated Potential ecological risk of various metals
- SE Baltic Sea – South-Eastern Baltic Sea
- SOM – Sedimentary organic matter

Sub-GES – Unacceptable environmental status

SSRI CPST – State Scientific Research Institute Center for Physical Sciences and Technology

SQG – Sediment quality guidelines

TEL – the Threshold effect level

TOC – Total organic carbon

TSM – Total suspended matter

T_r^i – Toxic response factor

WFD – Water Framework Directive (2000/60/EC)

w.w. – wet weight

INTRODUCTION

Processes supplying organic matter and hazardous substances to seawater are especially intensive in coastal areas and semi-enclosed seas. 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. Consequently, the Baltic has often been referred to as the most polluted sea in the world (HELCOM, 2010). Considerable amounts of organic substances enter the Baltic Sea from rivers, appear in sea-water due to photosynthesis and other natural processes (excretion, respiration or decomposition) related to biota activities and are finally deposited in deeper basins of the Baltic Sea by horizontal near-bottom transport processes (HELCOM, 2011; Maciejewska and Pempkowiak, 2015). 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), while the information on organic matter (OM) origin and on processes in ecosystems is essential for applying appropriate environmental policies for mitigation and/or for preventing eutrophication and dystrophic events (Guerra et al., 2013). Moreover, decomposition of organic matter both in the water column and bottom sediments causes an internal supply of dissolved nutrients and thus contributes to ongoing eutrophication of the Baltic Sea and its lagoons (e.g., Dolenc et al., 2006; Schneider, 2011; Löffler et al., 2011; Zilius et al., 2015). Although the Curonian Lagoon is well-characterized with respect to phytoplankton succession dynamics, water mass mixing and residence time (Pilkaityte and Razinkovas, 2006; Gardino et al., 2010; Zemlys et al., 2013; Umgiesser et al., 2016), however, dynamics and cycling of organic matter in terms of riverine and marine POM input remain not well understood in this large eutrophic system. Therefore, understanding the characteristics, nature of

the organic matter, its cycling and the major controlling factors in the coastal ecosystems can provide interesting insights into the occurrence of natural and anthropogenic processes in the lagoon and its drainage basin.

The natural marine environment of the Baltic Sea is also susceptible to pollution by hazardous substances. Among pollutants, metals are of particular concern because of their persistence, biogeochemical recycling and environmental risk (Dang et al., 2015). The concern has arisen regarding the effects of an organism's exposure to the more subtle chronic and subchronic concentrations of certain elements that industrial and other human activities are releasing into the environment. Metals enter the Baltic Sea either adsorbed onto suspended particles or in dissolved forms mostly through the rivers discharge (Yurkovskis and Poikāne, 2008). The significant input of cadmium, lead and mercury via atmospheric deposition was also reported by HELCOM (2010). An example, 47.5 tonnes of cadmium and 274.2 tonnes of lead entered the Baltic Sea as waterborne, 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 may be released with changing conditions in deposited sediments, such as changes in pH, dissolved oxygen, temperature, or biological activity (Glasby and Szefer, 1998; Leivuori, 2000; Dang et al., 2015). Sediments can be a direct source of metals to sediment-dwelling or sediment-ingesting animals. Tissue metal concentrations can reflect contamination, and molluscs in particular may therefore be sensitive biomonitors of anthropogenic metal inputs (Hendozko et al., 2010).

In general, eutrophication and pollution caused by hazardous substances is a major environmental concern in European waters and consequently is addressed by a number of EU legislative measures and policies (Ahtiainen et al., 2014; Tornero and Hanke, 2016). The Water Framework Directive (WFD, 2000/60/EC), Marine Strategy Framework Directive (MSFD, 2008/56/EC) and regional Helsinki Convention – HELCOM) establishes a framework to prevent

deterioration, protect aquatic ecosystems and establish good ecological-chemical conditions in river basins districts and marine environments. To maintain marine ecosystems, management plans considering any human-induced pollution should be established, where pollutant distribution and transport pattern, sources of pollution and behavior in ecosystems should be identified. Since metals, originating from natural (e.g., erosion) and anthropogenic sources, accumulate together in sediments, it is important (while difficult) to determine the ratio between the natural and artificial constituents of sediments (García et al., 2008; Ho et al., 2012).

Stable carbon and nitrogen isotope ratios ($^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, or $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) are robust tools that have been frequently used to elucidate sources, mixing and transformations of carbon and nitrogen in the terrestrial, estuarine and coastal regions, based on different signatures of the sources. Although many 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 and Struck, 1997; Voss et al., 2000; Jönsson et al., 2005; Szczepańska et al., 2012), the assessment for the south-eastern (SE) part of the Baltic Sea is missing. The study conducted by Lesutienė et al., (2008, 2014) focused on the particulate organic matter (POM) distribution in the Curonian Lagoon during vegetation season and none of the samples were collected from the Baltic Sea open waters. Therefore, there is still a need for researches covering the complete network of the SE Baltic Sea (Lithuanian zone). Moreover, a quantitative assessment of marine and freshwater organic matter contribution in the mixed organic matter is useful for the environmental management purposes in order to evaluate the riverine impact.

As regards the contamination with metals, there are some comprehensive studies on metal in sediments of the SE Baltic Sea (e.g., Jokšas, 1994; Mažeika et al., 2004; Jokšas et al., 2005; Pustelnikovas et al., 2007; Emelyanov, 2001; Emelyanov et al., 2001, 2014, 2015), while, up to now, there is a lack of information about an extent of pollution of sediments and

quantification of metal contamination. Moreover, not much data are reported concerning metals in organisms relative to their concentrations in the associated sediments in the SE Baltic Sea, except for those reported by Garnaga (2011).

Aim and objectives of the study

The main task of this work was to assess the distribution pattern of organic matter and metals and to evaluate an extent of contamination of the south-eastern Baltic Sea.

The main objectives of the study were:

1. to analyze spatial and temporal distribution of carbon and nitrogen stable isotope composition of the particulate and sedimentary organic matter of the SE Baltic Sea and to determine the major processes that influence their dynamics.
2. to evaluate the relative contribution by different sources (marine, freshwater) to particulate and sedimentary organic matter in the SE Baltic Sea based on the isotopic data.
3. to estimate the pollution with metals (Pb, Cu, Cd, Ni, Cr, Zn) level and potential ecological risk to biota based on the different geochemical indices (EF, I_{geo} , CF, C_d , E_r^i , RI) and to evaluate the sources of pollution.
4. to evaluate the significance of sediment characteristics (amount of organic matter and its origin, mineral constituent) on the variability in the concentrations of the trace elements.
5. to evaluate the metal (Cd, Cu, Pb and Zn) concentrations in biota tissue and to compare the accumulation capacity of each element by mussels *Macoma balthica* (L.) and *Dreissena polymorpha* (Pallas).

Novelty of the study

In the present study, a quantitative assessment of the particulate and sedimentary OM sources (freshwater vs. marine) for the SE Baltic Sea was made, and an extent of the riverine impact was evaluated. The geochemical indices and risk assessment factors (EF, I_{geo} , CF, C_d , E_r^i , RI) were calculated for the wide area of the SE Baltic Sea and the sediment pollution extent was evaluated. The biota tissue contamination with the metals (Cd, Cu, Pb and Zn) was assessed and metal accumulation from sediments by mussels *Macoma balthica* (L.) and *Dreissena polymorpha* (Pallas) was evaluated.

Scientific and practical significance of the results

The results of this study may be used revising and updating the Nemunas River Basin District Management Plan as well as the national Marine Strategy since this study reveals and confirms the most polluted sites, clarifies the transport and accumulation pattern of OM and trace elements in sediments and molluscs, as well as evaluates the impact of riverine discharge to the coastal ecosystem. Characterization of the organic matter may be used as a background information for the further studies on the distribution of OM, eutrophication or organic carbon transfer in a trophic web as well as for the studies in modelling the marine carbon cycle and the saline water intrusions.

Author's contribution

Planning research activities (sampling sites, sampling time), contribution to sampling and initial suspended matter pre-treatment, evaluation of the national monitoring and projects' data, publication of the results.

Defensive statements

1. The seasonal and spatial variability in isotopic signatures ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of organic matter is determined by the riverine input, phytoplankton dynamics and successional change, seawater intrusions and uptake of the available dissolved inorganic carbon and nitrogen.
2. About 50% of organic matter in the south-eastern Baltic Sea (Lithuanian zone) is of the freshwater origin with a larger amount (~75%) in the Curonian Lagoon outflow area.
3. The sediments in the Curonian Lagoon and in the open sea are most polluted with cadmium, lead, zinc and copper, whereas pollution with nickel and chromium in the study area is negligible.
4. Bioaccumulation of Cu and Zn is higher in *M. balthica*, while Cd accumulates more intensively in *D. polymorpha*. Both species show poor bioaccumulation capacities for Pb.

Scientific approval

List of publications:

1. **Remeikaite-Nikiene, N.**, Lujaniene, G., Garnaga, G., Joksas, K., Garbaras, A., Skipityte, R., Bariseviciute, R., Silobritiene, B., Stankevicius, A., 2012. Distribution of trace elements and radionuclides in the Curonian Lagoon and the Baltic Sea. Baltic International Symposium (BALTIC), 2012 IEEE/OES doi: 10.1109/BALTIC.2012.6249205 Publication Year: 2012 , Page(s): 1 – 12. IEEE CONFERENCE PUBLICATIONS; <http://ieeexplore.ieee.org/document/6249205/>
2. Lujanienė, G., Garnaga, G., **Remeikaitė-Nikienė, N.**, Jokšas, K., Garbaras, A., Skipitytė, R., Barisevičiūtė, R., Šilobritienė, B., Stankevičius, A., Kulauskaitė, I., Ščiglo. T., 2013. Cs, Am and Pu isotopes as tracers of sedimentation processes in the Curonian Lagoon–

- Baltic Sea system. *Journal of Radioanalytical and Nuclear Chemistry* 296, 787–792.
3. Lujanienė, G., **Remeikaitė-Nikienė, N.**, Garnaga, G., Jokšas, K., Šilobritienė, B., Stankevičius, A., Šemčuk, S., Kulakauskaitė, I., 2014. Transport of ^{137}Cs , ^{241}Am and Pu isotopes in the Curonian Lagoon and the Baltic Sea. *Journal of Environmental Radioactivity* 127, 40–49.
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Other publications:

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- waters off Lithuania and in the Gotland Deep. Journal of Radioanalytical and Nuclear Chemistry 307, 2231–2237. DOI 10.1007/s10967-015-4547-x.
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List of conferences and seminars:

1. **Remeikaite-Nikiene, N.**; Lujaniene, G.; Garnaga, G.; Jokšas, K.; Garbaras, A.; Skipityte, R.; Bariseviciute, R.; Silobritiene, B.; Stankevicius, A. Distribution of trace elements and radionuclides in the Curonian Lagoon and the Baltic Sea. IEEE/OES Baltic 2012 International Symposium. Ocean: Past, Present and Future. Climate Change Research, Ocean Observations & Advanced Technologies for Regional Sustainability, May 8 – 11, 2012, Klaipėda.
2. **Remeikaitė-Nikienė N.**, Lujanienė G., Garnaga G., Jokšas K., Garbaras A., Skipitytė R., Barisevičiūtė R., Stankevičius A. Distribution of metals in the environment of the Baltic Sea and the Curonian Lagoon. The 3rd Conference of the PhD students and Young Scientists of the Center for Physical Sciences and Technology. September 25 – 26, 2012, Vilnius.
3. **Remeikaitė-Nikienė N.**, Lujanienė G., Barisevičiūtė R., Garnaga G., Stankevičius A. Characteristics of the suspended organic matter in the Baltic Sea and the Curonian Lagoon (Lithuanian zone): $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures. Scientific-practical Conference “Sea and Coastal research–2013”. April 3 – 5, 2013, Klaipėda.
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 6. **Remeikaitė-Nikienė N.**, Lujanienė G., Barisevičiūtė R., Malejevas V., Garnaga-Budrė G., Stankevičius A. Origin of the sedimentary organic matter in the Baltic Sea and the Curonian: the measurements of the $\delta^{13}\text{C}$ signatures. Conference „Sea Sciences and Technologies – 2014”. April 23 – 25, 2014, Klaipėda.
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 8. **Remeikaitė-Nikienė N.** The origin of organic matter in the Baltic Sea and the Curonian Lagoon: an approach based on the $\delta^{13}\text{C}$ signatures. The 4th Conference of the PhD students and Young Scientists of the Center for Physical Sciences and Technology. October 28 – 29, 2014, Vilnius.
 9. **Remeikaitė-Nikienė N.**, Lujanienė G., Malejevas V., Barisevičiūtė R., Garnaga-Budrė G., Stankevičius A. Seasonal changes in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures of suspended organic matter in the Curonian Lagoon. Scientific-practical Conference “Sea and Coastal research–2016”. April 27 – 29, 2016, Klaipėda.

1. LITERATURE REVIEW

1.1 Investigations of composition and sources of organic matter

1.1.1 Stable carbon and nitrogen isotope ratios

Provided that primary producers have distinct isotopic signatures, carbon and nitrogen stable isotopes signatures ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) constitute a powerful tool for discriminating among organic matter sources (Table 1.1.1). Differences between primary producers are due to difference in both the isotopic composition of inorganic nutrient (DIN, DIC) sources and the magnitude of discrimination against heavy isotopes during nutrient uptake and subsequent fixation by the plant (Cifuentes, 1988; Bănaru et al., 2007). An example, the main N and C source for terrestrial biomass is atmospheric N ($\delta^{15}\text{N}=\sim 0\text{‰}$) and CO_2 ($\delta^{13}\text{C}=-8$ or -7‰), whereas the marine primary production is fueled by nitrate ($\delta^{15}\text{N}=4-6\text{‰}$) and bicarbonate ($\delta^{13}\text{C}=\sim 0\text{‰}$) (Voss et al., 2000 and references therein; Lamb et al., 2006; Bade et al., 2006).

Stable carbon isotopes signatures. The isotopic composition of carbon in coastal areas is influenced by the external carbon sources (e.g. river loads and atmospheric deposition), isotope fractionation during processes such as primary production and air-sea CO_2 exchange, as well as production/mineralization of organic carbon (Alling et al., 2012; Gustafsson et al., 2015). The primary producers assimilate dissolved inorganic carbon (DIC) which is incorporated into a complex food web involving production and consumption of different forms of particulate (POC) and dissolved (DOC) organic carbon (Allan, 1995; Alling et al., 2012). CO_2 and HCO_3^- are the main components of soil water DIC. At pH around 6 both species are equally abundant, CO_2 dominates at lower and HCO_3^- at higher pH (Lamb et al., 2006; Guerra et al., 2013). The primary producers prefer dissolved CO_2 for carbon uptake which has more negative $\delta^{13}\text{C}$ values ($\delta^{13}\text{C}=-8\text{‰}$ if in equilibrium with atmospheric CO_2) than bicarbonate does ($\sim 0\text{‰}$). Therefore, the high

availability of CO₂ in freshwater bodies results in lower δ¹³C values of the freshwater plankton (Table 1.1.1). In contrast, sea water plankton has to use the isotopically heavier bicarbonate once all dissolved CO₂ has been used up, and therefore, shows higher carbon isotope values (Müller and Voss, 1999 and references therein; Rolff, 2000; Lamb et al., 2006; Guerra et al., 2013).

During photosynthesis, plants preferentially acquire the lighter carbon isotope (¹²C) of DIC resulting in organic matter that is depleted in ¹³C compared to the initial C sources (Bade et al., 2006). The CO₂ diffusion model showed a decrease in the δ¹³C of plankton organic carbon relative to source CO₂ when CO₂ concentration increases and/or temperature decreases (Raven et al., 1993). The degradation of organic matter results release DIC that might be outgassed as CO₂ and leave isotopically heavier carbon of degraded OM (Alling et al., 2012). Some studies have shown that early diagenesis of OM resulted in a negative shift in δ¹³C (e.g., Gearing et al., 1984; Prahl et al., 1997; Bohlin et al., 2006), but other studies indicate that the δ¹³C of organic matter is resistant to isotopic alteration and changes of the carbon isotopic composition of the material usually are negligible (e.g. Schelske and Hodell, 1995; Chen et al., 2008).

In addition to variations in phytoplankton δ¹³C from the differing sources of inorganic carbon utilised in marine and freshwater environments, phytoplankton δ¹³C may also vary as a result of several physical and chemical characteristics of the environment, e.g. light intensity, temperature, pH and day length and by species (e.g., cell size and geometry) (Guerra et al., 2013 and references therein). For land plants, differences among photosynthetic pathways (e.g., C3 and C4) result in unique isotopic signatures among different types of plants (Bade et al., 2006). C4 plants are more common in tropical areas, especially the drier tropics, whereas C3 plants are common in temperate soils (Gliessman, 2000). An example the only C4 plant occurring in Poland is maize (corn) which occupies only 6% of cultivated land. Therefore, the contribution of C4 biomass to the isotopic composition of soil CO₂ must be negligible on the scale of the Vistula catchment (Wachniew, 2006). In a system

where soil CO₂ is primarily derived from decomposition of plant organic matter, the CO₂ produced has a δ¹³C in CO₂ value close to the initial substrate (i.e., -34 to -20‰ in the case of C3 plants and -16 to -9‰ in the case of C4 plants).

Stable nitrogen isotopes signatures. The initial source of all bioavailable-N to the oceans is the fixation of atmospheric N₂ by aerobic or anaerobic autotrophs, such as cyanobacteria, which transform molecular N₂ into organic matter (via NH₄⁺) with a small isotope fractionation (-4‰ to 0‰). Other primary photosynthetic organisms assimilate remineralized forms of nitrogen mostly as NO₃⁻ or NH₄⁺ (Ader et al., 2014 and references therein). Non N₂-fixing phytoplankton acquired N primarily as ammonium (82–98%), and secondarily as nitrate (15–18% in spring and autumn, but <5% in summer) (Ferber et al., 2004). The preferential assimilation of ¹⁴NO₃⁻ by phytoplankton produces PON that is deficient in ¹⁵N relative to the dissolved NO₃⁻ from which it is formed. Assuming a closed system, this phenomenon results in a progressive enrichment of ¹⁵N in the „pool“ of available NO₃⁻ in surface waters as the concentration of this nutrient decreases. As plankton continue to consume this NO₃⁻ rich in ¹⁵N, there is a progressive increase in the δ¹⁵N of their tissues (Waser et al., 1998; Savoye et al., 2003; Aguiñiga et al., 2010). Because of the lower rate of assimilation of ¹⁴NO₃⁻, under oligotrophic conditions the value of δ¹⁵N in the POM is less positive (i.e., lower) than it is during eutrophic conditions (Aguiñiga et al., 2010).

In contrast to C, the fluxes of N are substantially affected by human activities, including sewage discharge, agricultural activity (use of fertilizers and management of agricultural waste), and atmospheric inputs. Nitrogen is transported in several forms including particulate organic nitrogen (PON) and dissolved organic nitrogen (DON), nitrate, nitrite, and ammonium, and there is a substantial removal of N within catchments by denitrification. Stable nitrogen isotopes can thus be used to distinguish between natural and anthropogenic nitrogen sources in the ecosystems (Kuuppo et al., 2006; Dolenc et al., 2006).

The nitrate inputs from land, both diffuse runoff and riverine input, are isotopically enriched. Before industrialisation, $\delta^{15}\text{N}$ of dissolved inorganic nitrogen (DIN) in rivers have been between 2 and 4‰, similar to modern rivers draining pristine catchments in the northern Baltic Sea (Voss et al., 2005a), but increased N-input from fertilizer use and livestock farming over the last decades led to isotopic enrichment by isotope fractionation processes (Voss et al., 2005; Dähnke et al., 2008). An example, nitrate from rivers entering the German Bight have an elevated isotope signal with riverine signatures ranging from 8‰ to 12‰ (Dähnke et al., 2008; Johanssen et al., 2008).

The $\delta^{15}\text{N}$ transformations during bacterial decomposition of sedimentary organic matter usually result in an isotopically enriched (more positive) organic residue, probably due to kinetic isotope fractionation during protein hydrolysis (Thornton and McManus, 1994; Lehmann et al., 2002). As it was shown in the previous studies, the preferential loss of nitrogen during degradation of organic matter during early diagenesis and exposure to anthropogenic influences result in large variations in $\delta^{15}\text{N}$ signature and C/N ratio (Savoye et al., 2003; Dolenc et al., 2006; Chen et al., 2008; Brahney et al., 2014) making them sometimes problematic to be used as the tracers indicating organic matter origin. Since the measured $\delta^{15}\text{N}$ signals may reflect the extent of biogenic alteration they are, however, widely used in studies (e.g., Struck et al., 2004; Voss et al., 2005b; Lehmann et al., 2007; Serna et al., 2010) of major biogeochemical processes modifying $\delta^{15}\text{N}$ compositions of the various nitrogen pools (e.g., ammonification, nitrification, denitrification, nutrient assimilation, N_2 fixation).

It should be noted, that the $\delta^{15}\text{N}$ values of bulk suspended POM reflect planktonic organic matter, including each trophic compartment. The $\delta^{15}\text{N}$ signature increases with ca. 3–4 ‰, while the $\delta^{13}\text{C}$ signatures will increase up to 1 ‰ per trophic level (Schoeninger and DeNiro, 1984, Owens, 1987, Wada et al., 1991). Marine and freshwater zooplankton thus appear to have $\delta^{15}\text{N}$ values that are, on average, 3 ‰ more positive than those of phytoplankton, while the $\delta^{13}\text{C}$ values are quite similar (Table 1.1.1).

Table 1.1.1 Carbon and nitrogen isotopic signatures in several environmental objects.

Environmental component	$\delta^{13}\text{C}$, ‰	$\delta^{15}\text{N}$, ‰
Terrestrial C3 vegetation	range from -34 to -20 typically, -27 or -28	range from -5 to +18 typically, +3
Terrestrial C4 vegetation	range from -16 to -9 typically, -13	range from -5 to +18
Freshwater/estuarine phytoplankton	range from -35 to -25 typically, ~-30	typically, around 5
Marine phytoplankton	typically, range from -22 to -18	typically, range from 4 to 6
Freshwater zooplankton	from -32.6 to -29.3	typically, range from 8 to 14
Marine zooplankton	from -24.7 to -19.2*	typically, range from 6 to 10

Data compiled from: Meyers, 1994; France, 1994; Müller and Voss, 1999; Schubert and Calvert, 2001; Weiguo et al., 2003; Kritzberg et al., 2004; Goni et al., 2006; Bănaru et al., 2007 and references therein; Chen et al., 2008; Lesutienė et al., 2008; Böttcher et al., 2010; Ivanov et al., 2012; Guerra et al., 2013; Kuliński et al. 2014; Ogrinc et al., 2014; and references therein. *in copepods (Tamelander et al., 2008).

Even though the application of stable carbon and nitrogen isotopes is one of the techniques most commonly used for tracing organic matter, the distinguishing of sources is not straightforward since the isotopic composition is often induced by human activity causing overlapping of isotopic values. An example, the $\delta^{13}\text{C}$ values of sewage effluents overlap the values of terrestrial and marine sources and vary from -26‰ to -22‰ (Barros et al., 2010). POM from the sewage collectors of Brussels city, discharging into the Scheldt via the rivers Zenne and Rupel, had the average $\delta^{15}\text{N}$ value of +2.0‰ and $\delta^{13}\text{C}=-25.3‰$ (De Brabandere et al., 2002) relevant more to terrestrial C3 plants. Thus, a simple assignment of isotopic signatures of POM to different components without knowing of supporting environmental conditions and circumstances may lead to the wrong conclusions.

1.1.2 C/N and POC/Chl-a ratios

The use of other proxies such as the molar C/N and POC/Chl-*a* ratios in combination with the stable isotope compositions of organic carbon and nitrogen may be an additional tool to estimate relative contribution of terrestrial and marine sources and the fate of organic matter (Cifuentes et al., 1988; Maksymowska et al., 2000; Savoye et al., 2003). The C/N molar ratio generally ranges between 6 and 10 for phytoplankton and between 3 and 6 for

zooplankton and bacteria, and it is typically higher than 12 for terrestrial organic matter (Savoye et al., 2003; Szczepańska et al., 2012). The higher values of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ and lower C/N ratios, thus, would show an increased algal input to the organic matter. This ratio is therefore useful when one wishes to distinguish phytoplankton from heterotrophs and from terrigenous material. However, this tool must be used with caution because of its variation in the course of POM degradation: phytoplankton PON is preferentially degraded compared to POC, leading to a C/N increase, whereas terrestrial organic matter (high C/N ratio) colonized by bacteria (low C/N ratio) has lower C/N ratio. Thus degraded phytoplankton and bacteria-colonized terrestrial organic matter could have similar C/N ratios (Savoye et al., 2003; Guerra et al., 2013).

The POC/Chl-*a* ratios in phytoplankton may vary in a wide range from less than 10 to over 200 (Cifuentes et al., 1988; Erga et al., 2014 and references therein), while some authors (Barth et al., 1998; Maksymowska et al., 2000) suggest POC/Chl-*a* to be much lower than 100 as more indicative of photosynthetic activity with the higher values as typical of degraded material. Since chlorophyll *a* is degraded faster than the whole pool of POC, an increase in POC/Chl-*a* ratio during phytoplankton degradation exists (Cifuentes et al. 1988; Savoye et al., 2003).

1.2 Distribution and sources of organic matter in the Baltic Sea based on its isotopic and elemental composition

Source identification of organic matter by means of isotopic tracers as well as C/N ratios in the southern, central and northern parts of the Baltic Sea were previously described in many publications (e.g., Voss and Struck, 1997; Müller and Mathesius, 1999; Müller and Voss, 1999; Maksymowska et al., 2000; Rolff and Elmgren, 2000; Voss et al., 2000, 2005; Struck et al., 2000, 2004; Emeis et al., 2002; Miltner et al., 2005; Kuuppo et al., 2006; Savage et al., 2010; Szczepańska et al., 2012). The isotopic records were interpreted to trace the effects of eutrophication, riverine impact, diagenetical changes of OM

and an impact of the effluents, mostly by analyzing the sedimentary organic matter (SOM). Though, the amount of scientific studies addressing the origin of organic matter, its temporal and seasonal variability and the quantitative estimations of the sources in the SE part of the Baltic Sea is obviously scarce, whereas this area is highly impacted by discharge of the Nemunas River as well as other polluted southern rivers due to the prevailing westerly winds. The extent of the plume of the Nemunas River (Curonian Lagoon) into the Baltic Sea might be distinguished based on the salinity distribution, while the actual freshwater spreading zone might be masked due to rapid changes of physical-chemical variables (e.g., salinity and nutrients with changes of water masses). Therefore, the physical-chemical factors in relation with the biological variables might be the suitable indicators of the freshwater influence.

The previous results on the OM composition and sources reflected the variability in isotopic signatures of organic matter in the Baltic Sea on the temporal and spatial scales.

The **temporal** and **spatial** variability of the isotopic signatures in the OM was attributed to the seasonal changes in CO₂ in the water column as well as the assimilation of the “heavy” (enriched in ¹⁵N) riverine nitrate and “light” (depleted in ¹⁵N) atmospheric nitrogen (Maksymowska et al., 2000; Struck et al., 2000; 2004). The lower $\delta^{13}\text{C}$ values in POM during spring and autumn reflected the increasing riverine contribution and the increasing invasion of atmospheric CO₂ into the cold water. Because the lighter isotope is preferentially incorporated over the heavier one, nutrient uptake results in the enrichment of the heavier isotope in the remaining nutrient pool (i.e., $\delta^{13}\text{C}$ in DIC) and depletion in the product (i.e., $\delta^{13}\text{C}$ of POM). High C and N isotopic fractionation was observed when nutrients were in excess and did not limit primary production (Maksymowska et al., 2000; Struck et al., 2004).

The increase in $\delta^{15}\text{N}$ values in Baltic Sea coastal areas was related to higher nitrate contents of the river discharges and it was a sign of increasing use of artificial fertiliser in the catchment (Struck et al., 2000; Voss et al., 2000) as well as the impact of the waste water with the high $\delta^{15}\text{N}$ in nitrate

values (Voss et al., 2000; Kuuppo et al., 2006; Savage et al., 2010; Schubert et al., 2013). The nitrate which originate from sewage or agricultural runoff have the $\delta^{15}\text{N}$ values above 6‰, often between 8‰ and 12‰ and sometimes as high as 20‰ (Voss et al., 2000; Dolenc et al., 2006 and references therein). Therefore, the highest $\delta^{15}\text{N}$ in nitrate values were recorded in rivers with catchments dominated by fields and agricultural land and high population densities (>50 inhabitants km^{-2}). An example, the most highest $\delta^{15}\text{N}$ in nitrate values were reported for the Oder (7.6–8.3‰), Vistula (5.8 – 9.8‰), Peene (7.1‰) and the Nemunas (8.6‰) Rivers, while the reported $\delta^{15}\text{N}$ values for the Swedish-Finnish rivers as well as for the Neva River were lower (–0.1 to 3.1‰) (Voss et al., 2005b; Voss et al., 2006; Kuuppo et al., 2006; Korth et al., 2013). Nutrients often become enriched in heavy N isotopes during denitrification and nitrification which most often occur in the coastal areas and wastewater treatment systems (Cifuentes et al., 1988; Voss et al., 2005b; Kuuppo et al., 2006). The riverine nitrate and $\delta^{15}\text{N}$ signature are rapidly diluted towards open sea area to the $\delta^{15}\text{N}$ values of 3–5‰.

The riverine influence on the coastal and open areas was clearly reflected in the isotopic ($\delta^{15}\text{N}$, $\delta^{13}\text{C}$) signatures of suspended, dissolved and sedimentary organic matter (Voss and Struck, 1997; Voss et al., 2000; Maksymowska et al., 2000; Struck et al., 2004; Alling et al., 2008). Especially that was pronounced in the highly eutrophied southern part of the Baltic Sea. Voss and Struck (1997) reported $\delta^{15}\text{N}$ values of 10–14‰ in organic matter produced in the eutrophied coastal areas of the southern Baltic Sea, while the average $\delta^{15}\text{N}$ values in open sea were much lower (e.g., 6‰ in Arkona Basin or 3.4‰ in the Gotland Basin, Voss and Struck, 1997; Struck et al., 2004) (Table 1.2.1).

The primary producers will integrate available nutrients over time, depending on their growth rate and reflect those signatures. As it was demonstrated by Savage et al. (2010) for the Himmerfjärden and surrounding bays (along the Swedish coast), the wastewater N loads accounted for over half of the explained variance in SOM $\delta^{15}\text{N}$ values, which increased from 5.5‰ in

1974 when effluent discharge was initiated to 8.3‰ in 1990 when wastewater N loads peaked. Schubert et al. (2013) showed the usefulness of N isotopic signatures of wide spread eelgrass (*Zostera marina*) in the Baltic Sea as a proxy of sewage nitrogen. The authors showed that maximum values of $\delta^{15}\text{N}$ (up to 13.49‰) were from sites characterized by sewage N inputs, whereas minimum (−0.54‰) was close to those from relatively unaffected sites.

The average $\delta^{13}\text{C}$ values in POM and SOM in the Baltic Sea were mostly in the range from −30‰ to −21‰ (Table 1.2.1) with the most enriched carbon ($\delta^{13}\text{C} > -24\text{‰}$) in suspended matter and sediments towards open sea areas (e.g., Arkona Basin (Voss and Struck, 1997), Deeps of Gdansk and Gotland (Maksymowska et al., 2000; Voss et al., 2000; Struck et al., 2004) as well as Skagerrak, the Kattegat, the Danish Belts and Sounds (Miltner et al., 2005)). It was concluded that the $\delta^{13}\text{C}$ signature in OM in the western and central regions of the Baltic Sea was mostly determined by the marine phytoplankton with the $\delta^{13}\text{C}$ values of about −22‰.

The **vertical** changes of the isotopic signatures in sediment cores were also reported in many works (Voss and Struck, 1997; Müller and Mathesius, 1999; Müller and Voss, 1999; Struck et al., 2000; Voss et al., 2000; Miltner et al., 2005; Dähnke et al., 2008; Savage et al., 2010; Szczepańska et al., 2012). The previous studies focused on the relative importance of eutrophication and changes in organic matter provenance in sedimentary records from different depositional areas of the Baltic Sea (Kattegat and Skagerrak, Oder Lagoon and Pomeranian Bight, Arkona, Bornholm and Gotland Basins, Gulf of Riga, Gulf of Finland, Gdansk Deep and the Curonian Lagoon) by variation of the $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values and C/N ratios in the sediment cores through time.

Struck et al., (2000) showed that before 1900, the sedimentary records had the $\delta^{15}\text{N}$ values between 3 and 4‰ which nowadays are often recorded for the Baltic Proper sediments. The great overall difference between pre-industrial $\delta^{15}\text{N}$ values in coastal sediments and recent ones (2.3–10‰) was observed (Voss et al., 2000), but the amplitude of the change became less pronounced with increasing distance from land (Struck et al., 2000). The $\delta^{15}\text{N}$

values in the sediment cores showed distinct increases over the last 80–50 years in the Oder estuary, Arkona Basin and Bornholm Basin. In contrast, the Gotland Basin record showed increasing $\delta^{15}\text{N}$ signatures from 1900 to 1975 and decreased $\delta^{15}\text{N}$ values during the last 20 years. The switch to lower $\delta^{15}\text{N}$ values in the Gotland Basin sediment core after initially increasing values was explained by the increasing abundance of summer blooms of nitrogen fixing cyanobacteria. The $\delta^{13}\text{C}$ values of organic matter increased in the Oder estuary over the last 80 years and over the last 30 years in the Bornholm Basin and Gotland Basin (Struck et al., 2000).

An increasing accumulation rate of organic carbon and total nitrogen was also observed in the upper-most segments (10–15 cm) of the cores (Müller and Mathesius, 1999; Savage et al., 2010; Szczepańska et al., 2012; Winogradow and Pempkowiak, 2014) and it was explained by the increasing nutrient and organic matter load in particular over the last 50 years (Voss and Struck, 1997; Struck et al., 2000; Savage et al., 2010).

Based on the combined investigations of C/N ratios with the isotopic values of OM, macrophytes, macroalgae and seagrasses are considered as an important source of organic matter only in the shallow parts (e.g., Puck Lagoon, Curonian Lagoon, Oder Estuary) of the Baltic Sea (Müller and Mathesius, 1999; Müller and Voss, 1999; Maksymowska et al., 2000; Lesutienė et al., 2008). As it was shown by Müller and Mathesius (1999) for the southern Baltic Sea, the C/N ratios ranged between 10 and 85 in terrestrial plants, from 6 to 44 in aquatic macrophytes (with an average value of 17.5) and C/N values were close to 6 in plankton. A decreasing C/N ratio and $\delta^{13}\text{C}$ values in sediment cores towards the surface layer in the southern Baltic Sea reflected increasing eutrophication and a shift in the dominance of autochthonous organic matter sources from terrestrial vegetation to phytoplankton (Voss and Struck, 1997; Müller and Mathesius, 1999; Müller and Voss, 1999). Therefore, the C/N of OM, in conjunction with the $\delta^{13}\text{C}$ values, allow conclusions on organic matter provenance.

Table 1.2.1 Carbon and nitrogen isotopic signatures of POM and SOM measured in the Baltic Sea in the previous studies.

Sampling area	Sampling year and months	$\delta^{13}\text{C}$, ‰ Variability (from-to) or average \pm sd	$\delta^{15}\text{N}$, ‰ Variability (from-to) or average \pm sd	Reference
POM				
The Curonian Lagoon	2006, August – November	from –33.3 to –23.7	4–10	Lesutienė et al., 2008
Gdansk Deep	1996, annual mean	–22.3 \pm 0.4	1.5 \pm 0.8	Maksymowska et al., 2000
Gulf of Gdansk	2001, March, 2002, January	–26.0 \pm 1.0	6.0 \pm 1.5	Voss et al., 2005
Vistula River	1996, annual mean	–28.5 \pm 1.2	4.0 \pm 2.5	Maksymowska et al., 2000
The Gotland Deep, Baltic Proper*	1996, September – 1997, August	from –25.3 to –18.5 On the average, –21.7	0.4–6.7 On the average, 3.4	Struck et al., 2004
SOM (<10 cm)				
The Curonian Lagoon	2006, August – October	from –25.9 to –18.5	7.2–8.6	Lesutienė et al., 2008
Oder Lagoon and Pomeranian Bight	1993–1997	–27.5	10–14	Voss and Struck, 1997; Voss et al., 2000
Oder Lagoon	1994–1995	from –30.8 to –29.0	4.5	Müller and Voss, 1999
	1993–1997	~ –27.0; –28.0	~7–13	Voss et al., 2000
Arkona Basin	1997	–23.8	6	Voss and Struck, 1997
Gulf of Riga	1993–1997	from ~ –25.5 to –23.5	~6–8	Voss et al., 2000
Gulf of Finland	1993–1997	from ~ –25.5 to –23.0	~6–11	Voss et al., 2000
The Curonian Lagoon	1993–1997	from ~ –30.0 to –24.5	~6.0	Voss et al., 2000
Gulf of Gdansk, Gdansk Deep	1993–1997	–21.5; –22.0	~6	Voss et al., 2000
	2007	–24.61 \pm 0.22	-	Szczepańska et al., 2012
The Gotland Deep, Baltic Proper	2007	from –24.56 to –24.78	-	Szczepańska et al., 2012
	1993–1997	-	3–5	Voss et al., 2000

* Sedimenting particulate matter in 140 m water depth. Data from the sediment traps.

