
SUMMARY

Mercury (Hg) is a neurotoxin that has been a subject of research all over the world. Although, it occurs naturally in the environment, still developing anthropogenic activities cause an increase of its concentration in different environmental matrices such as air, soil, water, organisms and sediments. In the natural environment Hg occurs in three main forms: elemental mercury, inorganic mercury and organic mercury which differ from each other in terms of adsorption possibilities, distribution and accumulation in the human organism (Holmes et al., 2009). Mercury toxicity is various, and it depends on a form that occurs. The most toxic Hg form are dimethylmercury and methylmercury (Boeing, 2000). As a methylmercury ion is the most bioavailable, can bioaccumulate and biomagnify easily in organisms. Hg penetrates the human organism through dermal contact, inhalation but mostly by consumption of fish and seafood (Bernard et al., 2001). Mercury has a negative impact on the human nervous system and due to that causes irreparable brain damage and several neurological diseases such as Parkinsons and Alzheimers. Mercury also causes circulatory system issues, kidney disorders and its easy transferability through a bearing barrier causes damage to the human fetus (Bose-O'Reilly et al., 2010; Hong et al., 2012).

For many years (mostly '70s and '80s) mercury has been used in several industrial sectors and household products such as plant protection products (fungicidal and bactericidal preparations), dyes, thermometers, medicines and cosmetics. Due to that it caused a significant emission of this metal into the environment. Nowadays, the emission has been reduced by an implementation of several law regulations (HELCOM, 2013). Applied limits in mercury usage provided to 35% of a decrease of its emission from the Baltic Sea countries (Bartnicki et al., 2013). However, implemented changes are not proportional to the decrease of mercury concentration in the environment. Moreover, a significant Hg source into the atmosphere was and still is fossil fuel combustion (Pacyna et al., 2006; Pirrone et al., 2010). It means that for several years Hg undergoes a dry and wet atmospheric deposition on land and water surfaces (Beldowska et al., 2012; Saniewska et al., 2014). It is estimated that 75% of mercury originates from the atmosphere accumulates in the soil surface layer (Wang et al., 2003), which makes soil a mercury "land warehouse". Despite the fact that a significant part of mercury is deposited on land, its presence in soil has also an impact on Hg concentration in rivers and the sea. One of the reasons is that mercury is remobilized from land into the rivers, and then it is transported into the marine coastal zone (Shuster et al.,

2008; Svoray and Ben-Said, 2010). This process is stimulated by precipitation and thaws which cause surface runoff and mercury washing out from the soil into the water (Shuster et al., 2008; Selvendiran et al., 2008). Taking into account that presently we observe climate change as very intense precipitation along with floods, this problem became even more significant. Additionally, rivers where mercury is mostly washing out, consist a main Hg source into the Baltic Sea coastal zone.

Rivers are a complicated water body surrounded by different management type which significantly influences how high concentration of mercury is noticed in rivers and soils being a part of river catchment areas. The management type has an impact on the mercury form as well (Hurley et al., 1997; Lacerda et al., 2012). In soil mercury is available as a stable Hg (hardly soluble) and as a labile Hg (easily transformed and biomagnificated in organisms). The mercury is easily bounded by fine grain and organic matter. Binding of Hg in organic matter is mainly caused by the reduction of sulphur compounds in such functional groups as thiol or disulphide (Xia et al., 1991). One of the most stabile mercury compounds in soil is HgS and its concentration increases along with reduction condition occurrence (Bełdowski and Pempkowiak, 2003). Labile mercury forms include organic mercury such as methylmercury (MeHg) (Kibria, 2014). A higher MeHg concentration is noted in the area of pastures and wetlands, where methylation process easily occurs (Haynes et al., 2017).

