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Mercury deposit distribution in Minamata Bay

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Abstract — Half a century after the serious mercury spill from a chemical factory, an updated situation report on the distribution of mercury deposits in the sediment and benthos of the intertidal zone of Minamata Bay was undertaken in 1997. On two stations inside and two more outside the Bay, mercury distributions in the surface sediment and benthos of the boulder intertidal shore were quantified and compared with those in control regions. The results indicated that relatively higher than the natural level of mercury deposits remained at one station inside the Bay, with lower levels at three other stations. The control regions, however, showed even lower levels than at those three stations. Nevertheless, the two stations outside the Bay were nearer to the control levels. Methylmercury distribution at the station with the highest value indicated a low correlation with that of total mercury. That is unlike the situation in a metallic mercury polluted area such as is involved in gold mining. The mercury distribution in the benthos indicated the same gradient of concentration as that of sediment throughout western Japan.

Key words: smercury deposit, methylmercury, sediment, intertidal zone, benthos, Minamata Bay

Introduction

Since an acetaldehyde synthetic process had been ongoing in Minamata City since 1932, waste fluids including mercury had been discharged without any treatment into Minamata Bay for 34 years until 1966. The latest investigation (Nishimura and Okamoto 2001) indicated that methylmercury was present in the effluent, with the amounts released remarkably increasing during the 10 years beginning with 1951. As a result, more than 2,200 residents around Minamata Bay are suffering from Minamata Disease due to their consumption of fish and shellfish produced in the Bay and its vicinity.

When the Japanese Government identified the cause of the disease as methylmercury ingested through the fish and shellfish taken from the polluted sea area, mercury mainly remained in the sludge of Minamata Bay. Most of the sludge (approximately 1,510,000 m^3, including 150 tons of mercury reported by Kumamoto Prefecture) that contained more than 25 ppm of mercury was dredged and packed into a newly formed landfill during a prefectural pollution prevention project lasting for 14 years from 1977 (Kumamoto Prefecture, 1998). During the project implementation, since Minamata Bay was closed off by a dividing net to prevent the entrance and exit of fish, no fishing was done within the Bay. Thus that semi-closed area acted as a sanctuary for biota after sludge removal, which might prove beneficial to the diversity and biomass maintenance of biota within the Bay. The dividing net was removed in 1997, and the Minamata Bay environment has since recovered.

During the last few decades of the project mentioned above, the distribution of mercury deposits within the Bay was investigated by a few study groups. Their results demonstrated that there were still areas showing unchanged sediment mercury concentrations in the Bay for 20 years after dredging had been completed, indicating the very slow elimination of mercury deposit diffusions from the Bay. Moreover, the character of the Bay makes it an ideal field to study environmental mercury kinetics using the up-to-date methodology of mercury analysis.

In the present study, we compared mercury deposits in the sediment and benthos in the boulder shore intertidal zone of Minamata Bay with those in the control areas in western Japan (Figure 1).

Study Areas

Minamata Bay is located along the coast southeast of the Yatsushiro Sea in western Kyushu Island, Japan (Figure 1). The Bay is about 3 km^2 in area including the small inlet of Fukuro Bay and the islet of Koijishima, as shown in Figure 1.

