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ANTIMONY SURVEY IN YODO RIVER BASIN, JAPAN IN 1994–1995

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Antimony survey in Yodo river basin, Japan was conducted in 1994 and 1995. The concentration ranged from 0.3 μg/L to 4 μg/L in average. Background level of 0.3 μg/L were detected in Kizu river and Lake Biwa. On the other hand severe anthropogenic contamination in the lower reaches of Katsura river was observed, where 3 ~ 4 μg/L were detected in 1994. However, the contamination was presumably improved, as the concentration there decreased in 1995. Antimony load in 1995 was reduced by ca.30% compared to 1994.

Keywords: Antimony; fire retardant, water pollution

INTRODUCTION

Antimony is currently used not only in metal production but also as fire-retardant additive in plastics, artificial textiles etc [1]. The amount of usage of antimony as additives is ca.10000 ton/year in Japan, which is nearly the same as in the United States [1]. The interest of health effect by antimony is now growing [2,3]. In 1993 Japan government has noted antimony as "item requiring surveillance" whose guidance concentration is 2 μg/L. The importance to monitor antimony in fresh water has grown, especially, when utilized as a drinking water source. Therefore we have investigated antimony in Yodo river basin which is one of the largest basin in Japan.

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EXPERIMENTAL

Site Description

Yodo river basin is illustrated in Figure 1. Sample were collected from 19 points. Yodo river originates from the mouth of Lake Biwa and ends at Osaka Bay. In the middle reaches, it meets two large tributaries, which are Katsura river and Kizu river. In the upper reaches of Katsura river a large urban area "Kyoto City" is located. On the other hand Kizu river basin is a rural area which is agriculturally utilized. In the lower reaches of Yodo river basin, drinking water intake facilities are located. In Osaka urban area there are many small rivers, too.

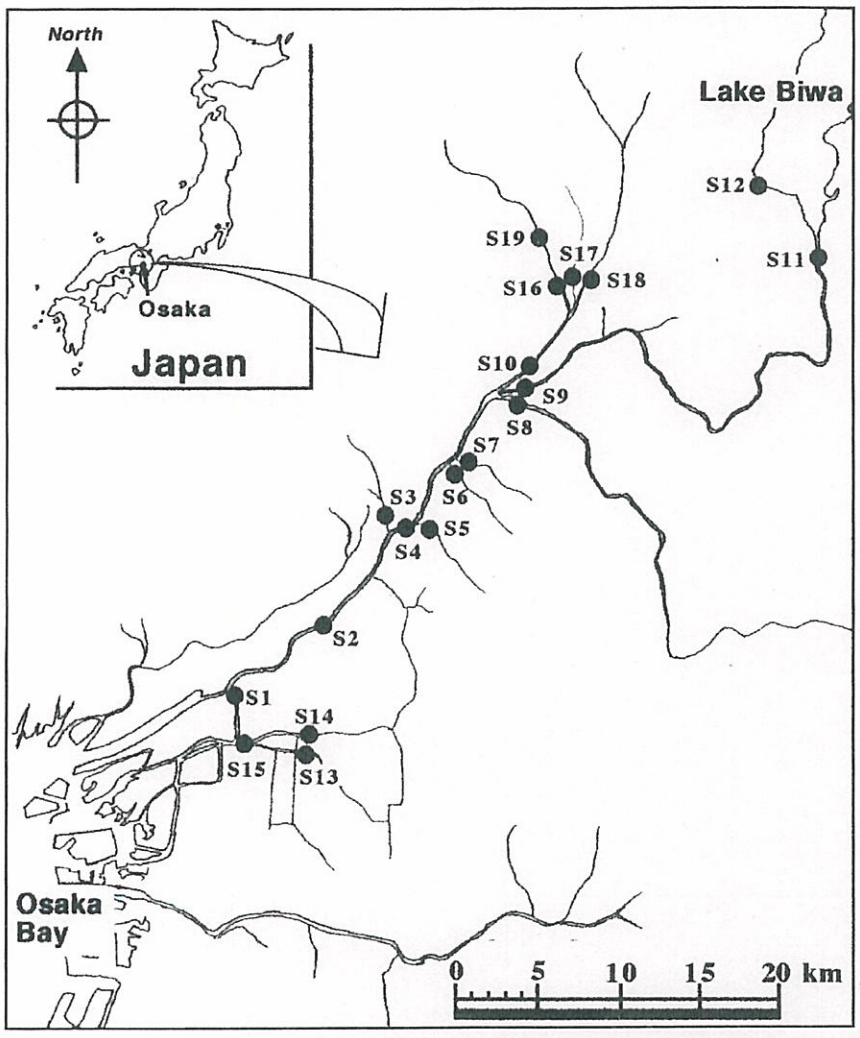

FIGURE 1 Yodo River Basin.

