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Elution of 1,4-Dioxane from Waste Landfill Sites

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1,4-Dioxane is one of polar, volatile and water-miscible compounds. It is used as an organic solvent for cellulose acetate, resins, oils, etc. Also, it has been used as a stabilizer for 1,1,1-trichloroethane, whose manufacturing was prohibited in 1996 by the Montreal Protocol. Its physical properties are as follows (Japan Ministry of Environment, 2001): d_4^{20}, 1.033; mp, 11.8 °C; bp, 101 °C; log P_{ow}, -0.27 or –0.42. According to the toxic data, its LD_{50} orally in mice and rats are 5.7 and 5.2 mL/kg, respectively. The IARC has classified 1,4-dioxane as a possible human carcinogen. US EPA presented a value of 30 μg/L as a concentration of drinking water at a 1/100000-risk level. In Japan, 1,4-dioxane is a designated chemical substance by the Chemical Substances Control Law amended in April 1987, because it has been recognized that it is a substance with low bioaccumulation but low biodegradability and a suspicion of chronic toxicity (Arai, 1986; Urushigawa, 1986). The production of 1,4-dioxane in Japan was ca. 4500 tons in FY 1999. 1,4-Dioxane has been frequently detected in landfill leachates (Lesage et al., 1990; Yasuhara et al., 1992; Yasuhara, 1995; Yasuhara et al. 1997; Yasuhara et al. 1999; Namegaya et al., 2002), 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).

Ministry of the Environment in Japan has annually monitored 1,4-dioxane in river and coast waters from 32 to 35 sites in Japan since FY 1990. However, there are few investigations upon variations of its concentrations in landfill leachates and upon its origin. This paper describes the variations of 1,4-dioxane concentrations in leachates and several aspects for origin of 1,4-dioxane.

MATERIALS AND METHODS

Two landfill sites were selected for sampling of leachates. One site A is a supervisory landfill whose area is 20,000 m^2 and is located in mountainous area in the Pacific Ocean side and the central region of Japan. The

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reclamation was carried out from April 1985 until March 1997. Waste buried was only ash from a stoker-fired MSW incinerator (the Incinerator E). Leachates were collected and dealt in coagulative precipitation treatment and activated sludge treatment. The other landfill B is a strictly controlled landfill whose area is 36,000 m^2 and is located in mountainous area in the Sea of Japan side and the central region of Japan. The reclamation has continued since 1998. Wastes buried are plastics, which have been pressed under heating and crushed into pieces in the Factory F. The recycling system, where well water is sprinkled on the waste and the leached water is sprinkled again on the waste after coagulative precipitation treatment and activated sludge treatment, is used in order to promote degradation of the waste. Sampling of leachates in both the landfill sites were performed once a month from May 2000 to March 2001 at site A and from May 2000 to December 2000 at site B. The leachates sampled were transferred to the laboratory in our institute under cooling at 5 °C within 24 hours and were immediately analyzed.

Bottom ash was obtained from a few incinerators including the Factory E. Various waste plastics were sampled from several landfill sites including the site B. Details of the samples are shown in Table 1.

1,4-Dioxane, 1,4-dioxane-d_8 and methyl acetate were purchased from Wako Pure Chemical Industries (Osaka, Japan). Dichloromethane, acetone, anhydrous sodium sulfate, and sodium chloride were of pesticide grade (Wako Pure Chemical Industries, Osaka, Japan). Pure water was prepared by Milli-Q system from Nihon Millipore Co. (Tokyo, Japan). Sep-Pak PS-2 cartridge and Sep-Pak AC-2 cartridge were purchased from Nihon Waters Co. (Tokyo, Japan) and were conditioned at the order of dichloromethane (10 mL), acetone (20 mL), and pure water (40 mL) immediately before use.

