

# Distribution and Variation of 1,4-Dioxane in Water from Rivers in Niigata Including the Shinano River

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Received: 23 September 2008 / Accepted: 26 February 2009 / Published online: 12 March 2009  
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**Abstract** The distribution of 1,4-dioxane in the waters from 27 sites in 12 rivers including the Shinano River, the longest river in Japan, was investigated in 2002. 1,4-Dioxane was detected in concentrations ranging from 0.02 to 0.49 µg/L. The monthly variations in the 1,4-dioxane concentrations at 6 sites along the Shinano River showed mutually different patterns, and the concentrations did not correlate with the concentrations of the biochemical oxygen demand and the suspended substances. The annual mean concentrations were from 0.02 µg/L at sites located in the middle reaches to 0.11 µg/L at the river mouth. The 1,4-dioxane concentration in the Shinano River has shown a downward trend from 1989 to 2003.

**Keywords** 1,4-Dioxane · River water · Annual trend · BOD · Suspended substances

1,4-Dioxane is a low-biodegradable hydrophilic organic compound used as an industrial solvent or solvent stabilizer (Zenker et al. 2003). The IARC has classified it as a possible human carcinogen (Group 2B). 1,4-Dioxane is produced as a result of the dimerization of ethylene oxide during the formation of polyethoxylated alcohols, which are used to synthesize sulfate surface active agents such as

alkylpoly(oxyethylene)sulfates (Zenker et al. 2003). Therefore, 1,4-dioxane is present in shampoos, liquid soap, hair lotions and other cosmetic products (Black et al. 2001; Tanabe and Kawata 2008). Recently, 1,4-dioxane has been reported to be found in incineration residues produced by the incineration of municipal solid waste (Yasuhara et al. 2003; Fujiwara et al. 2008) and industrial alcohols as an impurity (Japan Alcohol Association 2006). 1,4-Dioxane has been detected in sea water, river water, ground water (Abe 1999; Isaacson et al. 2006; Kawata et al. 2001), landfill leachates (Lesage et al. 1990; Yasuhara et al. 2003), and the effluent from sewerage systems (Abe 1999).

We have previously reported the distributions and variations of 1,4-dioxane in 11 rivers of Niigata, Japan (Kawata et al. 2003). In the report, 1,4-dioxane was estimated to be derived from the domestic effluents including sewage treatment plants. Therefore, we have evaluated the leaching of 1,4-dioxane from 36 wastes including fly and bottom ashes from incinerators as well as 1,4-dioxane concentrations in the leachates from two landfill sites (Yasuhara et al. 2003). We have also evaluated the behavior of 1,4-dioxane in the inflows and outflows of sewage treatment plants, and the impacts of 1,4-dioxane from the outflows of four sewage treatment plants on two major rivers in Niigata, Japan, including the Shinano River, the longest river in Japan (Tanabe et al. 2006). Moreover, we have estimated the 1,4-dioxane load from household detergents and cleaners in the domestic effluents in Japan (Tanabe and Kawata 2008).

In this paper, we first present the distributions of 1,4-dioxane in the waters from 27 sites in 12 rivers including the Shinano River as well as the small rivers in Niigata, Japan. Second, we present the monthly variations of 1,4-dioxane at 6 sites on the Shinano River. The Shinano River flows for 367 km through the Nagano Prefecture and the

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Niigata Prefecture to the Sea of Japan. The annual flow volume is  $1.59 \times 10^{10}$  cu m/year, and the contributory area is 11,900 sq km including cultivated areas and populated areas. The Shinano River water is used for agriculture, industry and drinking water as well as the generation of electricity. Third, the annual trend of the 1,4-dioxane concentrations at the river mouth and the estuary of the Shinano River are discussed on the basis of the concentrations previously reported and presented in this paper.

