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IDENTIFICATION OF ORGANIC COMPOUNDS IN MUNICIPAL LANDFILL LEACHATES

Cecilia Öman & Per-Åke Hynning

Swedish Environmental Research Institute, Box 21060, S-100 31 Stockholm, Sweden

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Abstract

Forty-five organic compounds have been identified in leachates from a Swedish municipal landfill. The samples were taken from the interior of the landfill to minimize alterations caused by contact with the surroundings and were identified and quantified by gas chromatography combined with mass spectrometry. Two analytical procedures were used, one for priority pollutants, the other for a wider range of phenolic and neutral compounds and acids. Analyses of the leachates for water quality parameters indicated that the part of the landfill which was sampled had reached an anaerobic stage in which methane was being produced. Possible origins for most of the compounds identified have been suggested.

Keywords: organic compounds, municipal landfill leachate, methane producing stage, gas chromatography/mass spectometry.

INTRODUCTION

Water percolating through a landfill will contain both organic and inorganic substances, released from the material deposited or as the result of biotic and abiotic reactions. These substances may be transported from the landfill with the leachate, and could present an environmental hazard. In order to evaluate this, the individual compounds must be identified. Individual organic compounds in landfill leachates have, however, been identified in relatively few previous investigations (Kahre & Dondero, 1977; DeWalle & Chian, 1981; Harmsen, 1983; Reinhard *et al.*, 1984; Sawhney & Kozloski, 1984; Schultz & Kjeldsen, 1986; Sridharan & Didier, 1988; Först, *et al.*, 1989; Murray & Beck, 1990), and there are substantial differences in the structures of the compounds that have been identified. This is at least partly due to the various factors that influence the leachate quality.

Different biological, chemical and physical processes take place successively in a municipal landfill, and these affect both the leachate and the production of gas. Several studies have investigated the biological degradation of solid waste (Farquhar & Rovers, 1973; Chian & DeWalle, 1976; Ehrig, 1983; Harmsen, 1983; Pohland *et al.*, 1983; Barlaz *et al.*, 1989; Ehrig, 1989), and these results make it possible to speculate on an idealized sequence of biological processes occurring in the landfill: these changes may be monitored by analysis of the leachate (Pohland *et al.*, 1983). Another important factor is the sampling point. For example, Ettala *et al.* (1988) found that the concentration of compounds in leachates sampled in basins and ditches connected to sanitary landfills did not correlate with concentrations in leachates from the interior of the same landfills. They suggest that analyses of leachates from basins and ditches are therefore of limited value in landfill management. Other factors influencing the leachate are, for example, the type of solid waste deposited on the landfill, its construction, and the amount of water that infiltrates.

The conclusions drawn from any study are influenced by a number of factors, including the sampling method, the way in which the samples were preserved before analysis, and the analytical procedures used. For example, Chian & DeWalle (1976) found that when leachates were exposed to atmospheric oxygen the chemical oxygen demand decreased, and the amount of suspended solids increased. In addition, organic compounds may be sorbed onto dissolved organic matter, colloids or suspended particles, so that the amount of such matter in a sample will influence the analytical result. Filtration of the sample may introduce significant errors since Harmsen (1983) found that membrane filtration retarded or adsorbed free volatile acids on the filters.

It is difficult to determine unambiguously the origin of the compounds identified in landfill leachate since they may have been released directly from the refuse originally deposited, or be the products of transformation processes, such as microbial degradation or abiotic hydrolysis.

The purpose of this study was to analyze leachates from the interior of a municipal landfill and to identify individual organic compounds. The leachates were analyzed for 62 compounds considered as priority pollutants (Sporstøl *et al.*, 1985), and for other phenolic and neutral compounds and acids. No attempt was

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made to identify or quantify volatile compounds such as hydrocarbons and haloalkanes. Possible origins for most of the compounds identified have been suggested, and chemical analyses were used to evaluate the degradation stage of the landfill and to provide a characterization of the leachate.