There are only several studies which report a quantitative assessment of terrestrial or lagoonal and marine OM contribution to the mixed POM (Voss and Struck, 1997; Rolff and Elmgren, 2000), SOM (Szczepańska et al., 2012) and DOM (Alling et al., 2008; Deutsch et al., 2012). Alling et al. (2008) estimated the share of terrestrial dissolved organic carbon in the water column

for the Bothnian Bay the Bothnian Sea, and the Baltic Proper of 87, 75, and 67%, respectively. Deutsch et al. (2012) provided the additional data during spring – summer and showed still high contribution of terrestrial DOM to the total DOM, ranging from 43 to 83%. Results demonstrated the high importance of the terrestrial DOM inputs for the Baltic Sea ecosystem and a decreasing contribution of terrestrial OM towards open sea.

1.3 Contamination of the Baltic Sea sediments with metals

Lead, copper, cadmium, chromium, nickel, zinc and aluminium are the naturally occurring metals usually found as mineral combined with other elements in the Earth's (continental) crust. However, in recent decades, there has been an increasing ecological and global public health concern associated with environmental contamination by heavy metals due to their intensive multiple applications. An example, about 79% of Cd, 52% of Pb, 31% of Cu, 50% of Zn and 77% of Hg accumulation in the northern part of the Baltic Sea is anthropogenically affected (Leivuori, 2000), while data of Glasby and Szefer (1998) showed that more than 90% of Cu, Zn and Pb were of anthropogenic origin. Reported sources of metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources. Environmental contamination can occur through metal corrosion, atmospheric deposition and sediment re-suspension. Natural phenomena such as volcanic eruptions have also been reported to significantly contribute to metal contamination (Nriagu, 1989).

The natural variability in trace metal content may be evaluated from the pristine (unpolluted) areas from deeper layer of sediment cores. In some studies, the trace metal concentrations from the sediment layers 24 – 25 cm (e.g., Leivuori, 1998, 2000) or 22 – 38 cm (Zalewska et al., 2015) were used as the reference or background values (Table 1.3.1). The average concentrations in the Earth's shale or crust (Table 1.3.1) have also been used for comparison with the metal concentrations in polluted sediments (e.g., Hamdoun et al., 2015).

Metals are considered as trace elements because of their presence in trace concentrations (ppb range to less than 10 ppm) in various environmental matrices (Kabata-Pendia, 2001). The term „heavy metals“ is usually applied to a group of metals and metalloids that are strongly toxic. They can be subdivided: (i) elements (Cu, Zn, Mn, Fe, Co, Mo) which are essential for the growth and life cycles of organisms, but are toxic at high concentrations; (ii) Hg, Cd and Pb – toxic even at low concentrations (Jakimska et al., 2011).

The metals are used in various industrial processes. An example, Cd is used in metallurgic industry, batteries, plastic production, phosphate fertilizers, detergents and refined petroleum products, as well as pigments, stabilizers for polyvinyl chloride (PVC), in alloys and electronic compounds. Cadmium coatings provide good corrosion resistance coating to vessels and other vehicles (Wuana and Okieimen, 2011; HELCOM, 2013). Lead ranks fifth behind Fe, Cu, Al, and Zn in industrial production of metals with about half of amount used in the U.S. for the manufacture of Pb storage batteries (Wuana and Okieimen, 2011). In the 1960s and 1970s, alkyl lead gasoline additives became the most important sources of atmospheric Pb pollution in the world. Lead additives (mainly tetraethyl lead) have been used in gasoline as anti-knocking agents since 1921. The EU banned leaded gasoline by the early 2000s (Zaborska, 2014). Cu and Zn are two important essential elements for plants, microorganisms, animals, and humans. Copper is the third most used metal in the world. Most Zn is added during industrial activities, such as mining, coal, and waste combustion and steel processing. The most common application of nickel is an ingredient of steel and other metal products. For animals Ni is an essential foodstuff in small amounts (Wuana and Okieimen, 2011).

Table 1.3.1 Metal concentration (mg kg⁻¹ d.w.) in the Earth's shale and some background values in sediments of the Baltic Sea.

	Pb	Cu	Cd	Ni	Cr	Zn	Al, %	Reference
The Earth's shale	20	45	0.3	68	90	95	8.00	Turekian and Wedepohl, 1961
Bothnian Sea (24-25 cm depth)	37	44	0.48	58	97	157	9.02	Leivuori, 1998
Bothnian Bay (24-25 cm depth)	30	35	0.32	48	41	99	7.6	Leivuori, 1998
Gulf of Finland (24-25 cm depth)	33	33	0.36	12	77	135	7.6	Leivuori, 1998
	21	25	0.11	-	-	100	-	Vallius and Leivuori, 1999
North Central basin, 24.5 cm	31.7	40.6	0.21	52.2	105	147	8.15	Kunzendorf and Vallius, 2004
Gdansk Deep, SE Gotland Basin, Bornholm Deep, (22 – 38 cm depth)	30	-	0.3	-	-	110	-	Zalewska et al., 2015
Eastern Gotland Basin, (mean in 25-31 cm depth)	35.3	68.8	-	-	-	134.5	6.37	Hille et al., 2005, 2006
Gotland Basin, 24.5 cm	52.5	45.1	1.01	53.7	84.4	159	6.87	Kunzendorf and Vallius, 2004
Bornholm Basin (mean in 24-35 cm depth)	19.7	25.5	-	-	-	115.8	-	Emelyanov et al., 2010
Bornholm Basin, 24.5 cm	57.2	36.2	0.3	42.2	69.4	125	7.24	Kunzendorf and Vallius, 2004
Mecklenburg Bay, (background)	25	23	0.15	25	60	70	5.20	Leipe et al., 2005

Trace metals are transported to the sea either via rivers, run-off in coastal areas, direct waterborne discharges to the sea or by wet and dry atmospheric deposition. The total cadmium load to the Baltic Sea in 2004 was 41 tonnes, of which 86% was waterborne and 14% airborne. The total load of lead to the Baltic Sea in 2004 was 567 tonnes, of which 59% was waterborne and 41% airborne (HELCOM, 2007). The total annual atmospheric deposition of metals to the Baltic Sea decreased from 1990 to 2006 by 45% for cadmium, 24% for mercury, and 66% for lead, which reflected the reductions in their emissions, increased use of unleaded fuel. Poland, Russia and Germany are the largest sources of these metal depositions, while the decreased contribution was observed due to the industrial restructuring, investments in cleaner technology and economic turn-overs in the catchment area (HELCOM, 2010 and references therein). As it was shown (SMOCS, 2012), high concentrations of metals were accumulated in harbours and, therefore, they might be the

source of internal pollution due to sediment dredging or other construction activities which reactivated the contaminants in the sediments.

Due to the long residence time of the water masses (25 – 35 years), once released into the Baltic Sea, metals can remain in the water for very long periods (Matthäus and Schinke, 1999). An example, the concentrations of metals in Baltic Sea water are up to 20 times higher compared to the North Atlantic. In water metals can accumulate in the marine food web up to levels which are toxic to marine organisms, particularly predators, and they may also represent a health risk for humans (HELCOM, 2007). On average, over 70% of lead, 50% of mercury, 40% of zinc, 30% of cadmium and 20% of copper loads are deposited in the sediments of the gulfs (Leivuori, 2000). Therefore, sediment as the largest storage and resources of metal plays a rather important role in metal transformations (Peng et al., 2009).

Many chemical and physical parameters have an influence on the accumulation of metals and major elements on the seafloor. The horizontal distribution of the metals is controlled by the physical and chemical properties of the metals, by the hydrographic properties of the water phase and by the chemical conditions in each individual area (e.g., Neumann et al. 1998; Vallius, 1999). The lateral transport of particulate matter, including organic matter, aims the increasing transport of metals (Müller, 1999). As it was shown for the Gulf of Finland (Vallius, 1999), some elements, like zinc, copper and cadmium, easily migrated far out to sea. Others, like chromium and cobalt were trapped close to the source (rivers). Close to the rivers mouth, in oxic environment, metals are transformed into the unstable iron and manganese oxyhydroxides. Under anoxic conditions the metals are reduced to lower oxidation states and mostly bound into sulphides. Contaminants are not necessarily fixed permanently in sediments but may be remobilized when physicochemical conditions change (an example, changes in oxic conditions) (Müller, 1999; Vallius, 1999; Leivuori, 2000). In most cases, obvious increases of metals are typical for the intensive accumulation zones of silty and clayey muds (Ebbing et al., 2002; Pustelnikovas, 2008; Emelyanov et al., 2015).

Table 1.3.2 Metal concentrations (mg kg⁻¹ d.w., variability (from-to) or average (\pm sd when given)) in surficial sediments (0 – 5 cm) of the Baltic Sea measured during the previous studies.

	Pb	Cu	Cd	Ni	Cr	Zn	Sampling year	Reference
The Curonian Lagoon (sand)	7.6	3.9	0.12	3.3	7	15.1	2013–2014	Jokšas et al., 2016
The Curonian Lagoon (silt)	28	28.9	0.64	19.8	28.7	76.4	2013–2014	Jokšas et al., 2016
Klaipėda Strait (sand)	8	3-29	-	-	37-74	16-140	1990–2004	Pustelnikovas et al., 2007
Klaipėda Strait (coarse silt, mud)	10	10-757	-	-	46-119	38-287	1990–2004	Pustelnikovas et al., 2007
Gulf of Finland	25.3-54.2	21.6-48.8	0.14-2.04	33.2-40.7	50.2-95.2	131-201	2007–2009	Vallius, 2012
	51	43	1.2	-	-	199	1992–1996	Vallius and Leivuori, 2003
Eastern Gotland Basin	45.6	99.3	6.97	72.9	37.6	448	1997	Kunzendorf and Vallius, 2004
	45-139	63-205	-	-	-	195-892	2003	Hille, 2005, 2006
Gulf of Gdansk	11.9 – 27.5*	6.0– 25.1*	0.19– 1.97*	-	-	33.5– 167.9*	2010	Dabrowska et al., 2013
	11-80	27-79	0.7-6.0	-	-	80-429	-	Glasby and Szefer, 1998
Gdansk Deep	77**	-	2.04**	-	-	230**		Zalewska et al., 2015
Port of Gdansk	2-93	1-131	0.14-2.0	1.7-11	1.7-38	9-334	1990–2004	Pustelnikovas et al., 2007
Vistula Lagoon	33-36	18-23	0.8-0.9	-	-	103-111	-	Glasby and Szefer, 1998
Bornholm Basin	56.7	38.5	1.09	38.7	56.4	167	1998–1999	Kuznezof and Vallius, 2004
	41	67	0.34	64	92	193	1997–2008	Emelyanov et al., 2010

*the range of the average concentrations, **maximal values.

Distribution of metals in sediments of the Baltic Sea have been reported widely (e.g., Pempkowiak, 1991; Neumann et al., 1998; Pohl et al., 1998; Glasby and Szefer, 1998; Leivuori et al., 2000; Ebbing et al., 2002; Glasby et al., 2004; Vallius, 2012, 2014, 2015; Zalewska et al., 2015). Results of the previous studies showed a higher marine and riverine sediment contamination with mercury, cadmium, lead, zinc and copper and a lower content of nickel and chromium. The sediments in different areas of the Baltic Sea differed in metal concentrations (Table 1.3.2), while the straight comparison should be

done with caution due to different sampling and analysis strategies (e.g., concentrations measured in bulk sediments, or only in small fraction, differences in sampling year, etc.). In general, results showed an enhanced deposition of Cd, Zn in Gotland Deep (Mälkki, 2001; Kunzendorf and Vallius, 2004; Hille, 2006) and elevated levels of Cd in sediments of the Gulf of Finland (Vallius, 2012, 2014, 2015) and the Gdansk Bay (Glasby and Szefer, 1998; Zalewska et al., 2015).

In spite of many geochemical studies in the bottom sediments in the SE Baltic Sea area (e.g., Jokšas, 1994; Radzevičius, 2002; Mažeika et al., 2004; Jokšas et al., 2005; Pustelnikovas et al., 2007; Garnaga, 2011; Emelyanov, 2001, 2014; Emelyanov et al., 2015), the results which concern the extent of the sediment pollution with metals in the Lithuanian zone are lacking. The reported bulk metal concentrations may show the natural geochemical peculiarities in the region, however, do not reflect the ratio between the natural and human-induced pollution of sediments. The HELCOM recommendations aim to achieve that pollution level is being reduced to the natural values (HELCOM introduces "target levels"). This means that pollutants of anthropogenic origin have zero contribution. Therefore, the quantitative sediment quality assessment taking into account the natural background (reference) values might help to evaluate an anthropogenic impact.

The most summarized view on the pollution of the entire Baltic Sea was presented by HELCOM (2010) using an integrated assessment tool CHASE. According to the results of the CHASE assessment, the entire Baltic Sea was highly contaminated in 1999–2007 because 137 out of the 144 assessed smaller areas were classified as being “disturbed by hazardous substances”. The main basin of the Baltic Sea (Northern Baltic Proper, Western and Eastern Gotland Basins) together with the Kiel and Mecklenburg Bights were the most contaminated areas (HELCOM, 2010). The all available data (e.g., mercury, cadmium, organochlorine pesticides, etc.) on pollutants were used in calculations. The method was based on the comparison of pollutant concentration in relation with the common admitted threshold criteria (i.e.,

environmental quality standards (EQSs) which are defined mostly only for the pollutant concentrations in water). However, sediment and biota are the most suitable matrices for many substances since they reflect the long-term exposure concentration. The Environmental Quality Standards Directive 2008/105/EC marks an important step in the use of sediments and biota as matrices for the chemical status assessment (Directive 2008/105/EC). Analysis of contaminants in sediments and biota indeed is widely recognized as a cost-effective approach in water-quality monitoring to describe the general contamination level, to supply reference values for local and regional monitoring and to identify areas of concern where additional monitoring effort is needed (Carere et al., 2012). In particular, biota is recognized as a preferential matrix for 14 and an optional matrix for 12 of the 41 substances listed under Directive 2008/105/EC. Concentrations in living tissues are expected to reflect the negative effects better than sediment concentrations (Binelli et al., 2015).

1.4 Metals in aquatic organisms of the Baltic Sea

Impacts of metals on marine ecosystems are not recognized as soon as they are introduced into the seawater. For this reason, frequent monitoring programs are needed to record changes in metal concentrations in environment which induce negative impacts on aquatic biota. In this sense, the accumulation of contaminants in biota is a time-integrated indicator of pollutant occurrence, bioavailability and its distribution in aquatic ecosystems (Szefer and Szefer, 1990; Szefer et al., 2006; Sokolowski et al. 2007; Zaldívar et al., 2011). Phytoplankton are known to accumulate certain metals and, therefore, have a crucial role in the trophic transfer of metals in the marine food chain (Revis et al., 1989). Two mechanisms of uptake are generally known to occur: adsorption of metal onto the external surface of the cells and absorption of metals by the phytoplankton from solution through cell walls against concentrations gradient. The presence of blooms of phytoplankton in the late

spring and summer provide ideal conditions for considerable metal accumulation.

The most common biomonitors in marine environment, however, are invertebrates including molluscs (e.g. bivalves and gastropods). In particular, molluscs have been used as bioindicators of pollution in coastal ecosystems because of their feeding behavior and their limited mobility, which make them particularly exposed to contamination both via the water column and sediment, either directly or after resuspension (Zaldívar et al., 2011). The metals are bioaccumulated in the mussels through dissolved uptake and particular ingestion and eliminated by depuration processes (Luoma and Rainbow 2005). Metals such as copper and zinc, are essential nutrients that are required for various biochemical and physiological functions. However, they may become harmful for organisms above critical levels (Rainbow, 2007).

No single species found in the Baltic Sea can be considered representative of the whole benthic environment, therefore, it is probable that effective coastal monitoring cannot be carried out by simply making use of a single benthic species (Bettinetti et al., 2009). The most common monitored species of molluscs for the pollution effect in the Baltic Sea are the blue mussel *Mytilus* spp. (Phillips, 1977, 1978; Szefer and Szefer, 1990; Broman et al., 1991; Szefer et al., 2002; 2006; Protasowicki et al., 2008; Przytarska et al., 2010; Dabrowska et al., 2013) and the Baltic clam *Macoma balthica* (e.g., Neuhoff, 1983; Szefer and Szefer, 1990; Sokolowski et al., 2002; Sokolowski et al., 2007; Thorsson et al., 2008; Hendozko et al., 2010). The data on metal concentrations in *Dreissena polymorpha* in the Baltic Sea region (Wiesner et al., 2001) are scarce, however, it is most representative benthic organism for the monitoring of pollutants accumulation in the Curonian Lagoon.

The tentative comparisons of the concentrations measured even in the same species of mussels must be done with the caution that any absolute comparisons are ruled out by different sampling years, different geographical areas determined by the different regimes of salinity, temperature, oxygen concentration, riverine discharge, etc. The small-scale differences in spatial

distribution of pollution are often much greater than those found on a regional scale (Bettinetti et al., 2009).

The results of previous study (Przytarska et al., 2010) using *Mytilus* spp. revealed that the southern Baltic Sea was much more polluted than the Northern Baltic. Accumulated metal concentrations in soft tissue of *Mytilus* spp. also showed significant spatial variations among sampling sites along the European coast with the highest Pb, Cu concentrations in mussels from the southern Baltic, and Zn in the Black Sea. The sampling station at the Mediterranean Sea, appeared to be the site with the lowest metal bioavailabilities among the coastal environments (Przytarska et al., 2010). The Baltic Sea is distinguished from the other seas by low salinity, elevated eutrophication, restricted water exchange with the oceanic system, and a relatively high metal load (Szefer et al., 2002; Przytarska et al., 2010).

In contrary, high concentrations of Cd, Pb and Zn in *Mytilus* spp. were reported by Phillips (1977, 1978), Broman et al. (1991) for the northern Baltic Sea (Table 1.4.1). Naturally occurring populations of *Mytilus edulis* in the Baltic Sea showed that at low salinities (e.g., the Gulf of Finland, Bothnian Sea) cadmium content of soft tissue was up to one order of magnitude higher (Table 1.4.1) than in more saline (e.g., Eastern Skagerrak) waters (Phillips, 1977; Broman et al., 1991). The same co-variation was shown for Zn by Phillips (1977), however, in study carried out by Broman et al. (1991) Zn did not show these salinity correlated differences. The results were explained by the higher accumulation of metals at low salinity or an actual difference in total metal concentrations in water together with the different salinity regime. Salinity of water was reported as an important factor influencing concentrations of selected metals in biota by other authors (Westernhagen and Dethlefsen, 1982; Szefer et al., 2002; DeForest et al., 2007). The enhancing effect of low salinity on uptake of cadmium has been described by Westernhagen and Dethlefsen (1982) in experiments with flounder from the Baltic Sea.

There are many other factors (organic carbon, temperature, pH, dissolved oxygen, sediment grain size and the hydrology of the system) which influence the uptake of metals from sediments. The metal accumulation in biota relies on uptake and other biological factors, such as feeding habits, age and individual size and it is the result of uptake and excretion rates (Hendozko et al., 2010, Pokorska, 2012). Elements can be excreted in different ways. A part of the elements that is taken up by molluscs is stored in the shells or can be eliminated by organisms through the binding of metals by metallothioneines and detoxification by storing metals in granules (Wiesner et al., 2001 and references therein).

Table 1.4.1 Metal concentrations (mean in mg kg⁻¹ d.w. (± sd) and/or range from-to (unless not indicated otherwise)) in *Mytilus* spp. in the Baltic Sea.

Area	Cd	Cu	Pb	Zn	Reference
The Bothnian Sea and the northern Baltic Proper	4.7–10.8	-	-	121–215	Broman et al., 1991
Eastern Gotland Basin (Lithuanian northern coast)	0.08–0.51*	1.69–2.21*	0.16–1.32*	6.12–113*	Garnaga, 2011
Southern Baltic Sea (Pomeranian Bight)	1.59–6.12	5.95–29.80	0.18–2.00	99.2–202.0	Szefer et al., 2002
Southern Baltic Sea (Gulf of Gdansk)	1.18–3.50	5.33–9.77	0.23–3.00	99.8–176.0	Szefer et al., 2002
Gulf of Gdansk	1.66–2.09**	4.2–8.3**	0.44–0.65**	86.3–114.7**	Dabrowska et al., 2013
Gulf of Gdansk	9.5–16.3	9.9–12.6	-	86–170	Przytarska et al., 2010

* the concentration unit for metals is mg kg⁻¹ wet weight.

** the translocated individuals of 2.5-3.5 cm in shell length were analyzed.

Several studies (e.g., Thorsson et al., 2008; Lin et al., 2016) have shown that increasing eutrophication and consequently organic matter settling to the seafloor can have a substantial effect on the increasing bioaccumulation of associated contaminants. Thus, in the Baltic Sea, there may be seasonal differences in the bioaccumulation of contaminants, with an increased bioaccumulation by benthic deposit-feeders following spring and summer blooms, if these blooms have associated contaminants and if they reach the seabed (Thorsson et al., 2008). The seasonal differences in metal

concentrations in mussels *Mytilus* spp. were most pronounced in summer and autumn. In most European coastal waters, summer–autumn is the post-spawning period when mussels recover after energy-demanding spawning and gather energy reserves; thus, they are highly dependent on external environmental conditions (Przytarska et al., 2010).

Pollutants accumulate differently in different tissues and organs of organisms. As found by other studies, fish muscles do not accumulate (or contain only small amounts) cadmium, while mercury concentrates in muscle (Westernhagen and Dethlefsen, 1982 and references therein; Szefer et al. 2002; Boalt et al., 2014). For the metal analysis the whole soft parts of mussels are used (e.g., Phillips, 1977, 1978; Hendozko et al., 2010; Dabrowska et al., 2013); while different accumulation pattern in different parts of molluscs (e.g., byssus, shell, gill) have been analyzed by many authors (Szefer and Szefer, 1990; Gundacker, 1999; Wiesner et al., 2001; Szefer et al., 2002; Szefer et al., 2006; Protasowski et al., 2008).

The negative, positive or insignificant relationships between body size and metal (e.g., Cd, Cu, Pb, Zn) tissue concentrations in molluscs and fish have been reported previously (Szefer et al., 1999a; Szefer et al., 2002; Polak-Juszczak, 2013; Tang et al., 2017). A positive correlation between fish length and mercury concentration was noted for cod, sprat, and herring in the Baltic Sea (Polak-Juszczak, 2009). In Baltic herring and perch, whole fish concentrations of cadmium and mercury also increased with increasing age and total length (Boalt et al., 2014). However, other authors reported that the accumulation of metals was generally higher in younger fish than in older ones (Canli and Atli 2003; Farkas et al. 2003). This indicates that these fish species have the ability to resist metal contamination with growth. A negative correlation between metal concentrations and size was detected when growth and the trace element uptake by smaller individuals were more rapid than metal uptake by large individuals (Szefer et al., 2002; Tang et al., 2017). No significant differences were detected in metal concentrations between different shell lengths of *Mytilus edulis* (Protasowicki et al., 2008) and *Dreissena* sp.

(Johns and Timmerman, 1998; Wiesner et al., 2001), however, Tang et al. (2017) reported, that tissue concentrations of Cd in *Dreissena polymorpha* tended to decrease with tissue weight.

In order to characterize bioavailability of metals more quantitatively, the biota – sediment (or biota – water) accumulation factors (**BAFs**) are estimated on the basis of both experimentally and environmentally derived data (Szefer et al., 1999a). Bioaccumulation is the process by which an organism concentrates metal from abiotic environment (e.g. water, sediment) and through food ingestion, resulting in body concentration that is many folds higher than the metal concentration in the environment (Al-Farsi et al., 2015). Knowledge of BAF values show the relative ability of organisms to adsorb and/or take up selected metals from the medium in which they live and allow to assess the proportions in which these metals occur in the organisms and in the associated sediments (Thorsson et al., 2008; Hendozko et al., 2010). The BAFs were widely applied in many studies on biota pollution with metals in natural conditions (e.g., DeForest et al., 2007; Gabriel et al., 2013; Al-Farsi et al., 2015; Battuello et al., 2017) and under laboratory conditions (Ruus et al., 2005; Guinot et al., 2012; Bonnail et al., 2016). For the Baltic Sea region, however, such a quantitative assessment was done only in several studies (Kļaviņš et al., 1998; Thorsson et al., 2008; Hendozko et al., 2010).

Since during this study the metal accumulation has been evaluated only in mussels *Dreissena polymorpha* and *Macoma balthica*, the short description of the mentioned species is presented below. The selection criterion regarding species representativeness for the research area was based on the species natural occurrence in the transitional, coastal and offshore areas of the SE Baltic Sea and the availability of the long-term dataset of metals.

The **zebra mussel** *Dreissena polymorpha* (**Pallas, 1771**) is a sessile suspension-feeder, attached with byssal threads to firm substrate (Gundacker, 1999). Zebra mussels were first introduced to the Baltic Sea in the 19th century likely by shipping canals for transportation from the Black Sea (Karatayev et al., 1997). They have established abundant populations in

several bays and estuaries except the northern part of the basin (Oganjan and Lauringson, 2014). Zebra mussels are now very abundant in the Curonian Lagoon, with the largest area occupied in the central part of the lagoon. The molluscs occur in the littoral zone down to 3–4 m depth on hard and soft substrates (Zaiko et al., 2010 and references therein).

The **Baltic clam *Macoma balthica* (Linnaeus, 1758)** is common in marine and estuarine habitats on both sides of the North Atlantic. In Europe, it occurs from the White Sea in the north to the Gironde estuary (Bay of Biscay) in the south, where it usually occupies sandy and muddy bottoms. *Macoma balthica* are sessile, facultative deposit-feeding organisms, widely distributed in low diversity Baltic Sea from a shallow sublittoral non-tidal zone to a deep-water anoxic zone, down to 91 m or more (Sokolowski et al., 2002; Janas et al., 2007). It lives buried a few centimeters down in the sediment and primarily feeds on organic particles deposited on the sediment surface (Thorsson et al., 2008).

1.5 Methods for evaluation of sediment and biota contamination with metals

In the literature, there are many indexes used to determine the sediment pollution intensity (e.g., enrichment factor – EF (Glasby and Szefer, 1998); geoaccumulation index – I_{geo} (Müller, 1979); contamination factor – CF, associated with the individual metal concentration (Håkanson, 1980) and the contamination degree of the study area (C_d). Furthermore, the potential ecological risk index can also be estimated for each metal (E^i_r , Håkanson, 1980) and the overall potential ecological risk of various metals (RI) in a study area based on the toxic responses in organisms. Sediment quality assessment guidelines (e.g., TEL, PEL, etc.) are also widely used in terms of revealing sediment contamination by comparing the sediment concentration with the corresponding quality guideline (Smith et al., 1996; MacDonald et al., 1996, 2000; Maanan et al., 2015).

The most common indexes, their calculations and levels used in sediment classification and organisms' contamination assessment are shown in the table 1.5.1.

- 1) **Enrichment factor (EF)**. A common approach to estimating the anthropogenic impact on sediments is to calculate an enrichment factor for metal concentrations above uncontaminated background levels (e.g., Glasby and Szefer, 1998; Selvaraj et al. 2010; Costa et al., 2015; Zalewska et al., 2015). The EF calculation seeks to reduce the metal variability associated with variations in granulometric particle size, and is a convenient tool for plotting geochemical assessment across the large geographic areas. The EF method normalizes the measured metal content with respect to a sample reference metal (local background values or continental crust/shale), most often relative to Al (Glasby and Szefer, 1998; Ebbing et al., 2002; Selvaraj et al. 2010; Dabrowska et al., 2013; Hamdoun et al., 2015). In the calculations of EFs, a normalization against Al is widely applied, mainly because it has a minor anthropogenic input and it is not influenced by changes in the redox potential and by early diagenetic processes comparing with iron or organic carbon (Ebbing et al., 2002). In this approach the Al is considered to act as a “proxy” for the clay content.

There are several classification systems based of the EFs values (Table 1.5.1). Enhanced values of EF indicate the increased metal concentrations resulting mainly from anthropogenic pressure (Zalewska et al., 2015). Glasby and Szefer (1998) have showed, that the EFs around 1 indicate that the element in the sediment is originated predominantly from lithogenous material, whereas EFs much greater than 1 show that the element is of anthropogenic origin.

- 2) **Geoaccumulation index (I_{geo})** is a coefficient, initially proposed by Müller (1979), and quite widely applied in assessments of sediment pollution with metals (Abraham and Parker, 2008; Garcia et al., 2008;

Hamdoun et al., 2015; Zalewska et al., 2015). The method assesses the degree of metal pollution in terms of seven enrichment classes based on the increasing numerical values of the index.

- 3) The method of **contamination factor (CF)** evaluates an enrichment in metal in relation to the background concentrations of each metal in sediment. CF is the ratio obtained by dividing the concentration of each metal in the sediment by the background value (Håkanson, 1980). The method of CF calculation is identical to EF calculation, except the fact that the CFs do not normalize concentrations against normalizing element. To facilitate pollution control, Håkanson (1980) proposed an integrated approach named the “**degree of contamination**” (C_d). C_d was determined as the sum of the CF for each sample.
- 4) **The potential ecological risk index (E^i_r)** was built by Håkanson (1980) and integrated the concentration of metals with ecological effect, environmental effect, toxicology. E^i_r was used to assess the metals pollution and ecological hazard for sedimentology. **RI** is a comprehensive potential ecological index, which equals to the sum of E^i_r . It represents the sensitivity of biological community to toxic substances and illustrates the potential ecological risk caused by the overall contamination.
- 5) **Assessment of sediment contamination according to sediment quality guidelines (SQG)**. Sediment quality assessment guidelines are very useful in terms of revealing sediment contamination by comparing the sediment concentration with the corresponding quality guideline (Smith et al., 1996; MacDonald et al., 1996, 2000). These guidelines evaluate the degree to which the sediment-associated chemical status might adversely affect marine organisms, and are designed to assist in the interpretation of sediment quality. According to MacDonald et al. (2000), the threshold effect level (TEL), probable effect level (PEL), lowest effect level (LEL), minimal effect threshold (MET), effect range low (ERL), threshold effect concentration (TEC), and probable effect

concentration (PEC) for assessing sediment quality conditions are determined. The TEL and PEL values for brackish and saline environments were widely applied in many studies (Bettinetti et al., 2009; Dabrowska et al., 2013; de Paula Filho et al., 2015; Maanan et al., 2016; Abreu et al., 2016).

In Lithuania, the boundaries for assessment of sediment chemical status were adopted by the Order of the Minister of the Environment as the threshold values between good environmental status (GES) and sub-GES according to the MSFD (Order No. D1-194 *On the Approval of the Characteristics of the Good Environmental Status of the Marine Region of the Republic of Lithuania* of the Minister of Environment of the Republic of Lithuania dated 4 March 2015). The GES limits defined are (Table 1.5.1): Cu = 10, Zn = 60, Cd = 0.5, Pb = 20, Cr = 30, Ni = 10 mg kg⁻¹. The metal concentrations which are equal and below those values show good environmental status (GES), while the concentrations higher than the agreed GES limits show unfavourable conditions (Sub-GES).

Those values for metal concentrations are also indicated in the Lithuanian national rules for sediment dredging and dumping (LAND 46A-2002) and show the threshold limits for the Ist (allowed to dispose at the coastal zone, <20 m depth) and IInd (allowed to dispose behind the coastal zone, at >20 m depth) sediment pollution classes. However, the last document regulates the method for disposal of sediments but not the possible cause for adverse environmental effects.

It is common that both background values of metals and sediment quality guidelines are used in sediment pollution assessment. As background concentrations reflect the pristine condition, these values should be lower than SQGs (Birch, 2017).

- 6) **Biota accumulation factor (BAF)** is used to estimate the degree of bioaccumulation of elements in biota with respect to their concentrations in the associated sediments and/or surrounding water

layer. In some studies (e.g., Szefer et al., 1999a) biota accumulation factor is named BSAF (biota sediment accumulation factor) when estimation is done with respect to the metal concentrations in sediment and BAF (with respect to the concentrations in water).

Table 1.5.1 Indexes and quality guidelines used in studies to assess sediment and organisms' contamination.

Index (Abbreviation)	Calculation	Classification or description
Enrichment Factor (EF) (Glasby and Szefer, 1998; Zalewska et al., 2015)	$EF = (C_s/N_s)/(C_{ref}/N_{ref}) \quad (1)$ <p>C and N – concentrations of element and normalizers in sediment sample (s) and reference material (ref).</p>	<p>EF < 1, no enrichment (I level) EF = 1–3, minor enrichment (II level) EF = 3–5, moderate enrichment (III level) EF = 5–10, moderately severe enrichment (IV level) EF = 10–25, severe enrichment (V level) EF = 25–50, very severe enrichment (VI level) EF > 50, extremely severe enrichment (VII level) (Zalewska et al., 2015)</p> <p>-----</p> <p>EF ≤ 1.5, lithogenous (natural) sources of metal; EF > 1.5, anthropogenic pollution (Mil-Homens et al., 2006; Garcia et al., 2008; de Paula Filho et al., 2014).</p> <p>-----</p> <p>0.5 ≤ EF < 2, the metals may be completely derived from natural or lithogenic processes. 2 ≤ EF < 5, a moderate portion of trace metals originated from an anthropogenic source or non-natural process. 5 ≤ EF < 20, a significant portion is from anthropogenic sources. 20 ≤ EF < 40, a high portion of contamination is derived from anthropogenic sources. EF ≥ 40, an extremely high portion of contamination Abreu et al., 2016).</p>
Geochemical Index (I_{geo}) (Müller, 1979)	$I_{geo} = \text{Log}_2(C_n/1.5B_n) \quad (2)$ <p>C_n and B_n - concentrations of element in sediment sample and the background or pristine value of the element, respectively. The factor 1.5 is introduced to minimise the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments (Abraham and Parker, 2008).</p>	<p>Pollution intensity</p> <p>$I_{geo} < 0$, uncontaminated (0 class) $I_{geo} = 0-1$, uncontaminated to moderately contaminated (1 class) $I_{geo} = 1-2$, moderately contaminated (2 class) $I_{geo} = 2-3$, moderately to strongly contaminated (3 class) $I_{geo} = 3-4$, strongly contaminated (4 class) $I_{geo} = 4-5$, strongly to extremely strongly contaminated (5 class) $I_{geo} > 5$, extremely contaminated (6 class).</p>
Contamination Factor (CF)	$CF = C_s/C_{ref} \quad (3)$ <p>C_s and C_{ref} - concentrations of element</p>	<p>Contamination degree of individual metal</p> <p>CF < 1, low 1 ≤ CF < 3, moderate 3 ≤ CF < 6, considerable</p>

(Håkanson, 1980)	in sediment sample and the background or pristine value of the element, respectively.	$6 \leq CF$, very high (Håkanson, 1980; Bonnail et al., 2016).
Degree of Contamination (C_d) (Bonnail et al., 2016)	$C_d = \sum CF$ (4)	Contamination degree of the environment $C_d < 5$, low $5 \leq C_d < 10$, moderate $10 \leq C_d < 20$, considerable $20 \leq C_d$, very high.
Potential Ecological Risk Index (E_r^i) (Benson et al., 2016)	$E_r^i = CF * T_r^i$ (5) T_r^i – Toxic response factor ^a	Grades of ecological risk of individual metal $E_r^i < 40$, low $40 \leq E_r^i < 80$, moderate $80 \leq E_r^i < 160$, considerable $160 \leq E_r^i < 320$, great $320 \leq E_r^i$, very great.
Potential Ecological Risk Index (RI) (Benson et al., 2016)	$RI = \sum E_r^i$ (6)	Grades of ecological risk of sum of metals $RI < 95$, low $95 \leq RI < 190$, moderate $190 \leq RI < 380$, considerable $380 \leq RI$, very high.
Threshold effect level (TEL), Probable effect level (PEL) (Smith et al., 1996; MacDonald et al., 1996, 2000)	TEL ^b , PEL ^c	Values $\leq TEL$, there are little or no toxic risks to organisms. PEL is the minimum value at which several adverse effects start to occur.
Good environmental status (GES)	GES ^d	The environmental status of marine waters where these provide ecologically diverse and dynamic oceans and seas which are clean, healthy and productive (MSFD, 2008/56/EC).
Bota Accumulation Factor (BAF)	$BAF = C_b / C_s$ (7) C_b and C_s - concentrations of element in biota and sediment sample, respectively	BAF value greater than 1 indicates bioaccumulation. Classification of species $BAF < 1$, deconcentrator $1 < BAF < 2$, microconcentrator $BAF > 2$, macroconcentrator (Dallinger, 1993). BAFs reported for plants $BAF < 1$, excluder; $1 < BAF < 10$, accumulator $BAF > 10$, hyperaccumulator (Ma et al., 2001).

^aToxic response factor calculated by Håkanson (1980): Cd = 30, Cr = 2, Cu = Ni = Pb = 5, Zn = 1.

^bTEL values determined by Smith et al. (1996); MacDonald et al. (2000): Cu =35.7, Zn =123, Cd =0.6, Pb =35, Cr = 37.3, Ni =18.

^cPEL values determined by MacDonald et al. (1996): Cu =108, Zn =271, Cd =4.21, Pb =112, Cr = 160, Ni =42.8.

^dGES values determined for the MSFD implementation in Lithuania: Cu =10, Zn =60, Cd =0.5, Pb =20, Cr = 30, Ni =10.

A crucial first step in evaluating the impact of sediment pollution and the level of contamination affecting a given area is to establish a reference background or baseline sample of known metal composition. Two methods are considered, firstly the use of average crustal/shale values or background values defined for similar region as reference concentrations, while the second method seeks to establish a local baseline by analysing comparable local

sediment unaffected by anthropogenic activity (Abraham and Parker, 2008; Birch, 2017). The average continental shale and crust values of metals were reported by Turekian and Wedepohl (1961) and Wedepohl (1995), respectively. They have been widely used as a baseline in many studies (e.g., Reimann et al., 2000; Nowrouzi and Pourkhabbaz, 2014; Hamdoun et al., 2015). The local geochemical background may be determined from the samples taken from pristine areas, using data of deep cores (Abraham and Parker, 2008; de Paula Filho et al., 2014; Costa et al., 2015; Maanan et al., 2016;) or by applying different statistical techniques (Reimann et al., 2005, Rodríguez et al., 2006).

