Bull Environ Contam Toxicol (2009) 83:841–845
DOI 10.1007/s00128-009-9857-7

Impact of *N*,*N*-Dimethylformamide from Domestic Effluents on River Waters

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Received: 7 May 2009 / Accepted: 28 August 2009 / Published online: 17 September 2009

Abstract The impacts of *N*,*N*-dimethylformamide (DMF) from domestic effluents on rivers were evaluated. The hourly DMF concentrations in the inflows (0.21–0.52 μg/L in mean) and the outflows (0.18–0.62 μg/L in mean) of two sewage treatment plants did not show any characteristic variations, and DMF was not removed at both plants. The monthly variations of DMF in the outflows of four sewage treatment plants (0.16–0.62 μg/L in mean) and three rivers (0.06–0.11 μg/L in mean) into which the outflows of the plants were discharged did not show any significant variations. The domestic DMF load per person was calculated to be 0.25 mg/d/person. The percent DMF loads of domestic effluents in the rivers were estimated to be below (8%–32%).

Keywords Dimethylformamide · River · Sewage treatment plant · Removal rate · Load

N,*N*-dimethylformamide (DMF) is a hydrophilic organic compound mainly used as a solvent for manufacturing synthetic leatherette and polymers. DMF has a markedly high skin adsorption rate. Although no guideline is given by the World Health Organization for drinking water, DMF is considered to be a potent liver toxin (Yan et al. 2002). DMF discharged into the water environment is expected to be mainly distributed in the water phase. Therefore, the monitoring of DMF in water is important for evaluating its impact on ecosystems and human health. DMF has been detected in sea water, river water, ground water and rain water (Ibaraki et al. 1999; Kadokami et al. 1993; Okamoto et al. 1992) as well as in the leachate from waste landfills (Yasuhara et al. 1992).

We have previously reported the distributions and variations of DMF in the rivers of Niigata, Japan (Kawata et al. 2001, 2003). The concentrations in the waters from 19 sites in 11 rivers were <0.03–0.33 μg/L, and in some rivers, DMF was estimated to be derived from anthropogenic sources such as the effluents from some of the factories (Kawata et al. 2003). The domestic effluents including sewage treatment plants is a potential source of DMF (Kadokami et al. 1993). However, there are few investigations on the impact of DMF from domestic effluents on rivers. Moreover, few reports have described the variations of the DMF concentrations in the inflows and outflows of sewage treatment plants, and the removal rates of DMF at the sewage treatment plants.

In this paper, we evaluate the impacts of DMF from the domestic effluents on rivers. For this purpose, we first present the hourly variations of the DMF concentrations in the inflows and outflows of two sewage treatment plants, and evaluate the removal effects of DMF at the sewage treatment plants. Second, we investigated the monthly variations of DMF in the outflows of four sewage treatment plants and three rivers into which the outflows of the plants were discharged. The target rivers were the Shinano River, the longest river in Japan, and the Agano River, the 10th longest river in Japan, as well as a small river, the Shin River, Niigata, Japan. The Agano River flows 210 km through the

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Fukushima Prefecture and the Niigata Prefecture to the Sea of Japan at 1.27×10^{10} cu m/yr, draining 7,710 km^2 including cultivated areas and civilized areas. The Shinano River is the longest river in Japan, and flows 367 km through the Nagano Prefecture and the Niigata Prefecture to the Sea of Japan at 1.53×10^{10} cu m/yr, draining 11,900 km^2 including cultivated areas and civilized areas. The Shin River flows for 13.5 km through the northwest part of the Niigata Plain, Niigata, Japan, to the Sea of Japan, draining 230 km^2. The contributory area includes 198 km^2 of cultivated areas and civilized areas.

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 × 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 DMF (100 and 20 μg/mL) were prepared in acetone. An acetone solution of $[^2H_7]$ *N*,*N*-dimethylformamide (DMF-d_7; 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 × 10 mm id) packed with 10 g of Activated Carbon Beads-L (20–30 mesh; specific surface area, 800–1200 m^2/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 h 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.

