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Journal of Chromatography A, 774 (1997) 321–332

JOURNAL OF
CHROMATOGRAPHY A

Determination of organic components in leachates from hazardous waste disposal sites in Japan by gas chromatography–mass spectrometry

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Abstract

This investigation was aimed at detecting the presence of several organic substances in landfill leachates in Japan. Approximately 190 compounds were detected using several analytical methods. High amounts of organic phosphates and phthalates were detected which originate from plastic additives. 1,4-Dioxane was detected in a range of 14–10 900 ng l⁻¹ in most leachates. Its origin is unknown. Only a few species of halogenated volatile organic substances were detected. A few species of chemicals used in agriculture such as pesticides were detected for the first time in Japan.

Keywords: Waste leachates

1. Introduction

In Japan, half of the wastes produced are incinerated and the other half is buried in landfills, without incineration. The fly ash and bottom ash from incinerators are disposed of in landfills. The wastes management act in Japan [1] classifies three types of landfills: open landfills, controlled landfills, and closed landfills, depending of the waste contents.

Wastes such as metal cans and glass bottles are buried in open landfills. Highly toxic wastes such as soils contaminated with polychlorinated biphenyls (PCBs) are buried in closed landfills. Weakly toxic or potentially toxic wastes such as incinerator ash or sewage sludges are buried in controlled landfills. The wastes which should be buried in an open landfill are very often buried in a controlled landfill, because an appropriate site for an open landfill is not available. Leachates from open or controlled landfills are expected to contain various types of chemicals. For

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waste management and regulating purposes, it is important to determine if landfill leachates are safe for human health and for other life forms. Identification of chemical components in leachates, their quantification, and toxicological information are essential to obtain reliable information on impact on human health. Several investigators have reported concentrations of chemical components in landfill leachates in America and in Europe [2–5]. However, only a few investigations have been reported in Japan [6,7]. A monitoring program for chemical components in leachates has started in 1994 in Japan to determine the number of species and their present concentrations of several chemicals in landfill leachates. This paper is an interim report on the program.

2. Experimental

2.1. Materials and samples

A flowchart of sample preparation is shown in Fig. 1. Leachates were sampled from eight landfills located in various area in Japan, whose details are shown in Table 1. One of the sites is an open landfill and the others controlled landfills. Reclamation has been accomplished at two sites (Nos. 3 and 6). All sites, managed legally, were ones recommended as a representative landfill by several local governments. All leachate samples were sent to National institute for Environmental Studies under cooling at 4°C within a day and 3 l of samples were delivered to the analytical institutes under cooling at 4°C within 2 days.

Dichloromethane, diethyl ether, hexane, acetone, ethanol, sodium chloride and anhydrous sodium sulfate were of pesticide grade (Wako, Osaka, Japan). Compounds used for identification and quantifications were purchased from Wako, Tokyo Kasei Industries (Tokyo, Japan) and Hayashi (Osaka, Japan). All the water used was distilled water purified through a Milli-Q System (Millipore, USA).

2.2. Determination of suspended solids (SS) (method 1)

Appropriate volumes of leachate were filtered with membrane filters (pore size, 0.45 μm; diameter, 47 mm), previously washed with 100 ml of pure water and oven-dried at 110°C, 1 h prior to filtering. After filtration, the filters were dried at 110°C for 2 h, followed by weighing on an analytical valance. The concentration of SS was calculated according to the following equation:

$$\text{Concentration (mg/l)} = 1000(A - B)/V$$

where *A*, *B* and *V* represent, respectively, the mass of filter+SS, the weight of the filter before filtration, and the volume of leachate filtered. The measurements were performed three times and the results were averaged.

2.3. Chemical oxygen demand (COD) (method 2)

Fifty millilitres of leachates were diluted with pure water to a total volume of 100 ml. Five ml of silver nitrate aqueous solution at a concentration of 200

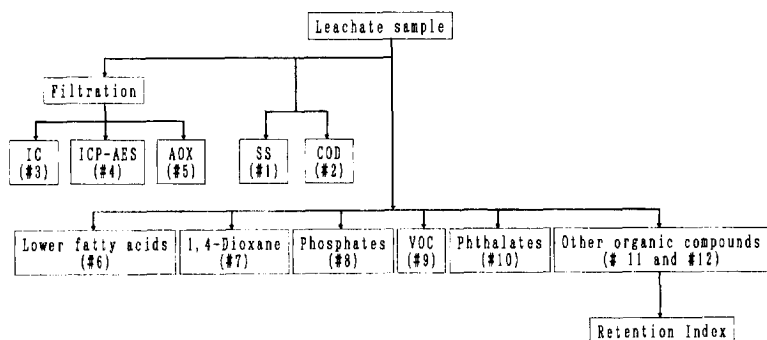


Fig. 1. Flowchart of sample preparation and analysis; method number is shown in parentheses.

Table 1
Details of landfill site and leachate

	Sample							
	1	2	3	4	5	6	7	8
Contents of wastes	Domestic incinerator ash from incinerator	Domestic incinerator, combustible waste, ash from incinerator, sewage sludge	Coal ash, slag	Waste plastics, metal waste, rubber waste, combustion residue	Ash from incinerator, sludge, waste plastics, building materials, waste	Waste plastics, rubber waste, metal waste, waste glasses, building materials, waste ceramics, building materials, waste	Ash from incinerator, domestic incinerator, waste, sewage sludge	Ash from incinerator, incombustible waste, waste plastics
Landfill type	Controlled	Controlled	Controlled	Controlled	Controlled	Open	Controlled	Controlled
Landfill situation	Under reclamation now	Under reclamation now	5 years after completion of reclamation	Under reclamation now	Under reclamation now	5 years after completion of reclamation	Under reclamation now	Under reclamation now
Odor	Odorless	Rotten odor	Odorless	Faint odor	Odorless	Burnt odor	Weakly rotten odor	Burnt odor
Color	Pale yellow	Black	Colorless	Pale yellow	Pale yellow	Brown	Pale yellow	Yellow-brown
BOD (mg l ⁻¹)	7.60	181.0	1.3	22.0	24.2	8.1	5.6	36.0
COD (mg l ⁻¹)	24.8	150.0	3.7	25.0	26.0	118.0	30.0	76.0
EC (mS cm ⁻¹)	8.3	28.5	3.7	1.2	19.0	2.8	8.2	25.3
TOC (mg l ⁻¹)	20.3	154.0	1.0	210.0	25.5	28.5	27.2	57.4
pH	7.47	7.48	10.7	7.94	10.6	6.8	7.38	7.36
SS (mg l ⁻¹)	6	250	5	51	14	418	6	153
AOX (μg l ⁻¹)	120	245	85.2	228	21.5	88.4	106	459

