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Impact of 1,4-Dioxane from Domestic Effluent on the Agano and Shinano Rivers, Japan

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1,4-Dioxane is a polar and low-biodegradable organic compound. It is used as an industrial solvent or solvent stabilizer that prevents the breakdown of chlorinated solvents during manufacturing processes (Zenker et al. 2003). Industrial solvents are used in degreasing, electronics, metal finishing, fabric cleaning, pharmaceuticals, herbicides and pesticides, antifreeze, paper manufacturing and many other applications. 1,4-Dioxane had been used as a stabilizer of 1,1,1-trichloroethane which was prohibited manufacturing in 1996 by the Montreal Protocol. 1,4-Dioxane is also produced as a by-product formed by the dimmerization of ethylene oxide during forming polyethoxylated alcohols which are used to synthesize sulfate surface activate agents (Zenker et al. 2003). Therefore, 1,4-dioxane is present in shampoos, liquid soap, hair lotions and other cosmetic products (Black et al. 2001).

The IARC has classified 1,4-dioxane as a possible human carcinogen (Group 2B); in the USA, the Environmental Protection Agency (EPA) has listed 1,4-dioxane as a probable human carcinogen. Although the EPA has not yet established a federal drinking water standard for 1,4-dioxane, it has issued a drinking water health advisory with an estimated lifetime cancer risk of 1 in 10,000 for a drinking water concentration of 300 μg/L (Zenker et al. 2003). The states Florida, North Carolina, Massachusetts, Maine and Michigan have established maximum contaminant levels for 1,4-dioxane at 5 μg/L, 7 μg/L, 50 μg/L, 70 μg/L and 85 μg/L, respectively; California State has set an advisory action level of 3 ppb (Haughton, 2003). In Japan, the Ministry of Health, Labor and Welfare has established a drinking water standard for 1,4-dioxane at 50 μg/L; the Ministry of Environment has classified 1,4-dioxane as a monitoring substance for the public water and has set a guideline for 1,4-dioxane at 50 μg/L.

1,4-Dioxane discharged into the environment is expected to be mainly distributed in the water phase because of its high hydrophilicity. Therefore, it has been frequently detected in the outflows from sewage treatment plants (Abe, 1999), landfill leachates (Yasuhara et al. 2003), seawater, river water, and ground water (Abe 1999; Kawata et al. 2001, Miyazaki et al. 2001). We have previously reported the distributions and variations of 1,4-dioxane in the rivers of Niigata, Japan (Kawata et al. 2003); the concentrations in the waters from 19

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sites in 11 rivers were <0.03 to 0.39 μg/L, and in some rivers, 1,4-dioxane was estimated to be derived from the domestic effluents including sewage treatment plants. In this study, we evaluate the impacts of 1,4-dioxane from the domestic effluent on two major rivers in Niigata, Japan, the Shinano River, the longest river in Japan, and the Agano River, the 10th longest river in Japan. For this purpose, we analyzed the behavior of 1,4-dioxane in the inflows and outflows of sewage treatment plants, and the concentration levels of 1,4-dioxane in the outflows and the river waters.

MATERIALS AND METHODS

Isco 6712 Portable Samplers (Elscolab, Utrecht, Nederland) were used for the sequential water sampling. A Waters Sep-Pak Concentrator (Nippon Millipore, Tokyo, Japan) and a J&W SPE Manifold (J&W Scientific, Folsom, CA, USA) were used for the solid-phase extraction and elution, respectively. A gas chromatograph–mass spectrometer, JEOL model Automass 50 (JEOL, Tokyo, Japan) was used for the quantitative analysis. A 30 m X 0.25 mm id (0.5 μm film thickness) fused-silica J&W DB-WAX column (Agilent, Palo Alto, CA) was used for the GC separation.

