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Distribution of 1,4-Dioxane and *N,N*-Dimethylformamide in River Water from Niigata, Japan

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1,4-Dioxane (dioxane) and *N,N*-dimethylformamide (DMF) are polar organic compounds mainly used as solvents miscible with water as well as several organic solvents. Dioxane had been used as a stabilizer of 1,1,1-trichloroethane which was prohibited manufacturing in 1996 by the Montreal Protocol. The IARC has classified dioxane as a possible human carcinogen; US EPA showed a value of 30 μg/L as a concentration of drinking water at a 1/100000 risk level. Dioxane is found in many industrial waste streams and by-products (Draper et al. 2000). For example, it can be formed as a by-product by dimmerization of ethylene oxide during forming polyethoxylated alcohols which may be used to synthesize sulfate surface activate agents for cosmetic products (Black et al. 2001). Dioxane is low-biodegradable (Abe 1999) and has been detected in landfill leachates (Lesage et al. 1990; Yasuhara et al. 1992; Yasuhara 1995; Yasuhara et al. 1997), effluent from sewerage systems (Abe 1999), sea water, river water, ground water (Abe 1999; Draper et al. 2000; Kadokami et al. 1993; Kawata et al. 2001) and rain water (Kadokami et al. 1993).

DMF, which is considered to be a potent liver toxin, is used as solvent for manufacturing synthetic leatherette and polymer as well as for toxicological studies (Yan et al. 2002). DMF was detected in sea water, river water, ground water and rain water (Kadokami et al. 1993; Okamoto et al. 1992; Ibaraki et al. 1999; Kawata et al. 2001) as well as leachate from wastes landfill (Yasuhara 1992).

Since dioxane and DMF are hydrophilic, both compounds discharged to the environment are expected to be distributed mainly in water phase. Therefore, monitoring of these toxic compounds in water is important for evaluating their impact on ecosystems and human health. Regarding dioxane, Ministry of the Environment, Japan (2001) has monitored annually dioxane in river and coast waters from 32 – 35 sites in Japan since FY 1990. However, there are few investigations upon variations of the compounds in recent river water. In this paper, we present distributions and variations of dioxane and DMF in rivers in Niigata, Japan.

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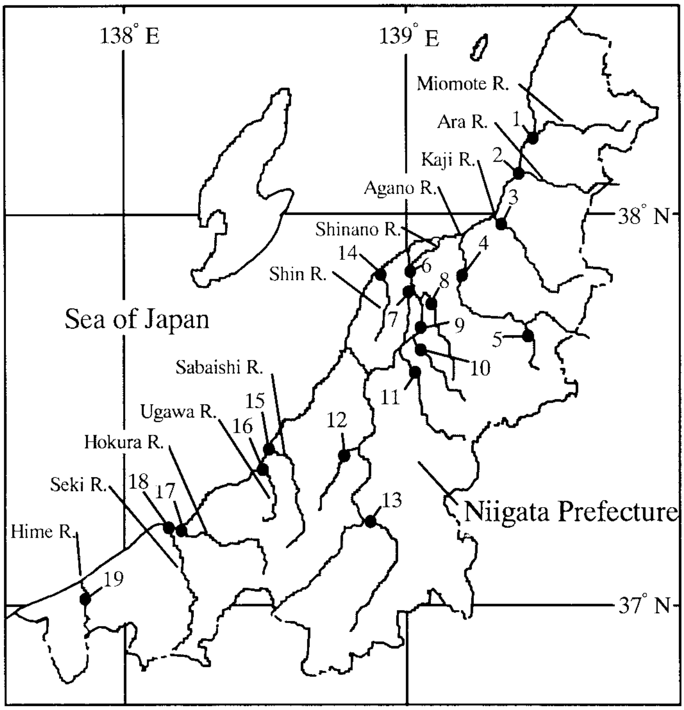

Figure 1. Sampling sites. 1, Senami Bridge; 2, Asahi Bridge; 3, Shidaihama Bridge; 4, Oun Bridge; 5, Shiroyama Bridge; 6, Heisei Bridge; 7, Nishishinano Bridge; 8, Oshima Bridge; 9, Shoze Bridge; 10, Ransen Bridge; 11, Nakazai Bridge; 12, Iizuka Bridge; 13, Kawaguchi Bridge; 14, Makio Bridge; 15, Ansei Bridge; 16, Yasaka Bridge; 17, Furushiro Bridge; 18, Naoetsu Bridge; 19, Yamamoto Bridge

MATERIALS AND METHODS

A Waters Sep-Pak Concentrator and a J&W SPE Manifold were used for solid-phase extraction and elution, respectively. A gas chromatograph/mass spectrometer Hitachi M9000 equipped with a fused-silica column J&W DB-WAX (0.5μm film thickness, 30m long, 0.25mm id) was used for quantitative analysis.

