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Chemical form of arsenic compounds and distribution of their concentrations in the atmosphere

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In order to understand the chemical form of arsenic compounds and their distribution in unpolluted areas, concentrations of arsenic compounds in the marine atmosphere were measured in several islands in several oceans. Furthermore, concentration of arsenic compounds were also measured between Tokyo and the Syowa station during a cruise by the Antarctic observation boat *Shirase*. Aerosols in the marine atmosphere were collected by a high-volume air sampler with a quartz fiber filter. After extracting a sample, an analysis of arsenic compounds in the sample solution was carried out by hydride generation atomic absorption spectrophotometry combined with a cold trap of liquid nitrogen. This technique has a high analytical sensivity, so that it is suitable to determine arsenic compounds at trace level.

The atmospheric concentrations of arsenic compounds were at the same level over the Pacific Ocean and the Atlantic Ocean. The concentration range of arsenic compounds over these oceans was 100–200 pg m^{-3} for inorganic arsenic, 10–20 pg m^3 for organic arsenic. It is considered that these values are the background concentrations in the northern hemisphere. On the other hand, over the Antarctic Ocean in the southern hemisphere, the atmospheric concentrations of inorganic arsenic were very low, and organic arsenics were little found. This fact indicates that arsenic in the atmosphere is strongly influenced by anthropogenic sources.

Keywords: Hydride generation, atomic absorption spectrophotometry, arsenic, monomethylarsonic acid, dimethylarsinic acid, trimethylarsine oxide, environment, marine atmosphere

INTRODUCTION

It has been reported that arsenic compounds exist in a variety of chemical forms, not only as inorganic arsenic but also as organic arsenic compounds such as monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA) and trimethylarsine oxide (TMAO).[1–4]

Atmospheric arsenic has two sources; one is a natural source and the other is an anthropogenic source. It originates from the biosphere, hydrosphere and lithosphere as natural sources, and from coal, light fuels and residual fuel burning, iron, copper, lead and zinc production, and agricultural use as anthropogenic sources.[5] Recently, also, arsenic has been used as a semiconductor material.[6,7] There are some reports that most organic arsenic is produced by biomethylation.[8–10] A bread mold produces trimethylarsine from inorganic arsenic.[11,12] A Fungi in sewage produce trimethylarsine from inorganic and methylarsenic compounds.[12,13] Dimethylarsine is synthesized by methanobacteria, including *Candida humicola*, *Gliocladium* and *Penicillium*.[14] Furthermore, trimethylarsine is oxidized into TMAO and DMAA, and dimethylarsine is changed to DMAA by oxygen.[15]

Emitted arsenic compounds in the atmosphere are washed out to the land and the ocean. As regards the cycling of arsenic in the atmosphere, there have been very few measurements of arsenic concentrations in the marine atmosphere. Therefore, it is very important to measure arsenic concentrations in the marine atmosphere.

In this study, we tried to collect aerosol samples at several sites in oceanic areas and measure various arsenic compounds in the marine atmosphere at trace levels. On the basis of these

analytical results, we discussed background concentration, distribution and seasonal variation of arsenic compounds. We also estimated the global tropospheric burden of arsenic compounds.

EXPERIMENTAL

1 Sampling

Airborne particulate matter was collected with a high-volume air sampler (1000–1500 dm^3 min^{-1}) for 1–7 day on a quartz fiber filter (Pallflex 2500 QAT-up). Sampling of aerosol in the marine atmosphere was carried out at several sites: Oahu (March 1987–December 1987), Midway (March 1982–December 1982), Fanning (January 1982–July 1982), Chichi-jima (December 1981) in the North Pacific Ocean and Bermuda (February 1989–August 1989) in the North Atlantic Ocean. The sampling was also carried out during a cruise by the Antarctic observation boat *Shirase*. Its cruise track was divided into three legs: the first one from Tokyo to Fremantle (November 1988), the second from Fremantle to Syowa station (December 1988) and the third from Syowa station to Sydney (March 1989). On the other hand, in order to compare with concentrations of arsenic compounds in the marine atmosphere, sampling was also carried out in an urban area, Yokohama (June 1987–November 1988).