A river catchment dominated by the areas with a high fossil fuel combustion in a heating season, are characterized by higher mercury concentration. Due to that the previous researches were focused on seasonal changes (spring, summer, autumn, winter) of Hg concentration in river catchments or were provided in heating or non-heating seasons. Taking into consideration the fact that mercury occurs in the environment in different forms (Boszke and Kowalski, 2008; Lacerda et al., 2012; Haynes et al., 2017), and all of these forms can be introduced into the Baltic Sea, it's important to estimate how big and enriched as well as in which form the Hg load is transported into the coastal zone as a result of changes in meteorological and hydrological conditions. A terrestrial origin suspended particulate matter (SPM) enriched with mercury is food for organisms living in the coastal zone, which ultimately also poses a threat to humans. It is caused because mercury undergoes bioaccumulation and biomagnification processes which cause mercury transportation into a higher trophic level, where humans consist in the top level.

Taking the above into consideration, there is a question if climate change provides to the increase or decrease of mercury concentration in the environment? Taking into account

the current state of knowledge, including literature studies, **the research hypotheses verified in this work were formulated as follows:**

- i. Changes of meteorological and hydrological conditions significantly influence mercury transformation in soil of river catchments;*
- ii. Extreme meteorological and hydrological phenomenon lead to an increase of suspended labile mercury load introduced into the southern Baltic Sea.*

In the term to verify the hypotheses following scientific aims were formulated:

- i. A recognition of processes influencing transformation of mercury compounds in the soil of river catchment areas;*
- ii. An identification of the impact of meteorological and hydrological phenomenon and types of the river catchments on washing out of labile mercury from the soil and its riverine transportation into the sea;*
- iii. An indication of the impact of meteorological and hydrological phenomenon on suspended particulate mercury fraction in rivers;*
- iv. Estimation of the impact of extreme phenomenon on inflow of suspended labile mercury into sea in the area of Puck Bay.*

The material for preliminary tests contained river water samples that were taken once a month from the mouth stations: January 2012-December 2013 from Reda river; December 2011-November 2012 from Zagórska Struga and Kacza river; December 2011-October 2013 from the Gizdepka river. In a term to conduct analysis referring to mercury transformation in river systems, water, soil and sediment samples were collected in the years 2015-2017 from four rivers being a part of the Baltic Sea catchment area: Reda - 7 stations; Zagórska Struga – 5 stations; Gizdepka – 5 stations and Płutnica – 4 stations. All of those stations represented different catchment types. Additionally, stations located in coastal zone about 200 m from the land were appointed. In the term to identify the impact of climate change on Hg transformation in the environment, samples were taken seasonally (spring, summer, autumn, winter) during the mean flow of the Reda river ($3.3-4.3 \text{ m}^3/\text{s}$) and after extreme meteorological and hydrological conditions such as low water flow ($<3.2 \text{ m}^3/\text{s}$) and high water flow ($>4.3 \text{ m}^3/\text{s}$) (fig. 1). Soil, river and marine water and sediment samples were collected. In the case of soil sampling, material was collected from two profiles: (i) periodically flooded located about 1-3 m from the river bed (river water was noticed only after intense precipitation/floods); (ii) often flooded profile located next to the river bed

(water was observed the whole year, an exception was drought period). From each profile, samples were taken from 3 depths: 0-20 cm, 20-40 cm, 40-60 cm. Each time the sediment samples were collected as well by using a manual Van-Veen gram sampler. In two years of research the total collected was: 1780 soil and sediment samples (river and marine) and 1330 water samples (river and marine). During both preliminary and detailed research (on mercury transformation) the base environmental parameters were measured: temperature, oxygen level, pH and conductivity in water samples. During detailed research Eh was checked in situ in sediments and soil and sediment pH in a laboratory. The sampling was carried out in accordance with guidelines dedicated for heavy metals analysis (US EPA 1996 and US EPA 1631) which reduced possibility to contaminate the collected material.

The samples of river and marine water were filtered through previously ignited and weighed glass fiber filters with 0.7µm pore diameter (Whatman GF/F). After that, the filters were frozen and then lyophilised.

