

ON MERCURY SPECIATION AND POSTSEDIMENTATION FATE IN PELAGIC SEDIMENTS OF THE SEA OF JAPAN

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The biogeochemical cycle of mercury (Hg) still remains in many respects unclear in spite of the intensive studies in last decades. Little is known about Hg postsedimentation behaviour and fate in deep sea pelagic sediments, which are final burial for both marine and terrestrial-bearing suspended materials.

The Sea of Japan shores and basin suffer diverse mining, industrial and agricultural activities of Japan, South and North Korea, and Pacific Russia. The western Kyushu I. is the exact place where the notorious Minamata Bay is situated.

The paper presents the results of investigation of Hg distribution, chemical speciation, and fate of recent pelagic sediments of the sea. Content of Hg in the chemical fractions, which are principal for Hg binding and mobility were studied, namely: H₂O, 0.05 M Na₂-EDTA pH 7, fulvic and humic acids, 1 N HCl, and humin (non-hydrolysing residue).



Fig. 1. Map of Sea of Japan showing sampling sites.

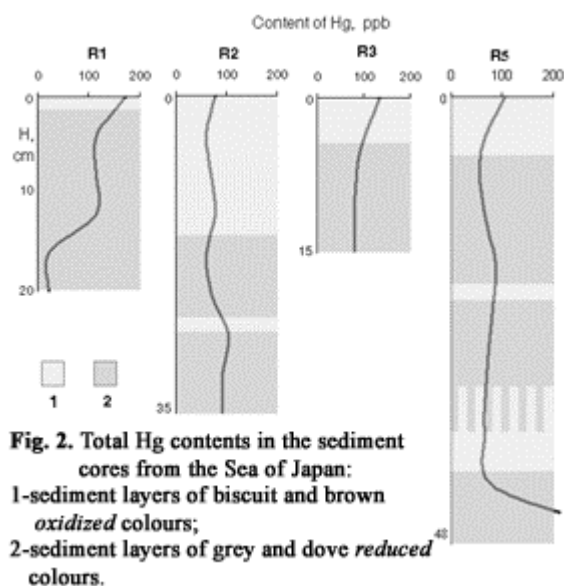
Materials and methods. Short 10-48 cm deep sediment cores were collected by a box-corer at 5 stations along the sea section from the SE to the NW (Fig. 1, Table 1). Detailed mineralogical and geochemical parameters of the cores are described by Astakhov & Polyakov (Geochem. Int., 2000, 9, 983). Methods and analytical scheme used can be found elsewhere (Kot & Matyushkina // J. Environ. Monit., 2002, 4, 803).

Results and discussion. The content of Hg in the sediment cores studied was rather low – 83 ± 30 ppb (21-173, n=25), with a single sizeable extreme in the downmost of core R5 of 445 ppb. The concentrations obtained are close to those reported for the contiguous inner Sea of Yatsushiro (Tomiyasu et al., 2000), and the inner Baltic Sea (Borg & Jonsson, 1996; Pempkowiak et al., 1998). Such content level indicates the absence of substantial specific sources of Hg to the deep part of the sea. Therefore, in spite of highly developed industrial and agricultural facilities based on the sea shores and the sea basin, and also a possible anthropogenic influence from the East China Sea via the Tsushima Current, Hg burden to the deep sea hasn't been affected noticeably during the industrial era.

Nevertheless, Hg distribution within the core depth evidently varies with a certain increase in the near-surface layers of cores R1, R3, and R5, and with a not so well-shaped peak in the near-surface layer of core R2 (Fig. 2). These peaks coincide with the near-surface layers of light brown and brown *oxidized* colours.

Table 1 Parameters of the sites sampled

Site index	Co-ordinates		Sea depth, m	Core depth, cm	Facies
	Latitude N	Longitude E			
R1	38°13,8'	137°21,8'	1104	0-20	slope, Honshu I.
R2	39°00,7'	136°34,8'	2650	0-35	bathyal, Yamato Basin
R3	39°45,9'	135°36,9'	1080	0-15	Yamato Height
R5	41°39,0'	133°32,8'	3540	0-48	bathyal, Japan Basin
R10	42°31,4'	132°20,6'	96	0-10	shelf, by the southern Primorye



To complicate matters, some Hg content peaks perfectly coincide with the oxidized-coloured middle and lower slices of R2 and R5.

