

Distribution of Indium, Thallium and Bismuth in the Environmental Water of Japan

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Received: 2 March 2012 / Accepted: 24 September 2012 / Published online: 5 October 2012
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Abstract Indium, thallium and bismuth are toxic and it is important to know the distribution of these elements in environmental water. The concentrations of these elements were measured in 50 sampling points in Japan and the reasons of high concentrations in several samples were discussed. The average concentrations (ng/L) of dissolved and particulate indium in river, lake and coastal seawater were 1.4–3.0 and 2.4–9.1, respectively. Those for thallium were 7.2–11.3 and 3.5–36.0. Those for bismuth were 12.7–24.0 and 12.1–52.7.

Keywords Indium·Thallium·Bismuth·Contamination · Average concentration

Recently, In, Tl and Bi have been widely used for the latest technologies such as information technology and advanced material technology etc. In has been used for the electrode of a display of television as an indium tin oxide (ITO). In addition, Tl has been used for an optical lens and rodenticide, and Bi has been used for the additives in the metallurgy. In addition, Bi has been used for a solder instead of lead, since the use of lead is strictly regulated by RoHS Directives and REACH Regulation etc.

Threshold limit value–time-weighted average (TLV–TWA) by American Conference of Industrial Hygienist (ACGIH) for In and Tl are 0.1 and 0.02 mg/m³, respectively (ACGIH 2011). TLV–TWA for bismuth telluride is

10 mg/m³ without the addition of selenium and 5 mg/m³ with the addition of selenium.

The demand of In metal in 2009 was the largest in the world. The import of Tl in 2009 increased to 4.4 times compared with that in 2006. The demand of Bi in 2009 increased to about 1.3 times compared with that in 2005 (JOGMEC 2010). Therefore, it is necessary to measure the concentrations of these elements in water environments before the contamination with these elements occurs in water environment.

We have measured the soluble and particulate these elements in rivers, lakes and coastal seawaters in Japan using inductively coupled plasma mass spectrometry (ICP–MS) (Miyazaki et al. 2005, 2008, 2009, 2010). In this paper, we report the concentrations at other sampling points in Japan and discuss on the source of contamination with these elements. In addition, we summarized the soluble concentrations of these elements in other countries in the world to estimate the situation of the contamination with these elements in the world.

Materials and Methods

All samples were collected according to the method reported previously (Miyazaki et al. 2005, 2008, 2009, 2010). Briefly, samples were collected using a polyethylene bucket with a nylon rope. After collection, 500 mL of samples were filtrated with a membrane filter (0.45 µm) into a polyethylene bottle. To the filtrate, 7.0 mL of high purity nitric acid (Kanto Chemical Co. Inc., Japan) was added and the bottle was stoppered tightly. The filtration residue was put into a plastic box and it was transported to the laboratory with the collected water samples. The residue was transferred into a beaker of polytetrafluoroethylene.

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One mL of high purity nitric acid and 3 mL of high purity perchloric acid (Kanto Chemical Co., Inc., Japan) were put into the beaker and it was heated to digest the residue. After the digestion, the residue was dissolved into 3 mL of 0.2 M high purity nitric acid. Then the solution was transferred into a 5 mL volumetric flask and made to the constant volume with 0.2 M high purity nitric acid. The ICP-MS instrument used was Agilent Technology 7500a. The operation conditions and measurement limits were the same as described previously (Miyazaki et al. 2009). Briefly, measurement limits (10σ , ng/L) were In 0.15, Tl 0.92, and Bi 0.60 for soluble components, and In 0.54, Tl 0.92 and Bi 2.21 for particulate components, respectively. In, Tl and Bi were measured with ^{115}In , ^{205}Tl , and ^{209}Bi . Since ^{115}In is interfered by ^{115}Sn , the measured value of ^{115}In was corrected by ^{115}Sn concentration in the samples. In the case of Bi, ^{208}PbH might interfere. However, even if 0.01 mg/L of lead (the environmental regulation value of Japan) exists, the effect to ^{208}Bi was only 0.018 ng/L. Hence, the measurement value of ^{208}Bi was not corrected.

Since we could not find a reference material which contains ng/L level of In, Tl and Bi, recovery test was undertaken using the seawater of Hitachi port sample (No. 32 in Table 3) in order to investigate the accuracy of ICP-MS analysis. Five hundreds mL of the sample was taken into a volumetric flask and 1 mL each of In, Tl and Bi standard solutions (10 ng/mL) were added to the sample. Then the concentrations of In, Tl and Bi were analyzed by ICP-MS and the recoveries were calculated. The recoveries were not less than 98.5 % for all of these elements.

