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Chapter

Mercury Cycling in the Gulf of Gdańsk (Southern Baltic Sea)

Dominika Saniewska

Abstract

The most efficient way of mercury (Hg) transport to the Gulf of Gdańsk was river runoff. Therefore, hydrological conditions were the most important factors controlling the inflow of Hg to the sea. The second most important Hg source in the Gulf was atmospheric deposition, which transported seven times smaller load than rivers. The Hg wet deposition dominated in the warm season, while during the heating season the predominant was dry deposition of mercury. The Hg source, which should not be neglected during the creation of the mass balance of Hg in aquatic ecosystems, was the coastal erosion. In the Gulf of Gdańsk, it accounts for 6% of the Hg load reaching the sea. The main sink of Hg was bottom sediments. Other important processes that reduced the Hg load in the Gulf water were re-emission of Hg to the atmosphere and export of this metal to the Baltic Proper. The mass balance of mercury in the Gulf of Gdańsk indicated that a larger load of this metal flowed into the Gulf than left it. Consequently, the Gulf of Gdańsk should be treated as a cleansing zone for the Baltic Proper.

Keywords: mass balance, sea, river, atmosphere, sediments, organisms

1. Introduction

Mercury (Hg) is considered to be one of the most toxic metals found in terrestrial and aquatic ecosystems around the world. This is due to the specific nature of this element—volatility, persistence, and strong toxicity of its organic forms. It has no known essential biological function. Hg is toxic in every form; however, its toxicity depends mainly on its chemical form. The most dangerous form of Hg is methyl mercury (MeHg). Hg has neurotoxic, mutagenic, cytotoxic, nephrotoxic, and allergenic properties. It can also affect the functioning of the muscular system and many enzymes and proteins. Mercury is particularly dangerous for pregnant women because MeHg can easily pass through the placenta via active transport by amino acid carriers, causing embryotoxic and teratogenic effects in the fetus [1]. The aquatic environment is particularly sensitive to Hg contamination because this metal accumulates and biomagnifies with increasing trophic level [2]. Consequently, the Hg concentration in tissues of fish, birds, and water mammals can be even 100,000 times higher than in surrounding water [2]. The most common cause of Hg poisoning is consumption of predatory fish and seafood with high levels of this metal in its tissues [2]. Therefore, an understanding of mercury cycling in the aquatic environments is of fundamental importance, especially in
coastal areas of densely populated countries which are usually exposed to pollutants from various human activities.

The Gulf of Gdańsk is located in the southern part of the Baltic Sea (Figure 1). Its northern boundary is the straight line connecting Cape Rozewie (54°50’N, 18°20’E) with Cape Taran (54°58’N, 19°59’E). The Gulf of Gdańsk (average depth 50 m, maximum depth 118 m) is often considered a separate natural region [3, 4]. Its area is 4940 km², while the volume of water is estimated at 291.2 km³ [4, 5]. The hydrological conditions in the Gulf of Gdańsk are largely influenced by river inflow, of which the Vistula is the most important. It is the longest river that flows into the Baltic Sea and the second, after the Neva, in terms of the size of the catchment [6]. The Vistula catchment (194 thousand km²) constitutes over 88% of the whole drainage basin of it of Gdańsk (220 thousand km²) [4]. Therefore, the Gulf is considered as an important transition between land and sea. In addition, urbanized and industrialized regions within its coast affect the level of pollutants in the sea.

Investigations performed in the 1970s and 1980s revealed that the Gulf of Gdańsk was one of the most polluted water bodies in the world [7, 8]. However, the latest research indicates that the Gulf of Gdańsk is not exceptionally contaminated, and contaminant concentration in the water generally indicates a good environmental state [9]. Such considerable differences between results within the last 40 years were the effect of both analytical errors and reduction of Hg load introduced from anthropogenic sources [6]. However, this situation has caused numerous studies of environmental pollution being carried out in this area for many years, including those relating to mercury. This enabled the creation of a large database containing the results of determinations of this metal in practically all the abiotic and biotic matrices. Therefore, the objectives of this study were to construct a multi-year mass balance of Hg in the Gulf of Gdańsk. This mass balance was used to identify and better understand the dominant mercury sources and sinks in the gulf and can provide an initial basis for future research in this region.

Figure 1.
The map of the study area.
2. Methods of mass balance calculations

The mass balance of mercury in the Gulf of Gdańsk was constructed on the basis of the analysis of Hg loads in precipitation, aerosols, river water, groundwater, sea water, cliff and marine sediment as well as in organism samples. In order to balance the loads of Hg in the gulf, it was assumed that the main sources of this metal were atmospheric deposition, river water, and coastal erosion, while the factors having impact on the decrease of Hg concentration in sea water were re-emission of gaseous Hg to the atmosphere, sedimentation processes, and exchange of water between the Gulf of Gdańsk and the Baltic Proper.