Abbreviations: BOD, biological oxygen demand; COD, chemical oxygen demand; EC, electric conductivity; SS, suspended solids; AOX, adsorbable organic halogens.

g l^{-1} and 10 ml of diluted sulfuric acid, prepared by mixing sulfuric acid and water at a ratio of 1:2, were added to the sample solution. Then, 10 ml of 5 mM KMnO_4 aqueous solution was added and heated for 30 min in a boiling water bath. Ten ml of 12.5 mM sodium oxalate aqueous solution was added. The solution was titrated with 5 mM KMnO_4 aqueous solution at a temperature of 60°C. For a blank test, pure water was used as a sample. The COD value was calculated from the following equation:

$$\text{COD} = 0.2(A - B)f/V$$

where 0.2, A , B , f and V represent, respectively, oxygen amount (mg) in 1 ml of 5 mM KMnO_4 aqueous solution, the volume (ml) of 5 mM KMnO_4 solution used in sample titration, the volume (ml) of 5 mM KMnO_4 solution used in blank titration, factor of 5 mM KMnO_4 solution and the volume (l) of sample leachate.

2.4. Ion chromatography (method 3)

Fifty millilitres of leachates were filtered on a 0.45- μm pore size membrane filter and a 50- μl aliquot of the filtered leachate was injected into a Dionex DX-100 ion chromatograph for fluoride, chloride, bromide, nitrate and sulfate analysis. The column was a model AS4A (250 mm \times 4 mm I.D.) from Dionex. The eluent was 1.8 mM sodium carbonate and 1.7 mM sodium bicarbonate at a flow-rate of 1.5 ml min^{-1} .

2.5. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) (method 4)

Fifty millilitres of leachates were filtered on a 0.45- μm pore size membrane filter before measurements. A Jarrell-Ash Model 750 ICP-AES was used under the following conditions: frequency, 27.12 MHz; radio frequency power, 1.1 kW; flow-rate of coolant gas (Ar), 20 l min^{-1} ; carrier gas flow-rate, 0.5 l min^{-1} ; observation height above coil, 18 mm; sample uptake rate, 1.2 ml min^{-1} ; integration time, 5 s. Analyzed elements were Al (0.03–300), As (0.001–1.0), Ba, (0.005–100), Be (0.005–100), Cd (0.005–100), Ca 80.05–300, Cr (0.01–100), Co (0.01–100), Cu (0.01–100), Fe (0.01–200), Pb (0.01–50), Mg (0.003–60), Mo (0.02–100), Ti

(0.01–100), Mn (0.005–100), Ni (0.01–100), K (1–500), Se (0.001–1), Na (0.5–300), V (0.02–200), Zn (0.01–100), B (0.005–100) and Sr (0.003–70), where quantitative ranges (mg l^{-1}) are shown in parentheses As and Se were determined by hydride generation method and Pb was measured by an ultrasonic nebulizer system. Calibration curves were made using 100 mg l^{-1} solutions of Na, K and Ca in 1% nitric acid aqueous solution, 10 mg l^{-1} solutions of other elements in 1% nitric acid aqueous solution and 1% nitric acid aqueous solution as a zero concentration..

2.6. Adsorbable organic halogens (AOX) (method 5)

Fifty millilitres of leachates were acidified with nitric acid, then passed at a flow-rate of 3.3 ml min^{-1} through two columns in series, each packed with 40 mg of activated charcoal. Next, 4 ml of KNO_3 aqueous solution (5 g l^{-1} as NO_3) was passed through the columns at a flow-rate of 2 ml min^{-1} to eliminate inorganic halide ions. Both columns were combusted separately at 900°C in a quartz container under oxygen flow. The incineration exhaust gas was passed through a electrolytic solution, made of 85% acetic acid and 0.136% sodium acetate, after removal of water in the gas by passing the gas through conc. H_2SO_4 . Concentration of halide anions in the electrolytic solution was determined by electrolysis titration using silver electrode using a Mitsubishi Kagaku Titration Model TOX-10. Duplicate measurements were done for each sample.

2.7. Lower fatty acid analysis by GC (method 6)

Ten millilitres of leachates were filtered on a 0.45- μm pore size membrane filter, then 10 μl of conc. phosphoric acid was added to a 1 ml aliquot of the filtered leachate. One microliter of this solution was directly injected into the GC system. The GC conditions were as follows: Instrument, Shimadzu GC15A; column, J&W DB-FFAP (30 m \times 0.53 mm I.D.); column temperature, 100°C for 1 min, 6°C min^{-1} ramp to 160°C, hold for 1 min; carrier gas, He, flow-rate, 12.5 ml min^{-1} ; injection temperature, 200°C; flame ionization detector, temperature, 200°C. Target compounds were acetic acid, propion-

ic acid, isobutyric acid, butyric acid, isovaleric acid, valeric acid, isocaproic acid and caproic acid. Quantitation limit for each acid was 1 mg l^{-1} .

