PERGAMON

Chemosphere 42 (2001) 415–418

CHEMOSPHERE

Bisphenol A in hazardous waste landfill leachates

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Received 8 December 1999; accepted 7 March 2000

Abstract

The levels of bisphenol A in hazardous waste landfill leachates collected in Japan in 1996 were determined by gas chromatograph/mass spectrometer (GC/MS). Bisphenol A was found in seven of 10 sites investigated. All the hazardous waste landfills with leachates contaminated by bisphenol A were controlled. The concentrations of bisphenol A ranged from 1.3 to 17,200 μg/l with a median concentration of 269 μg/l. The source of bisphenol A in landfill leachates may be the waste plastics in waste landfill. The concentrations of bisphenol A in some samples exceeded the EC_{50} or LC_{50} levels for aquatic biota. Landfill leachates may be a significant source of bisphenol A found in the environment.

Keywords: Bisphenol A; Endocrine disrupting chemicals; Hazardous waste landfill leachate; GC/MS

1. Introduction

Bisphenol A, 4,4′-(1-methylethylidene)bisphenol (CAS No. 80-05-7), is used as a monomer for polycarbonate or epoxy resin production. It is also used as an antioxidant or stabilizing material for plastics (Ash and Ash, 1995). Bisphenol A has a weak acute toxicity to aquatic biota. Examples of LC_{50} values are 1.1 mg/l for shrimp and 4.7 mg/l for minnow (Alexander et al., 1998) and of EC_{50} values are 10 mg/l for water flea and 1.0–3.1 mg/l for green algae. Bisphenol A also shows estrogenicity (Krishnan et al., 1993). Krishnan et al. (1993) reported that bisphenol A that had migrated from polycarbonate flasks increased the rate of proliferation of human breast cancer cells MCF-7. Therefore migration of bisphenol A from several kinds of plastic to foodstuffs is a significant problem (Brotons et al., 1995; Biles et al., 1997). Very few studies have been done on the environmental occurrence of bisphenol A. Kamiura et al. (1997) reported that the levels of bisphenol A in air ranged from 2.9 to 3.6 ng/m^3. Recently, the Environment Agency of Japan reported that environmental pollution by bisphenol A is widespread in Japan. The levels of bisphenol A in freshwater and sea water samples ranged from 0.010 to 0.268 μg/l (Environment Agency of Japan, 1997). Bisphenol A was also found in sediments and fish. Though these levels are lower than the toxic levels mentioned above, pollution by bisphenol A may be a significant environmental problem because of its estrogenic properties. The sources of bisphenol A found in environmental samples are not well described. One of the most likely sources is the leachate from hazardous waste landfill. When waste plastics containing bisphenol A are buried in a landfill, a hydrolytic or leaching process may occur to release the bisphenol A from these wastes to the leachate. Yasuhara et al. reported on the organic components of hazardous waste landfill leachates collected in Japan in 1994 and 1995. Bisphenol A was found at five sites out of the eight that were investigated in 1994. The concentration of bisphenol A ranged from 0.15 to 12.3 μg/l (median: 0.35 μg/l) (Yasuhara et al., 1997). In the study carried out in 1995, bisphenol A was found at seven sites out of 11, and the

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0045-6535/01/$ - see front matter
PII: S0045-6535(00)00079-5

levels of bisphenol A ranged from 6.32 to 2980 μg/l (median: 61.4 μg/l) (Yasuhara et al., 1999). These levels are much higher than the environmental levels of bisphenol A reported by the Environment Agency of Japan.

In this paper, the results of the investigation carried out in 1996 are presented.

2. Experimental

2.1. Samples and materials

Leachate samples were collected in the summer of 1996. The properties of the waste landfills and leachates are listed in Table 1. Landfills are classified into three types depending on the waste content: open landfills, controlled landfills, and closed landfills. Wastes such as metal cans and glass bottles are buried in open landfills. Highly toxic wastes, such as soils contaminated heavy metal, are buried in closed landfills where the wastes are completely isolated from the outer environment. Weakly or potentially toxic wastes, such as incinerator ash, are buried in controlled landfills. Controlled landfills are equipped with leachate treatment facilities. One of the sites examined in this study was an open landfill (#1) and the others were controlled. Reclamation has been completed in four sites (#4, #6, #7 and #10). All leachate samples were kept at 4°C and sent to the National Institute for Environmental Studies within a day of collection.

