

**Mercury fluxes  
through the sediment  
water interface and  
bioavailability of mercury  
in southern Baltic Sea  
sediments\***

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**KEYWORDS**

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JACEK BEŁDOWSKI\*  
MICHAŁ MIOTK  
JANUSZ PEMPKOWIAK

Marine Chemistry and Biochemistry Department,  
Institute of Oceanology,  
Polish Academy of Sciences,  
Powstańców Warszawy 55, PL-81-712 Sopot, Poland;

e-mail: hyron@iopan.gda.pl

\*corresponding author

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**Abstract**

Sediment cores collected in several areas of the southern Baltic were analysed for total mercury ( $Hg_{TOT}$ ) and five operationally defined mercury fractions:  $Hg_A$  – contained in pore waters,  $Hg_F$  – bound to fulvic acids,  $Hg_H$  – bound to humic acids,  $Hg_S$  – bound to sulphide, and  $Hg_R$  – residual. An effort was made to quantify mercury fluxes at the sediment/water interface in the study area. Net mercury input, calculated on the basis of sedimentation rate and concentration in the uppermost sediments, ranged from 1 to 5.5 ng cm<sup>-2</sup> year<sup>-1</sup>. Mercury remobilisation from sediments due to diffusion and resuspension was calculated from the proportion of labile mercury and the velocity of near-bottom currents. The results showed that the return soluble and particulate fluxes of mercury from the sediments to the water column constitute a substantial proportion of the input

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(20–50%), and are slightly higher than those found in pristine areas, although they are less than the values recorded in areas with a history of mercury contamination. In addition, an index was developed to assess the methylation potential of mercury in sediments. Mercury contained in pore waters, and mercury bound to fulvic and humic acids together with Loss on Ignition were used to calculate the semi-quantitative methylation potential ( $P_m$ ). Despite the simplicity of this approach,  $P_m$  correlates well with methyl mercury in fish from the study area.

## 1. Introduction

Mercury is a highly toxic metal. Because of its affinity to thiol groups it may react with proteins, affecting cellular membranes, inhibiting enzymes or damaging DNA and RNA helices. It is characterised by high bioaccumulation, and its organic species (i.e. methyl mercury) may be subject to biomagnification in food chains (Boening 2000). In the marine environment mercury, owing to its affinity for particulate matter, is readily scavenged from the water column (Laurier et al. 2003) and transferred to the bottom sediments (Forstner & Wittmann 1981, Cossa & Gobeil 2000). This is particularly evident in coastal regions, where concentrations of suspended matter – both biotic and abiotic – are high. One such area is the Baltic Sea.

In previous studies a sharp decrease in mercury concentration in the uppermost sediment layers in relation to subsurface sediments was reported (Beldowski 2004). This may be attributed to the reduced mercury load in recent decades, changes in the sedimentation regime or remobilisation of mercury from sediments to the water column. However, the roughly twofold reduction in concentration recorded in this region is greater than the known decrease in mercury emissions to the environment there (Borg & Jonsson 1996), and analyses of  $^{210}\text{Pb}$  activities do not show significant changes in the sedimentation rate (Beldowski & Pempkowiak 2008). Therefore, the observed concentration changes are likely to have resulted from the upward diffusion of labile mercury species from the uppermost sediment layers. As yet the process has been neither quantified nor investigated.

Remobilisation of mercury can be estimated mathematically. This requires that the concentrations of mobile mercury in the sediments be known (Boudreau 1997). Mercury is present in the bottom sediments in several physicochemical forms, differing in bioavailability and remobilisation potential. The latter can be readily assessed from mercury speciation studies (Beldowski & Pempkowiak 2003). The major mercury species in marine sediments were operationally divided into the fractions contained in the pore waters ( $< 0.45 \mu\text{m}$ ) ( $\text{Hg}_A$ ), bound to fulvic acids ( $\text{Hg}_F$ ), bound to humic acids ( $\text{Hg}_H$ ), bound to sulphides ( $\text{Hg}_S$ ) and residual ( $\text{Hg}_R$ ) (Wallschläger et al. 1998a, Beldowski & Pempkowiak 2003).

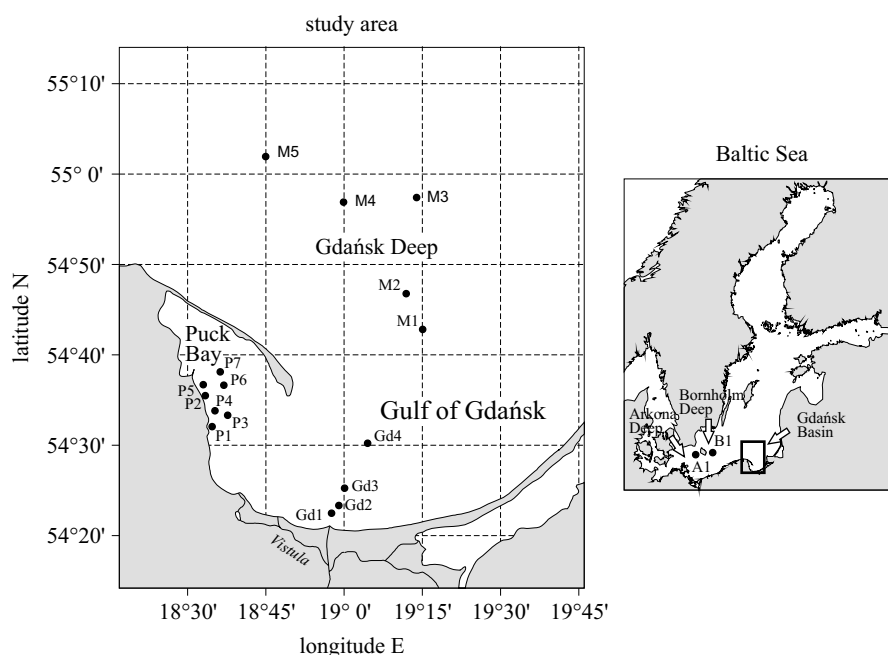
This paper gives the results of total Hg concentration measurements and of operationally defined mercury species in a series of sediment samples collected in the southern Baltic. On the basis of mercury concentration and speciation, bioavailability and fluxes resulting from diffusion and resuspension were calculated.

