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Mercury Distribution in Seawater of Kagoshima Bay near the Active Volcano, Mt. Sakurajima in Japan

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Abstract Kagoshima bay has a highly active volcano in its center. In the filtered seawater and suspended matter collected from 200-m deep fumaroles at the bottom of the inner bay, the geometric mean concentrations of total mercury were 7.6 and 65.0 ng/L, respectively. The surface seawater collected at the inner bay had a higher concentration of mercury when compared to that in the bay entrance (average: 1.0 vs. 0.5 ng/L). In July, however, no such difference was observed. The fumaroles seem to contribute to relatively high concentrations of mercury in the inner bay except in summer, when thermal cline is formed.

Keywords Mercury · Sea water · Volcano · Distribution

Kagoshima Bay is closely located to Mt. Sakurajima, a highly active volcano in Japan. In 1973, Kagoshima Prefectural government found total mercury concentration in 10 species of fish caught in the northern part of Kagoshima Bay to exceed 0.4 ppm, the provisional reference value for mercury contamination of fish, as determined by the Environment Agency of Japan. Consequently, the government urged local fishery cooperative associations to stop fishing these species of fish. However, the origin of the relatively high-level of mercury detected in the fishes was unknown. In 1977, a geological survey conducted by a manned submarine, Hakuyo, identified fluids and gases from the bottom of the bay at a depth of 80–200 m in the northern part of the bay. Moreover, high levels of mercury were found in gases and sediments collected from around the fumaroles located at 200 m (Sakamoto 1985; Sakamoto et al. 1995). Those results strongly suggested that elemental mercury (Hg°) released from volcanic vents of Mt. Sakurajima at the bottom of Kagoshima Bay was responsible for relatively high mercury concentrations of seawater in the bay. Note that the gas seeping site located at 100 m has not been confirmed to be fumaroles, which is related to volcanic activities. Mt. Sakurajima divides the Kagoshima Bay into northern and southern parts, making the northern part semi-closed-off and without any direct path to the ocean. In 1986 and 1993, Sakamoto and Kamada reported that mercury concentration in seawater around the fumaroles in the northern part of the bay was higher than in other parts of the bay (Sakamoto and Kamada 1986; Sakamoto and Kamada 1993), supporting the notion that the source of mercury is located in the northern bay and its surrounding areas. Recently, Tomiyasu et al. (2007) reported that mercury concentrations in sediments from 52 points in Kagoshima Bay were 23–679 µg/kg, and suggested that the fumaroles at 200-m depth were the main source of mercury in Kagoshima Bay.

In this study, the vertical mercury distribution in seawater columns of two gas-seeping sites, located at depths of 100 or 200 m in the northern part of the bay, and the

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horizontal mercury distribution of surface seawater collected from 26 offshore points in Kagoshima Bay were determined how mercury released from the fumaroles contributed to mercury levels in the bay.

Materials and Methods

At the sites of volcanic vents, which were located at depths of 100 and 200 m in the northern part of Kagoshima Bay, seawater samples were collected from the center of the gas seeping areas at the bottom, using the unmanned submarine, Dolphin 3 K, of Japan Marine Science and Technology Center (JAMSTEC) in October, 1994, July 1995 and September 1996. Two seawater samples were collected. Seawater samples from deep layers and bottom layers were collected from different depths of the seawater column of each of the two gas-seeping sites with two Bandon sampling bottles. From the surface and shallow depth layers, seawater samples were collected with a Niskin sampling bottle from the deck of R/V Natsushima (JAMSTEC). Surface seawater samples of offshore points in the bay were collected using a polyethylene bucket from the deck of the fishery training ship, Nansei-maru of Kagoshima University. Surface seawater samples were collected from 26 offshore sites in Kagoshima Bay in 6 different months; April, June, July, September, November and December, 1994. The sampling sites of offshore seawater were grouped into the following 4 areas in Fig. 1 (Site No.1–4: the bay entrance; Site No. 5–12: the southern part of the bay; Site No. 13–21: the coastal area of Mt. Sakurajima; Site No. 22–26: the northern part of the bay).