2.1 Sampling

Aerosols and precipitation samples were collected at a station located in Gdynia (Figure 1), at a distance of about 500 meters from the sea (54°30’N, 18°32’E). A detailed description of the station can be found in the publications [10, 11]. Precipitation samples were collected from August 2008 to May 2009 and from January to December 2012. In the first period, samples were collected using a bulk collector composed of a Teflon funnel of 20 cm diameter connected directly to a borosilicate glass bottle. In the second period, precipitation samples were collected using an automatic collector of wet deposition. After collection, samples were stored at −20°C until analysis. In each case, information about the amount of precipitation was obtained. Detailed information about sampling and storage methods can be found in the publications [11, 12].

Aerosol samples were collected from December 2007 to December 2008 in 24 h cycles using open-faced Teflon filter packs on 47 mm glass-fiber filters. Samples were then stored at −20°C until analysis. The collection and storage methods were described by Bełdowska et al. [10].

River water samples were taken from cross sections close to the mouth: the Vistula (12 km from mouth), the Reda (1.0 km from mouth), the Zagórska Struga (0.8 km from mouth), the Plutnica (0.4 km from mouth), the Kacza River (0.1 km from mouth), and the Gizdepka (0.6 km from mouth) (Figure 1). Sampling took place between 2008 and 2016 (with gaps). In each case, information about river flow was obtained. Water samples were collected directly into acid-washed borosilicate vials with Teflon screw cap. Samples were stored at 4°C until analysis. Detailed information on characteristics of the rivers as well as sampling and storage methods can be found in the publications [12–17].

The Hg concentration in groundwater was described by Szymczycha et al. [18]. The research was conducted in the Puck Bay (part of the Gulf of Gdańsk) in 2009–2010. Groundwater samples were collected directly into acid-washed borosilicate vials with Teflon screw cap and stored at 4°C until analysis. Detailed information on characteristics of the research area and sampling and storage methods can be found in the publication [18].

Information about Hg concentration in cliff deposits was presented in the work by Bełdowska et al. [12] and Kwasiagroch et al. [19]. Samples were collected in two periods: 2011–2014 [12] and 2016–2017 [19]. Materials within the colluvium were collected from three cliffs located on the west part of the Gulf of Gdańsk (Orłowo, Mechelinki and Osłonino cliffs) (Figure 1). Detailed information about sampling and storage methods can be found in the publications [12, 19].

Seawater samples were collected between 2006 and 2016 (with gaps) [14, 15, 20–22]. As part of these studies, samples were taken from various regions of the Gulf of Gdańsk (coastal and offshore areas) as well as from different depths.
(surface water and profiles). Water samples were collected directly into acid-washed borosilicate vials with Teflon screw cap. Samples were stored at 4°C until analysis. Detailed information on characteristics of the stations as well as sampling and storage methods can be found in the publications [14, 15, 20–22].

The Hg concentration in sediments from several areas of the southern Baltic Sea was described by Bełdowski et al. [23], Jędruch et al. [24], and Kwasigroch et al. [19]. Samples were collected in the periods 1999–2002 [23], 2011–2013 [24], and 2016–2017 [19]. Detailed information about sampling and storage methods can be found in the publications [19, 23, 24].

Information about Hg in marine organisms was obtained from the literature [25–33]. The Hg concentration in phytoplankton was measured by Bełdowska and Kobos between 2011 and 2013 [25, 26]. Phytoplankton samples were collected with 20 μm nets and then stored at −20°C until analysis. At the same time, zooplankton samples were collected by Bełdowska and Mudrak-Cegiołak [27]. The samples were collected vertically using a zooplankton net (mesh size 50 μm). The collected samples were transported to the laboratory in life-supporting conditions and after about 24 h (required for the acclimatization and defecation of the zooplankton) live zooplankton was separated from other material using the phototaxis phenomenon. Samples were then stored at −20°C until analysis. Detailed information about sampling and storage methods can be found in the publications [25–27].

The Hg concentration in macrophytobenthos was described by Bełdowska et al. [28]. Benthic plant samples were collected along the Gulf of Gdańsk coastal zone in the years 2006–2012. The collected material was taken to the laboratory, cleansed of epiphytes and organic and mineral particles, then rinsed in distilled water, and then stored at −20°C until analysis.

Information about Hg concentration in benthic macrofauna was presented by Jędruch et al. [29, 30] and Bełdowska et al. [31]. Samples were collected between 2011 and 2013 using a manual Van Veen grab sampler. In order to separate the benthic organisms, samples of marine sediments were sieved through a 0.5 mm mesh. Live biological material was placed in containers with sea water in situ and transported to the laboratory where they were stored at −20°C until analysis.

The Hg concentration in herring, sprat, and cod from the southern Baltic Sea was obtained from the study by Polak-Juszczak [32]. Samples were collected from 1994 to 2003. Fish were stored at −20°C until analysis.

Information about Hg concentration in gray seals (Halichoerus grypus) was presented by Bełdowska and Falkowska [33]. The studies were conducted in the Polish coastal zone of the Baltic Sea during the years 2001–2011. Seal’s tissues were obtained from dead individuals found along the coast.

2.2. Chemical analysis

The Hg concentrations in solid samples were determined via pyrolysis with the atomic absorption technique using a direct mercury analyzer [34]. This technique did not require any sample preparation (e.g. extraction/digestion) which would pose a risk of contamination. The analysis of certified reference materials produced both satisfactory recovery and precision.