The investigated sites were four sewage treatment plants in Niigata City, Niigata Prefecture, and the mouths of three rivers, the Agano River, the Shinano River (Tanabe et al. 2006) and the Shin 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 56,200 cu m/d. Plants B and C discharged their outflows into the Shinano River at 49,300 and 212,000 cu m/d, respectively. Plant D discharged its outflows into the Shin River at 4,200 cu m/d. 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.

Water samples were collected from the inflows and outflows of the sewage treatment plants A and D during 2 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 h 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 three 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 h 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 0.5 mL/min in the opposite direction of the extraction to test tubes with ground stoppers. The eluates were kept at −20°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. 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°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 73 and 44 for DMF, 80 for DMF-d_7 and 174 for 1-bromo-4-fluorobenzene. The ratios of the peak areas of the ions to those of the internal standards were used for quantification of the compounds. No DMF and DMF-d_7 were detected from the second AC-2 cartridges. The minimum detectable concentration of DMF was 0.02 μg/L. The overall recoveries and relative standard deviation of DMF-d_7 were 87% and 9.4%, respectively.

Results and Discussion

The hourly DMF concentrations in the inflows and outflows of sewage treatment plants A and D were analyzed in order to investigate the behavior of DMF for 24 h in the sewage treatment plants (Table 1). The *t*-test showed that the mean DMF concentrations in the inflows and the outflows of the two plants in summer were significantly higher ($p < 0.01$) than those in winter. The relative standard deviations (RSDs) of the DMF concentrations in the inflows and those in the outflows were 21%–59% and 17%–20%, respectively; these values were rather higher than the RSD value of the 1,4-dioxane concentrations in the inflows (11%–27%) and outflows (7.6%–14%) of the plants (Tanabe et al. 2006). The hourly variations of the DMF concentrations at plants A and D are shown in Fig. 1. The DMF concentrations in the inflows and the outflows did not show any characteristic variations at both plants, except for the increase of the DMF concentration in the inflow at plant D from 11 p.m. to 1 a.m. in the summer. This increase could be caused by the effluents flowing from the chemical plants using DMF into plant D.

The removal rates of DMF at 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 h, the DMF 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 0.23 ± 0.038 μg/L and 0.23 ± 0.024 μg/L in the winter, and 0.46 ± 0.17 μg/L and 0.44 ± 0.071 μg/L in the summer, respectively; those in the inflows and the outflows of plant D were 0.22 ± 0.076 μg/L and 0.17 ± 0.017 μg/L in the winter, and 0.42 ± 0.21 μg/L and 0.58 ± 0.10 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 ($p < 0.01$). Therefore, DMF was not removed at either plant. These results were due to the low biodegradability and high hydrophilicity of DMF.

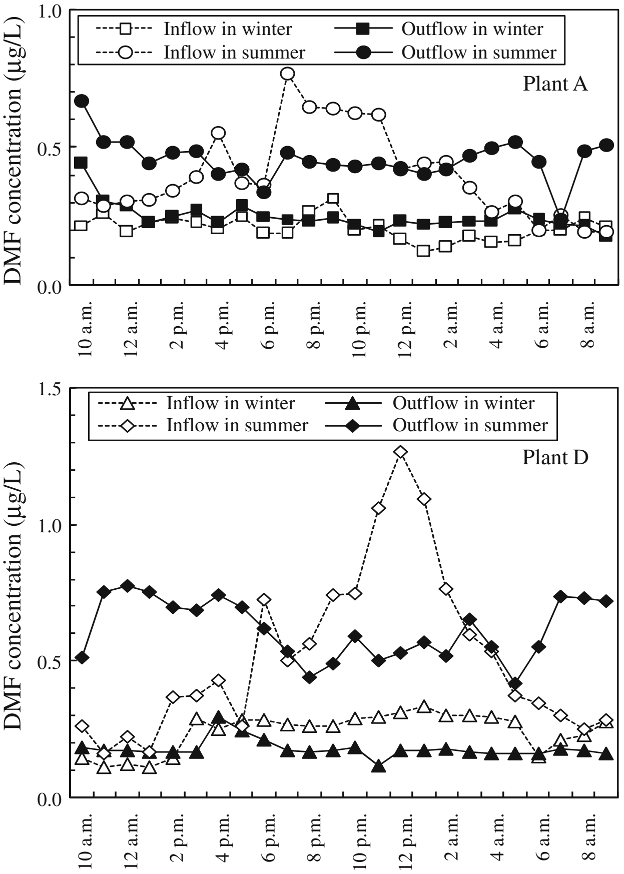

Fig. 1 Variation of DMF concentrations in inflows and outflows of sewage treatment plants A and D

