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Baseline

Total, methyl and organic mercury in sediments of the Southern Baltic Sea

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ABSTRACT

Distribution of sedimentary mercury in the Southern Baltic was investigated. Sediment samples were collected from the Southern Baltic in the period from 2009 to 2011, and concentrations of sedimentary total mercury (average 102 ng/g, range 5.8–225 ng/g) and methyl mercury (average 261 pg/g, range 61–940 pg/g) were measured in the manner that the influence of both patchiness and seasonal changes were assessed. Moreover, sedimentary mercury extracted with organic solvent- the so-called organic mercury was also analyzed (average 425 pg/g, range 100–1440 pg/g). There is a statistically significant dependence between organic mercury and both methyl mercury and total mercury concentrations in the sediments. Methyl mercury contribution to total mercury varied from 0.12% to 1.05%, while organic mercury contributed to 2% of total concentration on average. The area studied, although mercury concentrations exceed threefold the geochemical background, can be regarded as moderately contaminated with mercury, and methylmercury.

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Mercury has been a subject of environmental chemistry interest for several decades (Pacyna et al., 2006). Although all chemical forms of mercury are toxic, public health concerns are focused on methylmercury (MeHg).

Nowadays loads of mercury discharged to the environment from anthropogenic sources exceed several times these from natural ones (Pacyna et al., 2006). Much of the mercury originating from both anthropogenic and natural sources is, eventually, brought to the marine environment. There, owing to its affinity to particulate matter, mercury is readily scavenged from the water column (Laurier et al., 2003) and deposited to bottom sediments (Cossa and Gobeil, 2000) in particular in estuaries and coastal areas (Boening, 2000).

Distribution of mercury in marine sediments is influenced by physical transport, sediment texture, mineralogical composition, reduction/oxidation status of sediments, adsorption and desorption processes and organic matter content (Boening, 2000; French et al., 1999). Red-ox conditions are of particular interest as, in the reducing environment, mercury is readily transferred into organo-mercurial species (e.g. methylmercury-MeHg) that are both mobile and highly bioavailable. Thus, under specific conditions a fraction of mercury deposited to sediments re-enters the

overlying water and constitutes threat to living organisms. As a result, sediments can act as both sink and source for mercury in aquatic environment (Zoumis et al., 2001).

The Baltic Sea is a land locked basin surrounded by highly industrialized catchment area. Mercury concentrations in the surface Baltic sediments exceed the geochemical background by a factor of three to five (Bełdowski and Pempkowiak, 2009). According to the recent pollution load compilation (HELCOM, 2011) the input of mercury to the Baltic Sea had efficiently decreased within the previous two decades. Despite this, no corresponding decrease is observed in biota mercury concentrations (Saniewska et al., 2014). One of possible reasons is the re-emission of the previously accumulated mercury from sediments, in particular within sedimentation basins, due to anoxic conditions prevailing there (Bełdowski et al., 2009).

Mercury in the Baltic sediments has been a subject of investigations for several decades (Saniewska et al., 2010; Bełdowski and Pempkowiak, 2009; Bełdowski and Pempkowiak, 2007; Borg and Jonsson, 1996; Kannan and Falandysz, 1998; Pempkowiak, 1991; Pempkowiak et al., 1998). Concentration of the metal is well characterized (Bełdowski and Pempkowiak, 2007; Borg and Jonsson, 1996), as is the mechanism of mercury transport to the depositional basins of the sea (Bełdowski and Pempkowiak, 2007). However, MeHg in the Baltic sediments have been seldom studied. So far just one report indicated the presence of MeHg in the Baltic

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Sediments (Kannan and Falandysz, 1998). The authors of the report measured substantial contribution of MeHg to total mercury basing on several results of methyl mercury in the Baltic sediments. Thus little is known regarding both contemporary concentrations of MeHg in the sediments and factors affecting the concentrations. This, at least partly, may be caused by relatively extensive analytical procedure required to quantify sedimentary MeHg (Liang et al., 1994). Recently the so called organic mercury was suggested as a mercury fraction closely related to MeHg in fresh-water sediments (Boszke and Kowalski, 2008). The authors used methylene chloride to separate organic mercury from sediments. Other organic solvents were also used for the purpose: toluene (Miller et al., 1995), and chloroform (Eguchi and Tomiyasu, 2002; Tomiyasu et al., 2000). There are no reports regarding the usefulness of organic mercury as a substitute for MeHg in studies of marine sediments contamination.

The aim of this study was to investigate concentrations of total mercury, and selected mercury fractions: total organic mercury and methylmercury in sediments of the Southern Baltic Sea and to compare the results with concentrations measured in other marine coastal areas. As sampling stations characterized by varying red-ox conditions, sediment texture and organic matter content were collected in close proximity to one another, factors affecting sedimentary mercury concentration and speciation were assessed too, as were relations between the measured mercury fractions.

