



Seasonal changes of mercury speciation in the coastal sediments

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Received: 16 November 2017 / Accepted: 31 March 2018 / Published online: 14 April 2018
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Abstract

Purpose Mercury speciation in sediments is linked to environmental conditions and processes. Domination of particular mercury species depends on its source, displays considerable seasonal behavior, and may be further modified due to oxygen levels, icing conditions, or the input of fresh organic matter. The purpose of this study was to examine the coastal area of the Gulf of Gdańsk in terms of mercury contamination and the influence of seasonal environmental changes on its speciation.

Materials and methods In three highly dynamic coastal sites, mercury speciation in sediments was studied in relation to other environmental parameters (redox conditions, organic matter concentration, bacteria abundance, etc.). Sediment and water samples were collected monthly during a 3-year study. Sequential extraction of sediments was used for identification of four inorganic mercury species: dissolved, bound with fulvic and humic acids, mercury sulfide, and residual fraction. Cold vapor atomic fluorescence spectrometry (CV-AFS) was used for extracts and liquid sample analysis. Total mercury in sediments was measured with atomic absorption spectrometry (AAS). Changes in salinity were analyzed by measurements of chloride and sulfate ion concentrations using ion chromatography. Bacteria number and biomass were measured by direct counting using epifluorescence microscopy.

Results and discussion Seasonal changes in mercury speciation were observed at all sites and attributed to different processes. Labile mercury fraction contribution varied from 0 to 80%. The speciation patterns varied locally as the stations selected for the study are diversified in terms of anthropogenic impact, water dynamics, and output from land. Mercury concentrations at all stations fluctuated during phytoplankton blooms, icing of marine waters, precipitation, or increased surface runoff from the land. In this local scale, the global climate changes are visible already as environmental conditions in studied area changed in comparison to elder research.

Conclusions Obtained results suggest that although mercury emissions to the environment have decreased in recent years, local weather conditions, which may be intensified by climate change, seriously affect the bioavailability of past mercury deposits in coastal sediments.

Keywords Baltic Sea · Chemical speciation · Climate changes · Mercury · Sediments

1 Introduction

Mercury is for a long time recognized as a toxic metal for humans, showing both neurotoxic and embryotoxic properties.

Responsible editor: Paolo Porto

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Its primary source for humans is fish and seafood in general (Jackson 1998; Boening 2000). This is mostly related to the fact that mercury tends to accumulate in biota and undergoes biomagnification in food chains (Boening 2000). Both processes are related to bioavailability of mercury and hence to its speciation. Biogeochemical cycle of mercury is very dynamic, intense, and its transformations are complex, resulting from this element's properties. Once it reaches the sediments, mercury is exposed to entirely different conditions than in the water column in terms of Eh, abundance of organic matter, humic substances, clay minerals, and biota activity. These processes lead to the formation of specific equilibria among several inorganic mercury (II) species (Sunderland et al. 2006). Along with sediments and suspended matter, bacteria present in the environment are especially important for mercury sequestration in sediments (Baldi et al. 1989). Mercury uptake by microorganisms

includes absorption and complexation on bacterial cell walls. On the other hand, slight mercury increases in the environment may result from bacteria cells lysis (Frischmuth et al. 1993). Additionally, environmental changes may be linked to bacterial activity—including sulfate reduction, which influences mercury transformation and occurrence of its sulfidic fraction (Baldi et al. 1989, 2012). Microbial transformation of mercury is connected with bacterial metal resistance; these mechanisms lead to large-scale transformation of toxic target—mercury. Other important contributors of mercury cycling in the environment are sulfate-reducing bacteria (SRB), like marine *Desulfovibrio* or *Desulfobacter* genera (Purdy et al. 2002), which may methylate mercury to its most toxic, methylmercury form. Mercury resistance is considered the only bacterial metal resistance system which leads to large-scale transformation of this toxic agent (Barkay et al. 2003).

In the coastal zone, mercury speciation in sediments is also directly linked to environmental conditions and processes occurring in both maritime and terrestrial ambience. Mercury concentrations display considerable seasonal behavior due to high variability of input from land associated with river discharge, land erosion, and surface outflow (Jędruch et al. 2015). Its speciation may be modified in coastal sediments, due to oxygen consumption by decaying organic matter, icing conditions, or input of fresh organic matter from primary production. This may further lead to complex changes in mercury bioavailability, via direct uptake or methylation through the year in close connection to climate change and related meteorological conditions. Climate changes in the southern Baltic Sea region head towards shortening of icing period (Majewski 1990; Korzeniewski 1993; HELCOM 2013; IMGW PIB 2015). A warming of winter period (December, January, February) is already ongoing and as a consequence, ice cover in Baltic waters appears for shorter time or eventually it is non-existent at all (IMGW PIB 2015). Ice cover in coastal areas of the Gulf of Gdańsk was observed almost yearly in years 1946–1987, with average icing period for the Puck Lagoon lasting for 90 days, while icing of the Gulf of Gdańsk in vicinity of Gdynia lasted for 30 days (Girjatowicz 1988; Szeffler 1993). In the time period from 1987 to 2014, icing of the Puck Bay was observed only seven times and the ice-cover duration was shorter than in the past. As a consequence, fluxes of chemical substances in the surface sediments of coastal zone are affected (Bełdowska et al. 2013). The period in which mercury is reemitted from sediments into near bottom water and food chain lengthens, also due to the fact that elongated vegetative period for marine species accumulating mercury enhances transfer to the food chain (Bełdowska et al. 2015a, 2016a; Bełdowska and Kobos 2016). The reports regarding climate change in the Southern Baltic forecast increase of surface temperatures and therefore elongation of the vegetative period along with more intense rainfalls (HELCOM 2013; IMGW PIB 2015) which will

result in elution of contaminants from land surfaces. During fall and winter, intensive inflow of mercury from the atmosphere is observed and land outflow occurs after storms and erosion that they cause to the coastal cliffs (Bełdowska et al. 2014, 2016b). Marine sediments in the coastal zone are a subject of mixing by the wave action, bottom currents, and biota activity (Zaborska et al. 2014). Therefore, they experience considerable temporal variability, as compared to sediments in deep accumulation basins.

Shallow bays and coastal waters of Puck Bay are an example of very dynamic environments influenced by terrestrial processes (Jędruch et al. 2017). They are a habitat of many marine organisms susceptible to mercury intoxication (Boszke 1999). Therefore, identification of factors stimulating or limiting the mobility and assimilation of mercury is crucial to estimate the condition of the environment, especially when it is influenced by ongoing climate changes.