Leaching test was performed for 36 wastes shown in Table 1. Samples were divided into pieces as shape of square or cube so that one side length became around 1 cm. Samples of #1 to #11 were subjected to the leaching test method similar to the Japan Standard Leaching Test for Wastes, where samples are submerged in long-necked glass flasks containing deionized water at a solid-to liquid ratio of 1:10 under orbital-shaking with 200 rev./min for 6 hrs. Samples of #12 to 36 were submerged in separate Erlenmeyer flasks containing unbuffered deionized water without any shaking or stirring for 30 days. The aqueous layer was separated from waste by filtering immediately after the leaching period. The filtrate solution was analyzed in a manner described below.

Sodium chloride was dissolved in aqueous sample, so that amount of sodium chloride becomes 3 g per 100 mL of aqueous sample, after 15 μl of 1,4-dioxane-d_8 in methanol (1000 mg/L) was added to it. The solution was passed through a Sep-Pak PS-2 cartridge and a Sep-Pak AC-2 cartridge in

Table 1. Details of samples and leaching test.

#	Details of sample	Sample (g)	Water (mL)	Leaching time
1	Fly ash from the Incinerator E	20	200	6 hrs
2	Bottom ash from the Incinerator E	20	200	6 hrs
3	Waste plastics sampled at the Landfill B	20	200	6 hrs
4	Waste plastics sampled at the Landfill B	20	200	6 hrs
5	Waste plastics sampled at the Landfill B	20	200	6 hrs
6	Waste plastics sampled at the Landfill B	20	200	6 hrs
7	Waste plastics, pressed under heating, sampled at the Factory F	20	200	6 hrs
8	Bottom ash from the Incinerator C	20	200	6 hrs
9	Waste plastics, pressed under heating, sampled at the Factory D	20	200	6 hrs
10	Waste plastics, pressed under heating, sampled at the Factory D	20	200	6 hrs
11	Waste plastics, pressed under heating, sampled at the Factory D	20	200	6 hrs
12	White plastic bottle*	3.0	100	30 days
13	Gray synthetic leather	2.0	100	30 days
14	Brown synthetic leather with reverse cloth	2.0	100	30 days
15	Brownish gray synthetic leather with reverse cloth	5.1	100	30 days
16	Clear and thin plastic for foodstuff packing	2.0	100	30 days
17	White and hard plastic board	5.7	100	30 days
18	White and hard plastic board	9.8	100	30 days
19	Light blue and hard plastic board	9.9	100	30 days
20	Beige and hard plastic board	10.3	100	30 days
21	Beige and hard plastic board	10.9	100	30 days
22	White and hard plastic board	10.4	100	30 days
23	Blue and hard plastic board	10.3	100	30 days
24	Beige and hard plastic board	10.2	100	30 days
25	Dark gray synthetic leather with reverse cloth	5.1	100	30 days
26	Translucid and soft plastic film	1.0	100	30 days
27	Gray plastic fibers	0.51	100	30 days
28	Clear and thin plastic for foodstuff packing	2.0	100	30 days
29	Black and hard plastic board	5.0	100	30 days
30	Clear plastic sheet with reverse paper	3.0	100	30 days
31	Gray and hard plastic board	4.7	100	30 days
32	Mixture of gray plastic gum and black plastic gum	9.9	100	30 days
33	White and hard plastic board	10.0	100	30 days
34	Mixture of black and hard plastic board and white and hard plastic board	10.1	100	30 days
35	Clear and soft plastic film	2.0	100	30 days
36	Glassy hard plastic board*	5.0	100	30 days

*Samples were collected at the Factory D before pressing under heating.