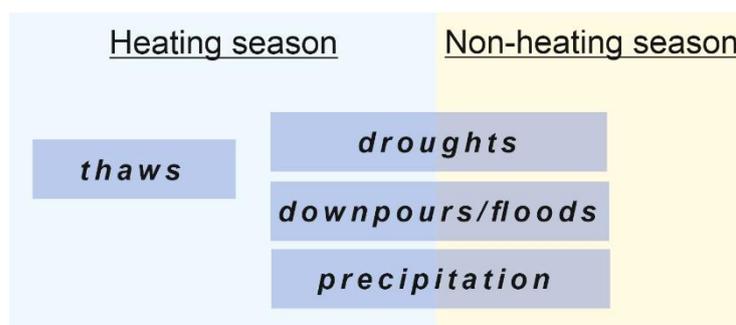


Fig. 1 Seasons (heating and non-heating) and periods (thaws, drought, downpours/floods, precipitation) of sampling

The concentration of total mercury in solid samples collected as part of a preliminary study was carried out by using an thermal-desorption automatic mercury analyzer AMA 245. Limit of detection of the applied method was 0.005 ng/g, RSD was 5% (**publication 1**). In the case of detailed research on mercury transformation, total mercury as well as mercury concentration forms were analyzed by applying a thermo-desorption method which is based on environmental samples burning in temperatures ranging from 175 to 750°C. The method was conducted by using thermal-desorption direct mercury analyzer DMA-80 (**publications 2-4**) (Saniewska and Bełdowska, 2017; Bełdowska et al., 2018). Due to that method, two groups containing mercury fractions which included different mercury forms were indicated (fig. 2): **labile mercury** (being easily transformed in the environment):

- Hg_{ads1} (mainly halides: $HgCl_2$, $HgBr_2$, HgI_2 , $Hg(CN)_2$ and Hg^0), mercury adsorbed on organic matter/fine grain, released in $175^\circ C$,
- Hg_{abs} (mainly organic forms: $MeHg$, $Hg(SCN)_2$, $(CH_3COO)_2Hg$, $Hg(NO_3)_2$, $Hg(ClO_4)$ and Hg bounded with organic matter), mercury absorbed on organic matter/fine grain, released in $225^\circ C$,
- Hg_{ads2} ($HgSO_4$, HgO , adsorbed on organic matter/fine grain), mercury adsorbed on organic matter/fine grain, released in $475^\circ C$,
and **stable mercury** (not easily transformed in the environment):
- HgS (released in $375^\circ C$),
- Hg_{res} (residual fraction), mercury in the mineral matrix; released in $750^\circ C$, (Bełdowska et al., 2018).

