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Mercury concentration variability in the zooplankton of the southern Baltic coastal zone

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ABSTRACT

Being a toxic element, mercury is introduced to the human organism through the consumption of fish and seafood, which in turn often feed on zooplankton. The bioaccumulation of Hg by zooplankton is an important factor influencing the magnitude of the mercury load introduced with food into the predator organism. Therefore the present article attempts to identify the processes and factors influencing Hg concentration in the zooplankton of the coastal zone, an area where marine organisms – an attractive food source for humans – thrive. This is particularly important in areas where climate changes influence the species composition and quantity of plankton. The studies were carried out on three test sites in the coastal zone of the southern Baltic Sea in the period from December 2011 to May 2013. The obtained results show that the shorting of the winter season is conducive to Hg increase in zooplankton and, consequently, in the trophic chain. High mercury concentrations were measured in genus *Synchaeta* and *Keratella* when *Mesodinium rubrum* were predominant in phytoplankton, while other sources of this metal in the plankton fauna were epilithon, epiphton and microbenthos. This is of particular importance when it comes to sheltered bays and estuaries with low water dynamics.

1. Introduction

The toxicity of mercury is widely documented (WHO, 1976; Ebinghaus et al., 1999; Langford and Ferner, 1999; O'Shea, 1999; Bose-O'Reilly et al., 2010). Its properties: nephrotoxicity, immunotoxicity, neurotoxicity and mutagenicity, mean that even the smallest concentrations of Hg introduced to the human body are harmful. The main route of Hg absorbtion is the consumption of fish and seafood, which is why the marine environment is so closely examined by researchers with respect to mercury concentration and its accumulation by organisms which inhabit the sea. One of the first links in the trophic chain is zooplankton, which acts as an intermediary between primary production (phytoplankton) and higher levels. Copepods, the predominant species in the plankton of the southern Baltic, constitute the food of many invertebrates, fish larvae and juvenile fish, including those consumed by humans (Bielecka et al., 2000).

A significant factor influencing Hg bioaccumulation is, among others, the species composition of zooplankton (Saniewska et al., 2010). In the southern Baltic region, in the Gulf of Gdańsk, the composition varies throughout the year and is largely dependent on water temperature. Zooplankton is a sensitive bioindicator of short- and long-term environmental changes (Bielecka et al., 2000). Marine coastal zones, particularly sheltered bays and estuaries, are areas where marine organisms thrive. Climate changes are leading to the warming of the winter season, which in turn results in a shorter icing period on the gulf, or a complete lack of ice. Relatively high temperatures that persist for longer periods of time bring about more intensive phytoplankton growth, even in late autumn and during winter. It is commonly thought that the vegetation season in the southern Baltic region starts at the end of March/beginning of April, but more and more frequently the first blooms, particularly in the coastal zone, appear much earlier - even at the end of January/beginning of February (Łysiak-Pastuszak, 1996; Witek and Pliński, 2000; Wasmund and Uhlig, 2003; Błaszczyk et al., 2013). In this situation, mercury from atmospheric deposition, the concentration of which is higher at this time of the year, becomes accumulated by algae. Because of this, despite the decrease of Hg input to the Baltic Sea (Bartnicki et al., 2010), the mercury load entering the trophic web per annum may be 30% higher compared to a cold year with a frosty winter, when phytoplankton growth is limited (Bełdowska and Kobos, 2016). The summer season is also getting warmer compared to a period spanning several years back. In the last 28 years, 21 summers were above the thermal norm (IMGW PIB, 2016). This influences

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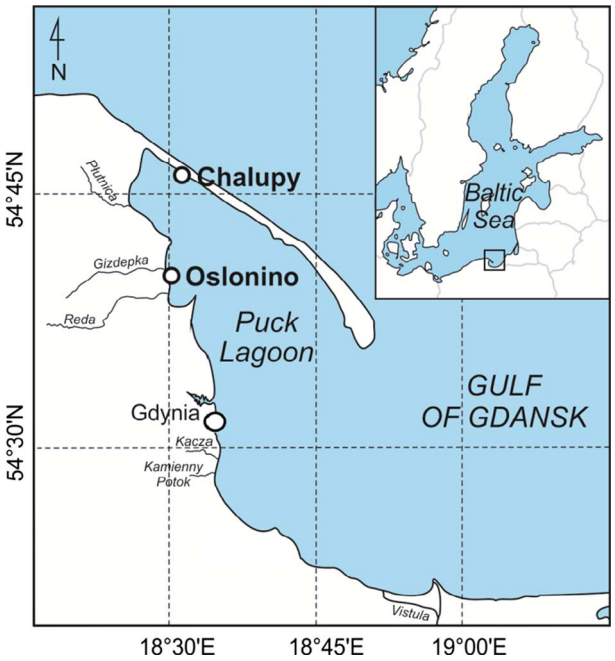

Fig. 1. Map of the study area.

phytoplankton growth, which thrives and multiplies more rapidly in warm water. In the southern Baltic area, there has been an increase of the number of days warmer than 5 °C and a decrease of days colder than 0 °C (Kożuchowski, 2009; IMGW PIB, 2016; HELCOM, 2013). According to Poland's Climate Monitoring Bulletin, years have been classified as being above the thermal norm with an increasing frequency since 1988–24 times over the last 28 years (IMGW PIB, 2016). All these factors influence species composition and quantity of plankton, which in turn affects the circulation of metals. For this reason, an attempt has been made to determine the factors influencing Hg concentration changes in one of the initial links of the trophic chain, i.e. zooplankton, in the coastal zone of a boreal environment.