The main criticism of using the global values is that they do not consider regional variability, geochemical heterogeneity and may do not represent local background concentrations (Abraham and Parker, 2008; Birch, 2017). The sediment quality criteria that are derived from site-specific data better predict toxicity in the environment, and therefore, this approach should be applied to sediment management (Abraham and Parker, 2008; Abreu et al., 2016; Birch, 2017). However, the global shale values may be similar to the mean metal concentrations from site-specific down core which represents reference (or uncontaminated, pre-industrial) period. The review study carried out by Birch (2017) showed that the global shale metal concentrations reported by Turekian and Wedepohl (1961) were similar to the pre-anthropogenic concentrations for the 23 worldwide studies. According to Sinex and Helz (1981), the enrichment factor is generally not very sensitive to the choice of background (reference) metal concentration. However, in the study carried out by Abraham and Parker (2008), the EF values for most of the elements were higher as compared to average values determined using the actual metal content in each core. The authors concluded that deep core data as baseline might be reliable in areas that had suffered relatively recent pollution such as in countries that have relatively young industrial histories (e.g. Australia and New Zealand). This approach may be not appropriate in old heavily industrialised countries such as in Europe, since the anthropogenic impact may

be recorded in several sediment meters. Therefore, the average continental shale and crustal data might be used for reference purposes. Christova et al. (2007) established the local background values for metals based on real results from quantitative chemical analyses published in Bulgarian geochemical studies during a period of 40 year. The background values for metals coincided (except Cd) with the averages of the studied elements in the upper continental crust.

Indeed, the data from the previous works compiled during this study (Table 1.3.1) showed that global Earth's shale values for metals (reported in Turekian and Wedepohl, 1961) were similar to the down core metal concentrations reported by many other authors. Based on that fact, it may be concluded, that the global values may be used when no data on the local reference metal concentrations exist.

Conclusions

Despite of increasing attention and many studies on the OM distribution and transformation in the Baltic Sea, the amount of scientific studies addressing the issues in the SE part of the Baltic Sea is scarce. The SE Baltic Sea is highly impacted by discharge of the Nemunas River as well as other polluted southern rivers (Vistula, Oder) due to the prevailing westerly winds, therefore, the OM distribution pattern, its seasonal and spatial dynamics and the main driving factors need to be scrutinized. The combined $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N, POC/Chl-*a* ratios approach leads to better identification of particulate organic matter provenance and fate as it was shown before, therefore, such a complex investigation may give the most comprehensive information. Moreover, the nature of the organic matter, its variability and cycling may be properly evaluated in relation with a complex of the environmental biotic (e.g., phytoplankton biomass) and abiotic factors (e.g., DIC, $\delta^{13}\text{C}_{\text{DIC}}$, DIN, pH, water temperature, salinity and riverine discharge). An assessment of the share of terrestrial-freshwater and marine OM contribution to the mixed POM and

SOM provides a quantitative assessment on the riverine impact to the marine waters, which is useful for the national plans and strategies on the reduction of the riverine pollution impact.

There has been an increasing ecological and global public health concern associated with environmental pollution with metals due to their intensive multiple applications. Many studies on sediment pollution in the SE Baltic Sea report bulk metal concentrations in sediments. They may show the natural geochemical peculiarities in the region, and do not reflect the real pollution level. The comparison between metal concentrations in sediments and the background values gives an idea on the extent of the sediment pollution and promotes an evaluation of natural and human-induced pollution. Many chemical and physical parameters have an influence on the accumulation of elements on the seafloor, therefore, the metal accumulation in relation with environmental factors need to be evaluated.

The sediment and biota are recognized as a cost-effective approach to describe the general contamination level due to the long-term metal accumulation in sediments and organism's tissue. Concentrations in living biota tissues are expected to reflect the negative impact better than sediment concentrations solely, however, there is a lack of such studies for the SE Baltic Sea.

2. MATERIAL AND METHODS

2.1 Study area

The area of this study includes the Lithuanian part of the Curonian Lagoon and the Baltic Sea (SE Baltic Sea). In order to test the impact of the Nemunas River, sampling was also performed in the Nemunas River, before it inflows to lagoon (Fig. 2.1.1).

The Curonian Lagoon is the largest coastal lagoon in the Baltic Sea (total area of 1584 km², mean depth 3.8 m, maximum depth 5 m). The lagoon is connected to the Baltic Sea through the narrow and artificially deepened Klaipėda Strait where Klaipėda Port is located. The width of the strait varies from 1.2 km to 0.4 km at the entrance to the Baltic Sea and the length of the strait is about 11 km (Žaromskis, 1996; Trimonis et al., 2003; Dailidienė and Davulienė, 2008). Freshwater input to the estuary is dominated by the Nemunas River discharge (mean annual runoff 632 m³ s⁻¹), averaging 21.8 km³, or 96 % of the total input (Jakimavičius and Kriaučiūnienė, 2013). The seasonal river runoff distribution is the following: 38 % of annual runoff belongs to spring, 16 % to summer, 20 % to autumn and 26 % to winter season (Jakimavičius and Kovalenkoviienė 2010). The northern part of the lagoon is influenced by an irregular sea water intrusion with the exposition for 250–364 days per year in the Klaipėda Strait and 25 days at a distance of 40 km from the sea entrance (Zemlys et al., 2013). As a consequence, the irregular salinity fluctuations (from 0 to 8 ‰) are observed in the northern part of the lagoon. Due to the extensive dredging activities in the Klaipėda Strait occasional increases in water salinity towards central part of the Curonian Lagoon are observed (Dailidienė and Davulienė, 2008). The average annual long-term inflow from the Baltic Sea to the Curonian Lagoon is 6.1 km³ (Jakimavičius and Kovalenkoviienė, 2010). About 70% of the total annual inputs of the brackish water intrusions occur during August to October. The Curonian Lagoon is a well mixed, highly turbid lagoon with a water residence time of about 80 days (Ferrarin et al., 2008).

The dominating winds along the Lithuanian coast are southwest, west, and southeast with the average wind velocity about 5 m s^{-1} . In the northern part of the Curonian Lagoon the flow is mostly moving towards the Baltic Sea, while the circulation pattern in the central part depends on the wind direction (Davulienė and Trinkūnas, 2004). A two-directional currents (saline water near-bottom flow to the lagoon and surface freshwater flow to the sea) were reported for the Klaipėda Strait (Zemlys et al., 2013).

The input of suspended particulate matter from the Nemunas River to the Curonian Lagoon equals to about 262 000 tonnes annually (Leipe and Gingele, 2003). The Nemunas River supplies mostly silty (0.1 – 0.01 mm) and clayey (< 0.01 mm) particles into the lagoon, while saline water intrusions bring sandy (0.25 – 0.1 mm) marine sediments (Pustelnikovas et al., 2007).

The Curonian Lagoon is hypereutrophic system with values of chlorophyll *a* concentrations up to $400 \mu\text{g l}^{-1}$, and recurring intensive blooms (biomass above 10 g m^{-3}) or hyperblooms (above 100 g m^{-3}) of cyanobacteria (Olenina, 1998; Zilius et al., 2014). Cyanobacteria (mainly *A. flos-aquae*) account for 70 – 97% of the phytoplankton (Jaanus et al., 2011; Lesutienė et al., 2014). It was estimated that the phytoplanktonic primary production reaches up to $1500 \text{ g C m}^{-2} \text{ year}^{-1}$ in the Curonian Lagoon, while in the Lithuanian coastal area it accounts about $370 \text{ g C m}^{-2} \text{ year}^{-1}$ (Tomczak et al., 2009).

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 the most of the lagoon area (Emelyanov, 2001; Chubarenko et al., 2002). In the Klaipėda Strait, different sedimentation zones (natural – western part and technogenic – eastern part) were distinguished with different predominant sediment types (coarse-grained and fine-grained, respectively) and pollution accumulation capacities (Pustelnikovas et al., 2007; Suzdalev and Gulbinskas, 2014).

The fresh water runoff from the Curonian Lagoon to the Baltic Sea through the Klaipėda Strait is approximately $27.7 \text{ km}^3 \text{ year}^{-1}$ (Jakimavičius and Kovalenkoviėnė, 2010). The northward currents are the predominant in the entire water column in the shallow Baltic coastal waters (up to 35 m isobaths), probably influenced by the outflow of the Curonian Lagoon (Žaromskis and Pupienis, 2003; 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 water salinity in the Curonian Lagoon outflow area is sometimes less than 1 ‰, while the water salinity in coastal waters varies in the range of 7 – 8 ‰. 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 $\mu\text{g l}^{-1}$, while much lower concentrations (2.23 – 20.16 $\mu\text{g l}^{-1}$) 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 $12.79 \pm 7.48 \text{ g m}^{-3}$, while about a threefold lower concentration ($3.84 \pm 1.59 \text{ g m}^{-3}$) was measured in the adjacent coastal waters (Vaičiūtė, 2012). 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 (Vaičiūtė, 2012; The Nemunas River Basin..., 2010).

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 hydrodynamics in the exposed coastal area prevents occurrence of hypoxia events (Olenin and Daunys, 2004; Conley et al., 2011) in this area. However, hypoxic conditions and appearance of hydrogen sulfide (H_2S) have often been recorded in the Gotland Deep (HELCOM, 2009; Emelyanov, 2014). Water depth in the open sea varies in the range of 30 – 120 m. Water salinity at the bottom water layer

(60 m) is about 7.0 – 7.3 ‰. A stable halocline occurs at 60–80 m, salinity at the bottom water layer of this zone reaches 10.5 – 12 ‰ (Vyšniauskas, 2008).

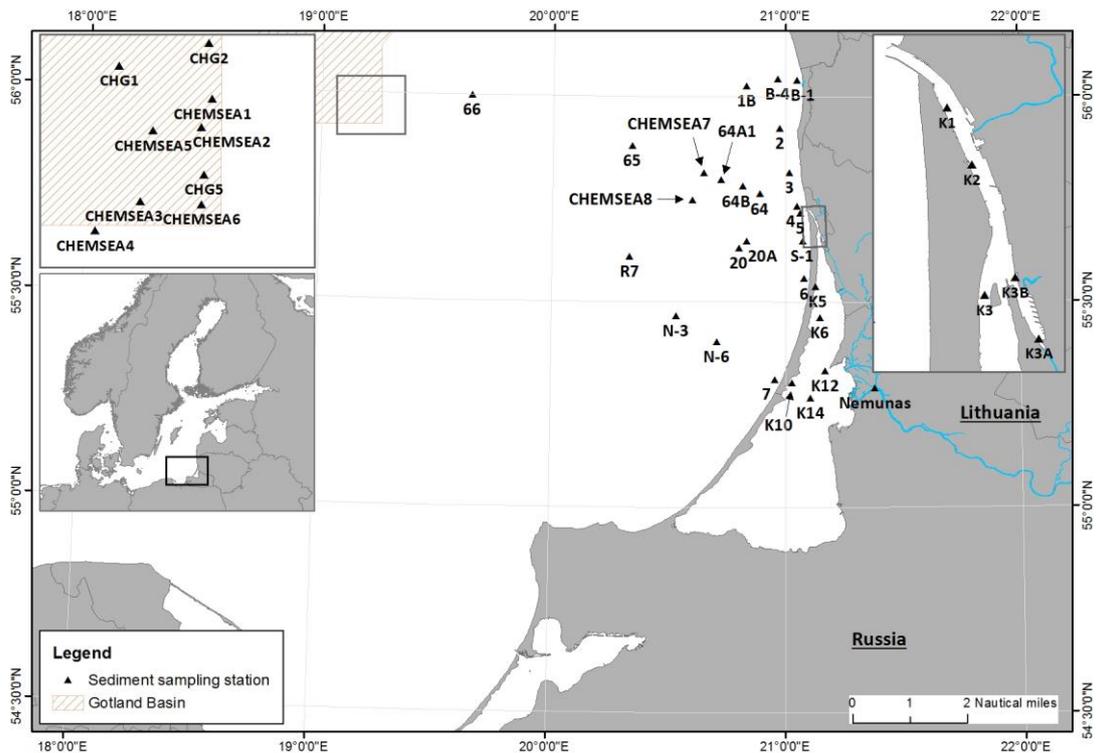


Fig. 2.1.1 The map of the study area in the Lithuanian part of the Curonian Lagoon and the Baltic Sea.

Besides the natural variability the Baltic Sea coastal area is markedly impacted by various anthropogenic activities and the national monitoring stations are distributed in the area of the main pressure e.g., freshwater discharge (st. 3, 4, 5), the Būtingė oil terminal (st. 1B, B-4) and dumping of dredged sediments in the territorial waters (st. 20 and 20A, Fig. 1). Since more than 90 % of disposed soil is stabilized in the dumping area (Pupienis and Žilinskas, 2005), occasional increase of pollution (e.g., with metals) are reported (Garnaga, 2011). The exposure to pollutants and vulnerability to human activities (oil discharge, soil dredging and disposal) at the coastal waters and offshore zone of the SE Baltic Sea were also reflected in the studies on biomarker responses and genotoxicity effects (Baršienė et al., 2006, 2012).

Table 2.1.1 Main morphometric and hydrological characteristics of the study area.

Research zones	Stations, No.	Salinity ‰	Water depth, m	Variability in sediment types
Central part of the Curonian Lagoon (CL-C)	K10, K12, K14	<0.5	2.4–5.6	Fine sand, silt, with shell deposits
Northern part of the Curonian Lagoon (CL-N)	K5, K6, K1, K2, K3, K3A, K3B	0.5–8	2–15	Fine sand, silt
Plume of the Curonian Lagoon waters into the Baltic Sea (BS-P)	3, 4, 5	0.5–8	15–18	Fine sand, pebble
Baltic Sea territorial – coastal waters (BS-CW)	2, 6, 7, 20, 20A, 1B, 64, 64A1, 64B, B-1, B-4, S-1, N-6	7–8	12–46	Fine sand, sand, gravel, aleurite, glacial deposits
Baltic Sea open waters (BS-OW)	65, 66, N-3, CHEMSEA1-8, CHG1, CHG2, CHG5, R7	7–12	40–117	Silt, aleurite, sand, gravel

The observed linear sedimentation rates mostly vary between 1.0 and 2.0 mm y⁻¹ in the open Baltic Sea waters (Mažeika et al., 2004; Hille et al., 2006) and 2.5 – 3.6 mm y⁻¹ or even 5 – 15 mm y⁻¹ (Pustelnikovas, 2008 and references therein) in the Curonian Lagoon. Therefore, the growth of a ~5 cm thick layer took 25–50 years in the open sea, and 3–20 years in the lagoon and the metal concentration indicated a recent pollution.

Stations (Fig. 2.1.1) were grouped according to the salinity zonation and taking into account the principal sedimentary environments (depth range and type of sediment) within the study area (Table 2.1.1).

2.2 Sampling and analysis

Data on the environmental parameters used in the study, as well as sampling period and analysing/measuring laboratory are briefly summarized in Table 2.2.1.

Table 2.2.1 Data on the environmental parameters used in the study.

Parameter	Research zone	Analyzed matrix	Period and months (or season)	Analysing/measuring laboratory
Water temperature, salinity, pH, oxygen	Nemunas River, Curonian Lagoon and Baltic Sea	Water	2011-2014 (monthly)	MRD of EPA
Salinity	Curonian Lagoon	Water	2012-2013 (daily)	MRD of EPA
Discharge of the Nemunas River	The Nemunas River	-	2012-2013 (daily)	LHS
Nutrients (NO ₂ -N, NO ₃ -N, NH ₄ -N)	Nemunas River, Curonian Lagoon and Baltic Sea	Water	2012-2013 (from May 2012 to April 2013)	MRD of EPA
POC, PN and its $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures, C/N ratio	Nemunas River, Curonian Lagoon and the Baltic Sea	Water	2012-2013 (from May 2012 to April 2013)	SSRI CPST
Chlorophyll-a	Nemunas River, Curonian Lagoon and the Baltic Sea	Water	2012-2013 (from May 2012 to April 2013)	MRD of EPA
Phytoplankton (biomass and taxonomic composition)	Nemunas River, Curonian Lagoon and the Baltic Sea	Water	2012-2013 (from May 2012 to April 2013)	MRD of EPA
Chlorophyll-a + additionally pH, temperature, salinity; DIC	Nemunas River and the Curonian Lagoon	Water	2012-2013 (from January 2012 to December 2013)	KU MSTC
$\delta^{13}\text{C}$ in DIC				SSRI CPST
TOC and its $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures, C/N ratio	Curonian Lagoon and Baltic Sea	Sediment	2012-2014 (once in spring, summer and autumn)	SSRI CPST
Metals (Pb, Cu, Cd, Ni, Cr, Zn, Al)	Nemunas River and Baltic Sea	Sediment	2011-2014 (spring, summer and autumn)	EPA
Metals (Pb, Cu, Cd, Ni, Cr, Zn, Al)	Nemunas River and Baltic Sea	Sediment	2011, 2013 (spring, summer)	GGI of NRC
Fe and S	The Baltic Sea	Sediment	2013 (spring)	GGI of NRC
Metals (Pb, Cu, Cd, Zn)	Curonian Lagoon and Baltic Sea	Biota	2006-2014 (spring, summer)	EPA
Granulometric size	The Curonian Lagoon	Sediment	2012 (spring, summer)	MRD of EPA

2.2.1 Water sampling

Samples of surface water (0.5 – 1 m) were taken for analysis of total suspended matter (TSM), POM, nutrients and chlorophyll *a* (Chl-*a*) at 10 stations in the Curonian Lagoon (Lithuanian part) from May 2012 to April 2013 and at 16 stations in the Baltic Sea coastal waters in May, August, October 2012 and February 2013. In addition, near-bottom water samples (depending on stations, depth range of 3 – 13 m in the Curonian Lagoon and 12 – 40 m in the Baltic Sea) for analysis of the POM isotopic composition were taken in August 2012 and February, April 2013. Samples from the Nemunas River were taken monthly in 2012 – 2013.

Marine and lagoon water sampling was carried out from research vessel “Vėjūnas” by using a Conductivity – Temperature – Depth (CTD) rosette equipped with 5 L and 1.7 L bathometers and sensors for water temperature, salinity and oxygen. Salinity was measured during the research cruises and automatically at three hydrometeorological observation stations in Klaipėda, Ventė and Nida. Phytoplankton biovolume and the species composition in the Baltic Sea were determined in integrated samples from the surface to the 10 meters depth. In the Nemunas River and the Curonian Lagoon, surface (0.2 – 0.5 m) water samples were taken for determination of phytoplankton parameters. Sampling was performed by the specialists from the Marine Research Department of the Environmental Protection Agency (MRD of EPA) in the frame of the national monitoring programme and implementing the project “Application of isotope methods to assess spreading of organic substances in the Baltic Sea” (financed by the Research Council of Lithuania). Samples from the stations 4, 5, 20A, N-3, N-6, 64, 65, 66, CHEMSEA and CHG were also taken in 2013 and 2014 implementing the EU part-financed project „Chemical munitions search and assessment (CHEMSEA).

Additionally, monthly samplings for DIC and $\delta^{13}\text{C}_{\text{DIC}}$ analysis, pH and Chl-*a* were performed from January 2012 to December 2013 at two sites, representing Nemunas River and the Curonian Lagoon outflow to the Baltic

Sea. Sampling was performed by the scientists from the the Marine Science and Technology Center, Klaipėda University (KU MSTC). Water samples (2 L) were collected at each site in triplicate by repeated Ruttner bottle sampling at surface layer (0.2 – 0.5 m). The two aliquots of 30 ml were immediately subsampled and filtered through pre-ashed GF/F filters into 12 ml exetainers (Labco, UK) allowing overflow two volumes. For isotopic analysis samples were fixed with 100 µl of 7 M ZnCl₂. *In situ*, water temperature and salinity were measured with a multiple probe.

2.2.2 Bottom sediment sampling and granulometric analysis

Bottom sediment samples were taken at 41 stations (Fig. 2.1.1) in the Baltic Sea coastal and open waters and in the Curonian Lagoon in 2011 – 2014 three times per year (once in spring, summer and autumn). Sediments were collected from cutter “Marinis” (in 2011) and research vessel “Vėjūnas” (since 2012) using a Van Veen grab sampler (sampling area of 0.1 m²). Sediments from the upper most layer (0-5 cm) were subsampled, stored in individual plastic containers and frozen on board (at -20°C) until further processing in the laboratory (Remeikaitė-Nikienė et al., 2016). The sediment samples for the granulometric analysis were taken in 2012. The types of bottom sediments of the Curonian Lagoon were distinguished on the basis of the decimal granulometric classification according to the dominant fraction and median diameter (Md) according to EN ISO 14688-1: 2004 and EN ISO 14688-2: 2004. Analysis was done at the MRD of EPA.

2.2.3 Biota sampling

Molluscs were sampled during the period of 2006 – 2014. Molluscs were collected: from the research vessels “Vėjas” and “Gintaras” until 2010, from vessel “Darius” and cutter “Marinis” in 2011 and from the research vessel “Vėjūnas” since 2012. Molluscs *Macoma balthica* from the Baltic Sea and

Dreissena polymorpha from the Curonian Lagoon were collected using a Van Veen grab sampler. *M. balthica* were collected at the Baltic Sea sites No. 7 (in 2006, 2012–2014) and 65 (2006–2010), whereas *D. polymorpha* were sampled at the lagoon station K12 (2006–2014). Living specimens were transported immediately to the laboratory and subsequently kept in the clean water from the area of collection at the temperature about 4 °C for 24 h to deplete gut contents.

2.2.4 Chemical and biological parameters

DIC measurements were done in the KU MSTC (Table 2.2.1). For DIC measurements the laboratory standard Li₂CO₃ (MERCK KGaA cat.# K40739280) was used. Standard was analyzed with every 6 samples. Standard solutions in degassed and deionized water were made. Standard was calibrated against IAEA-CO-8, NBS-18 and IAEA-LSVEC. Precision for carbon isotope analyses in DIC measurements is 0.1 ‰.

The nutrients, chlorophyll *a* and phytoplankton were analyzed at the MRD of EPA (Table 2.2.1). Dissolved nitrogen compounds (NO₂-N, NO₃-N, NH₄-N) were determined by flow analysis (FIA) according to the ISO 13395:1996 and ISO 11732:2005 standards. The samples for Chl-*a* determination were filtered through Whatman 47 mm GF/F filters (pore size 0.7 µm) and until analysis stored at -25 °C. Thereafter Chl-*a* was extracted with 90 % ethanol or with 90 % acetone during 24 h at 4°C and the concentration was analyzed by spectrophotometry (Jeffrey and Humphrey, 1975; HELCOM, 1988). The phytoplankton samples were fixed with acid Lugol's solution. Taxonomic species composition and biovolume were estimated using an inverted microscope (Utermöhl technique) according to the recommendations of HELCOM (1988).

2.2.5 Stable isotopic analysis of POM, SOM and DIC

Stable isotopic analysis of POM, SOM and DIC was done at the State Research Institute Center for Physical Sciences and Technology (Vilnius, Lithuania). The water samples for the particulate organic matter analysis were stored at 4 °C in the laboratory until further preparation. Water samples of 1.5-2.0 L (depending on the total suspended matter concentration) were filtered through a pre-combusted (at 450 °C, for 3 h) Whatman 47 mm GF/F filters (pore size 0.7 µm). After filtration the filters were dried at 50 °C for 4 h, reweighed and kept at room temperature in a desiccator until analysis (Lara et al., 2010). In order to remove inorganic carbon the filters were exposed to HCl fumes (Lorrain et al., 2003). After an acid treatment the filters were dried overnight at 60°C temperature, folded and placed into Ag capsules. DIC was determined within 24 hours via 6 end points 0.1 N HCl titration (Anderson et al. 1986).

Particulate organic carbon (POC), particulate nitrogen (PN) and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ isotopic signatures were measured using a Thermo Scientific Delta V Advantage mass spectrometer coupled to a Thermo Electron Corporation FlashEA 1112 elemental analyzer. The $\delta^{13}\text{C}$ measurements of DIC were done using a stable isotope mass spectrometer (Thermo Scientific Delta V Advantage) coupled with an online Finnigan Gasbench II interface (Thermo Scientific). DIC sample preparation and measurements were performed following the method presented in Torres et al. (2005). The 2 ml water samples were acidified with 0.5 ml 85% phosphoric acid to degas DIC as $\text{CO}_2(\text{g})$. The volume of water and amount of the acid was kept the same for all analyzed samples (Salata et al., 2000; Assayag et al. 2006). Samples were analyzed straight after a 15-24 h equilibration (Torres et al. 2005; Assayag et al., 2006). The amount of organic carbon (TOC, d.w. %) and isotopic signatures of SOM were measured after drying and homogenizing the sediment samples. The sediment samples were acidified with 2M HCl to remove carbonates, dried at 60°C overnight and pressed into pellets (Voss et al., 2000). Analyses were

made by using a Thermo Scientific Delta V Advantage mass spectrometer coupled to a Thermo Electron Corporation FlashEA 1112 elemental analyzer. The isotope ratios are expressed in the usual delta notations, i.e. the results were normalized to the Vienna PDB ($^{13}\text{C}/^{12}\text{C} = 0.0112372 \pm 0.0000090$) and atmospheric N_2 ($^{15}\text{N}/^{14}\text{N} = 0.0036765$):

$$\delta X = [R_s/R_{std} - 1] \times 10^3, \text{‰} \quad (8)$$

where δX - $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$, R_s is the sample, and R_{std} is the standard $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$.

For stable isotopic analysis of POM the reference gases CO_2 and N_2 were calibrated to the international standards from the International Atomic Energy Agency (Vienna) – IAEA-600, NBS-22 for ^{13}C and IAEA-600 for ^{15}N – were used. The repeated analyses of homogeneous material yielded standard deviations of less than 0.08‰ for $\delta^{13}\text{C}$ and 0.2‰ for $\delta^{15}\text{N}$.

2.2.6 Analysis of metals in sediment

The analysis of metals was performed in two laboratories. For the national monitoring purposes sediment samples were analyzed at the laboratory of the Environment Research Department of the Environmental Protection Agency (EPA, accredited according to the ISO/IEC 17025) in 2011–2014. The marine monitoring programme has been closely connected with the Baltic Sea monitoring programme prepared by the HELCOM. A 0.5 g of each dried sediment sample was leached with 6 ml nitric acid ($\geq 69,0 \%$) in a microwave, diluted to 50 ml, and then analyzed by atomic absorption spectrometry with the graphite furnace (AAS) or/and the inductively coupled plasma optical emission spectrometer (ICP-OES). Concentrations of Cd were analyzed by AAS according to ISO 15586:2003. The ICP-OES method (ISO 11885:2007) was used for the analysis of Cr, Zn and Al. Both methods were

used for the analysis of Pb, Cu and Ni depending on the concentrations of these metals in samples.

The precision of the analytical procedures, expressed as the standard deviation, ranged within approximately 5.2 – 14 % for AAS and 7.6 – 18 % for ICP-OES methods. The certified reference materials CRM BCR-277R (IRM) and ICP Multielement standard solution (Merck) were used. The limit of determination for the AAS method ranged from 0.01 mg kg⁻¹ for Cd to 0.10 mg kg⁻¹ for Pb and Ni; for the ICP method – from 0.20 mg kg⁻¹ for Cr to 4.5 mg kg⁻¹ for Cu (Table 2.2.2).

Since nitric acid only partly leaches mineral-bounded pollutants, the real contamination of the sediments might be not revealed. Despite that fact, it is often used to give a rough estimate of the anthropogenic share of the metal concentration (Vallius, 1999; Leivuori et al., 2000; Ebbing et al., 2002).

Table 2.2.2. Precision (%) and limits of determination (expressed in mg kg⁻¹) of the AAS and ICP-OES methods used by the EPA.

	Pb	Cu	Cd	Ni	Cr	Zn	Al
Precision (AAS)	5.2	-	8.5	14	-	-	-
Precision (ICP-OES)	13	10	-	10.5	18	7.6	15
Limit of determination (AAS)	0.10	0.080	0.010	0.10	0.050	-	-
Limit of determination (ICP-OES)	2.0	4.5	1.0	1.5	0.20	1.5	3.0

In order to compare a difference between sample pre-treatment methods, samples from several common stations (Nemunas, 4, 5, 6, 7, 20A, 65, 66, CHEMSEA2) and new stations (CHG1, R7) were taken and analyzed at the Institute of Geology and Geography of the Nature Research Center (GGI of NRC) in 2011 and 2013. For metal (Pb, Cu, Cd, Ni, Cr, Zn, Fe and Al) analysis the total digestion method was used. The split freeze dried sediments (0.25 g) were heated using microwave in concentrated acids mixture (HNO₃-HClO₄-HF) to fuming and taken to dryness. The residue was dissolved in HCl (Loring,

Rantala 1992). The content of trace elements in the bottom sediments was analyzed by Perkin Elmer Optima 7000 DV ICP-OES (Montaser 1998; Jokšas et al., 2016). For quality control of the results the NIST Standard reference material 2702 (Inorganics in Marine Sediments) was used. The following detection limits were established (in $\mu\text{g l}^{-1}$): Pb (1.4), Cu (0.9), Cd (0.07), Ni (0.4), Cr (0.25), Zn (0.2), Fe (0.2), S (0.2), Al (0.9). The precision of the analytical procedures, expressed as the standard deviation, was approximately up to 15 %.

2.2.7 Analysis of metals in biota

The length and weight of each mussel were measured. The sizes of the sampled molluscs were in the range of 15 – 24 mm for *M. balthica* and 16 – 33 mm for *D. polymorpha*. Wet soft tissue was isolated from each specimen. Soft tissues of particular individuals (up to ca. 100 – 200 specimens) were pooled for each size group to obtain means of the samples. Samples were stored in at < -20 °C until further analysis. For the analysis samples were thawed, weighed and homogenised with Ultra Turrax homogenizer and digested with nitric acid in a microwave oven. The content of Cd, Pb, Cu in analytical solutions was detected using atomic absorption spectrometry (AAS) with graphite furnace. Content of Zn was detected with AAS flame atomisation or ICP-OES. Sediment and biota samples until 2010 were analyzed at the Marine Research Department, after 2010 – at the laboratory of the Environment Research Department of the Environmental Protection Agency. Metal concentrations in molluscs soft tissue are presented as mg kg^{-1} dry weight (d.w.).

2.2.8 Data preparation and statistical analysis

Measurements below limits of determination (LOD) were treated as half the LOD value of the compound considered.

Spatial and temporal variations of studied physical-chemical and biological parameters in the research area were estimated by the analysis of variance (ANOVA). The Shapiro-Wilk test was applied to check the normality. Bartlett's test was performed to investigate homogeneity of variances. If data did not meet ANOVA conditions, logarithmic transformations were applied. When significant differences were observed, the post hoc Tukey HSD test was used. A non-parametric Kruskal-Wallis test (referred to as KW test) was used when data violated the normality assumption. T-tests were applied to compare the means of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of POM in surface and near-bottom water layers. The mean concentrations after partial and total leaching were also compared via the parametric *t*-test. Pearson's coefficient was used to identify the relationships between trace and major elements, TOC, carbon isotopic signatures, particle size, water depth and salinity. The analysis was performed applying SigmaPlot 12.5 software.

The Principal Component Analysis (PCA) was performed in order to evaluate the relative contribution of the variables that explain the temporal and spatial variance of particulate matter in the research area. Three datasets (for the central freshwater and northern-transitional part of the lagoon as well as for the territorial waters of the Baltic Sea) were considered separately. The PCA was also used in order to identify pollution with metals sources and to scrutinize distribution pattern. Four datasets were analyzed separately: 1) the Klaipėda Strait; 2) the Curonian Lagoon; 3) territorial waters of the SE Baltic Sea and 4) open waters. For the PCA, the data were arranged in matrix, where each column corresponds to one variable (e.g., metal) and each row represents sediment station. The number of factors extracted from the variables was determined according to Kaiser's rule. This criterion retains only factors with eigenvalues that exceed one. The analysis was performed applying Brodgar software (Highland Statistics Ltd.) and Statistica 7 software.

2.2.9 Estimations of freshwater and marine sources contributions to POM and SOM

End-member mixing analysis based on the $\delta^{13}\text{C}$ signatures of POM and SOM is often used to identify mixing proportions of different sources in a compiled sample. The values of $\delta^{15}\text{N}$ have been not used to distinguish between organic matter sources since they are affected by a number of processes such as N_2 -fixation, mineralization, nitrification and denitrification, resulting in changed isotopic signatures from different sources (Middelburg and Nieuwenhuize, 1998; Chen et al., 2008).

Three main organic matter pathways may be distinguished in the lagoons: riverine, autochthonous organic matter production and marine POM intrusion. Whereas the isotopic signatures of the riverine and marine end members can be characterized rather easily, the isotopic signatures of POM added by production in the lagoon are difficult to estimate, because of assimilation of biogenic elements from both marine and riverine sources. Indeed, the share of two sources (riverine and lagoon POM) was not possible to calculate due to similar $\delta^{13}\text{C}$ values in POM during this study.

Therefore, for the research area, freshwater POM was simply considered as a complete contribution of riverine and lagoonal sources the magnitude of which is described by the two end-members equation (e.g., Ivanov et al., 2012; Szczepańska et al., 2012):

$$F (\%) = [(\delta^{13}\text{C}_S - \delta^{13}\text{C}_M) / (\delta^{13}\text{C}_F - \delta^{13}\text{C}_M)] * 100 \quad (9)$$

where $\delta^{13}\text{C}_S$ is the measured signature of analyzed samples, $\delta^{13}\text{C}_M$ is the reference value of marine phytoplankton and $\delta^{13}\text{C}_F$ is the reference value of the freshwater organic matter.

It was assumed that the contribution of the marine source of organic matter to the mixed POM and SOM was negligible in the central part of the Curonian Lagoon, since no intrusion of saline waters (salinity $<0.5\%$, based on

the daily routine measurements at the coastal hydrometeorological stations, not shown) was observed during the study period.

Finding a suitable end-member for the freshwater and marine POM component is challenging, mainly due to the fact that the end-members are generally a mixture of several organic materials, which makes their composition variable over time. In this case, an annual average value ($\delta^{13}\text{C} = -30.4\text{‰}$) for freshwater POM found in the Nemunas River and the central part of the Curonian Lagoon was used. For the marine end-member, the value ($\delta^{13}\text{C} = -22\text{‰}$) found in the literature for the marine phytoplankton in the Baltic Proper (Maksymowska et al., 2000; Szczepańska et al., 2012) was used, which was in good agreement with results of this study. It was taken into account, that the end-members were unable to capture some data in the mixing model and therefore, the calculated values outside the percent scale (0 – 100%) were replaced by its minimum – maximum values.

In order to have a better estimation of freshwater POM percentage in surface sediment, the following end-member mixing model equations (Bănaru et al., 2007) were used:

$$F (\%) = [(\delta^{13}\text{C}_s - \delta^{13}\text{C}_m) / (\delta^{13}\text{C}_f - \delta^{13}\text{C}_m)] * 100 \quad (10)$$

$$F (\%) = [(\delta^{13}\text{C}_s) - (\delta^{13}\text{C}_m + 1)] / [(\delta^{13}\text{C}_f + 1) - (\delta^{13}\text{C}_m + 1)] * 100 \quad (11)$$

$$F (\%) = [(\delta^{13}\text{C}_s) - (\delta^{13}\text{C}_m + 1)] / [\delta^{13}\text{C}_f - (\delta^{13}\text{C}_m + 1)] * 100 \quad (12)$$

$$F (\%) = [(\delta^{13}\text{C}_s) - (\delta^{13}\text{C}_m)] / [(\delta^{13}\text{C}_f + 1) - \delta^{13}\text{C}_m] * 100 \quad (13)$$

where $\delta^{13}\text{C}_s$ is the measured signature of analyzed samples, $\delta^{13}\text{C}_m$ is the reference value of marine phytoplankton and $\delta^{13}\text{C}_f$ is the reference value of the freshwater organic matter. In equations (11-13), $\delta^{13}\text{C}_m + 1\text{‰}$ and $\delta^{13}\text{C}_f + 1\text{‰}$ correspond to sedimentary organic matter from primary consumers (zooplankton, bacteria) which have $\delta^{13}\text{C}$ values higher by $+1\text{‰}$ than those of the primary producers (Schoeninger and DeNiro, 1984). They were used in calculations in order to reduce uncertainties related to the plankton diversity.

2.2.10. Calculations of the metal pollution indices

The sediment pollution intensity indexes (enrichment factor – EF, geoaccumulation index – I_{geo} , contamination factors – CF, C_d) and potential ecological risk indexes (E_r^i and RI) were calculated in the study. The description and formulas were presented in the table 1.5.1. No background data of metals for uncontaminated marine sediment in the study area were available, therefore, the global Earth's shale values for metals reported by Turekian and Wedepohl (1961) were used as background values for metals.

3. RESULTS AND DISCUSSION

3.1 Distribution of particulate and sedimentary organic matter in the SE Baltic Sea

3.1.1 Hydrological, chemical and biological variables in water of the study area

The environmental variables which have an impact on the distribution of organic matter were evaluated. The averaged data and variability of the environmental parameters and characteristics of POM for distinct research zones are presented in Table 3.1.1, while the results are briefly described in the section 3.1.1.

A seasonal trend of water temperatures was observed in the marine waters with the lowest temperature in February (0.1 ± 0.1 °C) and the highest one in August (19.7 ± 0.2 °C). No significant difference (*t*-test, $t = -0.49$, $p > 0.05$) was observed between surface and near-bottom water temperature in the Curonian Lagoon, while the near-bottom water temperature in the Baltic Sea coastal waters was on average ~ 3 °C lower in comparison with the surface water. In the research area, the salinity showed significant differences depending on the station location and the sampling period (ANOVA, $F = 5.79$ and $F = 6.55$, respectively, $p < 0.05$). The average salinity was 0.14‰ at the central part of the Curonian Lagoon and increased seaward up to 11.6‰ with water depth (Fig. 3.1.1). In most stations near-bottom water salinity was consistently elevated as compared with that measured in the surface waters (Fig. 3.1.1).

