THE CONTENTS AND DISTRIBUTIONS OF ARSENIC, ANTIMONY AND MERCURY IN THE RIVERS AND THE HOT SPRING SEDIMENTS THAT FLOW INTO THE NORTHERN KAGOSHIMA BAY

著者	SAKAMOTO Hayao, TOMIYASU Takashi, YONEHARA Norinobu
journal or publication title	鹿児島大学理学部紀要. 数学・物理学・化学
volume	23
page range	159-167
別言語のタイトル	鹿児島湾北部に流入する河川と温泉底質中のヒ素・アンチモン及び水銀含有量とそれらの分布
URL	http://hdl.handle.net/10232/6482

THE CONTENTS AND DISTRIBUTIONS OF ARSENIC, ANTIMONY AND MERCURY IN THE RIVERS AND THE HOT SPRING SEDIMENTS THAT FLOW INTO THE NORTHERN KAGOSHIMA BAY

Rep. Fac. Sci., Kagoshima Univ., (Math., Phys. & Chem.)
No. 23, p. 159-167, 1990.

THE CONTENTS AND DISTRIBUTIONS OF ARSENIC, ANTIMONY AND MERCURY IN THE RIVERS AND THE HOT SPRING SEDIMENTS THAT FLOW INTO THE NORTHERN KAGOSHIMA BAY

Hayao SAKAMOTO*, Takashi TOMIYASU* and Norinobu YONEHARA*

(Received September 8. 1990)

Abstract

Arsenic, antimony and mercury were determined in the surface rivers and the hot spring sediments collected from Kirishima volcanic region and circumferece of northern Kagoshima Bay.

Arsenic, antimony and mercury contents in 23 samples were ranged $1.2_1 - 25._2$ (geometric mean 4.7_1), $0.16_2 - 3.0_7$ (geometric mean 0.58_0) and $0.006_4 - 63._5$ mg/kg (geometric mean 0.12_8 mg/kg), respectively.

The contents of arsenic, antimony and mercury in the surface river sendiments (derived from natural volcanic activity) and the hot spring sediments were higher than those in igneous rocks.

A high degree of correlation was found between arsenic and antimony in the hot spring sediments of Kirishima volcanic region, but no such close correlation existed among those in the river sediments.

River and hot spring sediments occur in the water system that moves violently. Accordingly it could not to find clearly trend that was seen among arsenic, antimony and mercury of marine sediments in the northern Kagoshima Bay.

Introduction

The volcanic activity in the northern Kagoshima Bay is high in comparison with the bay southern part. This is obvious that fumarolic gas of high temperature is discharged from the sea bottom.[1-4] High concentrations of arsenic, antimony and mercury around these fumaroles were reported already.[5] It was shown in this paper that arsenic concentration was high in marine sediments of Amori river estuary. The contribution of Kirishima volcano was considered as this cause.

The Kirishima volcanic region exists to the upstream of Amori river, and river waters and hot spring waters flow into the northern Kagoshima Bay. The influence of this volcanic activity reaches to river waters and river sediments. And it is conceivable that volcanic activity influences to sediments of the northern Kagoshima Bay. This re-

* Department of Chemistry, Faculty of Science, Kagoshima University, Kagoshima, 890, Japan

search planned the contribution of mercury from rivers and hot spring sediments to marine sediments of the northern Kagoshima Bay. Arsenic, antimony and mercury were determined in sediments collected from rivers and hot spring sediments, and their distributions were investigated.

Experimental

Methods of Collecting and Preserving Sediment Samples.

A powder scoop was used to collect surface sediments. The sediment samples were collected from Kirishima volcanic region and circumference of the northern Kagoshima Bay, during the period Nov. 4-5, 1976. The sediment samples were enclosed in a polystyrene bottle and then brought back to our laboratory. Each sample was then suction-filtered with a 0.45 μm Millipore filter, air-dried (taking care to avoid any extraneous contamination), and ground in an agate mortar. The uniform sediment samples thus obtained were preserved for the subsequent determination of arsenic, antimony and mercury.

Sampling stations. The sampling stations of rivers and hot spring sediments are shown in next section.

Apparatus. The apparatus used Shimadzu atomic-absorption spectrophotometer; Hitachi spectrophotometer; Iwaki-KM (Model V-D) shaker; Rigaku Mercury SP.

