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Mercury Partitioning Between Solid and Suspended Phases in the Southern Baltic Sea[1]

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1. Introduction

Mercury is a highly toxic metal. It can and does damage cellular membranes, inhibit enzymes, and damage DNA and RNA helixes. It is readily bioaccumulated, and organomercurials at least are biomagnified in food chains (Boening, 2000). In the aquatic environment mercury, being highly reactive, is readily associated with both organic and mineral particulate matter (Laurier et al., 2003), and majority of mercury transport in the coastal zone is believed to be through suspended matter (Forstner and Wittmann, 1981; Cossa and Gobeil, 2000).

The dynamics of mercury speciation in the course of its transport from sources to offshore depositional areas in the southern Baltic leads to partial remobilization of mercury to the water column, as described in Bełdowski and Pempkowiak (2006).

Some information about such processes and the mercury fate in the Baltic Sea may be derived from an examination of vertical profiles of total mercury concentration – both as particulate and dissolved in the water column. To this end stratified water column are best suited, since stratification hinders suspended matter settling.

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[1] The study was carried out as part of the statutory activities of the Institute of Oceanology, Sopot, grant No. II.2.06.

The Baltic Sea is characterized by the existence of permanent halocline at the depth of about 60-70 m, separating upper, brackish water from lower, more saline waters. The isolation of the two mentioned water masses in the presence of the suspended matter flux originating from eutrofication lead to oxygen depletion in waters below halocline, which can alter the trace metal cycles (Pempkowiak et al. 1998).

Previous studies report higher concentrations of dissolved mercury in water below halocline, which was attributed to mineralization of suspended matter at the halocline, wheras total mercury concentrations peaked at the halocline (Pempkowiak et al. 1998; Mason et al. 1994; Cossa et al., 1992, 1996). This suggests the importance of halocline in mercury remobilization, and the need to asses the influence of such factors as mercury source and actual magnitude of salinity gradient on the partitioning between suspended and dissolved forms of this metal.

2. Experimental

The study area is the southern Baltic, which is influenced by river run-off and urban activities. Conditions in the water column of the study area are both oxic and reducing and are expected to influence mercury speciation (Bełdowski and Pempkowiak, 2003).

Water and suspended matter samples were collected in several areas of the southern Baltic. Samples have been collected during the cruises of r/v "Oceania", ORP "Heveliusz" and ORP "Arctowski" in the years 2004-2005. Samples S1 and S4 were collected in August, samples S2 and S5 in September, and sample S3 in April. The main study area was the Gdańsk Basin, but single profile was also collected for comparison in the open Baltic Sea, close to the Slupsk Sill. Fig. 1 presents the location of the sampling stations.

Salinity and temperature measurements were recorded by CTD probes on a routine basis at each station, and displayed within this article in practical salinity units (PSU). Water samples were collected by means of whole PTFE pump with PFA hose and Teflon coated GO-FLO bathometer. Samples were transferred to acid cleaned borosilicate tubes, teflon capped and immediatly oxidized by the addition of BrCl solution according to Bloom and Crecelius (1983). Samples were then placed at 4 C and stored until analysis. Suspended matter samples were collected by means of filtration on ignited glas fibre whatman filters of the pore size of 0,45 um, transferred to double sealed polyethylene bags and frozen until the analysis.

Water samples were pre-reduced with 0,2% of NH_2OH addition and reduced to elemental mercury by $SnCl_2$ solution according to Bloom and Crecelius procedure (1988). Suspended matter samples have been digested in $HCl:HNO_3$ mixture (1:9) in teflon vessels at 90 C for 3h according to Laurier et al. (2003).