2 Analysis

For inorganic arsenic analysis, the aerosol sample was extracted with nitric acid and hydrogen peroxide prior to arsenic analysis. The extracted solution was filtered and diluted to 50 cm^3. For organic arsenic analysis, the aerosol sample was extracted ultrasonically with 25 cm^3 of 1.2 M HCl for 30 min. After filtering and dilluting to 50 cm^3, the sample solution was taken into a reaction vessel with 5 g of sulfanilamide as a masking agent of nitrate.[16]

Inorganic and organic arsenic analyses were carried out separately. The schematic diagram for the analytical system for arsenic compounds is shown in Fig. 1. Arsines were generated in a reaction vessel by injecting sodium tetrahydroborate solution, and then trapped in a U-tube immersed in liquid nitrogen. The use of column packing (OV-3 15% Chromosorb WAW DMCS 60/80 mesh) in this trap made it possible to separate organic arsenic compounds such as monomethylarsine, dimethylarsine and trimethylarsine. The arsines volatilized in order of their boiling points from the trap, and were transferred into a quartz cell and atomized by an air–hydrogen flame. The flow rate of helium as a carrier gas was 250 cm^3 min^{-1} and flow rates of hydrogen and air were 300 cm^3 min^{-1}, respectively. A Hitachi 180-70 atomic absorption spectrometer was used in this study. The analytical wave-

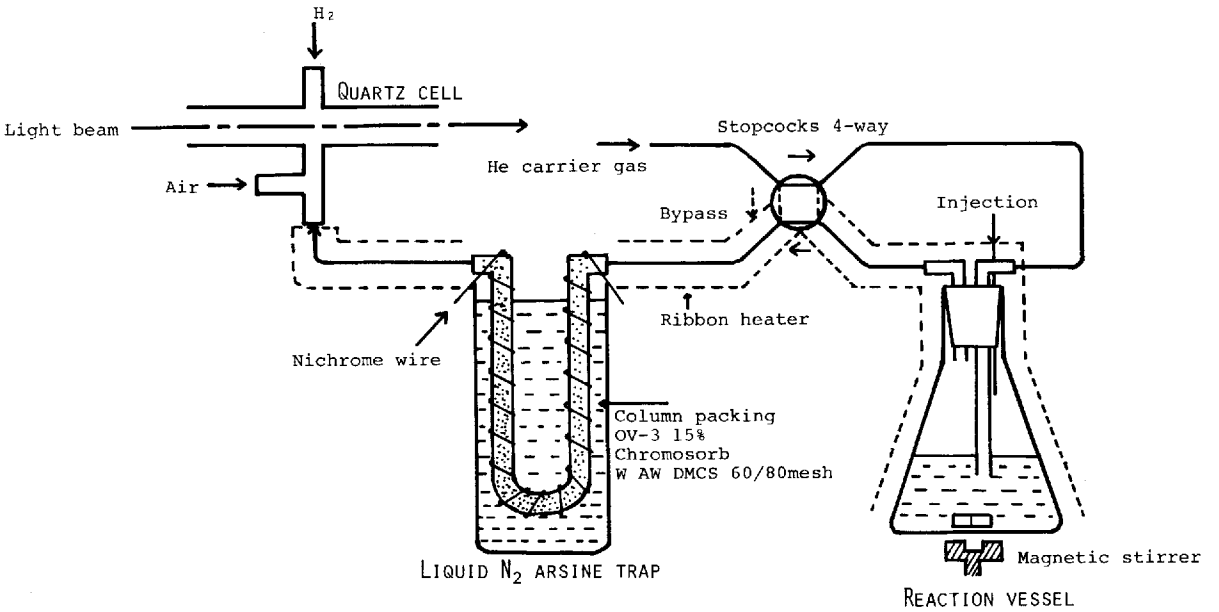

Figure 1 Schematic diagram of analytical system.

length was 193.7 nm and the lamp current was 18 mA. The details of this method are described in a previous paper.[6] Solutions of 6M hydrochloric acid (5 cm^3) and 5% sodium tetrahydroborate (5 cm^3) were used for inorganic arsenic analysis. Solutions of 6M hydrochloric acid (5 cm^3) and 5% sodium tetrahydroborate (5 cm^3) were used for organic arsenic analysis. Sample volume was 50 cm^3 for both organic and inorganic arsenic analysis. Inorganic arsenic was extracted with nitric acid and hydrogen peroxide. Organic arsenic was extracted under mild conditions using hydrochloric acid and ultrasonication, which also extracts inorganic arsenic.