Sample Collection

Samples were collected six times during September to December in 1994 and five times during July to November in 1995. Sampling date was chosen to low tide date in order to avoid the effect from sea water. River water was taken from the bridge with a polyethylene bucket and immediately transferred into a polycarbonate bottle. The sample were analyzed within a few days of collection.

Analysis

Antimony was analyzed by hydride generation atomic absorption spectrometry (HGAAS) in a batch mode [4]. Test tube of 18 mm in diameter was used as a hydride generator. Up to 10 mL of sample was added with 0.5 mL of 1 M potassium iodide solution, 0.5 mL of 0.1 M thiourea solution and 1 mL of 12 M hydrochloric acid. Injection of 1 mL of 0.2% sodium tetrahydroborate solution converted antimony in water into stibine, which was carried by nitrogen career gas (flow rate of 200 mL/min) to the electrothermal quartz tube (900 °C) on the burner head of atomic absorption spectrometer(Shimadzu AA-670). The quartz tube was treated with hydrofluoric acid prior to analysis(40% hydrofluoric acid, 10 min, room temperature). Analytical line of 231.15 nm was used with a slit width of 1.0 nm. Sample analysis was performed in continuous duplicate. Hydride generation was not interfered by any matrices in samples, which was confirmed by standard addition (Figure 2).

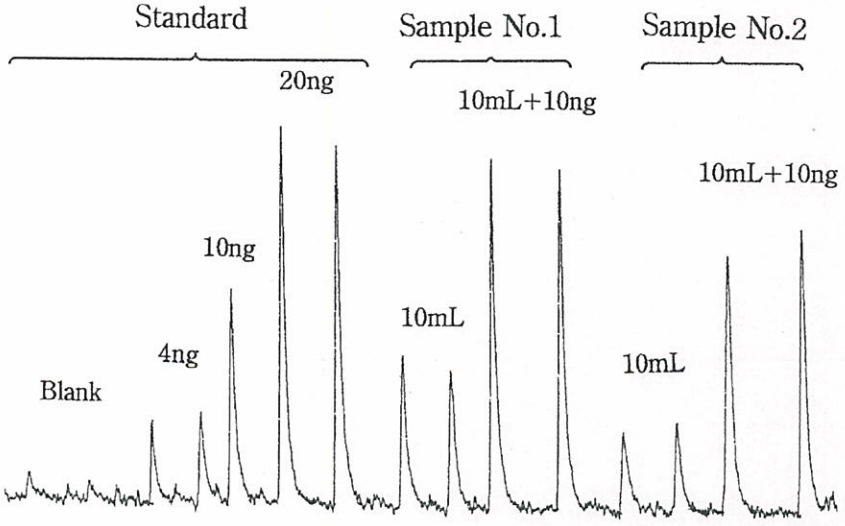

FIGURE 2 Analytical Chart.

RESULTS AND DISCUSSION

The summary of the data is given in Table I. Concentration level of antimony ranged from 0.3 μg Sb/L to 4 μg/L. The lowest concentration level were observed at Goko Br.-Kizu river(S8) and Sosui intake at Lake Biwa(S12), which have little artificial discharge in their upper reaches. Ambient level of antimony agreed with former reports[6–8]. On the other hand severe contamination was observed in the lower reaches of Katsura river(S16 and S10) as well as Osaka urban area(S13, S14 and S15).

Significant decrease was observed in concentration of antimony in the lower reaches of Katsura river in 1995. In the period of September 1994 to December in 1994 they were as high as 3.75±1.35 μg/L(S16) and 3.54±1.27 μg/L(S10), which had exceeded the guidance concentration set by Japan. The contamination occurred between Kuga Br.(S16) and Kuze Br.(S19), therefore, it was suspected some factories or the sewage treatment facilities located there as antimony sources. However, in the period of July to November in 1995, the concentration of the sample collected there decreased to lower than 2 μg/L.