2. Materials and methods

Samples were collected in triplicate, on a monthly basis at the coastal zone of the southern Baltic Sea, at two stations: Osłonino (n = 14) and Chałupy (n = 15), from December 2011 to May 2013, and also at Gdynia station (n = 11): from December 2011 to November 2012 (Fig. 1). In February 2012 (at all sites), December 2012–February 2013 at the Chałupy station and January–March 2013 at Osłonino, samples were not collected because of ice cover.

Osłonino and Chałupy are located in the Puck Lagoon, the average depth of which is 3 m. Stations were located in the shallow part of the bay, with an average sea level of 0.5 m (Korzeniewski, 1993). The Osłonino and Chałupy sites were remote from anthropogenic regions and, at the Osłonino station, the water exchange was restricted. Osłonino is a place of little interest to tourists and has a population of only 350 inhabitants (2007 year). The station is located about 300 m away from the outlet of the river Gizdepka, which has an average water flow of 0.2 $m^3 s^{-1}$ (catchment area: 37.2 m^2). The Chałupy station was situated close to the narrow Hel Peninsula with limited surface run-off. Chałupy is a small village of 380 inhabitants (2009 year) but, owing to high tourist attractiveness, that number is much higher between May and September. Sea currents in this area introduce marine suspended particulate matter (SPM) from the open sea (Nowacki, 1993). The Gdynia Orłowo station was located in the open part of the Gulf of Gdańsk near the Tricity Agglomeration, about 1.5 km from the mouth of the Kacza River, which has a mean water flow of 0.2 $m^3 s^{-1}$. Gdynia is a highly urbanised city: 250 thousand inhabitants in 2014 year. The study station was situated at a distance from the harbour and shipyard, as well as the storm water sewage system. Owing to the proximity of the cliff, which is close enough to cast shade on the beach, it isn't attractive for tourists. This is a region with high water dynamics and intensive water exchange.

The samples were collected vertically using a zooplankton net (mesh size 50 μm), from the pier about 10 m from the coast from subsurface water during 10–15 min. Mercury concentration was analysed only in live zooplankton organisms. To obtain this material, the collected samples were transported to the laboratory in life-supporting conditions and after about 24 h (required for the acclimatisation and defecation of the zooplankton) live zooplankton was separated from other material using the phototaxis phenomenon. (Staniszewska et al., 2014).

In addition, microorganisms were collected from stones (epilithon), plants (epiphyton) and from above the sediments (epipsammon) with methods used in the monitoring of floating waters (e.g. Kelly and Zgrundo, 2013). The biofilm from stones was scraped off using a toothbrush, while the biofilm from plants and above algae was extracted in an ultrasonic bath.

2.1. Hg analyses

The samples were freeze-dried and analysed with a triple replication, with an advanced mercury thermal desorption analyser (AMA 254). The dry weight of a single analytical sample was about 0.1000 g. Detection limit for solid materials, calculated as the triplicate of the standard deviation of Hg concentration in the blank substrate, was 0.005 ng g^{-1}. QA/QC included blank samples, replicates and reference materials. All measurements of Hg in the reference materials were within the certified ranges. The mean measured concentration of Hgtot (n = 20) was 264 ng g^{-1} in BCR 414 (plankton) and 46 ng g^{-1} in GBW 07314 (sediment), while the respective certified values were: 276 ng g1; 48 ng g^{-1}. Average errors did not exceed 5%.

2.2. Biological analyses of zooplankton

The material to be used for biological analyses was preserved in 4% formaldehyde and put through standard analysis according to HELCOM guidelines for Baltic Sea plankton (www.helcom.fi HELCOM Combine Manual Part C Annex C-7).

2.3. Statistical analysis

The bioaccumulation factor (BAF) was calculated following the formula suggested by Szefer et al. (1999):

$$BAF = Hgzoopl. / Hgw \quad (1)$$

where Hgzoopl. and Hgw represent concentrations of Hg in zooplankton and seawater, respectively.

Biomagnification factor was calculated as (Szefer et al., 1999):

$$BMF = Hgphytopl. / Hgzoopl.$$

where Hgphytopl. was mercury concentration in phytoplankton.

The data were not characterized by a normal distribution (Shapiro-Wilk test, $p < 0.05$). Dependences between the analysed variables were determined on the basis of the Spearman correlation coefficient at a confidence interval of 95%.

3. Results and discussion

3.1. Spatial and temporal variability of zooplankton

The taxonomic composition, abundance and variability of zooplankton during the study period were similar to those observed earlier in the Gulf of Gdańsk in the shallow coastal zone (Fig. 2) (Bielecka

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