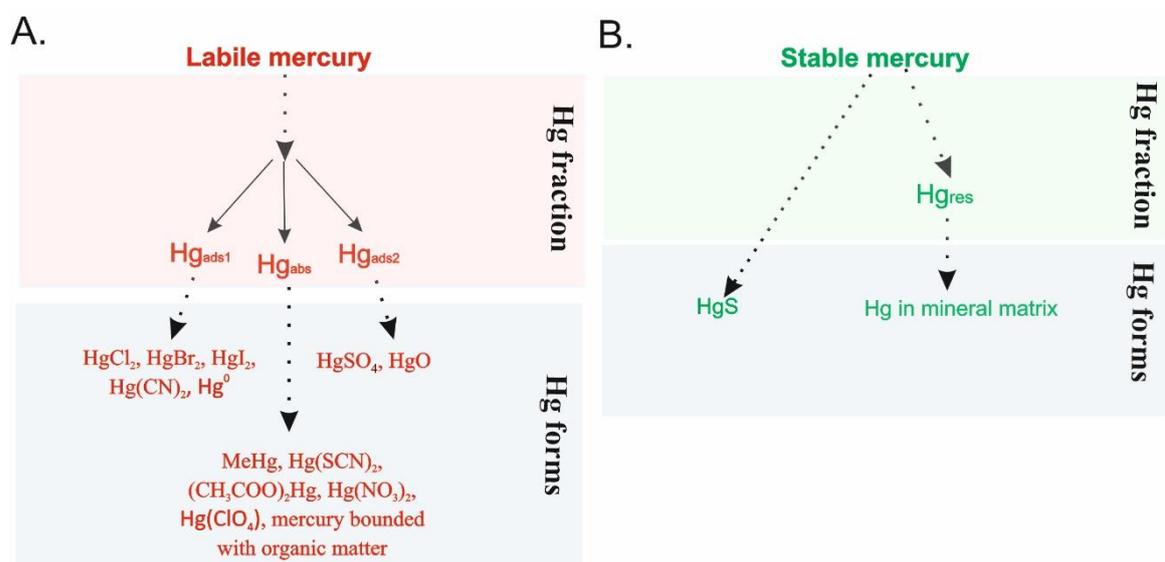


Fig. 2 Labile and stable mercury groups divided into fractions and forms

By adjusting the correct time to reach a target temperature (e.g. $175^\circ C$ in 9 minutes) the organic part of the sample was not burning at the beginning of the analysis. The limit of detection (LOD) in suspended particulate matter and soil samples were total mercury 0.05 ng/g d.w. ; mercury fractions 0.06 ng/g d.w. . The recovery of this method was 90% and it was obtained by the sum of 5-step of analysis and compared to the total Hg concentration. Additionally, this method is distinguished by a fact that the process of sample preparation is much shorter in comparison to the speciation method proposed by Wallshlager et al., (1998)

which reduces the possibility for contamination of samples (Beldowska and Saniewska, 2017; Beldowska et al., 2018).

Additionally, the analyses of total mercury concentration in river water were conducted by using a cold-vapor atomic fluorescence spectrometry (CVAFS) (TEKRAN 2600) (U.S. EPA method 1631). These analyses were carried out at the Marine Geotoxicology Laboratory of the Institute of Oceanology, Polish Academy of Sciences (**publication 1**). To obtain information about the suspended particulate matter in the river mouths origin the analysis of elemental composition was conducted (organic carbon (C_{org}) and total nitrogen concentration (N_{tot})) and carbon and nitrogen stable isotopes ($\delta^{13}C$, $\delta^{15}N$) ratio was determined. For this purpose, the Flash EA 1112 elemental analyzer (Thermo Scientific) combined with the mass spectrometer IRMS Thermo Delta V Advantage (Thermo Electron) was used (Kuliński et al., 2014). These analyses were carried out at the Marine Biogeochemistry Laboratory of the Institute of Oceanology, Polish Academy of Sciences (**publication 1**). Moreover, soil and sediment samples were tested to identify its humidity, granulometric composition and organic content matter expressed as the loss on ignition at $550^{\circ}C$ (LOI) (**publication 1 and 2**). The concentration of Mn and Fe in suspended particulate matter samples was analyzed by using flame absorption atomic spectroscopy (FAAS) with Perkin Elmer spectrometer (Lukawska-Matuszewska 2016) (**publication 4**).

In the term to determine particulate mercury load introduced into the sea a linear interpolation proposed by Niemirycz (2011) was used. A typical equation dedicated for rivers of Central Poland was used to determine the unitary volume intensity of bed sediment transport and then mercury load introduced into the sea (Skibiński, 1976, Dąbkowski i in., 1982).

The preliminary studies performed in the years 2011-2013 made it possible to identify processes influencing mercury washing out from the river catchments, which constitutes an element of the first scientific goal: A recognition of processes influencing transformation of mercury compounds in the soil of river catchment areas. Obtained results indicated that higher concentration of total mercury (Hg_{tot}) in suspended particulate matter as well as in river water was observed in the period of intense fossil fuel combustion (heating season) than in the non-heating season. Additionally, surface runoff caused by intense precipitation or thaws caused the washing out of mercury adsorbed on organic matter in the winter season, which led to the increase of Hg_{tot} in rivers and in consequences to the higher mercury load introduced into the coastal zone of the Puck Bay. The mercury load size that was introduced into the sea was not positively correlated with the river water flow but with

total mercury concentration. It indicates that the amount of metal that is introduced into the sea depends on different types of the river catchments, which mercury is washing out. Additionally, an increase of mercury in the Kacza river was observed in the non-heating season, which was caused by the fact that this river flows through the allotments area where plant protection products containing mercury are still in use (verbal information obtained from land's owners, 2018), and due to that it became an additional Hg source. Moreover, the Kacza river always flows through the area where summer houses are not connected to the municipal systems but only to the leaking cesspools that constitute the next mercury source in the environment. Due to the above, in this case, the Hg load introduced into the sea was not stimulated by the fuel combustion but by the washing out of mercury from allotments.

