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Mercury concentration in phytoplankton in response to warming of an autumn – winter season☆

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ABSTRACT

Among other climate changes in the southern Baltic, there is a tendency towards warming, especially in autumn-winter. As a result, the ice cover on the coastal zone often fails to occur. This is conducive to the thriving of phytoplankton, in which metals, including mercury, can be accumulated. The dry deposition of atmospheric Hg during heating seasons is more intense than in non-heating seasons, owing to the combustion of fossil fuels for heating purposes. This has resulted in studies into the role of phytoplankton in the introduction of Hg into the first link of trophic chain, as a function of autumn and winter warming in the coastal zone of the lagoon. The studies were conducted at two stations in the coastal zone of the southern Baltic, in the Puck Lagoon, between December 2011 and May 2013. The obtained results show that, in the estuary region, the lack of ice cover can lead to a 30% increase and during an “extremely warm” autumn and winter an increase of up to three-fold in the mean annual Hg pool in phytoplankton (mass of Hg in phytoplankton per liter of seawater). The Hg content in phytoplankton was higher when *Mesodinium rubrum* was prevalent in the biomass, while the proportion of dinoflagellates was small.

1. Introduction

The properties of mercury have resulted in its wide application in various industries, for centuries. However, its toxicity to humans was widely known in the second half of the last century. Since that time reduction of use and emissions of Hg into the environment have been undertaken. Mercury exhibits nephrotoxicity, immunotoxicity, neurotoxicity and mutagenicity (O'Shea, 1999). Mercury is introduced to the human organism mainly through consumption of fish and seafood, showing the marine environment to be especially sensitive to pollution of Hg. Mercury was used for ages by man. In the 20th century its usage increased rapidly in many branches of industry. For many years, the Baltic Sea was considered to be one of the most polluted basins in the world (Wrembel, 1997). However, according to HELCOM reports (2010), Hg emission in the Baltic region at the beginning of the 21st century was about 20%–30% lower than during the 1980s. The inflow of Hg via rivers into the Gulf of Gdańsk was estimated for the year 2012: via the Vistula 218 kg a^{-1} and the rest of rivers: 1.2 kg a^{-1}; with precipitation: 17.9 kg; witch dry deposition: 9.5 kg a^{-1}; by erosion of the coast (14.3 kg a^{-1}) (Bełdowska et al., 2016).

Climate changes have become manifest in the form of warmer winters (increased number of days warmer than 5 °C and decreased number of days colder than 0 °C) (Kożuchowski, 2009; HELCOM, 2013; IMGW PIB, 2015), thus contributing to a decreased load of mercury from the main source, which was identified in the southern Baltic Sea region as fossil fuel combustion (Bełdowska et al., 2012).

In Gdynia, situated on the southern Baltic Sea coast, during winter 2006, which was classified by the Climate Monitoring Bulletin (IMGW PIB, 2015) as a “very cold” winter, atmospheric dry deposition of Hg was nine times higher than in the “anomalous warm” winter of 2008 (Bełdowska et al., 2014a). In the Polish coastal zone of the Baltic, between 1951 and 2014, the average winter temperature was reported to be above the multiyear normal on 21 occasions (IMGW PIB, 2015), most of these coming within the past 15 years. The autumn season is also getting warmer and, from 1951 to 2014, the average autumn temperature was reported to be above the multiyear normal 33 times (IMGW PIB, 2015). This is of considerable significance as temperature, along with exposure to

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sunlight and the availability of biogenic compounds, is one of the key factors influencing the growth of phytoplankton – the first link in the trophic chain.

Research spanning many years has served to determine the sequence of the various systemic groups appearing in the yearly cycle of phytoplankton development in the waters of the southern Baltic. In general, together with chemical fluctuations in the Baltic, climate changes are considered responsible for anomalies in the composition, structure and numbers of phytoplankton. In the coastal zone of the southern Baltic, particularly in the Puck Bay, the concentration of nutrients is high enough for solar radiation and water temperature to determine algal growth (Kraśniewski et al., 2012). The relatively high temperatures that persist here lead to intense growth of phytoplankton even in late autumn or winter and winter temperatures are expected to increase more than summer temperatures (Lasseen et al., 2010). The beginning of the planktonic growth season is commonly thought to be at the end of March/beginning of April, yet increasingly the first algal blooms occur much earlier, particularly in the coastal zone – even as early as the end of January/beginning of February (Łysiak-Pastuszak, 1996; Witek and Pliński, 2000; Wasmund and Uhlig, 2003; Błaszczyk et al., 2013). Algal blooms have also been observed during the cold phase in other regions, such as San Francisco Bay (Cloern et al., 2007). In this situation mercury from atmospheric deposition, whose concentration is higher at this time of the year, does not deposit on the bottom of the bays as it is instead accumulated by suspended particulate matter including phytoplankton (Bełdowska, 2015). In this way, despite the decrease of Hg input to the Baltic Sea (Bartnicki et al., 2012), the annual mercury load entering the trophic web may be higher than that of a year featuring a cold winter, when the growth of phytoplankton is limited. The influence of climate warming on the growth of plankton and the consequent rise in mercury concentrations were observed in fish in the Mackenzie river (Carrie et al., 2009), as well as in the increased input of metals into the sediments in Kusawa Lake and some lakes in the Arctic (Sanei et al., 2009; Stern et al., 2009).