Reagents were purchased from Wako (Osaka, Japan) and Kanto Chemicals (Tokyo, Japan). Standard solutions of mixture of target compounds (100 and 20μg/mL) were prepared in acetone. An acetone solution containing 20 μg/mL of 1-bromo-4-fluorobenzene was prepared as an internal standard solution. $[^2H_8]$1,4-dioxane (dioxane-d_8) and $[^2H_7]$*N*,*N*-dimethylformamide (DMF-d_7) in acetone solution (20 μg/mL) was prepared as a surrogate solution.

Distilled water was purified by passing through a glass column (35 cm long, 10 mm id) packed with 10g of activated carbon beads-L (20/30 mesh), which was purchased from GL Sciences (Tokyo, Japan). A 1-μm pore size glass-fiber filter, Toyo GA-100 of 47 mm diameter was heated at 450℃ for 4 h before use. Waters Sep-Pak Plus AC-2 cartridge and C18 cartridge were washed with 5 mL of acetone, followed by 5 mL of the purified water prior to use.

Water samples were collected at 19 sites from 11 rivers in Niigata Prefecture, Japan (Figure 1). The surface water was sampled on June and November 1999. At Sites 6 and 14, samples were also taken once a month from December 1998 to October 1999. The collected samples were stored in a 1-L glass bottle with ground stopper at 4℃ without headspace.

Water samples were filtered through the glass-fiber filter. A 500-mL volume of the filtered water added with 20-μL of the surrogate solution was passed through a series of a C18 cartridge and two AC-2 cartridges at 10 mL/min. After the AC-2 cartridges were washed with 10 mL of purified water, the target compounds collected on the cartridges were eluted with 2 mL of acetone and 5 mL of dichloromethane at 0.5mL/min in the opposite direction of the extraction to test tubes with ground stoppers. The eluates were kept at -20℃ for 30 min to freeze water phases. After the remaining organic liquid phases were transferred to other test tubes, they were concentrated to 3 mL by blowing nitrogen gas. The internal standard solution of 20-μL was added to the solution and a 1-μL of the resulting mixture was analyzed by GC/MS.

GC/MS conditions were as follows: column temperature, programmed from 35℃ (held for 3 min) to 190℃ (held for 3min) at a rate of 5℃/min; injector temperature, 170℃; injection mode, splitless; helium carrier gas flow rate, 1.0 mL/min; interface temperature, 190°C. ion source temperature, 250°C; ionization current, 30 μA; multiplier voltage, 330 V; ionization time, 25 ms; mass scan range, 40–200 at 45 ms/scan. Ions used for analysis were 88 and 58 for dioxane, 73 and 44 for DMF, 96 for dioxane-d_8, 80 for DMF-d_7 and 174 for 1-bromo-4-fluorobenzene. The ratios of peak areas of the ions to those of the internal standards were used for quantification of the compounds.

Overall recoveries and relative standard deviation were 88 % and 8.6 % for dioxane-d_8, and 89 % and 9.2 % for DMF-d_7, respectively. The minimum detectable concentration was 0.03 μg/L for each the target compound.

RESULTS AND DISCUSSION

Concentrations of dioxane and DMF at sites 1-19 in June and November 1999 are shown in Table 1. Dioxane was detected from 10 sites in June and 11 sites in November, and ranged in concentrations from 0.06 μg/L at site 3 to 0.25 μg/L at site 6 in June and 0.04 μg/L at site 17 to 0.39 μg/L at site 6 in November.