Moreover, conducted analysis on isotopes such as $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N ratio indicated typical land origin of the SPM collected from the studied rivers which indicated that the terrestrial organic matter is a mercury carrier into the sea. No direct correlation between total mercury concentration and content of C_{org} , N_{tot} , $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C/N in suspended particulate matter was noted, and it suggests that specific Hg forms can be adsorbed on the terrestrial organic matter and then can be transported into the sea (**publication 1**).

Information obtained during preliminary study became a motivation to conduct more detailed analysis. Research carried out as a part of **publication 2** indicated that the greatest variability in the total mercury concentration in soil (Hg_{SOIL}) of Reda river catchment was noticed after intense precipitation in a flooded profile (located closer to the riverbed). In the case of the periodically flooded profile, the greatest variability in mercury concentration was observed in soil surface layer, 0-20 cm. The Hg_{SOIL} concentration changes were associated with the changes of individual mercury fractions share. The analysis indicated that the soil of the Reda river catchment area was mostly enriched with labile mercury: Hg_{ads1} , Hg_{abs} and Hg_{ads2} . Due to that it constitutes a potential source of the toxic mercury forms for organisms living in the marine coastal zone and in consequence for humans. However, in the case of the river source station, agricultural areas or pastures the significant share of the most stable mercury form (HgS) was noticed. Both appointed above labile Hg forms and mercury sulfide can be transported by the surface runoff closer to the riverbed and then can be washed out from the soil profile into the river water even from the subsurface layer (20-40 cm). It was confirmed by the decrease of Hg_{SOIL} concentration and the increase of mercury forms concentration in suspended particulate matter and river sediment. Besides a transportation of mercury forms into the river, an important role plays labile forms transformation into mercury sulfide. This situation was noted for example in flooded soil profile (layer 20-40

cm) in autumn and drought in the catchment dominated by pastures and in the agricultural area. In such conditions as a result of organic matter degradation or deficit in oxygen can occur and in consequence lead to the limitation of mercury bioavailability in the water environment (Bełdowski and Pempkowiak 2003). However, it was noticed that stable mercury sulfide was converted into labile mercury form ($\text{HgS} \rightarrow \text{HgSO}_4$). A similar situation was also observed by Bełdowski and Pempkowiak (2003), Lecher et al., (1997). In the last case, a reason of HgSO_4 share increase was riverbed rebuilding which included deepening and widening the river to prevent future flooding. As a result of those works, river sediment enriched in HgS was relocated from the riverbed and was placed on the riverbank. Along with the change of anaerobic conditions into aerobic bioavailable mercury was formed, which then could be washed out again into the river and constitute a potential danger for water organism. This issue was discussed in detail by Saniewska et al. (2019).

The above information is a highlighter for a significant role of surface runoff and catchment type in Hg washing out from the soil into rivers. Due to that, the second scientific aim was undertaken: An identification of the impact of meteorological and hydrological phenomenon and types of the river catchments on washing out of labile mercury from the soil and its riverine transportation into the sea as a part of **publication 3**. The performed analysis indicated that differences of total mercury concentration in surface soil between stations located in the Reda and Gizdepka rivers in typical seasons (heating and non-heating) are not statistically significant, and the content of mercury fractions are similar to the medians obtained for the whole catchment. Inverse dependencies were observed in the case of thaws, flood and drought periods which were also noted in two years study. In accordance with issues appointed in the **publication 1** and **2**, drought, precipitation, downpour/flood and thaw periods have a statistically significant impact on the mercury cycle between fluvial and marine systems. It is necessary to remember that every of the indicated periods occur in one or two typical seasons (heating and non-heating). It means that those seasons determine the initial mercury form in soil and occurring extreme conditions influenced on Hg transformation in the environment or further intensify the dominance of a particular metal form. In the period when flora is intensively developing, an increase of the share of Hg_{abs} in surface soil was noticed. While in a heating season soil of the study catchments was mostly enriched with Hg connected with halides (Hg_{ads1}), which was emitted during fossil fuel combustion which confirmed results obtained during research carried out in 2011-2013. Two years studies conducted for Reda and Gizdepka catchments also confirmed that what is typical for temporal zone intense precipitation does not also cause the change of total