A number of studies have been reported on interference in arsenic compound analysis using the hydride generation technique.[17] In order to measure accurately arsenic compounds in the atmosphere, it is necessary to eliminate the interference.[18] The level of nitrate typically found in natural waters interfered significantly in the determination of selenium species by the hydride generation technique. However, nitrate interference can be completely eliminated by addition of sulfanilamide, which reacts with nitrate to form a diazonium compound.[16] The typical nitrate level in sample solutions extracted from airborne particulate matter was 300 times as large as in natural waters. The nitrate similarly interfered in the determination of organic arsenic species in aerosol samples by hydride generation. Therefore, in the case of organic arsenic analysis, 5 g of sulfanilamide was added to the sample solution to elininate the interference.

Typical chromatograms are illustrated in Fig. 2: as shown, the separation among inorganic, monomethyl-, dimethyl- and trimethyl-arsine was good under these analytical conditions. However, inorganic arsenic exists at a concentration about 100 times higher than organic arsenic compounds in the atmosphere [Fig. 2(B)]. Therefore determination of organic arsenic and inorganic arsenic was done separately.

In the case of organic arsenic analysis, the U-tube was taken out of liquid nitrogen and stood at room temperature. Whilst arsine was released from the U-tube, most of the methylarsines remained in the U-tube at room temperature. Then, the U-tube was heated by a Nichrom wire heater. This heating results in a sequential release of methylarsines on the basis of their boiling points, and then the methylarsines are separately determined. On the other hand, for inorganic arsenic analysis the U-tube in which arsine collected was heated and arsine was released rapidly. As methylarsines are only a small proportion this does not cause a significant error in the results for inorganic arsenic.

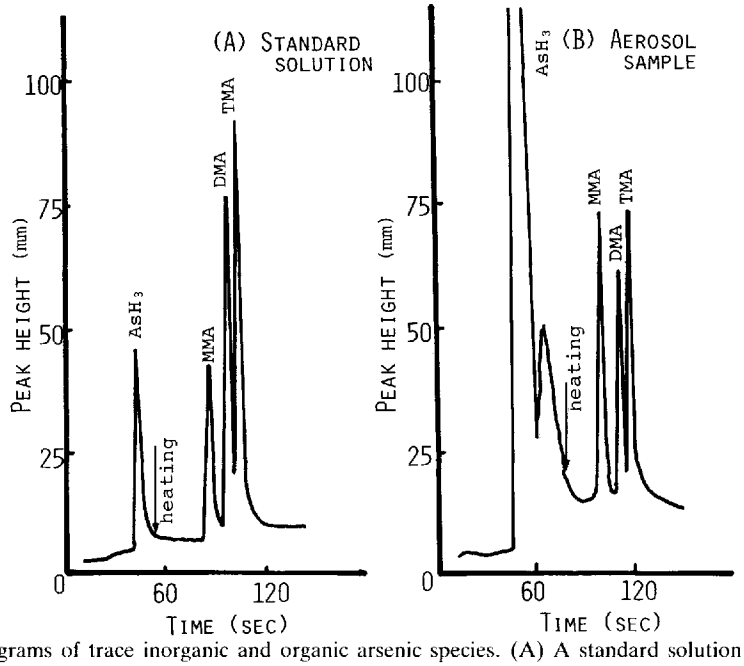

Figure 2 A chromatograms of trace inorganic and organic arsenic species. (A) A standard solution contained 10 ng each of arsenic in the form of monomethylarsonic acid, dimethylarsinic acid and trimethylarsine oxide; (B) aerosol sample collected at Hiyoshi, Yokohama, June 1987.