Water samples for mercury analysis were oxidized by the addition of BrCl and pre-reduced with hydroxylamine hydrochloride solution 1 h prior to analysis by the cold vapor atomic fluorescence technique, according to USEPA method 1631 [35]. Quality control procedures for water samples included blanks, and water spiked with mercury nitrate produced adequate rates of precision and recovery [11].
2.3. Calculations

The Hg concentration in precipitation was used to calculate wet deposition fluxes:

\[ F_{\text{wet}} = C \times R \]  

(1)

where \( F_{\text{wet}} \) is the wet deposition flux (ng m\(^{-2}\)); \( C \) is the Hg concentration in precipitation (ng dm\(^{-3}\)); and \( R \) is the amount of precipitation (mm = dm\(^3\) m\(^{-2}\)). The Hg load introduced to the Gulf of Gdańsk with wet deposition was calculated by multiplying the wet deposition flux by the area of the Gulf of Gdańsk (4940 km\(^2\)).

The Hg dry deposition fluxes were calculated using the formula previously described by Seinfeld and Pandis [36]:

\[ F_{\text{dry}} = C \times V_d \]  

(2)

where \( F_{\text{dry}} \) is the dry deposition flux of Hg (pg m\(^{-2}\) s\(^{-1}\)); \( C \) is the Hg concentration in aerosols (pg m\(^{-3}\)); and \( V_d \) is the deposition velocity (m s\(^{-1}\)). Deposition velocity was not measured during sampling. Therefore, this value was taken from the literature [37, 38] and was 0.005 m s\(^{-1}\). The Hg load introduced to the Gulf of Gdańsk with dry deposition was calculated by multiplying the dry deposition flux by the area of the Gulf of Gdańsk and time of sampling.

The Hg concentration in river water at cross sections close to the river mouth was used to calculate annual Hg load transported into the sea:

\[ L_r = C \times Q \]  

(3)

where \( L_r \) is the Hg load (kg s\(^{-1}\)); \( C \) is the Hg concentration in the river water (μg m\(^{-3}\)); and \( Q \) is the water flow during sampling (m\(^3\) s\(^{-1}\)). The annual Hg load was calculated assuming linear variability in time periods between measurements [39].

The Hg load associated with coastal erosion was calculated based on information presented by Bełdowska et al. [12]. The Hg load form the 1 km long section of the cliff (kg year\(^{-1}\)) was multiplied by the total length of the cliff sections in the area of the Gulf of Gdańsk (36 km).

The Hg load transported to the sea by the seeping groundwater was estimated by multiplying the Hg concentration in groundwater measured in the Puck Bay [18] by the submarine groundwater discharge rate to the Gulf of Gdańsk (0.07 km\(^3\)) [40].

Taking into account the annual air-water flux estimated by Wängberg et al. [41] and data presented by Marks and Bełdowska [42], the Hg load re-emitted from the Gulf of Gdańsk to the atmosphere was calculated.

The yearly Hg sedimentation flux presented by Bełdowski et al. [23] was used to calculate the load of mercury deposited in the Gulf of Gdańsk sediments.

Based on the model calculations [43], the export flux of water from the gulf was estimated. This value was assumed to be equivalent to the volume of water introduced into the gulf by rivers. The outflow of Hg from the Gulf of Gdańsk was calculated by multiplying this volume of water by the Hg concentration measured in the profile at the Gdańsk Deep [20, 21].

The Hg load in the Gulf of Gdańsk water was calculated by multiplying the median values of the Hg concentration in the open water of the gulf [20, 21] and the volume of water in the gulf [4, 5].

Based on the mean Hg concentration in the two types of sediment (sandy and silty), their wetness [24], density [44], and surface of the bottom of each type, the load of Hg deposited in the upper layer of the sediments (0–5 cm) in the Gulf of Gdańsk was estimated.
The amount of Hg bound to the phytoplankton was estimated by multiplying the median of the Hg concentration in phytoplankton in the coastal zone of the Gulf of Gdańsk [25] by the mean phytoplankton biomass in the Gulf [26, 45] and the volume of the water to a depth of 20 meters (where phytoplankton occurs most abundantly).

Taking into account the median of the Hg concentration in zooplankton in the coastal zone of the Gulf of Gdańsk [27], the mean zooplankton biomass in the Gulf [45] and the volume of water in the Gulf [4, 5], the Hg pool in zooplankton was estimated.

The calculation of the Hg load accumulated in macrophytobenthic plants was carried out based on the research conducted by Bełdowska et al. [28] (the Hg concentration in macrophytobenthos), Saniecki and Zalewska [46] (biomass of particular macrophytobenthic plants from the Gulf of Gdańsk) and the area on which these plants occur [4].