2.8. Determination of 1,4-dioxane (method 7)

One microgram of fully deuterated 1,4-dioxane spike was added to 200 ml of leachate after addition of sodium sulfate (30 g), followed by extraction with dichloromethane (40 ml) for 10 min. After separation of organic layer, the aqueous layer was extracted again with dichloromethane (20 ml). After separation of small amount of water by centrifugation, the combined organic layers were dried by passing through a layer of anhydrous sodium sulfate (30 g). This solution was concentrated to 1 ml using a rotary evaporator. Two microlitres of this solution were injected into a GC-MS. The running conditions were: Instrument, JEOL Model Automass 50; column, DB-1 ($30 \text{ m} \times 0.53 \text{ mm I.D.}$, $d_f = 3 \text{ } \mu\text{m}$); column temperature, 30°C for 2 min, $10^\circ\text{C min}^{-1}$ ramp to 100°C , hold for 2 min, followed by a second ramp of $20^\circ\text{C min}^{-1}$ to 200°C for 1-min hold; carrier gas (He) pressure, 7 p.s.i. (1 p.s.i. = 6894.76 Pa) at column head; injection temperature, 200°C ; 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.

2.9. Determination of organic phosphate by GC using flame photometric detection (method 8)

Three liters of leachates were extracted with dichloromethane (200 ml) for 15 min, and the organic layer was allowed to separate for 30 min. The aqueous layer was extracted again with dichloromethane (100 ml) following the same procedure. The organic layers were combined and dried with anhydrous sodium sulfate. The solution was concentrated to 2–4 ml by using a Kuderna-Danish concentrator under atmospheric pressure. After 3–5 ml of hexane was added to the concentrated solution, the solution was concentrated again to 3 ml by blowing nitrogen gas. When sulfur interfered with analysis, it was removed by mixing the extracted solution with copper powder in presence of small amount of water. The solution was combined with 5 ml of hexane,

dried by passing through a layer of anhydrous sodium sulfate (4 g) and concentrated to 3 ml by blowing nitrogen gas. Target compounds for analysis were triethyl phosphate, tributyl phosphate, tris(2-chloroethyl) phosphate, tris(2-chloropropyl) phosphate, tris(1,3-dichloro-2-propyl) phosphate, triphenyl phosphate, tris(2-butoxyethyl) phosphate, tris(2-ethylhexyl) phosphate, and tricresyl phosphate which is a mixture of many isomers. Quantification limits ranged from $2\text{--}15 \text{ ng l}^{-1}$. GC conditions were: instrument, HP5890A; column, J&W DB-1 ($30 \text{ m} \times 0.25 \text{ mm I.D.}$, $d_f = 0.25 \text{ } \mu\text{m}$); column temperature, 60°C for 1 min, $20^\circ\text{C min}^{-1}$ ramp to 180°C , followed by a second ramp of 2°C min^{-1} to 220°C , and finally a third ramp of 5°C min^{-1} to 280°C for 1-min hold; carrier gas, He, flow-rate, 1.4 ml min^{-1} ; injection mode, splitless; injection and detector temperatures, 280°C .

2.10. Determination of volatile organic compounds (VOCs) (method 9)

VOCs in leachates were analyzed immediately after sampling by automatic analytical system without removal of SS. The system was composed of Tekmar Model LSC-3000 purge-and-trap apparatus, HP5890 gas chromatograph and JEOL Automass mass spectrometer. The operational conditions were: sample temperature, 40°C ; sample volume, 5 ml; purge period for vaporization, 16 min; purge flow-rate, 35 ml min^{-1} ; cryo-focus temperature, -130°C ; purge period for drying, 2.5 min; desorption temperature, 220°C ; desorption time, 6 min; injection port temperature, 200°C ; injection time, 2.5 min; trap material, Tenax GR; baking temperature for trap material, 235°C ; baking time for trap material, 18 min; GC column, Aquatic ($60 \text{ m} \times 0.25 \text{ mm I.D.}$, $d_f = 1.0 \text{ } \mu\text{m}$); column temperature, 40°C for 1 min, followed by a 4°C min^{-1} ramp to 100°C , and a second ramp of 8°C min^{-1} to 200°C for 1-min hold; carrier gas, He, pressure, 1.2 kg/cm^2 at column head; interface temperature between GC outlet and MS inlet, 200°C ; ionizing current, 300 μA ; ionizing energy, 70 eV; scan speed, 30 ms/scan; ion-source temperature, 200°C . Target compounds: dichloromethane, chloroform, carbon tetrachloride, bromodichloromethane, chlorodibromomethane, bromoform, 1,2-dichloroethane, 1,1-dichloroethene, (Z)- and (E)-

1,2-dichloroethenes, 1,1,1- and 1,1,2-trichloroethanes, trichloroethene, tetrachloroethene, (Z)- and (E)-1,3-dichloropropenes, *p*-dichlorobenzene, benzene, toluene, *o*-, *m*- and *p*-xylenes.

2.11. Determination of phthalates by GC–MS (method 10)

Phthalates were determined according to the Japan official method for bis(2-ethylhexyl) phthalate [8]. Leachate (40 ml) was shaken vigorously with hexane (5 ml) after dissolution of sodium chloride (10 g). One microliter of the separated hexane layer was injected into the GC system. The operational conditions were: Instrument, Shimadzu QP5000 mass spectrometer; column, 5% phenylmethylsilicone (25 m×0.33 mm I.D., $d_f=0.5\ \mu\text{m}$); column temperature, 140°C for 2 min followed by a 15°C min⁻¹ ramp to 250°C for 16 min hold; injector temperature, 220°C; carrier gas, He, flow-rate, 1.6 ml min⁻¹ (flow velocity, 48 cm s⁻¹); injection mode, splitless; ion source temperature, 250°C; ionizing energy, 70 eV. Target compounds were dimethyl phthalate (quantification limit, 1 μg l⁻¹), diethyl phthalate (0.5 μg l⁻¹), diisobutyl phthalate (0.3 μg l⁻¹), dibutyl phthalate (2.5 μg l⁻¹), benzyl butyl phthalate (1 μg l⁻¹), diheptyl phthalate (2 μg l⁻¹), dicyclohexyl phthalate (1 μg l⁻¹), bis(2-ethylhexyl) phthalate (2.5 μg l⁻¹), dioctyl phthalate (2 μg l⁻¹) and dinonyl phthalate (2 μg l⁻¹).