Reagents. The acids used (sulfuric acid, nitric acid, hydrochloric acid, hydrofluoric acid, perchloric acid) and potassium permanganate were all analytical-special-reagent-grade for the measurements of the toxic metals.

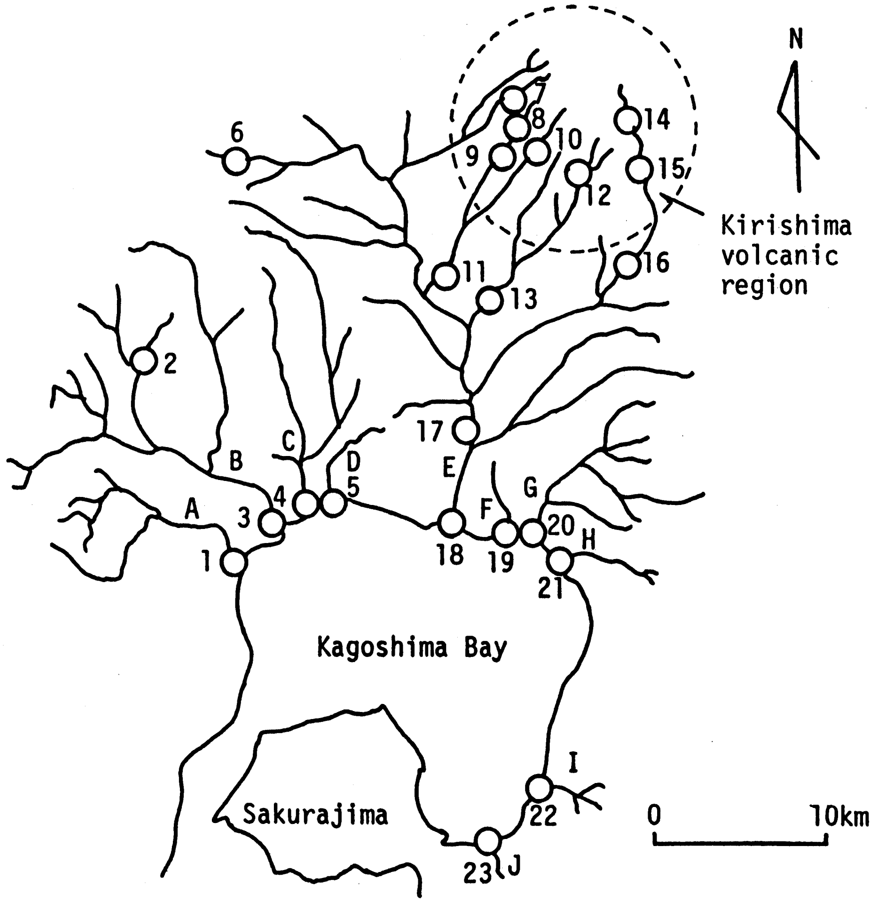
Procedure for the Determination of Arsenic. A sediment sample (0.05 to 0.20 g) was weighed out into a Teflon beaker; 4 ml of perchloric acid (60%), 3 ml of sulfuric acid (98%), 8 ml of hydrofluoric acid (46%), and 2 ml of potassium permanganate solution (2%) were then added, and the mixture was heated on a hot plate (100℃) to effect decomposition and subsequently evaporated to dryness. After cooling, 3 ml of 12 mol/l hydrochloric acid and 6 ml of redistilled water were added to dissolve the residue, and the solution was transferred into an arsine generator, where the arsenic was separated as arsine (AsH_3) by the addition of arsenic-free zinc and determined by the Ag-DDTC method.[6] The results of this method showed good agreement with those obtained by atomic-absorption spectrophotometry.[7]

Procedure for the Determination of Antimony. A sediment sample (0.05 to 0.50 g), weighed out into a porcelain crucible, was fused with 2.5 g of potassium pyrosulfate. After cooling to room temperature, 10 ml of 6 mol/l hydrochloric acid, 10 ml of 6 mol/l sulfuric acid, and 5 ml of redistilled water were added to dissolve the fusion product, the solution was transferred into a separating funnel, and the antimony was determined by the Rhodamine B method.[8]