Total mercury concentration in seawater was analyzed using the method reported by Akagi and Nishimura (1991) with slight modifications (Haraguchi et al. 2000). Each sample of seawater was filtered through a Whatman glass fiber filter (GF/C) to separate suspended matters from whole (unfiltered) seawater. After filtration, the suspended matters were digested by a mixture of HNO_3, HClO and concentrated H_2SO_4 (1:1:5; 3 mL) at 250°C for 20 min. Total mercury concentration in the digested sample was measured by cold vapor atomic absorption spectrophotometry (CVAAS). The lower limit of detection was 0.5 ng as mercury. For mercury analysis in filtered or whole water, two liters of seawater were mixed well with 10 M H_2SO_4 (10 mL) and 0.5% $KMnO_4$ solution (5 mL), and allowed to stand for 5 min. The sample was then neutralized with 10 M NaOH (20 mL) and 10% NH_2OH–HCl (5 mL) and allowed to stand for 20 min. After addition of 10% EDTA–4Na solution (5 mL), 0.01% purified dithizone in benzene (10 mL) was added to the sample. After vigorous shaking, the sample was allowed to stand for 40 min. During this process, mercury in the sample was extracted into the dithizone-benzene layer. The dithizone-benzene mercury-extract was evaporated to dryness, and then digested with a mixture of acids in the same manner described for the digestion of the suspended matter. Mercury concentration in the digested sample was again determined by CVAAS. The mercury analysis system was calibrated by the use of mercury standard solution prepared

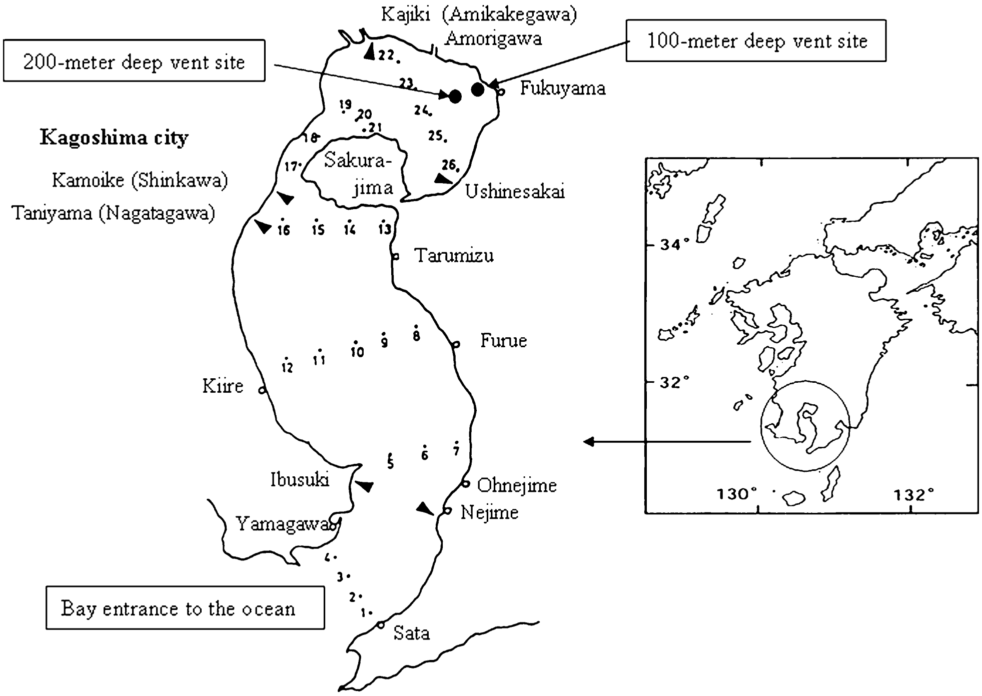

Fig. 1 Sampling sites in Kagoshima Bay. Site No. 1–4: the bay entrance; Site No. 5–12: the southern part of the bay; Site No. 13–21: the coastal area of Mt. Sakurajima; Site No. 22–26: the northern part of the bay