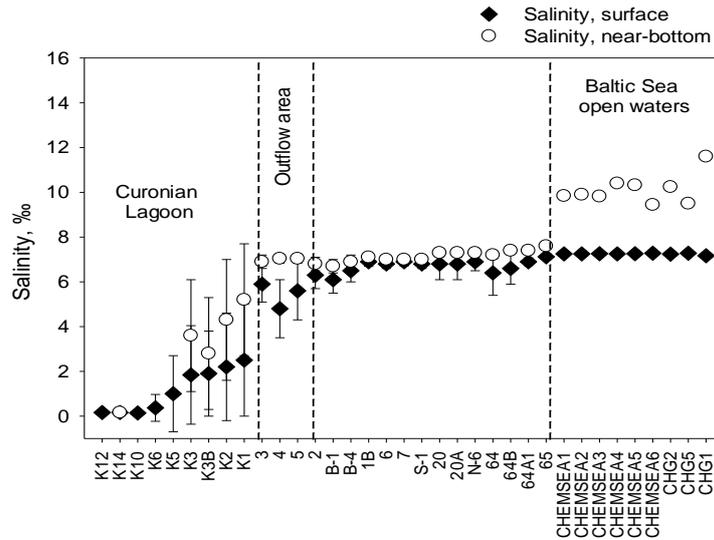


Fig. 3.1.1 Salinity distribution (mean \pm sd) in the Curonian Lagoon and the Baltic Sea stations in 2011–2014.

The highest variability in salinity was observed in the northern part of the lagoon (Fig. 3.1.1 and Table 3.1.1). More frequent marine waters intrusions to the northern part of the Curonian Lagoon were observed in June – November (Fig. 3.1.2); the obtained results coincided with the predominant southern direction of currents (not shown). No intrusion of saline waters (salinity $<0.5\text{‰}$, based on the data obtained during research cruises (Table 3.1.1) and daily routine measurements at the coastal hydrometeorological stations, not shown) was observed in the central part of the Curonian Lagoon during the study period. The Nemunas River discharge into the Curonian Lagoon ranged between $216 \text{ m}^3 \text{ s}^{-1}$ (October, 2012) and $2150 \text{ m}^3 \text{ s}^{-1}$ (April, 2013) with the average value of $525 \pm 305 \text{ m}^3 \text{ s}^{-1}$ (Fig. 3.1.2).

During the sampling campaigns in 2013 – 2014 at the open sea, a thermohaline stratification was observed in the deepest Baltic Sea stations at a depth of about 50–60 m. The upper water layer was characterised by lower salinity ($\sim 7\text{‰}$) and seasonal changes of water temperature. A more stable temperature (up to 6°C) and the highest salinity ($\sim 11\text{--}12\text{‰}$) were observed below halocline during spring and autumn cruises. The stratification in the water column impacted also the oxygen profile, with the oxygen concentration less than 3 mg l^{-1} below halocline (Fig. 3.1.3). The lower oxygen

concentrations at near bottom water layer were also measured at the stations in the Klaipeda Strait. Except for these occasions, oxygen concentration less than 3 mg l^{-1} was not measured during the sampling campaigns.

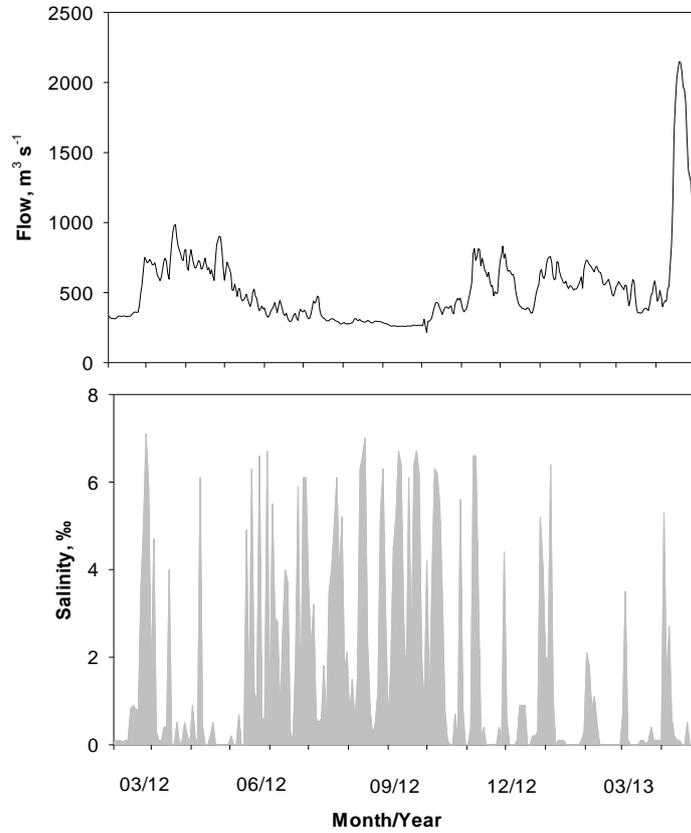


Fig. 3.1.2 Daily discharge of the Nemunas River (upper panel) and variability of salinity in the northern part of the Curonian Lagoon (lower panel) in 2012–2013.

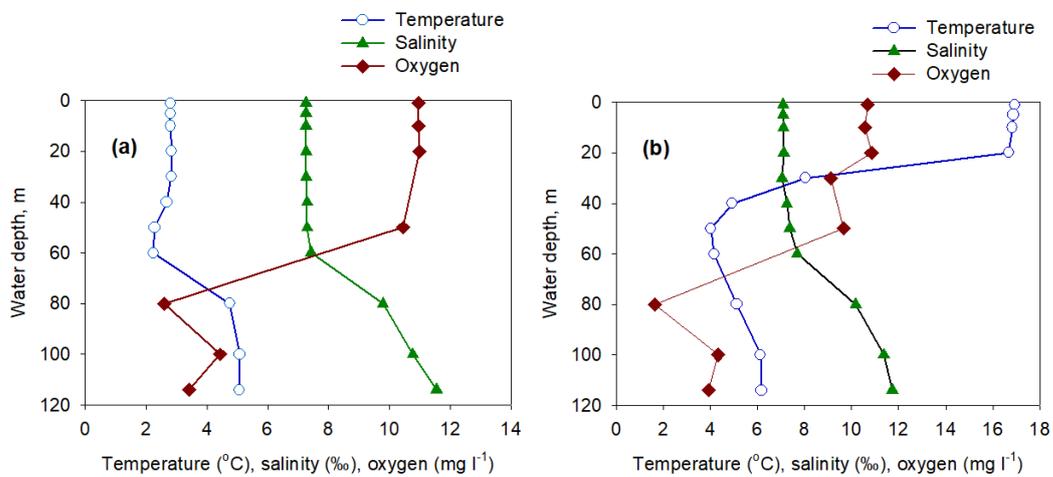


Fig. 3.1.3 Distribution of temperature, salinity and oxygen at station CHG1 (117 m water depth) in April 2013 (panel a) and in September 2014 (panel b).

Table 3.1.1 Water column characteristic (mean \pm sd) of the studied sites during the period of 2012 – 2014* (T – water temperature, DO – dissolved oxygen, DIN – dissolved inorganic nitrogen, POC – particulate organic carbon, PN – particulate nitrogen, Chl-*a* – chlorophyll *a*. The number of samples shown in the second parenthesis.

Parameters	<i>The Curonian Lagoon</i>			<i>The Baltic Sea</i>		
	The Nemunas River	Central part of the Curonian Lagoon	Northern part of the Curonian Lagoon – Klaipeda Strait	Plume of the Curonian Lagoon waters into the Baltic Sea	The Baltic Sea coastal waters	The Baltic Sea open waters
T, °C	10.7 \pm 7.8 (0.1 – 22.1) (12)	11.7 \pm 6.7 (0.1 – 18.9) (30)	12.2 \pm 6.2 (0.1 – 19.7) (72)	10.6 \pm 6.9 (0.3 – 18.9) (16)	11.1 \pm 6.2 (0.2 – 18.8) (54)	4.8 \pm 4.2 (2.0 – 17.1) (128)
Salinity,‰	-	0.16 \pm 0.06 (0.02 – 0.2) (30)	2.73 \pm 2.70 (0.02 – 7.2) (72)	5.3 \pm 1.4 (2.5 – 7.4) (16)	7.1 \pm 0.49 (4.1 – 7.4) (54)	7.8 \pm 1.2 (6.9 – 11.7) (128)
pH, (-)	8.46 \pm 0.37 8.02 – 9.27 (12)	8.68 \pm 0.27 8.32 – 9.22 (49)	8.58 \pm 0.29 7.78 – 9.19 (91)	8.18 \pm 0.29 7.44 – 8.48 (16)	8.31 \pm 0.27 7.46 – 8.57 (54)	8.37 \pm 0.23 7.82 – 8.57 (103)
DO, mg l⁻¹	-	5.68 \pm 1.49 (3.01 – 8.68) (21)	5.66 \pm 0.97 (3.99 – 9.04) (59)	6.49 \pm 1.06 (4.92 – 7.89) (9)	6.32 \pm 1.29 (5.11 – 9.12) (36)	8.85 \pm 2.98 (1.62 – 11.15) (118)
TSM, mg l⁻¹	14.6 \pm 10.7 (3.2 – 42.0) (12)	18.6 \pm 13.1 (2.5 – 46.0) (20)	14.1 \pm 6.1 (3.2 – 31.0) (51)	-	14.1 \pm 6.1 (3.2 – 31.0) (25)	-
DIN, μmol l⁻¹	75.58 \pm 75.41 (2.71 – 192.21) (12)	34.03 \pm 39.41 (0.71 – 162.14) (27)	32.19 \pm 40.17 (0.75 – 163.36) (63)	26.97 \pm 33.99 (1.46 – 105.79) (14)	5.09 \pm 6.98 (1.25 – 46.29) (51)	3.36 \pm 2.21 (0.93 – 8.78) (55)
POC, mg l⁻¹	1.97 \pm 1.60 (0.39 – 4.73) (12)	3.10 \pm 2.30 (0.30 – 8.40) (29)	1.60 \pm 1.07 (0.48 – 5.22) (62)	0.56 \pm 0.39 (0.16 – 1.53) (10)	0.24 \pm 0.23 (0.05 – 1.11) (41)	-
PN, mg l⁻¹	0.41 \pm 0.23 (0.07 – 0.71) (12)	0.50 \pm 0.40 (0.02 – 1.40) (29)	0.30 \pm 0.21 (0.05 – 0.92) (62)	0.09 \pm 0.08 (0.02 – 0.29) (10)	0.04 \pm 0.04 (0.004 – 0.18) (40)	-
Chl-<i>a</i>, μg l⁻¹	35.15 \pm 39.97 (1.85 – 113.66) (10)	42.05 \pm 26.87 (1.83 – 106.67) (27)	20.73 \pm 16.99 (0.21 – 94.39) (55)	7.59 \pm 7.60 (0.58 – 27.94) (16)	3.25 \pm 3.31 (0.14 – 17.62) (49)	2.50 \pm 1.20 (1.16 – 4.19) (12)

*Characteristics for the Nemunas River, the Curonian Lagoon and the Baltic Sea coastal waters include data from May 2012 to April 2013; for the Baltic Sea open waters – data obtained in April 2013 and September 2014.

The water displayed distinct temporal changes in pH, concentration of DIC and $\delta^{13}\text{C}$ in DIC. pH varied between 7.44 and 9.27 (Table 3.1.1) with the highest values observed in summer (Tukey HSD test, $p < 0.05$). There were no significant differences in pH values in samples from different locations (ANOVA, $F = 1.00$, $p > 0.05$). DIC, on the contrary, were the lowest ones in summer (Fig. 3.1.4) and inversely related to water temperature ($r = -0.79$ and -0.93) and pH ($r = -0.74$ and -0.87) for the central and northern parts of the Curonian Lagoon, respectively (Annex III, Tables A3.1, A3.2). Values of $\delta^{13}\text{C}_{\text{DIC}}$ in the Curonian Lagoon varied between -14.1‰ and -4.1‰ (Fig. 3.1.4) and they were inversely related to the DIC ($r = -0.98$, $n = 51$, $p < 0.001$, Annex III, Table A3.1). The mean $\delta^{13}\text{C}_{\text{DIC}}$ value of most samples of the Nemunas River during the study period was $-11.3 \pm 2.3\text{‰}$ (Fig. 3.1.4) and was in agreement to the $\delta^{13}\text{C}_{\text{DIC}}$ (from -12‰ to -10‰) reported for the European lowland rivers (Voss et al., 2005a; Gustafsson et al., 2015).

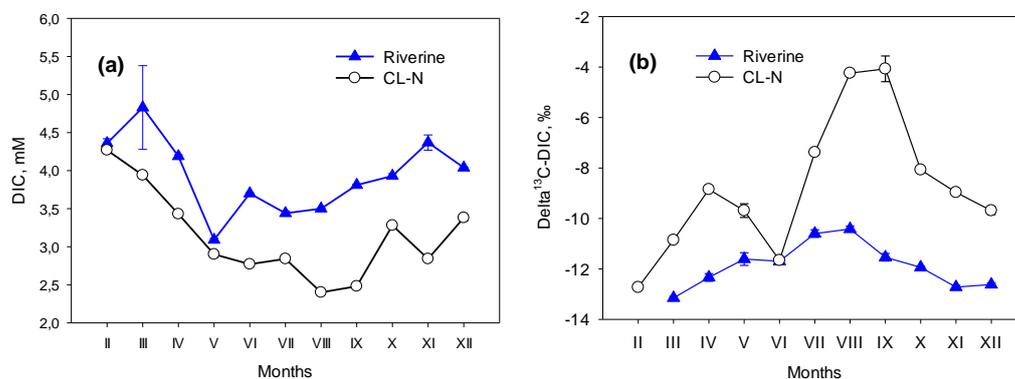


Fig. 3.1.4 Variability of DIC (mM) and $\delta^{13}\text{C}_{\text{DIC}}$ (‰) in the Nemunas River (Riverine) and the northern part of the Curonian Lagoon (CL-N). The average values ($n=3$) are presented.

Dissolved inorganic nitrogen (DIN) concentrations revealed a clear seasonal pattern with minimum values in summer and maximum values in winter – early spring (Tukey HSD test, $p < 0.05$, Fig. 3.1.5b,d). In the Curonian Lagoon the nitrates ($\text{NO}_3\text{-N}$) constituted 80–100% of DIN in November – May, whereas DIN consisted of ammonium ($\text{NH}_4\text{-N}$) in June – September ($78 \pm 18\%$ of DIN). There were no significant variations in DIN in samples from different locations (ANOVA, $F = 2.31$, $p > 0.05$). The averaged DIN

concentration in the Baltic Sea was about six-fold lower in comparison with that in the lagoon (Table 3.1.1); DIN was mainly composed of ammonium in August (up to $90 \pm 6\%$ of DIN) and nitrate in February ($80 \pm 10\%$ of DIN).

Chlorophyll-*a* (Chl-*a*) concentration, taken here as an indicator of productivity, varied from 0.21 to $113.66 \mu\text{g l}^{-1}$ (Table 1.3.1) with seaward decreasing values from the central part of the Curonian Lagoon (Tukey HSD test, $p < 0.05$) and a largely pronounced seasonal variability (Fig. 3.1.5b,d). The measured Chl-*a* concentrations (Table 1.3.1) agreed well with the previously reported values (e.g., on the average, $2.5 - 3.5 \mu\text{g l}^{-1}$ for the Gotland Basin and $24 - 113 \mu\text{g l}^{-1}$ for the Curonian Lagoon, Krevs et al., 2007; Wannicke et al., 2013). The peak of Chl-*a* was determined in May – July in the Nemunas River ($84.53 \pm 25.99 \mu\text{g l}^{-1}$) and in July – October in the central part of the Curonian Lagoon ($67.05 \pm 17.15 \mu\text{g l}^{-1}$). In the northern part of the lagoon, the highest Chl-*a* value ($36.22 \pm 17.20 \mu\text{g l}^{-1}$) in August was two-fold lower than in the central part and indicated the phytoplankton bloom. In the Curonian Lagoon outflow, an increase of Chl-*a* concentration was also observed during summer campaign ($12.55 \pm 8.50 \mu\text{g l}^{-1}$). In the Baltic Sea territorial waters, the highest value of Chl-*a* ($9.15 \pm 7.22 \mu\text{g l}^{-1}$) was also measured in August.

Regarding the phytoplankton composition, diatoms were dominant during the period of May – October (~80% of phytoplankton biomass) in the Nemunas River, while cyanobacteria accounted for 8% of phytoplankton biomass. No riverine phytoplankton data was available for the period from November to April 2013. The phytoplankton composition in the Curonian Lagoon followed the seasonal successional patterns with a dominance of diatoms in November – May (up to 90% of the total biomass in February) and it shifted towards more intensive development of cyanobacteria in June – October (up to 70 – 80% of the total biomass). The cyanobacteria bloom was observed in the central part of the lagoon in July – October (Fig. 3.1.5a) with a noticeable prevalence (up to 90% in August and up to 35% in October) of N₂-fixer *Aphanizomenon flos-aquae*. The intensive development of diatoms was

also observed during this period. The phytoplankton community in the northern part of the lagoon was represented by the same groups of phytoplankton with two-fold lower total biomass (Fig. 3.1.5c). In the outflow of the Curonian Lagoon the phytoplankton assemblage was dominated by diatoms which together with cyanobacteria constituted the majority (up to 80% of total biomass in August). In the Baltic Sea territorial waters, dinoflagellates dominated phytoplankton community in May (59% of the total phytoplankton biomass), diatoms in August (~75%) and in October (~35%), and both groups in February (~66% of total biomass). At the distinct research sites in the Baltic Sea coastal waters the biomass of cyanobacteria constituted from <1% to 36% with the average ~10% of the total phytoplankton biomass. Other algal groups were less abundant at the research sites.

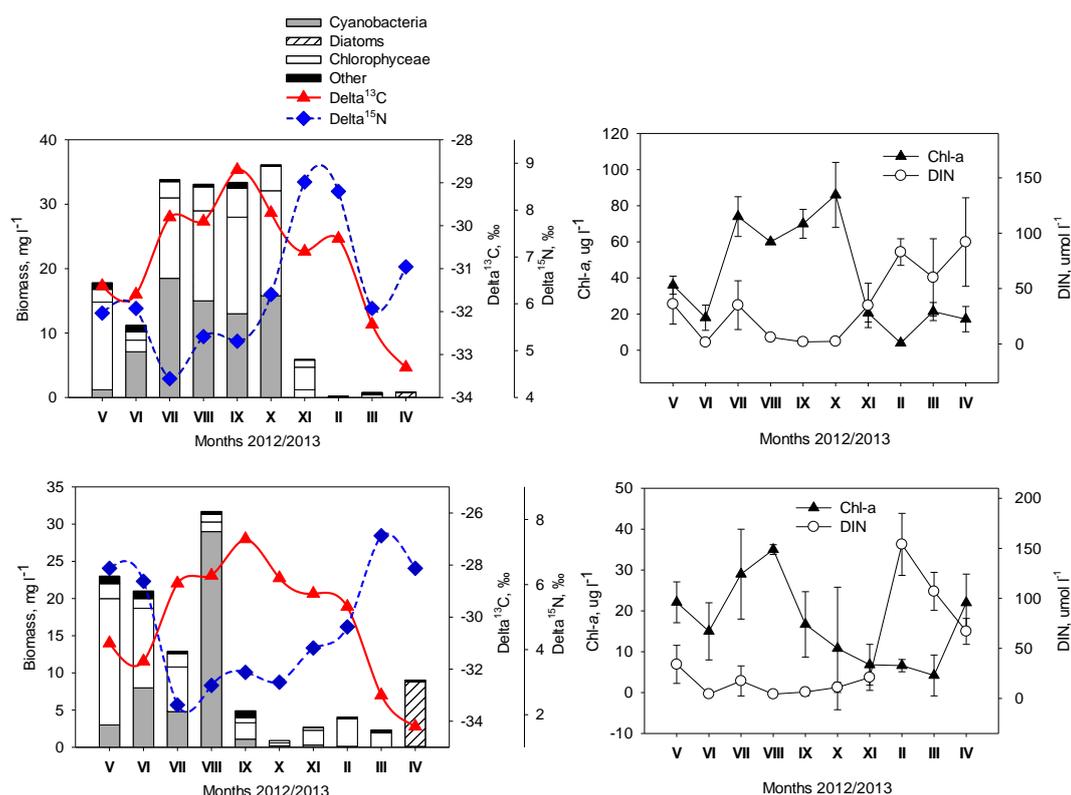


Fig. 3.1.5 Monthly variation of phytoplankton biomass and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ signatures of POM, chlorophyll a (Chl-*a*) and dissolved inorganic nitrogen (DIN) in the central part of the Curonian lagoon (a,b; $n=3\pm\text{sd}$) and the northern part of the Curonian Lagoon (c,d; $n=6\pm\text{sd}$).

3.1.2. Composition and fate of POM

The significant relationships between TSM, Chl-*a* and POC values ($r = 0.77\text{--}0.90$, $p < 0.001$) in the central part of the Curonian Lagoon suggested the presence of TSM with a high organic matter component attributed to the photosynthetic activity (*Annex III*, Table A3.1 and A3.2). As it was reported by Brescianni et al. (2014), more than 80 % of the TSM in the Curonian Lagoon consisted of organic matter. The correlations between TSM, POC and Chl-*a* values ($r = 0.35\text{--}0.42$, $p < 0.001$) were much weaker for the northern part of the lagoon, most probably due to the increasing contribution of inorganic particles to the TSM resulted from the active hydrodynamics and resuspension of the sedimentary matter in the transitional environment. Later, the loadings of TSM, cyanobacteria and riverine discharge on the principal component (PC4) for the transitional part of the Curonian Lagoon showed the summer situation: the low riverine discharge (Fig. 3.1.2) resulted in the reduced amount of TSM, while increasing biomass of cyanobacteria was contributing to the largest part of POC (Table 3.1.2). In the Baltic Sea territorial waters, the positive association between TSM, POC and Chl-*a* ($r = 0.40\text{--}0.58$, $n = 41$, $p < 0.05$, *Annex III*, Table A3.3) also indicated a significant contribution of organic component. The excellent positive relationship between organic carbon and total nitrogen content ($r = 0.99$, $p < 0.001$, Fig. 3.1.6) suggested that organic N was the predominant nitrogen source in particulate and sedimentary matter.

During the study the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in POM ranged from -36.1‰ to -21.3‰ and from -1.2‰ to 15.5‰ , respectively (Fig. 3.1.7), with the seasonal and spatial variability (Fig. 3.1.8). POM was significantly enriched in ^{13}C (increase of 4.5‰) and depleted in ^{15}N (decrease of $2\text{--}2.5\text{‰}$) in marine waters compared to the Curonian Lagoon samples (Table 3.1.4, Tukey HSD test, $p < 0.05$).

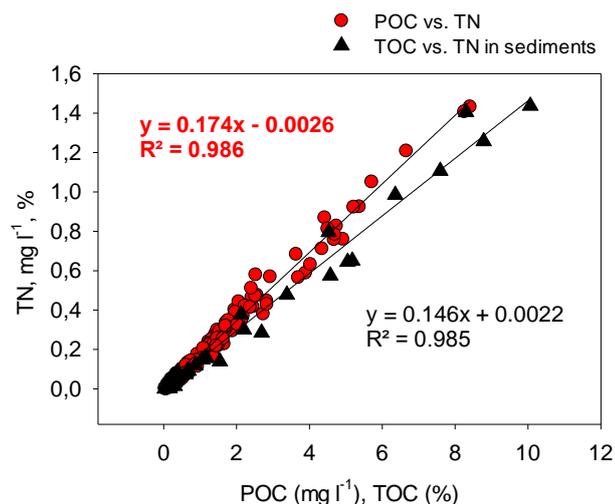


Fig. 3.1.6 The relationships between organic carbon and nitrogen content in POM (circles) and SOM (triangles). Concentrations are expressed in mg l⁻¹ in suspended phase and in % in sediments.

The stable isotopic signatures recorded in the research area (Fig. 3.1.7) indicated a mixed composition of POM including freshwater/estuarine phytoplankton ($\delta^{13}\text{C}$ from -35 to -25‰ and $\delta^{15}\text{N}$ around 5‰), marine phytoplankton ($\delta^{13}\text{C}$ from -22 to -18‰ and $\delta^{15}\text{N}$ $4\text{--}6\text{‰}$) and terrestrial vegetation ($\delta^{13}\text{C}$ around -27‰ and $\delta^{15}\text{N}$ around 3‰).

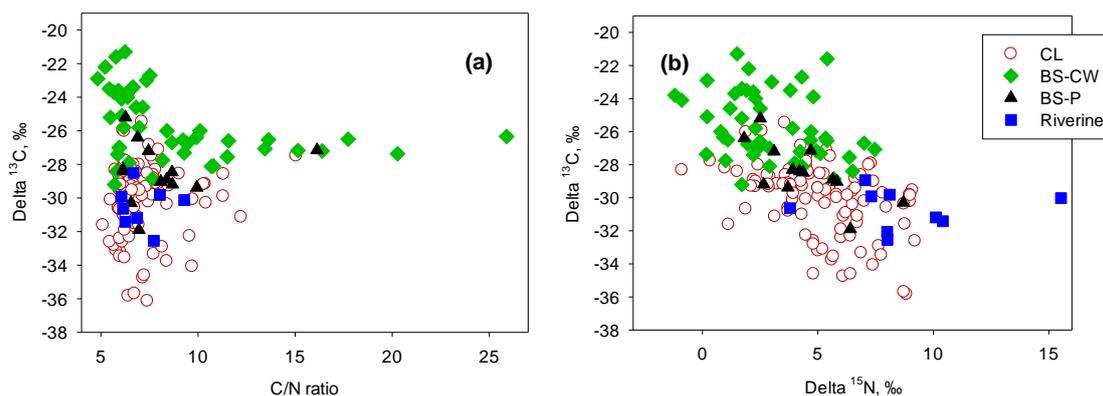


Fig. 3.1.7 Dual plots (panel a: $\delta^{13}\text{C}$ vs. C/N ratio in POM; panel b: $\delta^{13}\text{C}$ vs. $\delta^{15}\text{N}$ in POM) of organic matter. CL – Curonian Lagoon, BS-P – Plume of the Curonian Lagoon waters in the Baltic Sea, BS-CW – Baltic Sea coastal waters).

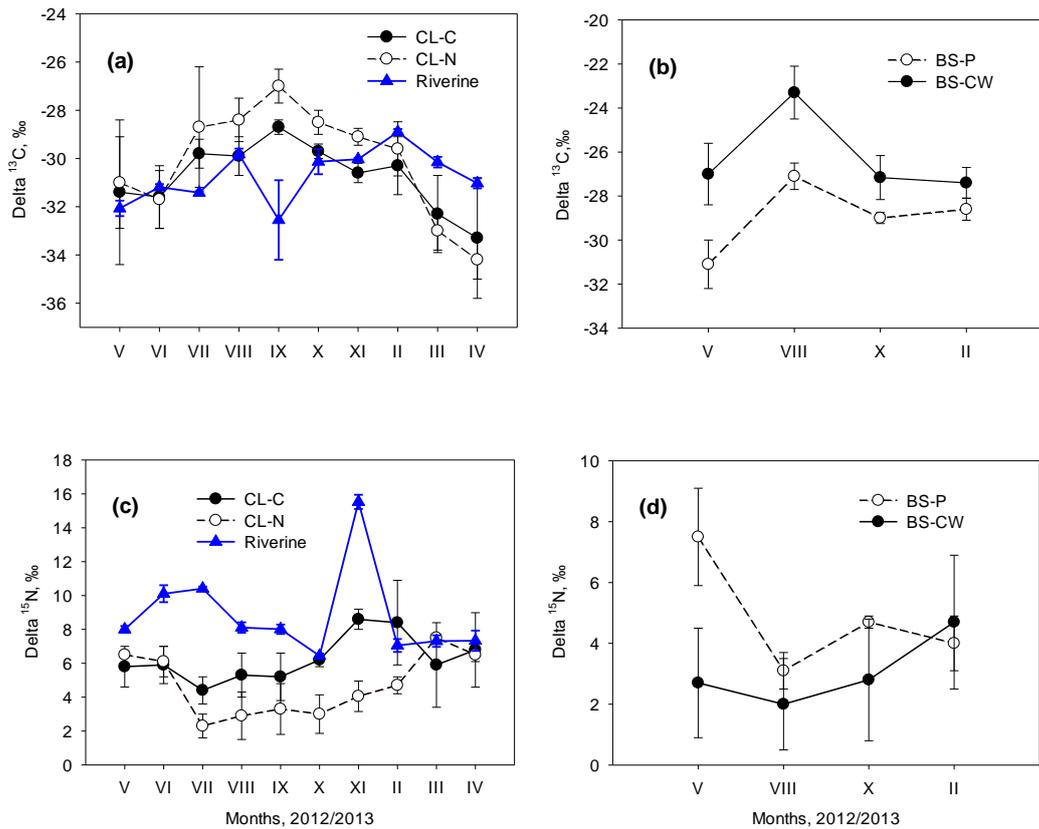


Fig. 3.1.8 Monthly mean values and standard deviation of the carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotope ratios of the surface waters POM (CL-C and CL-N – central and northern parts of the Curonian Lagoon, respectively; BS-P – plume of the Curonian Lagoon waters in the Baltic Sea, BS-CW – Baltic Sea coastal waters). The average values ($3 \leq n \leq 13$) \pm standard deviations are reported.

The average isotopic signatures of POM (Table 3.1.4) in the Curonian Lagoon were similar to those obtained in the previous study (on the average, $\delta^{13}\text{C} = -29.8\text{‰}$, $\delta^{15}\text{N} = 5.7\text{‰}$, Lesutienė et al., 2014). There is a lack of results of the isotopic signatures of POM in the coastal stations of the SE Baltic Sea, however, $\delta^{13}\text{C}$ in POM ($-25.7 \pm 2.1\text{‰}$, Table 3.1.4) was closer to the $\delta^{13}\text{C}$ value of -24‰ reported for the phytoplankton in the Baltic Sea Proper (Rolff and Elmgren, 2000). Moreover, the highest $\delta^{13}\text{C}$ signals in POM ($\sim -22\text{‰}$) measured in August at stations of the territorial waters (Fig. 3.1.8b) coincided with the marine phytoplankton end-member value ($\delta^{13}\text{C}$ of -22‰) used in other studies (Ivanov et al., 2012; Szczepańska et al., 2012).

The low C/N (~ 7) and POC/Chl-*a* values (< 100) in POM samples remained low throughout the year (Fig. 3.1.9), also suggesting dominance of

phytoplanktonic material. Although a significant increase of C/N (~10) and POC/Chl-*a* ratios (Tukey HSD test, $p < 0.05$) was observed during the cold period (Fig. 3.1.9), it was not indicative of terrestrial vascular plant detritus (C/N >12). Indeed, based on the previous studies (Galkus and Jokšas, 1997; Tomczak et al. 2009; Lesutienė et al., 2008, 2014), the contribution of terrestrial vegetation in the SE Baltic Sea rivers and the Curonian Lagoon was negligible.

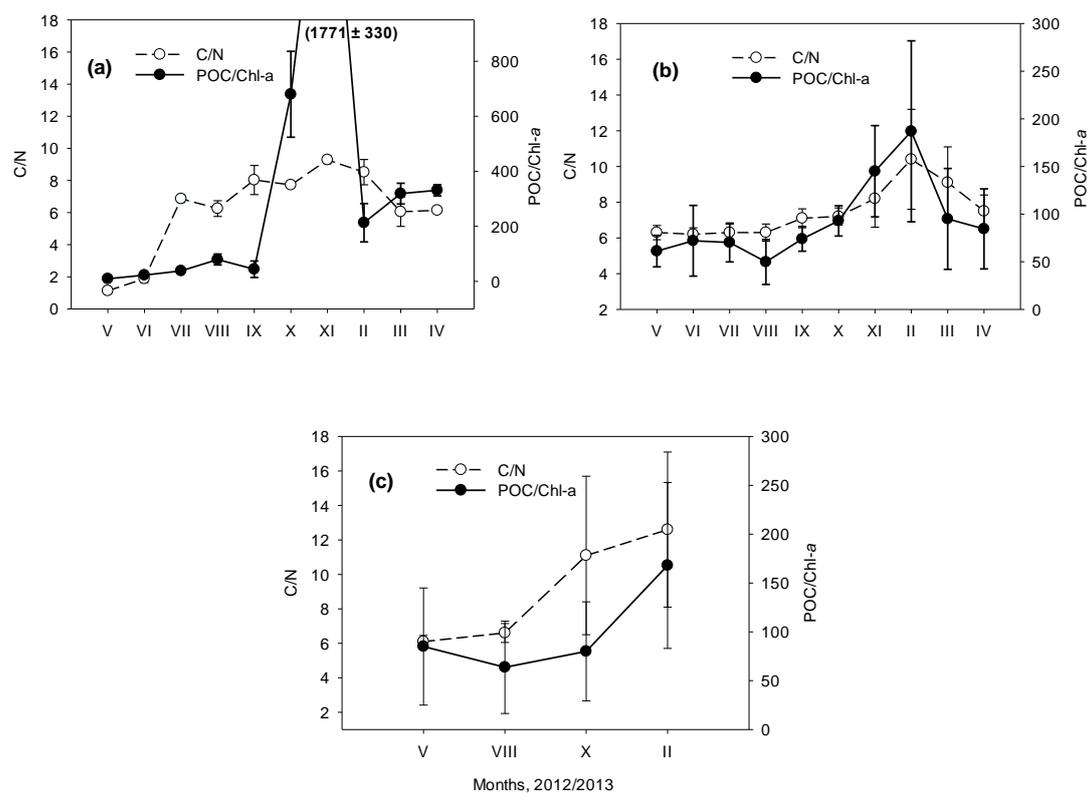


Fig. 3.1.9 Monthly mean values and standard deviation of the C/N and POC/Chl-*a* ratios (panel a – the Nemunas River ($n=3\pm sd$); panel b – the averaged values ($n=10\pm sd$) for the Curonian Lagoon; panel c – the averaged values ($n=16\pm sd$) for the Baltic Sea).

First of all, it was assumed that dominance of diatoms in the phytoplankton assemblage during the cold period could explain an increase of C/N and POC/Chl-*a* values. However, diatoms, with their larger biovolume (highest relative contribution to POC and Chl-*a*), would result in the lower POC/Chl-*a* and C/N ratios as it was shown by Lapoussi re et al., (2009) and in this study (Tables 3.1.2 and 3.1.3). It may be expected elevated POC/Chl-*a* and C/N values (Fig. 3.1.9) due to degradation of POM since the Chl-*a* and PON

are degraded comparatively faster than the whole POC pool (Cifuentes et al., 1988; Savoye et al., 2003). Thus, POM composed of phytoplankton is being degraded rapidly by losing labile compounds resulting in higher C/N and POC/Chl-*a* ratios (late autumn – winter period), whereas the POC and its $\delta^{13}\text{C}$ values remain still high in this period (Fig. 3.1.5a,c). The positive loadings of C/N and POC/Chl-*a* on the PC2 with POC and its $\delta^{13}\text{C}$ values (Table 3.1.2) in the central area of the lagoon give evidence of their simultaneous increase.

3.1.3 Temporal and spatial variability of isotopic signatures of POM

In order to assess distribution, temporal and spatial differences of POM, its isotopic signatures and the main controlling factors, the PCA was carried out for three datasets (the central freshwater part and the northern-transitional part of the lagoon and the Baltic Sea coastal waters). The PCA separated variables into groups according to different effects and driving factors (Fig. 3.1.10 and Tables 3.1.2, 3.1.3). The inter-parameter relationships (*Annex III*, Tables A3.1 – A.3.3) supported the results obtained from PCA and they have also been useful in revealing some new association of variables that were not properly stated in the PCA. The loading plots showed that first four Principal Components (PCs) with eigenvalues greater than 1 (Tables 3.1.2 – 3.1.3) explained 72.5%, 68.6% and 69.2% of the total variance in the central and northern parts of the lagoon and Baltic Sea coastal waters, respectively.