## 2. Material and methods

Surficial sediments were collected in several areas of the southern Baltic Sea in the period 1999–2002. Figure 1 shows the location of the sampling stations.

Samples from stations Gd1, Gd2 and Gd3 were collected with a Reineck-type box corer; those from the other stations were collected with a gravity corer. The top centimetre of sediment was sampled by cutting it away with a stainless steel blade, whereas the fluffy layer suspended matter covering the sediments was collected with a syringe.

Water samples for mercury analysis were obtained by siphoning near-bottom water onboard with an all-Teflon pump and passing it through ignited glass filters (pore size  $0.45 \mu\text{m}$ ). Samples were stored in borosilicate bottles with Teflon caps, pre-cleaned by storing 4M nitric acid in them for a week, then rinsed with 1%  $\text{HNO}_3$  in MilliQ water.



**Figure 1.** Location of sampling stations

Before mercury analysis all the sediment samples were homogenised and portions taken for the determination of moisture, organic matter and grain size distribution. Sediment cores from the sampling stations were  $^{210}\text{Pb}$  dated (Pempkowiak 1991). Sedimentation rates were calculated from the  $^{210}\text{Pb}$  profiles using the least squares procedure (Robbins 1978). The geochronology of the cores is dealt with elsewhere (Bełdowski & Pempkowiak 2008).

For total mercury analysis the samples were digested with acids ( $\text{HNO}_3:\text{HClO}_4:\text{HF}$ ) and the digests diluted with MilliQ water prior to analysis (for details – see Pempkowiak et al. 1998).

To assess the speciation of mercury in the samples, sequential extraction was performed employing a procedure adapted from Wallschläger et al. (1998a) (see Figure 2). As a result of the sequential extraction procedure solutions containing the following mercury fractions (either labile or stable) were isolated:

$\text{Hg}_A$  – Hg contained in pore waters ('dissolved' – labile);

$\text{Hg}_F$  – Hg bound to fulvic acids (fulvic – labile);

$\text{Hg}_H$  – Hg bound to humic acids (humic – labile);

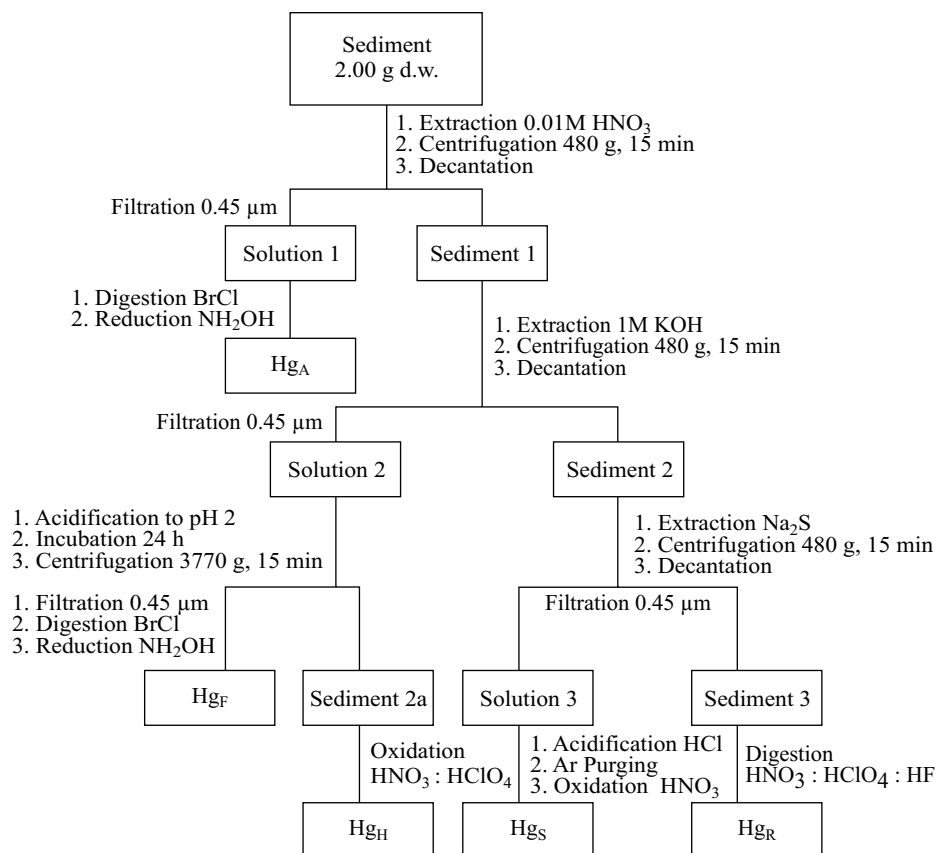
$\text{Hg}_S$  – HgS and Hg bound to sulphides (sulphidic – stable);

$\text{Hg}_R$  – Hg bound to humins and contained in a mineral matrix (residual – stable).

Quality assurance was provided by including attested samples (ABSS – Baltic sediment – obtained from the Baltic Sea Research Institute, Warnemünde, Germany) in each extraction run. The analyses of reference material NIES-2 (obtained from the National Institute of Environmental Studies, Japan Environmental Agency) proved satisfactory in terms of accuracy and precision of determination (recovery  $92.5 \pm 9.5\%$ ,  $n = 5$ ). For a detailed description of method validation against model compounds, see Wallschläger et al. (1996, 1998a,b); more information on the QA/QC procedures employed in this study has been published elsewhere (Bełdowski & Pempkowiak 2007).

Cold vapour atomic absorption spectrophotometry and cold vapour atomic fluorescence spectrophotometry were used to determine Hg in the extraction solutions. LODs were  $2 \text{ ng g}^{-1} \text{ d.w.}$  for CV-AAS and  $0.5 \text{ ng g}^{-1} \text{ d.w.}$  for CV-AFS.

Water samples for mercury analysis were oxidised by the addition of  $\text{BrCl}$  and pre-reduced with hydroxylamine hydrochloride solution 1 hour prior to analysis by CV-AFS, according to US EPA method 1631 (US EPA 2002).