MATERIALS AND METHODS

Landfill characteristics

The municipal landfill was situated in Gryta, Västerås, Sweden. It had an area of 40 ha, an average height of 15–20 m and was covered with about 1 m of fill. Each cell was about 3–4 m high and covered with 0·3 m of soil and gravel. The landfill had been compacted with a 27-ton compactor, but had not been vegetated. The sections investigated had been terminated at the time of sampling, and had, since the middle of 1970, received mainly domestic waste, but also some industrial waste, digested sludge from municipal wastewater treatment plants (after chemical and biological treatment), non-digested sludge from municipal wastewater treatment plants (after mechanical treatment), city drain sludge, construction waste and fill. No attempt was made to determine whether the water inside the landfill was groundwater or rainwater that had not yet percolated through the bottom of the landfill.

Sampling

The leachates were sampled in May 1990. Five polyvinylchloride (PVC) tubes had been vertically installed to the bottom of the landfill, and were originally used for gas collection. They were perforated throughout, and the upper 3 m was covered with unperforated metal tubes to prevent ingress of air. Leachates were collected from the bottom of the tubes using a hand-operated vacuum pump (Nalgene). Four of the tubes contained water, but water samples could be taken from only three of them (referred to as samples 1, 2 and 3) since the water level in the fourth was not sufficient for use of the vacuum pump. The tubes were not evacuated prior to sampling, so as not to diminish the number of sampling points, as the hydraulic conditions and therefore the time for refilling were unknown. The tubes were situated at distances of 70–150 m from each other. A control water sample was collected at a point 100 m south of the landfill area, where the same type of PVC tube was installed into the ground (referred to as control). The samples were pumped through Teflon tubing into 2-litre borosilicate glass bottles, fitted with glass stoppers, which were held in darkness: the bottles were completely filled leaving no air space. The temperature of the leachates was 19–20°C which corresponded closely with the ambient air temperature. Particles were allowed to settle during the 5-h transport to the laboratory, and the supernatants were then decanted. Borosilicate glass bottles with glass caps were filled to about three-quarters of their volumes and the samples were immediately frozen.

Glassware used for sampling and transport was: (i) washed with phosphate-free detergent, (ii) rinsed three times with deionized water, (iii) washed with 5% hydrochloric acid, (iv) rinsed three times with deionized water, (v) heated to 105°C for 1 h, (vi) rinsed with hexane, (vii) heated and then finally closed until use.

Solvents and chemicals

Solvents and reagents were of analytical quality and solvents were obtained from Burdick & Jackson (Muskegon, MI, USA). Standard compounds for comparison were purchased from the following suppliers: *N-n*-butylbenzenesulfonamide from ICN Biomedicals Inc. (Costa Mesa, CA, USA), benzoic acid from Merck (Darmstadt, Germany), 3,5-dimethylbenzoic acid, 3-phenylpropionic acid, *o*-cresol, 4-chloro-*o*-cresol, hexanoic acid and phenylacetic acid from Fluka Chemie AG (Buchs, Switzerland), 2-hydroxybenzothiazole from Pfaltz and Bauer Inc. (Waterbury, CT, USA), phenol, *p*-cresol, *m*-cresol, triethylphosphate, camphor (1,7,7-trimethylbicyclo[2.2.1]heptan-2-one),2,2'-dihydroxydiphenylmethane and tris(2-chloroethyl)phosphate from Janssen Chimica (Beerse and Geel, Belgium), chlorendic acid (1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-hept-5-ene-2,3-carboxylic acid) from TCI (Tokyo, Japan), 4-chloro-*m*-cresol from BDH (Poole, UK), cyclohexane-carboxylic acid, fenchon (1,3,3-trimethyl-bicyclo[2.2.1]heptan-2 one), 2-ethylhexanoic acid, *N,N*-diethyl-3-methylbenzamide, and tri-*n*-butylphosphate from Aldrich-Chemie (Steinheim, Germany), dehydroabietic acid from Helix Biotech Corporation (Vancouver, BC, Canada), tetradecanoic acid, hexadecanoic acid, octadecanoic acid, 2,4-, 2,6-, and 3,5-dimethylphenol, *tert*-butylphenol, 2-isopropylphenol from Alltech Associates (Deerfield, USA), 3,4-dimethylphenol, and 4,4'-dihydroxydiphenylmethane from Lancaster Synthesis (Morecambe, UK). 2-(4-chloro-2-methylphenoxy)propionic acid from Kemisk Vaerk Köge A/S (Denmark) and octasulfur from Merck (Darmstadt, Germany).