In recent years, a reduction of mercury loads entering the Baltic Sea is observed. Vallius (2014, 2015) reports a decrease of mercury concentrations in Gulf of Finland surface sediments reflecting the load from last two decades in comparison to sediment layers reflecting older loads. Still, the buried loads of mercury can undergo remobilization due to changing environmental conditions, related to oxy-redox fluctuations, mixing, etc. The aim of this study was to define dominating mercury species in the environment of shallow coastal waters of southern Baltic Sea and recognition of climate change influence on mobility and bioavailability of mercury species in shallow coastal areas of Puck Bay. Previous studies in this area were focused either on total mercury (Bełdowska et al. 2014, 2016b) or presented only single samples, missing seasonal aspect (Bełdowski and Pempkowiak 2003, 2006, 2007; Bełdowska et al. 2015a). In order to elucidate the mechanisms involved, sequential extraction was used throughout this work and the following mercury species were quantified: dissolved mercury (F1:HgA), mercury bound to fulvic (F2a:HgF) and humic acids (F2b:HgH), the sulfidic fraction (F3:HgS), and the residual fraction (F4:HgR). The dissolved fraction and the fractions bound to fulvic and humic acids are considered mobile and were recognized as substratum for mercury methylation (Bełdowska et al. 2015a), whereas the sulfidic fraction, containing insoluble mercury sulfide, and the residual fraction, containing insoluble humins and mercury bound to the mineral matrix, are considered stable in the environment (Wallschläger et al. 1998). Although methylmercury is not directly measured in this procedure, previous study shows correlation of this species and occurrence of lighter fractions (HgA, HgF, and HgH) (Bełdowska et al. 2015b). Monthly resolution of sampling allowed to observe the processes occurring in the uppermost sediment layers according to seasons and related environmental conditions changes. Some of those processes result from external forcing (including input variability, sediment erosion) (Bełdowska et al. 2014, 2016b),

while others reflect early diagenesis of organic matter and ongoing transformation of mercury species.

2 Materials and methods

2.1 Study area

Three diversified coastal sites of Gulf of Gdańsk (southern Baltic Sea)—Chałupy, Osłonino, and Gdynia—were studied in regard to mercury speciation in sediments from areas with different environmental conditions, water dynamics, and vicinity to anthropogenic sources of mercury. Location of sampling sites is presented in Fig. 1.

Chałupy station is located in a remote area of Puck Bay, inner part of the Gulf of Gdańsk, where no nearby large anthropogenic mercury sources are located. Surface runoff is limited, due to the fact that it is located on very narrow part of the Hel peninsula, only ca. 500 m across. It was therefore classified as a marine station because of the limited land influence.

Osłonino station is located away from anthropogenic mercury sources in a sheltered part of the Puck Bay, inner part of the Gulf of Gdańsk. This area is surrounded by forested cliffs, composed mainly of glacial till. The cliffs are geologically

active and erosion was observed within the study period, especially after intense rainfall and major storms. Average water depth in this site is 1.5 m. Prevailing currents cause macroalgae drift from the Puck Bay towards the Osłonino station, where large amounts of decaying algae are frequently shored on the local beaches during vegetative season. The study area is located ca. 0.5 km from Gizdepka river mouth, with mostly forested meadows and agricultural catchment area. This station was categorized as terrestrial, since land and river runoff influence the surrounding coastal waters.

Gdynia station is also located at the base of an active cliff and is located closer to the anthropogenically affected areas. This station is also categorized as terrestrial. In the south (ca. 1 km), there is a mouth of the Kacza River, transporting water from mostly urbanized catchment, while 2 km in the north a harbor and shipyards are located, which are considered as the main source of industrial emissions in close vicinity. However, the station may be influenced by the whole agglomeration of Gdańsk, Sopot, and Gdynia situated along the coastline. The area is also more open than Osłonino, at the unsheltered part of the Gulf of Gdańsk; therefore, the impact of storms and exchange of water with the open waters is more significant than in the two other stations (Majewski 1990).