**Figure 2.** The major steps in the sequential extraction procedure

To determine environmental parameters and to produce correlation and variability graphs (Figure 7), the following data sources were used: Korzeniewski (ed.) 1993, Siebert et al. 1999, Falandysz et al. 2000, Fant et al. 2001, Boszke et al. 2002, 2003, Voigt 2004, Ciesielski et al. 2006, IOW 2008, Millat 2008, SFI 2008.

The total mercury concentration in surface sediments, dry matter content in surface sediments and sediment accumulation rate were used to calculate the net mercury input, which is given by the following formula:

$$\Delta\text{Hg}_{\text{TOT}} = \frac{\omega}{10} \times \left(1 - \frac{W}{100}\right) d_s \text{Hg}_{\text{TOT}},$$

where

$\Delta\text{Hg}_{\text{TOT}}$  – net mercury input to bottom sediments [ $\text{ng year}^{-1} \text{cm}^{-2}$ ];

$\omega$  – sedimentation rate [ $\text{mm year}^{-1}$ ];

- W – water content in sediments [%];  
 $d_S$  – sediment density (for the study area the value of  $2.45 \text{ g cm}^{-3}$  was used);  
 $\text{Hg}_{\text{TOT}}$  – total mercury concentration in surface sediments.

One of the chief mechanisms responsible for mercury remobilisation from sediments is diffusion of mercury contained in pore waters. In the speciation scheme used in this study the pore water mercury was extracted as the first fraction –  $\text{Hg}_A$ . Diffusion, calculated according to Fick's first law of diffusion in porous media, is given by the following formula:

$$J = -\varphi D_S \left( \frac{dC}{dz} \right),$$

where

- J – diffusive flux [ $\text{ng cm}^{-2} \text{ s}^{-1}$ ];  
 $\varphi$  – porosity [dimensionless];  
 $D_S$  – diffusion coefficient [ $\text{cm}^2 \text{ s}^{-1}$ ];  
 $dC$  – concentration difference of soluble mercury ( $\text{Hg}_A$ ) in the uppermost sediment layer and in near-bottom water [ $\text{ng g}^{-1}$ ];  
 $dz$  – depth difference between uppermost sediment layer and near-bottom water [cm].

The diffusion coefficient was calculated according to Ullmann & Aller (1982), the assumptions for sediments of porosity  $< 70\%$  being that  $D_S = \theta^2 D_0$ , where  $\theta$  – sediment tortuosity [dimensionless] and  $D_0$  – molecular diffusion coefficient for mercury in seawater ( $= 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) (Gobeil & Cossa 1993). The tortuosity of the sediments was calculated according to Beekman's (1990) model:

$$\theta^2 = \varphi / (1 - (1 - \varphi)^{1/3}),$$

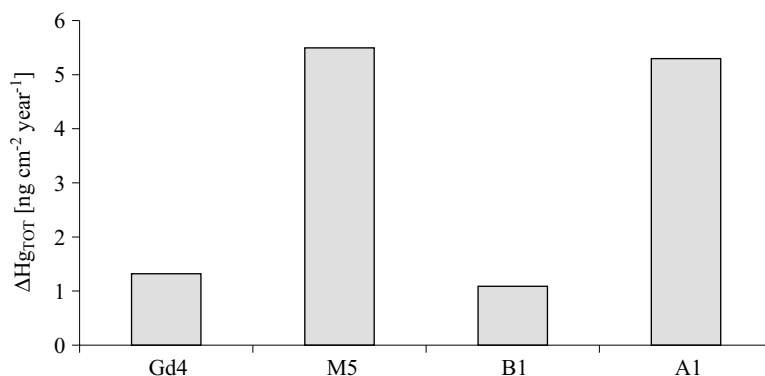
where  $\varphi$  – porosity [dimensionless].

The mercury concentrations in near-bottom water required to calculate the force driving diffusion were measured in filtered near-bottom waters collected from the Bornholm Deep, the Gdańsk Deep and the Vistula mouth (Figure 1).

### 3. Results and discussion

#### 3.1. Mercury input

Mercury delivered to the bottom sediments may be released to overlying water as a result of diagenetic speciation changes and physical processes



**Figure 3.** Net mercury input [ $\text{ng cm}^{-2} \text{ year}^{-1}$ ] to sediments in the study area

such as sediment mixing and resuspension, diffusion and dispersion. In order to demonstrate the importance of mercury remobilisation from the sediments, it is usual to relate it to the net mercury input to the sediments (Gagnon et al. 1997, Covelli et al. 1999). The ‘net input’ is the amount of mercury retained in the sediments in a given time period. Figure 3 presents the net mercury input to sediments in selected cores from the study area.

The highest net mercury inputs were recorded in sediments from the Arkona Deep. In Gdańsk Basin sediments, values similar to those from the Arkona Deep were found on the western slope of the Gdańsk Deep, an area fed with suspended matter carried by the bottom current flowing away from the Arkona Deep (Bełdowski & Pempkowiak 2007). Mercury input to sediments from both the central and eastern parts of the Gdańsk Deep is in the range of 1–2  $\text{ng cm}^{-2} \text{ year}^{-1}$ , and is similar to that in the Bornholm Deep. Such a low value could be the consequence of mercury remobilisation from the uppermost sediment layer.

### 3.2. Mercury remobilisation

Mercury can be remobilised from sediments as a result of physical processes like diffusion or sediment resuspension. Moreover, mercury can be extracted by benthic organisms, which may be consumed by pelagic predators, in which case mercury is removed from the sediments (macrozoobenthos, macrophytobenthos); these organisms may also move mercury within the sediments (bacteria, deposit feeders). Mercury remobilised from sediments can enter the food chain. In this paper physical processes are described quantitatively, whereas the potential transfer of mercury to the food chain is represented by an index related to the bioavailability of mercury in the uppermost sediments.

### 3.2.1. Diffusive fluxes

Tables 1 and 2 respectively list mercury concentrations and environmental parameters in near-bottom waters.