The amount of Hg accumulated in macrozoobenthos in the Gulf of Gdańsk was estimated based on the research conducted by Jędruch et al. [29, 30] (the Hg concentration in macrozoobenthos) and Włodarska-Kowalczuk et al. [47] (biomass of particular macrozoobenthic organisms from the Gulf of Gdańsk) and the area on which these organisms occur [4]. Jędruch et al. [29, 30] observed that the macrozoobenthos occurred most abundantly up to a depth of 80 m as well as the Hg concentration in macrozoobenthic organisms was dependent on the type of bottom. Therefore, the bottom area of the Gulf of Gdańsk to a depth of 80 m (3350 km$^2$) was divided into two types: bottom covered by macrophytobenthos (100 km$^2$) and bottom not covered by macrophytobenthos (3250 km$^2$) [Jędruch, personal comm.].

The fish resources of the Gulf of Gdańsk have not yet been reliably estimated. However, information about the biomass of the most common caught fish was available. Therefore, the Hg load exported from the sea with the fish was calculated by multiplying the median values of the Hg concentration in the particular species of the most commonly caught fish [32, 33] and the biomass of these fish [48].

Taking into account the median Hg concentration in the muscle [33], the wetness of the tissue (55%), the average weight of the gray seal (250 kg), and the size of population in the Gulf of Gdańsk [49], the load of Hg accumulated in the gray seals was estimated.

### 3. External sources and sinks of mercury in the Gulf of Gdańsk

An important source of mercury in the sea is atmospheric deposition. The Hg load introduced into the Gulf of Gdańsk with wet and dry deposition was 17.7 kg year$^{-1}$ and 9.5 kg year$^{-1}$, respectively (Figure 2) [10–12, 16]. The inflow of Hg with precipitation dominated in the warm season (May–September), while during the heating season (October–April) dry deposition of mercury associated with aerosols was predominant [10, 11, 16]. The key role in Hg dry deposition was played by the concentration of mercury bound in aerosols, while the particle deposition velocity was of marginal significance [10, 16]. Hg wet deposition flux depended mainly on the amount of precipitation. There was a significant statistical relationship between Hg wet deposition flux and the Hg concentration in the precipitation, only in the warm season [11, 16].

Another important source of Hg in the sea is riverine input. The average annual Hg load carried out into the Gulf of Gdańsk by rivers was estimated to be 200 kg (Figure 2) [12–16]. The riverine input of Hg to the Gulf varied between 180 and 220 kg per year [12–16]. A total of 99% of Hg carried out by the rivers was transported by the Vistula (average water flow 1047 m$^3$ s$^{-1}$), the longest river that flows into the Baltic Sea [6]. The small rivers (average water flow < 5 m$^3$ s$^{-1}$) provided about 2 kg of Hg [13, 15, 16]. The Hg load transported by rivers to the
sea depended on the amount of precipitation and retention capacity of the catchment. In areas of natural character, only 10–30% atmospheric Hg deposited to the catchment outflow from the soil to the river [13, 16, 50, 51]. However, in areas where the catchment was transformed by humans (fields and urban and industrialized areas), Hg outflow was considerably greater than in the natural areas and may have reached up to 65% [13, 16, 52–54]. Saniewska and colleagues [13] showed that in urbanized and agricultural areas, river water was two to three times more polluted with mercury than in the forests. This was influenced not only by the increased Hg outflow from the catchment, but also by the inflow of Hg from anthropogenic sources (e.g. combustion of fossil fuels and point sources). In this area, Hg is emitted into the atmosphere. Consequently, more Hg could be deposited in the catchment and then could be washed out to river water [13–16]. The Hg load transported by rivers to the sea depended on the river flow [13–16]. This was particularly visible during floods, downpours, and thaws, when river flow was much higher than the average value. At that time, water pours out of the riverbed, which causes local flooding and increased soil erosion [13–16]. During high flow, the Hg daily outflow from the catchment could increase over tenfold than during the period with average [13–16]. This was clearly visible during the Vistula flood of 2010. During the month of the flood, over 1197 kg of mercury flew into the Gulf of Gdańsk, which accounted for 75% of the Hg load transported through 2010 with the Vistula water [14]. During the flood, a very large load of dissolved mercury (around 314 kg) reached the sea. This can have a negative impact on the marine environment, especially on organisms inhabiting river estuaries [14].

An important source of mercury in the Gulf of Gdańsk, usually neglected during the creation of the mass balance of Hg in aquatic ecosystems, is the coastal erosion. Beldowska et al. [12] estimated that the 1-km long section of the cliff

Figure 2.
The mass balance of mercury in the Gulf of Gdańsk.
was responsible for the introduction of 0.4 kg of mercury into the sea every year. The total length of the cliff sections in the area of the Gulf of Gdańsk is 36 km. This allows estimating that due to the coastal erosion about 14.3 kg Hg year\(^{-1}\) was transported to the sea (Figure 2) [12]. A large Hg load introduced through the cliff abrasion into the sea as well as the labile form of mercury, which predominated in the material [19], makes it necessary to understand the consequences of the process for the marine food chain.

In recent years, attention has been paid to the submarine groundwater discharge as a source of mercury in the seas and oceans. The average dissolved mercury concentration in the seeping groundwater was 0.6 ng dm\(^{-3}\) [17]. Submarine groundwater discharge rate to the Gulf of Gdańsk was assessed at 0.07 km\(^3\) [40]. The Hg load to the Gulf was estimated to be 42 g year\(^{-1}\). This value is negligible in the Hg mass balance in the Gulf of Gdańsk. This is due to the fact that in this case, groundwater was characterized by lower concentrations of Hg than the sea water [17].