## Materials and Methods

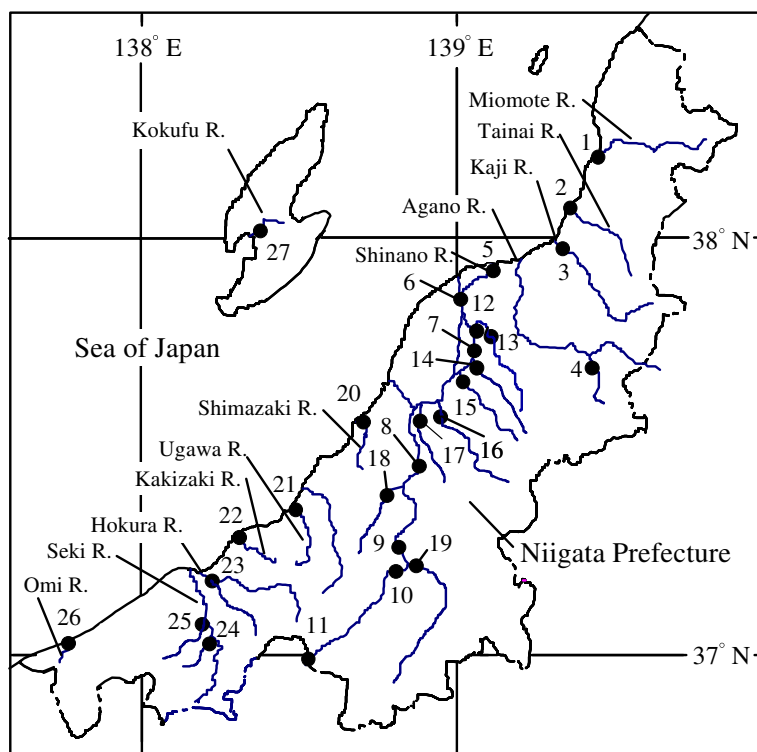
Water samples were collected at 27 sites from 12 rivers including the Shinano River in the Niigata Prefecture, Japan (Fig. 1). The surface water was sampled in February and June 2002. Samples were also taken once a month from January to December 2002 at sites 5–10 on the Shinano River. The collected samples were placed in 1-L glass bottles equipped with ground stoppers without a headspace and stored at 4°C in the dark. All samples were analyzed within 48 h after collection.

The determination of the compounds was performed using a previously published solid phase extraction and isotope-internal standard method (Kawata et al. 2003). Briefly, 500 mL of filtered water sample added with 0.4 µg of [ $^2\text{H}_8$ ]1,4-dioxane (1,4-dioxane- $\text{d}_8$ ) as the surrogate was passed through a series of a C18 cartridge (Waters Sep-Pak

Plus C18, Millipore, Bedford, MA) and two AC-2 cartridges (Waters Sep-Pak Plus AC-2, Nippon Millipore, Tokyo, Japan) at 10 mL/min using a Waters Sep-Pak Concentrator (Nippon Millipore). 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 in the opposite direction of the extraction to test tubes with ground stoppers using a J and W SPE Manifold (J and W Scientific, Folsom, CA). The eluates were kept at  $-20^\circ\text{C}$  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. A 0.4 µg weight of 1-bromo-4-fluorobenzene as an internal standard 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: instrument, JEOL model Automass 50 (JEOL, Tokyo, Japan); column, a 30 m  $\times$  0.25 mm id (0.5 µm film thickness) fused-silica J and W DB-WAX column (Agilent, Palo Alto, CA); column temperature, programmed from 35°C (held for 3 min) to 190°C (held for 3 min) at a rate of 5°C/min; injector temperature, 170°C; 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- $\text{d}_8$  and 174 for 1-bromo-4-fluorobenzene. The ratios of the

Fig. 1 Sampling sites



peak areas of the ions to those of the internal standards were used for quantification of the compounds. 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  $\mu\text{g/L}$ . The overall recoveries and relative standard deviation of 1,4-dioxane- $d_8$  were 87% and 12% ( $n = 114$ ), respectively.

