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On the Behavior of Mercury in Some Polluted Seawater

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Most of the mercury in coastal seawater polluted with waste water including mainly organic suspended matter is associated with suspended matter, especially particulate organic matter. The amount of mercury adsorbed on a given amount of particulate organic matter nearly obeys Freundlich's adsorption isotherm at mercury concentrations less than 15 ppm in particulate organic matter. The mercury in suspended matter is not much reduced by the addition of tin(II) chloride. Thus, to get the total value of the mercury concentration, the water samples must be heated with the addition of a sulfuric and nitric acid mixture to decompose the suspended matter.

Measurements of the mercury concentration in seawater have been made by several investigators; the values, however, are widely scattered. It may be most significant that almost all the samples were kept in polyethylene bottles after acidification. Matsunaga[1] has found that mercury at the nanogram level is given off from such bottles during sample storage, increasing the initial mercury level by a factor of 2 to 100, even if the container has been acid-rinsed. The mercury concentrations in uncontaminated natural waters are generally lower than 5 ng dm^{-3},[2–6] and that in the oceans was found to be constant at 5 ng dm^{-3}.[2,3] In studying the behavior of mercury in contaminated seawater, Carr and Wilknis[7] have reported a desorption rate of mercury from suspended matter. They added ^{197}Hg into seawater including a high concentration of suspended matter (7 mg dm^{-3}) and adjusted the pH of the water to 1.

Here we report on the behavior of mercury in coastal seawater polluted with waste water including mercury and fish meal.

Experimental

Reagents. 1000 ppm $HgCl_2$ stock solution: 1.345 g $HgCl_2$ was dissolved in distilled water; the volume was filled up to 1 dm^3. NaCl: To eliminate any contaminant mercury in the sodium chloride, the reagent was heated in a furnace at 500 °C for 2 h. 10 ppb $HgCl_2$ solution: Sodium chloride and sulfuric acid were added into the adequate amounts of the stock solution to become 3.5% and 0.2 mol dm^{-3}, respectively. This solution is stable for at least 3 months. Tin(II) chloride solution: 50 g $SnCl_2 \cdot 2H_2O$ was dissolved in 1 dm^3 of 1 mol dm^{-3} hydrochloric acid. The mercury in tin(II) chloride solution was eliminated by passing nitrogen gas at a flow rate of 1.4 dm^3 min^{-1} for 1 h. H_2SO_4 and HNO_3: Both the chemicals are of the analytical special reagent grade for measurements of toxic metals produced by Wako Chemicals Inc. Mercury contents in both acids were below 0.1 ppb in most cases, but we had to determine the amount before using because there is a difference of mercury concentration between lots.

Apparatus. Absorbances were measured on a Jarrell-Ash atomic absorption spectrophotometer, AA-780, with a quartz cell (2.0-cm diameter, 20-cm length).

Sampling and Analytical Methods. *Sampling Method*: About 30 samples of surface seawater were collected in the Hakodate Bay with a plastic bucket during a period from June to September 1976 at a station shown by the star mark in Fig. 1. Immediately after collection the sample was acidified to 0.2 mol dm^{-3} with sulfuric acid, and stored in a glass bottle. The mercury contents in the samples were analysed at the laboratory within 1 h. Samples were also collected vertically in the bay with a Van Dorn bottle on 12 August, 1976 at stations shown by a circle mark in Fig. 1.

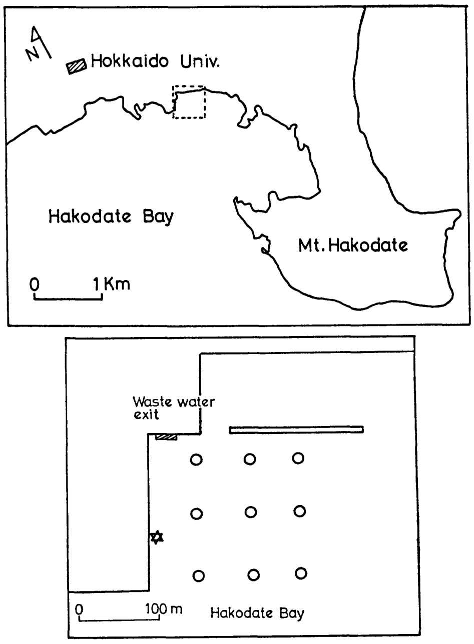

Fig. 1. Sampling stations for polluted seawater. Sampling station ☆: about 30 surface seawater samples were collected from Jun. to Sep. 1976, ○: samples were vertically collected at 12 Aug. 1976.

Analytical Method. *Ionic Mercury*: The outline of the analytical method is as follows:[8] Ionic mercury in 0.2—0.8 dm^3 sample is reduced with tin(II) chloride and the mercury vapor generated is transferred to gold particles, packed in a glass tube, by a stream of nitrogen gas. The metal is then heated to 500 °C in a furnace, and the vaporized mercury is determined with an atomic absorption spectrophotometer.