2.12. Simultaneous determination of multi-components by GC–MS (methods 11 and 12)

Several hundreds of organic compounds were selected as target substances for long-term monitoring [9], including a priority list [10] for hazardous compounds, edited by the Japan Environment Agency. Two methods, 11 and 12, were used for this purpose.

In method 11, 50 g of NaCl were added to 1 l of leachate, followed by two successive extractions with dichloromethane (100 ml and 50 ml). The organic layers were combined, dried with anhydrous sodium sulfate, and concentrated to around 5 ml with a Kuderna-Danish concentrator under atmospheric pressure. Internal standards of [²H₈]naphthalene,

[²H₁₀]acenaphthene, [²H₁₀]phenanthrene, [²H₁₀]fluoranthene, and [²H₁₂]chrysene solutions (100 ng ml⁻¹ in acetone each, 0.5 ml each) were added to the concentrated extracts. These solutions were further concentrated to 0.2 ml by blowing nitrogen and 1 μl of an aliquot was injected in a GC system. Quantification was carried out by calculating the ratios of target compound to internal standards by peak areas. Co-injection technique [11], where standard solution was injected in a GC system with small amount of polyethylene glycol (average M_r range 200–300) was used to correct abnormal change of peak area by matrix effects observed in actual samples. The GC–MS operational conditions were: instrument, a JEOL DX-303 MS equipped with a HP5790 GC; column, crosslinked 5% phenyl methyl silicone (25 m×0.31 mm I.D., $d_f=0.52\ \mu\text{m}$); column temperature, 60°C for 2 min followed by a 3°C min⁻¹ ramp to 270°C for 10-min hold; injector temperature, 250°C; carrier gas, He, flow rate, 2.0 ml min⁻¹ at 50 kPa; injection mode, splitless; ion source temperature, 250°C; ionizing energy, 70 eV.

In method 12, fractionation by silica gel column chromatography was used for accurate quantification. After addition of 150 g of NaCl to 1.5 l of leachate, the solution was successively extracted with dichloromethane (100 and 50 ml). Twenty milliliter of hexane was added to the combined organic layers. The solution was concentrated to ~1 ml using a rotary evaporator, followed by drying with anhydrous sodium sulfate. Hexane (10 ml) was added to the concentrated extracts and the solution was concentrated again, similarly to above, to remove traces of dichloromethane. The concentrated extracts were subjected to column chromatography using silica gel containing 5% water. Elution solvents were hexane (20 ml) for fraction 1, 10% acetone in hexane (20 ml) for fraction 2, and 5% ethanol in benzene (20 ml) for fraction 3. Each fraction was concentrated to 0.2 ml by a rotary evaporator and blowing nitrogen and 1 μl of the concentrated solutions was injected into a GC. The GC–MS operational conditions were: Instrument, a JEOL DX-303 MS equipped with a HP5890 GC; column, methyl silicone (15 m×0.25 mm I.D., $d_f=0.25\ \mu\text{m}$); column temperature, 50°C for 2 min followed by a 20°C min⁻¹ ramp to 120°C, and a second ramp of 7°C min⁻¹ to 310°C for 10-min hold; injector temperature, 250°C; carrier gas,

He, head pressure, 70 kPa; injection mode, splitless; ion source temperature, 240°C; ionizing energy, 70 eV.

2.13. Calculation of retention index

Retention indices were very important to confirm and to assign peaks. Retention indices used in this study for programmed temperature GC were defined by Guiochon [12]. A number of retention index data stored in the library search system of mass spectra [13], developed both by National Institute for Environmental Studies in Japan and the Japan Environment Agency, were used effectively for peak assignment.

3. Results and discussion

This was the first study in Japan that revealed the presence of several hundreds of chemical components in landfill leachates. Leachates 2 and 4 contained higher amounts of organic substances than

other six leachates, judging from their TOC values in Table 1. The TOC values in Table 1 were near to the lower values of those reported in the literature [14]. Leachates with high SS values (samples 2, 6 and 8) also showed high COD values. Relationship between TOC and AOX were not observed as reported elsewhere [15]. High pH values in leachates from sites 3 and 5 were due to high concentrations of alkaline metals in ash.

It is noteworthy that boron concentrations were high in all leachates (Table 2) from a point of view of regulation in the Japan wastewater act (limit: 0.2 mg l⁻¹). It is well known that coal ash or municipal incinerators ash is one of the sources for boron [16,17]. Concentration levels of inorganic components were similar to those found in other countries [2,3]. Their levels were under the regulation limits in the Japan wastewater act except for boron. The high salinity of the leachates (Table 2) is an important problem for irrigation and plant growth.