Reagents were purchased from Wako Pure Chemical (Osaka, Japan) and Kanto Kagaku (Tokyo, Japan). Standard solutions of 1,4-dioxane (100 and 20 μg/mL) were prepared in acetone. An acetone solution of [$^2H_8$]1,4-dioxane (1,4-dioxane-d_8; 20 μg/mL) and an acetone solution of 1-bromo-4-fluorobenzene (40 μg/mL) were prepared as a surrogate solution and an internal standard solution, respectively. Purified water for washing the extraction cartridges as well as the blank tests was prepared by passing water from a Milli-Q system (Millipore, Bedford, MA, USA) through a glass column (35 cm X 10 mm id) packed with 10 g of Activated Carbon Beads-L (20–30 mesh; specific surface area, 800–1200 sq m/g), which was purchased from GL Sciences (Tokyo, Japan). A 1-μm pore size glass-fiber filter, Toyo GA-100, with a 47 mm diameter was heated at 450°C for 4 hr before use. A Waters Sep-Pak Plus AC-2 cartridge (Nippon Millipore) and a Sep-Pak Plus C18 (Millipore) were washed with 5 mL of acetone, followed by 5 mL of the purified water prior to use.

Table 1. 1,4-Dioxane concentrations in inflows and outflows of plants A and D.

	Concentration (μg/L)							
	Plant A				Plant D			
	Winter		Summer		Winter		Summer	
	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow
Max	0.40	0.42	0.54	0.56	0.20	0.21	0.31	0.26
Min	0.26	0.32	0.39	0.39	0.11	0.08	0.10	0.14
Mean	0.32	0.35	0.46	0.45	0.15	0.16	0.19	0.20
SD	0.042	0.028	0.050	0.034	0.024	0.020	0.051	0.028
RSD (%)	13	8.0	11	7.6	16	13	27	14

SD = standard deviation

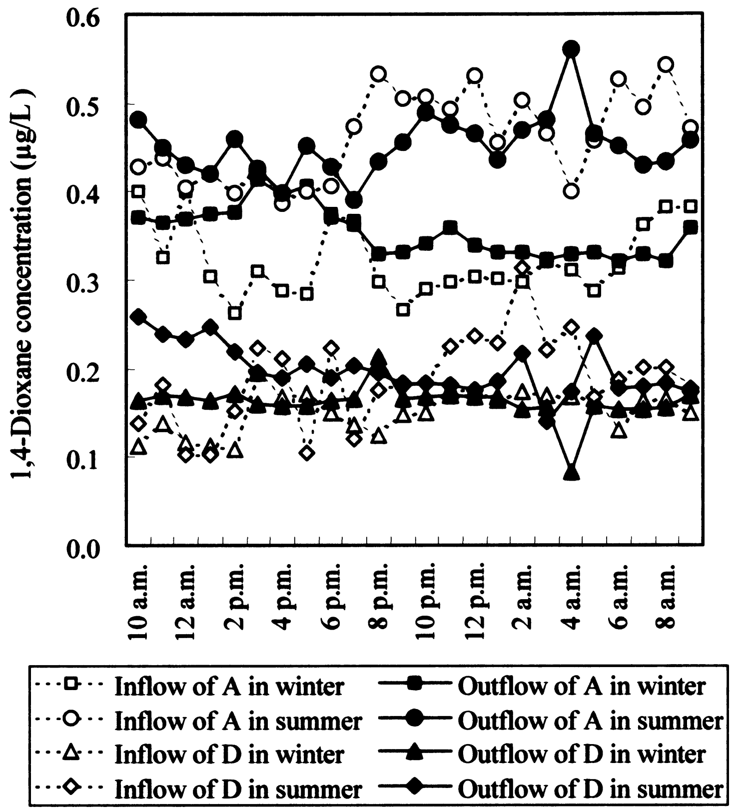

Figure 1. Variation of 1,4-dioxane concentrations in inflows and outflows of sewerage plants A and D.

The investigated sites were four sewage treatment plants in Niigata City, Niigata Prefecture and the mouths of two rivers, the Agano River and the Shinano River. The plants employed the conventional biological treatment system known as the activated sludge process to achieve the wastewater treatments. Plant A discharged its outflows into the Agano River at 56200 cu m/d (Niigata Prefectural sewerage Public Corporation 2005). Plants B and C discharged their outflows into the Shinano River at 49300 and 212000 cu m/d, respectively (Niigata City 2005). Plant D discharged its outflows into the Shin River at 4200 cu m/d (Niigata Prefectural sewerage Public Corporation 2005). Most of the inflows into plants A and D were domestic effluents, while the inflows into plants B and C were domestic effluents and rainwater.