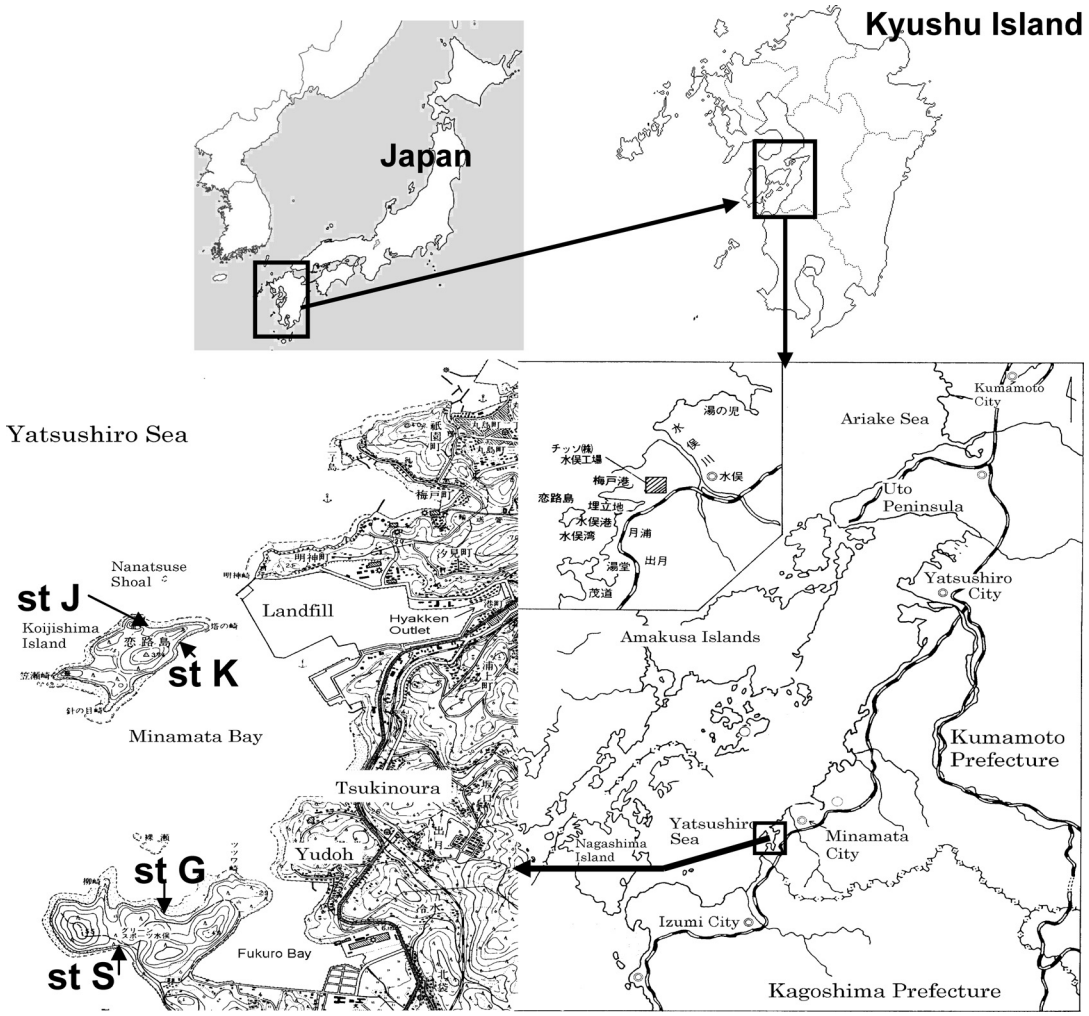

Fig. 1. Locations of Minamata Bay and sampling stations.

The shores of Minamata Bay are comprised of 48.9% boulders, 18.6% rocks and 31.8% artificial sea wall. In the present study, we focus exclusively on an investigation of the boulder shore. At the southern end of the Bay is the Nishinoura Peninsula, where two sampling stations were set up, one outside (st S) and another inside (st G) the Bay. In Koijishima, two more stations were established within (st K) and outside (st J) the Bay. The tidal range of this region (Yatsushiro Sea) reaches 4 m and is usually more than 3 m in the Bay, which provides a wide intertidal zone at each station.

As for control stations, several points were established in western Japan as shown in Figure 2. The locations of control stations were selected based on conditions relating to the ocean current and the situation of the shore. That is, all control station locates in inland sea as Minamata Bay, St. N and St. E are in Yatsushiro Sea opposite side of Minamata, St. W is at Wakamatsu Channel in north part of Goto Islands locates upstream of Tsushima Current and Kuroshio Current, and St. U locates at Urauchi Bay in north part of Koshiki Islands somewhat upper stream of Kuroshio Current than Minamata. St. H, on the other hand, locates at the opposite