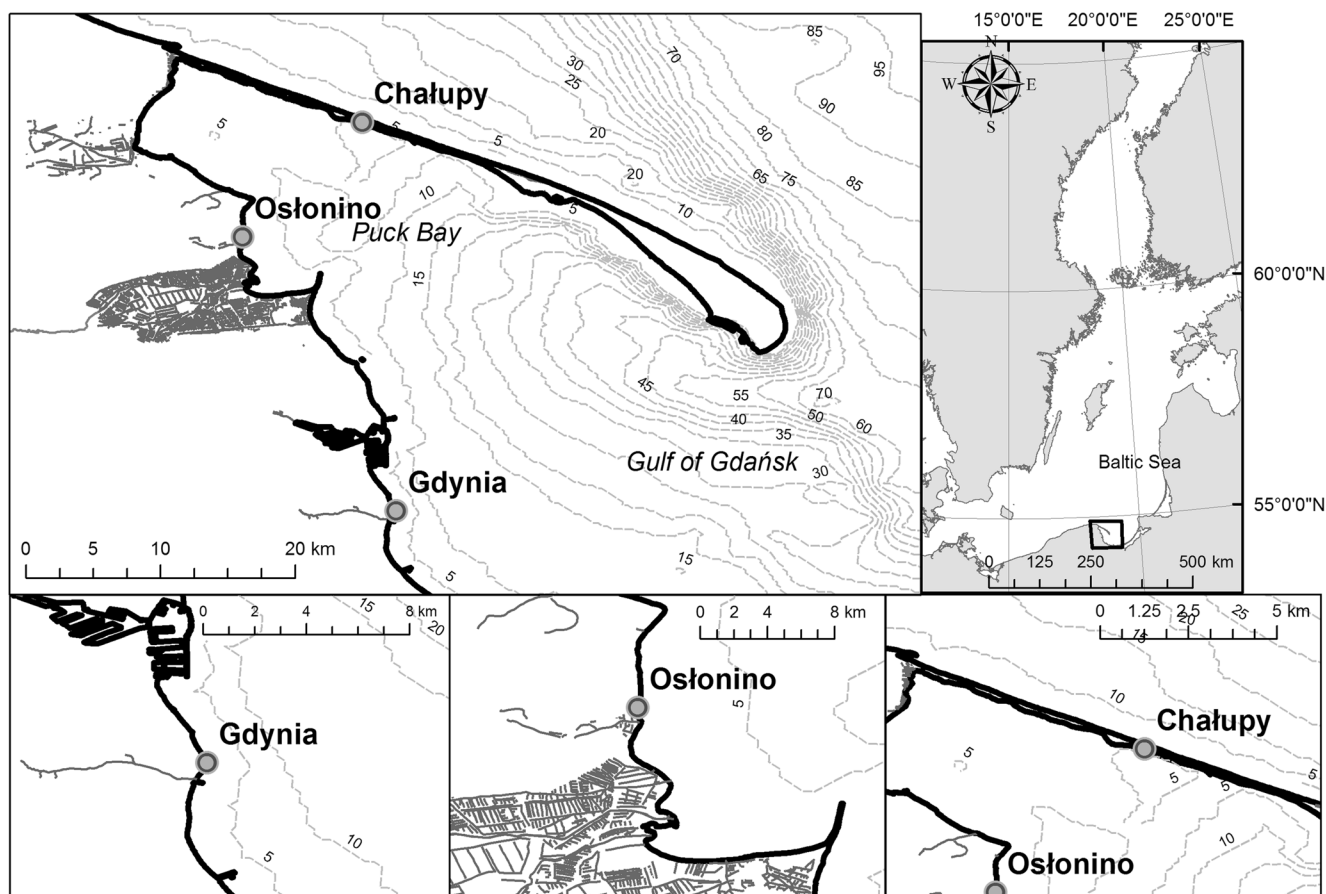


Fig. 1 Location of sampling sites in Gdynia, Osłonino, and Chałupy

Sediment samples for analysis were collected monthly, at the same position, from December 2011 until May 2013 at Puck Bay (Osłonino and Chałupy) and from December 2011 to June 2012 at Gdynia station (Gulf of Gdańsk). A handheld Van Veen grab, of 0.4-m² surface area, was used for sampling, and the top layer sediments of 5 cm thickness were collected. Sediments were put into polyethylene boxes and stored frozen until analysis. Pore waters were collected directly from the grab with the use of syringes equipped with Rhizon samplers consisting of microfiltration membrane with pore size of 0.15 µm. The pore water samples were used for biological analyses of bacteria biomass and determination of salinity in the environment, based on ion concentrations. In total, 48 sediment samples and 48 pore water samples underwent several stages of analytical procedures.

In February 2012, ice cover was observed at all stations and lasted for approximately 3 weeks. In the following winter, icing started in December 2012 in Chałupy and lasted until the end of January 2013. In Osłonino, ice appeared in January 2013 and lasted until the end of March, while Gdynia station was completely ice-free during this season.

2.2 Analytical procedures

Sediments for total mercury analyses were freeze-dried and homogenized with a ball mill before analysis. Total mercury determination was performed in triplicate, using pyrolysis in a stream of oxygen (mercury analyzer Leco AMA254, Czech Republic). The AMA254 is based on a technique of direct combustion features a combustion/catalyst tube where sediment (sample of approximately 500 mg) decomposes in an oxygen-rich environment and removes interfering elements. Both recovery and precision given as relative standard deviation proved satisfactory (97% ± 3% RSD) basing on a reference material analysis (NIST 2584). Detection limit of this method was calculated and equals 0.006-ng mercury.

For speciation analysis, fresh sediment samples underwent sequential extraction procedure developed by Wallschläger et al. (1998) and adapted to marine sediments by Beldowski and Pempkowiak (2003, 2006). Briefly, subsamples of wet sediments (containing approximately 2 g of dry matter) were placed in PTFE tubes and extracted overnight on a mechanical shaker with 20 ml of different extractants according to the sequence given in Table 1. After each step, the samples were centrifuged at 2500 rpm for 15 min. The supernatants were processed and used for the mercury determinations, while the solid residue was subjected to further extraction. The last step was acid digestion to obtain the residual mercury. Fractions F1 comprising mercury dissolved in pore waters and loosely adsorbed on sediment surface, and F2a—mercury bound to fulvic acids may be considered as mobile. Fraction F2b, representing mercury bound to humic acids, is also somewhat mobile and bioavailable, but less than the former two. Fraction F3, mercury sulfide and bound to

other metal sulfides (i.e., iron) and fraction F4—residual, containing mercury bound to mineral matrix and insoluble humins, may be considered stable and unavailable to biota. Each sample was extracted in triplicate.

The solutions obtained in the course of sequential extraction were analyzed in duplicate/triplicate (depending on the extract volume) with the CV-AFS method in a Tekran (model 2600) spectrophotometer using EPA 1631 rev. E procedure (EPA 2002). The analyses of the reference materials: CRM-579 (mercury in sea water) and QTMO56MS (provided by QUASIMEME Laboratory Performance Studies program) demonstrated both the satisfactory accuracy (recovery 90–95%, $n = 5$) and the precision of the determination (RSD equal to 10% of the mean).

Ion concentrations of sulfates and chlorides in pore waters were analyzed for sulfur occurrence and salinity estimation with high-performance ion chromatography using Metrohm 850 Professional IC. Each analysis was performed in triplicate after sample dilution (20 times). The average recovery of the ions was in the range of 95–100%. The precision, expressed as the relative standard deviation for $n = 5$, was < 4.5%.

The organic matter contents of sediments were calculated on the basis of the loss on ignition (LOI) performed in a muffle furnace. Typical precision of those measurements was ca. 3%.

The sediment redox potential was measured with a needle redox electrode (Microscale Measurements, The Netherlands, model MB 11 mV). Redox measurement precision expressed as the relative standard deviation for was estimated as < 4.5%. All environmental parameters were presented in Table 2.

2.3 Bacteria abundance

The total bacterial number and biomass were determined using direct counting of bacterial cells stained with 4',6-diamidino-2-phenylindole (DAPI), a popular nuclear and chromosome counterstain that binds strongly to A-T rich regions in DNA (Porter and Feig 1980) (Table 3). Pore waters were fixed with buffered formalin to a final concentration of 1%, DAPI stained at endpoint concentration of 2 µg cm⁻³, and then filtered through black nucleopore polycarbonate membrane filters (0.2-µm pore size).

Total bacterial number was estimated based on 20 subsequent fields of vision and appropriate algorithms. Results of automatic counting and measuring of bacterial cells were analyzed using macro definitions in MS Excel (Świątecki 1997). The biomass of bacteria was estimated from the mean volume of cells with the use of the Norland's formula (1993).

Significance of observed differences was evaluated using Kruskal-Wallis ANOVA, and correlations were assessed by Spearman rank correlation since distribution of data was not normal. Typically, values of p equal to 0.05 were used as a significance threshold. All statistics were performed using STATISTICA software.

Table 1 Procedure used for solid speciation of sedimentary mercury in marine sediments. Fractions description: Hg_A—dissolved; Hg_{F,H}—mercury bound to humic substances; Hg_S—sulfidic fraction, Hg_R—residual mercury

Fraction	Extractant	Extract treatment before CV-AAS measurement
F1	0.01-M HNO ₃	BrCl digestion (1 ml) followed by NH ₂ OH·HCl (1 ml of 20% solution). Hg dissolved and loosely adsorbed on sediment matrix
F2a and F2b	1-M KOH	BrCl digestion (1 ml) followed by NH ₂ OH·HCl (1 ml of 20% solution) Hg bound to fulvic acids—Hg _F Precipitation at pH 2 and HNO ₃ hot digestion—Hg bound to humic acids—Hg _H
F3	Na ₂ S in 1-M KOH	Acidification with HCl, purging of excess sulfide with Ar, oxidation overnight with HNO ₃
F4	HNO ₃ /HClO ₄ /HF	Oxidative digestion (120 °C/2 h in a Teflon bomb, HNO ₃ : HClO ₄ mixture 1.5 ml:3 ml)—Hg incorporated in clay minerals lattice, and bound to unextracted organic matter—Hg _R