## Results and Discussion

The concentrations of 1,4-dioxane at sites 1–27 in February and June 2002 are shown in Table 1. 1,4-Dioxane was detected from 22 sites in February and 19 sites in June, and ranged in concentrations from 0.02 to 0.39  $\mu\text{g/L}$  (0.072  $\mu\text{g/L}$  in mean) and 0.02 to 0.49  $\mu\text{g/L}$  (0.11  $\mu\text{g/L}$  in mean), respectively. 1,4-Dioxane was not detected in both months at sites 1, 10, 13 and 16. The Ministry of Environment (2002) reported that 1,4-dioxane was detected at 0.09–8.0  $\mu\text{g/L}$  from 16 sites out of the 33 investigated sites in Japanese rivers and coastal areas in 2001. The geomeans (0.049  $\mu\text{g/L}$  on February and 0.078  $\mu\text{g/L}$  on June) of the detected sites in this study were lower than the 0.12  $\mu\text{g/L}$  in geomean of the 16 sites in Japan. The investigated 27 sites included 13 sites where the 1,4-dioxane was determined in June and November 1999 (Kawata et al. 2003). Among the 13 sites, the concentrations were almost comparable at sites 1–4, 7, 9, 15 and 21. At sites 6, 13 and 16, the 1,4-dioxane concentrations in 2002 had decreased to less than 20% of those in 1999. On the other hand, 1,4-dioxane was detected (0.04–0.29  $\mu\text{g/L}$ ) at sites 18 and 19 where the 1,4-dioxane was not detected in 1999. The maximum concentrations, 0.30 and 0.49  $\mu\text{g/L}$ , were observed at sites 5 and 25 in February and June, respectively. These values were less than a tenth of the maximum concentration in the 2001 survey by the Ministry of Environment, and almost comparable to the maximum value, 0.39  $\mu\text{g/L}$ , in our 1998/1999 investigation.

1,4-Dioxane is reported to be provided by effluents from sewage treatment plants (Abe 1999; Tanabe et al. 2006), those from chemical plants using the compound as a solvent (Abe 1999) and leachates from hazardous waste disposal sites in Japan (Yasuhara et al. 1997). Effluents from factories using the industrial alcohol including 1,4-dioxane as an impurity could also provide the compound to the water environment. 1,4-Dioxane could be also present in the fly ash including that produced by municipal solid waste incinerators (Fujiwara et al. 2008). The 1,4-dioxane concentrations in February and/or June (Table 1) were higher or equal to 0.10  $\mu\text{g/L}$  at sites 5, 15, 17–20, and 23–25. The 1,4-dioxane could be derived from the institutions or companies mentioned above. Namely, there exist sewage treatment plants in the upper reaches of sites 2, 5 15 and 19; municipal solid waste incinerators were operated in the upper reaches or around sites 2, 19 and 23. Moreover, several factories including chemical plants exist in the upper reaches of sites 2, 15, 17, 18, 20, 23 and 24. Some could be using 1,4-dioxane or an industrial alcohol including 1,4-dioxane, and the others are equipped incinerators. On the other hand, there exist sewage treatment plants in the upper reaches of sites 13 and 16, where 1,4-dioxane was detected at a level higher or equal to 0.10  $\mu\text{g/L}$  in 1998/1999, but not detected in 2002. The ratios of the maximum 1,4-dioxane concentrations to the minimum ones in the effluents of the four sewerage plants in Niigata were 2.2–3.0, whereas the ratios in the waters from the rivers which the effluents flow into were 3.8–5.3 (Tanabe et al. 2006). Although the ratios of the concentrations in 1998/1999 to those in 2002 at sites 13 and 16 were more than five, the difference between the concentrations in 1998/1999 and 2002 at both sites could be within the range of the variations at the sites.