Procedure for the Determination of Mercury. A sediment sample (0.02 to 0.30), homogenized as much as possible under air-dried conditions, was weighed out into a porcelain boat previously ignited to exclude any trace of mercury that might be left adhered, and covered with an addition agent (calcium hydroxide and sodium carbonate, both ignited at ca. 700℃ and then mixed in a 1:1 volume ratio). The analytical sample thus prepared was heated in the furnace of a mercury analyzer at ca. 300℃ for three minutes, and then at ca. 700℃ for four minutes to complete the decomposition; the mercury vapor thus evolved was caught in a potassium permanganate solution acidified with sulfuric acid[9] or with a porous gold collector.[10]

Results and Discussion

The Arsenic, Antimony and Mercury Contents in the Rivers and the Hot Spring Sediments. The arsenic, antimony and mercury contents were determined for river and hot spring



A: Omoi river, B: Beppu river, C: Amikake river, D: Hikiyama river, E: Amori river, F: Sudo river, G: Kenkou river, H: Tkakahashi river, I: Matsuzaki river, J: Butsuseki river

Fig. 1. Sampling stations of rivers and the hot spring sediments in circumferece of the northern Kagoshima Bay.

Table 1. Analytical results of arsenic, antimony and mercury in the surface rivers and the hot spring sediments.

Stn. No.	Sampling station	Content mg/kg[a)]			Remarks
		As	Sb	Hg	
1	Omoi river Estuary	4.3_7	0.23_1	0.011_6	River Sediments
2	Kidzushi Kouzan	$10._6$	0.63_6	0.085_0	River Sediments
3	Airabashi	3.7_1	0.74_6	0.025_7	River Sediments
4	Amikake River Estuary	3.7_7	0.29_9	0.012_8	River Sediments
5	Hikiyama River Estuary	4.6_8	0.30_7	0.026_3	River Sediments
6	Yamanokouzan Downstream	1.9_0	0.82_5	0.53_7	River Sediments
7	Ginyu	8.3_1	3.0_7	$23._3$	Hot Spring Sediments
8	Oura Hot Spring	4.7_4	0.19_6	4.0_2	Hot Spring Sediments
9	Kinyu Hot Spring	2.3_2	0.71_0	0.89_7	Hot Spring Sediments
10	Tearai	3.6_2	0.96_4	3.5_2	Hot Spring Sediments
11	Matebara	7.8_6	1.3_1	0.21_5	River Sediments
12	Maruotaki	$25._2$	1.1_4	0.20_4	River Sediments
13	Arase	8.1_7	1.3_2	0.027_4	River Sediments
14	Shinyu Upper Stream	3.8_6	0.76_6	0.006_4	River Sediments
15	Yunono Hot Spring	2.7_2	0.61_1	$63._5$	Hot Spring Sediments
16	Hazeta	5.3_2	0.66_9	2.8_1	River Sediments
17	Himegi	5.0_3	0.16_2	0.043_2	River Sediments
18	Shinkawabashi	5.0_7	0.75_3	0.056_7	River Sediments
19	Sudo River Estuary	3.6_5	0.48_1	0.019_2	River Sediments
20	Kenkou River Estuary	1.2_1	0.17_2	0.014_7	River Sediments
21	Takahashi River Estuary	2.5_3	0.49_9	0.018_9	River Sediments
22	Matsuzaki River Estuary	3.5_6	0.56_7	0.012_4	River Sediments
23	Butsuseki River Estuary	$17._6$	0.59_4	0.009_8	River Sediments

a) The contents of arsenic, antimony and mercury are converted to these values when samples are heated at 110℃ for 6h.

Table 2. Arsenic, antimony and mercury contents in the surface rivers and the hot spring sediments.

Sample	Element	Range[a)]	$\overline{X_A}$[b)]	$\overline{X_G}$[c)]	n[d)]
River Sediments	As	1.2_1 −$25._2$	6.5_6	4.9_7	18
	Sb	0.16_2 − 1.3_2	0.63_8	0.53_8	18
	Hg	0.006_4− 2.8_1	0.23_0	0.041_9	18
Hot Spring Sediments	As	2.3_2 − 8.3_1	4.3_4	3.9_0	5
	Sb	0.19_6 − 3.0_7	1.1_1	0.75_9	5
	Hg	0.89_7 −$63._5$	$19._0$	7.1_6	5

a−c) in mg/kg for As, Sb and Hg. b) Arithmetic mean.
c) Geometric mean. d) Number of samples

sediments sampled from various areas around northern Kagoshima Bay. The sampling stations are illustrated in Fig. 1 and analytical results are tabulated in Table 1. Below, we discuss the data listed in Table 1.