3 Results and discussion

3.1 Environmental parameters

Values of chloride and sulfate ions in pore waters, redox potential of sediment, and organic matter contents may give additional information on processes occurring in the environment during sampling period. Parameters describing environmental conditions influencing mercury speciation are given in Table 2. Values of chloride ion concentration in pore waters were similar in all locations: in Oslonino and Chałupy ranged from 2.4 to 4.4 g dm⁻³, while in Gdynia, lower values were observed from 0.2 to 4.2 g dm⁻³. Also, sulfate ion concentrations were

comparable at all sampling stations and ranged from 0.43 to 0.65 g dm⁻³ in Gdynia, from 0.01 to 0.64 g dm⁻³ in Oslonino and from 0.32 to 0.61 g dm⁻³ in Chałupy. Those values are typical for brackish waters of Baltic Sea. Variations of chloride ion concentrations in time corresponded with changes in sulfate ion concentrations, which indicates changes in salinity connected to fresh water input from land and atmosphere. The lowest observed concentrations of chloride and sulfate ions in pore waters in Oslonino occurred during the thaw in the beginning of year 2013, directly after the ice cover extended to the area of inner Puck Bay (IMGW PIB 2015). Decrease of ion concentrations in pore waters from Gdynia occurred shortly after the period of the most intense precipitation in this region in June,

Table 2 Seasonal variability of environmental parameters: chlorides and sulfates, redox potential, organic matter on the basis of LOI (abbreviations stand for: Gd. —Gdynia, Os.—Oslonino, Ch. —Chałupy)

Month	Cl ⁻ (mg dm ⁻³)			SO ₄ ²⁻ (mg dm ⁻³)			Redox potential (mV)			Organic matter content (%)		
	Gd.	Os.	Ch.	Gd.	Os.	Ch.	Gd.	Os.	Ch.	Gd.	Os.	Ch.
2011.12	–	2391	2426	–	514	520	122	93	130	0.31	0.24	0.31
2012.01	2390	2481	2410	526	540	506	300	96	159	0.11	1.98	0.45
2012.02	4071	1286	3421	647	265	517	320	43	–	0.08	0.73	0.29
2012.03	2959	3816	3663	503	639	583	408	464	421	0.09	1.09	0.40
2012.04	3960	3994	3946	608	626	600	316	377	378	0.07	1.01	0.39
2012.05	3850	1946	4074	553	301	601	271	213	267	0.15	1.42	0.41
2012.06	3522	4219	4414	486	599	615	296	258	208	0.14	0.91	0.41
2012.07	2818	2580	2745	426	380	421	287	209	10	0.15	1.46	0.33
2012.08	3053	3153	3093	431	445	435	233	71	–435	0.12	0.92	0.32
2012.09	3140	3162	3100	470	478	478	144	436	312	0.10	1.08	0.42
2012.10	3480	3273	3423	500	474	500	288	326	205	0.08	1.05	0.28
2012.11	3227	2909	2995	620	557	562	–	445	349	0.10	1.17	0.26
2012.12	–	3245	2937	–	636	549	227	300	–	–	1.20	0.17
2013.01	–	802	3007	–	145	564	–	154	286	–	0.28	0.31
2013.02	–	232	3881	–	6	545	–	235	358	–	0.87	0.34
2013.03	–	1701	3678	–	289	520	–	297	363	–	0.23	0.17
2013.04	–	2929	2973	–	289	391	–	212	641	–	0.83	0.28
2013.05	–	1829	2332	–	260	324	–	176	695	–	0.67	0.31

Table 3 Seasonal variability of abundance of bacteria: total bacterial number and biomass (abbreviations stand for: Gd.—Gdynia, Os.—Osłonino, Ch.—Chałupy)

Month	Total bacterial number TBN $\times 10^6$ (cm ⁻³)			Bacterial biomass BBM ($\mu\text{g C dm}^{-3}$)		
	Gd.	Os.	Ch.	Gd.	Os.	Ch.
2011.12	2.69	–	2.318	97.9	–	57.9
2012.01	11.92	5.14	11.23	31.2	173.8	230.2
2012.02	0.53	7.47	18.07	15.4	121.3	526.9
2012.03	–	4.07	5.34	–	118	212.9
2012.04	4.08	5.52	13.21	126.5	164.6	439.8
2012.05	1.17	3.25	17.07	18.2	129.6	504.1
2012.06	4.41	2.77	9.09	91.2	68.2	220.7
2012.07	1.31	3.70	17.94	32	129.5	483.6
2012.08	2.07	7.17	13.85	43	231.5	632.2
2012.09	2.65	11.40	11.05	55.2	332.5	333.6
2012.10	1.82	6.46	14.26	34.7	202.6	332.3
2012.11	3.73	5.86	4.91	81.2	215.7	166.1
2012.12	0.63	8.88	7.83	16.8	298.3	253.4
2013.01	1.73	14.51	12.28	70.1	513.4	517.7
2013.02	0.36	18.16	–	22.1	471.7	–
2013.03	–	18.55	3.60	–	448.5	93.3
2013.04	2.61	8.16	18.07	79.2	209.6	459.3
2013.05	0.82	7.98	–	10.3	140.7	–

July, and August 2012, showing penetration of surface outflow to sediments (IMGW PIB 2015).

Organic matter contents in sediments ranged from 0.07% in Gdynia (April 2012) to 1.98% in Osłonino (January 2012). The highest mean organic matter content was observed in Osłonino (0.95%) which could emerge from the location of this sampling site—semi-enclosed area with limited water exchange with the open sea and additional source of organic matter from Gizdepka River (Jeđruch et al. 2017). In Chałupy and Gdynia, mean annual organic matter content was lower (0.33 and 0.16%, accordingly). In the case of Chałupy station, water currents are oriented along the peninsula and transport the material, which limits accumulation of organic matter in this site (Majewski 1990; Jeđruch et al. 2017). Location of Gdynia sampling station allows the water exchange with open sea, what results in lower organic matter contents, despite the additional source of sedimenting material from Kacza River outflow (Jeđruch et al. 2017).