Characterization of leachates

The water quality parameters pH, conductivity, BOD_7 (biochemical oxygen demand), COD_{Cr} (chemical oxygen demand with dichromate), Fe, Mn, N-NO_3^- + NO_2^-, chloride, N-NH_4^+, N-Kjedahl, P-tot, P-PO_4^{3-} and HCO_3^- were determined by Swedish Standard and SIS methods (NO_3^- + NO_2^- and chloride were automatized with FIA and N-NH_4^+, N-Kjeldahl, P-tot, P-PO_4^{3-} were automatized with an autoanalyzer) and sulphate was determined by standard methods (ion chromatography). Total carbon (TC), total organic carbon (TOC) and dissolved organic carbon (DOC) were analyzed with an Astro model 2001 instrument. Samples for DOC were filtered through a 0·2-μm polycarbonate filter (Millipore) before TOC analysis. Total inorganic carbon (TIC) was calculated from the difference between TC and TOC. Concentrations of adsorbable organic halogen (AOX) were determined using a combined pyrolysis–microcoulometer instrument (Euroglas, Delft, Holland) following a standardized procedure (DIN 38409, 1985).

Analysis of priority pollutants

One sample from each sampling point (control, 1, 2 and 3) was analyzed (Sporstøl *et al.*, 1985) for identification of priority pollutants (including mono-, bi- and polycyclic aromatic compounds, chlorinated aromatic compounds, pesticides, phosphate esters, phthalate esters, phenolic compounds, and aromatic nitrogen compounds). Deuterated internal standards (toluene-d_8, naphthalene-d_8, biphenyl-d_{10}, phenanthrene-d_{10}, pyrene-d_{10}, chrysene-d_{12}, and phenol-d_6) were added to 1-liter water samples, the solution made alkaline and extracted 3 times with 35 ml dichloromethane. The water phase was then acidified and extracted as above. The two groups of dichloromethane extracts were combined and dried (Na_2SO_4), the volume reduced to 1 ml, and analyzed by gas chromatography–mass spectrometry (GC–MS) using a 30-m DB-5 fused silica capillary column with a film thickness of 0·25 μm (J & W Scientific, Inc.). The following temperature program was used: the oven was initially held at 30°C for 5 min before rapidly raising the temperature to 70°C, thereafter the temperature was raised by 4°C per min to 300°C and held for 10 min. A VG TRIO-1 mass-spectrometer (VG MassLab, Altrincham, UK) coupled to a Hewlett-Packard 5890A gas chromatograph was used, and an automated computer search program.

Analysis of other organic compounds

Analysis of other compounds including phenolic and neutral compounds and acids were carried out as follows. Samples (500 ml) from each sampling point were acidified to about pH 2 with sulphuric acid and extracted twice with 40 ml hexane:*tert*-butyl methyl ether (2:1). The extract was dried (Na_2SO_4), evaporated to 10 ml and derivatized as described below:

(i) For analysis of phenolic compounds, 2-ml samples were acetylated as described by Hynning *et al.* (1989): the sample was evaporated almost to dryness, the residue dissolved in hexane and purified by chromatography on a silica gel column. The hexane eluate was discarded, and the desired compounds were eluted with benzene.

(ii) For aliphatic and aromatic acids, 2-ml samples were evaporated to dryness, and methylated with 0·3 ml HCl/MeOH at 75°C for 15 min. Water (4 ml) was added, and the samples extracted twice with hexane:*tert*-butyl methyl ether (2 × 1·5 ml), dried (Na_2SO_4) and purified as described above.

(iii) For phenolic acids, 2-ml samples were first methylated (HCl/MeOH) and then acetylated as described above.

(iv) For analysis of dehydroabietic acid and chlorendic acid, 2-ml samples were evaporated to dryness, dissolved in a small volume of diethyl ether, and derivatized with diazomethane.

Gas chromatography–mass spectrometry analyses were carried out as described previously (Hynning *et al.*, 1989) using a TRIO-2 mass spectrometer (VG Biotech, Altrincham, UK) coupled to a Hewlett-Packard 5890A gas chromatograph.

RESULTS

Water quality parameters for the leachates in this study and for those from published investigations are given in Table 1. Table 2 gives more comprehensive data from this study while Table 3 summarizes the concentrations of the priority pollutants found in the samples and Table 4 the organic analyses of other compounds.