in aqueous L-cysteine solution (Ando 1999; Ando et al. 2002). The recovery of mercury in the present method was confirmed to be ≈100% using standard mercury solution-spiked natural seawater samples. Mercury concentration in seawater samples was corrected for any contamination from chemical reagents by analyzing sample blanks and then deducting mercury content of the blanks from the final results of each sample. The difference between mercury levels in filtered water samples analyzed normally and those analyzed with double volume of the chemical reagents, except for dithizone-benzene solution, was considered as the reagent blank. The coefficients of variation of the measurements of mercury were approximately 5%.

Linear regression analysis was conducted, where log-transformed mercury concentrations were regressed on square root of distance or depth. When the data of 3 years were conducted, dummy variables for the year of survey were included in regression model as covariates. *p* values presented are two-sided unless otherwise specified.

Results and Discussion

Total mercury concentrations of seawater columns of the 100-m deep gas-seeping site are shown in Table 1. No statistically significant association between mercury

Table 1 Total mercury concentrations at various depths of seawater column of the 200-m deep gas-seeping vent site

Depth from the surface	October, 1994			July, 1995		September, 1996	
	pH	Filtered water	Suspended matters	Filtered water	Suspended matters	Filtered water	Suspended matters
0 m (surface)		1.6	0.8	0.6	0.8		
0 m (surface)		1.2	1.6				
0 m (surface)		0.8	0.9				
0 m (surface)		1.5	1.0				
10 m		1.0	0.6	0.3	0.5	0.2	0.3
20 m		2.2	0.4	1.0	0.6	1.3	3.0
30 m		1.2	0.7			0.3	0.8
100 m	7.40	0.8	2.3				
180 m	6.66	3.4	9.5				
190 m	6.62	3.6	6.4				
195 m	6.23	5.6	39.2	2.5	5.3		
200 m (bottom)	5.78	12.2	422.0	3.8	4.1	3.9	5.2
200 m (bottom)	6.28	4.7	10.0	4.1	5.5	2.9	2.5
p for trend		<0.001	<0.001	0.006	0.001	0.096	0.231

Table 2 Total mercury concentrations at various depths of seawater column of the 100-m deep gas-seeping vent site

Depth from the surface	October, 1994			July, 1995		September, 1996	
	pH	Filtered water	Suspended matters	Filtered water	Suspended matters	Filtered water	Suspended matters
0 m (surface)		2.2	2.3			0.7	0.8
0 m (surface)		1.1	1.5				
0 m (surface)		0.8	2.0				
0 m (surface)		0.5	1.8				
10 m		0.6	1.1	0.6	0.3	0.5	0.8
20 m		0.8	1.2	1.1	0.4	0.3	0.3
30 m		1.0	2.8	0.6	0.7	0.4	0.3
50 m	7.37	0.6	0.3				
80 m	7.30	0.5	0.2				
90 m	6.90	0.5	0.7				
95 m	6.57	0.7	0.3			0.5	0.3
100 m (bottom)	6.07	0.6	1.0	0.7	1.1	1.0	1.1
100 m (bottom)	5.88	0.8	1.2	0.7	1.1	1.1	1.0
p for trend		0.206	0.093	>0.5	0.204	0.084	0.449