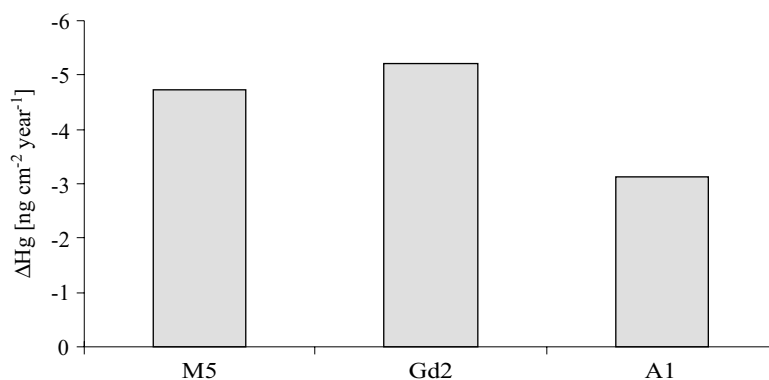
**Table 1.** Mercury concentration in the near-bottom water layer in the study area [ $\text{ng dm}^{-3}$ ]

Area	Concentration [ $\text{ng dm}^{-3}$ ]
Bornholm Deep	2.5
Central Gdańsk Deep	1.8
Vistula mouth	1.9

**Table 2.** Salinity and oxygen concentrations of surficial sediments in the near-bottom water layer and loss on ignition (LOI) in the study area

Region	Salinity [PSU]	Oxygen [ $\text{cm}^3 \text{dm}^{-3}$ ]	LOI* [%]	References
Puck Bay	7.65	7.38	0.48–41.67	Korzeniewski (ed.) 1993
Gulf of Gdańsk	9.34	0.25–3.95	18.11–23.54	SFI 2008
Gdańsk Deep	11.94	0	0.32–22.50	SFI 2008
Bornholm Deep	15.74	0.53	16.84	SFI 2008
Arkona Deep	15.46	3.42	14.92	IOW 2008

\* – this study.



**Figure 4.** Diffusion of mercury from sediments to overlying water shown as a negative flux [ $\text{ng cm}^{-2} \text{year}^{-1}$ ]



Fluxes were calculated only for the sediments in which  $Hg_A$  concentrations in the uppermost sediment layer exceeded LOD (see Figure 4).

The fluxes calculated in this manner are significantly smaller than those found in areas heavily polluted with mercury, such as the Gulf of Trieste (an area receiving a mercury load from a now closed mercury mine –  $1.78 \mu\text{g cm}^{-2} \text{ year}^{-1}$ ; Covelli et al. 1999) or Bellingham Bay (polluted by effluents from a chlor-alkali plant) –  $3.65 \mu\text{g cm}^{-2} \text{ year}^{-1}$ ; Bothner et al. (1980). However, fluxes calculated for the Baltic Sea exceed those calculated for the remote area of the Laurentian Trough –  $0.95 \text{ ng cm}^{-2} \text{ year}^{-1}$  (Gobeil & Cossa 1993). This could indicate that the study area is to some extent polluted with mercury.

The high values recorded at station Gd2 are due to the considerable mobility of mercury in the sandy sediments prevalent in this area. The substantial remobilisation in sediments from station M5 is due to the large proportion of the mercury fraction  $Hg_A$  contained in these sediments. The diffusive fluxes in sediments from the Arkona Deep and from the western slope of the Gulf of Gdańsk make up an important part of the input. This suggests that the input of mercury to these sediments is 50% higher in the Arkona Deep and even 100% greater at station M5 than the net input. The diffusive flux at station Gd2 exceeds the net input for the Gulf of Gdańsk (based on values for station Gd4). This can be attributed to both the grain size composition of the sediments from this station and to proven mercury transport to the sedimentation basin from those sediments (Bełdowski & Pempkowiak 2003).

### 3.2.2. Resuspension

Apart from diffusion, resuspension of the uppermost sediments is an important process causing remobilisation of metals from sediments (Boudreau 1997). Resuspension occurs when a shear stress exerted by water movement exceeds a critical value for a given sediment type. The upper layers of cohesive sediments are resuspended as a result of a fast bottom current, but resuspension of the fluffy layer suspended matter (FLSM) covering the sediments in the study area is also possible in the presence of currents with velocities of  $4\text{--}6 \text{ cm s}^{-1}$  (Pempkowiak et al. 2002).

The rate of sediment erosion can be roughly approximated by the following formula (Pruszek 1998, Lick 2008):

$$V_E = M(\tau_b - \tau_{\text{crit}}),$$

where

$V_E$  – sediment erosion rate [ $\text{g cm}^{-2} \text{ s}^{-1}$ ];

$M$  – proportionality parameter (from  $10^{-4}$  to  $2 \times 10^{-3}$ );

$\tau_b$  – bottom shear stress [dyne cm<sup>-2</sup>];  
 $\tau_{crit}$  – critical shear stress for a given sediment type [dyne cm<sup>-2</sup>].

The bottom shear stress was calculated according to Lund-Hansen et al. (1997) and, following conversion of units, was substituted in equation (5.6):

$$\tau_b = C_d \rho_w U^2,$$

where

$\tau_b$  – bottom shear stress [N m<sup>-2</sup>];  
 $C_d$  – bottom resistance coefficients =  $1.1 \times 10^{-3}$ ;  
 $\rho_w$  – seawater density (assumed 1.0025 g cm<sup>-3</sup>);  
 $U$  – current speed [cm s<sup>-1</sup>].

The critical shear stress ( $\tau_{crit}$ ) for FLSM in the southern Baltic was obtained experimentally by Christiansen et al. (2002); it was  $> 0.023$  N m<sup>-2</sup>.

Calculations of bottom shear stress used the approximate bottom current velocities at the stations from which FLSM samples were collected. The velocities were averaged for each month. The Princeton Ocean Model based on density fields, adopted by Jankowski (2002), was used to compute current speeds (Table 3).