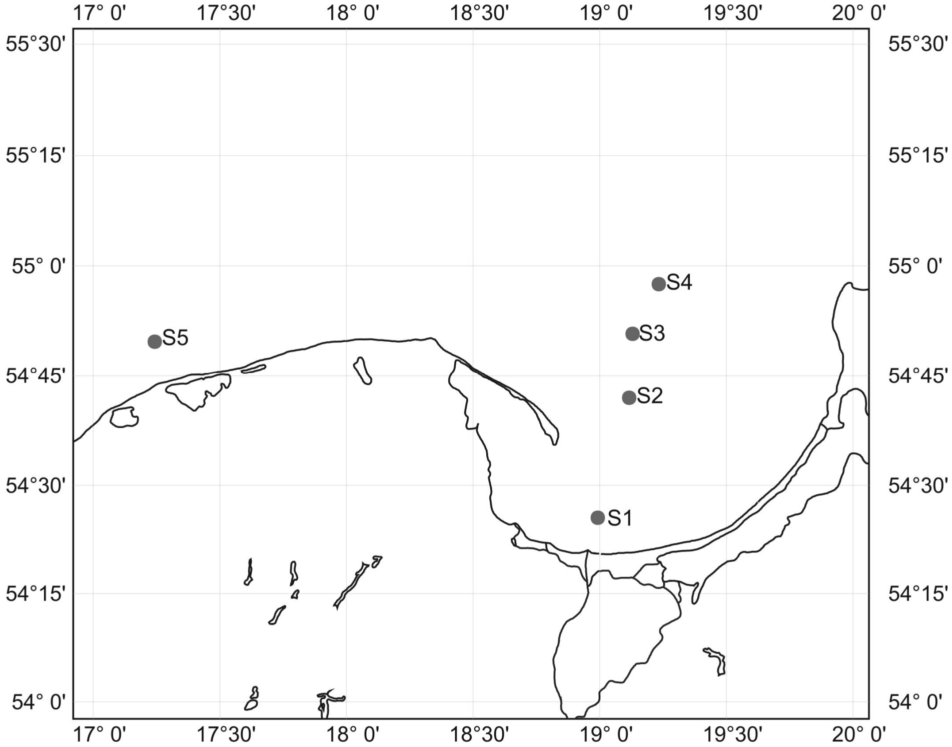

Fig. 1. Location of sampling stations
Rys. 1. Lokalizacja stacji pomiarowych

All samples have been analysed by means of either AFS (Tekran 2600) or AAS (Gardis 3a).

Quality control procedures for water samples included blanks and water spiked with mercury nitrate in the range of 0,5-100 ng/l, and produced adequate precision (1% RSD) and recovery (98-99%).

Because no suspended matter reference material was available, sediments with certified amount of mercury were utilized as a quality control. The analyses of the reference material QTMO56MS (from the QUASIMEME programme) demonstrated both the satisfactory accuracy (recovery 90–95%) and the precision of the determination (RSD equal to 10% of the mean).

3. Results and discussion

3.1. Hydrological conditions

The Baltic Sea is known from the stratification of its waters. The seasonal thermocline developes in early spring and erodes in autumn, separating mixed eufotic layer from deeper water and inhibiting the biogeochemical cycles of elements (Voipo, 1981). Permanent stratification exist in the deeper water, and results from the salinity gradient. The halocline exists at approximately 70 m, and disapears only periodically, due to events of saline water inflows from the North Sea (Voipo, 1981).

Salinity and temperature gradients recorded at the sampling stations are presented in figure 2. Temporal and spatial separation of the samples has resulted in quite different situation.

Station located closest to Vistula mouth, S1, presents mixed water column, with only gradual decrease of temperature towards the bottom. Station S2, visited in September, presents a well developed seasonal thermocline at 35mm, and a permanent halocline at 62m, while nearby S3, measured in April, exhibits no seasonal thermocline, with the halocline located slightly deeper, at 70 m. S4, located further in-basin and measured in August is quite similar to S2, with thermocline at 20 and Halocline at 60m. External station S5, located in the vicinity of Slupsk Sill Area, is characterized with a presence of thermocline at 16m, but the halocline does not exist, probably due to bottom current existent in the area (Beszczyńska-Moller, 2002).

Suspended matter concentration was characterized by large interseasonal variation. In spring (S3), in the surface layer it reached up to 23 mg/g, falling rapidly in the uppermost 5 meters and rising again from the halocline towards the bottom. In autumn suspanded matter content in the water varied from roughly 0,3 mg/g in midwater to approximately 3 mg/g in the vicinity of the Vistula mouth S1. Except of the S1, most profiles were characteristically U shaped, with elevated concentrations in the topmost and lowest layers (Fig 2.).