mercury concentration in soil, but it leads to changes in Hg fractions share. In precipitation, downpours/floods and thaws periods at the station located on Reda and Gizdepka rivers an intense surface runoff caused washing out of mercury weakly bounded with soil surface (Hg_{ads1}) and outflow of mercury absorbed on forest organic matter (Hg_{abs}) closer to the riverbank. In accordance with results obtained as a part of research described in the **publication 2**, precipitation, downpours and thaws detected in a heating season led to the transport of Hg_{ads1} adsorbed on tree leaves (Choi et al., 2008; Blackwell and Driscoll, 2015) and soil surface in the area dominated by individual houses closer to the riverbank. In the case of anthropogenic stations, surface runoff in a non-heating season also caused washing out of Hg_{ads1} from the roads and pavements into the river water. Despite the fact that soil of river catchments was mostly dominated by bioavailable mercury (labile), mercury sulfide which was detected in pasture, wetlands and arable lands soils was also transported with surface runoff to the riverbank and river water. In the anthropogenic catchments even, a slight precipitation was able to transport both Hg_{abs} and Hg_{ads1} closer to the riverbank, while in the natural catchments which are strongly covered by plants, soil erosion was observed only after downpours/floods (**publication 3**).

Meteorological and hydrological changes in a statistically significant way affected the content of mercury fractions and forms in river suspended particulate matter, which was determined during an implementation of the next, third scientific aim: An indication of the impact of meteorological and hydrological phenomenon on suspended particulate mercury fraction in rivers (**publication 4**). The differences in shares of Hg form in SPM in typical seasons (heating and non-heating) and after precipitation, downpour/floods, thaws and drought were noted. However, in this case there was no statistically significant differences between particular river stations located at rivers: Reda, Zagórska Struga, Gizdepka and Płutnica. The noted changes of mercury fractions content in surface soil caused by extreme meteorological and hydrological phenomenon (**publication 3**) were compatible with a share of Hg fraction observed in river SPM (**publication 4**). Correspondent to the changes observed in soil, in the season of intense fuel burning, the increased share of Hg_{ads1} was also observed in river suspended particulate matter. The highest content of Hg bounded with halides, similar to the results indicated in **publication 3**, was noted in river catchment dominated by individual houses. Along with the change of catchment development into the natural areas, share of Hg_{ads1} decreased. There were also cases when the content of Hg_{ads1} in SPM decreased with increase of HgS or Hg_{abs} , in every type of land use, what was probably connected to the inflow of another type of organic matter into the rivers. Correspondent to

results obtained in soil, the higher content of Hg_{abs} than Hg_{ads1} was typical for a non-heating season during which organic matter contains fresh flora (pollen and plant seeds). A different situation was observed in the drought period, when HgS was a dominant mercury in river SPM. It was caused by low water flow and high temperatures which led to the occurrence of anaerobic conditions in the river bottom. Consequently, as a result of resuspension process, organic matter enriched in HgS got into the column water again.

Periods after precipitation as well as after downpour/floods were one of the most dynamic periods in two years of study. These periods mostly caused a transportation of mercury forms from the whole catchment into river water which was indicated in **publications 1-3**. The increase of Hg forms in suspended particulate matter was determined by a dominance of specific metal fraction in soil, e.g. Hg_{ads1} in a heating season and Hg_{abs} in the non-heating season. The important fact is that the studied rivers flow through different type of land development. Even if there were no statistically significant differences between the content of suspended Hg forms between river stations, similarities were found between rivers. Due to that, SPM was enriched with mercury bounded with halides in the area dominated by individual houses and bigger cities, where mercury was weakly bounded with fine grain washed out from streets and pavements. The unclear results were noted in the case of all rivers after thaws when suspended particulate matter was enriched in Hg_{ads1} but also in Hg_{abs} , which was not detected in the previous studies. The increase of organic, bioavailable mercury (Hg_{abs}) in that period was probably a result of organic matter inflow, which degradation process was delayed by lower temperatures – frost occurrences. Thus, along with thaws organic matter with absorbed mercury (including methylmercury) was washed out into the river water causing an increase of Hg_{abs} share in river SPM.