Results of organic substance analysis are shown in Table 3, where the substances detected are listed according to order of high detection ratio which is

Table 2
Concentrations (mg l⁻¹) of inorganic components in leachates

	Sample							
	1	2	3	4	5	6	7	8
Al	0.30	0.40	6.2	0.20	1.4	0.47	0.20	0.80
As	nd	nd	0.027	nd	0.002	nd	nd	0.001
B	2.7	1.4	30	0.63	5.9	0.64	0.47	1.1
Ba	0.64	3.7	0.22	0.14	1.8	0.45	0.94	2.6
Ca	270	730	130	68	1500	370	280	980
Cd	nd	nd	nd	nd	nd	nd	nd	nd
Cu	0.06	nd	nd	nd	0.10	nd	nd	0.07
Fe	0.10	0.17	0.07	nd	0.26	0.13	0.07	0.43
K	220	1500	63	8	320	31	340	1900
Mg	120	85	0.4	70	2.1	44	27	47
Mn	2.3	3.6	0.01	0.16	0.05	0.89	2.4	11
Mo	nd	nd	3.3	nd	1.3	nd	nd	nd
Na	1100	4700	620	59	2500	240	1200	3600
Se	nd	nd	0.06	nd	nd	nd	nd	nd
Si	15	7.6	4.3	24	5.4	30	10	6.5
Sr	1.2	6.6	4.4	0.66	16	0.46	1.8	0.35
V	nd	nd	0.80	nd	0.20	nd	nd	0.20
Zn	0.10	nd	nd	nd	nd	nd	0.05	nd
Cl ⁻	2567	10 813	397	50.7	4980	49.6	2645	7834
NO ₃ ⁻	51.5	nd	nd	14.7	nd	15.5	105	nd
SO ₄ ²⁻	97.1	230	930	nd	537	1463	57.6	324

Table 3
List of compounds detected in landfill leachates

Name	Molecular formula	GC retention index		CAS reg. number	Det. ratio ^a (%)	Conc. range ^b (ng l ⁻¹)	Median conc. (ng l ⁻¹)	Method
		OV-1	5% Ph					
Aniline	C ₆ H ₇ N		977	62-53-3	100	15.1–3380	113	11
Tris(2-butoxyethyl) phosphate	C ₁₈ H ₃₉ O ₇ P	2364	2425	78-51-3	100	11.8–2320	260	8
Tris(1,3-dichloro-2-propyl) phosphate	C ₉ H ₁₅ Cl ₆ O ₄ P	2254	2329	13674-87-8	100	2.8–1890	99.2	8
3,5-Xylenol	C ₈ H ₁₀ O		1171	108-68-9	100	5.2–1360	30.9	11
<i>o</i> -Chloroaniline	C ₆ H ₆ ClN		1126	95-51-2	100	1.6–1590	37.9	11
<i>p</i> - <i>tert</i> -Butylphenol	C ₁₀ H ₁₄ O		1297	98-54-4	100	1.2–451	69.5	11
2-Methylnaphthalene	C ₁₁ H ₁₀	1277	1286	91-57-6	100	39.7–202	101	11
Benzothiazole	C ₇ H ₅ NS	1187	1220	95-16-9	100	16.9–281	83.6	11
Toluene	C ₇ H ₈		<900	108-88-3	100	10–180	65.5	9
1-Methylnaphthalene	C ₁₁ H ₁₀	1293	1301	90-12-0	100	24.7–95.5	61.3	11
2,6-Dimethylnaphthalene	C ₁₂ H ₁₂		1394	581-42-0	100	2.6–26.2	15.5	11
Fluorene	C ₁₁ H ₁₀		1568	86-73-7	100	0.5–43.1	3.7	11
Benzonitrile	C ₇ H ₅ N		981	100-47-0	100	0.5–5.1	2.9	11
Tris(2-chloroethyl) phosphate	C ₆ H ₁₂ Cl ₃ O ₄ P	1702	1766	115-96-8	100	17–907	343	8
4-Methyl-2,6-di- <i>tert</i> -butylphenol	C ₁₂ H ₂₄ O	1488	1519	128-37-0	100	0.1–0.2	0.1	11
1,4-Dioxane	C ₄ H ₈ O ₂		<900	123-91-1	87.5	1100–109 000	3900	7