The range, arithmetic and geometric mean of the arsenic, antimony and mercury contents and the number of samples determined, are shown in Table 2.

Arsenic, antimony and mercury contents in 23 samples listed in Table 1 were ranged 1.2_{1}-$25._{2}$ (mean 4.7_{1}), 0.16_{2}-3.0_{7} (mean 0.58_{0}) and 0.006_{4}-$63._{5}$ mg/kg (mean 0.12_{8} mg/kg), respectively.

Using the mean contents of arsenic, antimony and mercury in igneous rocks,

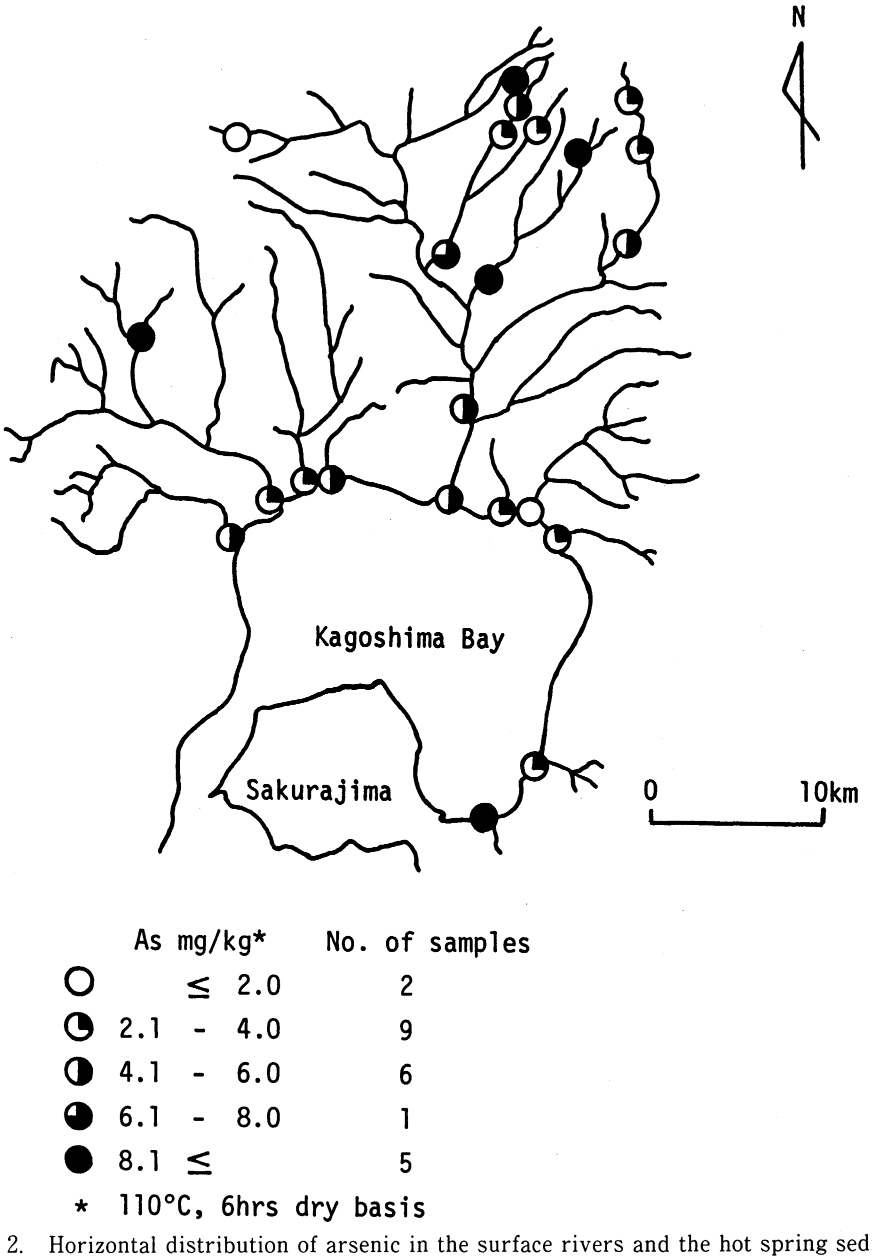


Fig. 2. Horizontal distribution of arsenic in the surface rivers and the hot spring sediments.