The last but in my opinion the most important part of this dissertation was a realization of the fourth scientific aim: Estimation of the impact of extreme phenomenon on inflow of suspended labile mercury into sea in the area of Puck Bay, which was achieved in **publication 3** and **publication 4**. Some part of mercury washed out by surface runoff into the river is deposited in the river bottom, which affects enrichment of river sediment in different Hg forms. Mercury is easily absorbed on grain fraction and due to that it can be transported with river sediment into the marine coastal zone. Even if some part of transported river sediment is again deposited at the bottom of the marine, a remobilization process leads to the inclusion of Hg in the water column which creates danger for marine organisms. Due to this load of mercury forms that was introduced into the Puck Bay with river sediment was estimated. Typical season as well as drought period were the most dynamic and the longest

out of the all appointed periods in two years study (respectively 240 and 241 days). It means that the load is being introduced for a long time with the same frequency. In consequence, it leads to the change in mercury forms content in marine sediment of the coastal zone. Probably, the introduced sediment was partly transported farther into the bay during a typical season that was confirmed by research conducted by Saniewska et al., (2019). On the other hand, SPM containing HgS during drought was probably partly diluted by marine suspended particulate matter before its deposition in marine sediment. Another situation was noted during the most dynamic periods, which were characterized by the much intense river water flow (downpour/floods: 47 days and thaws: 26 days). It caused the enrichment of marine sediment with labile mercury. In the case of downpours/floods sediments of coastal marine zone was more enriched with mercury bounded with organic matter (Hg_{abs}), and after thaws in Hg bounded with halides, what corresponded to the share of Hg fractions noted in Gizdepka catchment area. Probably it was caused by a much faster sedimentation of fine grain and then its flocculation (**publication 3**).

Suspended particulate matter is the most known contaminants carrier, which enrich marine coastal zone with Hg (Bełdowski and Bełdowska 2008). It was a reason to estimate also a load of suspended mercury form introduced into the Puck Bay by Reda, Zagórska Struga, Płutnica and Gizdepka in typical and extreme seasons. Adequate to the situation observed for all the studied rivers, SPM introduced into the Baltic Sea was mostly enriched with labile mercury (Hg_{ads1} , Hg_{abs}). Moreover, the highest load of bioavailable mercury was introduced by the biggest rivers (Reda and Zagórska Struga), which confirms results obtained in preliminary studies carried out in the years 2011-2013. Nevertheless, an important role in a size of bioavailable mercury load introducing into the Baltic Sea was subjected to the smaller rivers dominated by pastures and wetlands (Płutnica) and arable lands and forests (Gizdepka). The obtained results that Gizdepka (the smallest out of the all studied rivers) in the heating season introduced much higher loads of suspended mercury forms into the sea than Płutnica which is twice smaller than Gizdepka. It was mostly connected with the greater river water flow which caused washing out of labile mercury from catchments into the river. On the other hand, a catchment dominated by pastures and wetlands enhanced formation of organic mercury which significantly enriched a mercury load that was introduced by Płutnica into the sea. As the intensity of meteorological and hydrological phenomenon increased, the higher load of labile and stable Hg fractions was introduced into the Baltic Sea. The highest load was noted in a downpour/flood period and slightly less during precipitation. The high share of Hg_{ads1} in catchments soil and in river

SPM during the heating season led to the enrichment of the load introduced into the sea with mercury bounded with halides. The most enriched with Hg_{ads1} load was introduced by the Gizdepka river which is characterized by areas where individual houses are located. Nevertheless, the high Hg_{ads1} load was also noted in the summer season (July-downpours), which was probably a result of developing of phytoplankton which intense absorbs mercury (Bełdowska et al., 2015). One more time, it was observed that small rivers such as Płutnica and Gizdepka contribute to introducing the most bioavailable load of mercury bounded with organic matter (Hg_{abs}) into the coastal zone of the sea. Probably it was a result of intense washing out of mercury from the catchment rich in organic matter (**publication 4**).