Total Mercury: To a 0.5 dm^3 sample solution, sulfuric acid (2 cm^3) and nitric acid (5 cm^3) are added, and the solution is heated with a reflux condenser for 2 h to decompose particulate phases. The leached mercury is determined according to the procedure of ionic mercury determination. The acid decomposition method was compared with the decomposition method with potassium permanganate for the same samples. Table 1 shows that there is no significant difference between two methods for the significance level $(1-\alpha)=95\%$, $(\alpha=0.05)$.

Mercury in Suspended Matter: The sample was filtered through an HA type Millipore filter with a 0.45 μm pore size, and then

TABLE 1. THE COMPARISON OF TOTAL MERCURY CONCENTRATIONS DETERMINED BY TWO OXIDATION METHODS

Batch	Oxidant NHO_3-H_2SO_4 [Hg] (ng dm^{-3})	Oxidant $KMnO_4$ [Hg] (ng dm^{-3})
1	64.3	54.5
2	11.5	9.6
3	420	414
4	9.3	15.8
5	44.4	44.5
6	12.0	13.5
7	5.8	5.3
8	4.4	3.5
9	23.3	19.3
10	15.1	12.9

$t_0=1.25<t(9, 0.05)=2.26$.

the residue was decomposed with sulfuric and nitric acid mixture by heating. The mercury was determined by AAS, following the procedure described above.

Suspended Matter and Loss on Ignition: After the sample solution was filtered using the Millipore filter, the filter paper was rinsed with 100—150 cm^3 H_2O to remove sea salt, and dried in a desiccator until the weight of each filter reached a constant value within ± 0.2 mg. After weighing, the total weight of suspended matter was obtained using the difference in weight before and after filtration, and then the filter was ignited at 500 °C for 2 h. After weighing, the loss on ignition, assumed to be a measurement of the particulate organic matter, was determined from the difference in the values of the weight.

Results and Discussion

Student's t-test is useful to compare the data obtained by the use of two different methods. As already mentioned above, there is no significant difference between the two sets of data given in Table 1, for $\alpha=0.05$. Therefore, the method with sulfuric and nitric acid mixture can be applied to decompose suspended matters present in the samples in a simple and easy way. Some results on different forms are shown in Table 2. For the samples containing more than 10 mg dm^{-3} of suspended matter, quantities of mercury less than 11% of total mercury were detected in ionic form. Judging from the concentrations of mercury in suspended matters, evidently the rest of the mercury in those samples is adsorbed on, or coagulated with, suspended matter. Figure 2 shows the relationship between ionic mercury concentration and total mercury concentration. A remarkable deviation form the line which indicates the 1 : 1 relationship is observed with increasing the amounts of suspended matters. This means that the concentrations of ionic mercury decreased with

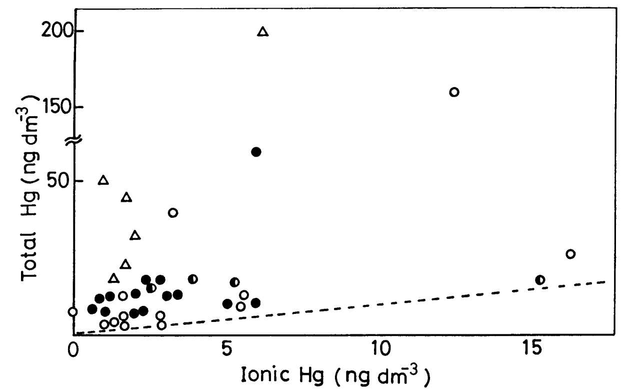

Fig. 2. The relationship between ionic mercury and total mercury. Marks denote the amounts of suspended matter.

○ 0—5; ● 5—10; ◐ 10—20; △ >20 mg dm^{-3}.

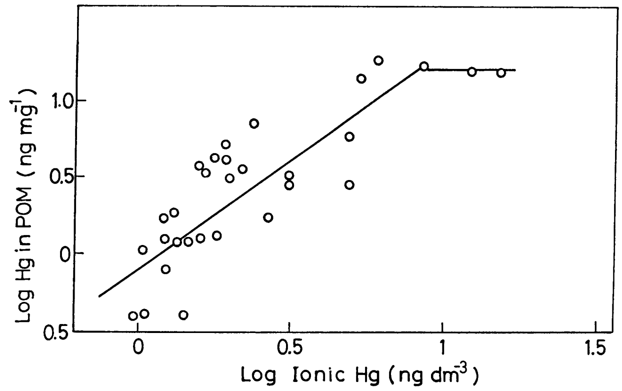

Fig. 3. Freundlich's adsorption isotherm between ionic mercury and mercury in particulate organic matter.