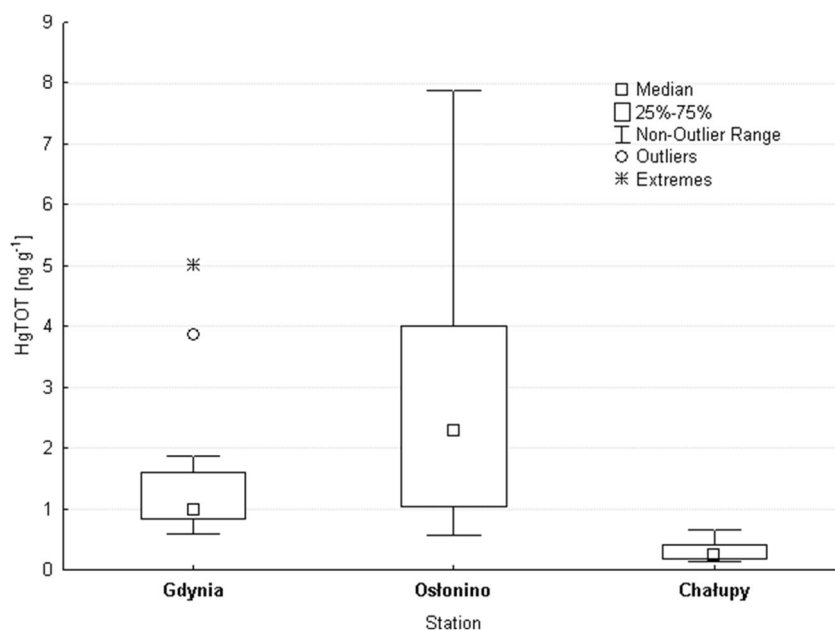
Sediments from Osłonino were also characterized by the highest mean contribution of fine grains (<63- μm diameter) which amounted to 3.6%. Fine fraction contribution in the sediments from Gdynia and Osłonino was significantly lower (below 1%). This could also result from station location fostering material accumulation. Also, mean humidity of the sediments was the highest in samples collected in Osłonino (23%) and slightly lower in Chałupy and Gdynia (20 and 21%, respectively).

3.2 Overall pattern of mercury concentration and speciation in the study area

Total mercury concentrations (Hg_{TOT}) in studied stations were low, but typical for sandy sediments from southern part of the Baltic Sea. The results ranged from 0.4 to 7.9 ng g^{-1} , with average concentration of 1.7 ng g^{-1} (median 0.9 ng g^{-1}). The highest concentrations were observed in the area of Osłonino and Gdynia stations (Fig. 2), which are located close to river mouths and near eroding cliffs, both of them being under the influence of terrestrial runoff. On all studied stations, stable fractions—sulfidic and residual (Hg_{S} and Hg_{R} , respectively) dominated, reaching on average 83% in Gdynia and up to 88% in Osłonino. This results from significantly high organic matter concentrations (Kruskal-Wallis ANOVA $p = 0.000$) and low average redox potential (Mann Whitney U test, $p < 0.05$) (Table 2).

Labile fractions—including Hg_{A} (dissolved and loosely bound), Hg_{F} (fulvic acid bound), and Hg_{H} (humic acid bound)—in sediments in the study area were characterized by considerable variability (Fig. 3). Observed differences result most likely from both variable delivery of organic matter and mercury associated with it and changes in environmental conditions, which will be further discussed in following sections. This shows that mercury speciation in coastal sediments reflects small-scale local processes, environmental dynamics, and exposure.

Fig. 2 Total mercury concentrations range in Gdynia, Osłonino, and Chałupy

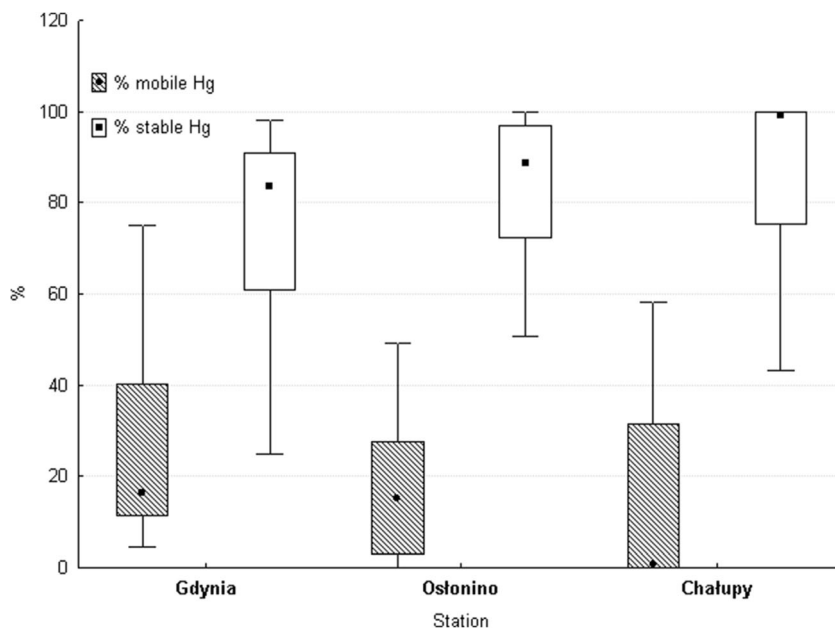


According to Zaborska et al. (2014), sandy sediments from coastal areas of the Gulf of Gdańsk can undergo mixing processes to the depth up to 11 cm below the sediment-water interface. Moreover, mercury associated with the fine mineral fraction of sediments, in dynamic bottom environment, can be transported via temporary resuspension or exchange of sediments with suspended matter. It seems that due to the mixing of uppermost sediments and export of the fine fraction to accumulation areas, coastal sediments are characterized by significant variability. Observed ranges of mercury concentration were clearly higher in two stations closer to land (Osłonino and Gdynia) than in Chałupy, which is considered a marine

station. This probably means that although surface sediments represent contemporary mercury concentrations, in the absence of variable input from land, mercury levels can remain fairly stable. Variable surface and river runoff (in Osłonino), cliff erosion and primary production (both Gdynia and Osłonino), and variable contribution of marine and terrestrial environments may result in considerable variability (Jędruch et al. 2017).

Observed total mercury concentrations are in the lower range of those previously reported in this area—ranging from 2 to 45 ng g⁻¹ in the Puck Bay at 10-m depth (Jędruch et al. 2015) and fit well in the range of concentrations reported for coastal sediments at this site (0.7–5.7 ng g⁻¹) (Falandysz et al. 1993).

