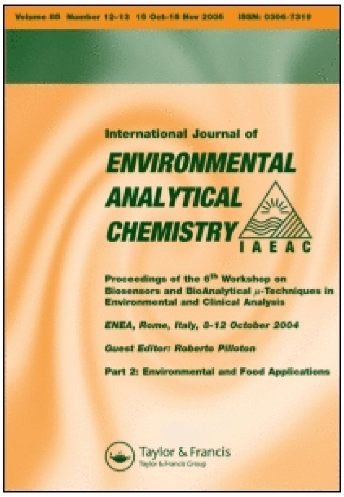

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Determination of Organic Contaminants in Landfill Leachates: A Review

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DETERMINATION OF ORGANIC CONTAMINANTS IN LANDFILL LEACHATES: A REVIEW

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Leachates derived from landfills constitute a potential risk of groundwater pollution because a variety of contaminants can be released by leaking from the contention system. Therefore, the leachate composition is of interest of their appropriate management. Although the leachate characterisation is usually carried out by global parameters (i.e. DOC, BOD, COD, AOX, etc), its characterisation at molecular level is of increasing interest and will be reviewed in the present article. Sample handling and determination techniques for a variety of organic contaminants is discussed and pitfalls as well as limitations of each analytical technique will be highlighted.

Keywords: Landfill leachates; Groundwater; VOCs; Organic contaminants; SPME; SPE; Purge and trap

INTRODUCTION AND SCOPE

Landfilling and incineration are the predominant practices in waste management within the OECD countries. About 60% of municipal and 68% of the hazardous wastes are currently landfilled [1]. Landfills can be classified according to the type of waste disposed of in hazardous, municipal (solid waste and sewage sludge) and inert waste. Capacity for non-hazardous waste in the EU is estimated to be about 1.2 billion tonnes in more than 8700 licensed landfills. In addition, over 3450 unlicensed landfills have been reported in the EU countries and 3091 landfills under operation were in US at 1996 [2]. Furthermore, in developing countries, landfills constitute a continuous source of atmospheric and groundwater pollution because the combustion of organic matter in an uncontrolled manner leads to atmospheric and soil contamination [3].

Landfill as a Point Pollution Source

Organic matter disposed off in landfills undergoes a variety of microbiological transformations and chemical reactions depending on the time scale since the waste

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is dumped. In the first diagenetic step, an aerobic transformation predominates while at longer residence time when oxygen is depleted, a transition from aerobic to anaerobic (i.e. sulphate reduction, denitrification acetogenisis processes) occurs reaching to strictly anaerobic conditions (i.e. methanogenesis) [4,5]. Methane and carbon dioxide gases are produced as a consequence of the organic matter transformation and released to the atmosphere depending on their physico-chemical properties of the compound, collection efficiency and combustion devices used.

In addition, landfills can contaminate groundwater if leaks in the insulation system occur. The state of the art of landfilling includes the use of high density polyethylene (i.e. geomembranes) and geotextile liners over clay layers. However, the relatively high temperatures reached during the organic matter biotransformation can deteriorate the insulation system, becoming at mid-term, a groundwater contamination potential [6]. Old landfills do not comply with such insulation technology and usually are an important source of groundwater pollution. Pollution monitoring is carried out in piezometers located at the vicinities of landfills to evaluate the plume direction and the extent of natural attenuation.

The composition of leachates depends on the landfill management, namely waste type, age, and leachate collection. Depending on the landfill, leachates can be reinjected with or without treatment in order to promote the biotransformation or can be discharged to surface waters following wastewater treatment processes.

A number of global parameters are currently determined for the characterisation of leachates (i.e. pH, electrical conductivity, TOC, DOC, COD, BOD, AOX, POX, total phenols, total petroleum hydrocarbons) [7]. These parameters can be useful but they do not provide information about the presence of toxic contaminants and their potential environmental impact if discharged to surface waters. Furthermore, to evaluate their migration potential to groundwater is necessary for their characterisation at molecular level. Therefore, leachate characterisation is usually carried out at both, molecular and chemical class levels [5–7].

The scope of the present review is the evaluation of the organic pollution derived from landfills. The analytes of interest will be the anthropogenic-specific organic compounds (ASOC) occurring in leachates or groundwater polluted by landfills but not those released to the atmosphere by landfill gases. This review will cover the literature published since 1985.