Tris(2-chloropropyl) phosphate	C ₉ H ₁₈ Cl ₃ O ₄ P	1750		6145-73-9	87.5	14–10 900	603	8
Caffeine	C ₈ H ₁₀ N ₄ O ₂	1768	1838	58-08-2	87.5	21.7–9280	517	11
2,6-Di- <i>tert</i> -butyl-1,4-benzoquinone	C ₁₄ H ₂₀ O ₂	1443	1464	719-22-2	87.5	58.5–827	216	11
<i>p</i> -Toluidine and <i>o</i> -toluidine	C ₇ H ₉ N		1068	106-49-0/95-53-4	87.5	2.5–618	124	11
Triethyl phosphate	C ₆ H ₁₅ O ₄ P	1091	1127	78-40-0	87.5	3.1–922	42.1	8
<i>m</i> - and <i>p</i> -Xylene	C ₈ H ₁₀		<900	108-38-3/106-42-3	87.5	10–150	10.0	9
1,3-Dimethylnaphthalene	C ₁₂ H ₁₂		1409	575-41-7	87.5	10.9–162	36.2	11
<i>p</i> -Dichlorobenzene	C ₆ H ₄ Cl ₂		1009	106-46-7	62.5	44.4–56	51.5	9
Naphthalene	C ₁₀ H ₈	1151	1177	91-20-3	87.5	18.4–35.0	33.0	11
Quinoline	C ₉ H ₇ N		1230	91-22-5	87.5	0.9–21.6	14.4	11
Acenaphthene	C ₁₂ H ₁₀	1439	1472	83-32-9	87.5	2.0–4.5	2.9	11
Phenol	C ₆ H ₆ O		980	108-95-2	75	38.6–82 900	140	11
<i>o</i> -Cresol	C ₇ H ₈ O		1052	95-48-7	75	4.9–1990	69.6	11
Acetophenone	C ₈ H ₈ O		1063	98-86-2	75	34.6–1600	123	11
Skatole	C ₉ H ₉ N		1381	83-34-1	75	0.4–834	25.1	11
Benzene	C ₆ H ₆		<900	71-43-2	75	65–400	105	9
BPMC	C ₁₂ H ₁₇ NO ₂	1567	1612	3766-81-2	75	9.0–510	53	11
Benzophenone	C ₁₃ H ₁₀ O		1621	119-61-9	75	6.3–72.3	24.3	11
N-Methylaniline	C ₇ H ₉ N		1062	100-61-8	75	1.2–35.6	6.2	11
Acridine	C ₁₃ H ₉ N		1784	260-94-6	75	2.2–20.5	5.5	11
Biphenyl	C ₁₂ H ₁₀		1371	92-52-4	75	2.9–17	4.4	11
<i>o</i> -Chlorophenol	C ₆ H ₅ ClO		989	95-57-8	75	0.6–273	3.4	11
Triphenyl phosphate	C ₁₈ H ₁₅ O ₄ P	2330	2392	115-86-6	75	0.8–2.3	1.6	8
Diheptyl phthalate	C ₂₂ H ₃₄ O ₄	2390	2453	3648-21-3	75	0.1–3	0.4	10
<i>p</i> -Cresol and <i>m</i> -cresol	C ₇ H ₈ O		1075	106-44-5/108-39-4	62.5	40.8–45 800	430	11
Bisphenol A	C ₁₅ H ₁₆ O ₂	2108	2181	80-05-7	62.5	149–12 300	350	11
Diethyl phthalate	C ₁₂ H ₁₄ O ₄	1549	1595	84-66-2	62.5	110–2800	230	10
<i>m</i> -Toluidine	C ₇ H ₉ N		1074	108-44-1	62.5	4.2–2570	10.3	11
Anthracene	C ₁₄ H ₁₀	1734	1771	120-12-7	62.5	0.8–414	18.1	11
Carbazole	C ₁₂ H ₉ N		1823	86-74-8	62.5	7.2–79.2	31.4	11
Anthraquinone	C ₁₄ H ₈ O ₂	1898	1950	84-65-1	62.5	6.1–83.1	11.6	11
1,2-Dimethylnaphthalene	C ₁₂ H ₁₂	1439		573-98-8	62.5	5.0–21	8.0	12
2,6-Dichlorophenol	C ₆ H ₄ Cl ₂ O		1199	87-65-0	62.5	3.0–15.5	6.8	11
2,4,6-Trichloroaniline	C ₆ H ₃ Cl ₃ N		1398	634-93-5	62.5	1.6–7.5	4.8	11
Dibenzofuran	C ₁₂ H ₈ O		1504	132-64-9	62.5	1.3–2.2	1.9	11
Dibenzothiophene	C ₁₂ H ₈ S	1728	1733	132-65-0	62.5	0.8–2.6	0.9	11