The Baltic Sea is a semi-enclosed water body surrounded by highly industrialized countries. Two main features characterize hydrology of the sea. Firstly, the surface water is brackish as a result of a large riverine input and the limited exchange of water with the North Sea. Secondly, there is a permanent halocline at a depth of about 70 m. The sub-halocline waters in the central basins are depleted of dissolved oxygen or even anoxic. Geochemical cycles in the Baltic have been strongly influenced by human activities since the beginning of the 20th century (Borg and Jonsson, 1996; Pempkowiak, 1991). Much of the anthropogenic load is carried to the Baltic Sea with the river runoff. Subsurface groundwater discharge plays substantial role in case of nutrients and organic matter, and a minor role in the case of mercury (Szymczycha et al., 2013). The major rivers entering the Baltic can be divided into two broad categories: those separated from the sea by a lagoon, and those entering the sea directly. The lagoons act as traps for suspended and dissolved riverine loads (Borg and Jonsson, 1996; Pempkowiak et al., 2000). Samples for this study have been collected from the Southern and central Baltic. This area is, on average, quite shallow – mean depth being 50 m (Voipo, 1981). Southern and central Baltic consists of series of deep basins separated by sills. Sedimentation regime in deep basins (>80 m) may be considered as stable (Zaborska et al., 2014). In the intermediate areas (>50 m) accumulation type of bed prevails, whereas in shallower regions erosion or no-accumulation bottoms predominate (Feistel et al., 2008; Voipo, 1981). Sediments consist of silt and mud in the Gdańsk Deep, the Bornholm Deep and the Gotland Deep-clay in the Słupsk Channel, and sand with occasional silt deposits in the Bay of Gdańsk, the Słupsk Sill and the Pomeranian Bay (Feistel et al., 2008). For this study, three sedimentation basins of the Southern Baltic were sampled – Bornholm, Gdańsk and Gotland Deeps, and two shallow areas adjacent to river mouths – the Gdańsk Bay, close to the Vistula mouth and the Pomeranian Bay, close to the Odra mouth during cruise on the R/V Oceania in Spring 2009 and 2010 from the Gdansk Deep, the Gotland Deep, the Pomeranian Bay and the Gdańsk Bay and in Autumn 2009 from the Gdańsk Deep and the Gotland Deep. Location of the sampling stations is shown in Fig. 1.

Samples were collected with a gravity corer. The top three centimeters of stratified sediments were sampled by cutting it away

with a plastic spatula, mixed, transferred into polyethylene bags and stored frozen (-20°C) until analyses in laboratory.

Before mercury analysis all the samples were homogenized under laminar flow hood and aliquots were taken for determinations of moisture, organic carbon and fine grain fraction contents. Moisture was used to calculate dry mass of sample, and all results are reported as mass per dry weight. Fine grained fraction (<0.067 mm) content was determined by sieving. Organic carbon content in sediments was determined after removal of carbonates (2 M HCl) using an Elemental Analyzer Flash EA 1112 Series combined with the Isotopic Ratio Mass Spectrometer IRMS Delta V Advantage (Thermo Electron Corp., Germany) and presented as percentage in the bulk of the dry sample. Quality control was carried out with standard materials supplied by the Thermo Electron Corp. The methodology used proved satisfactory accuracy and precision (average recovery $99.1 \pm 2.0\%$).

Total mercury determination was performed via sample (500 mg) pyrolysis in a stream of oxygen (Leco AMA 254, Czech Republic). The AMA254 technique of direct combustion features a combustion/catalyst tube where sediment decomposes in an oxygen-rich environment and removes interfering elements. Both recovery and precision given as Relative Standard Deviation proved satisfactory ($97\% \pm 3\%$ RSD) basing on a reference material analysis (NIST 2584).

Extractable fraction of mercury (organic mercury) was determined according to procedure described for river sediments (Boszke et al., 2007). In short, a sediment sample (5.0 g) was twice extracted with chloroform, reextracted by aqueous sodium thio-sulphate solution (0.01 M; 10 mL). From the aqueous layer an aliquot of 5 mL was collected, placed in a measuring flask (50 mL) and treated with $20\ \mu\text{L}$ 65% HNO_3 , 7.5 mL 33% HCl and 5 mL of a 1:1 solution of 0.0033 M KBrO_3 and 0.2 M KBr to oxidize all mercury species to Hg (II). Resulting solutions were analyzed by means of atomic fluorescence spectrophotometry on automated Tekran 2600 (Canada) apparatus, according to EPA 1631 method (EPA, 2002).

Methylmercury has been determined in the Josef Stefan Institute laboratories in Ljubljana (Slovenia), using the procedure developed by Liang et al. (1994) and used successfully by others (Logar et al., 2002; Quevauviller et al., 1998). Methylmercury defined by this procedure includes all monomethyl mercury species found in sediments (e.g. CH_3Hg^+ , CH_3HgCl , CH_3HgOH , and $\text{CH}_3\text{-HgS-R}$), which are amenable to complexation and extraction as CH_3HgBr . In short, 300 mg sample of wet sediment was sequentially eluted with 2.5 ml of 1.5 M HBr solution and 1 ml of 1 M CuSO_4 . Then MeHg was extracted into methylene chloride. 20 ml of deionized water were added, and the organic fraction was evaporated after dilution to a known volume with reagent water, further analysis was carried out by aqueous phase ethylation, and then analyzed using the GC/pyrolysis/CVAFS technique in a Brooks and Rand Model 1 Detector equipped with a gas chromatography column and a high temperature (300°C) desorption unit. All samples were analyzed in triplicate, and blank samples were run for every six samples. Recovery and precision of measurements were assessed by the use of certified reference material (NIST 2584 for total mercury and BCR 580 for organic/methyl mercury). Those were equal to 98% and 3% RSD, for total mercury, while for HgOrg and MeHg RSDs did not exceed 7.4% while recovery equaled 91%.

The common problem with mercury analysis in marine sediments is the random component, associated with the so called “patchiness” – mosaic properties of sediments, which vary, even on a very local scale. The Baltic sediments were reported to be characterized with substantial patchiness (Zaborska et al., 2014; Zalewska and Suplinska, 2013; Winterhalter, 2001), which may cause the measured concentration of mercury to be non-representative for a given area, if it is based on a single sample analyses.

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