Dioxane was determined at 1.1 to 109 µg/L in ground water in California (Draper et al 2000); dioxane concentrations in river water ranged from <0.024 to 0.69 µg/L in Kitakyushu, Japan (Kadokami et al. 1993) and 0.1 to 16 µg/L in Kanagawa, Japan (Abe 1999). Ministry of the Environment, Japan (2001) reported that dioxane in river and coast waters from 34 – 35 sites in Japan ranged from <0.08 to 46 µg/L during FY 1997 - 1999. The maximum concentration of 0.39 µg/L at site 6 was comparable to 0.4 µg/L at maximum in a river in Kanagawa, Japan (Abe 1999) and 0.31 – 0.33 µg/L at Katsura River, Kyoto, Japan (Ministry of the Environment, 2001). Medians of dioxane concentrations were 0.03µg/L in June and 0.05 µg/L in November. Mean of dioxane concentrations in arithmetic and geometric were 0.08 µg/L and 0.04 µg/L in June, and 0.06 µg/L and 0.04 µg/L in November, respectively. They were lower than the arithmetic mean (0.15 µg/L) in rivers in Kitakyushu (Kadokami et al. 1993) or the geometric means (0.18 – 0.28 µg/L) at the 34 - 35 sites in Japanese rivers and coastal areas (Ministry of the Environment, 2001).

Dioxane ranged in concentration from 1.1 to 109 µg/L in leachates from hazardous waste disposal sites in Japan (Yasuhara et al. 1997). Abe (1999) has reported that dioxane concentrations in effluents from chemical plants using the compound as a solvent, the combined collection treatments of apartment houses and river basin sewerage systems were 0.4 - 4020 µg/L, 0.8 – 46 µg/L and 1.0 – 97 µg/L, respectively. Among the investigated sites of this study, dioxane concentrations (>0.1 µg/L) at sites 2, 6, 8, 11, 14 and 17 were higher than those at the other sites. There exist sewage treatment plants at the upper reaches of sites 8 and 11. Therefore, dioxane derived from the effluents of sewage treatment plants was the most dominant at the two sites. On the other hand, chemical plants are located above site 17. Hence, the majority of dioxane at site 17 was derived from effluents from the chemical plants. Regarding sites 2, 6 and 14, there are no remarkable sewage treatment plants or chemical plants at the upper reaches of the sites; domestic effluents are most of inflows at the upper reaches of the sites. Therefore, dioxane at these sites appears to be derived mainly from the domestic effluents (Abe 1999).

Table 1. Concentrations of dioxane and DMF

Site	Concentration (µg/L)				Site	Concentration (µg/L)			
	Dioxane		DMF			Dioxane		DMF	
	June	November	June	November		June	November	June	November
1	<0.03	<0.03	0.07	<0.03	11	0.15	0.10	0.04	0.07
2	0.15	0.10	0.07	<0.03	12	<0.03	<0.03	0.08	<0.03
3	0.06	0.07	<0.03	<0.03	13	<0.03	<0.03	0.05	<0.03
4	0.03	<0.03	<0.03	<0.03	14	0.22	0.05	0.04	0.06
5	<0.03	0.06	0.08	0.03	15	<0.03	<0.03	<0.03	<0.03
6	0.25	0.39	0.05	0.33	16	<0.03	0.08	0.09	<0.03
7	<0.03	<0.03	0.05	0.04	17	0.13	0.04	0.09	<0.03
8	0.22	0.11	0.06	0.05	18	0.03	0.06	0.25	0.13
9	0.07	<0.03	0.06	<0.03	19	<0.03	<0.03	<0.03	<0.03
10	<0.03	0.05	<0.03	<0.03					

DMF was detected from 14 sites in June and 7 sites in November, and ranged in concentrations from 0.04 μg/L at sites 11 and 14 to 0.25 μg/L at site 18 in June, and 0.03 μg/L at sites 10, 12 and 15 to 0.13 μg/L at site 18 in November. DMF concentrations reported were from <0.062 to 1.0 μg/L (0.19 μg/L in arithmetic mean) in sea water and from <0.062 to 0.67 μg/L (0.17 μg/L in arithmetic mean) in river water in Kitakyushu, Japan (Kadokami et al. 1993), 0.47 μg/L at Tokyo Bay (Okamoto et al. 1992), 0.039 to 0.083 μg/L (0.07 μg/L in arithmetic mean) at Yamato River, Osaka, and 0.089 to 0.11 μg/L at Shimizu Bay, Shizuoka, Japan (Environmental Agency 1999). The maximum concentration of 0.25 μg/L at site 18 was comparable to 0.22 μg/L in a river in Kitakyushu (Kadokami et al. 1993). Medians of DMF concentrations were 0.05 μg/L in June and <0.03 μg/L in November. Mean DMF concentrations in arithmetic and geometric were 0.06 μg/L and 0.05 μg/L in June, and 0.05 μg/L and <0.03 μg/L in November, respectively. These values were almost one quarter of the arithmetic mean concentration (0.17 μg/L) in rivers in Kitakyushu (Kadokami et al. 1993).