The PCA analysis (Fig. 3.1.10, Tables 3.1.2 and 3.1.3) allowed to disentangle the mechanism responsible for variability of POM and its isotopic signatures in the research area. In the central part of the lagoon, POM dynamics and the stable C and N isotopic values were primarily influenced by strong seasonal dynamics of riverine inputs. Towards summer, the significantly decreased riverine inputs in the lagoon and an increased temperature shifted to N limitation (Vybernaite-Lubiene et al., 2017). As a result, diatoms were gradually replaced by N₂-fixing cyanobacteria (Fig. 3.1.5). An increasing biomass of phytoplankton in summer resulted in DIC pool depletion and

increment of $\delta^{13}\text{C}_{\text{DIC}}$ values due to fractionation during DIC uptake (Fig. 3.1.10, Table 3.1.2). It was obvious that seasonal variability in biological activity controls shift in the DIC and DIN pool, and it was confirmed by the significant correlations between Chl-*a* and either the DIC, $\delta^{13}\text{C}_{\text{DIC}}$ and DIN (Annex III, Table A3.1). The shift in phytoplankton assemblage and increasing phytoplankton (mainly cyanobacteria) biomass in summer – early autumn were reflected by the tendency to lower $\delta^{15}\text{N}$ and higher $\delta^{13}\text{C}$ values in the Curonian Lagoon (Fig. 3.1.5). Indeed, the biomass of cyanobacteria positively related with the $\delta^{13}\text{C}$ ($r = 0.56$, $n = 20$, $p < 0.05$) and inversely with the $\delta^{15}\text{N}$ values ($r = -0.76$, $n = 20$, $p < 0.001$) in the central part of the lagoon (Annex III, Table A3.1). N_2 -fixation by cyanobacteria is accompanied by little isotopic discrimination and produces organic matter with an isotopic composition similar to that of atmospheric nitrogen ($\delta^{15}\text{N} = \sim 0\text{‰}$). In the Baltic Sea, N_2 -fixation may contribute $\sim 50\%$ to primary production with the largest proportion of N_2 -fixer *Nodularia spumigena* and *Aphanizomenon flos-aquae* (Struck et al., 2004; Łysiak-Pastuszek et al., 2012; Wannicke et al., 2013 and references therein). The reduced $\delta^{15}\text{N}$ values in POM due to the intensive cyanobacteria development seem to be annually re-occurring phenomena in the Baltic Proper (e.g., Voss and Struck, 1997; Struck et al., 2004). However, in the Lithuanian zone of the SE Baltic Sea, the blue-green algae contributed about 10% of the total biomass, and no significant relationship was observed between cyanobacteria and the $\delta^{15}\text{N}$ values (Annex III, Table A3.3). The positive correlations of $\delta^{15}\text{N}$ values and either biomass of diatoms (Table 3.1.4) and dinoflagellates ($r = 0.53$, $n = 45$, $p < 0.05$, Annex III, Table A3.3) indicated that the variability in $\delta^{15}\text{N}$ values first of all was attributed to the variability of biomass of diatoms and dinoflagellates. Therefore, most probably that besides nitrogen fixation by cyanobacteria in summer, the $\delta^{15}\text{N}$ dynamics in the Baltic Sea by large part was attributed to dominance of diatoms and dinoflagellates and to the variability of available N sources: uptake of isotopically light nutrients in summer, and on the contrary, uptake of ^{15}N -enriched DIN during floods in May and February.

Table 3.1.2 Results of the PCA for the Curonian Lagoon. The dominant loadings in each PC are given in **Bold**.

Variables	The central area				The northern transitional area			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
TSM	0.237	0.301	0.324	-0.125	0.112	0.075	0.044	-0.377
DIC	-0.324	0.150	-0.065	-0.111	0.348	0.175	-0.286	0.143
$\delta^{13}\text{C}_{\text{DIC}}$	0.326	-0.111	0.017	0.122	0.235	-0.023	0.478	-0.223
pH	0.205	0.048	0.170	0.213	0.315	-0.205	0.301	0.136
Chl- <i>a</i>	0.328	0.136	0.066	0.176	0.272	-0.317	-0.030	0.150
$\delta^{13}\text{C}$	0.096	0.510	-0.275	0.280	0.201	0.352	0.192	0.191
POC	0.263	0.360	0.287	0.024	0.151	-0.401	-0.045	0.111
POC/Chl- <i>a</i>	-0.171	0.469	0.197	-0.375	-0.234	0.007	0.217	0.464
$\delta^{15}\text{N}$	-0.241	-0.173	0.353	0.301	-0.167	-0.395	0.009	-0.263
C/N	-0.235	0.350	-0.328	0.254	-0.278	0.059	0.425	0.049
DIN	-0.298	0.112	-0.064	0.205	-0.357	-0.119	0.153	0.283
Discharge	-0.228	0.125	0.531	0.188	-0.246	-0.173	0.181	-0.394
Cyanobacteria	0.299	0.197	-0.181	0.071	0.219	-0.233	0.152	0.409
Diatoms	0.236	-0.156	0.021	0.465	0.024	-0.208	-0.426	0.098
Temperature	0.281	-0.057	-0.192	-0.405	0.377	0.133	-0.269	0.027
Salinity	0.135	-0.042	0.291	-0.211	0.189	0.499	0.082	-0.079
Eigenvalues	7.372	1.699	1.385	1.143	4.715	2.941	1.535	1.095
% of variance	46.076	10.621	8.655	7.141	31.431	19.606	10.233	7.298
Cumulative %	46.076	56.696	65.351	72.492	31.431	51.036	61.269	68.567

Table 3.1.3 Results of the PCA for the Baltic Sea coastal waters. The statistically dominant loadings are given in **Bold**.

Variables	PC1	PC2	PC3	PC4
TSM	0.065	-0.148	0.243	0.457
Chl- <i>a</i>	0.274	-0.341	0.232	-0.092
$\delta^{13}\text{C}$	0.403	-0.018	0.110	-0.182
POC	0.204	-0.237	0.017	0.615
POC/Chl- <i>a</i>	-0.254	0.290	-0.118	0.319
$\delta^{15}\text{N}$	-0.234	0.051	0.448	0.324
C/N	-0.340	0.157	-0.378	-0.079
DIN	-0.347	-0.289	-0.239	-0.109
Cyanobacteria	-0.254	-0.502	-0.091	-0.173
Diatoms	0.001	-0.286	0.556	-0.251
Dinoflagellates	-0.361	-0.015	0.248	-0.013
Temperature	0.464	-0.070	-0.070	0.038
Salinity	0.172	0.516	0.252	-0.216
Eigenvalues	3.747	2.419	1.724	1.111
% of variance	28.825	18.611	13.260	8.543
Cumulative %	28.825	47.436	60.696	69.239

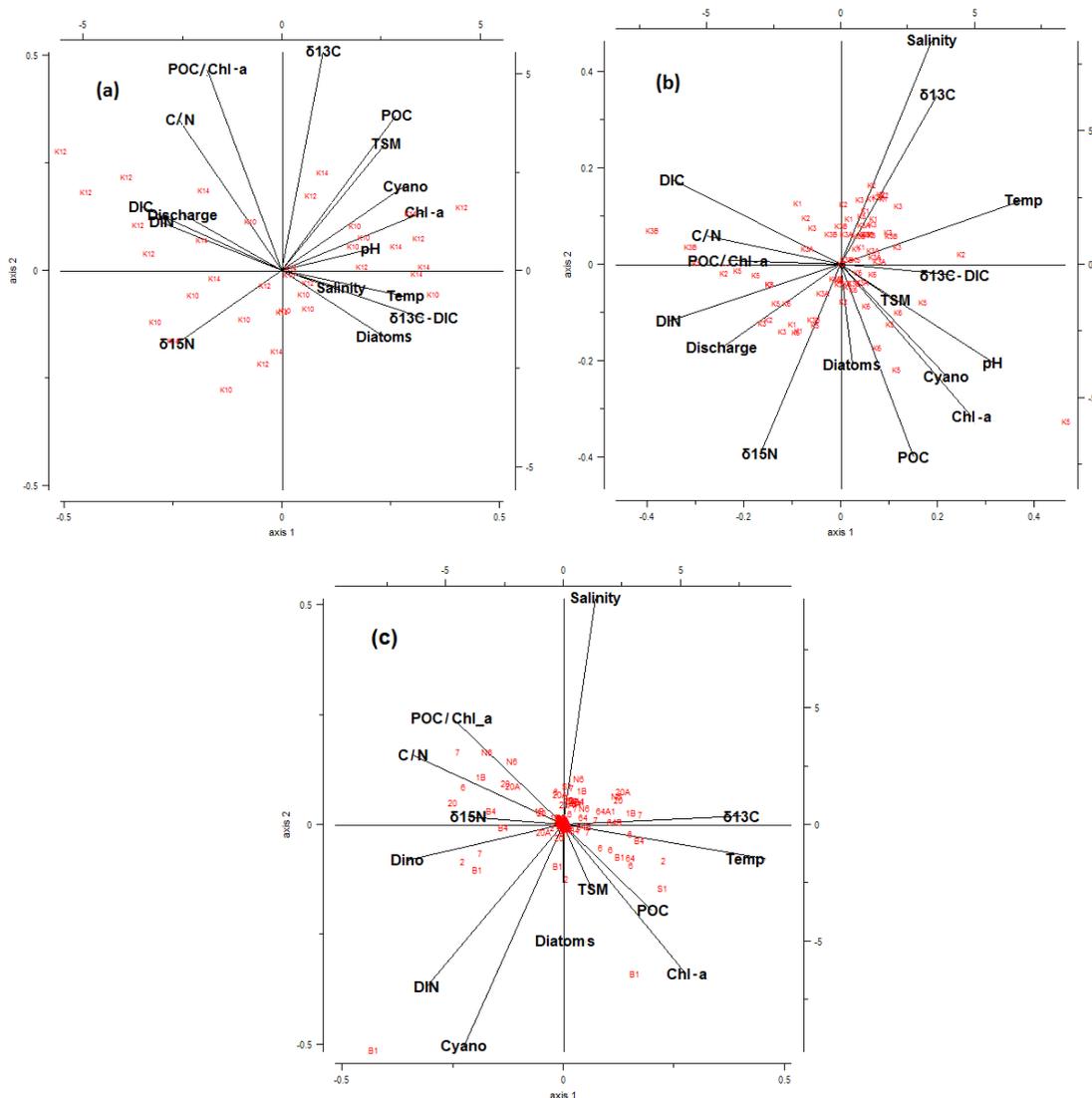


Fig. 3.1.10 The PCA biplots: panel a – central part of the Curonian Lagoon; panel b – northern part of the Curonian Lagoon; panel c – Baltic Sea territorial waters (without lagoon outflow). Loading plots report the distribution of the variables (where: Cyano – cyanobacteria, Dino – dinoflagellates, Temp – water temperature) on axes 1 and 2.

As regards the spatial variability of POM, the similarity between $\delta^{13}\text{C}$ values in riverine and lagoon POM (ANOVA, $F = 1.17$, $p > 0.05$, Table 3.1.4) indicated a commonality in POM distribution in the riverine – lagoonal system (Lesutienė et al., 2014). However, POM from the Nemunas River exhibited a higher $\delta^{15}\text{N}$ value (on the average, 8.6‰) relative to lagoon POM (in the central and northern parts 6.3‰ and 4.8‰, respectively, Table 3.1.4). This might also be explained by the high $\delta^{15}\text{N}$ values of the substrate (DIN) during nitrogen uptake by primary producers. According to the previous study (Korth et al., 2013), the eutrophied rivers in the south-eastern part of the Baltic Sea are

characterized by the elevated $\delta^{15}\text{N-NO}_3$ values ($\sim 8\text{‰}$) implying a sewage input and/or agricultural runoff with the $\delta^{15}\text{N}$ signal of $>8\text{‰}$ (Serna et al., 2010). In the Baltic rivers, the $\delta^{15}\text{N-NO}_3$ values of $6 - 8\text{‰}$ indicate that farmland and/or waste water effluents contribute $60 - 70\%$ of nitrate (Voss et al., 2006). A large part ($\sim 50\%$) of the catchment in Lithuania is an arable land (HELCOM, 2011). Despite the water quality improvement in the Lithuanian rivers, the Nemunas River is still affected by nitrate from diffuse sources (The Nemunas River Basin..., 2010), and large quantities of nitrogen are also stored in soil (Sileika et al., 2006). The significant relationships between the riverine discharge and both DIN ($r = 0.62$, $n = 20$, $p < 0.001$, *Annex III*, Table A3.1) and the $\delta^{15}\text{N}$ in POM ($r = 0.64$, $n = 30$, $p < 0.001$, Table A3.1 and Table 3.1.2) in the central part of the lagoon proved the land-derived sources of DIN. As it was shown previously (Žilius, 2011), the riverine nitrate is the main source of nitrogen for algae in spring and autumn in the Curonian Lagoon, whereas external sources such as nutrient release from sediment become more relevant during periods when the Nemunas flow diminishes.

The differences in $\delta^{15}\text{N}$ values in summer – autumn in the central and northern parts of the Curonian Lagoon can be probably explained by the seasonal variations in the phytoplankton communities and biomass (Fig. 3.1.5) as well as dilution of the riverine nitrate towards sea. However, in contrast to the central part of the Curonian Lagoon, the lower values of $\delta^{15}\text{N}$ during summer – autumn cannot result from the low biomass (except in August) of cyanobacteria in the transitional area of the lagoon (Fig. 3.1.5c). The multivariate analysis (Fig. 3.1.10b, Table 3.1.2) for the northern part of the lagoon pointed out that variation of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in POM occurred due to the saline water intrusion into the northern part of the lagoon and an increasing input of marine POM. The Pearson correlation coefficients ($r = 0.80$, $n = 72$, $p < 0.001$ and $r = -0.75$, $n = 72$, $p < 0.001$ between salinity and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively, *Annex III*, Table A3.2) also suggested a significant impact of sea water input. Results were consistent with the fact that the mean isotopic composition of POM in the outflow of Curonian Lagoon ($\delta^{13}\text{C} = -27.1 \pm$

1.3‰; $\delta^{15}\text{N} = 3.1 \pm 1.0\text{‰}$) in August was similar to that in the northern part of the lagoon ($\delta^{13}\text{C} = -28.1 \pm 2.0\text{‰}$; $\delta^{15}\text{N} = 2.9 \pm 1.9\text{‰}$). Since $\delta^{13}\text{C}$ values are lower in terrestrial DIC compared to marine one (Alling et al., 2012), the significantly higher $\delta^{13}\text{C}_{\text{DIC}}$ values with a peak up to -4‰ in the northern part of the lagoon (Fig. 3.1.4) may also confirm the influence of saline water intrusion into the carbon cycling in the Curonian Lagoon. Considering the increasing extent and duration of saline water intrusion into the northern part of the lagoon (Dailidienė and Davulienė, 2008) and future perspectives of the Klaipėda Port development, the investigation of the POM isotopic composition in the Curonian Lagoon and its outflow area for the modelling purposes might be very useful.

3.1.4 Distribution of SOM and its isotopic composition

During the study the amount of organic carbon in sediments ranged from $< 1\%$ to 10% dry weight (d.w.). The highest content of TOC was observed in the accumulation areas within the Curonian Lagoon and in the open Baltic Sea waters, indicating high organic matter supply and/or good preservation of OM. The obtained results were in agreement with the previously reported content of organic carbon in sediments in the Curonian Lagoon (from $<0.5\%$ to $>10\%$) and the Baltic Sea (e.g., from $<1\%$ up to 13% in the Gotland Basin) (Emelyanov, 2001; Zilius et al., 2015). A significant increase in the organic carbon content with the decreasing grain size was observed during this study and also reported by other authors (Emelyanov, 2001; Pustelnikovas et al., 2007; Galkus et al., 2012; Jokšas et al., 2016). Organic matter is known to be associated with fine-grained sediments because of the larger surface area which provides good binding sites for organic matter (Mayer, 1994).

The stable isotopic compositions of sedimentary organic matter (SOM) varied in a wide range ($\delta^{13}\text{C}$ from -31.3 to -23.3‰ , $\delta^{15}\text{N}$ from 0.6 to 11.2‰ , Fig. 3.1.11) with no significant differences during different seasons and

sampling years (KW, $H = 1.36$, $p > 0.05$). The average values (Table 3.1.4) were in agreement with those from the previous studies where similar values of $\delta^{13}\text{C}$ ($\sim -29\text{‰}$) and $\delta^{15}\text{N}$ ($\sim 6\text{‰}$) were found for the Curonian Lagoon surface (0–5 cm) and the Baltic Proper ($\delta^{13}\text{C}$ from -26.4‰ to -21.7‰ , $\delta^{15}\text{N}$ 3 – 5‰) sediments (Voss et al., 2000, Struck et al., 2004; Szczepańska et al., 2012). The low $\delta^{13}\text{C}$ values of SOM in the Curonian Lagoon showed the input of freshwater phytoplankton ($\delta^{13}\text{C}$ from -35‰ to -25‰) and terrestrial plants (on the average, $\delta^{13}\text{C}$ -28‰), with an increasing contribution of marine phytoplankton ($\delta^{13}\text{C}$ from -22‰ to -18‰) towards marine waters (Fig. 3.1.11).

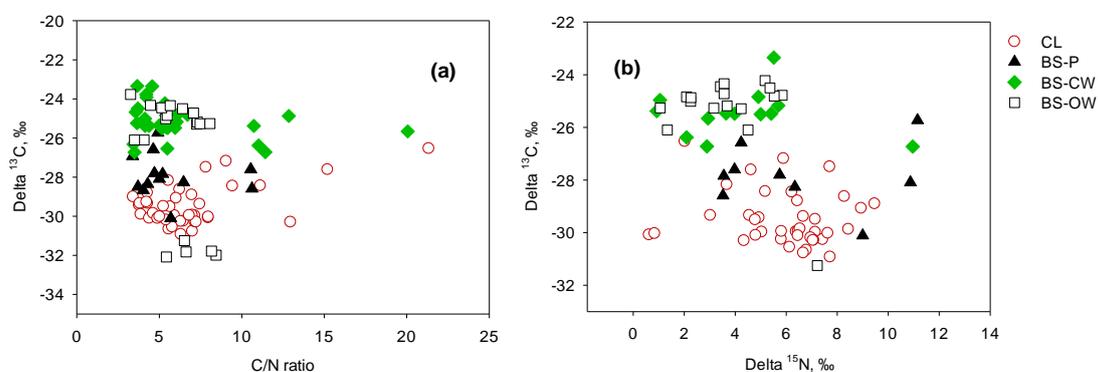


Fig. 3.1.11 Dual plots (panel a: $\delta^{13}\text{C}$ vs. C/N ratio in SOM; panel b: $\delta^{13}\text{C}$ vs. $\delta^{15}\text{N}$ in SOM) of organic matter (CL - Curonian Lagoon (for clarity data represent central and northern parts), BS-P – the Curonian Lagoon plume area, BS-CW – Baltic Sea coastal waters, BS-OW – Baltic Sea open waters).

However, the variability of C/N ratios in SOM (ranging from 3.3 to 21.3, with the mean of 6.4 ± 3) did not evidence any significant input of vegetation detritus in the research areas and might be explained by a higher abundance of bacteria and phytoplankton (C/N ratio $\sim 3-6$ and ~ 7 , respectively, Savoye et al., 2003). In some cases, the surface sediments revealed intermediate C/N ratios between 10 and 20 (Fig. 3.1.11) suggesting that SOM may be a mixture of river/lagoon phytoplankton and vascular plant debris. The sediment samples collected in the central part of the lagoon towards the northern coastal waters and in the Baltic Sea deep-water dumping area (20 and 20A st.) showed the C/N ratios to be above 10. Higher C/N ratios in samples towards the northern coast may be explained by the direction of

dominant currents due to prevailing south-westerly and westerly winds, freshwater outflow during the flood events and organic matter accumulation in the transitional zone (Galkus and Jokšas, 1997; Davulienė and Trinkūnas, 2004). Higher C/N ratios in SOM from the Baltic Sea deep-water dumping sites were probably attributed to detritus dumped from the Klaipėda Port area.

Table 3.1.4 The average and standard deviation of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ signatures and C/N ratios in POM and in SOM. The number of samples is shown in the parenthesis.

Water type	$\delta^{13}\text{C}$, ‰	$\delta^{15}\text{N}$, ‰	C/N ratio
Nemunas River POM	-30.4 ± 1.3 (10)	8.6 ± 3.0 (10)	6.2 ± 2.4 (10)
Curonian Lagoon POM (surface), central part	-30.4 ± 1.9 (30)	6.3 ± 1.9 (30)	7.4 ± 1.7 (30)
Curonian Lagoon POM (surface), northern part	-29.8 ± 2.5 (64)	4.9 ± 2.4 (64)	7.1 ± 1.2 (64)
Curonian Lagoon POM (near-bottom)	-30.3 ± 2.7 (10)	4.5 ± 3.0 (10)	6.5 ± 0.7 (10)
Curonian Lagoon SOM, central part	-29.6 ± 1.1 (17)	6.7 ± 1.9 (15)	6.8 ± 4.2 (15)
Curonian Lagoon SOM, northern part	-29.5 ± 0.88 (31)	5.6 ± 1.9 (27)	6.7 ± 2.7 (30)
Plume of the Curonian Lagoon POM (surface)	-28.4 ± 1.7 (14)	4.4 ± 1.9 (14)	8.2 ± 2.3 (14)
Plume of the Curonian Lagoon SOM	-27.9 ± 1.0 (14)	6.4 ± 3.0 (14)	5.6 ± 2.3 (14)
Baltic Sea coastal POM (surface)	-25.7 ± 2.1 (42)	2.8 ± 2.1 (38)	8.1 ± 2.5 (38)
Baltic Sea coastal POM (near-bottom)	-25.7 ± 1.8 (10)	3.7 ± 1.8 (10)	10.7 ± 6.0 (11)
Baltic Sea coastal waters SOM	-24.9 ± 0.9 (45)	4.3 ± 2.4 (20)	6.3 ± 1.7 (28)
Baltic Sea open waters SOM	-25.1 ± 1.4 (23)	3.5 ± 1.6 (14)	6.0 ± 1.4 (14)

SOM from one open sea station (St. R7) had the lowest $\delta^{13}\text{C}$ value ($-31.8 \pm 0.3\text{‰}$), low C/N ratio (7.1 ± 1.2) and a relatively high $\delta^{15}\text{N}$ value (6.8‰) (Fig. 3.1.12). Values were similar to the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signals in POM from the freshwater ecosystem (Table 3.1.4) and reflected an intensive accumulation of the freshwater organic matter. This site is located within the submarine valley of the Nemunas River with the terrigenous fine-grained sediments and a high organic carbon amount. It is well known that fine-grained sediments are not deposited on the seafloor in high-energy shallow water environments and are transported to the deeper zones (Emelyanov, 2001). Previously, the intensive accumulation of pollutants (e.g., metals) was reported

Rather uniform distribution of the isotopic composition of SOM within the lagoon (Table 3.1.4, ANOVA, $F = 1.92$, $p > 0.05$) probably might be caused by permanent resuspension and redistribution of organic matter in the ecosystem. The previous study demonstrated that the Curonian Lagoon area affected by resuspension ranges from 40 up to 100% (Emelyanov, 2001). No significant difference was also observed between the $\delta^{13}\text{C}$ in SOM and POM in the marine stations (t -test, $p > 0.05$, Table 3.1.4, Fig. 3.1.12), while the seabed samples from the Baltic Sea displayed more ^{15}N -enriched signatures (4.3 – 6.4‰, Table 3.1.4, Fig. 3.1.12; Remeikaitė-Nikienė et al., 2016) relative to the surface water particles (t -tests, $p < 0.05$). The similarity in $\delta^{13}\text{C}$ values in POM and SOM and the positive relationship ($r = 0.75$, $n = 22$, $p < 0.05$) might indicate the little changes in $\delta^{13}\text{C}$ signatures during diagenesis (~2‰) of sinking and sedimentary organic matter as it was shown previously (Gearing et al., 1984; Bohlin et al., 2006), while diagenesis of OM in sediments caused an increase in $\delta^{15}\text{N}$ signatures as reported in other studies (De Brabandere et al., 2002; Savoye et al., 2003).

3.1.5 Sources of POM and SOM using the end-member mixing model

According to the estimates based on the $\delta^{13}\text{C}$ end-member values, on the average marine source accounted about $13 \pm 14\%$ to the mixed POM in the northern part of the lagoon with the highest contribution (15 – 37%) in July – October (Fig. 3.1.13a). In the Baltic Sea, about $50 \pm 25\%$ of POM was of the freshwater origin: about $75 \pm 17\%$ in the plume area and about $45 \pm 23\%$ in the adjacent coastal waters (Fig. 3.1.13). A markedly higher contribution ($40 \pm 15\%$ in the plume area and $81 \pm 15\%$ in the coastal waters) of marine phytoplankton to POM was observed in summer (Tukey HSD test, $p < 0.05$; Fig. 3.1.13b).

According to the estimates based on the $\delta^{13}\text{C}$ in SOM, about $90 \pm 9\%$ of SOM in the northern part of the lagoon and $47 \pm 17\%$ of SOM in the Baltic Sea

were of the freshwater origin: about $75 \pm 12\%$ in the plume area, $41 \pm 11\%$ in the coastal waters, and $42 \pm 14\%$ in the open south-eastern Baltic Sea (Fig. 3.1.14). Overall, the contribution of freshwater organic matter to SOM in the studied area varied from 22% to 100% (Table A2.1 in *Annex II*).

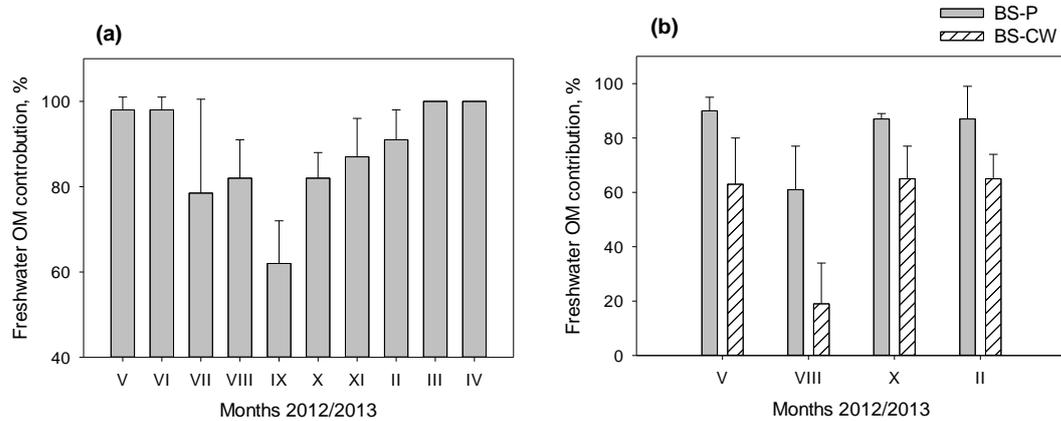


Fig. 3.1.13 Estimation of freshwater sources contribution to POM (panel a – the northern part of the Curonian Lagoon, panel b – plume of the Curonian Lagoon waters in the Baltic Sea (BS-P) and adjacent Baltic Sea coastal waters (BS-CW). The average values ($3 \leq n \leq 13$) \pm standard deviations are reported.

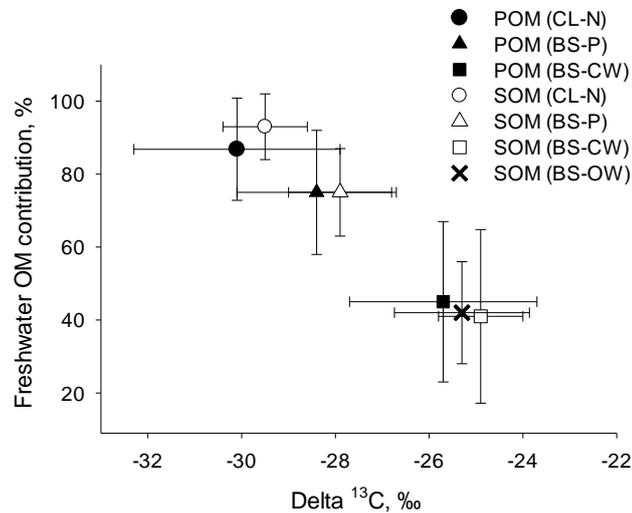


Fig. 3.1.14 Mean percentage of the freshwater source contribution (%) to the POM and SOM. The sticks show standard deviations.

The results (Fig. 3.1.14) indicated a retention of organic particles during the estuarine mixing and dilution of freshwater material with the increasing distance from the land. Nevertheless, it may be concluded that organic matter of the freshwater origin considerably contributes to eutrophication in coastal

areas of the SE Baltic Sea. The obtained results were comparable with those reported by Szczepańska et al. (2012) for the Gotland and Gdansk Deeps where the contribution of the terrestrial organic matter to SOM in the surface sediments was found to be about 43 – 47%. Using the $\delta^{13}\text{C}$ end-member approach, Szczepańska et al. (2012) reported a large proportion (41 – 73%) of terrestrial organic matter in sediments for the Gotland and Gdansk Deeps. Based on the stable nitrogen and carbon composition of suspended matter and surface sediments, Voss and Struck (1997) reported an input from the Oder River which accounted 50 – 95% into the Pomeranian Bight and 13 – 34% of PON-POC into the Arkona Basin.

Conclusions of the 3.1 section

During this study, the C and N isotopic signatures, the low C/N molar (~ 7) and POC/Chl-*a* ratios (< 100) of POM indicated that living freshwater and marine phytoplankton was the main contributor to POM in the SE Baltic Sea throughout the year, while the higher C/N (> 10) and POC/Chl-*a* (> 100) ratios were attributed to the increasing input of degraded POM in late autumn – winter.

The POM dynamics was influenced by the strong seasonal dynamics of riverine inputs into the lagoon which were reflected by uptake of ^{15}N -enriched DIN and higher $\delta^{15}\text{N}$ values in POM during floods period. An increasing biomass of phytoplankton in summer resulted in DIC and DIN pool depletion and increasing $\delta^{13}\text{C}_{\text{DIC}}$ values due to fractionation during DIC uptake. The changes in the phytoplankton composition and the increasing productivity of N_2 -fixing cyanobacteria in summer were reflected by the higher $\delta^{13}\text{C}$ values and lower $\delta^{15}\text{N}$ values. Additionally, in the northern – transitional area, the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in POM values significantly related with the water salinity ($r = 0.80$, $n = 72$, $p < 0.001$ and $r = -0.75$, $n = 72$, $p < 0.001$, respectively) and indicated an impact of marine POM intrusions into the northern part of the lagoon. The $\delta^{15}\text{N}$ dynamics in the Baltic Sea was attributed to the dominance

of diatoms and dinoflagellates and to the variability in available N sources: uptake of isotopically light nutrients in summer, and on the contrary, uptake of ^{15}N -enriched DIN during floods in May and February.

The similar $\delta^{13}\text{C}$ values and the significant relationship ($r = 0.75$, $n = 22$, $p < 0.05$) between POM and SOM indicated the permanent resuspension and redistribution of organic matter in the shallow ecosystems. An increase in $\delta^{15}\text{N}$ signatures (4.3 – 6.4‰) in coastal seabed samples relative to the surface water particles (2.8 – 4.4‰) showed the diagenesis of organic matter in marine sediments and the uptake of isotopically light nutrients in the surface water.

The results of the study indicated that the distribution of POM and SOM was predominantly controlled by the input of freshwater-derived organic matter. Annually, marine source accounted about 10 – 13% to the mixed SOM and POM in the northern part of the Curonian Lagoon with the highest contribution to POM (~15 – 37%) in July – October. In the Baltic Sea, about 50% of POM was of the freshwater origin with a markedly higher contribution (40% in the plume area and 81% in the coastal waters) of marine phytoplankton in summer. About 47% of SOM in the Baltic Sea was of the freshwater origin with a similar (41–42%) contribution in the territorial and open waters. According to the data obtained in this study and those reported in previous publications it may be concluded that organic matter of the freshwater origin considerably contributes to eutrophication in coastal areas of the SE Baltic Sea.

3.2 Distribution of metals in the SE Baltic Sea

3.2.1 Sediment quality

The formation of sediment deposits on the seafloor is not evenly determined and depends on the bottom morphology, hydrographical conditions, input of the river-borne material and increasing plankton production (Hille et al., 2006). The previous observations in the Baltic Sea

showed that sediments became finer from high-dynamic shallow-water to low-dynamic deep-water environments (Emelyanov, 2001; Bitinas et al., 2005). During this study, most of the surface sediments from the Curonian Lagoon were classified as fine sand (0.063–0.2 mm) and medium sand (0.2–0.6 mm) with the content in samples of $31 \pm 21\%$ and $52 \pm 27\%$, respectively (Fig. 3.2.1). Based on the results of other studies, in the Curonian Lagoon, the sand fraction covers more than half of the area with the prevalence in the central part of the lagoon between the Nemunas River delta and the Curonian Spit (Chubarenko et al., 2002; Emelyanov et al., 2015). The silty mud accumulates in the deepest places in the south-western part of the lagoon and in small areas close to the Nemunas River delta as well as in the vicinity of Nida settlement (near the st. K10) (Emelyanov et al., 2015).

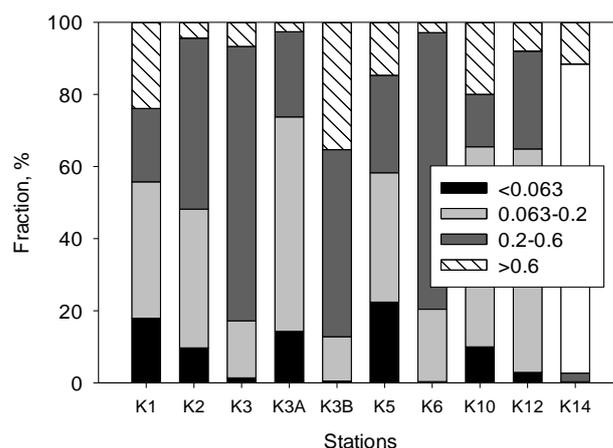


Fig. 3.2.1 Granulometric composition of sediment samples (size of particles in mm) taken from the Curonian Lagoon in 2012.

The metal (Pb, Cu, Cd, Ni, Cr, Zn, Al) in the sediments data obtained by using partial and total extraction methods were compared from nine stations (Nemunas, 4, 5, 6, 7, 20A, 65, 66 and CHEMSEA2) in order to have as much as possible reliable view on the contamination extent of the Lithuanian marine zone. The comparison of the pre-treatment methods in this study assumed to be important since: (i) the reference values (concentrations in the Earth's shale, Turekian and Wedepohl, 1961) showed the total concentrations; (ii) it was necessary to know if the national monitoring data on Al (partial digestion)

might be used for the normalization purposes. The mean concentrations for both pre-treatment methods are shown in Table 3.2.1.

Table 3.2.1 The average (\pm standard deviation) metal concentrations after partial and total leaching in the common stations (Nemunas, 4, 5, 6, 7, 20A, 65, 66 and CHEMSEA2) ($t = t$ -test, $*p < 0.05$).

Method	Pb	Cu	Cd	Ni	Cr	Zn	Al, %
Partial leaching ^a	3.81 \pm 1.4	1.4 \pm 0.9	0.04 \pm 0.02	2.8 \pm 1.1	8.4 \pm 3.6	12.1 \pm 3.4	0.19 \pm 0.07
Total leaching ^a	7.52 \pm 1.3	2.4 \pm 0.9	0.11 \pm 0.05	2.3 \pm 0.9	16.6 \pm 11.1	14.2 \pm 3.9	1.54 \pm 0.15
Statistics	$t=-5.18^*$	$t=-1.88$	$t=-3.29^*$	$t=0.79$	$t=-1.89$	$t=-0.99$	$t=-21.48^*$
Partial leaching ^b	16.6 \pm 13.1	8.4 \pm 4.5	0.33 \pm 0.30	10.4 \pm 6.5	20.3 \pm 5.3	42.3 \pm 29.1	0.79 \pm 0.50
Total leaching ^b	13.9 \pm 10.1	11.2 \pm 4.9	0.38 \pm 0.11	20.9 \pm 14.4	31.5 \pm 13.4	39.5 \pm 17.7	3.20 \pm 0.70
Statistics	$t=0.21$	$t=-0.31$	$t=-0.18$	$t=-0.63$	$t=-1.10$	$t=0.11$	$t=-3.94^*$

The stations with similar type of sediments (Fig. A1.1, *Annex I*) were grouped: ^a – Nemunas, 4, 5, 6, 7, 20A, 66 (fine sand, sand); ^b – 65, CHEMSEA2 (aleurites).

The comparison between the nitric acid extraction and the total digestion showed statistically different mean concentrations of lead and cadmium in sandy sediments (Table 3.2.1), while no differences were observed in aleurites. However, the concentrations of aluminium were about 4–8 times lower in the partial digestion than in the total leaching (Table 3.2.1) and, therefore, no Al-normalized enrichment factors (EFs) were calculated based on the national monitoring data. The results demonstrated that despite of different sediment pre-treatment methods, datasets of most metals might be comparable and be used for the chemical sediment status assessment in this study. However, the difference in metal concentrations determined using a partial and complete acid digestion methods may be considerable. As it was shown by Birch (2017), the sediment pre-treatment with the strong acids resulted in a 4–9 fold elevation in metal concentrations. Unfortunately, no national monitoring data on metal concentrations from the stations with the prevailing silt sediments (e.g., CHG1, R7) were available for the methodological comparison.

The concentrations of metals in sediments after the partial leaching varied: 0.69–26.5 mg kg⁻¹ for Pb, 0.08–70 mg kg⁻¹ for Cu, <0.007–1.1 mg kg⁻¹ for Cd, 0.26–22 mg kg⁻¹ for Ni, 0.89–78 mg kg⁻¹ for Cr, 0.25–106 mg kg⁻¹ for Zn, 0.03–1.86% for Al. The total concentrations varied: 5.4–49.9 mg kg⁻¹ for Pb, 1.2–56.5 mg kg⁻¹ for Cu, 0.02–0.60 mg kg⁻¹ for Cd, 1.73–15.87 mg kg⁻¹ for Ni, 2.0–85 mg kg⁻¹ for Cr, 7.0–160 mg kg⁻¹ for Zn, 1.35–6.99% for Al. Spatial variations of average contents of metals and the “metal pollution hotspots” are illustrated in Fig. 3.2.2.

Table 3.2.2 Metal concentrations (mg kg⁻¹ d.w., average±sd and/or variability (from-to)) in surficial sediments (0 – 5 cm, if do not indicated otherwise) of the Curonian Lagoon and other polluted lagoons/estuaries in Europe.