DISCUSSION

Transformation stages

Previous studies on the biological degradation of solid waste (Farquhar & Rovers, 1973; Chian & DeWalle, 1976; Ehrig, 1983; Harmsen, 1983; Pohland *et al.*, 1983; Barlaz *et al.*, 1989; Ehrig, 1989) make it possible to present a speculative idealized sequence of processes occurring in landfills. Although the situation may be considerably more complex in practice, for example with cells inside the landfill representing different ages, water content and refuse composition, Pohland *et al.* (1983) suggests that the transformation stages can be followed by leachate analyses, this is also indicated by the results of Ehrig (1983, 1989) and Harmsen (1983) at least concerning transformation stages III and IV.

Stage I

The period from initial refuse deposition to the time when significant degradation takes place. This stage may occur if degradation is inhibited, for example by drought or low ambient temperatures.

Stage II

A short period possibly of about 7 days (Barlaz *et al.*, 1989), when concentrations of oxygen and nitrate are reduced, and readily degradable organic matter is degraded with the production of carbon dioxide and a rise in temperature.

Stage III

Generation of volatile fatty acids resulting in high levels of TOC, COD and BOD in the leachate (Table 1). These acids may represent >95% of the TOC (Harmsen, 1983), and BOD_5/COD may lie between 0·8 and 0·4 (Ehrig, 1983, 1989). Carbon dioxide is produced.

Stage IV

Microbial reduction of sulphate to sulphide takes place and, subsequently, volatile fatty acids are converted to carbon dioxide and methane resulting in a low TOC in the leachate: also carbon dioxide and hydrogen are converted to methane. The TOC, COD, BOD decreases and the BOD_5/COD ratio decreases below 0·1 (Ehrig, 1989) while the absolute and relative amount of high molecular weight material ($M > 1000$) increases (Harmsen, 1983). The concentration of Fe and Mn decreases (Ehrig, 1989; Harmsen, 1983).

Table 1. Average values of leachate content from 20 landfills in Germany (A: Ehrig, 1983), values from two landfills in The Netherlands (B: Harmsen, 1983) and present results (C). Concentrations in mg liter^{-1}

	Parameter							
	pH	TOC	COD	BOD	BOD/ COD	SO_4^{2-}	Fe	Mn
Stage III								
A	6·1	—	22 000	13 000	0·58[a]	500[a]	925	24
B	5·7	20 000	60 000	30 000	0·5	—	1 120	53
Stage IV								
A	8·0	—	3 000	180	0·06[a]	80[a]	15	0·65
B	7·0	2 100	7 000	50	0·01	—	40	0·24
C: 1	7·6	190	600	64	0·11	<20	35	0·32
C: 2	7·2	130	460	43	0·09	<20	53	1·0
C: 3	7·4	630	2 100	910	0·43	<20	130	2·0
Control	6·8	12	<10	<5	—	—	10	0·51

—, not presented, not analyzed or not possible to calculate.

[a] Ehrig (1989).

Stage V

Only refractory organic matter remains in the refuse. The gas production is low and ambient air may diffuse into the landfill so that aerobic zones develop.

Chemical analysis of the leachate (Table 1) was compared with the results from previous studies in an attempt to estimate the transformation stage at the part of the landfill which was sampled. The low BOD_7 and COD_{Cr} values indicated that degradation was not inhibited (Stage I) and the age of the sampled area (about 15 years for sample points 1 and 2, and about 5 years for point 3) suggested that degradation had been proceeding sufficiently for oxygen and nitrate to be consumed (Stage II). Values of TOC, BOD_7 and COD_{Cr} correlated with those expected in stage IV. The ratio between BOD_7 and COD_{Cr} for samples 1 and 2 correlated well with stage IV, whereas values for sample 3 indicated that this section of the landfill lay between stages III and IV, which would be consistent with the shorter residence time. The low concentrations of sulphate, Fe and Mn were also consistent with those expected for stage IV. Methane production at the leachate sampling points (1, 2 and 3) was confirmed by the landfill personnel, indicating that stage V had not yet been reached. It therefore seemed that the tranformation stage at the part of the landfill which was sampled corresponded to stage IV with anaerobic production of methane.