Over the last 63 years, the average spring and summer temperatures were reported to be above the multiyear normal 25 times and 37 times, respectively (IMGW PIB, 2015). A warm summer in the coastal zone stimulates gaseous mercury air/sea exchange, which leads to a rise in gaseous mercury concentrations in the air which was measured in coastal zone of Puck Bay and Gulf of Gdańsk (Marks and Bełdowska, 2001; Bełdowska et al., 2008). High solar radiation supports growth of phytoplankton (Lewandowska et al., 2015), which intensively accumulate metals present in the water including mercury (Windom and Kendall, 1979). Warm water, on the other hand, encourages the blooming of cyanobacteria which are poor food for pelagic and benthic consumers (HELCOM, 2013), thus reducing the amount of mercury introduced into the trophic chain. Particulate, organic matter bound mercury can be released back into the water column through matrix degradation, or reduction of ionic mercury to its gaseous form. In this form, mercury may be transferred into the atmosphere (Bełdowska et al., 2007). The direction and rate of these processes depend on many parameters, such as solar radiation intensity, water temperature, wind-induced mixing, salinity, oxygen saturation, quality and quantity of organic matter and fraction of phytoplankton to total suspended matter (Costa and Liss, 2000; Bonzongo and Donkor, 2003). Previous semi-laboratory experiments indicated that phytoplankton species occurring in the Gulf of Gdańsk - *Aphanizomenon flos-aquae*, *Nodularia spumigena* (cyanobacteria), *Prorocentrum minimum* (Dinophyta), *Acutodesmus acuminatus* (green phytoplankton) and *Cyclotella meneghiniana* (diatom), adsorb and reduce mercury at different rates (Bełdowska and Falkowska, 2007; Magulski et al., 2007). Hence shifts in the composition of phytoplankton species, which may be induced by minute climate changes, as well as concentration and quality of dissolved organic carbon can significantly affect the mercury cycle (Pickhardt and Fisher, 2007).

Phytoplankton growth rates are also dependent on wind speed and direction. Calm sea conditions are optimal, whereas strong, long-lasting winds lead to the decline of blooms in the Baltic Sea region. During the past 200 years, storminess in the Baltic Sea has been dominated by large multidecadal variations rather than long-term trends (HELCOM, 2013). Composition and seasonal changes of phytoplankton in seas and oceans depend on salinity, temperature, sunlight and availability of nutrients. The oceanic water circulation caused by the currents may be important for the spread of various species. Global warming, which allows for faster growth and development of individual phytoplankton species, may allow both greater probability of taking mercury adsorption by these organisms.

According to reports about climate change in the Baltic Sea area, the annual mean air temperature anomalies from 1871 to 2011 were 0.8 °C per decade in the southern part of the sea (HELCOM, 2013). This value is larger than the trend of the global mean temperature (IPCC, 2001) and has led to an increase in annual mean sea-surface temperature of 0.6–0.8 °C per decade in the southern Baltic. In consequence, the length of the growing season has increased and the annual maximum ice extent of the Baltic Sea has decreased (by 20% over the past 100 years). For the last 30 years, especially in the southern Baltic, a decreasing trend in the number of days with ice per annum has been noted (HELCOM, 2013). Reports of future climate changes in the southern Baltic forecast air temperature increases of about 4 °C during summer and winter, as well as a 2.4–3.0 °C increase in sea-surface temperature, especially in the winter. Despite the period from late autumn to early spring getting warmer, in the southern Baltic this is nevertheless a cold time and fuel combustion continues to take place. This introduces a larger load of mercury into the sea via dry atmospheric deposition, in comparison with the non-heating season (in 2008: 1102 ngHg m^{-2} $season^{-1}$ and 356 ngHg m^{-2} $season^{-1}$ respectively) (Bełdowska et al., 2014a). The aim of this study was to evaluate the role of phytoplankton in Hg becoming introduced into the trophic chain, throughout the year, as a result of increasingly warmer climate in the coastal zone of the boreal environment.

2. Materials and methods

The samples were collected monthly from December 2011 to May 2013, at 2 coastal stations: Chałupy and Osłonino (Fig. 1). Chałupy and Osłonino are both located in the area of the Puck Lagoon (which is part of Gulf of Gdańsk), where the average depth is 3 m, and the stations were located in a shallow part of the bay with a mean depth of 0.5 m (Korzeniewski, 1993). Additionally, at the Osłonino station, there was a limited amount of water exchange. Both stations were remote from anthropogenic regions and the Chałupy station was situated close to the thin Hel Peninsula, where the surface run-off is limited. The main source of mercury to the seawater near Chałupy was atmospheric deposition (especially during heating season), while at Osłonino atmospheric deposition (especially during heating season) and surface run-off were of joint significance.

Samples were collected about 10 m from the coast. Phytoplankton for chemical and biological analysis was collected for 10–15 min, with 20 μm nets. The sub-samples for microscopic analyses of phytoplankton were collected from the net in 50 cm^3 bottles. The water samples for quantitative and quantitative analyses of phytoplankton were collected in 200 cm^3 bottles. The samples for microscopic analyses of phytoplankton were preserved