The Agano River flows 210 km through Fukushima Prefecture and Niigata Prefecture to the Sea of Japan at 1.27 x 10^{10} cu m/yr, draining 7710 sq km including cultivated areas and civilized areas. The Shinano River is the largest river in Japan, and flows 367 km through Nagano Prefecture to the Sea of Japan at 1.53 x 10^{10} cu m/yr, draining 11900 sq km including cultivated areas and civilized areas (Ministry of Land, Infrastructure and Transport 2005).

Water samples were collected from the inflows and outflows of the sewage treatment plants A and D during two days in December 2002 and August 2003; 24 samples each from inflow and outflow were collected from 10 a.m. on the first day to 9 a.m. on the second day at 1 hr intervals using the auto sampler. Outflows of the four sewage treatment plants were sampled once a month from January to December 2003. River waters from the mouths of the two rivers were also sampled once a month on the same day of the month from January to December 2003. The collected samples were transported and stored in separate 1-L glass bottles equipped with ground stoppers at 4 °C without any headspace. All samples were analyzed within 48 hr after collection.

The determination of the compounds was performed using a previously published isotope-internal standard method (Kawata et al. 2003). Briefly, water samples were filtered through the glass-fiber filter. A 500-mL volume of the filtered water added with 20-mL of the surrogate solution was passed through a series of the C18 cartridge and the 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 the 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 in the selected-ion monitoring mode.

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, 200°C. ion source temperature, 200°C; ionization current, 300 µA; ionization energy, 70 eV. Ions used for the analysis were 88 and 58 for 1,4-dioxane, 96 for 1,4-dioxane-d_8 and 174 for 1-bromo-4-fluorobenzene. The ratios of the peak areas of the ions to those of the internal standards were

Table 2. 1,4-Dioxane concentrations in outflows of sewerage plants and in river waters.

	Concentration (µg/L)					
	Outflow from sewage treatment plant				River water	
	A	B	C	D	Agano R.	Shinano R.
Max	0.66	0.36	0.29	0.36	0.26	0.10
Min	0.30	0.12	0.10	0.16	0.05	0.03
Mean	0.39	0.19	0.19	0.21	0.11	0.05
SD	0.11	0.072	0.049	0.058	0.063	0.025
RSD (%)	28	38	25	28	58	50

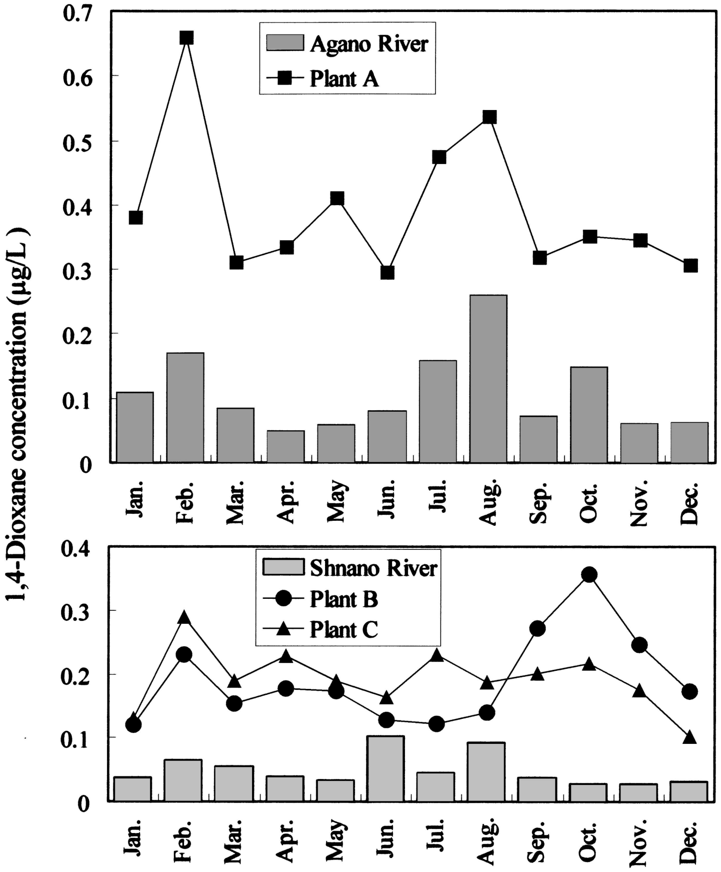

Figure 2. Variation of 1,4-dioxane concentrations in outflows of sewerage plants and River waters.

used for quantification of the compounds. The overall recoveries and relative standard deviation of 1,4-dioxane-d_8 were 88 % and 8.6 %, respectively. No 1,4-dioxane and 1,4-dioxane-d_8 were detected from the second AC-2 cartridges. The minimum detectable concentration of 1,4-dioxane was 0.02 μg/L.