Table 1 *Concentrations of arsenic compounds in the marine atmosphere.*

Site	Date	Concentration (pg m $^{-3}$)				
		Inorganic As	Total organic As	MMAA	DMAA	TMAO
North Pacific Ocean						
Oahu	Mar.–Apr. 1987	39–520	1.2–14	—	1.2–5.5	1.3–8.8
		Av. 190 ($n=6$)	4.6 ($n=5$)	—	2.6 ($n=5$)	5.1 ($n=2$)
Midway	Mar.–Dec. 1982	13–190				
		Av. 74 ($n=11$)				
Fanning	Jan.–Jul. 1982	41–140				
		Av. 80 ($n=8$)				
Tokyo–Fremantle	Nov. 1988	18–950	3.6–32	1.5–8.6	2.1–8.3	4.7–16
		Av. 160 ($n=11$)	13 ($n=11$)	3.9 ($n=6$)	4.7 ($n=11$)	11 ($n=6$)
Chichi-jima	Dec. 1981	380 ($n=1$)				
Antarctic Ocean						
Fremantle–Syowa st.	Dec. 1988	12–160	2.0	—	2.0	—
		Av. 45 ($n=9$)	2.0 ($n=1$)	—	2.0 ($n=1$)	—
Syowa st.–Sydney	Mar. 1989	13–210				
		Av. 58 ($n=12$)				
North Atlantic Ocean						
Bermuda	Feb.–Aug. 1989	17–450	0.94–33	1.1–2.5	0.94–7.1	1.7–25
		Av. 130 ($n=28$)	7.7 ($n=21$)	2.1 ($n=8$)	3.2 ($n=21$)	6.0 ($n=13$)
Urban area						
Yokohama	Jan.–Nov. 1988	1000–5100	1.1–64	0.5–18	0.6–12	10–43
		Av. 2500 ($n=36$)	13 ($n=26$)	4.2 ($n=26$)	3.2 ($n=21$)	22 ($n=6$)

[a] The sampling was carried out during cruising by Antarctic observation boat *Shirase*.

RESULTS AND DISCUSSION

1 Concentrations of arsenic compounds in the marine atmosphere

Concentrations of arsenic compounds in the marine atmosphere are summarized in Table 1, and the distribution of their concentrations is shown in Fig. 3. Concentrations of arsenic compounds were measured in several islands in the Pacific Ocean and the Atlantic Ocean; Oahu, Midway, Fanning, Chichi-jima and Bermuda. Furthermore, they were also measured between Tokyo and the Syowa station during cruising by the Antarctic observation boat *Shirase*.

The average concentration of inorganic arsenic in the urban area, Yokohama, was 2500 pg m^{-3}. However, the average values of the concentrations of inorganic arsenic at several sites in the marine atmosphere were very low, 45–380 pg m^{-3}. Among these sampling sites, in Midway, Fanning, Fremantle–Syowa station and Syowa station–Sydney, the concentrations of inorganic arsenic were lower than those in Bermuda, Oahu, Chichi-jima and Tokyo–Fremantle. This is because Fanning and Midway are about 4000–5000 km from continents which have many anthropogenic arsenic sources. The average concentrations of inorganic arsenic in Midway, Fanning, Fremantle–Syowa station and Syowa station–Sydney were 45–80 pg m^{-3}, and these values might be the background concentration levels of inorganic arsenic in the marine atmosphere.

The concentrations of organic arsenic compounds in the marine atmosphere were 1.1–8.6 pg m^{-3} for MMAA, 0.94–8.3 pg m^{-3} for DMAA, 1.3–25 pg m^{3} for TMAO, and 0.94–33 pg m^{-3} for the total organic arsenic as shown in Table 1. On the other hand, in the urban area Yokohama, the concentrations of organic arsenics were 0.5–18 pg m^{-3} for MMAA, 0.6–12 pg m^{-3} for DMAA, 10–43 pg m^{-3} for TMAO and 1.1–64 pg m^{-3} for total organic arsenic. Therefore, it was found that there is a small difference of *organic* arsenic concentration between marine areas and urban areas, compared