Results and Discussion

The concentrations of In, Tl and Bi in river waters are shown in Table 1. The standard deviations ($n = 5$) for the determination of concentrations of In, Tl and Bi were 3.8 %, 3.2 % and 3.2 %, respectively. In river water, most of the concentrations of metals in particulate components were higher than those in dissolved components except for some exceptions. The sampling point sample No. 7 was the bridge in the downstream region of Yodogawa river. Yodogawa river flows through Osaka city whose population is about 2,670,000 which is the second largest population among the Japanese cities. This city is also active in the field of chemistry, nonferrous metal, electronic components and devices, and textile etc. Thus, high concentration of Bi in the dissolved component at this point is possibly due to the industrial effluents. The concentration of lead (Pb) in 2008 at this sampling point was 0.004 mg/L (Ministry of Land, Infrastructure and Transport, Japan, 2008). The values of Pb at Kunijima where is about 8 km upstream from the sampling point No. 7 were 0.001 mg/L

(Ministry of Land, Infrastructure and Transport, Japan, 2008). Thus, concentration of Pb at the sampling point No. 7 was 4 times higher than that of other point. Such high concentrations of Pb and Bi at the sampling point No. 7 indicate that the point was more contaminated with metals than other points. Antimony (160 kg/per year) had been discharged from a factory of electrical equipment manufacturing into the port near sampling point No. 18 (The Ministry of the Environment, Government of Japan 2006). The high dissolved and particulate concentration Bi at this sampling point might be due to the factory, since antimony belongs to the same group as Bi in the periodic table.

As for particulate components, the sample No. 5 had high concentrations of In, Tl and Bi. There is a big chemical factory near this sampling point. Hence, the high concentration of these metals might be due to this factory. The sample No. 10 had also high concentrations of In, Tl and Bi. This point was under the intersection of a big highway. Thus, those high concentrations might be due to the heavy traffic of cars. The sample No. 18 had high concentration of Bi. The reason might be the fact that described for dissolved components. Although sample No. 13 had high concentration of particulate Bi, the reason was not clear. The samples No. 21, 22 and 23 were collected in the Okinawa Island where is located in the southern part of Japan. All of the samples had about twenty ng/L level of Bi concentration in particulate component. Since we could not find any big factories etc. in this area, it might be due to the natural geological abundance.

The results on the Biwako lake that is the largest lake in Japan are shown in Table 2. The samples were collected at the surface level of the lake. The concentrations of particulate components were also generally higher than those of dissolved component except for sample No. 24. The sample No. 24 had high concentrations of Tl and Bi in the dissolved component (Miyazaki et al. 2010) and high concentration of Bi in the particulate component. The sample No. 25 had also high concentration of Tl in the dissolved component (Miyazaki et al. 2010) and in the particulate component. Near the sampling point No. 24, there is a large chemical factory which is producing textile, medicine, plastics, electronics, carbon material etc. Thus, high concentration of Tl and Bi might be due to this factory. Near the sampling point No. 25, there is a large hospital. The effluent from this hospital comes into the Biwako lake through a water channel. Therefore, high concentration of Tl at the sampling point No. 25 might be due to this hospital, since thallium compounds are used for an injection and some inspection. And the rodenticide also might be the reason which has been used in the hospital.

The concentrations of the surface level of costal seawaters are summarized in Table 3. In the coastal seawater samples, the concentrations of many dissolved components