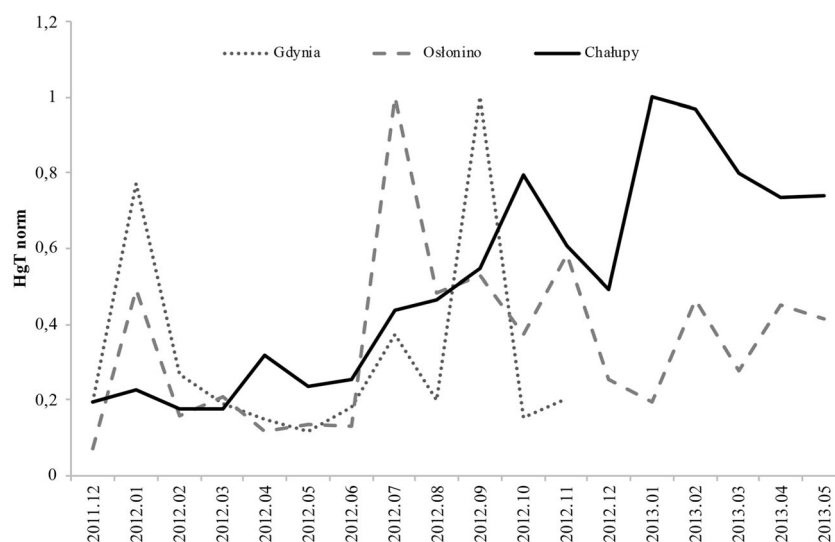
Fig. 3 Contribution of mobile and stable mercury fractions in total mercury concentrations according to sampling area



They are however smaller than those observed in the Vistula mouth coastal area (40–109 ng g⁻¹) (Bełdowski and Pempkowiak 2007), what may result from the fact, that Vistula River is a major mercury source in the Baltic Sea, making its signal visible even in sandy sediments of its estuary (Saniewska et al. 2014). Obtained Hg_{TOT} results are also lower than reported by Vallius (2014, 2015) in the sediment cores collected in the Gulf of Finland (10–100 ng g⁻¹ of surface sediment). However, the sediments from the Gulf of Finland were characterized as muddy clay and this area is relatively more contaminated. Also, Leipe with coworkers (2013) report that mercury concentrations in the Baltic Sea are lower in the coastal areas and increase with the distance from the shore, reaching the highest values in accumulative areas.

Obtained results correlate also with mercury concentrations in sandy sediments from different marine coastal environments from other parts of the globe. Chakraborty et al. (2014) studied mercury speciation in coastal areas of India and obtained Hg_{TOT} concentrations within the range from 5 to 66 ng g⁻¹. In their study, Hg_{TOT} concentrations in sandy sediments collected close to the shore did not exceed 10 ng g⁻¹ and consisted in 12 to 60% of the residual fractions. Meng et al. (2014) in China and Hwang et al. (2016) in South Korea measured Mercury concentrations in coastal sediments obtaining concentration ranges 7–398 and 8–120 ng g⁻¹ (respectively). Both authors point out the dependencies between mercury accumulation and sediment grain size (the lowest concentrations—around 10 ng g⁻¹ and less—are always noted in sandy sediments) and occurrence of local anthropogenic contamination sources. Garcia-Ordiales with coworkers (2018) came to the same conclusions when measured mercury concentrations in the range of 100–1330 ng g⁻¹ in the region of northern Spain (Asturian Coast, Nalón Estuary), but the area stays under a strong anthropogenic pressure—authors bring up the background values for mercury concentrations equal 12 ng g⁻¹ (Fig. 4).

Fig. 4 Seasonal variability of total mercury concentrations in Gdynia, Oslonino, and Chalupy—presented as a ratio of actual concentration to its maximum value at each station



3.3 Seasonal variability of mercury speciation in differing coastal areas

The spatial variability of mercury concentrations and speciation is a resultant of many environmental drivers. Each sampling site has different dynamics, and various events influencing coastal biochemistry were observed. Weather conditions, e.g., precipitation, ice cover occurrence, and increased fresh water inflow, may consequently affect environmental processes (Bełdowska 2014). Moreover, bacterial transformations and redox conditions play an important role in transformations of mercury fractions (Avramescu et al. 2011).

3.3.1 Terrestrial area influenced by riverine runoff and massive plankton blooms

The most interesting phenomena occurred at the Oslonino station, which was classified as a terrestrial area, highly impacted with massive plankton blooms. This is the most dynamic site among all the sampling stations, in terms of changing conditions and a large number of factors influencing mercury cycle. At this station, total mercury concentrations were the highest among all the sampling sites and ranged between 0.6 and 8 ng g⁻¹ (median value 2.6 ng g⁻¹). Likewise, in the whole study area, stable mercury species were prevailing at Oslonino station, and the sulfide-bound Hg_S fraction was dominant (51% on average). At the same time, fulvic bound (Hg_F) was dominant within the mobile mercury species (on average 55%). In Oslonino, the dissolved fraction (Hg_A) is virtually non-existent and appears only twice during the sampling period—after the icing in March 2012 and March 2013. This may result either from removal of dissolved fraction by precipitation as insoluble cinnabar in low-oxygen conditions in Oslonino or absorption on abundant organic matter in the sediments. Methylation of dissolved mercury is not excluded, although used procedure would not indicate that directly.

Elevated Hg_{TOT} concentration in sediments was observed in Ośłonino during the plankton blooms and may be connected with the delivery of mercury assimilated by phytoplankton from the water column. Additionally, Ośłonino represents an enclosed bay and is a subject to shoring of decaying filamentous algae transported with the currents from the vast areas of the Puck Bay. This results in delivery of mercury accumulated by those algae and its slow release during algae decomposition, which would naturally extend a mercury bound to humic material pulse coming from primary production. Phytoplankton blooms in this area started in April–May in 2012 and 2013 (Beldowska and Kobos 2016). A maximum increase of Hg_{TOT} concentration in sediments during spring bloom in more sheltered waters close to Ośłonino is observed in July 2012 together with occurrence of Hg_H and increase of Hg_F . Mercury included in alive or relatively fresh phytoplankton cells is associated with labile organic matter and is therefore extracted as fraction Hg_F , which can be further transformed into Hg_H in sediments, during early diagenesis. If the plankton material enters the sediments already in decomposed form, then mercury will be present in Hg_H fraction. Also, during autumn algal bloom—November 2012, slightly elevated Hg_{TOT} was noted. The highest values however are observed at the end and after the blooms, while the organic matter decay takes place together with intensified bacterial production. Such situation is clearly visible in August–September 2012, when especially high Hg_H contribution instead of Hg_R which dominates in the other periods (Fig. 5). Input of dead phytoplankton after massive *Mesodinium rubrum* bloom in July 2012, *Bacillariophyceae* in 2013, and *Dinophyta* bloom in

May 2013 (Beldowska and Kobos 2016) caused increased contribution of Hg_F and Hg_H fractions. Heterotrophic microorganisms (bacteria and fungi) are responsible for decomposition up to 90% of net primary production. In marine sediments, rate of organic matter decay under different redox conditions depends mainly on its age and origin, thus chemical composition of organic matter (Kristensen et al. 1995). Such situation is observed in Ośłonino in September 2012. Increased total number of bacteria in sediment samples, along with decreased values of redox potential (Table 2) in this site, indicates that conditions in sediment are hypoxic or anoxic. Under such conditions, sulfate reduction plays key role in the mineralization of organic matter (Parkes et al. 1989) and presence of mobile mercury fractions could cause mercury methylation (Avramescu et al. 2011). The highest contribution of Hg_H and a decrease in Hg_R concentration is observed at that time. This is typical during the decomposition of organic matter—a release of mercury from mobile fractions (Hg_F and Hg_H). This mercury may then be observed in dissolved fraction, methylated, or may be bound to sulfides, creating insoluble cinnabar if available sulfide ions are present in pore waters. Sulfides appear in the sediments due to reduction of sulfate by bacteria. According to Schartup et al. (2014), cinnabar formation may compete with methylation—it seems to be the case in this area, due to the fact that Hg_S fraction contribution, representing mercury sulfide and mercury bound to other metal sulfides, increases when dissolved fraction disappears. It can be expected that the equilibrium between dissolved, mobile and sulfidic fractions should be highly related to the abundance of bacteria and redox potential. However, no significant correlations were observed between those