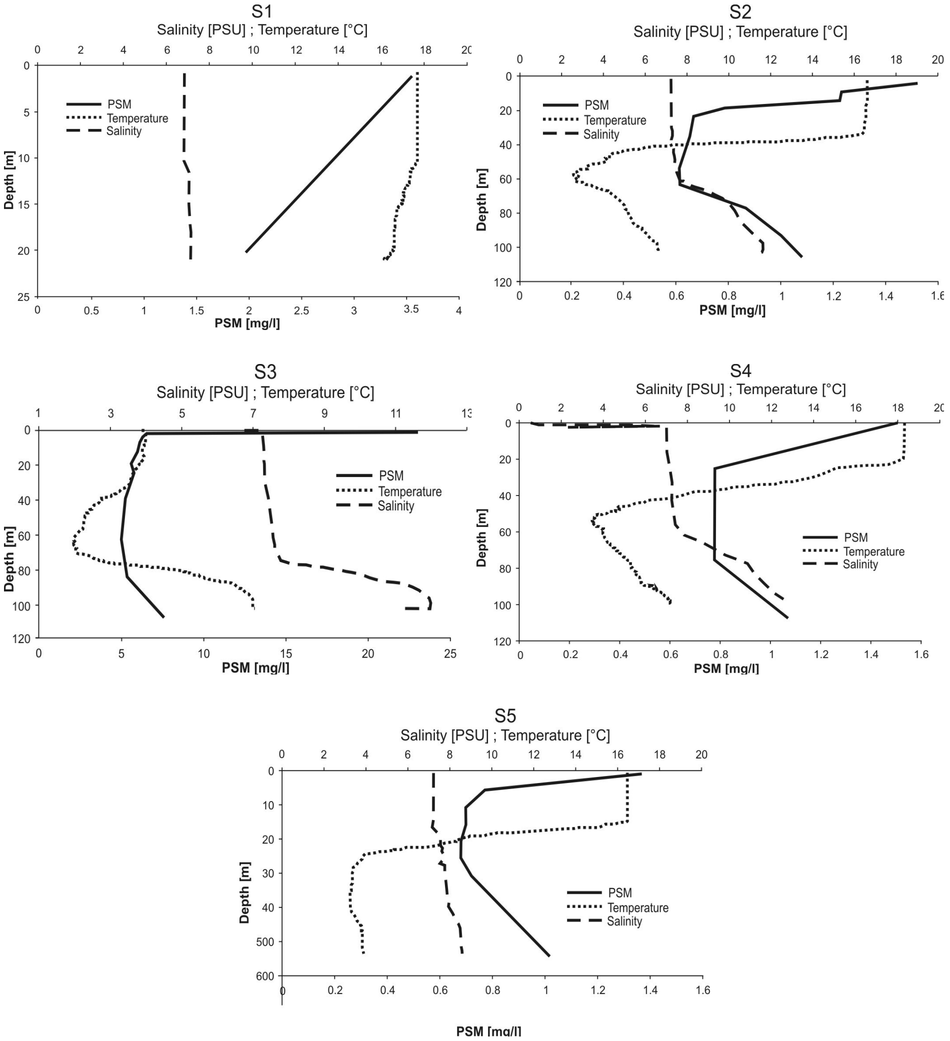

Fig. 2. Salinity [PSU], Temperature [°C] and particulate suspended matter (PSM) concentration [mg/l] depth profiles at the sampling stations

Rys. 2. Zasolenie [PSU], temperatura [°C] i stężenie materii zawieszonej – PSM [mg/l] w profilach pionowych na stacjach pomiarowych

3.2 Dissolved and particulate mercury partitioning

Dissolved and particulate mercury concentrations in the water profiles are presented on the figure 3.

Dissolved mercury concentration in the water column varied from 2 at S1 station to over 60 ng/l in samples S2 and S3 close to the bottom. These values are well in range reported by other authors for other areas in the Baltic (Pohl and Hennings 2005; Helcom 2004), but higher than those reported by Pempkowiak et al. (1998) for southern Baltic. The differences may arise from the fact of sampling in different season. Mercury concentration in the water column are a subject of large interseasonal variation (Laurier et al. 2003). This is caused mainly by varying river discharge and atmospheric mercury concentration variation (Schroeder and Munthe, 1998, Jackson, 1998).

The profile of mercury concentration close to Vistula mouth (S1) suggests the separation of the suspended matter in the course of transport from the river mouth – and association of mercury with larger particles with higher sinking speed. Decreasing dissolved mercury concenytration suggests scavenging of this metal from the surface waters by sinking particles. Similar phenomenon can be also observed ato other stations – S4, and upper layer of S5 station. Due to its affinity to particulate matter mercury is long recognized as a scavenged element (Forstner and Wittmann, 1981).