The 1,4-dioxane concentrations from the 6 sites of the Shinano River are summarized in Table 2. We have already reported the monthly variations of 1,4-dioxane at site 5 from January to December 2003 (Tanabe et al. 2006)

**Table 1** 1,4-Dioxane concentrations in river waters in February and June

Site	Concentration ( $\mu\text{g/L}$ )		Site	Concentration ( $\mu\text{g/L}$ )		Site	Concentration ( $\mu\text{g/L}$ )	
	Feb.	June		Feb.	June		Feb.	June
1	<0.02	<0.02	10	<0.02	<0.02	19	0.19	0.04
2	0.11	0.07	11	0.02	<0.02	20	0.07	0.22
3	0.02	<0.02	12	<0.02	0.02	21	0.03	0.02
4	0.05	<0.02	13	<0.02	<0.02	22	0.02	0.09
5	0.30	0.05	14	0.03	<0.02	23	0.10	0.22
6	0.02	0.08	15	0.15	0.03	24	0.08	0.15
7	0.02	0.06	16	<0.02	<0.02	25	0.08	0.49
8	0.03	0.03	17	0.03	0.10	26	0.03	0.08
9	0.03	0.04	18	0.16	0.29	27	0.02	0.09

**Table 2** Summary of 1,4-dioxane concentrations at sites 5–10

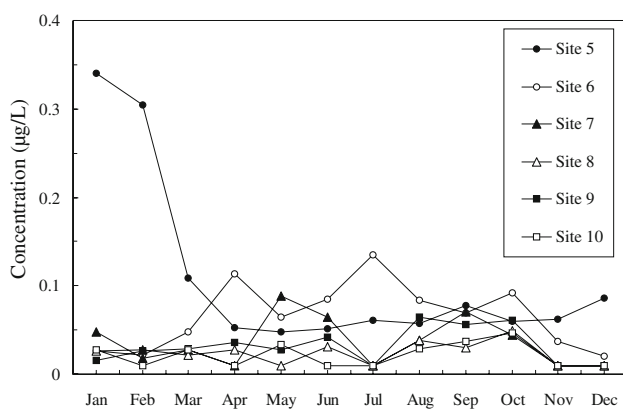
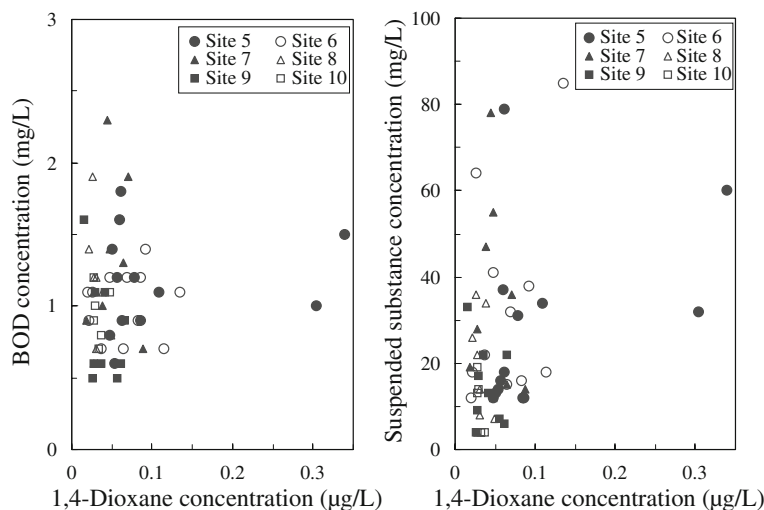
Site	Concentration ( $\mu\text{g/L}$ )						RSD (%)
	Min	Max	Mean	Geomean	Median	SD	
5	0.05	0.34	0.11	0.08	0.06	0.10	93
6	0.02	0.13	0.07	0.06	0.07	0.037	56
7	<0.02	0.09	0.04	0.03	0.03	0.027	74
8	<0.02	0.05	0.02	0.02	0.03	0.012	52
9	<0.02	0.07	0.03	0.03	0.03	0.020	62
10	<0.02	0.05	0.02	<0.02	<0.02	0.013	61