Classes of Organic Contaminants Occurring in Landfill Leachates

Organic contaminant classes occurring in landfill leachates (LL) are very broad and their concentration range span in several orders of magnitude (Table I) depending on the waste disposed, age, and their management [4,27]. Contaminant concentration and detection frequency follow different trends in leachates.

Phthalate esters are usually the most abundant ASOC in LL since three components (e.g., dibutyl phthalate, bis(2-ethylhexyll)phthalate and diethyl phthalate) can exceed the hundreds of mg/L attributable to them use as plasticisers in PVC containers [26]. However, very low concentrations can be found in aged leachates because they can be degraded to monoester derivatives and phthalic acid during the biodegration of the organic matter [24]. However, their frequency of detection is moderate because its relatively easy biodegradation both in aerobic and anaerobic conditions.

TABLE I Organic contaminants identified in landfill leachates

Contaminant class	*Concentration range* $\mu g\,L^{-1}$	*Total number samples (frequency of detection)*	*References*
Volatile aromatics			
Toluene	0.01–41 000	30 (100%)	[8,9]
Trimethylbenzenes	1.9–37 000	19 (100%)	[10,13]
Benzene	0.065–3800	36 (95%)	[8,10,14,15]
Total xylenes	4–170 000	20 (80%)	[12,15]
Ethylbenzene	1–2300	22 (75%)	[8–15]
Dichlorobenzene	10–517	14 (57%)	[8,12,15]
Chlorobenzene	1.5–4620	12 (50%)	[15,16]
Chlorinated hydrocarbons			
Trans-1,2-dichloroethane	2.1–570	10 (100%)	[8,15]
1,1-Dichloroethane	0.6–180	12 (85%)	[11,15]
Cis-1,2-dichlorethylene	1.4–60	21 (80%)	[8,15–16]
1,1,2-Trichloroethylene	0.03–9500	36 (91%)	[12,15,16]
Tetrachloroethylene	0.03–23 600	33 (91%)	[7,13,18,29]
Dichloromethane	15–21 290	36 (68%)	[7,8,12,15,16,29]
Trans-1,2-dichloroethylene	3.8–2200	28 (62%)	[8–12,15,16]
1,2-Dichloroethane	5.5–34 000	34 (58%)	[12,15,16]
1,4-Dichlorobenzene	7.7–516	12 (58%)	[12,15,16]
1,1,1-Trichloroethane	1.9–2400	26 (50%)	[15,16]
Chloroform	0.01–4550	39 (25%)	[12,15,16,29]
1,2-Dichloropropane	2.0–650	26 (25%)	[11,12,15–17]
Vinylchloride	20–32 500	14 (25%)	[12,15,16]
Bromomethane	170	5 (20%)	[15,16]
Dichlorodifluoromethane	180–1 70 000	14 (20%)	[15,16]
1,1,2-Trichloroethane	500	5 (20%)	[15,16]
1,1,2,2-Tetrachloroethane	0.01–125	14 (20%)	[15,16]
Cis-1,3-dichloropropene	18–2 10 000	15 (20%)	[7,15,16]
Trichlorofluoromethane	15	6 (17%)	[15,16]
Phenols			
Chlorophenol	1–3	5 (100%)	[7]
Phenol	30–17 000	8 (100%)	[11,15]
Cresols	2100	9 (100%)	[11,15]
Ethylphenols	5.2–300	8 (100%)	[11,13]
Pentachlorophenol	0.01–3000	6 (100%)	[15,18]
p-Tert-butylphenol	0.001–0.451	7 (71%)	[13]
2,4,6-Trichlorophenol	0.08–1.87	7 (71%)	[18]
2,3,4,6-Tetrachloropenol	0.08–20.4	7 (71%)	[18]
2,4-Dichlorophenol	0.34–12.8	8 (57%)	[18]
3,4-Dichlorophenol	0.27–14.3	7 (57%)	[18]
Anilines			
Aniline	0.015–870	16 (100%)	[13,15]
2-Chloroaniline	0.001–36	10 (100%)	[13,15]
4,2-Toluidines	0.002–0.62	8 (88%)	[13]
N-Methylaniline	0.001–0.035	8 (75%)	[13]
3-Toulidine	0.004–2.57	8 (62%)	[13]
2,4,6-Trichloroaniline	0.001–0.007	8 (62%)	[13]
3,4-Dichloroaniline	0.005–0.278	8 (50%)	[13]
2,4-Dichloroaniline	0.002–0.016	8 (50%)	[13]
Alkylphosphates			
Tris(2-butoxyethyl)phosphate	0.011–2.32	8 (100%)	[13]
Tris(1,3-dichloro-2-propyl)phosphate	0.003–1.9	8 (100%)	[13]
Tris(2-dichloroethyl)phosphate	0.017–0.907	8 (100%)	[13,15]
Tris(2-chloropropyl)phosphate	0.014–10.9	8 (88%)	[13]
Triethylphosphate	0.03–15	17 (88%)	[13]
Phthalates			
Dibutyl phthalate	0.8–1 50 000	17 (75%)	[6,13,15]