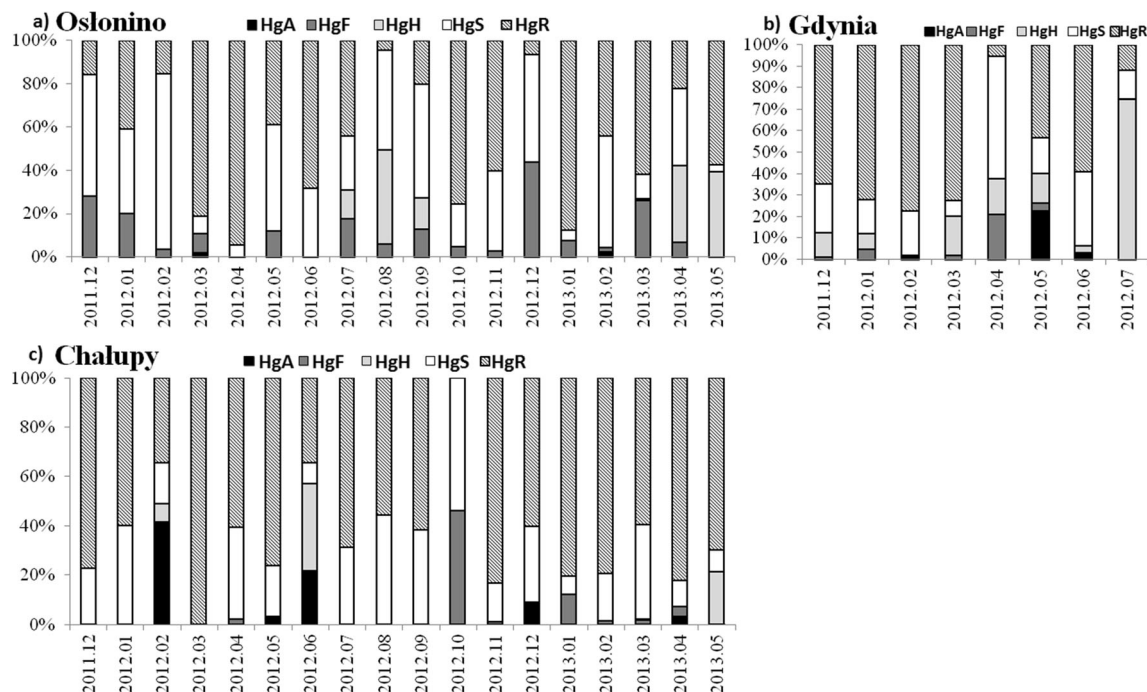


Fig. 5 Seasonal variability of mercury speciation in a Ośłonino, b Gdynia, and c Chalupy

parameters and respective mercury forms. This can be attributed to the dynamic changes in the surface sediments in the study area. It seems that the lack of sediment accumulation in the coastal sediments and transport of fine fraction out of the area towards the accumulation basins is too fast to be reflected in monthly resolution measurements.

A second important factor influencing mercury load in this site is the sea level change. The phenomena is induced by strong winds, which can affect mercury cycling via two processes: Long-lasting winds from one direction can cause an inflow of waters to the eastern part of the Puck Bay, not only inundating the beach but also transporting considerable amount of mercury-rich fine particles from deeper areas; beach inundation and wave action are responsible for the second process—land abrasion and enhanced cliff erosion could additionally contribute to terrestrial load of mercury associated with clay minerals. Such scenario—an increase of mercury concentration in coastal sediments—is observed in Ośłonino in January 2012 when exceptionally high sea level was recorded (IMGW PIB 2015; Bełdowska et al. 2016b). Transportation of abrasive material is reflected in elevated Hg_R contribution during this period, as the residual mercury fractions can be identified as connected with clay minerals.

Another phenomena influencing mercury distribution occurring at this site is icing of the water column. A single event of icing reaching to the bottom of the reservoir was observed in Ośłonino in February 2012. The changes in salinity were reflected in decreased concentration of chloride ions and sulfates (Table 2). On this station, winter icing led to hydrogen sulfide occurrence and hence to domination of stable mercury fraction— Hg_S . Both during the icing events in February 2012 and in the period from December 2012 to January 2013, there is a reduction of Hg_R and domination of Hg_S . Total mercury concentrations at this time decreased, probably as a result of separation of coastal sediments from atmospheric air and material transport from the land. After the thaw, the Hg_{TOT} concentrations increased slightly and Hg_R fraction prevailed again, what could be a result of transportation of land material with the melting snow runoff.

3.3.2 Marine area with limited land input

The area of Chałupy station is in a complete opposition to the Ośłonino station. Chałupy is the most remote from anthropogenic influence among all the sampling sites; it is not affected with land input and currents transfer the decaying matter to the other areas of the Puck Bay. In the marine station of Chałupy, mercury concentrations ranged between 0.1 and 0.8 ng g⁻¹ (median value 0.4 ng g⁻¹), which is a result of limited land and anthropogenic influence. The lowest Hg_{TOT} concentrations among all the sampling stations were observed at this site (Fig. 2), which is mainly influenced by a very narrow strip of land separating it from the Baltic Sea open waters. The location

of this station (Fig. 1) suggests that there is only a minor influence of surface runoff (Jędruch et al. 2017). Additionally, low levels of organic matter and low contribution of fine fraction of sediments (Table 2) does not foster mercury accumulation, as mercury is characterized with high affinity for organic matter (Wallschlager et al. 1996; Jackson 1998).

Changes in mercury concentrations and speciation are relatively small in this area when comparing to Ośłonino and Gdynia. Small increase of Hg_{TOT} concentration in sediments during spring bloom was observed (May–June 2012 and 2013). In May 2013, large *M. rubrum* bloom was recorded in Chałupy (Bełdowska and Kobos 2016). This was accompanied by an increase of Hg_A fraction contribution in sediments. In June that year, when the bloom continued, Hg_A contribution remained at the same level and additionally Hg_H appeared, most likely originating from decomposed plankton material or transformed from Hg_A , which amounted up to 50% contribution of labile mercury forms. Hg_A represents mercury absorbed on the plankton cells and loosely associated with organic matter. Similar phenomenon may be observed in April/May 2013 (Hg_A followed by Hg_H , respectively), during *Bacillariophyceae* bloom (Bełdowska and Kobos 2016). Autumn bloom also caused mobile mercury contribution increase in fraction Hg_F in October, which suggests stronger mercury binding in plankton blooming at that time or its further decomposition. As a result in summer 2012 in Chałupy, organic matter decomposition processes were observed (decreasing organic matter contents in comparison to organic matter inflow from March to June 2012), which leads to oxygen consumption, clearly visible in lowering redox potential values. This may enable anaerobic bacteria growth in examined site, including sulfate reducing bacteria which are considered the principal mercury methylators in natural anaerobic sediments (King et al. 2000; Barkay et al. 2003). Consequently, in Chałupy, no mobile mercury fractions are observed in summer period of 2012 (from July to September). Very low and negative values of the redox potential were observed in July and August 2012 in Chałupy, what indicates that methylation of mercury can take place at this site.