Table 3 (continued)

Name	Molecular formula	GC retention index		CAS reg. number	Det. ratio ^a (%)	Conc. range ^b (ng l ⁻¹)	Median conc. (ng l ⁻¹)	Method
		OV-1	5% Ph					
2-(Methylthio)benzothiazole	C ₈ H ₇ NS ₂	1589		615-22-5	62.5	0.1–1.2	0.3	12
2,4-Dichlorophenol	C ₆ H ₄ Cl ₂ O	1164		120-83-2	62.5	9.6–387	43.9	11
Dibutyl phthalate	C ₁₆ H ₂₂ O ₄	1915	1960	84-74-2	50	800–1100	920	10
Tri- <i>n</i> -butyl phosphate	C ₁₂ H ₂₇ O ₄ P	1617	1655	126-73-8	50	64–600	86	8
Dimethyl phthalate	C ₁₀ H ₁₀ O ₄	1406	1458	131-11-3	50	37–290	120	10
3,4-Dichloroaniline	C ₆ H ₃ Cl ₂ N	1423		95-76-1	50	5.0–278	41.4	11
Biphenyl-4-ol	C ₁₂ H ₁₀ O	1708		92-69-3	50	3.1–56	24.8	11
2,4-Dichloroaniline	C ₆ H ₃ Cl ₂ N	1323		554-00-7	50	1.6–16.4	11.2	11
Acetic acid	C ₂ H ₄ O ₂			64-19-7	37.5	4 700 000–46 300 000	14 800 000	6
CAT	C ₇ H ₁₂ C ₁ N ₅	1714	1741	122-34-9	37.5	138–1110	1000	11
Simetryn	C ₈ H ₁₅ N ₂ S	1843	1899	1014-70-6	37.5	64–880	181	11
1-Naphthol	C ₁₀ H ₈ O		1504	90-15-3	37.5	24.2–575	223	11
Cyclohexanone	C ₆ H ₁₀ O		896	108-94-1	37.5	19.4–494	259	11
Isoprothiolane	C ₁₂ H ₁₈ O ₂ S ₂	2101	2172	50512-35-1	37.5	32.3–543	54.1	11
Biphenyl-2-ol	C ₁₂ H ₁₀ O		1507	90-43-7	37.5	12.8–417	179	11
<i>p</i> -Chloroaniline and <i>m</i> -chloroaniline	C ₆ H ₆ ClN		1201	106-47-8/108-42-9	37.5	24.1–437	111	11
2-Naphthol	C ₁₀ H ₈ O		1497	135-19-3	37.5	11.3–234	222	11
Chloroform	CHCl ₃	<900		67-66-3	37.5	62–240	140	9
Benthiocarb	C ₁₂ H ₁₆ C ₁ NOS		1966	28249-77-6	37.5	26–312	59.4	11
<i>N</i> -Ethylaniline	C ₈ H ₁₁ N		1128	103-65-5	37.5	2.1–204	14.0	11
Dichloromethane	CH ₂ Cl ₂	<900		75-09-2	37.5	54–63	62.0	9
Molinate	C ₉ H ₁₇ NOS		1528	2212-67-1	37.5	24–100	34.0	11
γ -Picoline	C ₆ H ₇ N		854	108-89-4	37.5	15.9–80.4	54.7	11
Diisopropyl-naphthalene	C ₁₆ H ₂₀			24157-81-1	37.5	13–37	30.0	12
Diphenylamine	C ₁₂ H ₁₁ N		1616	122-39-4	37.5	6.4–25.5	10.1	11
Diazinon	C ₁₂ H ₂₁ N ₂ O ₃ PS	1766	1811	333-41-5	37.5	5.1–23.7	6.4	11
Flutolanil	C ₁₇ H ₁₆ F ₃ NO ₂	2105	2168	66332-96-5	37.5	3.5–14.5	7.1	11
Pyrene	C ₁₆ H ₁₀		2044	129-00-0	37.5	4.9–11.4	9.0	11
Oxadiazon	C ₁₅ H ₁₈ C ₁₂ N ₂ O ₃		2198	19666-30-9	37.5	3.4–10.1	7.3	11
<i>trans</i> -Decaline	C ₁₀ H ₁₈		1049	493-02-7	37.5	2.4–8.7	4.3	11
<i>n</i> -Nonacosane	C ₂₉ H ₆₀		2900	630-03-5	37.5	0.3–1.8	0.3	12
<i>p</i> -Cymene	C ₁₀ H ₁₄		1012	99-87-6	37.5	0.2–1.2	0.5	12
<i>n</i> -Octacosane	C ₂₈ H ₅₈		2800	630-02-4	37.5	0.3–1.1	0.3	12
<i>n</i> -Heptacosane	C ₂₇ H ₅₆		2700	593-49-7	37.5	0.1–0.9	0.2	12
1,2,3-Trichlorobenzene	C ₆ H ₃ Cl ₃		1207	87-61-6	37.5	0.3–0.5	0.4	12
Benz[<i>a</i>]anthracene	C ₁₈ H ₁₂		2403	56-55-3	37.5	0.3–2.0	1.9	11
<i>p</i> - <i>tert</i> -Octylphenol	C ₁₄ H ₂₂ O		1601	140-66-9	37.5	0.2–0.4	0.4	12
2,4-Xylenol	C ₈ H ₁₀ O		1150	105-67-9	37.5	0.2–0.2	0.2	12
Isovaleric acid	C ₅ H ₁₀ O ₂			503-74-2	25	2 400 000, 3 500 000		6
Benzyl alcohol	C ₇ H ₈ O		1031	100-51-6	25	766, 933		11
Atrazine	C ₈ H ₁₄ C ₁ N ₅		1696	1912-24-9	25	13.2, 166		11
<i>o</i> -Xylene	C ₈ H ₁₀		<900	95-47-6	25	60, 64		9
Indeno[1,2,3- <i>cd</i>]pyrene	C ₂₂ H ₁₂		3086	193-39-5	25	9, 19		11
<i>N</i> -Phenyl-1-naphthylamine	C ₁₆ H ₁₃ N		2135	90-30-2	25	9.7, 13.5		11
Benzo[<i>ghi</i>]perylene	C ₂₂ H ₁₂		3144	191-24-2	25	8, 12		12
1,2,4-Trichlorobenzene	C ₆ H ₃ Cl ₃		1172	120-82-1	25	7, 9.2		11
Phenanthrene	C ₁₄ H ₁₀		1724	1761	25	7, 8.4		11
Fluoranthene	C ₁₆ H ₁₀		1996	206-44-0	25	6, 9		11
Benzo[<i>e</i>]pyrene	C ₂₀ H ₁₂		2737	129-97-2	25	5, 10		12
Benzo[<i>a</i>]pyrene	C ₂₀ H ₁₂		2743	50-32-8	25	4, 9		12
2-Aminodiphenyl	C ₁₂ H ₁₁ N		1584	90-41-5	25	3.8, 4.6		11

(Continued on p. 330)

Table 3 (continued)