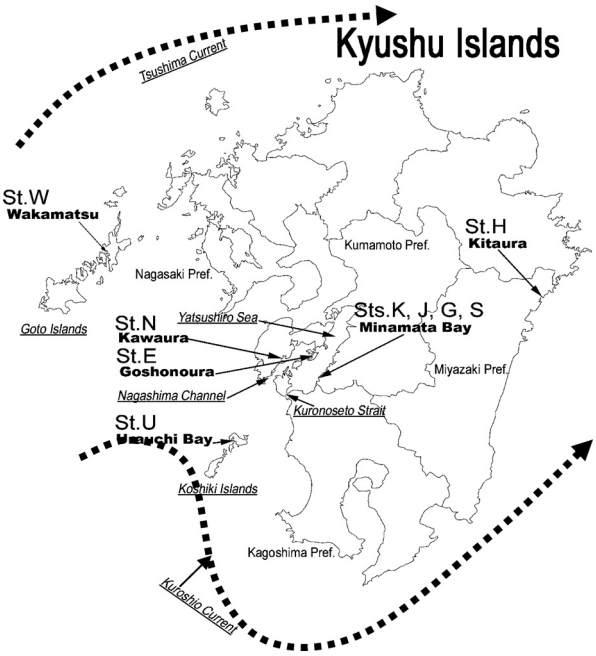

Fig. 2. Locations of control sampling stations.

shore of Kyushu Island, the position of which is out of stream of both Kuroshio and Tsushima Currents (See Figure 2).

Methods

Sampling

Sampling at Minamata Bay was conducted every spring from 2003 to 2007, while in the control region it was done once or twice at each point from 2003 to 2006. Sampling was conducted at ebb tide, dividing the shore into three zones (high, middle and low tide) parallel to the beach. In 2003 Minamata Bay sediment sampling as well as in all control region, sediment was taken from 3 points separated by 20 m distance with each other at low tidal zone.

Random samplings of several species of benthos were conducted to simultaneously determine traces of mercury in snails (carnivores, *Thais* and herbivores, *Lunella*), crabs (carnivores, *Leptodius* and omnivores, *Gaetice*) and worms (omnivores, *Nereis*). Biota samples for mercury determination were identified, recorded individually as to weight and size, dissected if needed, and lyophilized. The dried biota samples were weighed again to verify their moisture content. They were then ground with a glass mortar and used for mercury determination. Sediment samples were stored at −80°C until use, and ground with an agate mortar under chilled with ice just before use. Aliquots of the ground sediment samples were collected in glass tubes weighed and heated overnight at 110°C with an aluminum block heater to obtain their dried weights.

Mercury analysis

After appropriate pre-treatment, mercury determination was performed using cold vapor atomic absorption spectrometry (CVAAS) for total mercury and gas-chromatography with an electron capture detector (ECD-GC) for methylmercury. Water used in the mercury determination was purified by a three-step treatment, i.e. an ion exchange column, reverse osmosis membrane and distillation. All reagents used in the mercury analysis were of a grade suitable for analyzing pesticide or trace metals. All the equipment was cleaned with detergent, 10% potassium permanganate, 2% hydroxylammonium chloride and water. After washing, the glassware used was heated at 210°C for 2 hours before use.

Pre-treatment of samples for total mercury determination

Ground samples were weighed and put in 30-ml test tubes (with glass caps), after which 1 ml water, 2 ml acid mixture (nitric and perchloric acid, 1 : 1), and 5 ml sulfuric acid were added. The tubes were then heated in an aluminum block heater at 230°C for 30 min. After cooling, each sample was filled to a 30-ml level with pure water.

Total mercury analysis

Mercury in the aliquots (usually 2 ml) of the sample solution was vaporized by reduction in the presence of 0.l5% (w/v) stannous chloride under vigorous bubbling for 30 sec, and then sent to the atomic-absorption analyzer. This preparation was carried out in an automated circulating airflow system (Akagi and Nishimura, 1991, assembled by Sanso Seisakusho Co. Ltd., Tokyo, Japan; see the Mercury Analysis Manual, 2004).