accepted to be 1.5[11], 0.2[12] and 0.08[13] ppm (mg/kg), respectively. The contents of arsenic and antimony in the rivers and the hot spring sediments are higher compared to the mean content of igneous rocks. Mercury content in hot spring sediments is higher compared to the mean content of river sediments. Especially, mercury was concentrated in the hot spring sediments of Kirishima volcanic region. The abnormally high concentrations of arsenic, antimony and mercury were found in part surface rivers and hot spring sediments. It may be considered that it derived from natural volcanic activity of the past.

Horizontal Distribution of Arsenic, Antimony and Mercury in the Surface Sediments. Figure

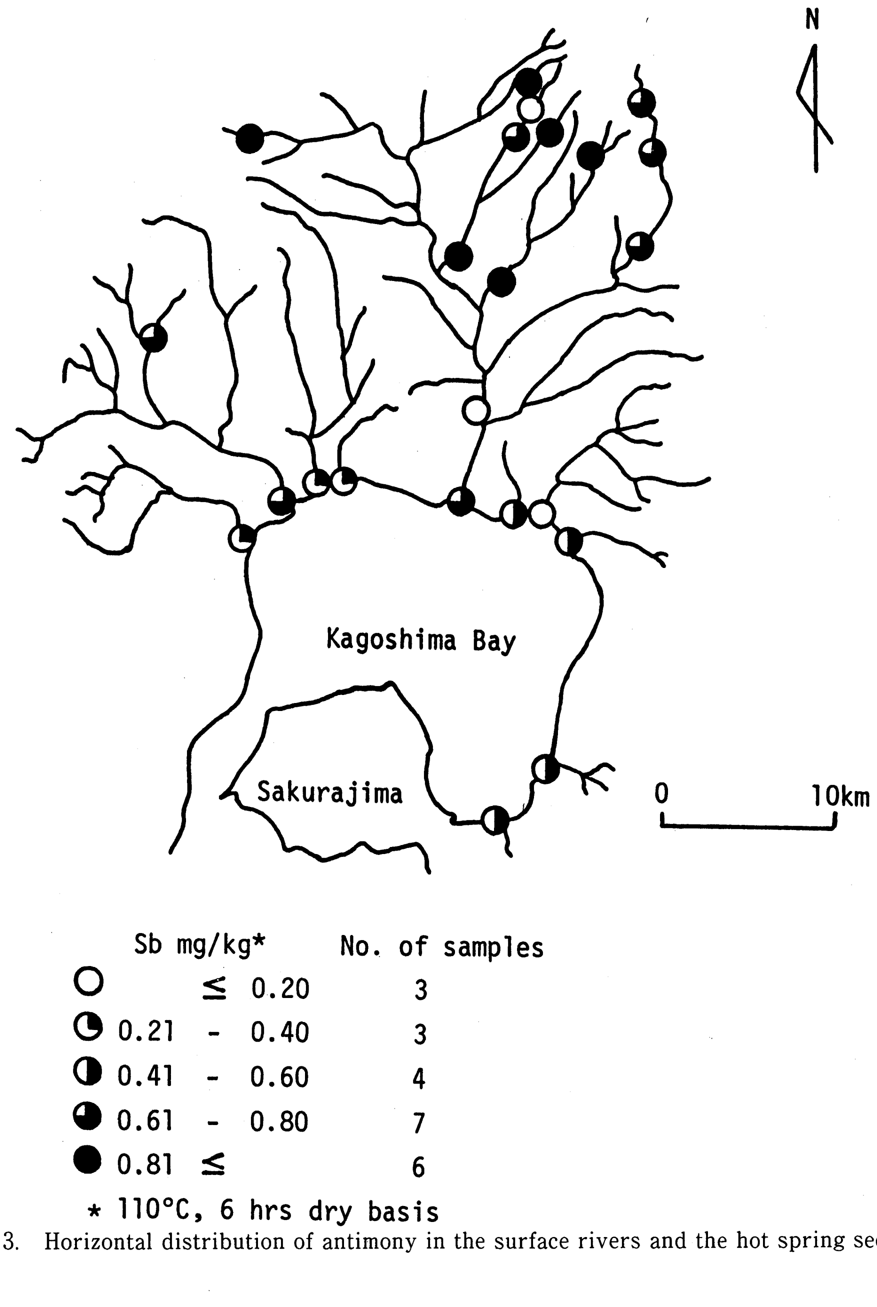


Fig. 3. Horizontal distribution of antimony in the surface rivers and the hot spring sediments.