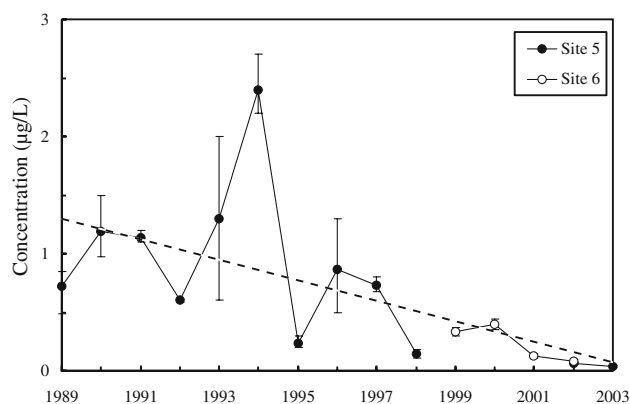
and at site 6 from December 1998 to November 1999 (Kawata et al. 2003). The mean value at site 5 in 2003 (0.05  $\mu\text{g/L}$ ) and that at site 6 in 2002 (0.07  $\mu\text{g/L}$ ) were about twice that in 2002 (0.11  $\mu\text{g/L}$ ) and that in 1998/1999 (0.18  $\mu\text{g/L}$ ). The maximum values at sites 5 and 6 also decreased from 0.34  $\mu\text{g/L}$  in 2002 to 0.10  $\mu\text{g/L}$  in 2003 and from 0.39  $\mu\text{g/L}$  in 1998/1999 to 0.13  $\mu\text{g/L}$  in 2002, respectively. Therefore, the 1,4-dioxane concentrations at

both sites did decrease during these years. The RSDs of the annual 1,4-dioxane concentration at site 5 (93%) in 2002 was greater than that (50%) in 2003, whereas that at site 6 (56%) in 2002 was almost same as that (55%) in 1998/1999.

Figure 2 shows the variations in the 1,4-dioxane concentrations at sites 5–10 in the Shinano River waters. The concentrations at the 6 sites did not show the characteristic variations. The variation at site 5 showed a different pattern from that in 2003 (Tanabe et al. 2006). In addition, the concentrations at site 5 in January and February exceeded 0.3  $\mu\text{g/L}$ , which caused a significant variation with an RSD of 96%. The variation at site 6 also showed a different pattern from that in 1999 (Kawata et al. 2003). The relations between the 1,4-dioxane concentrations and the biochemical oxygen demand (BOD) values at sites 5–10 are given in Fig. 3. The 1,4-dioxane concentrations did not correlate with the BOD values; those at sites 5 and 6 did not correlate with the chemical oxygen demand values. These uncharacteristic variations indicate that the target compounds could be derived from anthropogenic sources as mentioned above, which are not the major sources of the BOD. Regarding the total organic carbon (TOC) contents, Yasuhara et al. (2003) reported that the 1,4-dioxane was independent of the TOC values in the leachates from landfill sites. Moreover, the relations between the 1,4-dioxane concentrations and the concentrations of the suspended substances at sites 5–10 are also given in Fig. 3. The 1,4-dioxane concentration had no correlation with the suspended substances, indicating that 1,4-dioxane in the river water mainly exists in the water phase and not in the solid phase.

The annual 1,4-dioxane concentrations were reported by the Ministry of Environment (2002) in September or October from 1989 to 1998 at site 5 and from 1999 to 2001 at site 6. Figure 4 shows the annual variations at sites 5 and 6. The

**Fig. 2** Variation in 1,4-dioxane concentrations in Shinano River waters**Fig. 3** Relations of 1,4-dioxane concentrations with BOD concentrations and concentrations of suspended substances



**Fig. 4** Annual variation in 1,4-dioxane concentrations at sites 5 and 6. The dashed line indicates the regression line calculated by the least-squares method

values at site 5 in 2002 and 2003, and site 6 in 1999 and 2003 were those of the corresponding concentrations in September and October (Fig. 2). Although the concentrations at sites 5 and 6 had considerable variations, they showed a downward trend. All the concentrations significantly correlated ( $p < 0.01$ ) with the year ( $r = 0.789$ ). This implies that the consumed amounts of 1,4-dioxane and the industrial alcohol including 1,4-dioxane as well as those released from incinerators decreased during this period.

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