These Hg content maxima evidenced two redox-type geochemical barriers for Hg, namely (1) the near-surface oxidized layers, and (2) the buried ones that Strakhov (1954) described as depleted in organic matter and microbial activity. These maxima confirm that Hg is capable of noticeable redox processes-conditioned post-depositional redistribution in sediments. Nevertheless, Hg burden in the near-surface sediments in all probability is caused by both factors: (1) global anthropogenic Hg dispersion during the industrial era that is proved clearly in

an extensive set of works, and (2) diagenesis processes. The effects of anthropogenic inputs *vs.* diagenetic redistribution on Hg enrichment of the near-surface sediment layers warrant further research.

Hg chemical speciation. Hg content in chemical fractions/extracts reflects, to a greater or lesser extent, Hg binding to different chemical and physical-chemical sediment constituents (groups of compounds/associates/formations) consisting the complex heterogeneous material of bottom sediments (Förstner & Wittmann, 1983) and, thus, gives evidence on the element potential mobility/bioavailability in the bottom sediments/water ecosystems.

Results of Hg chemical speciation are given in Fig. 3. Extracting with (1) H₂O and 0.05 M EDTA, (2) 1 N HCl, and (3) humus fractions and humin was carried out from three separate aliquots.

It appears that the extracting with distilled H₂O reflects the content of the most mobile and labile sediment components. As some authors stated H₂O extract reflects to some degree the composition of sediment interstitial solutions (Wilken & Hintelmann, 1990), and, thus, the portion of the most reactive and bioavailable sediment compounds. For the pelagic sediments studied the portion of Hg-H₂O fraction constituted merely 1.5-3% of the total Hg in the near-surface slices. And it dramatically dropped to the analytical zero with the first cm of the core depth (Fig. 3). However, the content of Hg in this fraction was far above comparing to the pristine and contaminated soils of the Middle Amur (Kot & Matyushkina, 2002), as well as

comparing to the lake sediments of the Middle Amur (Kot et al., unpublished) analysed in accord with the same speciation scheme. In addition, all H₂O extracts were more or less intensively yellow-tinged, and Hg turned to be bound to water-soluble so-called *yellow* organic acids (Jonasson, 1977), as Hg becomes detectable as soon as the extract was oxidized-

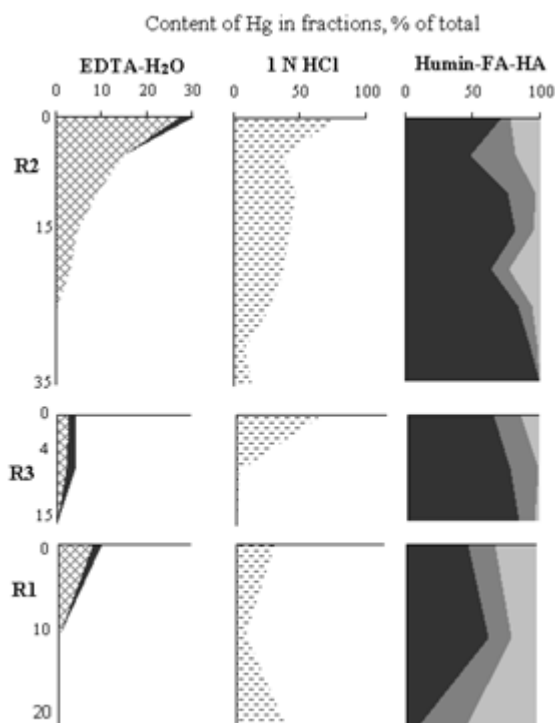


Fig. 3.