Dichloromethane, acetone, sodium chloride and anhydrous sodium sulfate were of pesticide analysis grade and purchased from Wako Pure Chemical Industries, Japan. Hydrochloric acid was of analytical grade. Bisphenol A was purchased from Wako Pure Chemicals Industries. For preparing the standard stock solution, bisphenol A (50 mg) was dissolved in acetone (50 ml). Standard solutions for calibration were prepared by diluting the standard stock solution with acetone.

2.2. Methods

Sodium chloride (50 g) was added to the leachate sample (500 ml) and completely dissolved. The leachate was then acidified with hydrochloric acid and extracted twice with dichloromethane (50 ml) by shaking for 5 min. The combined extracts were dried with anhydrous sodium sulfate, evaporated to ca. 5 ml by rotary evaporation, transferred to a test tube and concentrated to 1 ml under a flow of nitrogen. The concentrated extract was analyzed by gas chromatograph/mass spectrometer (GC/MS). An HP Model 5890A (Hewlett–Packard, USA) gas chromatograph equipped with a splitless injector (250°C) and a PTE-5 capillary column (Supelco, USA, 30 m × 0.25 mm i.d., 0.25 μm film thickness) was

Table 1
Properties of hazardous waste landfill sites and leachates

Sites	1	2	3	4	5	6	7	8	9	10
Contents of wastes	Waste plastics, construction waste, waste rubber, scrap metal,	Domestic incombustible waste, incinerator ash	Coal ash, slag, sewage sludge, construction waste	Incinerator ash, incombustible waste	Waste plastics, sewage sludge, slag, construction waste, waste glass	Waste plastics, waste rubber, incinerator ash, waste ceramics, construction waste	Waste plastics, paper, wood, waste rubber, scrap metal,	Waste plastics, rubber waste, incinerator ash, scrap metal	Domestic incombustible waste, incinerator ash, construction waste	Domestic incombustible waste, incinerator ash, construction waste
Landfill type	Open	Controlled	Controlled	Controlled	Controlled	Controlled	Controlled	Controlled	Controlled	Controlled
Reclamation	Continuing	Continuing	Continuing	End in 1995/3	Continuing	End in 1984/1	End in 1993/3	Continuing	Continuing	End in 1987/3
pH	7.0	7.9	9.1	7.5	7.1	6.9	8.1	7.2	7.9	7.4
SS (mg/l)	15	3.8	69.1	4	24.3	23.7	18	3.5	37.3	24.3
TOC (mg/l)	6.9	33.5	11.8	39	132	16.5	25.3	10.3	104	107
BOD[a] (mg/l)	8.6	20.8	6.3	54.9	46.7	5.7	18	5.6	118	23.6

[a] 5 days, 20°C.

used. Helium was used as the carrier gas with a flow rate of 1 ml/min. The initial column temperature was 50°C and was raised to 250°C at a rate of 6°C/min and then held for 5 min. For quantitative analysis, a JMS-DX302 mass spectrometer (JEOL, Japan) was used in selected ion monitoring (SIM) mode. Ionization was by EI (70 eV). The ionization current was 300 μA. The ionization chamber temperature was maintained at 230°C. Mass numbers of monitored ions were *m/z* 213 and 228. For qualitative analysis, the mass spectrometer was operated in scan mode and the scan range was from *m/z* 35–500.

3. Results and discussion

The concentrations of bisphenol A in hazardous waste landfill leachates are shown in Table 2. Bisphenol A was found at seven sites out of the 10 that were investigated. The concentrations of bisphenol A ranged from 1.3 to 17,200 μg/l. The median concentration was 269 μg/l. The total ion chromatogram of landfill leachate extract #9 is presented in Fig. 1. In comparing these results with those reported by Yasuhara et al. (1997, 1999) investigated in 1994 and 1995, the detection frequency is almost the same and the maximum and median concentrations have increased much. In 1994, the maximum and median concentrations of bisphenol A were 12.3 and 0.35 μg/l (Yasuhara et al., 1997), respectively. In 1995, they were 2980 and 61.4 μg/l (Yasuhara et al., 1999). Since the waste landfills investigated in this study are not the same as those reported previously, it is difficult to be sure whether pollution by bisphenol A is worsening. Several landfills were investigated repeatedly. Landfill #4 (1.3 μg/l) was investigated in 1994 and 1995, the levels of bisphenol A in the leachates from this landfill were 12.3 and 61.4 μg/l, respectively. Landfill #5 (6960 μg/l) was investigated in 1995, the level of bisphenol A was 2980 μg/l. Landfill #8 (1.6 μg/l) was also investigated in 1994 and 1995, the levels were 0.8 and 2.36 μg/l, respectively. Yamada et al. (1999) reported the levels of bisphenol A in leachates from seven landfill sites. The levels of bisphenol A ranged from not detected (detection limit is not presented) to 5400 μg/l.