series, so that the Sep-Pak AC-2 cartridge is a back up, at a rate of 5 mL/min by using a Waters Sep-Pak concentrator system obtained from Nihon Waters Co. (Tokyo, Japan). 1,4-Dioxane was adsorbed on Sep-Pak AC-2 cartridge, but not on Sep-Pak PS-2 cartridge. The Sep-Pak AC-2 cartridge was detached and then the residual water in the cartridge was removed by passing air through the cartridge. 1,4-Dioxane adsorbed in the cartridge was eluted with methyl acetate (3 mL). The eluates were composed of two phases, aqueous phase and organic phase. Anhydrous sodium sulfate (1 g) was added to the eluate mixture in order to eliminate the aqueous layer. After 30 min, 2 μL of the elute was injected into an Agilent 6890A gas chromatograph/5973 mass spectrometer, whose operational conditions were as follows: column, FFAP (30 m length, 0.25 mm I.D., d_f=0.30 μm); column temperature, 35 °C for 4 min, 30 °C/min ramp to 200 °C, and hold for 10 min; injector temperature, 250 °C; carrier gas (He) flow rate, 1.8 mL/min at 97.4 kPa; carrier gas flow velocity, 49 cm/sec; injection mode, splitless; detector temperature, 230 °C; detection mode, selected ion monitoring (SIM); ionizing current, 300 μA; ionizing energy, 70 eV; monitor ions, m/z 88 and 58 for 1,4-dioxane and m/z 96 and 64 for deuterated 1,4-dioxane.

RESULTS AND DISCUSSION

A typical method for analysis of 1,4-dioxane has been reported in the literature (Abe, 1997). The same method was used in this research except for elution solvent, GC column and column temperature. Average recovery of 1,4-dioxane-d_8 in aqueous samples was 93 %. All measurement values were corrected by comparison with an internal standard quantification using 1,4-dioxane-d_8.

Analytical results of 1,4-dioxane in leachates from landfill sites are shown in Tables 2 and 3. Concentrations of 1,4-dioxane in leachate from the landfill site A were below 1 μg/L, but ones from the landfill site B were over 1 μg/L. The landfill site A, where wastes buried were ash from MSW incinerator, has already been closed. On the other hand, the landfill site B is now under operation. Therefore, the reason for the large difference in 1,4-dioxane concentration between the two sites is assumed to be depended on operation period of the landfills as well as wastes buried.

Concentration ranges of 1,4-dioxane in leachates reported in the literatures are as follows: leachates in Japan in FY 1994, 1.1 to 109 μg/L (Yasuhara et al., 1997); leachates in Japan in FY 1995, 0.8 to 198 μg/L (Yasuhara et al., 1999); leachates in Japan in FY 2001, 19.6 to 775 μg/L (Namegaya et al., 2002); anoxic groundwater at the landfill in Canada, 300 to 2000 μg/L (Lesage et al., 1990).

Concentrations of 1,4-dioxane in this research were fairly low, compared with ones in the literatures described above. However, the concentrations in

Table 2. Concentrations of 1,4-dioxane in leachates from landfill site A.

Sampling Date (m/d/y)	Leachate before treatment			Effluent after treatment		
	pH	TOC (mg-C/L)	Dioxane (μg/L)	pH	TOC (mg-C/L)	Dioxane (μg/L)
5/17/2000	7.4	3.3	0.47	8.2	1.2	0.35
6/20/2000	7.5	2.5	0.46	8.5	1.6	0.45
7/24/2000	7.5	4.6	0.56	8.2	1.2	0.36
8/24/2000	7.4	1.5	0.18	8.2	1.1	0.21
9/20/2000	7.5	2.6	0.19	8.2	1.6	0.20
10/19/2000	7.5	3.9	0.16	8.4	3.5	0.16
11/21/2000	7.5	2.0	0.08	8.0	1.7	0.19
12/20/2000	7.6	1.5	0.62	7.9	1.7	0.21
1/30/2001	7.4	1.9	0.16	8.2	3.1	0.40
2/20/2001	7.4	1.3	0.12	7.6	3.6	0.50
3/19/2001	7.4	1.5	0.15	7.6	1.5	0.37

Table 3. Concentrations of 1,4-dioxane in leachates from landfill site B.