Methylmercury analysis

Methylmercury concentrations in each sample were determined by an electron-capture detector type gas chromatograph (GC-ECD) after extraction in KOH-ethanol (1 : 1) and concentration by dithizone, Na_2S and dithizone extraction (Ikingura and Akagi, 1999; the Mercury Analysis Manual, 2004). Each measurement was conducted twice with duplicate determinations.

Measurement quality was checked using the standard materials distributed by IAEA, BCR and NRC (Table 1). The detection limit for MeHg was 0.12 ng/g. Difference of mer-

Table 1. Measurement of reference materials.

Materials	Reference Number		Certified values (ng/g)	*Measured values [average (ng/g)±CI]
Dogfish meat by NRC	DORM-2	THg	4,640±260	4,670±110
		MeHg	4,470±320	4,260±100
Sediment by BCR	CRM-580	THg	132,000±3,000	132,000±2,000
		MeHg	75.5±3.7	76.0±2.6
Sediment by IAEA	IAEA-405	THg	810±40	853±13
		MeHg	5.49±0.53	5.52±0.34

*Values are shown as means of 6 times repetitions
CI: 95% confidence interval
IAEA: International Atomic Energy Agency
NRC: National Research Council of Canada
BCR: Commission of the European Communities

cury concentrations between stations is evaluated with the student's t test.

Results

Mercury deposit distribution in surface sediment of boulder shore

Mercury concentrations in the Minamata Bay boulder shore sediment were higher than those in control areas (Table 2). Among total mercury concentrations, the highest value was obtained in the samples of st K, followed by the st G value (at both stations inside the Bay). The difference was more than a thousand-fold between st K and a control such as st N. The same tendency was found in the methylmercury distribution. As shown in Figure 3, methylmercury concentrations decreased with their distance from Minamata Bay, and were somewhat related with the Kuroshio Current, since station U at Koshiki (#8 in Table 2) located downstream of Minamata Bay exhibited a higher value than the st W at Wakamatsu (#9 and #10) located upstream of the Bay in the Kuroshio and Tsushima Currents (Figure 2), respectively.

At each station in Minamata Bay, mercury distributions in the surface sediment at the boulder shore were recorded in 2005 and 2007. The order of the average concentration level between stations was the same as that in 2003 (Table 2 and Figure 4). At the station with the highest level, st K, the distribution of total mercury increased from the high tide to the low tide zones, while the reverse was true of the methylmercury distribution. In contrast, in st S, the slope of methylmercury concentrations rose at low tide (Table 3), while the lev-

Table 2. Mercury concentrations in the sediment taken at three points in the lowest tidal zone of each station in 2003.

	THg ng/g			MeHg ng/g		
*1. st K**	3452.2	3708.3	3953.3	0.74	1.15	1.64
2. st G	540.6	1039	1101.6	0.63	0.84	0.57
3. st J	344.4	374.4	314.3	0.42	0.39	0.44
4. st S	307.8	305.7	327.6	1.42	1.44	1.79
5. st E**	11.1	7.8	9.9	0.35	0.35	0.3
6. st N**	2.1	2.4	2.3	0.53*	0.31*	0.37*
7. st H**	10	9.1	8.2	0.19	0.07	0.11
8. st U**	4.8	5.6	5.2	0.38	0.28	0.33
9. st Wa**	13.7	5.4	4.8		0.1	0.08
10. st Wb**	5.9	5	4.4	0.25	0.2	0.13

*See Figure 2 for station numbers
Difference between values in Minamata Bay and control stations are significant ($p<0.05$**) for THg. As an exception, MeHg in st N indicated $p<0.1$*.