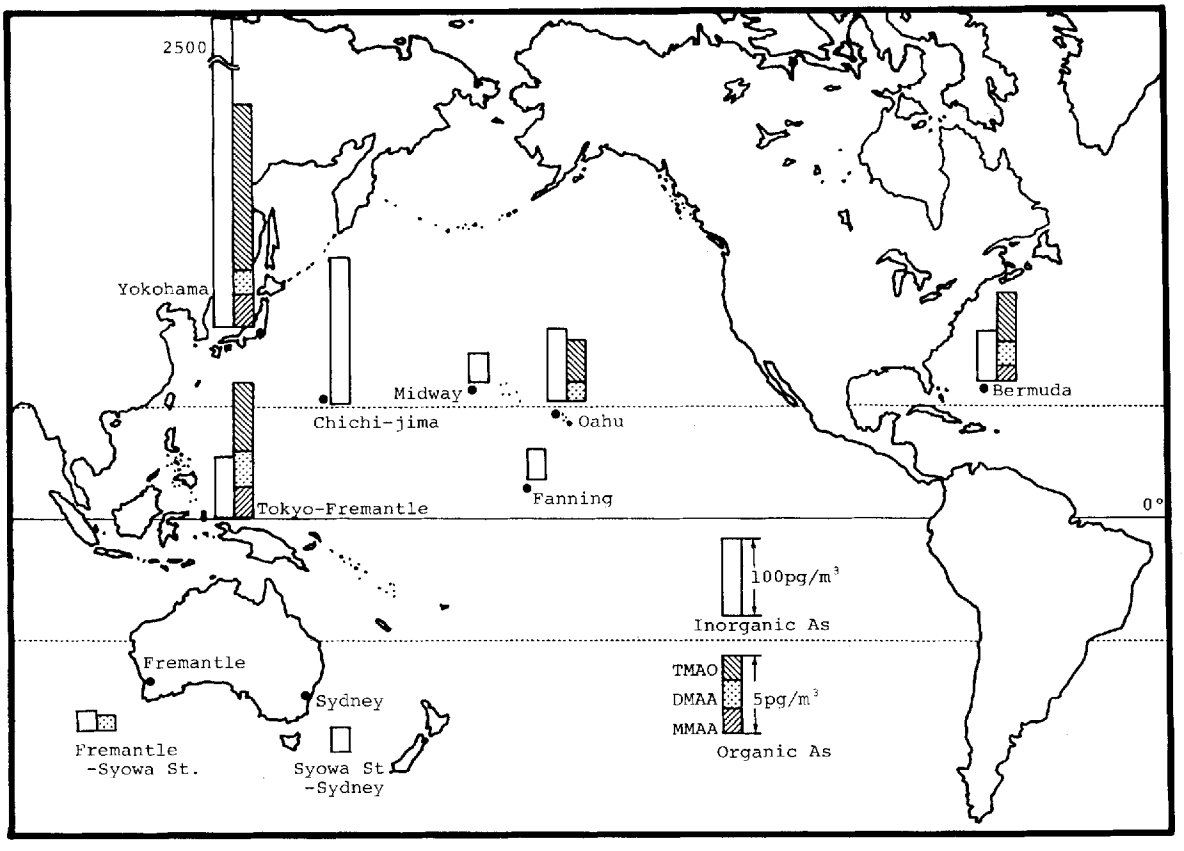

Figure 3 Distribution of arsenic compounds in the atmosphere.

with a large difference of *inorganic* arsenic concentrations. This fact indicates that the sources of organic arsenic compounds in both marine areas and urban areas might be the same. It has been reported that the production of DMAA and trimethylarsine could be due to methylation of inorganic arsenic through biological processes in natural waters.[10,19,20] Volatile methylarsenic compounds such as dimethylarsine and trimethylarsine are emitted in a gaseous form from natural water, and then these organic arsines are oxidized in the air and condense to airborne particules. The fact that the concentrations of DMAA and TMAO in marine areas and urban areas were at almost the same levels, suggests that DMAA and TMAO have a homogeneous distribution in the atmosphere. On the other hand, MMAA is used in agriculture[21] and its distribution in the atmosphere might be different from DMAA and TMAO.