TABLE 2. MERCURY CONCENTRATIONS IN SEVERAL FORMS

Sample	Ionic Hg (ng dm^{-3})	Total Hg (ng dm^{-3})	Hg on a filter (ng dm^{-3})	SM[a] (mg dm^{-3})	Hg in SM (ppm)	POM[b]/SM (%)
1	1.7	45	45	76.4	0.59	72.4
2	8.9	416	370	28.2	13.12	87.9
3	13.0	122	106	12.6	8.41	63.4
4	5.3	11	9.1	2.2	4.14	36.4
5	1.1	11	6.5	8.2	0.79	73.2
6	1.8	8.2	6.4	4.2	1.52	89.6
7	3.3	42	41	15.0	2.73	76.0
8	3.3	12	10	6.8	1.47	58.8
9	1.8	4.0	3.6	3.6	1.00	33.3
10	1.4	23	19	14.4	1.32	90.2

Sampling was done at the station shown by the star mark in Fig. 1 from June to Sept. 1976. a) SM means suspended matter. b) POM means particulate organic matter.

increasing the amounts of suspended matters. Figure 3 shows the relationship between mercury concentrations in ionic form and in particulate organic matters. The amount of mercury adsorbed on particulate organic matters per unit weight nearly obeys Freundlich's adsorption isotherm at the concentrations lower than 15 ppm mercury.

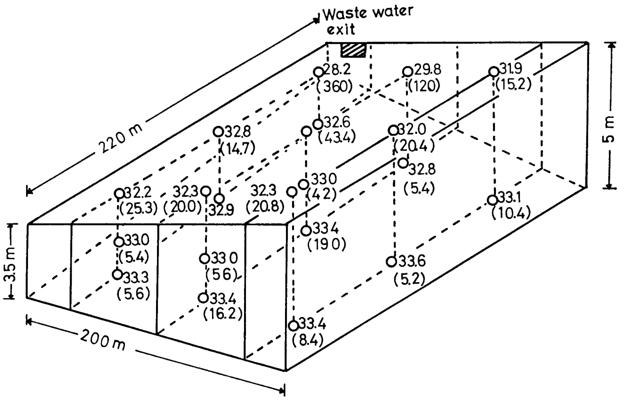

Fig. 4. Salinity, ‰ and the amount of suspended matter (mg dm^{-3}).

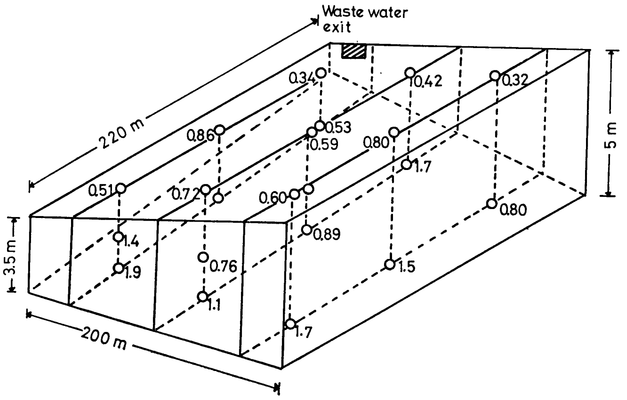

Fig. 5. The amount of mercury in suspended matter.

The salinity and the amount of suspended matter, and the amount of mercury in the suspended matters are shown in Figs. 4 and 5, respectively, for the samples at different depths collected in the area shown in Fig. 1. In the area, waste water diffuses from east to south, as is seen in the salinity distribution (Fig. 4) around the waste water exit. However, the salinity near the bottom is scarcely affected by waste water, except for the area adjacent to the discharge. The same tendency is observed in the suspended matter distribution, though suspended matters settle downward. The mercury concentration in suspended matters is about 0.1 ppm level in samples near the surface, while the concentration occasionally approaches 1 ppm level with increasing depth. This suggests that suspended matters adsorb and remove mercury from the water. The concentrations of ionic mercury in seawater samples are below 2 ng dm^{-3} in all of the samples measured; such values are about half of the values in unpolluted sewater at Hakodate Bay. The present results suggest that most of mercury in highly polluted waters is associated with suspended matter. As mentioned above, the determination of mercury can be simplified by treating water samples with a nitric and sulfuric acid mixture. For samples with salinity higher than 30‰ and acidified to 0.2 ml dm^{-3} with sulfuric acid, no adsorption of mercury on the walls of the glass container was observed. But significant adsorption of mercury occurred for samples with salinity less than 30‰, even if they were acidified to more than 0.2 mol dm^{-3}. Generally coastal seawater has a salinity lower than 30‰. Therefore, sodium chloride preheated at 500 °C must be added to the sample solutions to bring its salinity up higher than 30‰, unless the samples are quickly processed after sampling. By these procedures, adsorption of mercury on the walls of the container was avoided.[1)] For open seawater samples, acidification to 0.2 mol dm^{-3} with sulfuric acid for a month at room temperature was found to be sufficient for quantitative determination of mercury.[1)] However, this treatment yielded only 40% of the total mercury for samples with suspended matters concentration higher than 30 mg dm^{-3}. For polluted seawater samples, the treatment with sulfuric and nitric acid mixture is necessary for quantitative determination of mercury.

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