Table 1 Concentrations in rivers in Japan

Sampling point	Sampling date	Dissolved (ng/L)			Particulate (ng/L)		
		In	Tl	Bi	In	Tl	Bi
(1) Kitakamigawa river, shinkitakamiohashi bridge	2008.8.01	0.3	6.1*	n.m.*	2.1	2.7	10.6
(2) Kyukitakamigawa river, Ishinomakiohashi bridge	2008.8.01	n.m.	16.0*	n.m.*	0.7	n.m.	n.m.
(3) Kujigawa river, kujiohashi bridge	2008.8.01	0.3	3.2*	n.m.*	n.m.	1.3	7.1
(4) Sekikawa river, sekigawa bridge	2008.9.27	1.1	2.9	4.5	3.3	6.0	9.1
(5) Hokuragawa river, minatobashi bridge	2008.9.27	2.5	4.2*	5.5*	11.3	19.2	48.0
(6) Yodogawa river, yodogawashinbashi bridge	2008.6.14	n.m.	n.m.	n.m.	2.4	1.1	5.9
(7) Yodogawa river, denpouhashi bridge	2008.6.14	n.m.	n.m.*	121.1*	5.2	2.5	10.8
(8) Yamatogawa river, hankaiobashi bridge	2008.6.14	1.4	2.5	5.3	3.0	4.9	15.8
(9) Ujigawa river, upstream of kumiyama drainage pumping station	2008.6.14	1.1	2.7	4.5	4.7	5.0	9.2
(10) Kizugawa river, kizugawaohashi	2008.6.14	3.2	6.5	7.8	12.8	27.4	30.3
(11) Katsuragawa river, miyamae bridge	2008.6.14	n.m.	2.3*	n.m.*	2.9	4.4	9.5
(12) Kinokawa river kinokawaohashi bridge	2008.6.15	1.1	3.5	5.4	11.8	6.3	10.5
(13) Kinokawa river takebusabashi bridge	2008.6.15	n.m.	n.m.	2.9	2.9	n.m.	366.9
(14) Mukogawa river, nanbubashi bridge	2008.6.15	1.3	n.m.	16	4.8	2.9	8.5
(15) Suzukagawa river, suzukaohashi bridge	2008.6.15	n.m.	n.m.	n.m.	1.5	2.2	3.6
(16) Kumanogawa river, shinkumanoohashi bridge	2008.6.15	n.m.	n.m.	n.m.	2.3	3.5	3.3
(17) Yoshinogawa river, yoshinogawaohashi bridge	2008.12.14	3.2	3.1*	5.1*	5.3	2.1	6.4
(18) Nakagawa river, shinnakagawa bridge	2008.12.14	1.5	2.1	79.0	7.5	3.3	42.1
(19) Monobegawa river, shinmonobegawa bridge	2008.12.14	2.6	1.3	1.1	4.3	3.2	6.3
(20) Shimantogawa river, watarigawaohashi bridge	2008.12.14	n.m.	n.m.*	n.m.*	1.1	1.2	2.5
(21) Kokubagawa river, nahaohashi bridge	2008.9.12	n.m.	n.m.	n.m.	1.9	4.3	17.9
(22) Hijyagawa river, hijyabashi bridge	2008.9.12	n.m.	n.m.	n.m.	1.0	2.6	18.7
(23) Okukubigawa river, okukubibashi bridge	2009.9.12	n.m.	n.m.	n.m.	1.5	6.7	25.5

n.m. stands for the value under the measurement limits

* Data already reported in the reference, Miyazaki et al. (2010)

Table 2 Concentrations in Biwako lake in Japan

Sampling point	Sampling date	Dissolved (ng/L)			Particulate (ng/L)		
		In	Tl	Bi	In	Tl	Bi
(24) Biwako lake, Tamanoura	2008.6.13	3.2	39.4*	402.7*	1.5	20	201.5
(25) Biwako lake, Kihankitabashi bridge	2008.6.13	1.1	28.1*	n.m.*	3.2	30.1	3.5
(26) Biwako lake, in front of the Hotel biwako puraza	2008.6.13	1.4	7.7*	n.m.*	2.9	11.1	5.6
(27) Biwako lake, Otsu city, Yanagigasaki	2008.6.13	1.1	3.1*	n.m.*	2.5	6.6	4.9

n.m. stands for the value under the measurement limits

* Data already reported in the reference, Miyazaki et al. (2010)

were higher than those of particulate components. This phenomenon was contrary to those in river or lake water samples. The reason might be that particulate components of these elements in the coastal seawaters were more easily precipitated than river and lake waters.

In the dissolved components, the sample No. 30 had very high Bi concentration. This might be due to a large thermoelectric power plant located near this sampling point

(Miyazaki et al. 2010). The samples of Hitachi port (sample No. 32) had high dissolved concentrations of In, Tl and Bi. Near this port, a big factory of company that deals with heavy industry and electro industry etc. is located. Therefore, these high concentrations are possibly due to this factory. The sample No. 36 and 37 those were collected in the Tokyo Bay had high concentrations of In and Bi. There are many chemical factories, big thermoelectric