Mercury in the sea may also come from point sources such as municipal wastewater treatment plants, industrial plants or fish farms, etc. In the case of the Gulf of Gdańsk, point sources located in the coastal zone were of little importance in the transport of mercury to the sea [55]. This was also confirmed by HELCOM [6]. However, it should be emphasized that contaminants transported this way may adversely affect adjacent ecosystems.

Some part of Hg present in the sea can be re-emitted into the atmosphere. Wångberg et al. [41] estimated that in the southern Baltic, an annual re-emission flux of Hg was equal 9.5 µg m\(^{-2}\) year\(^{-1}\). It was calculated that approximately 47 kg Hg may be re-emitted from the Gulf of Gdańsk every year (Figure 2). This value was 1.7 as high as Hg atmospheric deposition; however, it could still be underestimated. The value of the re-emission flux depends on the weather conditions [41, 42, 56, 57]. The research was conducted in calm conditions, while stormy weather increased emission of both gases and aerosols from the water to the atmosphere. Therefore, detailed studies are necessary to allow an accurate estimation of the re-emission flux of Hg.

Sediments are important sink of Hg in the sea. According to Beldowski et al. [23], the net mercury input, calculated on the basis of sedimentation rate and concentration in the uppermost sediments, was estimated at 1.3 ng cm\(^{-2}\) year\(^{-1}\). It follows that every year, about 64 kg of mercury was retained in the sediments (Figure 2).

On the basis of the water balance in the Gulf of Gdańsk, the export flux of Hg from the Gulf to the Baltic Proper was estimated. Based on the model [43], it was calculated that the annual export of water from the Gulf of Gdańsk was about 32 km\(^3\). This value was obtained from the difference between the outflow of water from the Gulf to the Baltic Proper and inflow of water from the Baltic Proper to the Gulf. Considering the Hg concentration measured in the profile at the Gdańsk Deep [20, 21], it was estimated that the export of Hg from the Gulf of Gdańsk to the Baltic Proper was about 58 kg year\(^{-1}\) (Figure 2). It follows that the Gulf was a source of Hg to the sea.

Herring (Clupea harengus), sprat (Sprattus sprattus), cod (Gadus morhua), and flounder (Platichthys flesus) are the most frequently caught fish in the Polish part of the Baltic Sea (Table 1) [48]. Of the fish caught, the lowest Hg concentration was measured in the sprat, and the highest in flounder (Table 1) [32, 33]. The Hg load associated with the caught fish was dependent on the biomass of fish. Approximately 52,796 tons of fish were caught annually in the Gulf of Gdańsk [48]. The highest Hg load was accumulated in the sprat (which accounts to 78% of the total fish biomass taken out), which constituted 61% of the Hg being carried out of the sea with fish (Table 1). On the basis of these data, the load of Hg exported from the sea within caught fish was estimated at 937 g (Figure 2).
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4. Mercury in different environmental compartments in the Gulf of Gdańsk

The surface water of the offshore part of the Gulf of Gdańsk was characterized by low Hg concentrations (< 2 ng dm$^{-3}$), which was typical for the Baltic Proper [13–15, 20–23, 58, 59]. The major factor influencing mercury distribution in the water column was suspended matter. Therefore, the Hg concentration was higher in the areas of the density stratification (thermo- and halocline) and in the layer of maximum chlorophyll $a$ concentration than in surface water [20, 21]. Higher concentration of Hg in the water in comparison with the offshore water was measured in the vicinity of the coastline—near the industrialized shore as well as in the area of the river mouths; however, the median of the Hg concentration in those areas was still relatively low (< 8 ng dm$^{-3}$) compared to coastal zones in different parts of the world [60, 61]. Based on the median values of the Hg concentration in the open water of the Gulf of Gdańsk (1.7 ng dm$^{-3}$) and the volume of water in the Gulf (291.2 km$^3$) the total amount of Hg in this water body was estimated at 495 kg (Figure 2).

In the Gulf of Gdańsk, 4–79% (average 27%) of Hg in sea water was bound to suspended matter [15, 20–22]. This is a relatively high value compared to ocean water, where suspended mercury usually constitutes less than 20% [61, 62]. This is due to the specific properties of the Baltic Sea—low salinity and high content of organic matter (both DOC and POC) in the sea water [63, 64]. Therefore, in this region, suspended particulate matter (SPM) plays a particularly important role in Hg cycling—it acts as the carrier for mercury in the marine environment [20–22]. Organic matter transports Hg toward greater depths and accelerates its sedimentation to the benthic sediments. Taking into account the total amount of Hg in the Gulf of Gdańsk (495 kg) and percentage of Hg bound to suspended matter (27%), it was estimated that about 134 kg Hg in the Gulf was presented in the particulate form.