concentration and depth from the surface was observed. Total mercury concentrations of seawater columns of the 200-m deep gas-seeping site are shown in Table 2. A statistically significant depth-dependent increase (one-sided $p < 0.001$, linear regression analysis) was observed in total mercury concentrations of filtered water and suspended matters from the seawater column on the vent of 200-m deep fumaroles in October, 1994 and in July, 1995. A similar trend was observed in September, 1996, although statistical significance was not attained. Those observations confirmed the previous reports (Sakamoto and Kamada 1986; Sakamoto and Kamada 1993; Tomiyasu et al. 2007), supporting the notion that 200-m deep fumaroles contribute to the relatively high mercury concentrations in the closed-off section of the bay. Hg$^\circ$ released from the fumaroles can be oxidized to form mercuric chloride complexes in seawater under acidic conditions (Yamamoto 1996). A part of soluble mercury species in the ambient seawater may simultaneously precipitate as insoluble mercury sulfide with hydrogen sulfide released from the vents.

Mercury concentrations in the surface seawater collected from 26 offshore points across the Kagoshima Bay in 1994 were also examined in order to assess the effect of fumaroles on mercury levels in the Kagoshima Bay (Table 3). The mercury concentration in the surface unfiltered seawater of Kagoshima Bay was 0.8 ng/L on average. Interestingly, the mercury concentrations of surface seawater samples increased with increasing distance from the bay entrance ($p < 0.001$), suggesting that mercury released from volcanic vents contributed to relatively high mercury

Table 3 Total mercury concentration of the surface seawater in Kagoshima Bay

Total mercury concentration (ng/L)								
Site No.	Distance from the bay entrance (km)	April	June	July	Sept.	Nov.	Dec.	Annual geometric mean
	Bay entrance							
1	0	0.4	0.4	0.6	0.8	0.4	1.8	0.6
2	0	0.5	0.1	0.4	0.2	1.8	1.8	0.5
3	0	0.2	0.1	0.3	0.5	0.6	1.2	0.4
4	0	0.9	0.5	0.5	0.2	1.0	1.5	0.6
	Southern part of the bay							
5	18	0.7	1.3	0.6	0.3	2.0	0.5	0.7
6	18	0.3	0.5	0.5	0.3	0.2	2.3	0.5
7	18	0.4	0.2	0.6	0.4	0.8	1.6	0.5
8	31	0.1	1.3	0.8	0.6	1.0	1.3	0.7
9	31	0.5	0.7	0.4	0.7	0.2	2.3	0.6
10	31	3.2	1.0	0.5	0.3	0.2	1.1	0.7
11	31	2.4	0.3	0.7	0.1	0.1	3.9	0.5
12	31	2.0	0.5	0.6	0.7	0.6	1.8	0.9
	Coastal area of Mt. Sakurajima							
13	45	1.3	1.6	1.0	0.6	0.1	2.8	0.8
14	45	1.8	0.8	0.7	0.5	0.4	1.4	0.8
15	45	2.8	1.2	0.6	0.6	0.2	1.4	0.8
16	45	2.8	1.7	0.7	1.6	1.0	1.4	1.4
17	51	1.4	1.3	0.3	1.0	2.2	5.0	1.3
18	51	1.5	0.5	0.2	0.6	1.3	3.7	0.9
19	59	1.2	0.4	0.6	0.2	1.8	3.6	0.8
20	59	3.1	0.5	0.1	1.0	3.2	2.0	1.0
21	59	1.5	0.4	0.3	1.7	1.6	1.9	1.0
	Northern part of the bay							
22	67	2.8	0.5	0.2	1.0	0.6	2.5	0.9
23	67	2.2	0.4	0.2	0.6	1.2	2.2	0.8
24	67	1.6	0.8	0.1	1.7	1.8	3.6	1.1
25	67	2.2	1.5	0.1	0.8	1.8	6.1	1.2
26	67	1.7	1.3	0.2	0.7	0.8	2.0	0.9
p for trend		0.001	0.003	−0.057	0.019	0.520	0.029	<0.001

geometric mean. * two-sided *p* values obtained from regression analysis, where log-transformed mercury concentrations were regressed on distance from the bay entrance. The negative *p* value stands for a negative coefficient. ** log-transformed mercury concentrations were regressed on the square root of distance

levels in seawater in the semi-closed-off section of the Kagoshima Bay even in the 1990s.