Name	Molecular formula	GC retention index		CAS reg. number	Det. ratio ^a (%)	Conc. range ^b (ng l ⁻¹)	Median conc. (ng l ⁻¹)	Method
		OV-1	5% Ph					
Xanthone	C ₁₃ H ₈ O ₂		1844	90-47-1	25	3.4, 4.7		11
<i>o</i> -Chloronitrobenzene	C ₆ H ₄ ClNO ₂		1241	88-73-3	25	2.3, 7.9		11
Chrysene and triphenylene	C ₁₈ H ₁₂	2443	2441	218-01-9/217-59-4	25	3, 3		12
<i>o</i> -Bromophenol	C ₆ H ₅ BrO		1064	95-56-7	25	2.4, 3.2		11
N-Nitrosodibutylamine	C ₈ H ₁₈ N ₂ O		1320	924-16-3	25	1.9, 2.1		12
<i>trans</i> -Chlordan	C ₁₀ H ₆ Cl ₂		2089	5103-74-2	25	1.0, 1.3		11
1,3-Dichloro-2-propanol	C ₃ H ₆ Cl ₂ O		<900	96-23-1	25	0.6, 0.9		12
<i>n</i> -Dotriacontane	C ₃₂ H ₆₆	3200		544-85-4	25	0.1, 1		12
<i>n</i> -Hexacosane	C ₂₆ H ₅₄	1600		630-01-3	25	0.2, 0.6		12
Isobutyric acid	C ₄ H ₈ O ₂			79-31-2	12.5	3 400 000		6
Propionic acid	C ₃ H ₆ O ₂			79-9-4	12.5	2 600 000		6
Di(2-ethylhexyl) phthalate	C ₂₄ H ₃₈ O ₄	2505	2546	117-81-7	12.5	2510		10
<i>p</i> -Chlorophenol and <i>m</i> -chlorophenol	C ₆ H ₅ ClO		1198	106-48-9/108-43-0	12.5	251		11
Isophorone	C ₉ H ₁₄ O		1117	78-59-1	12.5	147		11
N-Phenyl-2-naphthylamine	C ₁₆ H ₁₃ N		2222	135-88-6	12.5	80		11
MBPMC	C ₁₇ H ₂₇ NO ₂	1851	1898	1918-11-2	12.5	71.2		11
1,2-Dichloroethane	C ₂ H ₄ Cl ₂		<900	107-06-2	12.5	61		9
<i>p</i> -Bromophenol	C ₆ H ₄ BrO		1286	106-41-2	12.5	31.3		11
2,4,6-Trichlorophenol	C ₆ H ₃ Cl ₃ O		1347	88-06-2	12.5	20		11
<i>o</i> -Nitrophenol	C ₆ H ₅ NO ₂		1127	88-75-5	12.5	13.2		11
Bis(2-chloroisopropyl) ether	C ₆ H ₁₂ Cl ₂ O	1023	1055	108-60-1	12.5	3.8		12
N,N-Dimethylaniline	C ₈ H ₁₁ N		1086	121-69-7	12.5	3.7		11
2-Methylbenzothiazole	C ₈ H ₇ NS		1288	120-75-2	12.5	2.8		12
α -Terpineol	C ₁₀ H ₁₈ O	1171	1197	98-55-5	12.5	2.4		12
2,4,6-Tribromophenol	C ₆ H ₃ Br ₃ O		1624	118-79-6	12.5	1.8		11
<i>n</i> -Triaccontane	C ₃₀ H ₆₂	3000		638-68-6	12.5	1.7		12
<i>n</i> -Hentriacontane	C ₃₁ H ₆₄	3100		630-04-6	12.5	1.7		12
Benzo[f]quinoline	C ₁₃ H ₉ N		1807	85-02-9	12.5	1.6		11
Benzothiophene	C ₈ H ₆ S	1155	1189	95-15-8	12.5	1.0		12
<i>m</i> -Terphenyl	C ₁₈ H ₁₄	2091	2140	92-06-8	12.5	0.5		11
<i>n</i> -Tricosane	C ₂₃ H ₄₈	2300		638-67-5	12.5	0.2		12
<i>n</i> -Pentacosane	C ₂₅ H ₅₂	2500		629-99-2	12.5	0.2		12
<i>n</i> -Nonadecane	C ₁₉ H ₄₀	1900		629-92-5	12.5	0.1		12

^a Detection ratio is a ratio of the number of sites, where compound was detected, in the eight sites.

^b Concentration range shows a range from the lowest concentration to the highest concentration of detected concentrations.

defined as a ratio of the number of sites, where compound was detected, in the eight sites investigated. Concentration range is a range from the lowest concentration to the highest detected concentrations among detected values. Median values are shown as a mean concentration in cases where compound was determined in three sites or more. Concentrations of acetic, propionic, isobutyric, and isovaleric acids were high compared with other components. Analysis of lower fatty acids is important to estimate the decomposition stage of the biodegradable organic materials.

Several organic phosphates such as tris(2-butoxy-

ethyl) phosphate, tris(1,3-dichloro-2-propyl) phosphate, tris(2-chloropropyl) phosphate, tris(2-chloroethyl) phosphate, and triphenyl phosphate were detected very frequently. Some were also in high concentration compared to phthalates. These phosphates were widely used in plastic additives. For example, tris(2-chloroethyl) phosphate was found in water contacting several types of plastics [18]. Water pollution problems with organic phosphates have already been reported in Japan [19–21].

1,4-Dioxane was detected both at high detection ratio (87.5%) and at a maximum concentration of 109 $\mu\text{g l}^{-1}$. Dioxane has been previously reported in

leachates [7] and in river water [22]. Trichloroethane was not detected in this work, even though dioxane is used as a stabilizer for trichloroethane. Dioxane must come from sources other than trichloroethane, and since dioxane is a controlled and toxic substance in Japan and it is non-biodegradable, the search of sources for this compound is an urgent and important problem.

Several phthalates such as diheptyl phthalate, diethyl phthalate, dibutyl phthalate and dimethyl phthalate were detected frequently. Detection ratio of di(2-ethylhexyl) phthalate was 12.5%. The reason for low detection ratio was the presence of peak in blank samples. These phthalates supposedly originate from plastics.

4-Methyl-2,6-di-*tert.*-butylphenol and bisphenol A were detected in most leachates. Fukui et al. [23,24] have reported that these compounds are commonly used as additives in plastics and rubber.

The number of polar substances detected was more than that of non-polar substance species such as alkanes. Most alcohols, phenols, carbonyl compounds, and lower fatty acids come from the natural decay of organic matter and are useful for characterization of landfill nature.

Several pesticides or herbicides such as BPMC, CAT, and benthocarb were detected for the first time in Japan. Most known pesticides or herbicides were not detected. Compared with leachates in USA, contamination with agricultural chemicals in Japan was similar [2].

Small concentrations of chlorinated volatile organic compounds were detected in this study, although they were detected frequently in USA [4,5]. It is possible that chlorinated volatile organics could be found in illegal landfills, because of underground water pollution near these sites [25,26].

Median concentrations of 1,4-dioxane, tris(2-chloropropyl) phosphate, caffeine, dibutyl phthalate, acetic acid and CAT were over 500 ng l⁻¹.

4. Conclusion

Approximately 190 organic compounds were detected in leachates from eight landfills in Japan. Many organic phosphates and phthalates, used as

plastic additives, were detected in a range of 0.8–10 900 ng l⁻¹ and 0.1–2800 ng l⁻¹ respectively in most leachates. Detection of 1,4-dioxane in most leachates was important because the compound is one of the compounds listed as toxic environmental contaminants by Japan Law [27], as the origin of dioxane is unknown. A few species of agricultural chemicals were detected for the first time in Japan. Only a few species of halogenated volatile organic compounds were detected.

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