	Pb	Cu	Cd	Ni	Cr	Zn
The Curonian Lagoon (without Klaipėda Strait), this study	6.8±5.5 0.69-22	4.4±5.5 0.08-18	0.21±0.31 <0.007-1.1	6.1±7.3 0.26-22	11.7±12.1 0.89-42	25.6±24.1 0.25-100
The Curonian Lagoon (sand), Jokšas et al., 2016	7.6	3.9	0.12	3.3	7.0	15.1
The Curonian Lagoon (mud), Jokšas et al., 2016	28.0	28.9	0.64	19.8	28.7	76.4
Klaipėda Strait, this study	6.0±4.3 0.94-16	10.3±12.4 0.22-70	0.13±0.12 0.01-0.5	9.4±7.0 0.57-21	15.4±14.3 1.7-78	31.8±26.8 0.25-106
Klaipėda Strait (sand), Galkus et al., 2012*	10.9	5.5	<0.4	5.3	14.0	28.6
Klaipėda Strait (mud), Galkus et al., 2012*	22.0	21.9	0.84	12.1	31.5	109.0
Vistula Lagoon, Szefer et al., 1999b	36	22	0.8	39	91	111
Szczecin Lagoon, Glasby et al., 2004	108	64	3.8	37	-	762
Berre Lagoon, Accornero et al., 2008	41	28	0.6	36	102	93
Venice Lagoon, Masiol et al., 2014	11.8	15.7	0.96	17.7	50.5	91.3
Elbe Estuary, Wetzel et al., 2013	81	44	2	42	83	392
Loire Estuary, Coyne et al., 2016	1.49-104	<LOD-84	0.01-3.33	0.88-68.6	2.02-315	3.87-349
Gironde Estuary, Larosse et al., 2010	4.97-83.8	0.493-40.1	0.011-2.09	0.883-48.4	1.34-140	3.95-323

*0-10 cm sediment layer

The comparison of metal concentrations in the water bodies revealed that the amount of elements accumulated in the Curonian Lagoon sediments was 1.4–4.0 times higher than in the sediments of the Baltic Sea and might

show that the lagoon acts as a sink for many pollutants entering from the catchment. The mean concentrations of metals in the Curonian Lagoon sediments (partial leaching method) were comparable to the total concentrations obtained during the previous studies (e.g., Galkus et al., 2012; Jokšas et al., 2016). Results also showed similar or even lower metal concentrations than in the polluted lagoons and estuaries elsewhere (Table 3.2.2).

Among the stations, the higher concentrations of metals (Tukey HSD test, $p < 0.05$) exceeding the threshold metal concentrations were measured in sediments of the Klaipėda Strait (st. K1, K3A, K3B), the central part of the Curonian Lagoon (st. K10) and the open sea (st. CHEMSEA2, CHG1 and R7) (Fig. 3.2.2). The prevalent metal accumulation in sediments in most cases coincided with the increase of its organic (TOC) and mineral (Al, silt fraction) constituents (Table 3.2.6). As was presented before, TOC values in sediments ranged from <1% to 10% dry weight (d.w.) with a consequently higher amount in sediments from the accumulation areas in the Curonian Lagoon (8.40% at the st. K10) and the open sea (7.59% at the st. R7). Results might be explained by the affinity of metals to the organic matter and the clay fraction of the sediment as well as formation of e.g., organic complexes (Pustelnikovas et al., 2007; Zalewska et al., 2015; Emelyanov et al., 2015). Sorption of metals to organic matter in organic soils can exceed sorption to mineral soil constituents by several times (Lair et al. 2007). The concentration and retention of metals in the sediments are also affected by the oxygen saturation and occurrence of hydrogen sulphide, which periodically accumulates in the bottom of the Gotland and Gdansk Deeps (Emelyanov, 2014; Zalewska et al., 2015). In exposed and oxic waters, iron/manganese-oxides/hydroxides are important carriers for metals in sediments, while under reducing conditions, part of the iron fraction can be fixed in sediment layers in the form of iron sulphides (Müller, 1999; Emelyanov, 2014). The higher sulphur concentrations in the most remote stations (Fig. 3.2.3) as well as the strong correlation (Table

3.2.10) with all metals might indicate binding of metals with insoluble sulphides.

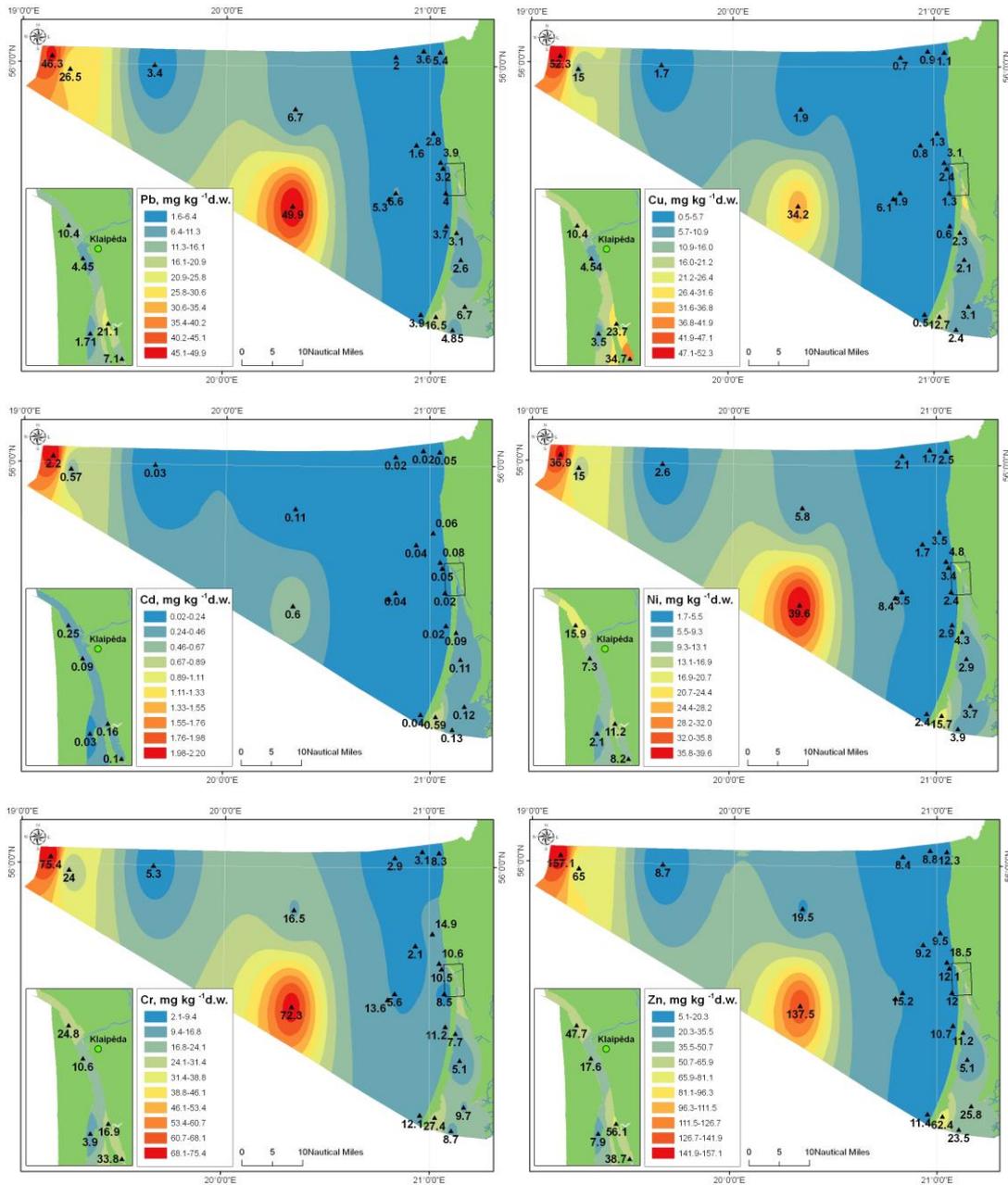


Fig. 3.2.2 Distribution of Pb, Cu, Cd, Ni, Cr and Zn (the average values) in the SE Baltic Sea in 2011–2014. The maps are prepared based on the concentrations after partial leaching; total concentrations are shown only in R7 and CHG1 sites.

No significant variations were observed between the metal concentrations in sediments during different seasons and sampling years of the period 2011–2014 (KW, $H = 0.31-4.85$, $p > 0.05$). The mean metal data of two sampling periods (2006 – 2010 (MRD database, unpublished) and 2011 – 2014

(this study)) were compared in order to see changes of contamination with metals. Several common research sites were selected: in the Curonian Lagoon – K10 (near Nida) and K1 (the Klaipėda Strait entrance), in the Baltic Sea – 4 (plume of the lagoon), 65 (open sea station), 20A (sediments dumping site) and 7 (southern coastal waters).

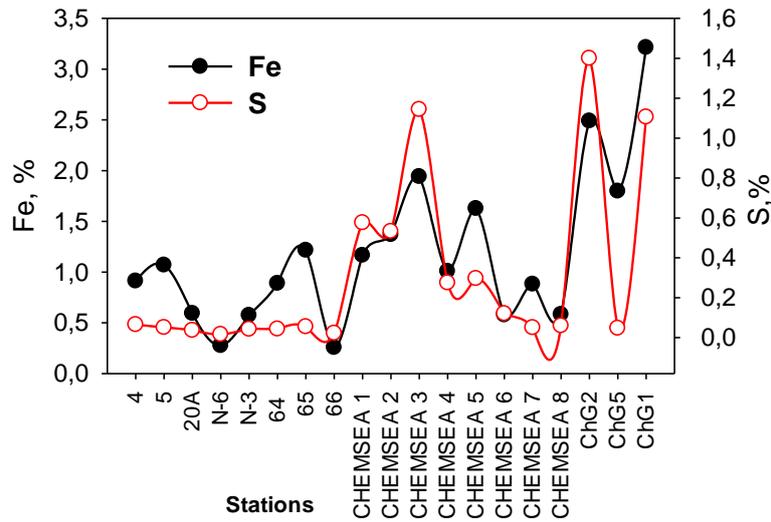


Fig. 3.2.3 Iron (Fe) and sulphur (S) concentrations in sediments of some sites in 2013.

Results (Fig. 3.2.4) showed that sediment concentrations of most harmful metals remained at similar levels over the last decade. The Baltic Sea is an inert system with the long time scales and it may take some time to improve the water quality. The estimated range for the residence times for the Eastern Gotland Basin were estimated to be ~0.5–1.3 years for Pb; ~2–11 years for Zn, ~7–36 years for Cd and 42–89 years for Cu until they were exported to the deep water and buried in the sediment (Pohl et al., 2006). This demonstrates that measures for Pb and Zn concentrations reduction give quick results on the improving environmental status, while for cadmium and copper it takes longer time.

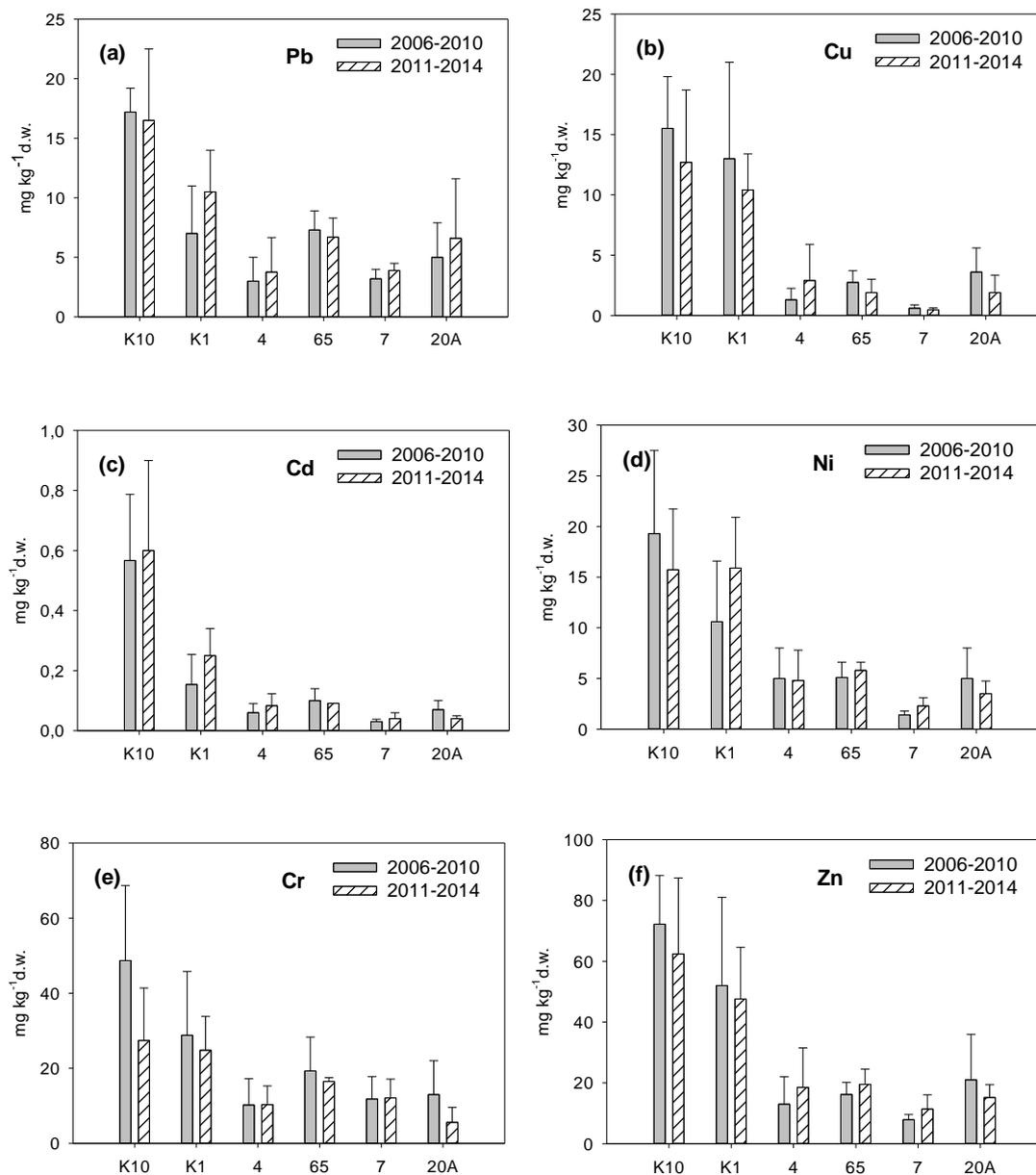


Fig. 3.2.4 Metal concentrations (mean, mg kg⁻¹ d.w. ± sd) in sediments of the selected sampling sites during the periods 2006–2010 and 2011–2014.

The metal concentrations were compared with the sediment quality levels defined by MacDonald et al. (1996) and those defined by the Order of the Minister of the Environment of the Republic of Lithuania as the threshold values between good environmental status (GES) and sub-GES according to the MSFD. In aquatic toxicity studies, the threshold effect level (TEL) represents the concentration threshold below which there are little or no toxic risks to organisms. The probable effect level (PEL) is the minimum value at

which several adverse effects start to occur. Results showed, that the concentrations of elements in most samples were below TEL values (on the average, 96% of sediment samples, Table 3.2.3).

Table 3.2.3 Comparison between sediment quality levels and metal concentrations (mg kg⁻¹ d.w.) of all samples in studied area.

Sediment quality levels	Pb	Cu	Cd	Ni	Cr	Zn
Average Earth's shale ^a	20	45	0.3	68	90	95
TEL ^b	35	35.7	0.6	18	37.3	123
PEL ^b	112	108	4.21	42.8	160	271
GES ^c	20	10	0.5	10	30	60
Samples ≤ Earth's shale (total%)	95.8	98.5	88.5	100	99.6	97.3
Samples > Earth's shale (total%)	4.2	1.5	11.5	0.0	0.4	2.7
Samples ≤ TEL (total%)	98.5	97.3	96.7	92.6	96.6	98.8
Samples between TEL and PEL (total%)	1.5	2.7	3.3	7.4	3.4	1.2
Samples ≥ PEL (total%)	0.0	0.0	0.0	0.0	0.0	0.0
Samples ≤ GES boundary (total%)	95.8	83.7	93.4	83.4	90.5	91.9
Samples > GES boundary (Sub-GES) (total%)	4.2	16.3	6.6	16.6	9.5	8.1

^aTurekian and Wedepohl, 1961; ^bMacDonald et al. (1996); ^cOrder No. D1-194 *On the Approval of the Characteristics of the Good Environmental Status of the Marine Region of the Republic of Lithuania* of the Minister of Environment of the Republic of Lithuania dated 4 March 2015.

None of the contaminants measured in sediments exceeded the PEL values developed by MacDonald et al. (1996). About 90% of samples met GES conditions, while the remaining sediments showed the sub-GES status (Table 3.2.3). As background concentrations reflect the pristine condition, these values should be lower than sediment quality levels for metals in sediments (Birch, 2017). However, the GES boundaries defined under the MSFD requirements for many metals are much lower than those reported for the average Earth's shale (Table 3.2.3) or even the background values reported for the Baltic Sea (Table 1.3.1). In this context, the GES values defined for the marine environment management purposes seem to be too strict and probably need to be reconsidered.

3.2.2 Assessment of sediment contamination

The distribution and variability of metal concentrations in sediments were presented in the section 3.2.1. However, the information on bulk metal concentrations did not allow to quantitatively evaluate the pollution extent. Even though values of metal concentration can be very valuable and have been used as direct indicators of toxicological risk, they are not sufficient on their own for the evaluation of toxicological risk at a particular study site (Garcia et al., 2008).

The metal pollution sediment assessment was performed in order to define the comparable pollution level and in some extent – to determine what proportion of the sedimentary metal load might be natural and what proportion was human-induced. The metal concentrations were compared with the background (reference) values (Turekian and Wedepohl, 1961) by applying various indexes (EF, I_{geo} and CF). The potential ecological risk to biota was also estimated by applying the indexes (E^i_r – for the individual metal, RI – an integrated assessment of all metals) based on the toxicity of metal.

The enrichment factors (EFs) for this study were calculated based only on the total metal concentrations since the significant differences between Al content after partial and total extraction methods were observed (Table 3.2.1). The several classification systems based on the EFs values were presented in the Table 1.5.1. The EF values lower than 1.5 (Garcia et al., 2008; de Paula Filho et al., 2014) or <2 (Abreu et al., 2016) indicate that the metal is entirely from crustal materials or natural processes, whereas EF values higher than 1.5 or 2 suggest an increasing portion of the anthropogenic sources (Garcia et al., 2008; de Paula Filho et al., 2014; Abreu et al., 2016). In this study, the average EFs for the studied metals varied between 0.1 and 9.9 (Table 3.2.4). The mean EFs for the study sites were: Cd (3.3) > Pb (2.2) > Cr (1.1) > Zn (1.0) > Cu (0.5) > Ni (0.3) and showed the anthropogenic sources (EF > 1.5–2.0) of Cd and Pb.

Table 3.2.4 EFs of elements* in selected sediments from the SE Baltic Sea.

Station and research area	Pb	Cu	Cd	Ni	Cr	Zn
Nemunas	2.1	0.2	0.9	0.1	0.1	0.4
4	1.7	0.4	2.2	0.2	1.3	0.7
5	2.0	0.3	3.5	0.2	3.5	1.1
Mean EF in the Curonian Lagoon outflow area	1.9	0.4	2.9	0.2	2.4	0.9
6	2.3	0.2	2.3	0.1	1.2	0.8
7	2.6	0.3	2.0	0.1	1.4	0.9
20A	1.7	0.4	1.7	0.2	0.6	0.8
Mean EF in the Baltic Sea coastal waters	2.2	0.3	2.0	0.1	1.1	0.8
64A1-65	2.1	0.4	2.9	0.2	0.8	0.9
66	1.8	0.2	-	-	0.4	0.4
CHEMSEA2	2.3	0.8	4.1	0.5	1.0	1.2
CHG1	3.1	1.6	9.9	0.7	1.2	2.2
R7	3.1	0.9	2.4	0.7	1.1	1.8
Mean EF in the Baltic Sea open waters	2.5	0.8	4.8	0.5	0.9	1.3
<i>Mean EFs for the study sites</i>	<i>2.2</i>	<i>0.5</i>	<i>3.3</i>	<i>0.3</i>	<i>1.1</i>	<i>1.0</i>

*the total leaching method.

EF < 1, no enrichment; 1 ≤ EF < 3, minor enrichment;

3 ≤ EF < 5, moderate enrichment; 5 ≤ EF < 10, moderately severe enrichment;

10 ≤ EF < 25, severe enrichment; 25 ≤ EF < 50, extremely severe enrichment (Glasby and Szefer, 1998).

In detail, the mean EF values (<1) for Cu, Cd, Ni, Cr and Zn indicated no enrichment in the Nemunas River sediments, while the EF value of Pb showed a “minor enrichment” (1 ≤ EF < 3) which might be attributed to the human impact (EF =2.1). In the Baltic Sea territorial waters, Pb, Cd and Cr showed a “minor enrichment” (EF < 3), while no anthropogenic pollution with Cu, Ni, Cr and Zn was observed (EF < 1.5). In the open sea area, the average EF for Cd (EF = 4.8) indicated a moderately severe enrichment, EFs for Pb and Zn – minor enrichment with those elements and no enrichment with Cu, Ni and Cr (EF <1).

Based on the I_{geo} index, contamination levels of each metal for each station are shown in Table A4.1 (*Annex IV*). In general, the geoaccumulation index values were very low (<0) for all metals (except Cd, Pb and Zn at the several stations), implying that these trace metals have not contaminated SE

Baltic Sea sediments. The calculated I_{geo} values ($0 \leq I_{geo} < 1$) for Cd at the K10, CHEMSEA2 and R7 sites, for Pb at the CHG1 and R7 sites and for Zn (only CHG1 site) indicated that sediments from the investigated locations were uncontaminated to moderately contaminated with Cd, Pb and Zn. The highest I_{geo} value (2.3) calculated for Cd at the station CHG1 indicated moderately to highly polluted sediments (Table A4.1, *Annex IV*).

The sediment pollution extent based on the EFs and I_{geo} values was comparable with the most recent data reported for the southern Baltic Sea by Zalewska et al. (2015). Compared the average EFs values, the Baltic Sea open waters showed a higher contamination with Cd (EF=4.8 in this study and EF=1.7 reported by Zalewska et al., 2015), but similar contents of Pb (EF=2.5 and EF=2.2, respectively) and Zn (EF=1.3 and EF=1.5, respectively) for the SE Gotland Basin. Based on the I_{geo} values obtained during this study and those reported by Zalewska et al. (2015), the SE Gotland Basin was uncontaminated to moderately contaminated with Pb and Zn ($0 \leq I_{geo} < 1$), while the values of I_{geo} for Cd were in a wider range (from <0 to 2.3) during this study. The adjacent Gdansk Deep was also minor contaminated with Zn and Pb (EF=2.2 and 2.7, respectively), while the EF for Cd (EF=7.2) indicated a moderately severe enrichment (Zalewska et al., 2015). Based on the results of Dabrowska et al. (2013), the Gulf of Gdansk was more contaminated with Zn (EF=5.0–5.1), and Cd (EF=7.5–10.6), indicating a significant load of metals with a discharge of the Vistula River. The obtained results pointed to the similar sediment pollution with Zn and Pb extent in the Gdansk and Gotland Deeps, and a higher contamination with Cd in the Gdansk Deep. The similarity may be determined by the riverine pollution loads, dominant direction of the currents, as well as similarities in sediment characteristics and their formation rate in the basins (Zalewska et al., 2015; Golenko et al., 2017).

The state of sediment contamination based on the CF values (Table A4.2, *Annex IV*) showed that sediments exhibited low levels of contamination (CF < 1) for Ni and Cr (at all locations); moderate ($1 \leq CF < 3$) for Cd (K10, CHEMSEA2, R7), Cu (only CHG1), Pb (CHEMSEA2, CHG1 and R7) and Zn

(CHG1 and R7); and very high contamination ($6 \leq CF$) for Cd (at CHG1) (Fig. 3.2.5).

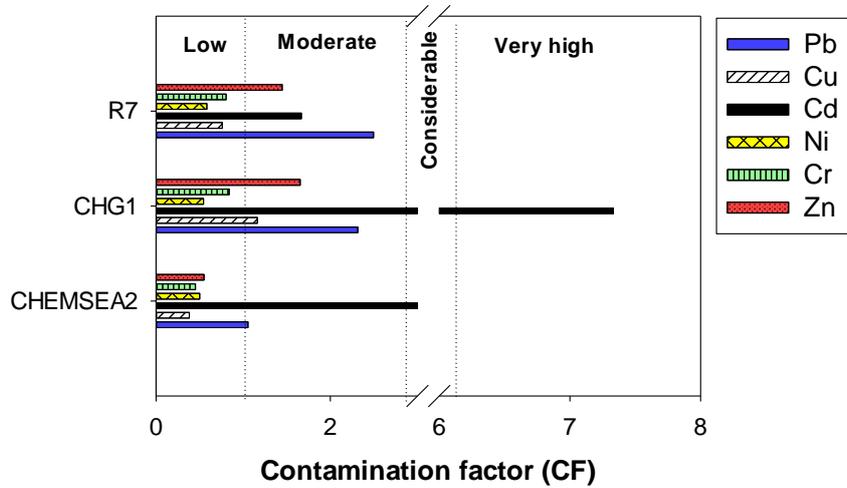


Fig. 3.2.5 Contamination factors (CFs) of sediments from the R7, CHG1 and CHEMSEA2 sites.

In contrast to the non-biological sediment contamination factors, ecological risk indexes (E_r^i and RI) indicate ecological risk of surrounding environment (sediment in this study) to the living organisms. The estimated ecological risk (E_r^i and RI) for metals in sediments from the SE Baltic Sea is presented in Table A4.3 (*Annex IV*). Based on the E_r^i values, Pb, Cr, Ni and Zn probably pose low levels of eco-risk at all sites, whereas Cd and Cu pose moderate – to great ecological risk in the surface sediments of the several stations. The E_r^i values for Cd ranged from ~2 to 220 and showed great risk ($160 \leq E_r^i < 320$) at CHG1 and moderate ($40 \leq E_r^i < 80$) risk at the stations K10, CHEMSEA2 and R7. Copper exhibited moderate ecological risk in K10 and CHEMSEA2 sediment, considerable risk ($80 \leq E_r^i < 160$) in K3B and a great ecological risk ($160 \leq E_r^i < 320$) in K3A, CHG1 and R7 sediments. Among metals (Pb, Cu, Cd, Ni, Cr, As, Zn), cadmium has the highest toxic response factor ($T_r^i = 30$, Håkanson, 1980) which results higher ecological risk even at the low concentrations in sediments. It is likely that ecological risk from Cu might be also determined due to its toxicity unit ($T_r^i = 5$) since pollution with Cu was not obvious in the SE Baltic Sea based on the

contamination factors EF, I_{geo} and CF. It should be, however, noted that the potential ecological risk index (E_r^i) related to toxicity is based on the standardized values and provides information on biological responses from the previous studies (Bonnail et al., 2016; Benson et al., 2016). However, toxic effects and responses can vary among species, the threats differ among metals and the influences may be determined by the complex of environmental variables (Luoma and Rainbow, 2005; Bonnail et al., 2016).

Comparing the results from the I_{geo} and CF assessment, and that from the EFs, similar conclusions on sediment contamination level were reached (Table 3.2.4 and Tables A4.1–A4.9 in *Annex IV*). Generally, the results of metal contamination factors suggested that higher differences in assessment status occurred and indexes were less effective in contamination differentiation when the pollution level of a given metal was low. A discrepancy between results may also be explained by the lack of normalization, since EFs normalize concentrations against geochemical sediment properties (in this study against Al).

As it was shown in the previous section (3.2.1), the significant higher concentrations of metals (Tukey HSD test, $p < 0.05$) were measured in sediments at the stations K1, K3A, K3B, K10, CHEMSEA2, CHG1 and R7 (Fig. 3.2.2). Based on the different contamination and risk factors (EF, I_{geo} , CF and E_r^i), the sediment from those seven stations in some extent were classified as being polluted or at risk with the individual metals (Tables A4.5–A4.9, *Annex IV*). Therefore, the integrated contamination degree (C_d) and potential ecological risk index (RI) for these sites were calculated and presented in the Table 3.2.5. The C_d was calculated taking into account the CF values of individual metals to further examine an integrated level of pollution in sediments (Table A4.2, *Annex IV*). An integrated C_d index showed low pollution at K10, K3A, K3B, K1 and CHEMSEA2 ($C_d < 5$) and moderate-considerable contamination at R7 ($C_d = 7.8$) and CHG1 ($C_d = 13.8$) sites (Table 3.2.5).

Table 3.2.5 The integrated contamination degree (C_d) and potential ecological risk index (RI) for the stations K10, K3A, K3B, K1, CHEMSEA2, CHG1 and R7.

Stations	C_d	Assessment ^a	RI	Assessment ^b
K10	4.3	Low	130	Moderate
K3A	2.4	Low	187	Moderate
K3B	2.4	Low	138	Moderate
K1	2.6	Low	82	Low
CHEMSEA2	4.8/ <u>2.4</u>	Low	140/ <u>97</u>	Moderate
CHG1	<u>13.8</u>	Considerable	<u>499</u>	Very high
R7	<u>7.8</u>	Moderate	<u>239</u>	Considerable

The underlined values – calculations based on the data obtained by applying a total leaching method.

^a $C_d < 5$ – low; $5 \leq C_d < 10$ – moderate; $10 \leq C_d < 20$ – considerable; $20 \leq C_d$ – very high (Bonnail et al., 2016).

^bRI < 95 – low ecological risk for all factors; $95 \leq RI < 190$ – moderate; $190 \leq RI < 380$ – considerable, $380 \leq RI$ – very high (Maanan et al., 2015).

Based on the integrated RI values (Table A4.3, *Annex IV*), sediments from six stations (K10, K3A, K3B, CHEMSEA2, CHG1 and R7) exhibited from moderate to very high ecological risk, while sediments only at K1 showed low risk ($RI < 95$). The integrated potential ecological risk estimated from metals was dominated by Cd and Cu (Table A4.3, *Annex IV*). Results (Table 3.2.5) showed that potential ecological risk level was tending to show class worse by one level as compared with C_d level. Even at low contamination sediments can pose a moderate ecological risk to organisms. Especially it was pronounced for Cu, since none of the indexes (EF, I_{geo} and CF) proved sediment enrichment with copper. Taking into account the results on the contamination indexes (EF, I_{geo} and CF) presented before, and high risk to environment posed by Cd, pollution with Cd should be widely concerned. Cadmium may accumulate in the soil as a result of the application of agricultural inputs such as fertilizers, pesticides, and sewage sludge, the disposal of industrial wastes or the deposition of atmospheric contaminants (Marrugo-Negrete et al., 2017 and references therein).

3.2.3 Identification of pollution sources

The principal component analysis (PCA) and the Pearson correlation matrix used in the study provided important tools for a better understanding of source identification and the dynamics of the pollutants. The PCA extracted a small number of factors (Principal Components, PCs) for exploring the similarity of distribution behaviour of metals and analysing the relationships among the observed variables. This technique clusters variables into groups, such that variables belonging to one group are highly correlated with one another (Table 3.2.6 and Fig. 3.2.6).

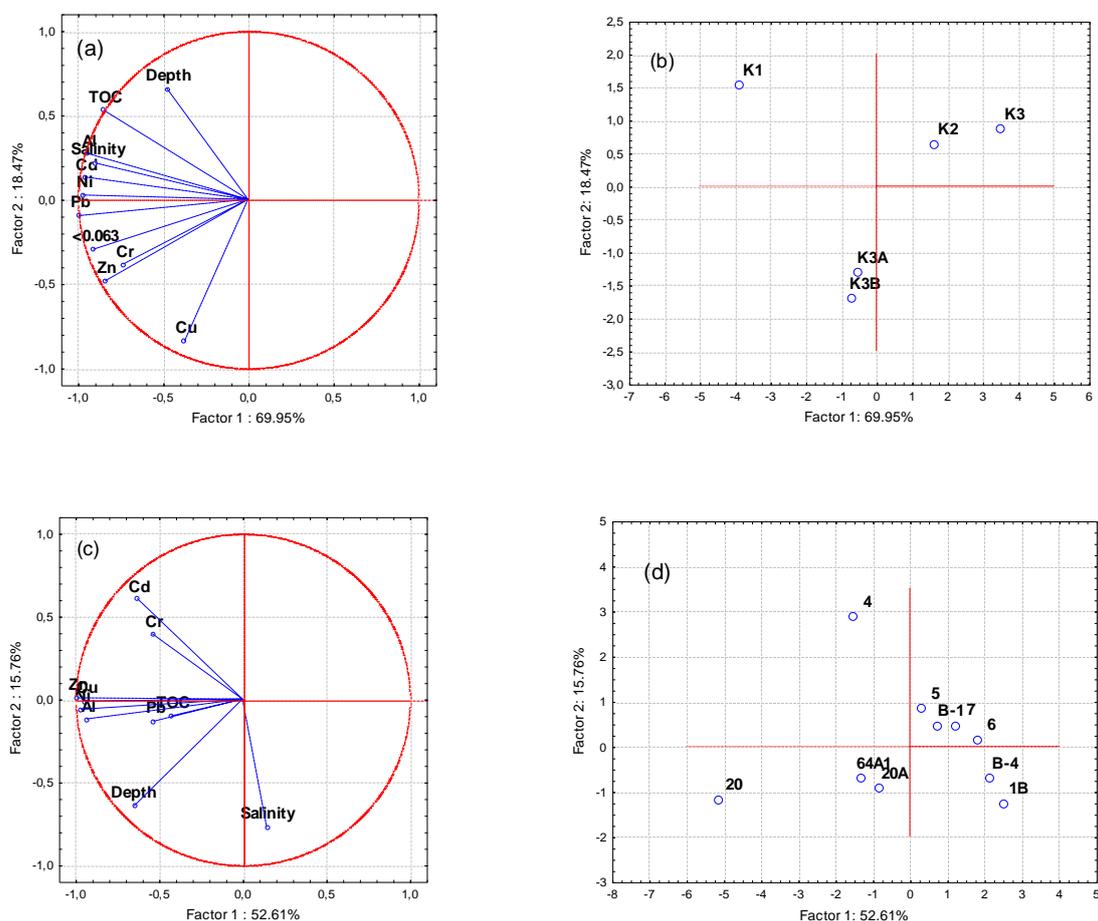


Fig. 3.2.6 Plot of PCA loadings and scores: the Klaipėda Strait (a,b), the territorial waters of the Baltic Sea (c,d).

Four datasets were analyzed separately: 1) the Curonian Lagoon; 2) the Klaipėda Strait; 3) territorial waters of the SE Baltic Sea and 4) open waters.

The PCs with eigenvalues >1 were extracted for metal in sediments datasets, accounting for about 82 – 92% of the total variance (Table 3.2.6). Positive scores in PCA indicate that sediment samples are affected by the presence of the parameters that are significantly loaded on a specific PC, whereas negative scores suggest that sample is essentially unaffected by those parameters (Fig. 3.2.6).

Table 3.2.6 Results of the PCA for the distinct research zones. The statistically dominant loadings are given in **Bold**.

Variables	Curonian Lagoon	Klaipėda Strait		Territorial waters			Open sea
	PC1	PC1	PC2	PC1	PC2	PC3	PC1
Pb	-0.97	-0.98	0.04	-0.53	-0.14	-0.24	0.98
Cu	-0.99	-0.37	-0.84	-0.94	-0.01	0.15	0.99
Cd	-0.99	-0.96	0.13	-0.64	0.60	-0.36	0.99
Ni	-0.98	-0.98	0.03	-0.97	-0.06	0.19	0.99
Cr	-0.99	-0.73	-0.38	-0.54	0.39	0.56	0.98
Zn	-0.95	-0.84	-0.48	-0.99	0.01	0.04	0.98
Al	-0.98	-0.95	0.27	-0.93	-0.12	0.29	0.98
TOC	-0.98	-0.85	0.53	-0.43	-0.10	-0.79	0.99
<0.063*	-0.71	-0.91	-0.30	-	-	-	-
Depth	-0.20	-0.48	0.66	-0.65	-0.64	-0.31	0.80
Salinity	0.06	-0.90	0.22	0.15	-0.77	0.35	0.36
Fe**	-	-	-	-	-	-	0.99
S**	-	-	-	-	-	-	0.99
Eigenvalues	8.25	6.69	1.74	5.26	1.58	1.48	8.12
% of variance	91.68	69.95	18.47	52.61	15.76	14.84	81.25
Cumulative %	91.68	69.95	88.42	52.61	68.36	83.20	81.25

*Data on the particle size were available only for the Curonian Lagoon.

**Data on Fe and S were available only for the open sea stations.

The Curonian Lagoon (without Klaipėda Strait). Only one PC (with eigenvalue >1) was extracted from database which explained about 92% of the total variance of metals (Table 3.2.6). The PC1 was loaded on Pb, Cu, Cd, Ni, Cr, Zn, Al, TOC and amount (%) of fine particles (<0.063) which were significantly distributed in K10 site. The strong relationships among metals (Table 3.2.7) suggested their similar source and mechanism of distribution in sediments, while each source type was not defined. In some studies, a lithogenic (natural) origin is presumed for metals related with Al, since it is a common element in soil parent materials (e.g., Levei et al., 2014). However, the significant correlations might show the supply of aluminosilicate of

mainland origin contaminated with metals from intensive agricultural activities and thus reflect an anthropogenic source. The highest amount of pollutants enters the Curonian Lagoon with the riverine discharge, affected by the municipal sewage discharge, industrial and agricultural activities within catchment areas (The Nemunas River..., 2010). Pb, Cu, Cd and Zn are well-known elements of agricultural activities, specifically related to application of pesticides and phosphate fertilizers (Wang et al., 2015; Marrugo-Negrete et al., 2017 and references therein). Consequently, metals originated from mainland sources accumulate in the central part of the lagoon characterized by slower dynamic and high primary production resulting in high TOC amount. Besides the pollution of mainland origin, close to the sampling station K10 there is a marina for small boats, which may contribute to the inputs of metals, as well as the fuel residues to the sediment. An example, Costa et al., (2015) reported moderate to strong relationships ($r = 0.66\text{--}0.85$, $p < 0.05$) between metals (Zn, Cd, Cu and Pb) and petroleum markers (e.g. hopanes) for the estuary of Southern Brazil which is exposed to high ship traffic.