2 Seasonal variation of concentrations of arsenic compounds

Figure 4 showed a seasonal variation of inorganic, total organic arsenic and MMAA concentrations, in Bermuda and Yokohama. As for the concentrations of inorganic arsenic, a seasonal change was not observed at both sites as shown in Fig. 4. However, a high concentration was observed in summer as for total organic arsenic at both sites.

The production of organic arsenic by biomethylation is active during the warm season, since the biomethylation depends on the temperature. The fact that the high concentrations of organic arsenic are observed in summer indicates that organic arsenic could be produced by biomethylation. However, as shown in Fig. 4, the concentration of MMAA strongly increased during the summer in Yokohama, while the concentration of MMAA was very low and unchanged during all the

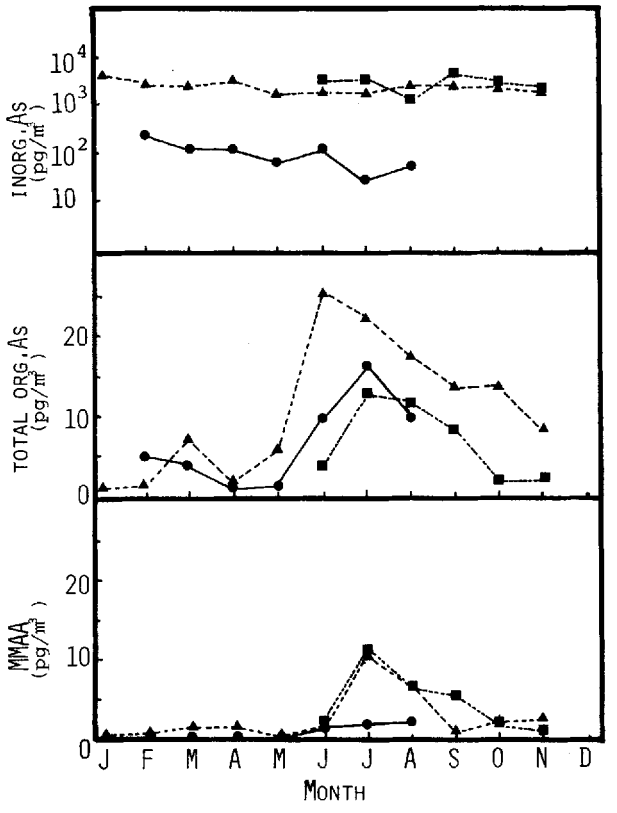

Figure 4 Seasonal variation of concentrations of inorganic, total organic and MMAA (Monomethylarsonic acid) in Bermuda (1989) and Yokohama (1987, 1988): ●, Bermuda (1989); ■, Yokohama (1987); ▲, Yokohama (1988).

seasons in Bermuda. It is considered that the emission source of MMAA in Yokohama is different from that of MMAA in Bermuda. Iron methanearsonate is used as an agricultural agent in fields before summer, and Yokahama has some agriculture. Therefore, the high concentration of MMAA in Yokohama might be influenced by agricultural agents such as iron methanearsonate.

3 Organic and inorganic arsenic concentrations as percentage of total arsenic concentration in the atmosphere

The percentage of each arsenic compound in the atmosphere was calculated on the base of the results of Table 1, and are shown in Table 2.

Table 2 Organic and inorganic arsenic concentrations as percentages of total arsenic concentrations.

Site	Date	Inorganic As	MMAA	DMAA	TMAO
Oahu	Mar.–Apr. 1987	96.1	—	1.3	2.6
Tokyo–Fremantle	Nov. 1988	89.1	2.2	2.6	6.1
Fremantle–Showa st.	Dec. 1988	95.8	—	4.2	—
Bermuda	Feb.–Aug. 1989	92.0	1.5	2.3	4.2
Yokohama	Jan.–Nov. 1988	98.8	0.2	0.1	0.9

Table 3 Estimate of atmospheric influxes and effluxes for arsenic.