Gileva (1968) showed that 0.05 M EDTA suppressed Hg accumulation by plants, thus indicating binding of Hg bioavailable compounds with the EDTA solution. On the contrary, Silanpää & Oikari (1996) found out that the complexation with EDTA had no or only slight effects on the toxicity of Hg to bacteria. In the present work the treatment with 0.05 M Na₂-EDTA pH 3 has yielded a noticeable Hg portion from the near-surface sediment slices only (2.5-27.5% of total) (Fig. 3). Nevertheless, it is much more comparing to the heavily contaminated soils of the Middle Amur (up to 0.5%) (Kot & Matyushkina, 2002), and comparing to the pristine lake sediment cores of the Middle Amur (median 0.0%) (Kot et al., unpublished). Thus, it appears that the near-surface pelagic sediments possess considerable quantities of (potentially) bioavailable/biotoxic Hg comparing to soils and lacustrine sediments treated with the same procedure. Hg content in the EDTA extracts decreased sharply with the first centimetres of the sediment depth as well, showing a tendency of Hg immobilization with the sediment depth and, probably, age of sedimentation.

1 N HCl solution appeared to be a much more effective extractant. The maximum Hg content was also yielded from the near-surface oxidized layers (up to 79% of total Hg), though with a noticeable portion beneath, in the reduced sediment slices (Fig. 3). Many authors suppose that it is a partial dissolver of Fe/Mn amorphous formations. Zvonarev & Zyrin (1983) found that 1 M HCl solution extracts Hg bound in the sites with the lesser binding capacity. These authors also noted an inverse dependency of Hg contents in the extract and con-

digested. Thus, Hg exerts its maximum bio-/geochemical activity in the near-surface oxidized layers as a component of soluble organic matter.

0.05 M Na₂-EDTA pH 3 solution was used to estimate a portion of Hg bound weakly to the sediment particles, presumably, in the adsorbed forms and in the forms bound to amorphous Fe/Mn formations (Förstner & Wittmann, 1983). Moreover, though EDTA solution is an extractant of rather uncertain chemical selectivity as regards to soil and bottom sediments it can probably be used to estimate a portion of bioavailable Hg compounds. Some authors evidenced a clear dependency of 0.05 M EDTA extractable metals (Cu, Zn, Cd, Pb, others) on those in plants (Förstner & Wittmann, 1983; Sanders et al., 1986; Clayton & Tiller, 1987). Experiments with ²⁰³Hg labels by Makhonina &

tent of $C_{org.}$ in soils. According to Leventhal & Taylor (1990) 1 M HCl solution extracts *reactive* phases of Mn, Fe and Hg. Some authors have noted that 1 M HCl can partially desorb Hg from humus because Cl⁻-anion efficiently competes with the functional groups of humus in binding this element (Varshal et al., 1998; Zvonarev & Zyrin, 1983). 1 M HCl turned out to be even more efficient in extracting Hg from the sediment material of R2 and R3 as compared to the pyrophosphate solution despite of its complexing capacity for Fe (Ponomareva & Plotnikova, 1971). The effectiveness of 1 N HCl solution to bind Hg is determined by partial acid dissolving of Fe (Fe/Mn) formations and strong complexation ability of Cl⁻-anion toward Hg either. It is interesting to mark that 1 N HCl and Na₂P₂O₇ solutions evidently extracted Hg from the same binding sites of the sediment matter since Hg portion in the both procedures has sometimes been overlapped (the 18-20 cm slice of R1, 0-3 cm of R2). Thomson & Robinson (*cit.* Strakhov, 1954) marked already that the fate of Fe in marine waters associates with dissolved organic matter, presumably, as colloidal micelles protected by organic matter (Strakhov, 1954). Thus, 1 N HCl removes and binds Hg from a portion of amorphous Fe (Fe/Mn) formations and, most likely, weakly organically bound Hg.

Presumably, Hg bound to fulvic and, especially, humic acids are the most definite Hg fractions considered in this work, though only so far as humic and fulvic acids themselves are definite fractions of humus. The crucial role of humic and fulvic acids in binding and mobilization of metals has been widely discussed. In this work the portion of Hg in the 0.1 M Na₄P₂O₇ + 0.1 M NaOH pH 13 extracts yielded average 14±10% (<2-34) for humic and 12±15% (<2-56) for fulvic acids out of total Hg content. Most Hg-humic acids and Hg-fulvic acids fractions were found within the near-surface sediment layers. Portion of the two fractions decreased with the core depth, though not as abruptly as the labile ones (*i.e.*, Hg-H₂O and Hg-EDTA). It is well-known that humus undergoes considerable material changing during postsedimentation diagenesis. Probably, having a strong binding capacity for certain humus functional groups (especially, to reduced sulphur-bearing ones) Hg could be used as an additional characterizing agent for humus nature and fate. For example, in this work a noticeable quantity of Hg in the extracted humic and fulvic acids has being released directly by SnCl₂ solution, omitting the preliminary oxidizing of aliquot, and yielded a so-called *reactive*, *i.e.* relatively weakly bound Hg-humic and Hg-fulvic acids portion (Fig. 2 – top layers in the core R2 and the entire core R3).