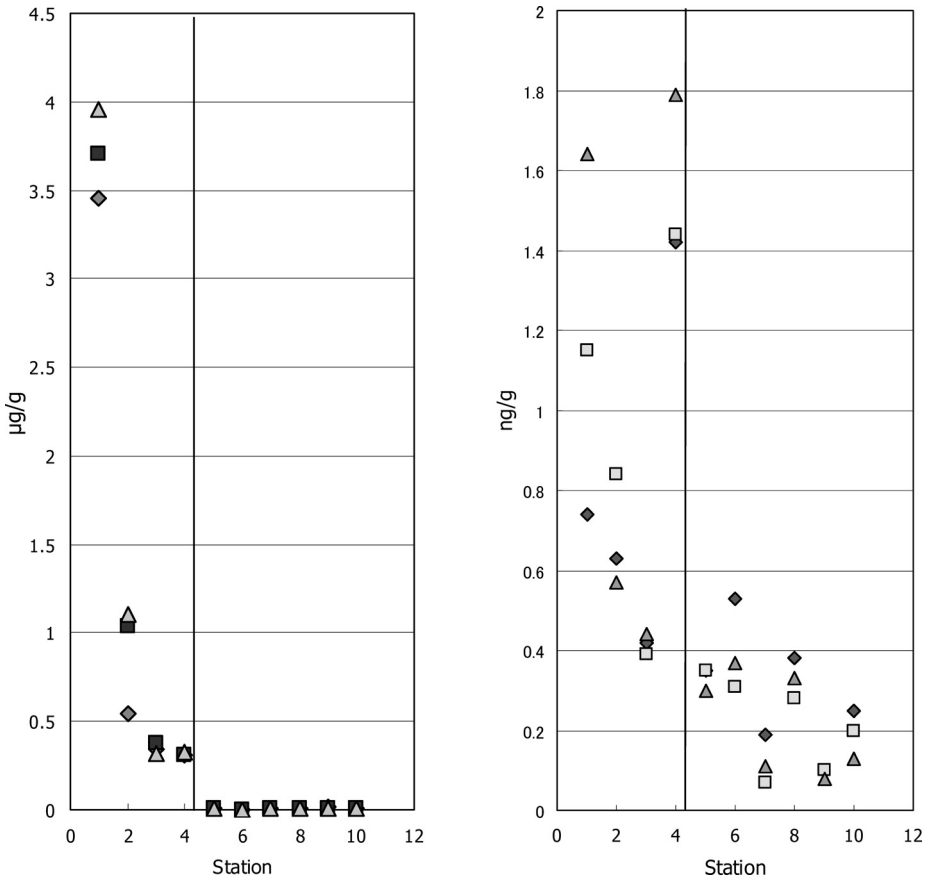

Fig. 3. Profiles of the data in Table 2. Number at abscissa indicates station listed in Table 2.

Table 3. Mercury distribution on the surface sediment of boulder shore in Minamata Bay in 2007.

Tidal zone			High tide		Middle tide		Low tide	
			Geomean	95% limit	Geomean	95%limit	Geomean	95% limit
1. st K	MeHg	ng/g	0.96	0.63–1.45	1.26	1.14–1.40	1.28	1.08–1.52
	THg	μg/g	2.71	2.22–3.31	4.36	3.68–5.16	5.14	4.69–5.62
2. st G	MeHg	ng/g	0.61	0.5–0.75	0.43	0.32–0.59	0.31	0.20–0.48
	THg	μg/g	1.24	1.00–1.53	1.37	1.23–1.53	1.48	1.33–1.65
3. st J	MeHg	ng/g	0.51	0.45–0.58	0.85	0.74–0.97	0.72	0.55–0.94
	THg	μg/g	0.41	0.38–0.44	0.46	0.43–0.49	0.45	0.42–0.47
4. st S	MeHg	ng/g	0.10	0.07–0.16	0.95	0.86–1.05	1.20	0.92–1.57
	THg	μg/g	0.27	0.24–0.30	0.20	0.19–0.22	0.33	0.28–0.40