2-4 show the horizontal distribution of arsenic, antimony and mercury in the surface rivers and the hot spring sediments collected at 23 stations, are shown in Fig. 1. Higher contents of arsenic, antimony and mercury were observed in the Kirishima volcanic region, particularly in the vicinity of geothermal areas and in marine sediments[5] near the estuary of the Amori river, flowing down from the Kirishima volcanic region.

Correlations among Arsenic, Antimony and Mercury in the Surface Sediments in Kirishima Volcanic Region and Circumference of the Northern Kagoshima Bay. Table 3 shows the correlation coefficients among the contents of arsenic, antimony and mercury in the surface rivers and the hot spring sediments in the Kirishima volcanic region and circumference of

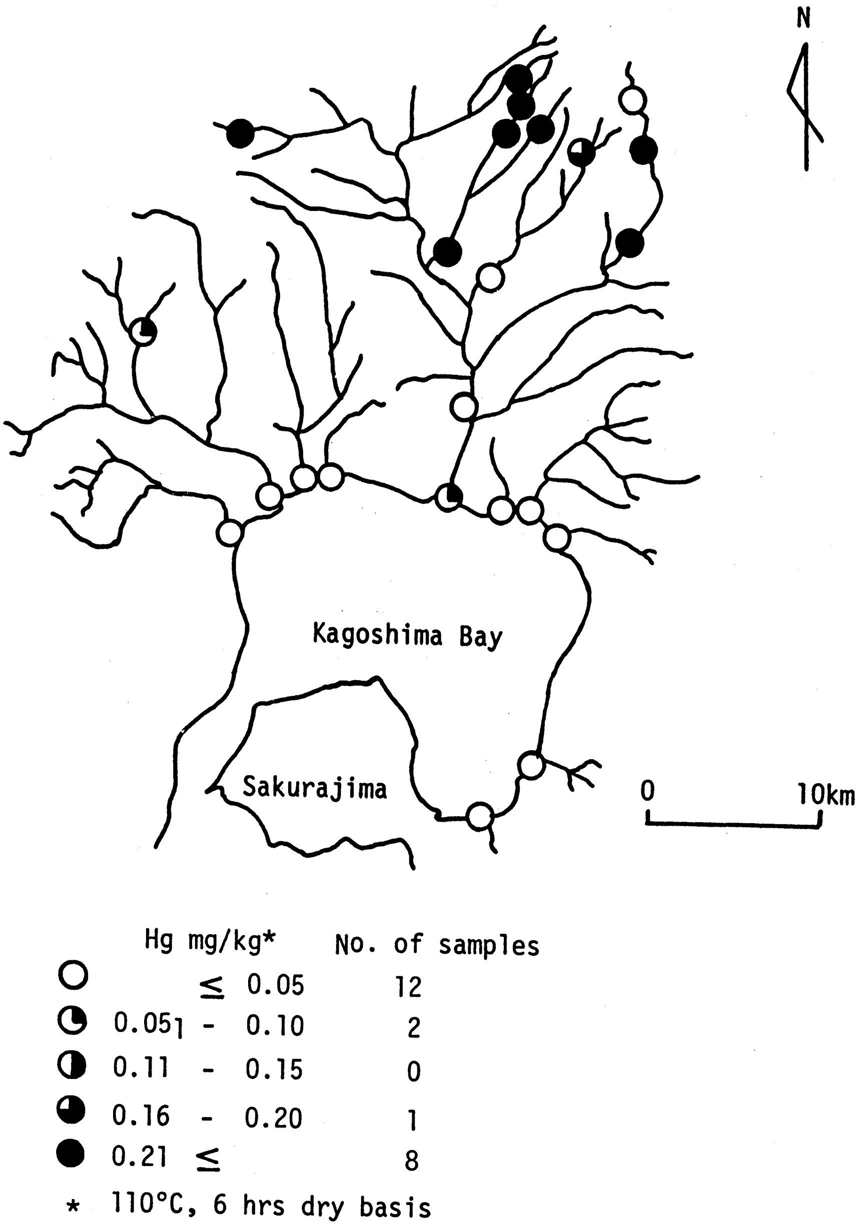


Fig. 4. Horizontal distribution of mercury in the surface rivers and the hot spring sediments.