Table 3.2.7 The Pearson's correlation between metals* (mg kg^{-1} d.w.), TOC (%), $\delta^{13}\text{C}$ values (‰), amount (%) of sediment fraction <0.063 mm in sediments, water salinity (Sal) and water depth (m) of sites in the *Curonian Lagoon (without Klaipėda Strait)*. The significant relationships ($p < 0.05$) are given in **Bold** (n=23–60).

	Pb	Cu	Cd	Ni	Cr	Zn	Al	TOC	<0.063	$\delta^{13}\text{C}$	Depth
Pb	1.00										
Cu	0.98	1.00									
Cd	0.97	1.00	1.00								
Ni	0.93	0.98	0.92	1.00							
Cr	0.93	0.98	0.92	0.98	1.00						
Zn	0.97	0.94	0.93	0.97	0.98	1.00					
Al	0.96	0.97	0.99	0.97	0.98	0.93	1.00				
TOC	0.96	0.98	0.89	0.88	0.90	0.96	0.95	1.00			
<0.063	0.82	0.82	0.96	0.70	0.72	0.73	0.75	0.78	1.00		
$\delta^{13}\text{C}$	-0.20	-0.28	-0.25	-0.22	-0.08	-0.19	-0.12	-0.40	-0.43	1.00	
Depth	0.12	0.20	0.30	0.11	0.16	0.27	0.05	0.26	0.31	0.14	1.00
Sal	0.16	0.25	0.35	0.10	0.12	0.06	0.08	0.22	0.30	0.21	0.15

*the partial leaching method.

The Klaipėda Strait. The PC1 explained about 70% of total variance with high loadings of Pb, Cd, Ni, Cr, Zn, Al, TOC, salinity and amount (%) of

fine particles (<0.063 mm) in sediments. On the plot of scores the relatively higher concentrations of elements appeared in the K1, K3A and K3B sites (Fig. 3.2.6a,b). The positive strong correlations among those metals (Table 3.2.8) suggested that they had common geochemical behaviors and probably originated from similar pollution sources, while the possibility to identify a clear origin of metal was limited. On the one hand, contaminants collected from the rivers catchment area are carried into the harbor basin, on the other hand, pollution also enters from sources in the port itself (Galkus et al., 2012 and references therein).

The increasing accumulation of trace metals in sediments at the station K1 might be greatly influenced by the flocculation processes which are often amplified by the increase of pollution. When colloidal particles move downwards from freshwater into the marine environment, flocculation causing larger particles to form and settle on the seafloor takes place. Flocculation processes in the marine water-freshwater interface have been widely reported in other studies (Palanques et al., 1995; Karbassi et al., 2013). The significant relationships between metal concentrations in sediments and salinity ($r = 0.83-0.87$, $p < 0.05$; Table 3.2.8) might support this explanation. Despite of significantly high metal concentrations at K1, K3A and 3B sites, the contamination factors (I_{geo} , CF) indicated uncontaminated/low contaminated sediments. Nevertheless, the potential risk assessment showed that concentrations of Cu in sediments of the K1, K3A and K3B sites posed moderate ($E_r^i = 52.1$) to great ($E_r^i = 173.3$) ecological risk (*Annex IV*).

Factor two accounted for 19.4% of the total variance and was dominated by Cu (Table 3.2.6). Copper occurred as important parameter in sites K3A and K3B (Fig. 3.2.6a,b) probably might be related to the urban and industrial activities taking place in the Klaipėda Port. In the technogenic sedimentation zone of the Klaipėda Strait metal concentrations may be 5-50 times greater than in the natural sedimentation zone (Pustelnikovas, 2007). The station K3B was established to track the impact of domestic and industrial effluent inputs, whereas st. K3A was located in the semi-enclosed Malku Bay in order to

evaluate the impact of the floating docks of the ship repair company. Stagnation and low oxygen conditions are prevalent at these sites (Pustelnikovas et al., 2007). The high E_r^i values for copper showed a considerable ($E_r^i = 118.7$) and great ($E_r^i = 173.3$) ecological risk at those sites. The elevated concentrations of metals in sediments and moderate pollution with copper level were indicated previously by other authors (Jokšas et al. 2005; Garnaga, 2011; Galkus et al., 2012).

Table 3.2.8 The Pearson's correlation between metals* (mg kg^{-1} d.w.), TOC (%), $\delta^{13}\text{C}$ values (‰), amount (%) of sediment fraction <0.063 mm in sediments, water salinity (Sal) and water depth (m) of sites in the *Klaipėda Strait*. The significant relationships ($p < 0.05$) are given in **Bold** (n=20–52).

	Pb	Cu	Cd	Ni	Cr	Zn	Al	TOC	<0.063	$\delta^{13}\text{C}$	Depth
Pb	1.00										
Cu	0.44	1.00									
Cd	0.94	0.14	1.00								
Ni	0.97	0.25	0.99	1.00							
Cr	0.76	0.81	0.51	0.59	1.00						
Zn	0.88	0.64	0.80	0.84	0.67	1.00					
Al	0.92	0.06	0.98	0.97	0.51	0.69	1.00				
TOC	0.79	-0.14	0.89	0.84	0.39	0.47	0.95	1.00			
<0.063	0.94	0.47	0.91	0.94	0.62	0.97	0.83	0.62	1.00		
$\delta^{13}\text{C}$	-0.13	-0.36	-0.27	-0.29	-0.18	0.35	-0.13	-0.09	-0.51	1.00	
Depth	0.40	-0.14	0.40	0.36	0.42	-0.05	0.54	0.70	0.06	0.05	1.00
Sal	0.87	0.29	0.83	0.77	0.71	0.60	0.84	0.87	0.64	0.41	0.75

*the partial leaching method.

Territorial waters. Three main PCs explained about 83% of the total variance (Table 3.2.6). The PC1 (53 % of the total variance) distinguished a large group of variables containing all metals together with a water depth, thus confirming the distribution of elements depending on the water depth. Results (Table 3.2.9) show that in the case of Cu, Ni and Zn, the major source for accumulation in coastal sediments has lithological material (Al), while material of biotic origin (TOC) probably has a secondary importance. The PC2 explained 15.8% of total variance with moderate loadings of Cd, salinity and water depth (Table 3.2.6). On the score plot, the elements defined by the PC1 and PC2 were related to the stations 64A1, 20, 20A and 4 (Fig. 3.2.6d) and it probably showed the mainland origin of metals: an input with the freshwater

discharge (stations 4 and 64A1) as well as sediment dumping from the Klaipėda Port area (st. 20 and 20A) (Fig. 3.2.6a,b).

Table 3.2.9 The Pearson's correlation between metals* (mg kg⁻¹ d.w.), TOC (%), δ¹³C values (‰), water salinity (Sal) and water depth (m) of sites in the territorial waters of the SE Baltic Sea. The significant relationships ($p < 0.05$) are given in **Bold** (n=55–93).

	Pb	Cu	Cd	Ni	Cr	Zn	Al	TOC	δ¹³C	Depth
Pb	1.00									
Cu	0.36	1.00								
Cd	0.25	0.47	1.00							
Ni	0.40	0.97	0.49	1.00						
Cr	0.19	0.48	0.46	0.54	1.00					
Zn	0.50	0.92	0.62	0.97	0.98	1.00				
Al	0.38	0.97	0.39	0.99	0.53	0.94	1.00			
TOC	0.27	0.27	0.62	0.25	0.12	0.38	0.16	1.00		
δ¹³C	0.10	-0.42	-0.60	-0.36	-0.36	-0.26	-0.25	-0.18	1.00	
Depth	0.16	0.35	0.04	0.38	0.38	0.38	0.37	-0.12	0.26	1.00
Sal	-0.48	-0.31	-0.13	-0.15	0.11	-0.22	0.05	0.10	0.41	0.18

*the partial leaching method.

Open waters. Only one PC (with eigenvalue >1) was extracted from the database which explained about 81% of the total variance of metals (Table 3.2.6). The PC1 was highly loaded on all metals, TOC, water depth, amount of sulphur and iron, which were significantly distributed in CHG1, R7 and CHEMSEA2 sites. Since Cd and Pb are scarce in rocks, their presence in the marine environment is usually related to anthropogenic inputs from the atmosphere and rivers (Palleyi et al., 2015). As it was shown in Section 3.2.2, the concentrations of Pb and Cd in the open waters were clearly higher than the concentrations in the Earth's shale and it showed an anthropogenic origin of pollutants (EFs >1.5–2.0 and the highest I_{geo} , CF values, *Annex IV*). Regarding nickel, Renner et al. (1998) claimed that Ni as well as Mn and Co entered the southern Baltic as a result of natural erosion processes. Therefore, the strong correlations among all elements should refer to a similar distribution pattern and a combination of natural and anthropogenic sources.

Table 3.2.10 The Pearson's correlation between metals* (mg kg⁻¹ d.w.), S, TOC (%) and $\delta^{13}\text{C}$ (‰), water salinity (Sal) and water depth (m) in sites of the *Baltic Sea open waters*. The significant relationships ($p < 0.05$) are given in **Bold** (n=16–47).

	Pb	Cu	Cd	Ni	Cr	Zn	Al	Fe	S	TOC	$\delta^{13}\text{C}$	Depth
Pb	1.00											
Cu	0.98	1.00										
Cd	0.99	0.98	1.00									
Ni	0.97	0.97	0.99	1.00								
Cr	0.98	0.96	0.98	0.95	1.00							
Zn	0.90	0.95	0.97	0.97	0.98	1.00						
Al	0.96	0.97	0.97	0.99	0.95	0.94	1.00					
Fe	0.98	0.98	0.96	0.96	0.96	0.96	0.98	1.00				
S	0.98	0.98	0.98	0.97	0.98	0.97	0.96	0.97	1.00			
TOC	0.98	1.00	0.99	0.99	0.99	0.96	0.95	0.96	0.99	1.00		
$\delta^{13}\text{C}$	0.34	-0.47	-0.29	-0.60	-0.47	0.14	-0.57	-0.60	0.13	-0.33	1.00	
Depth	0.62	0.84	0.89	0.65	0.71	0.71	0.62	0.80	0.98	0.79	0.13	1.00
Sal	0.28	0.27	0.22	0.27	0.42	0.28	0.39	0.38	0.40	0.39	0.12	0.39

*the total leaching method.

Although PCA applied to the data set provides a qualitative information about distribution pattern of elements and probably common sources, it seems that it is not adequate for supplying a qualitative and quantitative information regarding the contributions of each source type. Based on the PCA results, the metal accumulation in sediments is affected by the grain-size, amount of TOC, depth variability, and thus the anthropogenic component is not easily discernible by the lithogenic one. The PCA results showed that the only Cu might be attributed to the anthropogenic source in the Malku Bay.

The sources of metals and their distribution pathways might be indicated indirectly by the C and N isotopic signatures of organic matter. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures, as well as low C/N ratio (~ 7), suggested that the SOM in the SE Baltic Sea was mostly derived from a contribution of marine and freshwater algae. The trace elements from water might be incorporated in living phytoplankton cells and, in this context, phytoplankton plays an important role in the transport of metals (Aigars et al., 2014) as well as other toxic pollutants (e.g., TBT compounds, Filipkowska et al., 2014) from the water column to the bottom sediments. Since the decrease of terrestrial organic matter towards offshore is observed (Figs. 3.1.12 and 3.1.14), the influence of terrestrial contaminants is believed to decrease towards open waters. Since the lower $\delta^{13}\text{C}$ signatures are characteristics of freshwater phytoplankton, the weak

correlation between metals and $\delta^{13}\text{C}$ values (Table 3.2.9) might show a general tendency of decreasing transport of contaminants in association with freshwater organic matter. In general, no correlation between metals and $\delta^{13}\text{C}$ values was observed for the open sea area. Considering an increase of organic matter from marine sources at the open sea stations (Remeikaitė-Nikienė et al., 2016), it is believed that marine phytoplankton is probably not directly involved in the metal transport from terrestrial sources, although it uptakes metals deposited from the atmosphere and is likely involved in the further sedimentation and redistribution processes of fine-grained particles. An exception was R7 site which was characterized by the lowest $\delta^{13}\text{C}$ value ($-31.8 \pm 0.3\text{‰}$) and a relatively high $\delta^{15}\text{N}$ value (6.8‰) (Fig. 3.1.12) similar to those, reported for the freshwater ecosystems (Lesutienė et al., 2014; Remeikaitė-Nikienė et al., 2016). Apparently, this site is influenced by the considerable amounts of elements discharged to the sea by the Vistula River. In the Gdansk Deep, an intensive accumulation of trace metals supplied by the Vistula River was reported in other studies (Emelyanov, 2014; Zalewska et al., 2015).

A clear picture of the metal inputs entering the Baltic Sea via riverine discharge cannot be established due to the shortcomings in national monitoring programmes. In spite of the lack of data, the results from the HELCOM countries showed the highest riverine metal (Cd, Pb, Cu, Cr, Ni, Zn) loads from Russia, Poland, Finland and Sweden (HELCOM, 2011). The modeling results showed that levels of annual total atmospheric deposition of metals to the surface of the Baltic Sea have substantially decreased in the period from 1990 to 2014 which reflects the reductions in their emissions (Gusev, 2016). An example, the atmospheric deposition decreased by 69% for lead from 1990 to 2007 (HELCOM, 2010) and 54% for cadmium from 1990 to 2014 (Gusev, 2016). The greatest reductions in the emissions of cadmium occurred in Estonia (88%) and Lithuania (90%). The decrease in waterborne loads was also reported to be 91% for cadmium and 50% for lead (HELCOM, 2010). Despite the decreasing trends, significant transboundary pollution loads of waterborne metals still originate in Belarus, the Czech Republic and Ukraine (HELCOM,

2010 and references therein). Riverine inputs to the sea also include natural background losses of metals, the extent of which is highly uncertain (HELCOM, 2007).

3.2.4 Metal accumulation in molluscs

Monitoring of contaminant concentrations in biota has an advantage compared with the measurement of the total contaminant concentration in the water column and sediments, since marine organisms are characterized by a greater spatial ability to accumulate some metals and the hazard compounds may be found at very low levels (Szefer and Szefer, 1990; Szefer et al., 2006; Sokolowski et al. 2007; Przytarska et al., 2010; Zaldívar et al., 2011). During this study, the metal accumulation was analyzed in two mollusc species – Baltic clam *Macoma balthica* and zebra mussel *Dreissena polymorpha*. Despite of different feeding pattern (zebra mussel – suspension feeders, Baltic clam – facultative suspension – deposit feeders) both species have a strong interaction with the surrounding sediments, and the deposit-feeding organisms (such as Baltic clam) are exposed directly to sediment-bound metals.

During this study, molluscs exhibited wide ranges of metal concentrations (Table 3.2.11). The higher level of Zn was measured in soft tissue of *Macoma balthica* (Table 3.2.11), while no significant difference was observed between Baltic clam from the stations 65 and 7 ($t = 0.29$, $p > 0.05$). Cu concentrations in *M. balthica* showed a site-dependent difference ($t = 6.09$, $p < 0.05$), since the highest mean concentration was measured in molluscs sampled at the st. 65 ($168.2 \pm 86.5 \text{ mg kg}^{-1}$) as compared with st. 7 ($36.8 \pm 6.9 \text{ mg kg}^{-1}$). Results probably might be explained by the composition of bottom sediments (aleurites and sand, respectively) and, therefore, different capacity to accumulate metals. Neuhoff (1983) showed that uptake of Cu by *M. balthica* is enhanced by low dissolved oxygen concentrations, which most probably may occur in fine grained sediments in the open sea. The difference between concentrations of Cd and Pb in Baltic clam and zebra mussel was not significant (KW, $H = 0.69$, $p > 0.05$).

Table 3.2.11 Metal concentrations (mean in mg kg⁻¹ d.w. ± sd and/or range from-to unless indicated otherwise) in soft tissue of molluscs.

Area	Sampling period	Cd	Cu	Pb	Zn	Reference
<i>Dreissena polymorpha</i>						
The Curonian Lagoon (st. 12)	2006–2014 August	0.81±0.37 (0.41–1.71)	22.3±13.5 (8.9–77.1)	0.95±1.05 (0.20–4.95)	80.2±35.5 (25.7–150.0)	This study
The Curonian Lagoon (st. 12)	1998–2000 August	0.07±0.05* 0.7**	1.3±1.2* 13.0**	0.44±0.35* 4.40**	16.9±15.7* 169.0**	Garnaga, 2011
Szczecin Lagoon, Kleines Haff	1996 May, July, August and September	0.232–0.955	-	0.48–4.95	-	Wiesner et al., 2001
<i>Macoma balthica</i>						
The SE Baltic Sea (st. 65)	2006–2010 August	0.49±0.22 (0.11–0.89)	168.2±86.5 (11.0–340.0)	0.92±0.18 (0.70–1.10)	604.6±206.8 (295–985)	This study
The SE Baltic Sea (st. 7)	2006, 2012–2014 August	0.40±0.09 (0.27–0.48)	26.2±4.6 (18.8–32.0)	0.82±0.49 (0.33–1.91)	517.2±86.9 (408–650)	This study
The SE Baltic Sea (st. 65)	1999–2000 August	0.07±0.04* 0.35**	25.8±13.6* 129**	1.01±0.05* 5.05**	24.2±11.9* 121.0**	Garnaga, 2011
Gulf of Gdansk and central southern Baltic	2006 July - August	0.31–3.39	19.19–376.6	-	337.8–762	Hendozko et al. (2010)

*original data expressed in mg kg⁻¹ wet weight (Garnaga, 2011). The conversion of mean concentrations to a dry weight basis** was made assuming a moisture content of about 90% and 82% as it was estimated for dreissena and macoma for this study.

The levels of Cd and Cu measured in molluscs were similar to those reported earlier for the same species by Garnaga (2011), whereas concentrations of Pb were considerable lower in 2006–2014 as compared with the average concentrations in 1998–2000 (Table 3.2.11). Results could be probably explained by the phaseout of tetraethyl lead from road vehicle fuels since the early 2000s, however, Pb concentration in sediments remained at similar levels over the last decade (Fig. 3.2.4). The variations in Cu and Zn concentrations found in this study for the Baltic clam were comparable with

the recent data reported for *M.balthica* from the Gdansk Basin (Hendozko et al., 2010), while the concentrations of Cd in *M.balthica* from the open sea (st. 65) were in a narrower range as compared with the Gdansk Basin (Table 3.2.11). Concentrations of Cd and Pb in *D.polymorpha* from the Curonian Lagoon were similar to those reported earlier for zebra mussel from the Szczecin Lagoon (Table 3.2.11).

The transfer of metals from sediment to molluscs was evaluated based on the **bioaccumulation factor (BAF)**.

In this study, the average BAFs in molluscs were:

D. polymorpha: Cu > Cd > Zn > Pb;

M. balthica (st. 65): Cu > Zn > Cd > Pb;

M. balthica (st. 7): Zn > Cu > Cd > Pb (Table 3.2.12).

The estimated values for Cd, Cu, and Zn were above 1.0, indicating tendency of these metals to accumulate in molluscs (Table. 3.2.12). The analyzed benthic organisms showed poor bioaccumulation capacities for lead (Table. 3.2.12). The average concentration of Pb in tissue was 5 to nearly 8 times lower than in the surrounding sediment (Fig. 3.2.7). According to Dallinger (1993), the species can be classified based on the BAF values which include the macroconcentrator (BAF>2), microconcentrator (1<BAF<2) and deconcentrator (BAF<1). Results of this study showed that molluscs are macroconcentrators of Cd, Cu and Zn and deconcentrators of Pb. Assuming that concentrations in biota should reflect the environmental contamination degree, results might show the decreasing pollution with Pb extent and/or the strong ability of organisms to excrete Pb as non-essential element.

Table. 3.2.12 Bioaccumulation factors (BAFs) calculated for metals in soft tissue of molluscs (*Dreissena polymorpha* and *Macoma balthica*).

	Cd	Cu	Pb	Zn
<i>D. polymorpha</i> n=22	30.6 ± 17.2 (11.8 – 82.5)	35.6 ± 29.0 (4.2 – 124.2)	0.32 ± 0.20 (0.05 – 1.21)	4.5 ± 2.4 (1.5 – 10.3)
<i>M. balthica</i> (st.65) n=14	6.0 ± 4.1 (0.7 – 15.1)	70.7 ± 42.1 (2.9 – 194.3)	0.13 ± 0.02 (0.10 – 0.16)	38.2 ± 13.7 (16.4 – 56.6)
<i>M. balthica</i> (st.7) n=11	17.0 ± 6.9 (9.2 – 29.7)	44.9 ± 30.4 (13.9 – 101.4)	0.23 ± 0.10 (0.09 – 0.47)	99.5 ± 67.2 (37.1 – 235.8)

n – number of samples.

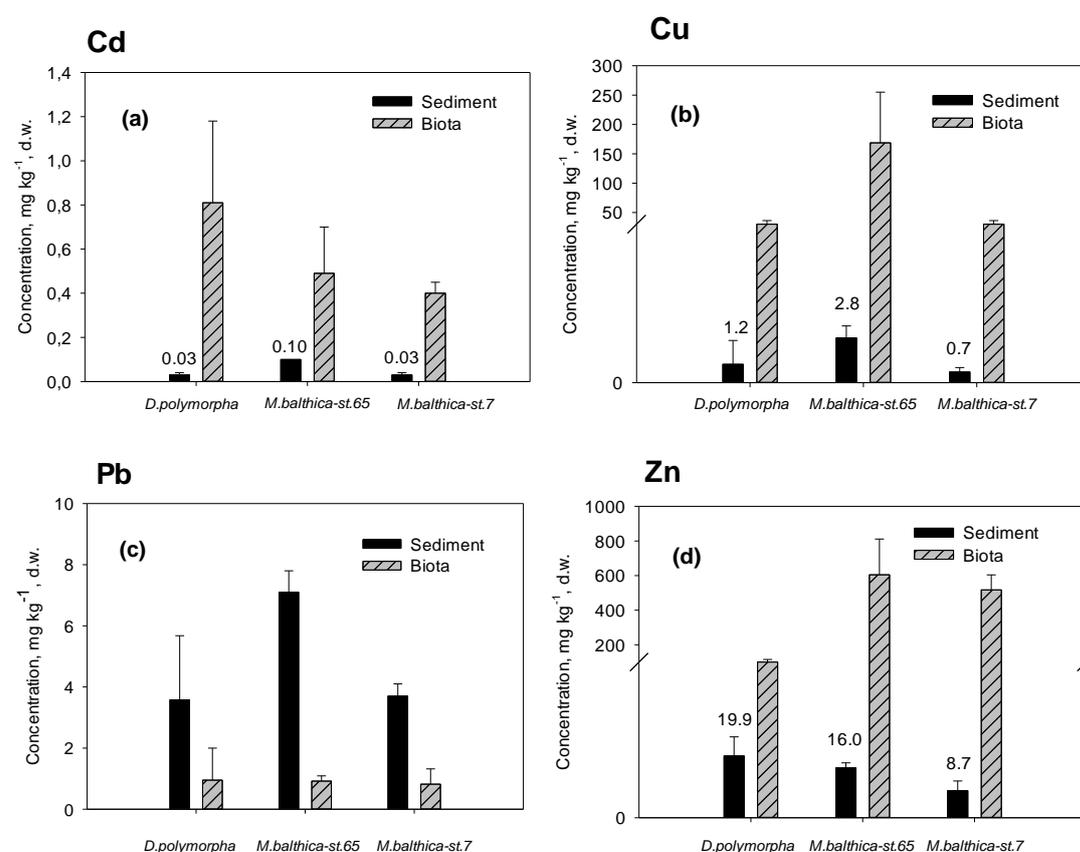


Fig. 3.2.7 Mean concentrations of Cd, Cu, Pb and Zn in soft tissues of molluscs (*D. polymorpha* and *M. balthica* at the stations 65 and 7) and adjacent sediment collected from the SE Baltic Sea during the period of 2006–2014. Data are mean ± sd in mg kg⁻¹ dry weight.

A considerable ability of *M. balthica* to accumulate Cu and Zn was also reported by other authors (Szefer and Szefer 1990; Hendozko et al., 2010). It seems that the trace elements accumulate differently in different organs. Szefer et al., (2006) analyzed distribution patterns of trace elements in molluscs *Mytilus* from different geographical regions all over the world. The authors

concluded that Pb mainly accumulates in byssus of molluscs (that function to attach the mollusc to a solid surface and it is composed of a protein component, collagen) relative to the soft tissue. That might be the explanation, why low Pb accumulation in molluscs' soft tissue was observed. In contrast, Cd strongly accumulates in soft tissue as it was shown for the molluscs *Macoma balthica* and *Mytilus edulis* (Szefer and Szefer, 1990; Gundacker, 1999; Szefer et al., 2002).

The average BAFs for Cd (6–17) and Cu (~45–71) calculated in this study for the *M.balthica* (Table 3.2.12) were comparable with those reported by Hendozko et al. (2010) for the Baltic clam from the Gdansk Basin (5–10 for Cd and 20–55 for Cu). BAF for Zn (~38–100) calculated in this study was about two times higher as compared with the maximum value of BAF (25–45 for Zn) reported by Hendozko et al. (2010). The results indicated the similar metal pollution extent and metal accumulation abilities by *M.balthica* in the southern Baltic Sea.

A clear relationship between external and internal metal concentrations is one of the most important requirements of a metal accumulating organism need in bio-monitoring studies (Ravera et al., 2003). However, no relationships between metal concentrations in the species (and BAFs) and those in the sediment were found or the relationships were not strong (Fig. 3.2.8). That were contrary to the prediction (i.e., a simultaneous increase in sediment contamination and the concentrations in biota). It seems that sediments which suffer higher contamination may not necessarily result in higher metal concentration in organisms. Similarly, Cd, Cu, Pb and Zn were reported to exhibit weak or no relationships to metal exposure concentrations (i.e. metal levels in the surrounding environment) in natural conditions and laboratory by other authors (e.g., Ravera et al., 2003; Anderson et al., 2004; DeForest et al., 2007).

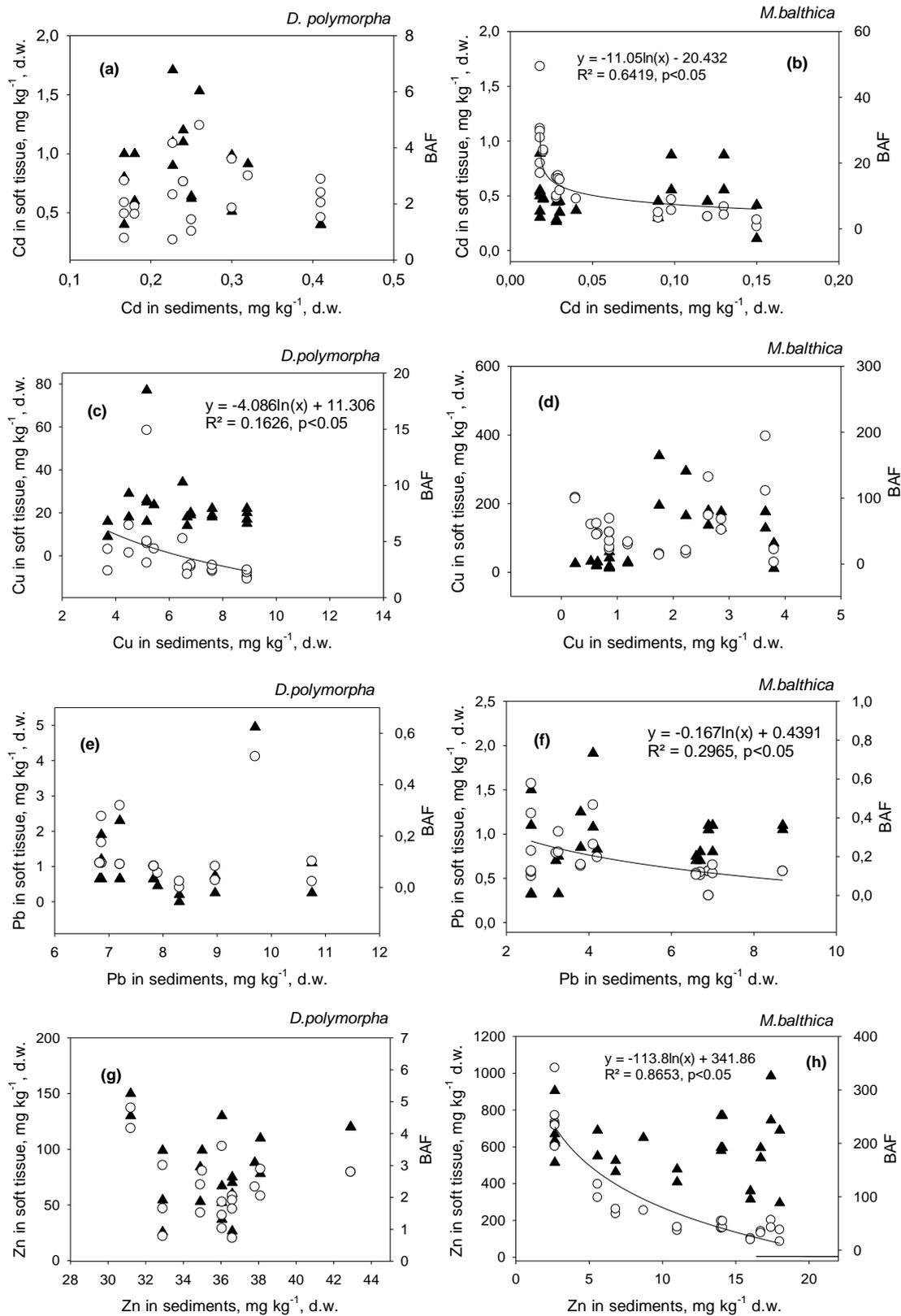


Fig. 3.2.8 Relationships between BAFs (open circles), concentrations of Cd, Cu, Pb and Zn in molluscs (filled triangles) and sediments. The solid line represents the correlation between BAFs and metal concentrations in sediments.

Several explanations for these results exist. Firstly, the pollutant concentrations in the organism are the result of the past as well as the recent pollution level of the environment in which the organism lives, while the pollutants concentrations in the environment may not always indicate the long-term situation (Ravera et al., 2003). Even using tissue and environmental (water, sediment) concentrations sampled at the same time from the same location are uncertain because the water and sediment concentration might not reflect the average exposure concentration to which the organism and its food were exposed to in the days, weeks, or months leading up to the sampling time. In some cases a relationship may not have been observed because the metal exposure concentrations did not bracket a sufficient range as it was shown before (DeForest et al., 2007).

Secondly, it should be noted, that metal accumulation was evaluated taken into account only metal concentrations in sediment, whereas dissolved and suspended material from the near bottom water column offer also potential sources of trace metals to the deposit-suspension feeder bivalve. Unfortunately, no BAFs related to metal concentrations in water may be calculated during this study based on the national monitoring data because: (i) metal concentrations in water are expressed in dissolved phase (filtered), whereas molluscs also accumulate metals bound to suspended solids; (ii) dissolved metal concentrations in water are mostly below the limit of determination, therefore, calculation of BAF is incorrect.

Thirdly, other factor such as metal regulation by organisms may be as important. It is well documented, that many species have a more or less effective capacity for regulating their tissue metal (particularly, the essential metals, like Cu and Zn) concentrations (e.g., White and Rainbow, 1982; Szefer and Szefer, 1990; Ravera et al., 2003; Anderson et al., 2004; DeForest et al., 2007; Jakimska et al., 2011; Livingstone, 2013). An example, the reductions in nickel concentrations in freshwater mussels (*Elliptio complanata*) with the increasing Ni values in sediment were observed and explained by regulation mechanism. Perhaps in Ni-poor environments mussels may store Ni for future

use. Upon exposure to Ni rich environments, mussels may release Ni as they no longer need to store it and then the sudden drop in tissue Ni concentrations can be observed (Anderson et al., 2004). White and Rainbow (1982) applied an experiment with shrimps *Palaemon elegans* and showed that total body concentrations of copper and zinc were regulated on exposure to dissolved metal concentrations up to 100 $\mu\text{g l}^{-1}$. Exposure to higher levels of dissolved copper and zinc after 21 days produced an increase in the metal concentration of the shrimps. The experimental results, however, showed that cadmium concentrations were not regulated, the body concentration of metal was proportional to the external metal concentration.

Other studies also showed, that molluscs and fish are able to control the level of the essential zinc and copper in their tissues while the non-essential metals cadmium and lead in the organisms depend mainly on their environmental level and, therefore, are accumulated by organisms to steady-state (e.g., Bordin et al., 1992; Gundacker et al., 1999 and references therein; Przytarska et al., 2010; Gabriel et al., 2013 and references therein). However, Kļaviņš et al. (1998) showed a decreasing accumulation trend of lead (non-essential element) by chironomids with the increasing sediment contamination in lakes of Latvia and it was explained by the induction of metal excreting mechanisms in biota in cases of environmental contamination.

Another explanation for no relationships between internal and external metals concentrations might be that the bioavailable metal fraction might represent only a part of the total metal concentration in sediments (Ravera et al., 2003; Zhang et. al., 2015).

In conclusion, it appears that in most cases the use of correlations between metal concentrations in biota and in sediments to evaluate transfer of metals from sediments to organisms in natural waters is limited and meaningless. The results reflect in general the long-term accumulation of metals in marine biota and do not directly reflect the level of environment contamination at the time of sampling. The underlying processes and other contamination with metals sources (e.g., water) must also be evaluated.

Conclusions of the 3.2 section

The sites most polluted with metals were identified in the Curonian Lagoon (stations K1, K3A, K3B in Klaipėda Strait and K10 near the Nida settlement) and in the Baltic Sea open waters (CHEMSEA2, CHG1 and R7). The prevalent metal accumulation in sediments coincided with the increasing amount of TOC and silt fraction ($r = 0.88\text{--}1.00$, $p < 0.05$), increasing water depth ($r = 0.26\text{--}0.98$, $p < 0.05$) as well as the variability was determined by the iron and sulphur ($r = 0.96\text{--}0.98$, $p < 0.05$) concentrations.

The different geochemical indices and risk factors (EF, I_{geo} , CF, E_r^i) allowed to quantify the contamination levels and they showed that concentrations of *cadmium*, *lead*, *zinc* and *copper* were of a particular concern in sites (K1, K3A, K3B, K10, CHEMSEA2, CHG1 and R7), located in different sedimentation zones, while sediment enrichment with *nickel* and *chromium* was negligible. An integrated C_d index showed low contamination ($C_d < 5$) at K10, K3A, K3B, K1 and CHEMSEA2, moderate at R7 ($C_d = 7.8$) and considerable contamination at CHG1 ($C_d = 13.8$) sites. RI values showed that sediments exhibited low ($RI < 95$, at st. K1), moderate ($95 \leq RI < 190$ at st. K10, K3A, K3B, CHEMSEA2), considerable ($190 \leq RI < 380$, at st. CHG1) and very high ($380 \leq RI$, at st. R7) ecological risk to biota.

The results of multivariate analysis might show combined sources of natural leaching and anthropogenic pollution with metals (Pb, Cu, Cd, Ni, Cr, Zn, Al) which were distributed in stations K10, K3A, K3B, K1, 4, 20, 20A, 64A1, CHEMSEA2, CHG1 and R7. The only accumulation of copper in the stations K3A and K3B was attributed to the anthropogenic sources (urban and industrial activities).

The highest concentrations of Zn (604.6 ± 206.8 mg kg⁻¹ d.w.) and Cu (168.2 ± 86.5 mg kg⁻¹ d.w.) were measured in soft tissue of mollusc Baltic clam *Macoma balthica* sampled at 65 site, while the most elevated level of Cd (0.81 ± 0.37 mg kg⁻¹ d.w.) was measured in zebra mussel. Pb concentrations in molluscs were similar, with an average of about 0.90 mg kg⁻¹ d.w.

The mean bioaccumulation factor (BAF) for the analyzed metals decreased in the following order: *D. polymorpha*: Cu > Cd > Zn > Pb; *M. balthica* (in 65 site): Cu > Zn > Cd > Pb; *M. balthica* (in 7 site): Zn > Cu > Cd > Pb. The higher bioaccumulation factors of Cu (on the average, 44.9–70.7) and Zn (38.2–99.5) were calculated for *M. balthica* as compared with *D. polymorpha*, while Cd (30.6 ± 17.2) accumulated more intensive in zebra mussel. Based on the BAFs values both molluscs species are macroconcentrators (BAF >1) of Cd, Cu and Zn and deconcentrators of Pb (BAF <1).

4. CONCLUSIONS

1. The low C/N molar (~ 7) and POC/Chl-*a* ratios (< 100) of POM indicate that living freshwater and marine phytoplankton are the main contributors to particulate and sedimentary organic matter in the SE Baltic Sea throughout the year, while the higher C/N (> 10) and POC/Chl-*a* (> 100) ratios indicate an increasing input of degraded POM in late autumn – winter period.
2. The seasonal and spatial co-variations of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in POM in the research area are determined by the riverine input, phytoplankton dynamics and successional changes and the uptake of the available DIN and DIC sources. The lower $\delta^{13}\text{C}$ and the higher $\delta^{15}\text{N}$ signatures coincide with the increasing riverine discharge and show an uptake of ^{15}N -enriched DIN of riverine origin. In the Curonian Lagoon, the shift in phytoplankton assemblage towards summer and the increasing biomass of N_2 -fixing cyanobacteria are reflected by the higher $\delta^{13}\text{C}$ values and lower $\delta^{15}\text{N}$ values. Additionally, in the northern – transitional area of the Curonian Lagoon, seawater intrusion affects dynamics of POM and isotopic signatures of $\delta^{13}\text{C}$ ($r = 0.80$, $n = 72$, $p < 0.001$) and $\delta^{15}\text{N}$ ($r = -0.75$, $n = 72$, $p < 0.001$). The $\delta^{15}\text{N}$ dynamics in the Baltic Sea largely is attributed to dominance of diatoms and dinoflagellates.
3. Annually, marine source accounted for about 10 – 13% to the mixed SOM and POM in the northern part of the lagoon with the highest contribution to POM ($\sim 22\%$) in July – October. In the Baltic Sea, about 50% of POM is of freshwater origin with a markedly higher contribution (40% in the plume area and 81% in the coastal waters) of marine phytoplankton in summer. About 47% of SOM in the Baltic Sea is of the freshwater origin with a similar (41–42%) contribution in the territorial and open waters. It is concluded that organic matter of the freshwater origin considerably contributes to eutrophication in coastal areas of the SE Baltic Sea.