General leachate characteristics

Except for concentrations of nitrate and nitrite, all parameters in Table 2 were higher in the leachate samples (1, 2 and 3) than in the control sample. Sample 3 had higher concentrations of BOD_7, COD_{Cr}, TC, TOC and DOC, chloride, Fe and Mn than samples 1 and 2, and this may be consistent with the very low water level in the sampling tube (3 cm) which resulted in a sample with much suspended material. The DOC analyses showed that the main part of the organic carbon had a particle size of less than 0·2 μm, and N-Kjedahl analyses compared with $N\text{-}NH_4^+$ analyses showed that ammonia represents the main part of nitrogen with oxidation level three. Phosphate represented less than 2% of the total amount of phosphorus, and AOX represented less than 0·3% of the total chloride concentration in the leachate samples (1, 2 and 3).

Table 2. Characterization of three leachate samples and one control sample. Concentrations in mg liter^{-1}

Parameter	Samples			
	Control	1	2	3
Conductivity (mS m^{-1})	14·5	631	425	811
TC	12	830	530	1 200
TOC	6·3	190	130	630
TIC	5·4	640	400	530
DOC	4·6	180	120	580
$N\text{-}NO_3^- + NO_2^-$	0·032	<0·02	<0·02	<0·02
$N\text{-}NH_4^+$	0·25	430	280	370
N-Kjedahl	0·52	460	300	420
$P\text{-}PO_2^{3-}$	0·003	0·040	0·034	0·071
P-tot	<0·1	2·3	2·6	3·9
Chloride	15	380	280	1 200
AOX	0·024	0·90	0·50	1·3

Priority pollutants

Automated identification and quantification of the target compounds were performed using a computer search program. Each compound has its own library entry with a simplified mass spectrum containing three characteristic fragments, the name of the compound, library number, retention time, relative retention time, molecular weight, formula and single mass for quantification. Unknown samples were analyzed first by library search within a given retention window (50 s) centered on the theoretical relative retention time of the compound versus the deuterated internal standard. The unknown compound is then positively identified if the mass spectrum of a given scan within the retention window matches that in the library. Quantification was based on multilevel response factors which took into account differences in extractability, volatility, and the GC–MS response of the compounds and the internal standards. Only compounds not identified in the control sample were considered to originate from the landfill wastes and hence were sought in the leachate samples (samples 1, 2 and 3). The quantification limit was in the range of 1–10 μg liter^{-1}, except for benzene (50 μg liter^{-1}) and toluene (130 μg liter^{-1}). The detection limits were generally 10 times lower than the quantification limits, but the level of precision (standard deviation) was rather low and for some analyses exceeded 20% (Table 3). The precision of the GC/MS method was estimated (Sporstøl *et al.*, 1985) from values for four replicate samples at four concentrations: 1, 5, 25 and 100 μg liter^{-1} water. The precision ranged from 1% to 38% with an average of 14%. The highest standard deviations were found for the monoaromatic hydrocarbons, the phenols and diphenyl-

Table 3. Priority pollutants identified and quantified in samples of leachate. Concentrations in μg liter^{-1}. None of the listed compounds could be detected in the control sample

Substance [Chemical Abstracts Registry number]		Samples			Quantification limit	Precision S.D.(%)	Possible origin
		1	2	3			
Non-chlorinated aromatic compounds							
Naphthalene	[91-20-3]	11	4·5	3·8	1	13	B, C, D, E, G, asphalt, tar, creosote
1-Methylnaphthalene	[90-12-0]	1·6	1·1	<1	1	18	B, C, asphalt, creosote
2-Methylnaphthalene	[91-57-6]	2·1	1·4	<1	1	24	Tar, creosote
Phenanthrene	[85-01-8]	1·1	<1	<1	1	10	C, creosote
Chlorinated aromatic compounds							
1,2-Dichlorobenzene	[95-50-1]	1·3	<1	1·1	1	7	B, C, G, F
1,4-Dichlorobenzene	[106-46-7]	1·1	<1	<1	1	9	A, B, C
Phosphate esters							
Tri-*n*-butylphosphate	[126-73-8]	<2	<2	7	2	22	C, D, H
Phthalate esters							
Diethylphthalate	[84-66-2]	<10	<10	94	10	8	A, B, C, food packaging
Di-*n*-butylphthalate	[84-74-2]	<5	<5	14	5	15	A, B, D, H, ink, paper coating
Butylbenzylphthalate	[85-68-7]	<5	<5	8·1	5	6	D, H
Phenolic compounds							
Phenol	[108-95-2]	<1	<1	27	1	7	A, B, C, D, degr. lignin, creosote
m/*p*-Cresol	*m*: [108-39-4] *p*: [106-44-5]	<1	<1	34	1	25	*m*: B, creosote *p*: Creosote
p-Nonylphenol	[106-44-5]	<10	<10	107	1	38	B, C, D, E, H, surfactant
Aromatic nitrogen compounds							
Diphenylamine	[122-39-4]	2·3	3·5	<2	2	32	A, B, C, D