Other processes which seem to influence observed profiles are bioaccumulation and organic matter decomposition. Bioaccumulation is especially pronounced at S3 profile, sampled in the time of spring algae bloom. Resulting particulate mercury concentrations – max 648 ng/g (per gram of suspended matter dw.) are above of those recorded in natural suspended matter – max 470 ng/g (Laurier et al., 2003), but close to that found in the plankton (up to 1400 ng, Helcom 1987; Aubreu et al., 2000).

Decomposition of organic matter might be accompanied by the release of particulate-bound mercury into water column (Jackson, 1998), however , in the aboundance of particulate organic matter it can be partially readsorbed on the particles (Laurier et al., 2003). The release can be observed below a halocline at the S3 and S5 stations. This might result from the planktonic origin of suspended matter and fast decomposition which it undergoes. Profile at S5 ststion suggest an existence of a phytoplanktonplankton bloom near the termocline, which are known to happen in the area due to nutrient regeneration. Organic matter decomposition at the halocline releases mercury, which seems to affected by the resorption suspended matter despite its abundance (Fig. 2, Fig. 3). This can be probably explained by the existence of relatively fast bottom currents in the area (Beszczyńska-Moller, 2002), which could suggest, that part of suspended matter origins due to resuspension, and dissolved mercury resorbed on particles might be balanced by mercury liberated from the porewaters.