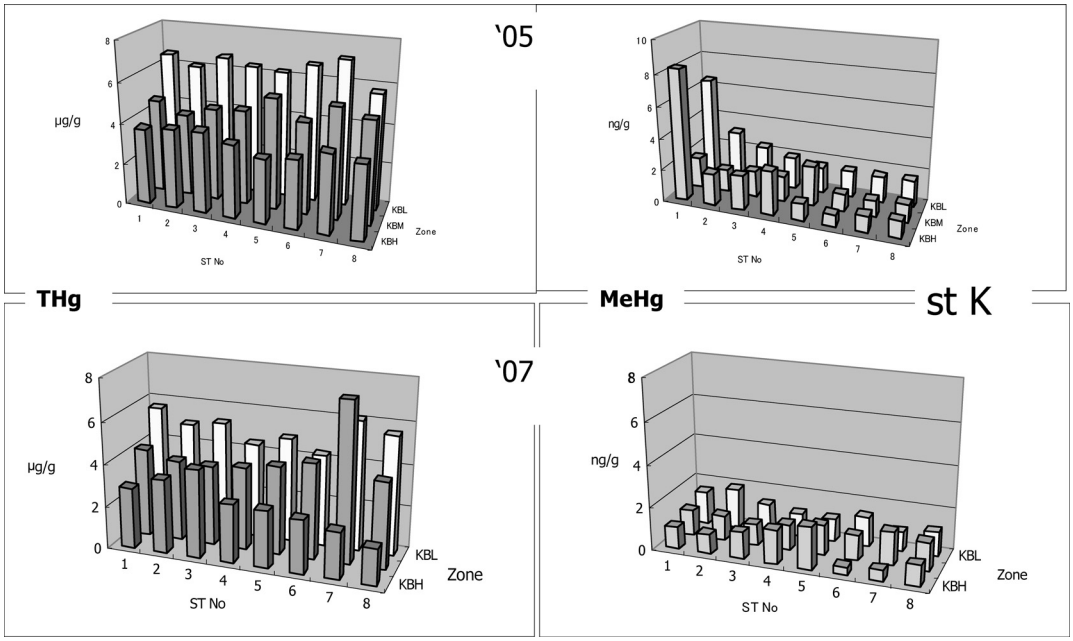

Fig. 4. Mercury distribution in surface sediment of st K boulder shore in 2005 and 2007.

els of the lower two zones were the same as those in st K. The level of total mercury concentration in st S was lowest at the four stations in 2007.

From comparing the mercury distributions of surface sediments in the st K boulder shore between 2005 and 2007, the levels were the same on average, but the concentration profiles, in particular those for methylmercury, were different in the high tide zone as shown in Figure 4.

Mercury distribution in biota

A small omnivorous crab, *Gaetice depressus* (Gaetice), was employed as one of the indicators of mercury distribution in the intertidal shore, since it is one of the main bait favored by an indicator fish, *Sebastiscus marmoratus* (Rock fish), that still contains around 0.4 ppm of mercury in Minamata Bay. A carnivorous snail, *Thais clavigera* (Thais), was also used to compare mercury distribution profiles. The results are shown in Figure 5, which indicates that the mercury concentration decreases with the distance from Minamata. Moreover, via the accumulation of methylmercury through the food web, it can be seen that the carnivorous snail Thais contains 0.2 ppm of methylmercury in the boulder shore of st K. As for the herbivorous snail Lunella, the methylmercury concentration in st K was less than 0.03 ppm even in its muscle tissue (data not shown).

Discussion

According to the latest study by Nishimura and Okamoto (2001) of Minamata Bay pollution, the modification of a co-catalyst in the reaction matrix of acetaldehyde production (from manganese to iron compounds) in 1951 as well as renovation trials during the production process, the amounts of methylmercury discharged increased 10 to 20 times over a 10–year period, during which the victims of