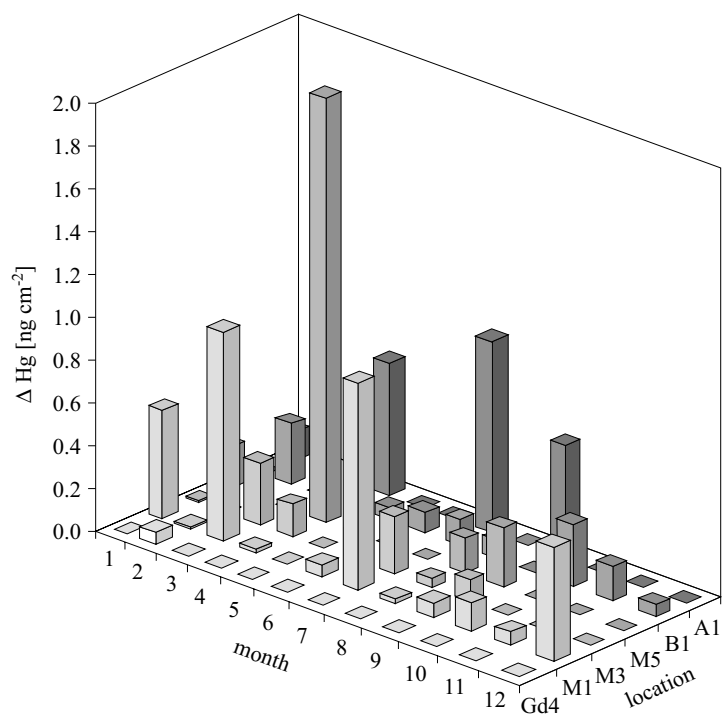
**Table 3.** Average bottom current velocities at sampling stations, calculated for each month using the POM model

Month	Bottom current velocities [cm s <sup>-1</sup> ] at sampling stations						
	A1	M3	B1	M1	Gd4	M5	Gd2
January	5.0	4.6	4.2	9.9	2.9	5.5	2.8
February	1.7	2.5	14.5	4.6	5.8	2.2	1.7
March	3.1	8.4	1.7	12.8	0.2	4.4	1.7
April	6.2	6.8	4.5	4.0	1.0	10.3	3.4
May	1.7	1.2	7.3	3.8	3.5	2.6	4.1
June	1.2	6.5	8.8	5.4	2.9	2.3	2.4
July	6.7	8.0	9.5	12.4	10.0	2.0	4.5
August	2.8	5.3	8.1	4.9	2.7	5.3	1.9
September	6.0	6.0	3.9	5.5	2.9	5.8	0.6
October	2.8	1.6	13.8	6.3	2.9	3.4	3.0
November	1.5	3.1	10.7	5.4	2.1	6.2	2.3
December	3.4	3.2	7.3	9.5	3.2	4.2	1.78

The mass of resuspended FLSM calculated on the basis of computed current velocities must be regarded as a potential value. It indicates that the current is capable of raising the solid particles contained in the FLSM

**Table 4.** Potential mass of fluffy layer suspended matter (FLSM) resuspended monthly in successive resuspension events at each station

Month	Mass of FLSM resuspended monthly at sampling stations [mg cm <sup>-2</sup> month <sup>-1</sup> ]					
	A1	M3	B1	M1	Gd4	M5
January	126	23		2279		268
February			5118	17	332	
March		1483		4209		
April	533	760		71		2489
May			993			
June		628	1641	223		
July	731	1319	2052	3909		
August		210	1305	92		198
September	455	465		289		362
October			4912	529		
November			2826	238		
December			936	2001		

**Figure 5.** Fluxes of mercury [ng cm<sup>-2</sup>] released each month from sediments as a result of resuspension

in a single resuspension event. Resuspension equalling the calculated value is only possible as the sum of several resuspension/deposition events (Table 4).

To assess the amount of mercury released during resuspension, the partition coefficient ( $K_D$ ) between the particulate and dissolved mercury concentrations in the FLSM was used. The coefficient was calculated during experiments with resuspended sediment:  $\log K_D = 5.35$  (Kim et al. 2004); for these calculations, the total mercury concentrations ( $Hg_{TOT}$ ) in FLSM were used. These fluxes, based on the calculated mass of resuspended FLSM, represent potential maximum monthly values (see Figure 5).

Monthly fluxes of mercury released in the course of resuspension varied from  $0 \text{ ng cm}^{-2} \text{ month}^{-1}$ , when no resuspension took place, to  $1.9 \text{ ng cm}^{-2} \text{ month}^{-1}$  at station M5 in April. In the Gdańsk Basin larger fluxes were recorded in autumn, as a consequence of the faster current speeds in that season. The sediments collected from the southern rim of the Gdańsk Deep (M1) contained the greatest sum of remobilised mercury fluxes ( $3.33 \text{ ng cm}^{-2} \text{ year}^{-1}$ ); this is the effect of frequent resuspension. Fluxes for the central part of Gdańsk Deep (M3) were comparable in magnitude and variation to those from the Bornholm Deep.

### 3.2.3. Mercury bioavailability

The bioavailability of mercury depends on the proportion of labile species, which in turn, is a function of environmental and biological factors. Methyl mercury ( $CH_3Hg$ ) is considered to be the most readily bioavailable mercury species. Mercury is methylated by microbial activity during the degradation of organic matter, mainly in bottom sediments (Jensen & Jernelov 1969, Compeau & Bartha 1985, Benoit et al. 1999). Quantitative relationships between the methylation rate and mercury speciation have not been unequivocally defined. The methylation rate is governed by several factors, including sulphide availability, pH and temperature (Jackson 1998). Since the pH in sediment pore waters of the study area is stable and close to that of seawater ( $\approx 8.1$ ), whereas sulphide availability is a function of Eh in sediments (Emylyanov 1995, Sternbeck & Sohlenius 1997), the redox potential Eh appears to be a crucial parameter for mercury methylation. In southern Baltic sediments, the reducing environments required for mercury methylation are associated with high concentrations of organic matter (Pempkowiak 1994). Therefore, it can be safely assumed that the methylation rate is directly proportional to the concentration of organic matter, a factor closely related to the microbial activity. The latter is not only directly responsible for mercury methylation, but also controls Eh,  $O_2$  concentration and sulphide production.