amine. Concentrations of the quantified compounds were generally similar for all sampling points, except phthalate esters and phenolic compounds which were present in concentrations exceeding the quantification limit only in sample 3.

The high concentrations of the plasticizer di(2-ethylhexyl)phthalate found in all water samples (1797, 2014, 9775 and 2444 μg liter^{-1} in the control, 1, 2, and 3, respectively) suggest that this compound originates from the PVC tubes: it is therefore not further discussed.

No attempt was made to identify volatile organic compounds such as low molecular weight halogenated aliphatic hydrocarbons, so that their contribution to the group of priority pollutants cannot be assessed.

Other organic compounds

One sample from each of the four sampling points was analyzed for phenolic and neutral compounds and acids. For an unequivocal identification, it was necessary that the gas chromatographic relative retention times and mass spectra were identical with those of reference compounds. Only compounds not identified in the control sample were considered as originating from the landfill wastes and were hence sought in the leachate samples (1, 2 and 3) (Table 4). The detection limit was in the range of 1–10 μg liter^{-1} for all compounds.

The following compounds were also detected: tri-*n*-butylphosphate in samples 1, 2 and 3, phenol and *p*-cresol in all samples (trace amounts of phenol in the control and sample 1), *m*-cresol in sample 3. These compounds are presented as priority pollutants.

Origin of identified compounds

Compounds identified in the leachate have widely different origins: they may have been released from the material deposited onto the landfill, or may be the result of transformation processes including microbial degradation and abiotic hydrolysis (Tables 3 and 4).

Several of the compounds identified are used as starting materials for manufacture of products that ultimately may have been deposited onto the landfill (Tables 3 and 4). Examples include products commonly found in domestic waste: pharmaceuticals, cosmetics and soaps (A); pesticides, insect repellents, disinfectants, food-, textile-, and leather preservatives (B); dyestuffs, varnishes, lacquers (C); plastics, resins, rubber (D); motor- and other oils, lubricants (E); polishes (F); solvents (G); plasticizers (H) and flame retardants (I) (Merck Index, 1983; Verschueren, 1983; Swedish National Chemicals Inspectorate; Stowell & Jensen, 1991). Other compounds may originate from tar and creosote (Sundström *et al.*, 1986; Swedish National Chemicals Inspectorate). It should be pointed out that not all product mixtures have been analyzed as thoroughly as creosote. It is not, therefore, implied that creosote is the principal source of the compounds listed in the table. It is, however, difficult to determine the source of compounds which might have originated from industrial wastes, various kinds of sludge, construction wastes and fills placed in the landfill.

Some of the organic compounds that were identified may be produced by microbial degradation of waste products (Tables 3 and 4). For example, phenylacetic acid, benzoic acid, cyclohexane carboxylic acid, 3-

Table 4. Other identified organic compounds. None of the listed compounds could be detected in the control samples