The DMF 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 a summary of the DMF concentrations in the outflow from sewage treatment plants A–D. The concentrations of DMF in the outflows ranged from 0.02 μg/L at plants B and C to 1.3 μg/L at plant A. Although there were no statistically

Table 1 DMF concentrations in inflows and outflows of plants A and D

	DMF concentration (μg/L)							
	Plant A				Plant D			
	Winter		Summer		Winter		Summer	
	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow
Max	0.32	0.44	0.77	0.67	0.34	0.29	1.3	0.78
Min	0.12	0.18	0.19	0.24	0.11	0.12	0.16	0.42
Mean	0.21	0.25	0.40	0.46	0.24	0.18	0.52	0.62
SD	0.044	0.050	0.16	0.078	0.071	0.033	0.31	0.11
RSD (%)	21	20	40	17	29	18	59	18

SD standard deviation

Table 2 DMF concentrations in outflows of sewage treatment plants and river waters

	DMF concentration (µg/L)						
	Outflow from plant				River water		
	A	B	C	D	Agano R.	Shinano R.	Shinano R.
Max	1.3	0.50	0.85	0.99	0.24	0.40	0.22
Min	0.22	0.02	0.04	0.31	<0.02	<0.02	<0.02
Mean	0.53	0.16	0.29	0.62	0.06	0.11	0.10
SD	0.35	0.14	0.26	0.22	0.06	0.13	0.06
RSD (%)	65	87	91	36	120	110	58

significant differences ($p < 0.01$) in the mean concentrations of plants A and D, and in those of plants C and D, the mean concentrations of plants A and D were significantly higher than those of plants B and C ($p < 0.01$). The RSDs of the annual DMF concentrations in the outflows of plants A–D were 35%–91%. These values were rather lower than the RSD values (25%–58%) of 1,4-dioxane in the outflows from the sewage treatment plants, and almost comparable to the RSD values (92% and 56%) of the biochemical oxygen demand (BOD) in the outflows of plants B and C, respectively (Tanabe et al. 2006). The relations between the DMF concentrations and the BOD values at plants B and C were evaluated. The DMF concentrations did not correlate with the BOD values, suggesting that DMF could be derived from anthropogenic sources which are not the major sources of the BOD.

The DMF concentrations in water samples from the mouths of the rivers are summarized in Table 2. The detected concentrations of DMF ranged from 0.02 µg/L in the Agano River to 0.40 µg/L in the Shinano River. The mean concentration (0.06 µg/L) in the Agano River was 10% of that in the outflow from sewage treatment plant A (0.53 µg/L). The mean concentration (0.11 µg/L) in the Shinano River was 71% and 39% of those in the outflow from plants B and C, respectively; the mean concentration (0.10 µg/L) in the Shin River was 17% of that in the outflow from plant D (0.62 µg/L). The RSDs of the annual DMF concentrations in the rivers were 58%–120%. The RSDs values were greater than those in the outflows from the plants flowing into the rivers, and those of the BOD and the chemical oxygen demand (COD) in the Agano River, 47% and 30%, and the Shinano River, 66% and 29% (Tanabe et al. 2006), respectively. The DMF concentrations did not correlate with the BOD values or the COD values.

Variations of the DMF concentrations in the outflows of the plants and the river waters are given in Fig. 2. The DMF concentrations did not show any characteristic variations at all the investigated sites. The concentration in the water from the Agano River and Shinano River did not correlate to those in the outflows of plant A and B, respectively. On the other hand, the concentration in the water from the Agano River significantly correlated with that in the outflow of plant C ($r = 0.929$; $p < 0.01$).