		($\times 10^8$ g y^{-1})	Arsenic flux (%)
To atmosphere			
From land[a]	Particle weathering	2.4	0.8
	Anthropogenic sources	236	64
	Forest wild fires	1.6	0.4
	Terrestrial biosphere	2.6	0.8
From ocean		56	15
From volcanoes[a]		70	19
Total		355	100
From atmosphere			
To land	Dry deposition	81	24
	Rainfall	162	49
To ocean	Dry deposition	30	9
	Rainfall	60	18
Total		333	100

[a] Data from Ref. 5.

While most arsenic in the marine atmosphere was inorganic arsenic, 3.9–10.9% of the total arsenic was organic, such as MMAA, DMAA and TMAO. However, in Yokohama, 98.8% of total arsenic was inorganic arsenic and organic arsenic was about 1%. Because Yokohama is strongly influenced by anthropogenic sources, this may be the reason why the concentration of inorganic arsenic is ten times higher than that in the marine area.

4 Atmospheric cycling of arsenic in the environment

Table 3 shows the estimate of atmospheric influxes and effluxes for arsenic by using the results of this study and previous papers.[5,22–26] We especially tried to estimate the strength of influx from the oceans to the atmosphere by using the work of Mosher *et al.*[27] and Koblentz-Mishke *et al.*,[23] who divided the seas in the world into five types of water: Oligotrophic, Transitional, Equatorial Divergence, Inshore and Neritic. On the basis of the results in this study, concentrations of arsenic in the marine atmosphere in the above five areas were assumed to be 0.13 ng m^{-3} for Oligotrophic, 0.053 ng m^{-3} for Transitional, 0.096 ng m^{-3} for Equatorial Divergence, 0.22 ng m^{-3} for Inshore and 1.7 ng m^{-3} for Neritic, respectively. Then, an atmospheric arsenic burden for each area was calculated by multiplying the assumed arsenic concentration by the surface area and the mix layer height (3900 m). The flux was finally obtained from the calculated burden and the residence time of arsenic in the atmosphere (15 days).[5]

Total atmospheric influxes were estimated at 355×10^8 g y^{-1} including the influx from the oceans to the atmosphere. The major source of atmospheric arsenic was anthropogenic volatization processes, and the major natural source of arsenic was volcanoes. Influx from anthropogenic volatilization processes were estimated at 236×10^8 g y^{-1} and were 64% of total arsenic influxes. On the other hand, total atmospheric effluxes were estimated at 333×10^8 g y^{-1}. Effluxes from the atmosphere to the land and the oceans were estimated at 243×10^8 g y^{-1} and 90×10^8 g y^{-1}, respectively, so that these effluxes were 73% and 27% of total arsenic effluxes.

Walsh *et al.*[5] reported that the flux from the oceans to the atmosphere and the flux from the atmosphere to the oceans were 1% and 10% of total arsenic. However, these fluxes estimated in this study were 15% and 27%, respectively. This suggests that the fluxes between ocean and atmosphere might be larger than those estimated by Walsh *et al.*

CONCLUSIONS

The concentration of inorganic arsenic in marine atmospheres was about one-tenth of that in an urban area, Yokohama, Japan. Inorganic arsenic

concentrations at several sites over the ocean were at almost the same level. Especially over the Antarctic ocean, the inorganic arsenic concentration was very low, 45–58 pg m^{-3}. It is considered that this value is the background concentration of inorganic arsenic in the marine atmosphere. A small difference between organic arsenic concentrations in the atmosphere was found between urban and marine areas, compared with a large difference of inorganic arsenic concentrations between these two areas. This fact indicates that organic arsenics such as DMAA and TMAO could be produced by biomethylation in the environment and have a homogeneous distribution in the atmosphere, while MMAA might be emitted by a pesticide spread which is an anthropogenic source.

Seasonal variation of concentrations of organic arsenic compounds were observed in Yokohama and Bermuda. The concentration of organic arsenic increased during summer in both sites. This suggests that the production of organic arsenic is strongly affected by biomethylation. In this study, the estimated flux of arsenic between ocean and atmosphere was larger than the estimate by Walsh *et al.*[5] It is considered that a large emission of arsenic might be occurring from ocean to atmosphere.

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