DMF could be discharged from factories using DMF as solvent. DMF was detected in leachate from a waste disposal site at 7.8 μg/L (Yasuhara et al. 1992). DMF was also detected in effluents from sewerage treatment plants at <0.062 - 0.17 μg/L (0.14 μg/L in arithmetic mean) in Kitakyushu, which is comparable to the arithmetic mean (0.17 μg/L) in river water in the district (Kadokami et al. 1993). Among the investigated sites of this study, DMF concentrations (>0.1 μg/L) at site 18 were higher than those at the other sites. Since there are several factories at the upper reaches of site 18, the majority of DMF at the site was derived from effluents from some of the factories.

Concentrations of dioxane and DMF at sites 6 and 14 are summarized in Table 2. Arithmetic mean concentrations of dioxane (0.18 μg/L at site 6 and 0.19 μg/L at site 14) and DMF (0.08 μg/L at site 6 and 0.07 μg/L at site 14) were almost comparable to 0.15 μg/L at rivers in Kitakyushu (Kadokami et al. 1993) and 0.07 μg/L at Yamato River, Osaka (Environmental Agency 1999), respectively. The maximum concentrations of dioxane (0.29 μg/L) and DMF (0.26 μg/L) at site 14 were almost comparable to those at site 6 discussed above.

Variations of dioxane and DMF concentrations at sites 6 and 14 are given in Figure 2. DMF concentration show rather intense variations; the ratios (*R*) of the maximum concentration of DMF to the minimum one during the investigated

Table 2. Summary of dioxane and DMF concentrations at sites 6 and 14

Site	Concentration (μg/L)									
	Dioxane					DMF				
	A mean	G mean	Median	Min	Max	A mean	G mean	Median	Min	Max
6	0.18	0.16	0.14	0.08	0.39	0.08	0.05	0.05	<0.03	0.33
14	0.19	0.17	0.21	0.05	0.29	0.07	0.05	0.05	<0.03	0.26

A mean, arithmetic mean; G mean, geometric mean

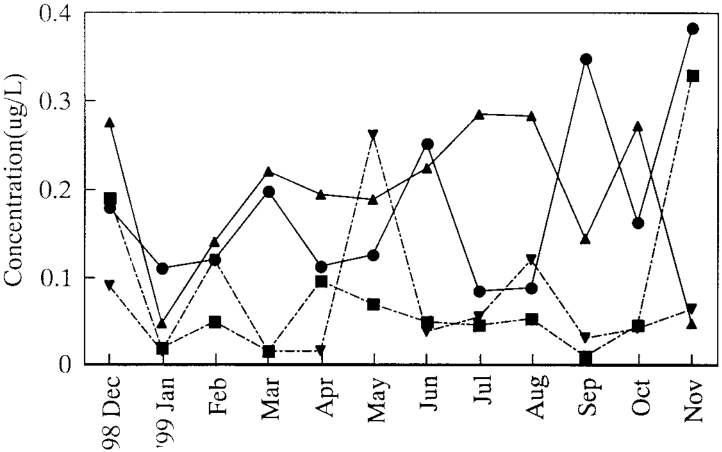

Figure 2. Variations of 1,4-dioxane and DMF at sites 6 and 14. ●, 1,4-dioxane at site 6; ■, *N,N*-dDMF at site 6; ▲, 1,4-dioxane at site 14; ▼, DMF at site 14.

periods (Table 2) were >11 at site 6 and >8.7 at site 14, On the other hand, dioxane concentration gives a relatively temperate variation compared to DMF; *R* values for dioxane were 4.9 at site 6 and 5.8 at site 14. These *R* values were larger than those of BOD of 3.6 at site 6 and 2.6 at site 14. At both sites, the concentrations of dioxane and DMF did not show characteristic variations. This indicates that the target compounds could be derived from anthropogenic sources as mentioned above. However, additional investigation is required to conclude exactly the origins of the target compounds in the rivers.

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