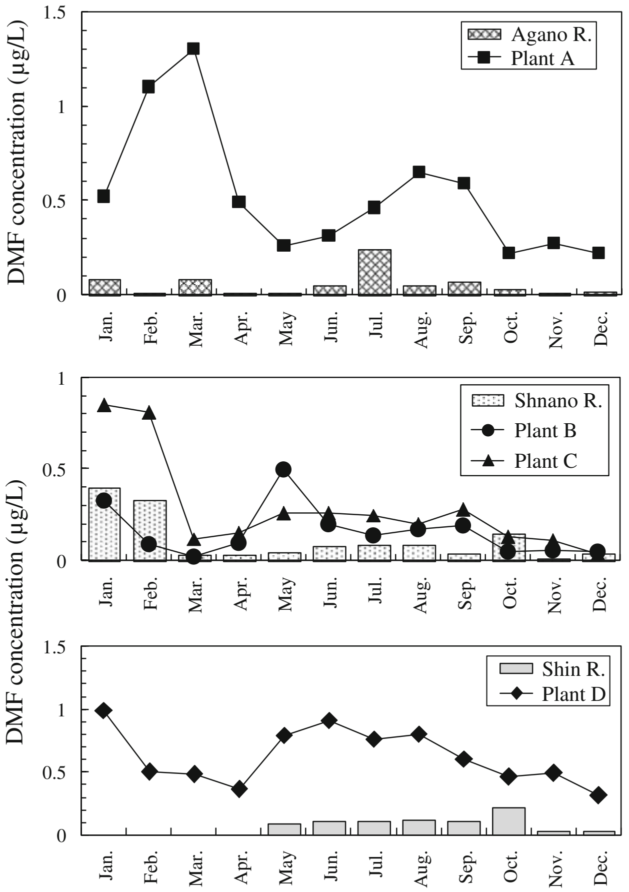

Fig. 2 Variation of DMF concentrations in outflows of sewage treatment plants and river waters

The DMF loads of the outflows from sewage treatment plants A–D were calculated based on the mean concentrations of DMF in the outflows and flow rates of the outflows. The loads of DMF per person were calculated based on the loads and populations of the drainage areas. These results are given in Table 3. The loads of DMF per person were 0.19–0.32 mg/d/person at plants A–C whereas 0.84 mg/d/person at plant D. This implies that there could be non-domestic sources discharged into plant D.

Table 3 DMF loads of outflows of sewage treatment plants

	Sewage treatment plant			
	A	B	C	D
Mean concentration of DMF (μg/L)	0.53	0.16	0.29	0.62
Flow rate of outflow (cu m/d)	59,300	49,300	212,000	4,200
DMF load (mg/d)	31,600	7,800	61,000	2,600
Population	162,000	35,300	191,000	3,100
DMF load per person (mg/d/person)	0.19	0.22	0.32	0.84

Table 4 DMF loads of domestic effluents on river water

	Agano R.	Shinano R.	Shin R.
Mean concentration of DMF (μg/L)	0.06	0.11	0.10
Water flow rate (cu m/d)	32,300,000	30,300,000	1,200,000
DMF load (mg/d)	1,780,000	3,390,000	120,000
Population	590,000	3,350,000	150,000
DMF load of domestic effluents (mg/d)	140,000	820,000	38,000
DMF load of others (mg/d)	1,630,000	2,560,000	78,000
DMF load of domestic effluents (%)	8	24	32

Since DMF in the inflows was not removed at either plant as described above, we cited the mean value (0.25 mg/d/person) of plants A–C as DMF load per person of the untreated domestic effluent. The DMF 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 given in Table 4. The percent DMF load of domestic effluents in the Agano River was extremely low (8%). Therefore, the major portion of the DMF loads originated from other sources. The percent loads in the Shinano River (24%) and the Shin River (32%) were three and four times higher than that in the Agano River, while 76% and 68% of the loads were derived from the other sources, respectively. Moreover, the DMF loads of the outflows from the sewage treatment plants (Table 3) to the river waters (Table 4) were estimated. The DMF loads at the investigated plants were calculated to be 1.8% from plant A into the Agano River, 0.23% and 1.8% from plants B and C, respectively, into the Shinano River, and 2.3% from plant D into the Shin River. The chemical plants were suggested as the sources of the DMF. Therefore, further studies need to be carried out for evaluating these other sources.

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