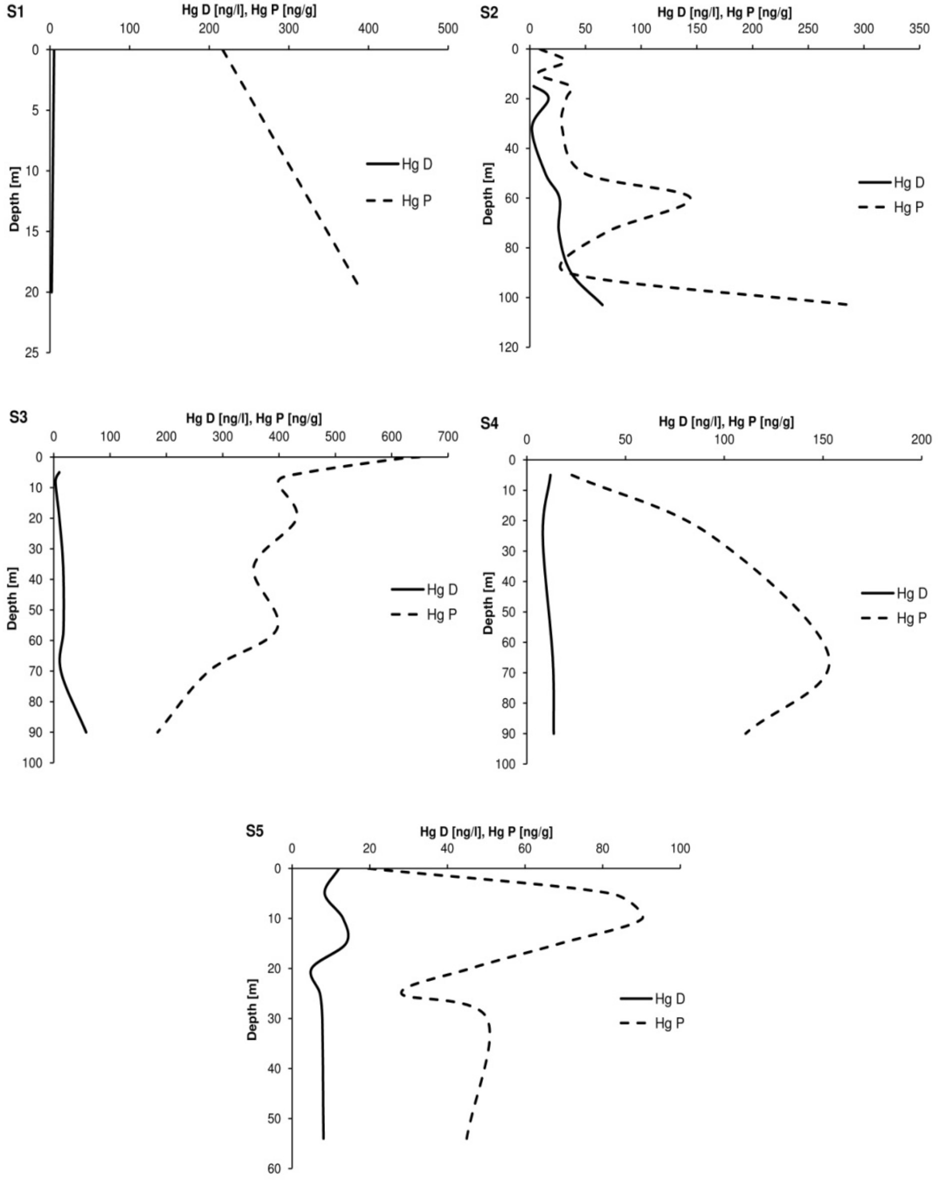

Fig. 3. Dissolved (HgD [ng/l]) and particulate (HgP [ng/g PSM] mercury concentrations depth profiles at the sampling stations

Rys. 3. Profile pionowe stężeń rozpuszczonej (HgD [ng/l]) i zawieszonej (HgP [ng/g PSM] rtęci na stacjach pomiarowych

Partitioning coefficients have been calculated according to formula (1).

$$K_D = \frac{HgP[ng/g]}{HgD[ng/l]} \tag{1}$$

Log K_D values vary in range from close to 0 to approximately 2.5 (Fig. 4), which differs from global average [2.2-3.5] (Allisson and Alisson, 2005), and is probably caused by specific conditions in the Baltic Sea.

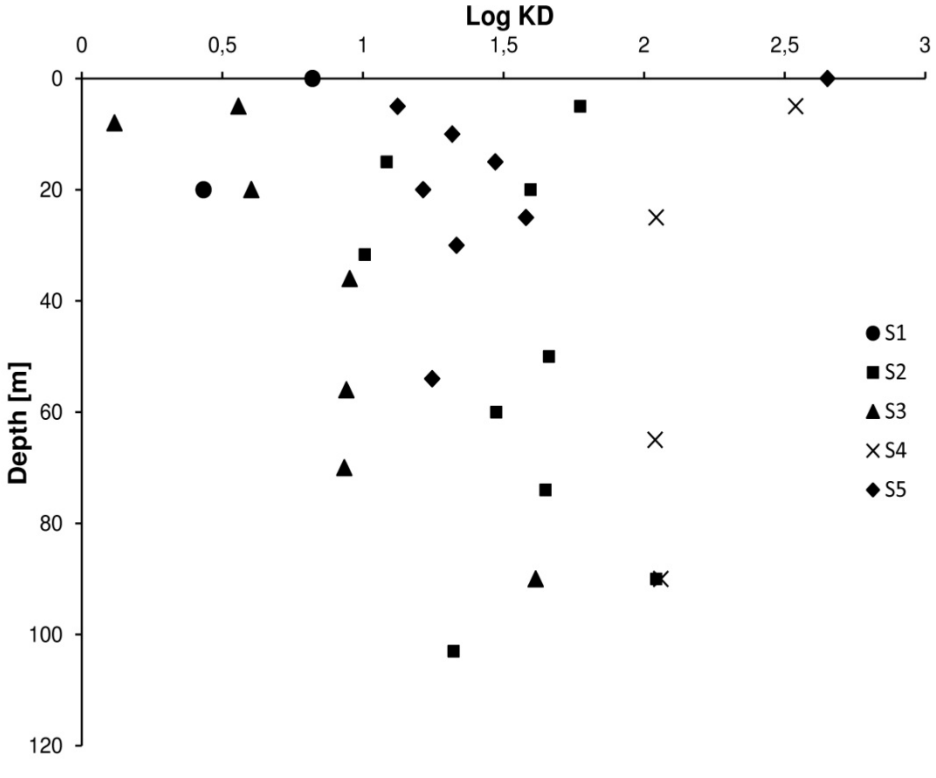

Fig. 4. Partitioning coefficient log K_D depth profiles at the sampling stations
Rys. 4. Profile pionowe współczynników podziału log K_D rtęci na stacjach pomiarowych

Log K_D seem to depend from several factors, one of them definitely being the season of sampling, and thus biological activity. A steady, decreasing log K_D profile can be observed only in spring profile (S3). Other samples show significant peak of K_D at halo- and thermocline, suggesting the occurrence of resorption at this point, or some sort of accumulation of mercury rich suspended matter before deposition, and following mercury release in deep, anoxic waters. As a matter of fact, both processes are known to occur in the coastal zone (Laurier et al. 2003; Barghiani and Ristori, 1995), however the latter has been suggetsed to be dominant in southern Baltic (Pempkowiak et al., 1998).