Humic and fulvic acids demonstrate different capacity to bind Hg. Despite fulvic acids domination among extractable humus fractions (evaluated per organic carbon $C_{org.}$ content in) humic acids concentrated much more Hg per $C_{org.}$. The specific Hg content found for humic acids is 188-233 $\mu\text{g Hg g}^{-1} C_{org.}$ comparing to fulvic acids – 0-79 $\mu\text{g Hg g}^{-1} C_{org.}$

Nevertheless, the principal pool of Hg in the sediments studied has been found to be bound with the most refractory non-hydrolysing residue (humin). It comprised from 47% in the top layers to 98% of total Hg downward core R2, from 72 to 81% in core R3, and from 57 to 88% in core R5, correspondingly. In core R1 a portion of the Hg-humin fraction decreased from 46% in the top layers to analytical zero at the deep layer, following general decrease of total Hg content in the core.

Humin is regarded to be comprised of the highest molecular mass organic groups that are highly polymerised and largely insoluble in aqueous solutions (Jonasson, 1977). In the strict sense non-hydrolyzing residue does not correspond to organic humin fraction directly. Non-hydrolysing residue consists of a complex hardly-separated mixture of compound associates that are refractory to dilute alkaline and acidic solutions. It includes humin itself, as well as clay minerals, authigenic sulphides and pyrites, crystallised Fe/Mn minerals, and accessory minerals. Humin, sulphides, Fe/Mn minerals, and humic compounds enclosed within inter-packet gaps of clay minerals, as well as some accessory minerals can to a greater or lesser extent be capable to bind metals. Though, it is a further task to divide this fraction into components as carrier matrixes for Hg.

The results on the Hg extractability from the studied pelagic sediments evidenced a complex Hg behaviour and fate in the sediment postdepositional environment. Hg demonstrated clearly different binding preferences to various sediment compounds/associates within the sediment depth. One general regularity was observed in the cores studied, namely the decrease of Hg extractability within the core depth. One can see that Hg content in the entire specific (fulvic and humic acids) and non-specific (H₂O, 0.05 M Na₂-EDTA pH 3, and 1 M HCl) extracts decreased down the core profile. Moreover, Hg content in the extracts that comprised most mobile and labile Hg compounds, *i.e.* H₂O-soluble and EDTA-complexing, demonstrated the sharpest decrease, and Hg content in the lasts dropped below the analysis precision just below the near-surface oxidized-coloured slices.

All the revealed regularities prove the fact that mobility and lability of Hg in recent pelagic sediments are abated with sediment depth and, consequently, time of sedimentation. Thus, the principal tendency in Hg postdepositional fate is its immobilization within non-hydrolysing residue - a group of compounds/associates that are the most refractory to chemical and microbiotic attacks.

CONCLUSIONS

Content of Hg in the pelagic sediments studied was rather low and indicated the absence of substantial specific sources of the element to the deep sea. Distribution of Hg within the cores evidenced Hg redox-sensitive diagenetic redistribution resulted in formation of Hg content peaks in near-surface and buried layers of oxidized conditions. Hg content in all extractable fractions (H₂O, 0.05 M Na₂-EDTA pH 3, 1 N HCl, humic and fulvic acids) decreased with the core depth, thus indicating Hg immobilization as a principal tendency during diagenesis. Grey humic acids were much more efficient concentrator for Hg comparing to other extractable humus fractions. The most refractory to microbiotic and chemical attacks non-hydrolyzing residue (humin) contained the principal Hg pool in the sediments.