The pool of mercury available for methylation comprises both inorganic, dissolved mercury and mercury in complexes with organic matter (Wallschläger et al. 1998). The methylation rate is faster in anoxic conditions, but is limited by the presence of free sulphide ions, which react with mercury to form highly stable, insoluble HgS (WHO 1987).

Mercury methylation in bottom sediments is adequately described in the literature (Forstner & Wittmann 1981, Jackson 1998, Boening 2000), but a mathematical description of this process is lacking. In this study, an attempt was made to conceive a quantitative measure of the phenomenon. For this purpose, a semi-quantitative index – the ‘methylation potential ( $P_m$ )’ – is proposed to describe potential mercury methylation in the uppermost sediments. As a ‘potential’ this index does not include demethylation. Since the study area is limited in space, and the environmental conditions (salinity, temperature and material input) varied within a narrow range, it was assumed that the demethylation rate remains in constant proportion to methylation. The methylation potential was calculated according to the following formula:

$$P_m = \frac{(\text{Hg}_A + \text{Hg}_F + \text{Hg}_H) \text{ LOI}}{100},$$

where

$P_m$  – methylation potential [dimensionless];

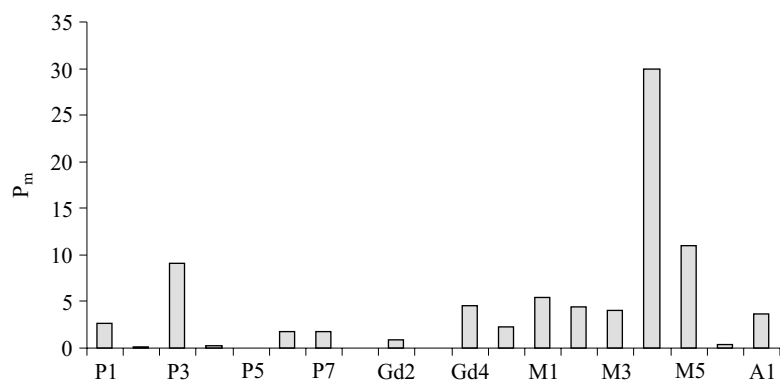
$\text{Hg}_A$  – dissolved mercury [ $\text{ng g}^{-1}$ ];

$\text{Hg}_F$  – fulvic-bound mercury [ $\text{ng g}^{-1}$ ];

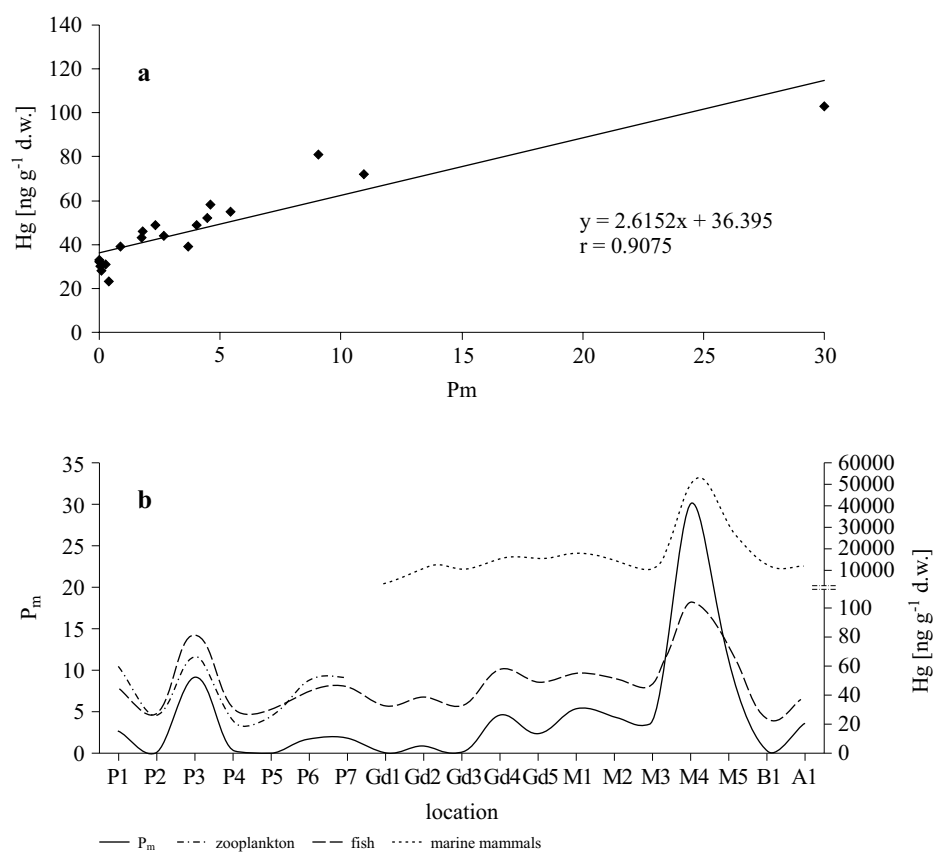
$\text{Hg}_H$  – humic-bound mercury [ $\text{ng g}^{-1}$ ];

LOI – loss on ignition [%].

It was assumed that the species obtained by sequential extraction ( $\text{Hg}_A$ ,  $\text{Hg}_F$  and  $\text{Hg}_H$ ), representing dissolved, fulvic-bound and humic-bound mercury, are a substratum for methylation, and the concentration of organic matter (represented by loss on ignition – LOI) served as an index of microbial activity. The choice of LOI as a proxy for organic matter was possible because of the similar mineral composition of the sediments of the study area, and hence, the similar LOI:TOC ratio (Emylyanov 1995, Pempkowiak et al. 2006). It was assumed that free sulphide ions, mercury sulphide and ionic mercury(II) were in equilibrium. Since HgS and mercury bound to sulphides were included in a discrete fraction, it was assumed that sulphide ions had no limiting effect on the labile fractions used in the equation as a substratum for methylation. Figure 6 shows calculated methylation potentials for the topmost sediments.