4. Conclusions

Both dissolved and particulate mercury levels are no doubt connected to input variability, and vicinity to mercury source. This is demonstrated by higher mercury levels close to the Vistula mouth, as well as elevated concentrations in spring, which follows enhanced water discharge by rivers and elevated atmospheric mercury concentrations due to winter heating. However, part of the particulate mercury seasonal variability is caused by biotic factors, namely plankton abundance and mercury acumulation therein.

The partitioning of mercury is a function of organic matter decomposition and particulate matter settling rate, possibly influenced by the oxic conditions below the halocline and sediment/water interaction. Longer residence times of mercury in density anomalies area results in increase of particulate mercury content in SPM, regardless of SPM concentration in the water column.

References

1. **Allison J.D., Allison T.L.:** *Partition Coefficients for Metals in Surface Water, Soil, and Waste.* U.S. Environmental Protection Agency, Athens, GA. Publication No. EPA/600/R-05/074, 2005
2. **Aubreau S.N., Pereira E., Vale C., Duarte A.C.:** *Accumulation of mercury in Sea Bass from a contaminated lagoon (Ria de Aveiro, Portugal).* Mar. Poll.Bull., 40, 293-297, 2000.
3. **Barighigiani C., Ristori T.:** *Preliminary results on the role of rivers in total Hg concentrations in marine sediments and benthic organisms of coastal area of Italy.* Water Air Soil Poll., 80, 1017-1020, 1995.
4. **Bełdowski J., Pempkowiak J.:** *Horizontal and vertical variabilities of mercury concentration and speciation in sediments of the Gdansk Basin, Southern Baltic Sea.* Chemosphere, 52, 645-654, 2003.
5. **Bełdowski J., Pempkowiak J.:** *Mercury concentration and speciation changes along source/sink transport pathway (Southern Baltic).* Est. Coast Shelf. Sci., in press, 2006.
6. **Beszczyńska-Moller A.:** *Dynamika wód wlewowych w Bałtyku Południowym.* Ph D. Institute of Oceanology PAS, 168 pp, 2002.

7. **Bloom N.S., Crecelius E.A.:** *Determination of mercury in seawater at subnanogram per liter levels.* Mar Chem 14, 49-59, 1983.
8. **Boening D.W.:** *Ecological effects, transport, and fate of mercury: a general review.* Chemosphere, 40, 1335-1351, 2000.
9. **Cossa D., Coquery M., Gobeil C., and Martin J. M.:** *Mercury fluxes at the ocean margins. In Global and Regional Mercury cycles: Sources, Fluxes and Mass Balances.* (eds. W. Baeyens, R. Edbinghaus, and O. Vasiliev), Kluwer, Dordrech, pp. 229-247, 1996.
10. **Cossa D., Gobeil C.:** *Mercury Speciation in the Lower St. Lawrence Estuary.* Can. J. Fish. Aquat. Sci., 57, 138-147, 2000.
11. **Cossa D., Michel P., Noel J., Auger D.:** *Vertical profile of total mercury in relation to arsenic, cadmium and copper distributions at the eastern North Atlantic ICES reference station (46 N; 6 W).* Oceanol. Acta, 15, 603-608, 1992.
12. **Forstner U., Wittmann G.:** *Metal pollution in the aquatic environment.* Springer, Berlin, 1981.
13. HELCOM, *Progress Reports on Cadmium, Mercury, Copper and Zinc.* BSEP 24, 71-100, 1987.
14. HELCOM, *The Fourth Baltic Sea Pollution Load Compilation (PLC-4).* Balt. Sea Environ. Proc. No. 93, 2004.
15. **Jackson T.A.:** *Mercury in aquatic ecosystem.* In: Langston, J., Bebiano, M.J. (Eds.), Metal metabolism in Aquatic Environment. Chapman & Hall, London, pp. 178-249, 1998.
16. **Laurier F.J.G., Cossa D., Gonzalez J.L., Breviere E., Sarazin G.:** *Mercury transformations and exchanges in a high turbidity estuary: the role of organic matter and amorphous oxyhydroxides.* Geochim. Cosmochim. Acta, 67, 3329-3345, 2003.
17. **Mason R.P., Fitzgerald W.F., Morel F.M.M.:** *The biogeochemical cycling of elemental mercury: Anthropogenic influences.* Geochim. Cosmochim. Acta 58, 3191-3198, 1994.
18. **Pempkowiak J., Cossa D., Sikora A., Sanjuan J.:** *Mercury in water and sediments of the southern Baltic Sea.* Sci. Tot. Environ., 213, 185-192, 1998.
19. **Pohl C., Hennings U.:** *The coupling of long-term trace metal trends to seasonal diffusive trace metal fluxes at the oxic-anoxic interface in the Gotland Basin; (57;19,20`N; 20;03,00E) Baltic Sea.* J. Mar. Sys. 56, 207-225, 2005.
20. **Schroeder W.H., Munthe J.:** *Atmospheric Mercury – an Overview.* Atmospheric Environment 29, 809-822, 1998.
21. **Voipo A.:** *The Baltic Sea.* Elsevier Sci., New York, 1981.