Taking loads introduced into the coastal zone of the sea with both river sediment and suspended particulate matter into account it was confirmed that SPM is a more effective contaminates' carrier. The load introduced with sediment fine grains constituted less than 1% of the load introduced with SPM in the same period and by the same river (**publication 3, publication 4**). Intense meteorological and hydrological phenomenon in a significant way caused an increase of the total suspended mercury containing bioavailable Hg introduced into the coastal zone of Puck Bay. It is particularly important because suspended particulate mercury constitutes food for organisms living mainly in that area. The result of a research carried out by Jędruch et al., (2020) and Jędruch et al., (2018) revealed that the organism of the lowest trophic chain (e.g. macrozoobenthos) and those from the higher trophic level contain even 90% of organic mercury. It indicates that there is a correlation between mercury forms in sediment and suspended particulate matter and the share of Hg in water organisms. It is significantly important because mercury undergoes a biomagnification process which means that Hg can be transferred into the human organisms at the top of the trophic chain.

The results obtained in this research allowed formulation of the following conclusions:

- i. The following processes affecting Hg transformation in soil of river catchments were determined (**publication 2**):
 - a. Conversion of labile compounds (Hg_{ads1} , Hg_{abs}) into stable mercury (HgS) along with the changing of aerobic into anaerobic conditions in soil profiles;
 - b. Transformation of stable mercury into labile form ($HgS \rightarrow HgSO_4$) in river sediment relocated to the riverbank along with the changing of anaerobic conditions into aerobic as a result of deepening and widening of the river.

- ii. Washing out of mercury (emitted during fossil fuel combustion) from the surface soil caused the significant increase of mercury concentration in rivers. Washing out process of Hg was observed from both surface and subsurface soil layers (20-40cm) (**publication 1, publication 2**).
- iii. Even a light precipitation caused the transportation and washing out from the anthropogenic catchment mercury adsorbed and absorbed on organic matter into the river. While in the case of natural catchment this process was limited by strongly developed root systems which caused the limitation of soil erosion. Due to the above, more effective washing out of labile mercury was observed during intensive precipitation/floods. Rivers located in the catchments dominated by wetlands and pastures introduced the highest load of particulate mercury enriched in organic Hg as well as mercury bounded with organic matter, which can be bioaccumulated in the trophic chain (**publication 2, publication 3, publication 4**).
- iv. Surface runoff caused by thaws affect enrichment of suspended particulate matter as well as river sediments with mercury bounded with halides (Hg_{ads1}). While surface runoff intensified by precipitation in the non-heating season caused the enrichment of SPM and river sediments with Hg_{abs} , which in consequence led to the increase of the share of labile mercury forms in marine sediments (**publication 3, publication 4**).
- v. Downpours contributed to the introducing of highest suspended labile mercury load into the southern Baltic. However, the most enriched in bioavailable Hg forms load was introduced during thaws by small rivers characterized by forest and arable lands. While the drought periods caused the limitation of labile mercury introduced into the coastal zone of the sea (**publication 4**).

Achievement of the assumed scientific goals permitted positive verification of the hypothesis. The conducted research significantly affected the understanding of the impact of the climate change (long term drought and intense precipitation) on the transformation of mercury in fluvial systems as well as at the interface between land and sea. Due to the fact, that rivers constitute the main source of mercury in the southern Baltic Sea (Jędruch et al., 2017), changes occurring in river catchments in a significant way affect the form of mercury

in that it is introduced into the sea with suspended particulate matter. Conducted research indicated that the main form is labile Hg which is intensively introduced into the sea during intense meteorological and hydrological phenomenon. It is especially important due to the fact, that the coastal zone of the sea is enriched in water organisms for which SPM constitutes nourishment (Jeđruch et al., 2017, 2018, 2020). Consequently, it leads to the increase of Hg concentration in the next level of trophic chain where the human is at the top.

The conducted research also revealed that there are still several environmental matrices that should be analyzed. It is important to indicate the correlation between the share of labile mercury introduced into the sea and its content in organisms living in the area of river mouths. And it will allow the comprehension of the direct response of the environment to the climate change.