RESULTS AND DISCUSSION

The 1,4-dioxane concentrations in the inflows and outflows of the sewage treatment plants A and D were analyzed in order to investigate the behavior of 1,4-dioxane during the 24 hr in the sewage treatment plants. These results are summarized in Table 1. The t-test showed that the mean concentrations of 1,4-dioxane in the inflows (0.32 and 0.46 μg/L) and the outflows (0.35 and 0.45 μg/L) of plant A were significantly higher ($p < 0.01$) than those (0.16 and 0.19μg/L in the inflows and 0.16 and 0.20 μg/L in the outflows) of plant D, respectively. The relative standard deviations (RSDs) of the 1,4-dioxane concentrations in the inflows were 11 to 27 %; those in the outflows were 7.6 to

14 %. These values were lower than the RSD value (56 %) of the biological oxygen demand (BOD) in the effluents of plant C (Niigata City 2005). The hourly variations of the 1,4-dioxane concentrations at plants A and D are shown in Figure 1. The concentrations of 1,4-dioxane in the inflows and the outflows did not show any characteristic variations at both plants. 1,4-Dioxane in the inflows could be derived from commercial detergents, shampoos and cosmetic products containing surface activate agents (Black et al. 2000) used in the household, because most of the inflows into the plants were domestic effluents.

The removal effects of 1,4-dioxane on the sewage treatment plants were evaluated by the t-test. Since the delayed time of the outflows to the inflows at the investigated plants was 11 hr, the 1,4-dioxane concentrations in the inflows from 10 a.m. to 10 p.m. on the first day and those in the outflows from 9 p.m. on the first day to 9 a.m. on the second day were used for the evaluation. The concentrations (mean ± standard deviation) in the inflows and the outflows of plant A were 0.32 ± 0.049 μg/L and 0.33 ± 0.012 μg/L in the winter, and 0.44 ± 0.048 μg/L and 0.47 ± 0.033 μg/L in the summer, respectively; those in the inflows and the outflows of plant D were 0.14 ± 0.027 μg/L and 0.16 ± 0.023 μg/L in the winter, and 0.16 ± 0.045 μg/L and 0.18± 0.023 μg/L in the summer, respectively. There were no statistically significant differences between the mean concentrations of the inflows and those of the outflows in the winter as well as in the summer at both plants ($p < 0.05$). Therefore, 1,4-dioxane was not removed at either plant. The results were due to the low biodegradability and high hydrophilicity of 1,4-dioxane. The removal rates of 1,4-dioxane at the sewage treatment plants were reported as 0 - 31 % at a plant in Kanagawa, Japan (Abe 1999) and 8.5 % at a plant in Ibaraki, Japan (Makino et al. 2005). The differences in the removal effects between the results in the present study and the reported values could mainly depend on the conditions of the biological treatments.

The 1,4-dioxane concentrations in the outflows from sewage treatment plants A - D were investigated in order to evaluate their impact on the river waters. Table 2 shows the summary of the results. The concentrations of 1,4-dioxane in the outflows ranged from 0.10 μg/L at plant C to 0.66 μg/L at plant A. These values were lower than those (1.0 - 97 μg/L) from three sewage plants in Kanagawa, Japan (Abe 1999) and those (2.4 - 3.1 μg/L) from a plant in Ibaraki, Japan

Table 3. 1,4-Dioxane loads of outflows of sewage treatment plants.