Współczynniki podziału rtęci między fazę rozpuszczoną a cząsteczkową w Bałtyku Południowym

Streszczenie

Rtęć dostarczana do środowiska trafia do morza, gdzie, na wskutek swojego powinowactwa do materii zawieszonej jest usuwana z kolumny wody i ulega depozycji do osadów dennych. Ze względu na gradienty gęstości występujące w Morzu Bałtyckim, rtęć związana z zawiesiną może zatrzymywać się na halo klinie lub termoklinie, gdzie na wskutek dekompozycji materii organicznej może zostać uwolniona do środowiska.

Wyznaczono współczynniki podziału rtęci między fazę zawieszoną a rozpuszczoną w kolumnie wody w rejonie Ujścia Wisły, Zatoki Gdańskiej, Głębi Gdańskiej i otwartego Bałtyku Południowego. Zarówno stężenie rtęci zawieszonej jak i rozpuszczonej było powiązane z sezonem pobierania prób jak i bliskością do źródeł rtęci. Najwyższe stężenia odnotowano w ujściu Wisły, a także w próbach z obszaru Zatoki Gdańskiej pobieranych wiosną. Było to prawdopodobnie wywołane zwiększonym spływem rzecznym oraz podwyższonym, na wskutek okresu grzewczego, stężeniem rtęci atmosferycznej.

Zmienność sezonowa została odnotowana także pod względem współczynników podziału. Zwiększony udział cząsteczkowej frakcji rtęci zauważono w próbach wiosennych, co zostało przypisane głównie bioakumulacji rtęci przez fitoplankton.

Równowaga między rozpuszczoną a cząsteczkową formą rtęci zmieniała się w profilu pionowym w kolumnie wody. Współczynnik podziału między frakcję rozpuszczoną a cząsteczkową wydaje się być funkcją dekompozycji materii organicznej i prędkości opadania zawiesiny. Dłuższy czas rezydencji zawiesiny w obszarach anomalii gęstościowych (halo- i termokliny) związany jest z dekompozycją zawartej w zawiesinie materii organicznej i uwalnianiem rtęci do wody. Jednakże równoległy proces resorpcji prowadzi do kształtowania się specyficznej równowagi w obszarze klin jesienią, co skutkuje wyższymi niż w kolumnie wody stężeniami rtęci w zawiesinie, zaś proces przechodzenia rtęci do fazy rozpuszczonej dominuje w głębszych warstwach wody, co najprawdopodobniej jest skutkiem warunków redukcyjnych panujących poniżej halokliny.

Dystrybucja rtęci jest funkcją rozkładu materii organicznej i prędkości sedymentacji cząstek stałych, prawdopodobnie również wpływ mają warunki tlenowe poniżej halokliny oraz interakcja między wodą i osadem. Dłuższy czas przebywania rtęci w obszarach anomalii gęstościowych powoduje wzrost zawartości rtęci cząsteczkowej w materii zawieszonej, niezależnie od stężenia materii zawieszonej w kolumnie wody.