Table 3 Concentrations in coastal seawaters in Japan

Sampling point	Sampling date	Dissolved (ng/L)			Particulate (ng/L)		
		In	Tl	Bi	In	Tl	Bi
(28) Onagawa omae beach	2008.8.01	2.9	7.9*	18.6*	0.8	2.6	8.2
(29) Onahama port	2008.8.01	4.1	3.2*	12.6*	4.1	1.6	10.7
(30) Hirono, Yamada beach	2008.7.31	2	13.9*	163.9*	1.2	5.8	35.9
(31) Ohotsu port	2008.7.30	1.7	12.8*	3.2*	3.1	n.m.	3.9
(32) Hitachi port	2008.7.30	19.4	28.5*	25.4*	4.1	3.5	10.1
(33) Oharai port	2008.7.30	0.8	2.7*	17.7*	1.3	2.4	4.9
(34) Tokyo bay, Tekeshiba pier	2008.6.27	2.5	3.6*	22.6*	4.7	5.7	25.5
(35) Tokyo bay, Higashi ohgishima higashi park	2008.6.27	0.3	4.2*	12.9*	n.m.	n.m.	4.6
(36) Tokyo bay, Ushigome beach	2008.6.27	10.6	3.5*	102.1*	1.8	1.2	10.6
(37) Tokyo bay, Biotopu sogu	2008.6.27	34.8	4.3*	71.3*	3.9	1.1	18.6
(38) Shimizu port	2008.6.12	2.2	4.2*	10.3*	3.1	2.1	2.3
(39) Nagoya port	2008.6.13	3.1	9.3*	12.5*	2.8	4.5	8.9
(40) Yokkaichi port	2008.12.12	2.9	7.3*	19.9*	0.8	2.6	8.2
(41) Toba city toba bay ohamachyo	2008.12.13	2.0	2.9*	9.8*	3.1	4.2	11.3
(42) Ohsaka port	2008.6.14	3.6	10.4*	19.5*	4.1	1.6	10.7
(43) Ohsaka minami port	2008.6.14	4.3	14.3*	10.5*	1.2	5.8	35.9
(44) Kushimoto, Hashiguiwa	2008.12.13	1.1	2.2*	8.8*	4.1	1.6	10.7
(45) Shinwakanoura	2008.12.14	2.6	2.3*	10.6*	3.1	0.9	3.9
(46) Kobe shiosai park	2008.12.14	1.9	3.2	6.9	1.4	2.7	10.6
(47) Takamatsu port	2008.12.15	3.2	8.5	15.5	3.9	7.6	13.3
(48) Kochishin port	2008.12.15	2.9	6.3*	11.3*	3.5	5.5	10.6
(49) Okinawa, Naha port	2008.9.12	0.2	5.1*	20.9*	0.6	5.1	15.3
(50) Okinawa, Bibibeach	2008.9.12	0.5	2.6*	47.7*	0.8	n.m.	4.5

n.m. stands for the value under the measurement limits

* Data already reported in the reference, Miyazaki et al. (2010)

Table 4 Average concentrations in Japan

	River (ng/L)		Lake (ng/L)		Coastal sea (ng/L)		References
	Dissolved	Particulate	Dissolved	Particulate	Dissolved	Particulate	
In	1.9 ± 4.4(229)	9.1 ± 35.5(179)	1.4 ± 1.8(25)	4.8 ± 14.8(25)	3.0 ± 6.4(38)	2.4 ± 1.5(24)	Alibo et al.(Alibo et al. 1998), Miyazaki et al. (2005, 2008, 2009), this paper
Tl	7.2 ± 15.2(178)	25.3 ± 104.4(178)	11.3 ± 19.6(25)	36.0 ± 105.1(25)	8.2 ± 5.6(31)	3.5 ± 3.1 (24)	Iwashita et al.(1994), Miyazaki et al. (2005, 2008, 2009) this paper, Nukatsuka et al. (2004), Shimizu et al. (1998)
Bi	12.7 ± 43.4(164)	28.1 ± 103.2(162)	17.7 ± 82.0(24)	52.7 ± 167.9(23)	24.0 ± 34.3(29)	12.1 ± 9.1(23)	Miyazaki et al. (2008, 2009, 2010), this paper, Shijo et al. (1992), Yoshimura et al.(1995)

power plants and petroleum refining plants etc. around these areas. Thus, these high concentrations are probably due to these facilities.

As for the particulate components, the concentration of Bi in the sample No. 30, 34, and 43 were higher than 25 ng/L. The sample No. 30 is probably due to a large thermoelectric power plant as described above. The sample No. 34 is collected at a big port where many ships anchor. And there is a very big hotel at this point. Hence, the high Bi concentration might be due to these ships and the facility. The sampling point sample No. 43 was the ferry terminal for many directions. Around this point, there are a large thermoelectric power plant and a large shipyard. The high concentration of Bi might be due to these ferries and the facility.

We calculated the average concentrations of In, Tl and Bi in the environmental waters in Japan including our data previously reported and data reported by other authors after 1990. The results are shown in Table 4. The percentage of particulate component for the coastal seawater is lower than those in river and lake waters. The value of n.M. in Tables 1, 2, and 3 were regarded as zero in these calculations.

The average concentrations of In, Tl and Bi in Japan are low right now, but sub ppb levels of these elements were observed at some points. We think that the concentrations of these elements in water environment should be monitored continuously, since the demands of these elements and the dosages to water environment will increase hereafter.

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