Sampling Date (m/d/y)	Leachate before treatment			Effluent after treatment		
	pH	TOC (mg-C/L)	Dioxane (μg/L)	pH	TOC (mg-C/L)	Dioxane (μg/L)
5/22/2000	8.1	25.5	2.05	8.6	5.8	0.91
6/27/2000	8.1	60.0	6.34	8.8	38.4	4.74
7/26/2000	7.8	69.6	7.16	8.5	54.8	4.78
8/19/2000	7.7	78.0	7.17	8.4	56.4	3.92
9/18/2000	8.1	105	8.60	8.8	60.6	4.58
10/23/2000	8.1	75.3	13.8	8.6	57.7	10.6
11/20/2000	8.0	42.0	7.20	8.6	53.1	7.15
12/4/2000	8.4	51.3	9.87	8.7	48.4	9.23

Table 2 were comparable with ones detected in aqueous environment, that is, <0.024 to 0.69 μg/L in river water in Kitakyushu of Japan (Kadokami et al., 1993), 1.1 to 18 μg/L in ground water in California (Draper et al., 2000), <0.08 to 46 μg/L in river and coast waters from 34-35 sites in Japan during FY 1997-1999 (Ministry of the Environment, Japan, 2001), 0.13 to 0.23 μg/L in river waters in Niigata of Japan (Kawata et al., 2001), 0.1 to 16.0 μg/L in river waters and 0 to 94.8 μg/L in groundwaters in Kanagawa of Japan (Abe, 1999), and 0.42 to 1.47 μg/L in river waters in Nagano of Japan (Kakegawa et al., 1995).

Concentration of 1,4-dioxane was independent on pH or total organic carbon, since 1,4-dioxane is a neutral compound and freely miscible with water. Concentrations in leachates and effluents were in the same level, since biodegradability of 1,4-dioxane is very low. Seasonal variation of 1,4-dioxane was not observed.

Leaching test of 1,4-dioxane from various wastes was carried out in order to

Table 4. Results of leaching test

#	1,4-Dioxane in leaching solution (μg/L)
1	21.6
2	6.86
3	38.0
4	9.36
5	13.4
6	14.0
7	8.57
8	6.58
9	10.4
10	18.1
11	8.69
12	<0.10
13	<0.10
14	<0.10
15	<0.10
16	<0.10
17	<0.10
18	<0.10
19	<0.10
20	<0.10
21	<0.10
22	<0.10
23	<0.10
24	<0.10
25	<0.10
26	<0.10
27	<0.10
28	<0.10
29	<0.10
30	2.43
31	0.86
32	<0.10
33	<0.10
34	<0.10
35	<0.10
36	<0.10

clarify an origin of 1,4-dioxane in leachate from landfill. Any difference was not observed between the Japan Standard Leaching Test for Wastes, which was applied to samples #1-11, and the static leaching test, which was applied to samples #12-36, according to the result that concentrations of 1,4-dioxane in aqueous solutions (300 mL) obtained from plastic samples #17, 23, and 31 (each 30 g) by the Japan Standard Leaching Test for Wastes were <0.10 μg/L, <0.10 μg/L, and 0.92 μg/L, respectively.

The results of leaching tests are shown in Table 4. Fly ash (sample #1) and bottom ash (sample #2) from the Incinerator E, bottom ash from the Incinerator C (sample #8) contained 1,4-dioxane. Various waste plastics sampled at the Landfill B (sample #3-6), which have been pressed under heating and crushed into pieces, and waste plastics, pressed under heating, sampled at the factories D (sample #9-11) and F (sample #7) also contained 1,4-dioxane. However, all plastic wastes sampled at the Factory D (sample #12-36) without heating process, did not contain any 1,4-dioxane except for two samples (samples #30 and #31). Therefore, heating process appears to produce 1,4-dioxane. The formation mechanism of 1,4-dioxane in landfill or disposal process of waste plastics is still unknown.

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