4. The sites most polluted with metals are identified in the Curonian Lagoon and in the Baltic Sea open waters. The prevalent metal accumulation in sediments coincides with the increase of TOC and amount of the fine particles ($r = 0.88-1.00$, $p < 0.05$), the water depth ($r = 0.26-0.98$, $p < 0.05$), as well as concentrations of the iron and sulphur ($r = 0.96-0.98$, $p < 0.05$) and indicates a sorption of metals and organic matter to the clay fraction of the sediment and binding of metals with iron-oxides/hydroxides in oxic and with sulphides in anoxic sediments. The strong correlations among all the elements refer to a similar distribution pattern and a combination of natural and anthropogenic sources.
5. The calculated geochemical indices and risk factors (EF, I_{geo} , CF, E_r^i , C_d and RI) show that concentrations of cadmium, lead, zinc and copper are of a particular concern in the research area, while the sediment enrichment with nickel and chromium is negligible.
6. The mean accumulation of metals from the sediments by molluscs decreases in the following order: *D. polymorpha*: Cu > Cd > Zn > Pb; *M. balthica* (station 65): Cu > Zn > Cd > Pb; *M. balthica* (station 7): Zn > Cu > Cd > Pb. The higher bioaccumulation factors of Cu (on the average, 44.9–70.7) and Zn (38.2–99.5) are calculated for *M. balthica* as compared with *D. polymorpha*, while Cd (30.6 ± 17.2) accumulates more intensively in *D. polymorpha*. Based on the BAFs values both species are macroconcentrators (BAF >2) of Cd, Cu and Zn and deconcentrators of Pb (BAF <1).

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ANNEX I

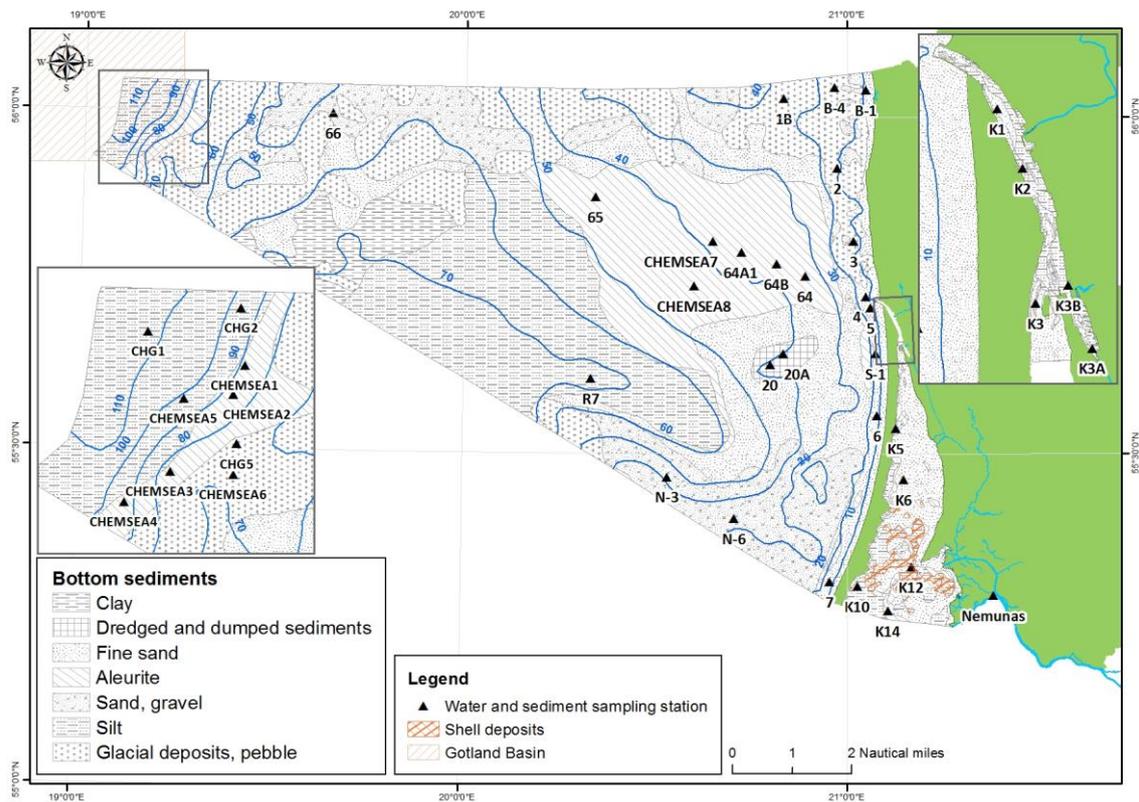


Fig. A1.1 Research stations and the bottom sediment types. The map was prepared based on the results of Gelumbauskaitė, 1998; Trimonis et al., 2003.

Table A1.1 Coordinates (decimal degrees) of the stations in the Curonian Lagoon and the Baltic Sea and variables used in this study.

Station	Latitude	Longitude	Measurements/analysis
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Nemunas	55.2912	21.3779	Complex I*, Chl- <i>a</i> , TSM, Complex II**, DIC
Curonian Lagoon			
K12	55.3333	21.1667	Complex I, Chl- <i>a</i> , TSM, Phytoplankton, particle size of sediment, Complex II, metals (Cu, Cd, Zn, Pb) in <i>D.polymorpha</i>
K14	55.2633	21.0783	Complex I, Chl- <i>a</i> , Phytoplankton, particle size of sediment, Complex II
K10	55.3050	21.0267	Complex I, Chl- <i>a</i> , TSM, particle size of sediment, Complex II
K6	55.4632	21.1474	Complex I, Chl- <i>a</i> , particle size of sediment, Complex II
K5	55.5300	21.1367	Complex I, Chl- <i>a</i> , TSM, Phytoplankton, particle size of sediment, Complex II, DIC
K3	55.6667	21.1333	Complex I, Chl- <i>a</i> , TSM, particle size of sediment, Complex II
K3A	55.6464	21.1617	Complex I, TSM, particle size of sediment, Complex II
K3B	55.6467	21.1633	Complex I, Chl- <i>a</i> , TSM, particle size of sediment, Complex II
K2	55.6851	21.1200	Complex I, Chl- <i>a</i> , Phytoplankton, particle size of sediment, Complex II
K1	55.7117	21.1117	Complex I*, Chl- <i>a</i> , TSM, particle size of sediment, Complex II**
Baltic Sea			
1B	56.0283	20.8333	Complex I, Chl- <i>a</i> , Phytoplankton, Complex II
B-1	56.0417	21.0500	Complex I, Chl- <i>a</i> , TSM, Phytoplankton, Complex II
B-4	56.0450	20.9667	Complex I, Chl- <i>a</i> , TSM, Phytoplankton, Complex II
2	55.9250	20.9750	Complex I, Chl- <i>a</i> , Phytoplankton
3	55.8167	21.0167	Complex I, Chl- <i>a</i> , Phytoplankton, Complex II
4	55.7350	21.0500	Complex I, Chl- <i>a</i> , Phytoplankton, Complex II, S, Fe
5	55.7183	21.0617	Complex I, Chl- <i>a</i> , TSM, Phytoplankton, Complex II, S, Fe
6	55.5583	21.0783	Complex I, Chl- <i>a</i> , Phytoplankton, Complex II
7	55.3117	20.9567	Complex I, Chl- <i>a</i> , Phytoplankton, Complex II, metals (Cu, Cd, Zn, Pb) in <i>M.balthica</i>
20	55.6333	20.8000	Complex I, Chl- <i>a</i> , TSM, Phytoplankton, Complex II
20A	55.6500	20.8333	Complex I, Chl- <i>a</i> , TSM, Phytoplankton, Complex II, S, Fe
S-1	55.6500	21.0750	Complex I, Chl- <i>a</i> , TSM, Phytoplankton, Complex II
N-6	55.4050	20.7067	Complex I, Chl- <i>a</i> , Phytoplankton, Complex II (without metals), S, Fe
N-3	55.4667	20.5333	Complex II (without metals), S, Fe
64	55.7650	20.8917	Complex I, Chl- <i>a</i> , Phytoplankton, Complex II (without metals), S, Fe
64B	55.7834	20.8162	Complex I
64A1	55.7999	20.7246	Complex I, Chl- <i>a</i> , Phytoplankton, Complex II
65	55.8817	20.3417	Complex II, S, Fe, metals (Cu, Cd, Zn, Pb) in <i>M.balthica</i>
66	56.0000	19.6500	Complex II, S, Fe
R7	55.7999	20.7246	Complex II
CHG1	56.0200	19.1467	Complex II, S, Fe
CHG2	56.0350	19.2433	Complex II, S, Fe
CHG5	55.9550	19.2417	Complex II, S, Fe
CHEMSEA1	56.0013	19.2484	Complex II, S, Fe
CHEMSEA2	55.9840	19.2374	Water temperature, salinity, oxygen, pH, Complex II, S, Fe
CHEMSEA3	55.9378	19.1733	Complex II, S, Fe
CHEMSEA4	55.9191	19.1259	Complex II, S, Fe
CHEMSEA5	55.9810	19.1855	Complex II, S, Fe
CHEMSEA6	55.9369	19.2394	Complex II, S, Fe
CHEMSEA7	55.8166	20.6500	Complex II, S, Fe
CHEMSEA8	55.7500	20.6000	Complex II, S, Fe

*Complex I (complex of variables of water layer: water temperature, salinity, pH, dissolved oxygen, DIN, POC, PN, $\delta^{13}\text{C}_{\text{POM}}$, $\delta^{15}\text{N}_{\text{POM}}$) – measurements during the period of 2012–2013;

**Complex II (complex of variables of bottom sediments: TOC, PN, $\delta^{13}\text{C}_{\text{SOM}}$, $\delta^{15}\text{N}_{\text{SOM}}$, metals – Pb, Cu, Cd, Ni, Cr, Zn, Al) – measurements during the period of 2011–2014 (metals) and 2012–2014 (C, N and their isotopic signatures); Other analysis: particle size of sediment analyzed in 2012; S and Fe – in 2013; research at the stations CHEMSEA1–8, CHG1, CHG2, CHG5 were conducted in 2013 and 2014, at R7 – in 2011 and 2013. Metals in molluscs investigated: *D.polymorpha* in 2006-2014; *M.balthica* at st. 7 in 2006, 2012-2014, at st. 65 in 2006-2010.

ANNEX II

Table A2.1 Freshwater organic matter (OM) proportion (%) \pm sd in the research sites of the Curonian Lagoon (K stations) and the Baltic Sea.

Station	Freshwater OM (%) in POM	Freshwater OM (%) in SOM
K6	90.6 \pm 11.5	96.8 \pm 1.2
K5	89.8 \pm 12.5	92.5 \pm 13.1
K3	84.8 \pm 16.7	98.2 \pm 1.3
K3A	90.9 \pm 11.2	-
K3B	91.5 \pm 9.4	89.0 \pm 6.3
K2	80.7 \pm 18.7	92.7 \pm 7.1
K1	82.4 \pm 17.6	91.6 \pm 13.5
4	75.9 \pm 17.2	73.6 \pm 15.8
5	83.2 \pm 15.2	79.0 \pm 4.3
3	63.7 \pm 21.9	-
2	60.0 \pm 34.4	-
1B	45.8 \pm 19.3	38.8 \pm 11.3
B-1	58.8 \pm 23.8	57.2 \pm 8.7
B-4	48.2 \pm 30.9	36.5 \pm 7.5
64	40.5 \pm 26.9	45.2 \pm 1.5
64A1	32.2 \pm 18.6	37.7 \pm 3.6
64B	31.7 \pm 8.9	-
20	50.4 \pm 19.7	51.7 \pm 9.0
20A	50.3 \pm 17.5	44.3 \pm 5.7
6	37.6 \pm 31.3	36.7 \pm 9.8
7	41.0 \pm 24.5	40.6 \pm 3.9
S-1	22.1 \pm 10.5	40.3 \pm 0.9
N-6	42.1 \pm 14.5	22.0 \pm 0.5
65	-	37.6 \pm 2.9
CHEMSEA1	-	34.9
CHEMSEA2	-	40.7 \pm 5.9
CHEMSEA3	-	46.7 \pm 11.4
CHEMSEA4	-	42.4
CHEMSEA5	-	40.9 \pm 3.9
CHEMSEA6	-	34.8 \pm 1.6
CHEMSEA7	-	41.8
CHEMSEA8	-	33.6
CHG1	-	45.1
CHG2	-	38.7 \pm 5.8
CHG5	-	35.7 \pm 0.5
R7	-	100

ANNEX III

Table A3.1 Pearson correlation matrix for the variables (n = 20–39) from the central part of the Curonian Lagoon.

	TSM	DIC	$\delta^{13}\text{C}_{\text{DIC}}$	pH	Chl- <i>a</i>	$\delta^{13}\text{C}$	POC	POC/ Chl- <i>a</i>	$\delta^{15}\text{N}$	C/N	DIN	S	T	Cyano	Diatoms
TSM															
DIC	-0.62 ^a														
$\delta^{13}\text{C}_{\text{DIC}}$	0.66 ^a	-0.98 ^b													
pH	0.76 ^a	-0.74 ^b	0.71 ^b												
Chl-<i>a</i>	0.77 ^b	-0.86 ^b	0.91 ^b	0.77 ^b											
$\delta^{13}\text{C}$	-	-	-	-	0.35 ^a										
POC	0.84 ^b	-0.64 ^b	-0.65 ^b	0.63 ^a	0.80 ^b	0.39 ^a									
POC/Chl-<i>a</i>	-	0.58 ^a	-0.59 ^a	-	-0.42 ^a	-	-								
$\delta^{15}\text{N}$	-0.48 ^a	0.53 ^a	-0.65 ^b	-	-0.55 ^b	-	-0.33 ^a	-							
C/N	-	0.69 ^b	-0.63 ^b	-	-0.44 ^b	-	-0.35 ^a	-	-						
DIN	-0.48 ^a	0.90 ^b	-0.72 ^b	-	-0.51 ^b	-	-0.53 ^b	-	-	0.63 ^b					
S	-	-0.57 ^a	0.51 ^a	-	-	-	-	-	-	-	-				
T	0.51 ^a	-0.79 ^b	0.78 ^b	-	0.51 ^b	-	0.38 ^a	-	-0.55 ^a	-0.65 ^b	-0.63 ^b	-			
Cyano	0.82 ^b	-0.82 ^b	0.85 ^b	0.81 ^a	0.80 ^b	0.56 ^a	0.62 ^a	-	-0.76 ^b	-	-0.54 ^a	-	0.69 ^b		
Diatoms	-	-0.79 ^b	0.79 ^b	0.96 ^b	0.76 ^b	-	0.53 ^a	-0.67 ^b	-0.59 ^a	-	-0.51 ^a	-	0.51 ^a	0.61 ^b	
Discharge	-	0.62 ^b	-0.65 ^b	-	-0.50 ^b	-	-	0.51 ^b	0.64 ^b	-	0.62 ^b	-	-0.66 ^b	-0.58 ^b	-

^a $p < 0.05$, ^b $p < 0.001$, (-) – not significant. S – salinity, T – water temperature, Cyano – cyanobacteria, Discharge – discharge of the Nemunas River.

Table A3.2 Pearson correlation matrix for the variables (n = 20–73) from the northern part of the Curonian Lagoon.

	TSM	DIC	$\delta^{13}\text{C}_{\text{DIC}}$	pH	Chl- <i>a</i>	$\delta^{13}\text{C}$	POC	POC/ Chl- <i>a</i>	$\delta^{15}\text{N}$	C/N	DIN	S	T	Cyano	Diatoms
TSM															
DIC	-														
$\delta^{13}\text{C}_{\text{DIC}}$	-	-0.68 ^a													
pH	-	-0.87 ^b	-												
Chl-<i>a</i>	0.32 ^a	-0.68 ^a	-	0.70 ^b											
$\delta^{13}\text{C}$	-	-	-	-	-										
POC	0.41 ^b	-0.77 ^b	-	0.79 ^b	0.77 ^b	-									
POC/Chl-<i>a</i>	-	0.57 ^a	-	-	-0.41 ^b	-	-								
$\delta^{15}\text{N}$	-	-	-	-	-	-0.54 ^b	0.36 ^b	-							
C/N	-	0.80 ^b	-	-0.63 ^a	-0.44 ^b	-	-0.27 ^a	0.55 ^b	-						
DIN	-0.31 ^a	0.89 ^b	-	-0.64 ^a	-0.31 ^b	-0.45 ^b	-	0.57 ^b	0.30 ^a	0.53 ^b					
S	-	-	-	-	-	0.80 ^b	-0.42 ^b	-	-0.74 ^b	-	0.57 ^b				
T	-	-0.93 ^b	-	0.79 ^b	0.42 ^a	0.43 ^b	-	-0.48 ^b	-0.48 ^b	-0.69 ^b	-0.84 ^b	0.48 ^b			
Cyano	-	-	-	0.72 ^a	0.84 ^b	-	0.74 ^b	-	-	-	-	-	-	-	-
Diatoms	-	-	-	-	-	-	-	-	-	-	-	-0.51 ^a	-	-	-
Discharge	-	-	-	-	-	-0.47 ^b	-	-	0.39 ^b	0.43 ^b	0.37 ^b	-0.28 ^a	-0.64 ^b	-	-

^a $p < 0.05$, ^b $p < 0.001$. (-) – not significant. S – salinity, T – water temperature, Cyano – cyanobacteria.

Table A3.3 Pearson correlation matrix for the variables (n = 20–50) from the Baltic Sea.

	TSM	Chl-<i>a</i>	δ¹³C	POC	POC/ Chl-<i>a</i>	δ¹⁵N	C/N	DIN	S	Cyano	Diatoms
TSM											
Chl-<i>a</i>	0.40a										
δ¹³C	-	0.38 ^a									
POC	0.50 ^a	0.58 ^b	-								
POC/Chl-<i>a</i>	-	-0.51 ^b	-0.37 ^a	-							
δ¹⁵N	-	-	-0.32 ^a	-	-						
C/N	-	-	-0.46 ^b	-0.29 ^a	-	-0.48 ^b					
DIN	-	-	-0.41 ^b	-	-	-	0.34 ^a				
S	-	-0.31 ^a	0.38 ^a	-0.38 ^b	-	-	-	-0.52 ^b			
Cyano	-	-	-	-	-	-	-	-	-0.65 ^b		
Diatoms	0.58 ^a	0.45 ^b	-	-	-	-	-	-	-	-	
Dino	-	-	-0.48 ^b	-	0.35 ^a	0.53 ^b	0.55 ^b	-	-	0.33 ^a	-

^a*p*<0.05, ^b*p*<0.001. (-) – not significant. S – salinity, Cyano – cyanobacteria, Dino – dinoflagellates.

ANNEX IV

Table A4.1 I_{geo} of trace metals in selected sediments from the SE Baltic Sea.

In Bold - the values >0 ; the underlined values – calculations based on the GGI's data (total leaching method); n.d. – not determined.

Stations	Pb	Cu	Cd	Ni	Cr	Zn
Nemunas	-4.1/ <u>-2.3</u>	-6.6/ <u>-5.6</u>	-4.1/ <u>-3.2</u>	-6.5/ <u>-4.5</u>	-5.6/ <u>-6.1</u>	-3.9/ <u>-4.3</u>
K12	-2.2	-4.3	-1.9	-4.8	-3.8	-2.5
K14	-2.6	-4.6	-1.8	-4.6	-4.1	-2.6
K10	-0.9	-2.4	0.4	-2.7	-2.3	-1.2
K6	-3.5	-5.1	-1.7	-5.1	-4.8	-4.8
K5	-3.3	-5.1	-2.3	-4.6	-4.2	-3.6
K3	-4.1	-4.3	-4.1	-4.8	-5.3	-4.2
K3A	-2.1	-0.9	-2.2	-3.6	-2.0	-1.9
K3B	-2.0	-1.5	-1.5	-3.2	-3.0	-1.4
K2	-2.7	-3.8	-2.3	-3.8	-3.7	-3.1
K1	-1.5	-2.7	-0.8	-2.7	-2.5	-1.6
4	-2.9/ <u>-2.5</u>	-4.6/ <u>-3.3</u>	-2.4/ <u>-2.2</u>	-4.6/ <u>-5.6</u>	-3.7/ <u>-5.9</u>	-2.9/ <u>-3.3</u>
5	-3.2/ <u>-3.2</u>	-5.1/ <u>-4.6</u>	-3.2/ <u>-1.2</u>	-5.1/ <u>-6.6</u>	-3.7/ <u>-1.2</u>	-3.6/ <u>-2.9</u>
B-1	-2.5	-5.6	-3.2	-5.6	-4.1	-3.5
B-4	-3.1	-6.6	-4.6	-5.9	-5.6	-4.1
1B	-4.1	-7.2	-4.7	-5.7	-5.6	-4.1
6	-3.1/ <u>-1.8</u>	-7.2/ <u>-5.4</u>	-4.5/ <u>-2.2</u>	-5.6/-6.6	-3.5/ <u>-2.9</u>	-3.6/ <u>-3.5</u>
7	-3.1/ <u>-1.6</u>	-7.2/ <u>-5.1</u>	-3.3/ <u>-2.2</u>	-5.6/ <u>-6.1</u>	-3.5/ <u>-2.6</u>	-3.6/ <u>-3.2</u>
20	-2.6	-3.5	3.2	-3.6	-3.3	-2.5
20A	-2.2/ <u>-1.9</u>	5.1/ <u>-4.1</u>	-3.6/ <u>-2.2</u>	-5.1/ <u>-4.9</u>	-4.6/ <u>-3.6</u>	-3.2/ <u>-3.3</u>
64A1	-2.8	-5.6	-2.7	-4.8	-4.1	-3.1
65	-2.2/ <u>-1.0</u>	-5.6/ <u>-3.7</u>	-2.3/ <u>-0.5</u>	-4.1/ <u>-4.4</u>	-3.1/ <u>-2.6</u>	-2.8/ <u>-2.4</u>
66	-3.2/ <u>-2.2</u>	-6.1/ <u>-5.6</u>	-4.1/ <u>n.d.</u>	-5.3/ <u>n.d.</u>	-4.6/ <u>-4.5</u>	-4.1/ <u>-4.3</u>
CHEMSEA2	-0.2/ <u>-0.5</u>	-2.2/ <u>-2.5</u>	0.3	-2.8	-2.5/ <u>-1.7</u>	-1.1/ <u>-1.4</u>
CHG1	n.d./ 0.6	n.d./ <u>-0.4</u>	n.d./ 2.3	n.d./ <u>-1.5</u>	n.d./ <u>-0.8</u>	n.d./ 0.1
R7	n.d./ 0.8	n.d./ <u>-0.9</u>	n.d./ 0.2	n.d./-1.4	n.d./ <u>-0.9</u>	n.d./ <u>-0.1</u>

$I_{geo} < 0$, uncontaminated;

$0 \leq I_{geo} < 1$, uncontaminated to moderately contaminated;

$1 \leq I_{geo} < 2$, moderately contaminated;

$2 \leq I_{geo} < 3$, moderately to heavily contaminated;

$3 \leq I_{geo} < 4$, heavily contaminated;

$4 \leq I_{geo} < 5$, heavily to extremely contaminated;

$5 \geq I_{geo}$, extremely contaminated (Müller, 1979).

Table A4.2 The contamination factor (CF) and degree of contamination (C_d) for investigated trace metals in sediments from the SE Baltic Sea.

In Bold - the values >1 ; the underlined values – calculations based on the GGI's data; n.d. – not determined.

Stations	CF						C_d
	Pb	Cu	Cd	Ni	Cr	Zn	
Nemunas	0.02/ <u>0.30</u>	0.02/ <u>0.03</u>	0.09/ <u>0.17</u>	0.02/ <u>0.01</u>	0.02/ <u>0.02</u>	0.09/ <u>0.07</u>	0.26/ <u>0.59</u>
K12	0.34	0.07	0.39	0.05	0.11	0.27	1.23
K14	0.24	0.05	0.43	0.06	0.10	0.25	1.12
K10	0.82	0.28	1.99	0.23	0.30	0.66	4.29
K6	0.13	0.05	0.36	0.04	0.06	0.05	0.68
K5	0.15	0.05	0.29	0.06	0.09	0.12	0.76
K3	0.09	0.08	0.09	0.03	0.04	0.08	0.41
K3A	0.35	0.77	0.32	0.12	0.38	0.41	2.35
K3B	0.37	0.53	0.53	0.17	0.19	0.59	2.37
K2	0.22	0.10	0.30	0.11	0.12	0.18	1.04
K1	0.52	0.23	0.84	0.23	0.28	0.50	2.59
4	0.19/ <u>0.35</u>	0.6/ <u>0.07</u>	0.28/ <u>0.33</u>	0.07/ <u>0.03</u>	0.11/ <u>0.25</u>	0.19/ <u>0.15</u>	0.90/ <u>1.18</u>
5	0.16/ <u>0.38</u>	0.05/ <u>0.06</u>	0.17/ <u>0.67</u>	0.04/ <u>0.04</u>	0.12/ <u>0.64</u>	0.12/ <u>0.19</u>	0.67/ <u>1.98</u>
B-1	0.27	0.02	0.16	0.04	0.09	0.13	0.71
B-4	0.18	0.02	0.07	0.03	0.03	0.09	0.42
1B	0.10	0.01	0.06	0.03	0.03	0.09	0.32
6	0.19/ <u>0.41</u>	0.01/ <u>0.04</u>	0.07/ <u>0.33</u>	0.03/ <u>0.02</u>	0.13/ <u>0.20</u>	0.11/ <u>0.14</u>	0.54/ <u>1.14</u>
7	0.19/ <u>0.49</u>	0.01/ <u>0.05</u>	0.15/ <u>0.33</u>	0.04/ <u>0.02</u>	0.13/ <u>0.25</u>	0.12/ <u>0.17</u>	0.64/ <u>1.31</u>
20	0.26	0.13	0.17	0.12	0.15	0.27	1.11
20A	0.33/ <u>0.39</u>	0.04/ <u>0.09</u>	0.13/ <u>0.33</u>	0.05/ <u>0.05</u>	0.06/ <u>0.12</u>	0.16/ <u>0.16</u>	0.77/ <u>1.14</u>
64A1	0.22	0.04	0.23	0.05	0.09	0.18	0.81
65	0.33/ <u>0.69</u>	0.04/ <u>0.12</u>	0.30/ <u>0.99</u>	0.09/ <u>0.07</u>	0.18/ <u>0.25</u>	0.21/ <u>0.29</u>	1.15/ <u>2.41</u>
66	0.16/ <u>0.34</u>	0.02/ <u>0.04</u>	0.09/ <u>0.02</u>	0.04/ <u>0.01</u>	0.06/ <u>0.07</u>	0.09/ <u>0.07</u>	0.46/ <u>0.51</u>
CHEMSEA2	1.33/<u>1.05</u>	0.33/ <u>0.38</u>	1.90/n.d.	0.22/ n.d.	0.27/ <u>0.45</u>	0.65/ <u>0.55</u>	4.80/ <u>2.43</u>
CHG1	n.d./ <u>2.32</u>	n.d./ <u>1.16</u>	n.d./ <u>7.33</u>	n.d./ <u>0.54</u>	n.d./ <u>0.84</u>	n.d./ <u>1.65</u>	n.d./ <u>13.84</u>
R7	n.d./ <u>2.50</u>	n.d./ <u>0.76</u>	n.d./ <u>1.67</u>	n.d./ <u>0.58</u>	n.d./ <u>0.80</u>	n.d./ <u>1.45</u>	n.d./ <u>7.75</u>

CF <1 , no/low contamination; $1 \leq CF < 3$, moderate; $3 \leq CF < 6$, considerable; $6 \leq CF$ – very high (Håkanson, 1980; Bonnail et al., 2016).

$C_d < 5$, low contamination; $5 \leq C_d < 10$, moderate; $10 \leq C_d < 20$, considerable; $20 \leq C_d$ – very high (Bonnail et al., 2016)

Table A4.3 The potential ecological risk factor (E_r^i) and index (RI) for the investigated trace metals in sediments from the SE Baltic Sea.

In Bold - the values ≥ 40 (for E_r^i) and ≥ 95 (for RI); the underlined values – calculations based on the GGI's data; n.d. – not determined.

Stations	E_r^i						RI
	Pb	Cu	Cd	Ni	Cr	Zn	
Nemunas	0.1/ <u>1.4</u>	0.1/ <u>6.0</u>	2.7/ <u>5.0</u>	0.1/ <u>0.1</u>	0.1/ <u>0.1</u>	0.1/ <u>0.1</u>	3/ <u>13</u>
K12	1.7	15.2	11.7	0.3	0.2	0.3	29
K14	1.2	12.1	12.8	0.3	0.2	0.3	27
K10	4.1	63.3	59.8	1.2	0.6	0.7	130
K6	0.6	10.5	10.7	0.2	0.1	0.1	22
K5	0.7	11.1	8.8	0.3	0.2	0.1	21
K3	0.4	17.7	2.8	0.2	0.1	0.1	21
K3A	1.8	173.3	9.7	0.6	0.8	0.4	187
K3B	1.9	118.7	15.9	0.8	0.4	0.6	138
K2	1.1	22.7	9.1	0.5	0.2	0.2	34
K1	2.6	52.1	25.1	1.2	0.6	0.5	82
4	0.9/ <u>1.7</u>	14.6	8.3	0.3	0.2	0.2	25/ <u>29</u>
5	0.8	11.2	5.0	0.2	0.2	0.1	18/ <u>38</u>
B-1	1.3	5.2	4.7	0.2	0.2	0.1	12
B-4	0.9	4.6	2.0	0.1	0.1	0.1	8
1B	0.5	2.3	1.7	0.2	0.1	0.1	5
6	0.9	2.1	2.0	0.2	0.3	0.1	6/ <u>21</u>
7	1.0	2.4	4.4	0.2	0.3	0.1	8/ <u>25</u>
20	1.3	29.9	5.0	0.6	0.3	0.3	37
20A	1.7	9.5	3.8	0.3	0.1	0.2	16/ <u>33</u>
64A1	1.1	8.1	6.9	0.3	0.2	0.2	17
65	1.7	9.3	9.1	0.4	0.4	0.2	21/ <u>61</u>
66	0.8	5.2	2.6	0.2	0.1	0.1	9/ <u>10</u>
CHEM SEA2	6.6/ <u>6.3</u>	75.0/<u>86.6</u>	57.0/n.d.	1.1/ <u>n.d.</u>	0.5/ <u>0.9</u>	0.7/ <u>0.6</u>	140/97
CHG1	n.d./ <u>11.6</u>	n.d./ <u>261.5</u>	n.d./ <u>220</u>	n.d./ <u>2.7</u>	n.d./ <u>1.7</u>	n.d./ <u>1.7</u>	<u>499</u>
R7	n.d./ <u>12.5</u>	n.d./ <u>171</u>	n.d./ <u>50</u>	n.d./ <u>2.9</u>	n.d./ <u>1.6</u>	n.d./ <u>1.4</u>	<u>239</u>

$E_r^i < 40$ – Low; $40 \leq E_r^i < 80$ – Moderate; $80 \leq E_r^i < 160$ – Considerable; $160 \leq E_r^i < 320$ – Great; $320 \leq E_r^i$ – Very great.

RI < 95 – low ecological risk for all factors; $95 \leq \text{RI} < 190$ – moderate; $190 \leq \text{RI} < 380$ – considerable, $380 \leq \text{RI}$ – very high (Maanan et al., 2015).

Table A4.4 The sediment contamination with lead (Pb) at the stations K10, K3A, K3B, K1, CHEMSEA2, CHG1 and R7.

Stations	EF	Assessment	I_{geo}	Assessment	CF	Assessment	E^i_r	Assessment
K10	-	-	<0	Uncont.	0.82	low contamination	4.1	low risk
K3A	-	-	<0	Uncont.	0.35	low contamination	1.8	low risk
K3B	-	-	<0	Uncont.	0.37	low contamination	1.9	low risk
K1	-	-	<0	Uncont.	0.52	low contamination	2.6	low risk
CHEMSEA2	2.3	minor enrichment	<0	Uncont.	1.05 - 1.33	moderate contamination	6.3-6.6	low risk
CHG1	3.1	moderate enrichment	0.6	Uncont. to moder. contam.	2.32	moderate contamination	11.6	low risk
R7	3.1	moderate enrichment	0.8	Uncont. to moder. contam.	2.50	moderate contamination	12.5	low risk

Uncont. – uncontaminated; Uncont. to moder. contam. – uncontaminated to medarately contaminated.

Table A4.5 The sediment contamination with copper (Cu) at the stations K10, K3A, K3B, K1, CHEMSEA2, CHG1 and R7.

Stations	EF	Assessment	I_{geo}	Assessment	CF	Assessment	E^i_r	Assessment
K10	-	-	<0	Uncont.	0.28	low contam.	63.3	moderate risk
K3A	-	-	<0	Uncont.	0.77	low contam.	173.3	great risk
K3B	-	-	<0	Uncont.	0.53	low contam.	118.7	considerable risk
K1	-	-	<0	Uncont.	0.23	low contam.	52.1	moderate risk
CHEMSEA2	0.8	no enrichment	<0	Uncont.	0.33 - 0.38	low contam.	75.0-86.6	moderate risk
CHG1	1.6	minor enrichment	<0	Uncont.	1.16	moderate contam.	261.5	great risk
R7	0.9	no enrichment	<0	Uncont.	0.76	low contam.	171.0	great risk

Uncont. – uncontaminated; low contam. – low contamination

Table A4.6 The sediment contamination with cadmium (Cd) at the stations K10, K3A, K3B, K1, CHEMSEA2, CHG1 and R7.

Stations	EF	Assessment	I_{geo}	Assessment	CF	Assessment	E^i_r	Assessment
K10	-	-	0.41	Uncont. to moderately contaminated	1.99	moderate contam.	59.8	moderate risk
K3A	-	-	<0	Uncont.	0.32	low contam.	9.7	low risk
K3B	-	-	<0	Uncont.	0.53	low contam.	15.9	low risk
K1	-	-	<0	Uncont.	0.84	low contam.	25.1	low risk
CHEM SEA2	-	-	0.34	Uncont. to moderately contaminated	1.90	moderate contam	57.0	moderate risk
CHG1	9.9	moderately severe enrichment	2.30	Moderately to heavily contaminated	7.33	very high contam.	220.0	great risk
R7	2.2	minor enrichment	0.20	Uncont. to moderately contaminated	1.67	moderate contam.	50.0	moderate risk

Uncont. – uncontaminated; Uncont. to moderately contaminated - uncontaminated to moderately contaminated; contam. – contamination.

Table A4.7 The sediment contamination with nickel (Ni) at the stations K10, K3A, K3B, K1, CHEMSEA2, CHG1 and R7.

Stations	EF	Assessment	I_{geo}	Assessment	CF	Assessment	E^i_r	Assessment
K10	-	-	<0	Uncont.	0.23	low contam.	1.2	low risk
K3A	-	-	<0	Uncont.	0.12	low contam.	0.6	low risk
K3B	-	-	<0	Uncont.	0.17	low contam.	0.8	low risk
K1	-	-	<0	Uncont.	0.23	low contam.	1.2	low risk
CHEM SEA2	-	-	<0	Uncont.	0.22	low contam.	1.1	low risk
CHG1	0.7	no enrichment	<0	Uncont.	0.54	low contam.	2.7	low risk
R7	0.7	no enrichment	<0	Uncont.	0.58	low contam.	2.9	low risk

Uncont. – uncontaminated; contam. – contamination.

Table A4.8 The sediment contamination with chromium (Cr) at the stations K10, K3A, K3B, K1, CHEMSEA2, CHG1 and R7.

Stations	EF	Assessment	I_{geo}	Assessment	CF	Assessment	E_r^i	Assessment
K10	-	-	<0	uncontaminated	0.3	low contamination	0.6	low risk
K3A	-	-	<0	uncontaminated	0.4	low contamination	0.8	low risk
K3B	-	-	<0	uncontaminated	0.2	low contamination	0.4	low risk
K1	-	-	<0	uncontaminated	0.3	low contamination	0.6	low risk
CHEMSEA2	1.0	minor enrichment	<0	uncontaminated	0.3	low contamination	0.5	low risk
CHG1	1.2	minor enrichment	<0	uncontaminated	0.8	low contamination	1.7	low risk
R7	1.1	minor enrichment	<0	uncontaminated	0.8	low contamination	1.6	low risk

Table A4.9 The sediment contamination with zinc (Zn) at the stations K10, K3A, K3B, K1, CHEMSEA2, CHG1 and R7.

Stations	EF	Assessment	I_{geo}	Assessment	CF	Assessment	E_r^i	Assessment
K10	-	-	<0	uncontaminated	0.7	low contamination	0.7	low risk
K3A	-	-	<0	uncontaminated	0.4	low contamination	0.4	low risk
K3B	-	-	<0	uncontaminated	0.6	low contamination	0.6	low risk
K1	-	-	<0	uncontaminated	0.5	low contamination	0.5	low risk
CHEMSEA2	1.2	minor enrichment	<0	uncontaminated	0.6-0.7	low contamination	0.6-0.7	low risk
CHG1	2.2	minor enrichment	<0	uncontaminated	1.7	moderate contamination	1.7	low risk
R7	1.8	minor enrichment	<0	uncontaminated	1.5	moderate contamination	1.5	low risk