According to Jędruch et al. [24], the Hg concentration in the sediments varied in a wide range (1.0–325.3 μg g$^{-1}$). However, this large difference resulted from the properties of the sediments—silty sediments were characterized by much higher Hg concentration (98.8 ng g$^{-1}$) than sandy one (7.3 ng g$^{-1}$) [24]. Based on the mean Hg concentration in the two types of sediments, the surface of the bottom and density of each (Table 2), it was estimated that the load of Hg deposited in the upper layer of the sediments (0–5 cm) in the Gulf of Gdańsk was 11,595 kg (Figure 2). It is worth mentioning that 88% of this load was deposited in silty sediments. Therefore, bottom sediments should be considered as the important Hg reservoir in the sea.

Due to the fact that mercury accumulates and biomagnifies in the marine trophic chain, aquatic organisms should also be considered as Hg reservoir. The median of the Hg concentration in phytoplankton in the coastal zone of the Gulf of Gdańsk was 51 ng g$^{-1}$ [25]. The values depended both on the quantity and species.

<table>
<thead>
<tr>
<th>Group</th>
<th>Median of Hg concentration [32, 33] (μg g$^{-1}$)</th>
<th>Mass of caught fish [48] (Mg)</th>
<th>Hg load (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sprat (Sprattus sprattus)</td>
<td>0.014</td>
<td>40,442</td>
<td>566.2</td>
</tr>
<tr>
<td>Herring (Clupea harengus)</td>
<td>0.025</td>
<td>5279</td>
<td>132.0</td>
</tr>
<tr>
<td>Cod (Gadus morhua)</td>
<td>0.034</td>
<td>4329</td>
<td>147.2</td>
</tr>
<tr>
<td>Flounder (Platichthys flesus)</td>
<td>0.054</td>
<td>1689</td>
<td>91.2</td>
</tr>
</tbody>
</table>

Table 1. The Hg load accumulated in the caught fish from the Gulf of Gdańsk.
composition of phytoplankton and on mercury sources in the Gulf [25, 26]. The mean phytoplankton biomass in the Gulf of Gdańsk was assumed to be 85 mg m\(^{-3}\) [26, 45] and the volume of the water to a depth of 20 m (where phytoplankton occurs most abundantly) was 10.9 km\(^{3}\) [4]. This information allowed to estimate the amount of Hg bound to the phytoplankton at 47 g (Figure 2).

Slightly higher Hg concentrations than in phytoplankton were measured in zooplankton (66 ng g\(^{-1}\)) [27]. The Hg concentration in zooplankton presented by Beldowska and Mudrak-Cegiołka [27] was about 4-fold lower than that measured 20 years earlier by Boszke et al. [65]. This was the result of a systematic reduction of the Hg emission into the environment [6, 66], which in turn caused a decrease of metal concentrations in the water as well as in marine organisms. Taking into account the mean zooplankton biomass in the Gulf of Gdańsk (150 mg m\(^{-3}\); [45]) and the volume of water in the Gulf (291.2 km\(^{3}\)), the Hg pool in zooplankton was estimated at 2.9 kg (Figure 2).

Lower Hg concentrations than in plankton were measured in macrophytobenthic plants [28, 29]. The Hg concentration in macrophytobenthos depended on the species and the area of research. The highest Hg concentration was measured in the red algae, while the lowest in the brown algae (Table 3). Similar to zooplankton, also in case of phytothentic plant, the Hg concentrations were found to be much lower than those determined in 1995–1998 in the Puck Bay region [65]. Based on the research conducted by Beldowska et al. [28] (the Hg concentration in macrophytobenthos) and Saniewski and Zalewska [46] (biomass of particular organism), the Hg load accumulated in macrophytobenthic plants was estimated at 13.9 g (Table 3). This value was very low compared to the Hg load presented in zooplankton organisms and was unnoticeable in the Hg mass balance in the Gulf (Figure 2). The highest Hg load among macrophytes was accumulated in the vascular plants (8.2 g) (Table 3). This group also had one of the highest biomass among discussed organisms. Therefore, subsequent rise in biomass of vascular plants, which has been observed in the Gulf of Gdańsk in recent years, may play a significant role in increasing concentration of this metal in more advanced organisms.

The Hg concentration measured in macrozoobenthos in the Gulf of Gdańsk varied in a wide range (Table 4) [29–31]. The Hg level in macrozoobenthos was dependent on its trophic preferences as well as biotic (i.e. primary production and

<table>
<thead>
<tr>
<th>Type of the sediments</th>
<th>Hg concentration [24] (ng g(^{-1}))</th>
<th>Surface [4] (km(^{2}))</th>
<th>Density [44] (g cm(^{-3}))</th>
<th>Wetness <a href="%25">24</a></th>
<th>Hg load (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silty sediment</td>
<td>98.8 (38.0–325.3)</td>
<td>3124</td>
<td>2.45</td>
<td>73</td>
<td>10,209</td>
</tr>
<tr>
<td>Sandy sediment</td>
<td>73 (1.0–29.0)</td>
<td>1816</td>
<td>2.55</td>
<td>18</td>
<td>1386</td>
</tr>
</tbody>
</table>

Table 2. The Hg load deposited in the upper layer of the sediments (0–5 cm) in the Gulf of Gdańsk.

