NOTE

Mercury in sediments from the Okhotsk Sea and Funka Bay

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Mercury and organic nitrogen were determined in sediment cores taken from the Okhotsk Sea and Funka Bay in northern Japan. The concentrations of mercury and organic nitrogen in the cores decrease from the surface to a nearly constant value below 20-50cm depth. Mercury is strongly correlated with organic nitrogen in each core, showing association of mercury with organic matter. Copper, zinc, iron and lead were also determined in some cores but showed no systematic variation with depth. Methylmercury both in interstitial waters and in solid phases was determined for some Funka Bay cores. The profiles appear to suggest that the mercury is lost from the sediments during early diagenesis by forming methylmercury or its sulfur derivatives.

INTRODUCTION

Vertical distributions of mercury concentration in lake and marine core sediments have been reported by ASTON *et al.* (1973) and YOUNG *et al.* (1973). The profiles showed that the mercury concentrations were high in the surface and decreased with depth. Based on the observations, they suggested that the high mercury concentration in the surface sediments is due to increasing supply by man's activities on a global scale. Recently COWGILL (1975) reported similar results in recently deposited Hueh Lake muds.

On the other hand, SIKES and DRAIN (1973) have demonstrated that, except for sediments from areas known to have been contaminated with mercury, the higher mercury concentration in the surface sediments is due not to increased anthropogenic loading but to natural processes. They suggested that corpora of aquatic organisms, which can concentrate mercury in their bodies, are deposited on the surface of sea bottom, thus adding significant amounts of mercury to the upper sediments. Further they suggested that the life cycle of benthic organisms offers a particularly striking pathway whereby mercury could be carried upward and ultimately deposited at the sediment-water interface. Obviously, more investigations are needed to solve the mechanism of mercury enrichment in the surface of sediments.

Here we report the results on mercury, organic nitrogen and trace metals in marine sediments taken from the Okhotsk Sea and Funka Bay. Based on the results, an alternative explanation for high mercury concentrations in the surface sediments is presented.

EXPERIMENTAL

Core samples: Twelve core samples were collected by a gravity corer from the Okhotsk Sea during the 13 cruise of the R/V Mendelev from August to September, 1974. The sampling sites are shown in Fig. 1. In addition, three cores were collected in August, 1975 at two stations in Funka Bay (Fig. 1), which are presumably uncontaminated by human activities. The core samples from the Okhotsk Sea and one of the cores from each station in the Bay were kept at -20°C prior to analysis. In the laboratory the cores were sliced into 5cm intervals and vacuum dried. Other core samples from Funka Bay were also cut into blocks of 5cm in length, and interstitial waters were separated by centrifugation. Methylmercury was determined in both sediments and interstitial waters.

The outline of the analytical method for total mercury is as follows (NISHIMURA *et al.*, 1975): 0.1-0.5g of sediment passed through a 100 μ m sieve was heated for 2hr in a reflux condenser after adding 2ml of concentrated

Fig. 1. Sampling stations in the Okhotsk Sea and Funka Bay.

sulfuric acid and 5ml of concentrated nitric acid. Mercury was then reduced with stannous chloride and any ensuing mercury vapour was transferred by nitrogen gas to gold particles packed in a glass tube. The resulting amalgam is heated in a furnace at 500°C, and the vapourized mercury is determined by atomic absorption spectrophotometry. Methylmercury was extracted into benzene, back-extracted into glutathione-ammonia solution and measured by atomic absorption spectrophotometry (MATSUNAGA and TAKAHASHI, 1976). Identification of methylmercury in some samples was carried out by gas chromatography with an electron capture detector. It was found that organic mercury extracted into benzene was all methylmercury. Organic nitrogen and carbon were determined by a carbon nitrogen analyser. After a total digestion in hydrofluoric/perchloric/nitric acid, copper, zinc, iron and lead were measured by atomic absorption spectrophotometry. The relative standard deviations of 5 replicate determinations of elements in a marine sediment sample were 20, 15, 1 and 1% at 2ng methylmercury, 100ng inorganic mercury, 10mg carbon and 2mg absolute level of nitrogen, respectively. The relative standard deviations of 5 replicate determinations of other heavy metals in a marine sediment sample were less than 15%.