Judging from the decrease of concentration of antimony, one may think that antimony discharge decreased to less than 50%. However, we must take river flow rate into account, when we discuss antimony load. Table II shows the

TABLE I Concentration of Antimony in Yodo River Basin

No.	*Location*	*Sep.-Dec.1994*		*Jul.-Nov.1995*	
		Average±	*SD.*	*Average±*	*SD.*
S1	Kema Br.			0.78 ±	0.22
S2	Torigai Br.			0.77 ±	0.28
S3	Sagiutshi Br.			0.64 ±	0.17
S4	Hirakata Br.	0.86 ±	0.23	0.74 ±	0.17
S5	Kasasagi Br.	0.62 ±	0.18	0.90 ±	0.37
S6	Makino Br.	0.71 ±	0.20	0.85 ±	0.60
S7	Kuzuha Br.	0.77 ±	0.33	0.78 ±	0.31
S8	Goko Br.-Kizu River	0.28 ±	0.07	0.29 ±	0.08
S9	Goko Br.-Uji River	0.61 ±	0.13	0.56 ±	0.16
S10	Miyamae Br.	3.54 ±	1.27	1.66 ±	0.61
S11	Nango Araizeki			0.36 ±	0.06
S12	Sosui Intake at Lake Biwa			0.32 ±	0.08
S13	Bandokobashi Br.			1.68 ±	0.65
S14	Neyagawaohashi Br.			1.46 ±	0.37
S15	Kyobashi Br.			1.61 ±	0.34
S16	Kuga Br.	3.75 ±	1.35	1.71 ±	0.95
S17	Kyokawa Br.-Nishitakase River	1.71 ±	0.66	1.77 ±	0.38
S18	Kyokawa Br. -Kamo River	0.69 ±	0.15	0.90 ±	0.40
S19	Kuze Br.	0.53 ±	0.15	0.35 ±	0.05

unit: μg/L

TABLE II Antimony Load at Lower Reaches of Katsura River in 1994 and 1995

	1994							*1995*					
	9/2	*10/17*	*11/9*	*11/27*	*12/12*	*12/18*	*Avg. ±S.D.*	*7/17*	*8/7*	*9/11*	*10/4*	*11/15*	*Avg. ±S.D.*
Flow Rate(m^3/sec)	9.07	13.24	13.07	10.10	11.69	10.08	11.21 ± 1.58	(60.4)*	15.28	13.17	15.64	18.11	15.55 ± 1.75
Kuze Br.(S19)													
Concentration(μgSb/L)	0.66	0.64	0.39	0.59	0.26	0.62	0.53 ± 0.15	N.A.	0.32	0.29	0.42	0.38	0.35 ± 0.05
Load of Sb(mgSb/sec)	6.0	8.5	5.1	6.0	3.0	6.2	5.8 ± 1.6		4.9	3.8	6.6	6.9	5.5 ± 1.2
Kuga Br.(S16)													
Concentration(μSb/L)	5.54	2.63	3.88	4.64	1.44	4.37	3.75 ± 1.35	N.A.	0.93	1.01	3.28	1.61	1.71 ± 0.95
Load of Sb(mgSb/sec)	50.2	34.8	50.7	46.9	16.8	44.0	40.6 ± 11.9		14.2	13.3	51.3	29.2	27.0 ± 15.4
Miyamae Br.(S10)													
Concentration(μSb/L)	4.66	2.03	3.66	4.49	1.62	4.75	3.54 ± 1.27	(1.00)*	1.25	1.29	2.57	2.19	1.83 ± 0.57
Load of Sb(mgSb/sec)	42.3	26.9	47.8	45.3	18.9	47.9	38.2 ± 11.2	(60.4)*	19.1	17.0	40.2	39.7	29.0 ± 11.0

*This data is excluded in calculating the average, because of the storm.

daily river flow rate [8], the concentration of antimony and calculated antimony load. The river flow rate were measured at Miyamae Br.(S10), however the contribution of Nishitakase river and Kamo River are very small, so that we consider the flow rate constant along the lower reaches of Katsura river. If we ignore the data of July 17th 1995, which was the next day of storm caused by a typhoon, antimony load are calculated to be 38.2 ~ 40.6 mgSb/sec and 27.0 ~ 29.0 mgSb/sec for former and later period, respectively. Moreover, antimony load at Kuze Br.(S19) was the constant during 1994–1995. This may suggest discharge improvement took place by ca.30% between 1994 and 1995. It is rather possible that announcement by Japan government in 1993, in which antimony was noted as "item requiring surveillance", had affected antimony — using industrial attitude in some extent.

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