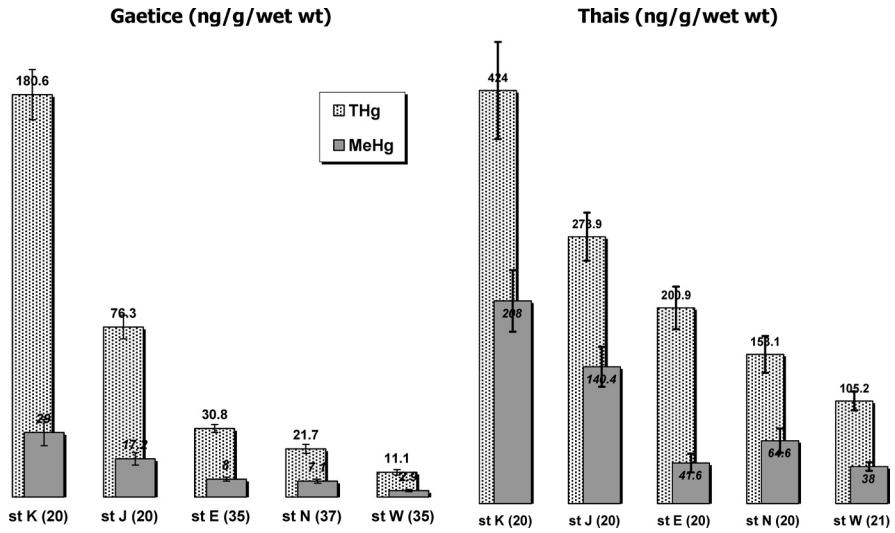

Fig. 5. Comparison of mercury concentration in biota among stations.

methylmercury intoxication (Minamata Disease) emerged around Minamata Bay. That time-frame coincides well with the period when methylmercury releases increased during the situation described above. After most of the sludge containing mercury in Minamata Bay was sequestered in a landfill as a result of the pollution prevention project that continued for 14 years from 1977, traces of severe pollution can still be detected using up-to-date analytical techniques of mercury and methylmercury as described in the present study.

The characteristics of the mercury deposit distribution profile in Minamata Bay's boulder shore are partly elucidated in the present study, which differs slightly from those in other regions where mercury pollution is still a cause for worry. At present, most cases of mercury pollution are associated with the diffusion of elemental mercury from gold amalgamation techniques used in gold mining (UNEP, Lasut and Yasuda 2008). That is a cause of enormous anxiety, since elemental mercury turns to methylmercury in environment which could be absorbed and accumulated in biota, including those in humans, through the food web. One such example can be found in north Sulawesi, Indonesia. In the Talawaan watershed, a region in which many small-scale gold mining operations are concentrated, we have investigated the sediment mercury distribution in rivers originating in this region (Yasuda and Lasut, in preparation). In that study, it was found that the methylmercury concentrations in river sediment are highly correlated with the total mercury concentration ($r=0.87$ in Talawaan River). That result suggests that methylation of the mercury deposits occurs at each sampling point at the same level. On the other hand, in the present study, any correlation between methylmercury and total mercury in the surface sediment of the boulder shore in Minamata Bay was found to be weak ($r=0.34$ in st K and st S).

One of the causes of the above difference might derive from the difference in the chemical situation between seawater and fresh water (Goulet et al. 2007). Such a difference, however, may also arise from the difference in the chemical composition of effluent, elemental mercury in a gold mine compared to the factory effluent containing various types of chemical forms of mercury, including methylmercury in Minamata Bay. Methylmercury in the environment is thought to be de-methylated by various factors such as UV irradiation, oxygen and bacterial activity, though the reverse is also occurring. In Minamata Bay, however, traces still remain of the deposit of methylmercury derived from the waste fluids of acetaldehyde production (containing a huge amount of methylmercury, as described by Nishimura and Okamoto 2001), after completion of the pollution prevention project, as a conjugate with organic particles in water and sediment and as a member of the body burden of biota in the Bay. About 490 tons of polluted fish in the Bay were artificially removed during the pollution prevention project, with the result that the current level of fish mercury concentration has fallen below the provisional control value (0.4 ppm). Nevertheless, the average level of mercury in fish remains still slightly higher than in other regions, such as in st U, st W and st H. The circulation of mercury compounds in the Minamata Bay environment has thus attained a somewhat higher level than in other regions where no such pollution catastrophe has occurred.

The methylmercury distribution in biota decreased with distance from the Minamata site (Figure 5). The slight difference between st U and st W can be explained by the presence of a diffusion of methylmercury carried by biota (presumably larva) of Minamata origin. At each station, mercury thus brought could enter a new cycle at each concentration. That speculation, however, requires further investigation concerning mercury circulation in the coastal environment.

Acknowledgements

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