<table>
<thead>
<tr>
<th>Group</th>
<th>Hg concentration [28] (ng g(^{-1}))</th>
<th>Biomass [46] (g m(^{-2}))</th>
<th>Surface [4] (km(^{2}))</th>
<th>Hg load (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green algae (Chlorophyta)</td>
<td>10.1 (0.8–371)</td>
<td>0.668</td>
<td>20.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Brown algae (Phaeophyta)</td>
<td>5.2 (4.3–6.8)</td>
<td>41.860</td>
<td>20.4</td>
<td>4.4</td>
</tr>
<tr>
<td>Red algae (Rhodophyta)</td>
<td>11.0 (1.3–43.3)</td>
<td>5.391</td>
<td>20.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Vascular plant (Spermatophyta)</td>
<td>8.3 (1.3–572)</td>
<td>12.497</td>
<td>78.6</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Table 3. The Hg load accumulated in the macrophytobenthic plants in the Gulf of Gdańsk.
Mercury Cycling in the Gulf of Gdańsk (Southern Baltic Sea)
DOI: http://dx.doi.org/10.5772/intechopen.86159

The Hg load accumulated in the macrozoobenthos in the Gulf of Gdańsk.

<table>
<thead>
<tr>
<th>Group</th>
<th>Hg concentration [29, 30] (ng g⁻¹)</th>
<th>Biomass [47]</th>
<th>Surface [4]</th>
<th>Hg load (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom not covered by</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>macrophytobenthos</td>
<td>Bivalvia</td>
<td>46.0 (74.1–123.3)</td>
<td>14.6</td>
<td>3250</td>
</tr>
<tr>
<td>Crustacea</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gastropoda</td>
<td></td>
<td>128.1 (8.2–410.2)</td>
<td>61.1</td>
<td>3250</td>
</tr>
<tr>
<td>Polychaeta</td>
<td></td>
<td>9.8 (26.2–110.5)</td>
<td>14.7</td>
<td>3250</td>
</tr>
<tr>
<td>Oligochaeta</td>
<td></td>
<td>34.0 (9.3–157.4)</td>
<td>48.3</td>
<td>3250</td>
</tr>
<tr>
<td>Insect larvae</td>
<td></td>
<td>36.3 (9.7–223.4)</td>
<td>9.6</td>
<td>3250</td>
</tr>
<tr>
<td>sum</td>
<td></td>
<td>50.3 (10.9–979)</td>
<td>1.8</td>
<td>3250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>34.8</td>
</tr>
<tr>
<td></td>
<td>sum</td>
<td>46.0 (74.1–123.3)</td>
<td>14.6</td>
<td>3250</td>
</tr>
<tr>
<td>Bottom covered by</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>macrophytobenthos</td>
<td>Bivalvia</td>
<td>44.3 (32.7–76.9)</td>
<td>22.2</td>
<td>100</td>
</tr>
<tr>
<td>Crustacea</td>
<td></td>
<td>49.0 (8.5–213.7)</td>
<td>79.2</td>
<td>100</td>
</tr>
<tr>
<td>Gastropoda</td>
<td></td>
<td>58.0 (30.7–185.6)</td>
<td>69.0</td>
<td>100</td>
</tr>
<tr>
<td>Polychaeta</td>
<td></td>
<td>21.6 (12.6–39.7)</td>
<td>99.6</td>
<td>100</td>
</tr>
<tr>
<td>Oligochaeta</td>
<td></td>
<td>21.8 (8.6–521.2)</td>
<td>13.2</td>
<td>100</td>
</tr>
<tr>
<td>Nemertea</td>
<td></td>
<td>59.2 (23.2–460.2)</td>
<td>3.0</td>
<td>100</td>
</tr>
<tr>
<td>Insect larvae</td>
<td></td>
<td>179 (14.9–1779)</td>
<td>13.8</td>
<td>100</td>
</tr>
<tr>
<td>sum</td>
<td></td>
<td>44.3 (32.7–76.9)</td>
<td>22.2</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 4.

The amount of Hg accumulated in macrozoobenthos in the Gulf of Gdańsk was in the same range like those determined by Boszke et al. in 1995–1998 in the Puck Bay [65]. This indicates that sediments—habitat of macrozoobenthos—need much more time to reduce the Hg than sea water [67]. The amount of Hg accumulated in macrozoobenthos in the Gulf of Gdańsk based on the research conducted by Jędruch et al. [29, 30] (the Hg concentration in macrozoobenthos), Włodarska-Kowalczuk et al. [47] (biomass of particular macrozoobenthic organisms from the Gulf of Gdańsk), and the area on which these organisms occur [4] was estimated at 35.9 kg (Figure 2, Table 4). A total of 96% of this load was contained in the organisms dwelling at the bottom not covered by macrophytobenthos (Table 4). The organisms that were most responsible for accumulation of Hg were Crustacea, while Gastropoda and insect larvae were of a marginal importance (Table 4).

The fish resources of the Gulf of Gdańsk have not yet been reliably estimated. Therefore, estimation of the Hg load associated with the fish was impossible.