	Sewage treatment plant			
	A	B	C	D
Mean concentration of 1,4-dioxane (μg/L)	0.39	0.19	0.19	0.21
Flow rate of outflow (cu m/d)	59,300	49,300	212,000	4,200
1,4-Dioxane load (mg/d)	23,000	9,400	41,000	880
Population	162,000	35,300	191,000	3,130
1,4-Dioxane load per person (mg/d/person)	0.14	0.27	0.21	0.28
Mean ± standard deviation (RSD)	0.23 ±	0.066	(29 %)	

(Makino et al. 2005). The concentration levels in all the outflows in this study were far lower than the drinking water standard in Japan as well as the maximum contaminant levels and the advisory action level in the USA. The mean concentration of plant A was significantly higher than those of plants B, C and D ($p < 0.01$). On the other hand, there were no statistically significant differences in the mean concentrations of plants B, C and D ($p < 0.05$). The RSDs of the annual 1,4-dioxane concentrations in the outflows of plants A - D were 25 - 38 %. These values were quite higher than those during the 24 hr as mentioned above, and were lower than the RSD values (92 % and 56 %) of the BOD in the effluents of plants B and C, respectively (Niigata City 2005).

The 1,4-dioxane concentrations in water samples from the mouths of the two rivers were monitored. These results are summarized in Table 2. The RSDs of the annual 1,4-dioxane concentrations in the Agano River and the Shinano River were 58 %, and 50 %, respectively. These values were larger than those in the outflows from plants A, B and C as mentioned above, and the RSD values of the BOD and COD (Ministry of Land, Infrastructure and Transport 2005) in the Agano River (47 % and 30 %) and the Shinano River (66 % and 29 %), respectively. The 1,4-dioxane concentrations in the rivers did not significantly correlate with those of the COD and BOD.

Variations of the 1,4-dioxane concentrations in the river waters are given in Figure 2. Those in the outflows of plants A - C are also given in the figure. The concentration in the water from the Agano River significantly correlated with that in the outflow of plant A ($r = 0.739$; $p < 0.01$). On the other hand, the concentration in the water from the Shinano River did not correlate with that in the outflow of plant B or plant C. The 1,4-dioxane loads at the investigated sites were calculated to be 0.66 % from plant A into the Agano River, and 0.62 % and 2.7 % from plants B and C, respectively, into the Shinano River.

The 1,4-dioxane loads of the domestic effluents to the river waters were estimated. The 1,4-dioxane loads of the outflows from sewage treatment plants A - D were calculated based on the mean concentrations of 1,4-dioxane in the outflows and flow rates of the outflows. The loads per person were calculated based on the loads and populations of the drainage areas. These results are given in Table 3. The mean of the 1,4-dioxane load per person was estimated to be 0.23 mg/d/person. This value was almost the same as the estimated value of 0.25

Table 4. 1,4-Dioxane loads of domestic effluents on river water.

	Agano R.	Shinano R.
Mean concentration of 1,4-dioxane (μg/L)	0.11	0.05
Water flow rate (cu m/d)	32,200,000	30,300,000
1,4-Dioxane load (mg/d)	3,520,000	1,500,000
Population	590,000	3,350,000
1,4-Dioxane load of domestic effluents (mg/d)	140,000	770,000
1,4-Dioxane load of others (mg/d)	3,380,000	730,000
Percentile 1,4-dioxane load of domestic effluents (%)	4.0	51

mg/d/person at Kanagawa, Japan (Abe 1999).

The percentages of the domestic effluent treated in the sewage treatment plants were 53.4 % in Niigata Prefecture, and 67.4 % in Niigata City. As described above, 1,4-dioxane in the inflows was not removed at either plant. Therefore, we cited the value (0.23 mg/d) as 1,4-dioxane load per person of the untreated domestic effluent. The 1,4-dioxane loads of the domestic effluents on the river water were then calculated based on the mean of the load per person and the populations of the catchments of the rivers. These results are shown in Table 4. The percentile 1,4-dioxane load of domestic effluents in the Agano River was extremely low (4.0 %). Therefore, the major parts of the 1,4-dioxane loads originated from other sources. The percentile load in the Shinano River (51 %) was 10 times higher than that in the Agano River, while 49 % of the loads were derived from other sources. Chemical plants (Abe 1999) and waste landfill sites (Yasuhara et al. 2003) were estimated as the sources of 1,4-dioxane. Therefore, further studies need to be carried out for evaluating these other sources.

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