Substance (Chemical Abstracts Registry Number]		Samples			Possible origin
		1	2	3	
Aliphatic acids					
Hexanoic acid	[142-62-1]	(+)	+	+	E, hydrolysis of phthalates
2-Ethylhexanoic acid	[149-57-5]	–	–	+	Detergent, hydrol. of phthalates
Tetradecanoic acid	[544-63-8]	–	–	+	A, E
Hexadecanoic acid	[57-10-3]	–	(+)	+	A, E, natural fats & oils, creosote
Octadecanoic acid	[57-11-4]	–	–	(+)	A, D, E, F, food package, creosote
Neutral aliphatic compounds					
Triethylphosphate	[78-40-0]	+	(+)	+	
Tris(2-chloroethyl)phosphate	[115-96-8]	–	–	+	I
Alicyclic acids					
Cyclohexanecarboxylic acid	[98-89-5]	–	–	+	B, D, degradation of lignin
Chlordenic acid	[115-28-6]	+	+	+	I
Dehydroabietic acid	[1170-19-8]	+	+	+	D
Neutral alicyclic compounds					
Fenchon	[4695-62-9]	+	+	+	A, flavor in food
Camphor	[76-22-2]	+	+	+	A, B, C, D, H, odorant household
Aromatic acids					
Benzoic acid	[65-85-0]	–	–	+	A, B, C, D, H, creosote, degr. lignin
3,5-Dimethylbenzoic acid	[499-06-9]	+	+	–	
Phenylacetic acid	[103-82-2]	–	–	+	A, B, degradation of lignin
3-Phenylpropionic acid	[501-52-0]	–	–	+	Degradation of lignin
2-(4-Chloro-2-methylphenoxy) propionic acid (Mecoprop)	[93-65-2]	+	–	–	B
Neutral aromatic compounds					
N,*N*-Diethyl-3-methylbenzamide	[134-62-3]	+	+	+	B
N-*n*-Butylbenzenesulfonamide	[3622-84-2]	+	+	+	
Phenolic compounds					
o-Cresol	[95-48-7]	–	(+)	+	A, B, C, D, G, surfactant, creosote
2-Isopropylphenol	[88-69-7]	+	+	–	Creosote
2,4-Dimethylphenol	[105-67-9]	+	+	–	A, B, C, D, G, creosote
2,6-Dimethylphenol	[576-26-1]	+	+	(+)	D, creosote
3,4-Dimethylphenol	[95-65-8]	+	+	–	Creosote
3,5-Dimethylphenol	[108-68-9]	+	+	+	Creosote
4-Chloro-*o*-cresol	[1570-64-5]	+	+	(+)	Degrad. and impur. in MCPA
4-Chloro-*m*-cresol	[59-50-7]	(+)	(+)	+	B
tert-Butylphenol	[98-54-4]	+	+	–	A, E
2-Hydroxybenzothiazole	[934-34-9]	+	+	+	Hydr. 2-mercaptobenzothiazol
2,2'-Dihydroxydiphenylmethane	[2467-02-9]	+	–	–	
4,4'-Dihydroxydiphenylmethane	[620-92-8]	+	–	–	
Miscellaneous compounds					
Octasulfur		+	+	+	Oxidation of S^{2-}, creosote

–, not detected.
+, identified.
(+), identified but occurring only in trace amounts.

phenylpropionic acid and phenol may be degradation products of lignin (Tables 3 and 4; Young & Frazer, 1987). 4-chloro-*o*-cresol is an established microbial degradation product of the herbicide MCPA (4-chloro-2-methylphenoxyacetic acid) (Verschueren, 1983) which has been identified in landfill leachate by Schultz & Kjeldsen (1986), and may be a microbial metabolite of the analogue 2-(4-chloro-2-methylphenoxy)propionic acid which was identified in this study.

Three of the identified compounds were probably the result of hydrolysis of the compounds initially deposited, i.e. hexanoic acid and 2-ethylhexanoic acid by hydrolysis of phthalates and 2-hydroxybenothiazole from 2-mercaptobenzothiazole, which is a vulcanizing agent.

Octasulphur is almost certainly produced by oxidation of sulphide produced by microbial reduction of sulphate in transformation stage IV.

Comparison with previous studies

In previous studies, a variety of organic compounds has been identified in leachates from municipal landfills (Kahre & Dondero, 1977; DeWalle & Chian, 1981; Harmsen, 1983; Reinhard *et al.*, 1984; Sawhney &

Kozloski, 1984; Schultz & Kjeldsen, 1986; Sridharan & Didier, 1988; Först *et al.*, 1989; Murray & Beck, 1990). Of more than 150 compounds, only 29 have, however, been identified in more than one of these studies, and of the 45 organic compounds identified in this study, 21 have been reported previously.

CONCLUSIONS

A wide range of organic compounds was identified in leachates from a municipal landfill representing the anaerobic methane-producing stage. Only a small amount of total organic carbon has yet been identified and the results of this and previous studies showed considerable differences in the nature of the organic compounds identified in landfill leachates, so that examination of leachates from a variety of landfills, and more extensive identification are clearly merited. The wide range of compounds identified illustrates that analytical methods must take into account the possible existence of compounds with widely differing chemical structures.

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