Table 3. Mutual correlation coefficients of arsenic, antimony and mercury in the surface rivers and the hot spring sediments.

(I)[a]

	As	Sb	Hg
As			
Sb	0.44		
Hg	-0.030	0.10	

($n^{c)}$=18)

(II)[b]

	As	Sb	Hg
As			
Sb	0.84		
Hg	-0.052	0.079	

($n^{c)}$=5)

a)(I) is river sediments. b)(II) is hot spring sediments.
c)n is the number of determined samples.

the northern Kagoshima Bay. As may be apparent from Table 3, a higher degree of positive correlation is only found between the contents of arsenic and antimony in the hot spring sediments. Such trends were seen to arsenic and antimony of hot spring water.[14] There was a little positive correlation between arsenic and antimony in river sediments. But, between aresenic and mercury, antimony and mercury a correlation was not admitted at all.

Conclusion

The horizontal distributions of the contents of arsenic, antimony and mercury in the surface rivers and hot spring sediments collected from Kirishima volcanic region and circumference of the northern Kagoshima Bay have been studied. The results may be summarized as follows: (1) The distribution of arsenic, antimony and mercury contents in the surface sediments of the Kirishima volcanic region and circumference of the northern Kagoshima Bay revealed high concentrations of these components in a limited area. (2) A high degree of correlation was found between arsenic and antimony in surface hot spring sediments, but no such close correlation existed among those in the river sediments. (3) Abnormal concentrations of arsenic and mercury were found at the hot spring sediments or in the river sediments that was derived from natural volcanic activity. (4) Rivers and hot spring sediments occur in the water system that moves violently.

Accordingly it could not to find clearly trend that was seen among arsenic, antimony and mercury of marine sediments in the northern Kagoshima Bay.

The authors are indebted to the Environmental Government and Environmental Pollution Control Section of Kagoshima Prefecture and the Institute of Environmental Pollution and Public Health of Kagoshima Prefecture for their practical assistance, such as in the collection of samples, as well as for their endlessly helpful discussions during this investigation.

References

1) M. Kamada, T. Onishi and H. Sakamoto, "Study of the Submarine Volcanic Activity of Northern Kagoshima Bay and Influences in Environment", 55 (1976).
2) M. Kamada, H. Sakamoto and N. Yonehara, "Study of the Submarine Volcanic Activity in the Northern Area of Sakurajima", 64 (1977).
3) Kagoshima Prefecture, "Report of Environmental Survey on Mercury Pollution in Kagoshima Bay" (1977).
4) Kagoshima Prefecture, "Report of Environmental Survey on Mercury in Kagoshima Bay" (1978).
5) H. Sakamoto, *Bull. Chem. Soc. Jpn.*, **58**, 580 (1985).
6) Testing Methods for Industrial Wastewater, JIS K0102, 176 (1981).
7) M. Yamamoto, K. Urata, K. Murashige and Y. Yamamoto, *Spectrochimica Acta*, **36B**, 671 (1981).
8) Testing Methods for Industrial Wastewater, JIS K0102, 182 (1981).
9) H. Sakamoto and M. Kamada, *Rep. Fac., Kagoshima Univ.*, (*Math., Phys. & Chem.*), **13**, 63 (1980).
10) H. Sakamoto and M. Kamada, *Nippon Kagaku Kaishi*, **1981**, 32 (1981).
11) "Handbook of Geochemistry", Springer, Vol. II-4, 33-E-4 (1969).
12) "Handbook of Geochemistry", Springer, Vol. II-4, 51-E-3 (1969).
13) "Handbook of Geochemistry", Springer, Vol. II-5, 80-E-1 (1969).
14) H. Sakamoto, M. Kamada and N. Yonehara, *Bull. Chem. Soc. Jpn.*, **61**, 3471 (1988).