Seasonal variations were also noted. The average mercury concentrations in April, June, July, September, November and December were 1.1, 0.6, 0.4, 0.5, 0.7, and 2.0 ng/L, respectively. Note that the mercury concentration in December was determined from the sum of mercury concentration in filtered water and suspended matter, which were measured separately. It is unlikely, however, that this approach increased the mercury concentration in this month, since the mercury levels in November were also relatively high in many sampling sites. Seasonal variations were most evident in the northern bay area; p values for seasonal variation calculated by ANOVA were 0.086 for the bay entrance, 0.051 for the southern part of the bay, 0.003 for the coastal area of Mt. Sakurajima, and <0.001 for the northern bay.

In month-specific analysis, a distance-dependent increase was observed in all months except for July and November. It should also be of note that mercury concentrations of seawater in July did not increase with the increasing distance from the bay entrance. Possible explanations for this seasonal variation are (1) high intensity of solar radiation; (2) the ambient high temperature of the air parcel above the seawater; and (3) the high water temperature in July. Since seasonal variations were less evident in the southern part of the bay and in the bay entrance, the most plausible explanation is the thermal cline, formed at the depth of about 20–65 m in summer due to the shape of underwater caldera in the interior part of the bay. The thermal cline covers the entire closed-off section of the bay, and prevents the mercury released from the 200-m deep fumaroles to reach the surface. The absence of evident difference of mercury concentrations in the northern and the southern parts of the bay in the summer suggests that the relatively high mercury concentrations in the northern part of the bay in other seasons can be attributed to mercury released from underwater fumaroles. Further assessment on the contribution of mercury released from 200-m deep fumaroles to mercury levels in the bay seems to be warranted.

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References

Akagi H, Nishimura H (1991) Speciation of mercury in the environment. In: Suzuki T, Imura N, Clarkson TW (eds) Advances in mercury toxicology. Plenum Press, New York, pp 53–76

Ando T (1999) The metal measured in the marine pollution.-Mercury and tin-. Rinsho Kensa 43:1281–1286 in Japanese

Ando T, Yamamoto M, Tomiyasu T, Hashimoto J, Miura T, Nakano A, Akiba S (2002) Bioaccumulation of mercury in a vestimentiferan worm living in Kagoshima Bay, Japan. Chemosphere 49:477–484

Haraguchi K, Ando T, Sato M, Kawaguchi C, Tomiyasu T, Horvat M, Akagi H (2000) Detection of localized methylmercury contamination by use of the mussel adductor muscle in Minamata Bay and Kagoshima Bay, Japan. Sci Total Environ 261:75–89

Sakamoto H (1985) The distribution of mercury, arsenic, and antimony in sediments of Kagoshima Bay. Bull Chem Soc Jpn 58:580–587

Sakamoto H, Kamada M (1986) Mercury contents in sea waters of the Kagoshima Bay. Rep Fac Kagoshima Univ Math, Phys & Chem 19:49–68 (in Japanese; abstract in English)

Sakamoto H, Kamada M (1993) Mercury contents and its distribution in sea water of Kagoshima Bay. Rep Fac Kagoshima Univ Math, Phys & Chem 26:75–91

Sakamoto H, Tomiyasu T, Yonehara Y (1995) The contents and chemical form of mercury in sediments from Kagoshima Bay, in comparison with Minamata Bay and Yatsushiro Sea, southwestern Japan. Geochem J 29:97–105

Tomiyasu T, Eguchi T, Yamamoto M, Anazawa K, Sakamoto H, Ando T, Nedachi M, Marumo K (2007) Influence of submarine vents on the distribution of mercury in the sediment of Kagoshima Bay, Japan. Mar Chem 107:173–183

Yamamoto M (1996) Stimulation of elemental mercury oxidation in the presence of chloride ion in aquatic environments. Chemosphere 32:1217–1224