**Figure 6.** Methylation potential ( $P_m$ ) of sediments in the study area

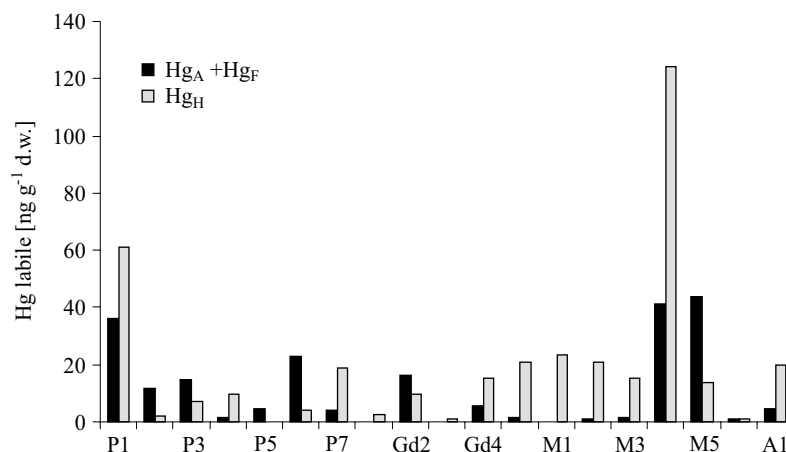


**Figure 7.** Results of correlation analysis between mercury in fish muscles and the methylation potential ( $P_m$ ) (a), and the variability of  $P_m$  and mercury in zooplankton, fish and marine mammals (b) in the study area

The highest potentials were recorded for sediments from Puck Bay (P3) and from the western slope of the Gdańsk Deep (M4, M5). The methylation potentials of sandy sediments (P2, P4, P5, Gd1 and Gd3) and muddy sand sediments (Gd2) are clearly lower than those in most muddy sediments. This is due to the natural conditions in sandy sediments where, because of their oxic character and lower organic matter content, mercury methylation is limited (Jackson 1998). Sediments with high  $P_m$  come from deeper areas, where the toxicity and bioavailability of methyl mercury are less important as the biomass of the zoobenthos is low in these areas (HELCOM 2003). However, methyl mercury released from the sediments in this area has been recorded in water tens of meters above the sea bed (Pempkowiak et al. 1998). The abnormally high methylation potentials recorded at station P3 could be due to the specific pollution caused by the wreck of the German ship 'Stuttgart' lying nearby (BHMW 2001).

There was a significant ( $r = 0.9075$ ) positive linear correlation between  $P_m$  and mercury in fish muscles (Figure 7a).

Because of the scarcity of data for zooplankton and marine mammals, only the correlation for fish is shown. A comparison of mercury concentration change in zooplankton and marine mammals with  $P_m$  change for areas where such data are available is shown in Figure 7b. The variability of Hg values in zooplankton from Puck Bay and in marine mammals from the Gdańsk Basin, Bornholm Basin and Arkona Basin was similar to  $P_m$ . Both the high correlation with MeHg in fish and the similar variability of  $P_m$  and methyl mercury in other environmental compartments suggest that despite its simplicity, this index could be used for a semi-quantitative comparison of



**Figure 8.** Bioavailable mercury fraction concentrations [ $\text{ng g}^{-1}$  d.w.] in sediments in the study area

methyl mercury exposure of marine organisms, at least in areas not differing much in term of sediment origin and environmental parameters.

Inorganic forms of mercury(II) are also bioavailable, but to a lesser extent than methyl mercury (Jackson 1998). This refers to dissolved mercury(II) and mercury(II) bound to fulvic acids, and to some extent also to mercury bound to humic acids (Wallschläger et al. 1998a,b, Boening 2000). Figure 8 gives the concentrations of these species.

The highest concentrations of easily bioaccumulated mercury species were recorded in Puck Bay (P1, P2, P3, P6), in the vicinity of the Vistula mouth (Gd2) and on the western slope of the Gdańsk Deep (M4, M5). Apart from the last area, mercury in sediments located closer to the shore is more readily bioavailable than that in offshore sediments.

### 3.3. Scenarios

Calculated methylation potentials, diffusive fluxes and fluxes caused by resuspension were used to predict changes in mercury remobilisation and bioavailability in response to increased input of mercury to the sediments. Two scenarios were considered –

1. Input up by 10%
2. Input up by 50%

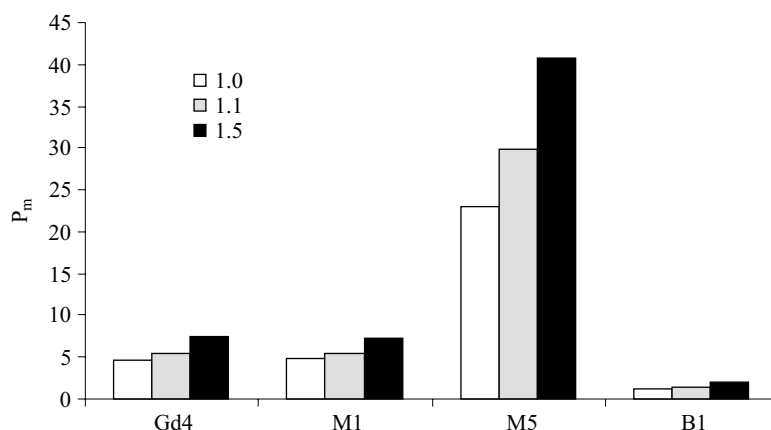
In both cases, the concentrations of total mercury and mercury species in the uppermost sediments were calculated on the assumption that mercury speciation remains the same. From these  $P_m$  and remobilisation potential were calculated.

#### 3.3.1. Mercury bioavailability change ( $P_m$ )

Methylation potential is a function of mercury species concentration, hence an increase in input (spread between species according to the proportions measured) will result in a higher value of this index. Figure 9 presents the calculated values.

The changes in methylation potential at the southern rim of the Gdańsk Deep (M1) and in the Bornholm Deep (B1) resemble the input changes. In sediments from the western slope of the Gdańsk Deep (M5) and from the Gdańsk Basin (Gd4), changes in  $P_m$  are greater than the input change: they are respectively equal to 22% and 16% for an input increase of 10%, and to 77% (M5) and 58% (Gd4) for a 50% increase. This indicates that an elevated mercury input will induce greater bioavailability of mercury, in some cases greater than the input change.