The gray seal (Halichoerus grypus) is a species representing the highest level of the trophic chain, which most frequently occurs in the Gulf of Gdańsk. The size of its population in the Gulf is estimated at 150 specimens [60]. The median Hg concentration in seal’s muscle was 1.81 μg g⁻¹ [59]. This value was 130-times higher than in sprat, the main diet of seals (Table 1). Taking into account the median Hg concentration in the muscle, the wetness of the tissue (55%), the average weight of the gray seal (250 kg), and the size of population in the Gulf of Gdańsk [60], the load of Hg accumulated in the gray seals was estimated at 31 g.

5. Mass balance of mercury in the Gulf of Gdańsk

Every year around 242 kg of mercury was introduced into the Gulf of Gdańsk (Figure 2). The most efficient way of Hg transport to the Gulf of Gdańsk was river runoff, which constituted 83% of Hg flowing into the Gulf (Figure 3). This is a typical situation for water bodies, where there is a relatively high ratio of catchment area to the surface of the reservoir itself [68]. A similar tendency was observed in the whole Baltic Sea, where 86% of Hg came from surface runoff, while 14% of Hg came from atmospheric deposition [69, 70].
Figure 3. The percentage share of the main mercury sources in the Gulf of Gdańsk.

The second most important source of Hg in the Gulf of Gdańsk was atmospheric deposition (Figure 3). Wet and dry deposition accounts for 7% and 4% of the Hg load reaching the Gulf, respectively. This is a typical situation, because wet deposition of mercury prevails in moderate latitudes. Dry deposition usually accounts for less than 30% of the Hg atmospheric input. Atmospheric deposition introduced much lower Hg load than the rivers; however, considering that the “atmospheric” Hg is much more bioavailable than “riverine” Hg, it played a crucial role in incorporating Hg into the marine trophic chain.

Another source of mercury in the Gulf of Gdańsk, which should be taken into account during the creation of mass balance of Hg is the coastal erosion. In the Gulf of Gdańsk, it accounts for only 6% of the Hg load reaching the sea (Figure 3). However, in regions where there are no such large rivers as the Vistula, the significance of this source will increase considerably [12, 19].

Point sources and submarine groundwater discharge have a negligible impact on the Hg load of this metal getting to the Gulf of Gdańsk. Hg transported to the Gulf only in a small extent reached the open sea water (58 kg—24%). Consequently, the Gulf of Gdańsk should be treated as a cleansing zone for the Baltic Proper. Most Hg was removed from the water through the sedimentation of the metal bound to suspended particulate matter and its deposition into the sediments. This process caused that the bottom sediments are the main Hg reservoir in the Gulf of Gdańsk (Figure 2). The third most important process decreasing the Hg load in the Gulf of Gdańsk was re-emission of this metal to the atmosphere (Figure 2) [41, 42]. This indicated that seawater was an important source of mercury to the coastal atmosphere. Fishing as a process of removing mercury from the sea can be omitted in the mercury mass balance in the Gulf of Gdańsk (Figure 2).

6. Conclusions

The main sources of mercury in the Gulf of Gdańsk were river runoff, atmospheric deposition, and coastal erosion, while the most important processes that reduced Hg load in the Gulf were deposition of Hg to the sediments, re-emission of Hg to the atmosphere, and export to the Baltic Proper. The resultant of all discussed
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processes was the mercury load accumulated in water and marine organisms. It was estimated that 495 kg of Hg was contained in the sea water. About 12 times smaller load was incorporated into marine organisms. The Hg concentrations in the different environmental compartments in the aquatic ecosystem of the Gulf of Gdańsk measured in 2010s were lower than measured 20 years earlier [65]. This was the result of a reduction of the Hg emission into the environment [6, 66]. This makes that nowadays the Hg concentration in the Gulf of Gdańsk are similar to values observed in different unpolluted coastal regions [60, 61]. However, climate change occurring in the southern Baltic region could change this tendency [71, 72]. On the one hand, the forecasts of climate change in this region anticipate an increase in total annual precipitation as well as an increase in the intensity and frequency of extreme phenomena i.e. storms and floods [31, 73]. These processes lead to the washing out of Hg from both the atmosphere (wet deposition) and from land (river runoff and coastal erosion) [12, 13–16, 19, 22]. In consequence, in the next few decades we can expect an uncontrolled increase in the Hg load transported into the sea. On the other hand, climate warming (especially mild winters without the ice cover) stimulates the growth of marine organisms during the prolonged vegetative season (more frequent blooms and higher biomass). Consequently, this process increases the Hg accumulation by organisms and an increase of the Hg load introduced into the marine trophic chain. Research conducted by Beldowska et al. [26, 31] indicated that the mean annual Hg pool in phytoplankton, macrophytobenthos, and macrozoobenthos communities in a year without icing was higher compared to an estimated previous year in which the icing period lasted approximately 90 days (by 30%, 30% and 25%, respectively). This can have a negative impact on the marine environment, especially on organisms inhabiting river estuaries.

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Conflict of interest

The author declares that she has no conflict of interest.

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