Table 2
Concentrations of bisphenol A in hazardous waste landfill leachates

No.	Bisphenol A (μg/l)	No.	Bisphenol A (μg/l)
1	nd[a]	6	269
2	nd	7	330
3	nd	8	1.6
4	1.3	9	17,200
5	6960	10	50.8

[a] Detection limit is 0.5 μg/l.

The levels of bisphenol A in hazardous waste landfill leachates depend on the kind of waste reclaimed in the landfills. Yamamoto and Yasuhara (1999) reported that some kinds of waste plastics collected at a waste landfill site contained bisphenol A and it readily migrated to water. The levels of bisphenol A leached from several waste plastics (cord covering or synthetic leather) ranged from 700 to 12,300 μg/l. Therefore waste plastics might be an important source of bisphenol A found in landfill leachate. As waste plastics or domestic incombustible waste (mainly waste plastics) was the major type of waste in landfills #5 and #9, these landfill leachates are polluted by bisphenol A to high levels (6960 and 17,200 μg/l, respectively). On the other hand, at landfill #3, coal ash or slag was mainly buried. Since these wastes do not

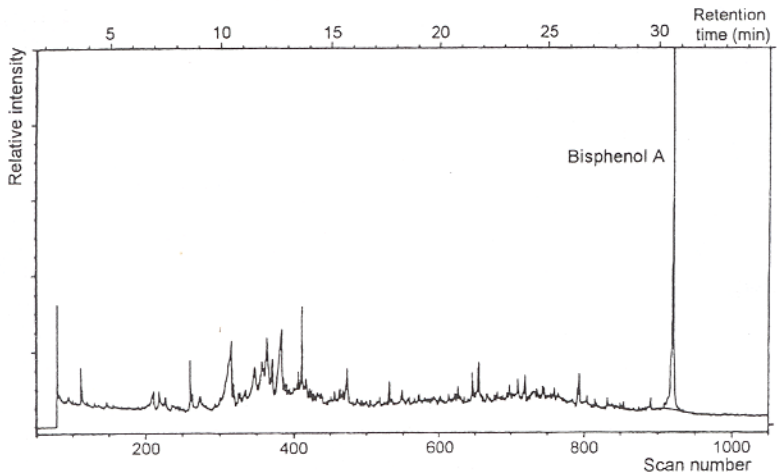

Fig. 1. Total ion chromatogram of landfill leachate extract #9.

contain bisphenol A, this compound was not found in leachate #3. The TOC and BOD values in the leachates which are highly contaminated by bisphenol A were relatively high. But there seems to be no obvious relationship between TOC or BOD values and bisphenol A levels.

The concentrations of bisphenol A in leachate #5 and #9 exceeded the LC_{50} or EC_{50} values for aquatic organisms mentioned above. Krishnan et al. (1993) reported that 10–25 nmol/l (2.3–5.7 μg/l) of bisphenol A induced progesterone receptors in cultured MCF-7 cells. They also reported that 25 nmol/l of bisphenol A increased the rate of proliferation of MCF-7 cells (Krishnan et al., 1993). The concentration of bisphenol A in leachate #5, #6, #7, #9 and #10 exceeded these values. Therefore, these landfill leachates may be estrogenic. Moreover, hazardous waste landfill leachates also contain many chemicals such as alkylphenols or phthalate esters which are potentially estrogenic (Yasuhara et al., 1999). Therefore hazardous waste landfill leachates may be one of the important sources of endocrine disrupting chemicals found in the environment.

All leachates found to be contaminated with bisphenol A were from controlled landfills. Since the leachate from a controlled landfill is treated in a water treatment facility before being discharged, the concentration of bisphenol A in the discharged water may be less. Yamada et al. (1999) reported that bisphenol A in landfill leachates was easily removed by water treatment. The concentrations of bisphenol A in influent and effluent of a certain water treatment facility (biological treatment, coagulating sedimentation and activated carbon absorption) were 3400 and 0.5 μg/l, respectively. Shindo et al. (1998) reported that the concentrations of bisphenol A in effluents from waste disposal sites ranged from not detected (detection limit is 1 ng/l) to 67.1 μg/l. Since the concentrations in these effluents are lower than these in landfill leachates, water treatment is effective in reducing contamination by bisphenol A. However, because these concentrations are still higher than these found in environmental samples, landfill leachates are likely to be an important source of the bisphenol A found in the environment.

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