RESULTS AND DISCUSSION

The vertical profiles of mercury, organic nitrogen and carbon in the core from Stn. 938 are shown in Fig. 2. Mercury and organic nitrogen in other cores except for the one from Stn. 932 which is diatomaceous ooze show similar depth profiles. The relationship between mercury and nitrogen in some selected cores are shown in Fig. 3. In these cores, mercury correlates with organic nitrogen at 95% confidence limit and in some other core samples there is also a strong correlation between mercury and organic carbon. The core from Stn. 932, however, shows that mercury, nitrogen and carbon concentrations are nearly constant with depth within the limits of analytical errors.

The vertical distributions of methylmercury concentrations both in sediments and in interstitial waters for the cores from Funka Bay are shown in Fig. 4. Methylmercury in interstitial waters increases with depth, whereas that in sediments decreases with depth. The sharp increase of methylmercury in interstitial waters suggests that the significant amount of mercury diffuses out of the sediment.

Methylation of inorganic mercury in sediments (JENSEN and JERNELOV, 1969; JERNELOV, 1970; LANGLEY, 1973; SPANGLER *et al.* 1973) and its existence in natural sediments (ANDREN and HARRISS 1973; BATTI *et al.*, 1975) have been reported. Recently ROWLAND *et al.* (1977)

Fig. 2. Total mercury, organic nitrogen and carbon concentrations in sediments at Stn. 938. □: Hg; ○: organic N; ●: organic C.

Fig. 3a

Fig. 3b

Fig. 3. Relation between total mercury and organic nitrogen or carbon. Hg is plotted for organic N (○) and for organic C (●).

a : Stn. 921, 58-34.0N, 148-14.0E, water depth is 128m.

$r = 0.965$ for N, $r = 0.987$ for C

b : Funka Bay (Stn. 1), 42-16.2N, 140-36.0E, water depth is 90m.

$r = 0.971$ for N, $r = 0.942$ for C

Fig. 4a

Fig. 4b

Fig. 4. Total and methylmercuric mercury concentrations in sediments and in interstitial waters from the Funka Bay.

a : Stn. 1, 42-16.2N, 140-36.0E, water depth is 90m.

□ : Total Hg; ○ : CH₃Hg-Hg in interstitial water; ● : CH₃Hg-Hg in sediment

b : Stn. 2, 42-24.0N, 140-31.0E, water depth is 96m.

□ : Total Hg; ○ : CH₃Hg-Hg in interstitial water; ● : CH₃Hg-Hg in sediment

showed that methylmercury reacts with hydrogen sulfide to produce a volatile sulfur derivative of methylmercury. It is generally assumed that methylmercury exists in natural waters and that aquatic organisms concentrate it, because it has been detected in all aquatic organisms. Attempts to detect methylmercury in natural waters have been made by CHAU and SAITO (1973) and ANDREN and HARRISS (1975).

If the high mercury concentration in the upper sediment is due to accumulation of mercury by benthic organisms, similar distributions may be seen for the other heavy metals. As shown in Fig. 5, however, the concentrations of copper, zinc, iron and lead in the sediments from Stn. 938 show no variation with depth. Similar results were obtained in the other samples from both the Okhotsk Sea and Funka Bay.

Another possibility must be examined: Significant amounts of mercury may be introduced to the surface sediments by industrialization accelerated since 1,900 A.D. According to LISITSYN (1975), the sedimentation rate is $3\text{--}10\text{ cm } 1,000^{-1}\text{ y}^{-1}$ in the Okhotsk Sea. If man's activities since 1,900 caused the increase in mercury concentration in the surface sediments, then the anthropogenically derived mercury should be observed only in the top 1 cm of the cores. In addition, the mercury concentration in present sea water with normal salinity is nearly constant at 5 ng l^{-1} regardless of depth

(MATSUNAGA, *et al.*, 1975) and also there was no variation of mercury concentration in the oceans at least during the last several decades (MATSUNAGA, 1976).

Based on the above arguments, we favour an early natural diagenetic process as a cause of mercury enrichment in the surface sediments. Mercury is transported to the sediment by associating organic matter (MATSUNAGA, *et al.*, 1976). During bacterial decomposition of organic matters, mercury may be released into interstitial waters and eventually lost from the sediment by forming soluble mono- or di-methylmercury or by volatilizing as its sulfur derivatives.

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Fig. 5. Copper, zinc, iron and lead concentrations in sediments at Stn. 938.

○: Cu; ●: Zn; △: Fe; □: Pb

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