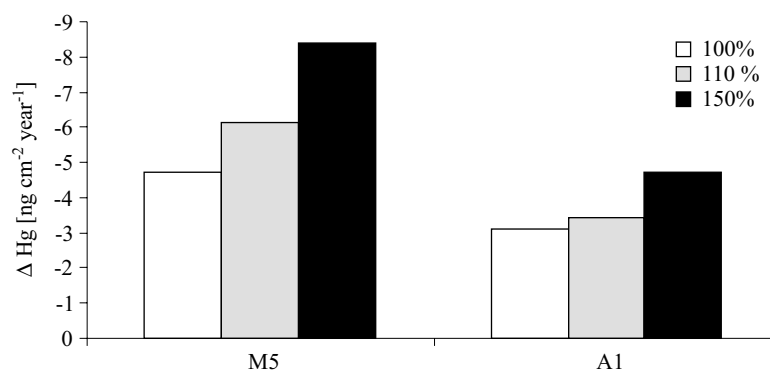




**Figure 9.** Methylation potential changes [%] due to mercury input increases of 10% (110%) and 50% (150%)

### 3.3.2. Remobilisation change

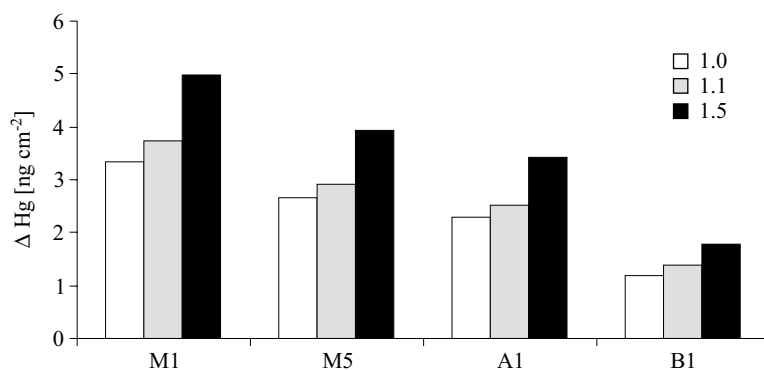
Diffusive fluxes changes were calculated only for sediments fulfilling two conditions: 1)  $Hg_A$  concentration above the detection limit; 2) Net input values calculated (see Figure 10).



**Figure 10.** Mercury diffusion fluxes from surface sediments (100%), and the change in mercury diffusion fluxes due to input increases of 10% (110%) and 50% (150%)

Mercury diffusion from the Arkona Deep sediments (A1) changed in proportion to input change – by 10% and 50%, respectively. Values of 30% and 77% were calculated for sediments from the western slope of the Gdańsk Deep (M5). This indicates that increased input may cause some sediments to become important sources of dissolved mercury.

Changes of fluxes associated with resuspension were calculated for sediments A1, B1, M1 and M5 (see Figure 11). Changes in remobilisation are in most cases proportional to input changes; in some areas (the western slope of the Gdańsk Deep), however, re-emission was stronger than the input change.

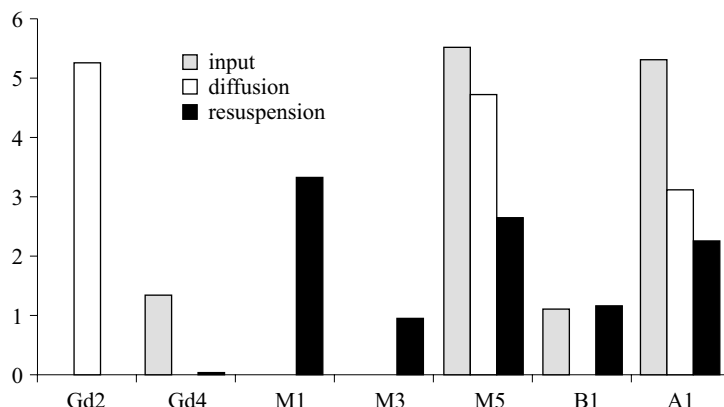


**Figure 11.** Mercury fluxes due to sediment resuspension (1), and flux change due to input increases of 10% (1.1) and 50% (1.5)

#### 4. Conclusions

The yearly load of mercury deposited in the southern Baltic sediments is highly variable (Gdańsk Deep  $\approx 6 \text{ ng cm}^{-2} \text{ year}^{-1}$ , Gdańsk Basin  $\approx 3 \text{ ng cm}^{-2} \text{ year}^{-1}$ , Arkona Deep  $\approx 6 \text{ ng cm}^{-2} \text{ year}^{-1}$ ). Mercury contained in the sediments is involved in a number of processes (biochemical transformations, diffusion and resuspension) causing its release to the overlying water. The return flux of mercury (according to calculations) may account for up to 50% of the mercury load deposited annually in the muddy sediments of the Gdańsk Deep (western slope) and Arkona Deep. A similar magnitude of the return flux has been calculated for sandy sediments (Gd2) from the Gulf of Gdańsk. It is clearly higher than the mercury inputs calculated for other muddy sediments from this area (Figure 12).

Mercury speciation analysis enabled different phenomena related to the presence of mercury in the environment to be modelled mathematically. Knowledge of labile mercury species concentration enabled the quantification of mercury bioavailability and mobility in the study area. Two indices are proposed in this respect: one, indicating the concentration of bioavailable mercury species, takes the highest values in areas close to anthropogenic mercury sources – in sediments in the vicinity of urban areas and close to the mouth of the River Vistula, and the other, representing the



**Figure 12.** A summary of mercury input and release fluxes in the study area

potential of mercury to be methylated in sediments. This second index takes higher values in deeper areas, especially in sediments below the halocline. In the sediments of the study area, the highest values were calculated for the bottom sediments of Gdańsk Deep. Our calculations showed an increase in bioavailability (given by the methylation potential) and return fluxes (by both diffusion and resuspension) exceeding the simulated increase in mercury load reaching the study area.

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