Stable species of mercury dominated at this station, and residual fraction Hg_R prevailed, reaching on average 50% through the study period. At the same time, the most mobile fraction Hg_A amounted up to 6%. During the whole study period, the Hg_R fraction dominated at this site and in a lesser extent Hg_S .

The situation changed only in two cases: in February 2012 when icing occurred together with highly intensified bacterial production. The replacement of sulfidic fraction, significant increase of soluble Hg_A with simultaneous occurrence of hydrogen sulfide accompanied by Eh drops (Table 2), took place during this icing period. In anaerobic environments, mercury bound with sulfides (Hg_S) may be transformed into polysulfides with the releases of mercury in labile forms— Hg_A (Bełdowski et al. 2009). In deeper layers of the

sediments, sulfates are consumed in organic matter decomposition processes and thus are reduced to sulfides. Part of those sulfides may precipitate to sediments as mercury sulfides, while the rest gets into surface sediment layers where it undergoes oxidation to sulfates. An increase of soluble fraction suggests methylation of mercury there. Competing effects of excess sulfates (Schartup et al. 2014) should be reflected by the conversion of mercury to Hg_S fraction, which was not observed.

Also, an increase of mobile Hg_F fraction was observed in Chałupy in October 2012. At this time, only Hg_S and Hg_F were observed at this station, together with relatively high bacterial production, reflected in bacteria biomass. This situation could result from ongoing mineralization processes of the organic matter remaining after the summer blooms.

3.3.3 Terrestrial area close to anthropogenic mercury sources

The station in Gdynia could be assumed as moderate while compared to marine station of Chałupy and the enclosed bay of Osłonino. Total mercury concentrations in Gdynia ranged from 0.6 to 5 $ng\ g^{-1}$, with a median value of 1 $ng\ g^{-1}$. Obtained results are lower than in Osłonino and higher when comparing with Chałupy station. Just like in Chałupy and Osłonino, among the stable mercury species in Gdynia, Hg_R fraction prevailed (49%). Among mobile fractions, humic acid bound (Hg_H) dominated (on average 60% of mobile mercury) and Hg_A amounts to 3% on average. It is characterized by more terrestrial influence. Surface runoff is more efficient in elution of loosely bound mercury, associated with fulvic acids, which was observed, i.e., on Elbe river floodplains (Wallschläger et al. 1998). The station in Gdynia can be also affected by algal blooms like the Osłonino station and is located in the area of the strongest anthropogenic activity among all the sampling sites chosen for this study. Yet, the relatively low concentration of mercury in this area may be caused by large water volume exchange, as the station is located in an area under the influence of Gdańsk Basin open waters. The sampling campaign in Gdynia was shorter than in other stations; however, during 12 months, several events influencing mercury cycle were observed, including abrasion, icing, bacterial production, and phytoplankton blooms.

A constant increase of Hg_{TOT} concentrations in sediments was observed since the spring bloom, which started in June 2012. At the same time, the bacterial production is highly intensified and increased contribution of soluble and bioavailable Hg_A is observed. In July, the concentrations of Hg_{TOT} remained elevated, yet the speciation has changed significantly. Mercury bound with fulvic acids is prevailing reaching up to nearly 80% of total mercury, while Hg_S and Hg_R remain on the level of 10%. At the same time, the number of bacteria decreased rapidly, what may indicate that the elevated mercury concentrations are a result of decaying both phytoplankton

and bacterioplankton, which assimilated the bioavailable mercury in former weeks.

Also, sea level change, resulting in land abrasion, enhanced cliff erosion and potential deep sediment transport due to substantially higher wave action, probably additionally contributed to an observed increase of mercury concentration in coastal sediments in Gdynia in January 2012 when exceptionally high sea level was recorded (IMGW PIB 2015; Bełdowska et al. 2016b). At this period, the highest total mercury concentrations are observed, and similarly to Osłonino, the abrasive material, associated with clay minerals, mainly contributes of Hg_R —reaching up to 80% of total mercury.

Also, ice cover occurs in Gdynia in February 2012 and similarly like in Osłonino, the total mercury concentration in sediments is lower, probably due to the cutoff from the surface runoff from the land. As for the mercury speciation, the pattern does not reflect the changes observed at other stations. Stable Hg_R remains at the same prevailing level in Gdynia, while in Osłonino, Hg_S is dominant and in Chałupy mobile mercury fractions reach 50% of total mercury, which is the highest labile mercury contribution at this site.

4 Conclusions

Nowadays, when anthropogenic mercury emissions are limited, the importance of reemission and remobilization of mercury increases. It is especially significant in the coastal zone, in areas away from large industrial facilities. In such areas, spatial and seasonal mercury concentration and speciation variability were observed in surface sediments.

Depending on environmental specificity and local mercury sources, the patterns of mercury speciation varied between the study sites. In highly dynamic, open waters of remote marine station in Chałupy the changes were the least, probably due to mixing of the surface sediments. In Gdynia, the changes were moderate, and in semi-closed Osłonino, every weather or climatic event was reflected in the sediments. It appears that plankton blooms and a subsequent microbial decomposition of organic matter are the most important factor influencing mercury concentrations and transformations in all studied areas. However, in the areas unaffected with massive algal blooms (Chałupy and Gdynia), the events of water column icing seem to be the most important drivers changing mercury speciation.

Also, extreme events, as major storms and sea level rise, contribute to an increase of mercury concentration in surface coastal sediments. Influence of extreme events, such as sea level rise due to strong winds, and enhanced cliff erosion caused by storms were reflected in the speciation pattern in surface sediments. This may be important in terms of observed global climate change, which in the Baltic Sea area

may cause further decrease of icing and raise of extreme events frequency (IMGW PIB 2015).

According to the results of this study, the coastal areas could be affected with changing environmental conditions. Especially, enclosed areas can be affected with the weather, and thus climate changes, as all the transformations ongoing in such places are condensed in comparison to more dynamic environments like open waters. In this respect, the whole Baltic Sea should be considered as more susceptible to ongoing climate changes than the open seas and mercury transformations connected with that process.

Funding information This study has been performed within the framework of the Polish National Science Centre Project: No. 2011/01/B/ST10/07697.

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