(*continued*)

TABLE I Continued

Contaminant class	*Concentration range* $\mu g\,L^{-1}$	*Total number samples (frequency of detection)*	*References*
Dimethyl phthalate	0.037–55 000	17 (50%)	[13,15]
Bis(2-ethylhexyl)phthalate	2.5–1 50 000	17 (12%)	[8,13,15]
Diethyl phthalate	10–3 00 000	10 (12%)	[6,8,15]
Phenoxy acids			
MCPP	1–805	8 (100%)	[7,20]
2,4-DP	< 0.1–7	17 (24%)	[7,20]
Silvex	< 0.1–10	17 (15%)	[20]
PAHs			
Fluorene	0.001–12	8 (100%)	[13,15]
Naphthalene	0.001–19 000	14 (88%)	[8,9,13–15]
PCDD/PCDFs			
I-TE (ng L^{-1})	0.038–0.364	3 (100%)	[21]
I-TE (ng L^{-1})	0.022	1 (100%)	[22]
I-TE	623	1 (100%)	[23]
Aromatic sulphonates			
Naphthalene disulphonates	< 2.0–397	12 (67%)	[25]
p-Toluene sulphonate	< 7.6–48 800	12 (58%)	[25]
Naphthalene sulphonates	< 3.2–1190	13 (38%)	[25]
Aminonaphthalene disulphonates	< 7.3–109	12 (25%)	[25]

Volatile aromatics (e.g. BTEX) is another class of contaminants found at high concentrations in LL reaching the tenths of mg/L in case of toluene and hundreds in case of total xylene isomers. They exhibit a broad distribution in LLs depending on their management being particularly relevant because of their groundwater pollution potential [9]. Polycyclic aromatic hydrocarbons (PAHs) occur in LL but at lower concentrations than BTEX. Their lower solubility than BTEX, increases the association to the contaminated soil and solid waste especially in areas where poor waste management practices are used.

Aromatic sulphonates such as toluene and naphthalene sulphonates have been detected at very high concentrations but they are associated to a specific solid waste [25]. Until now, very few studies have reported on their occurrence in LL and consequently with a low to moderate detection frequency.

Chlorinated volatile hydrocarbons are constituted by a large number of components belonging to one of the most widely distributed chemical classes of contaminants. Depending on the LL management, they may occur at high concentrations in LL because they are degraded slowly. However, if leachates are stored at the open air, they can be volatilised. Since most of them belong to the priority contaminant lists, they are currently measured in monitoring programmes (Table I).

Phenols and cresols are another important class of contaminants in LL because they can be found at high concentrations and exhibited high frequency of detection. In fact, they are usually determined as total in most of the monitoring programmes [1]. Their occurrence is associated with the degradation of the organic matter and polymers. Chlorinated phenols are found at several orders of magnitude lower concentrations and with lower detection frequency than the alkylphenols, except pentachlorophenol, which is the most abundant component of this contaminant class [15].

Anilines, alkyl, and chloro-substituted exhibit a widely distribution in LL but their concentrations at several orders of magnitude lower than the former classes of contaminants [13]. They are intermediates in several chemical processes and are the degradation products of azodyes.

Alkylphosphates are not frequently determined but they are widely distributed in LL samples but at lower concentrations than the former contaminants, probably because they can be hydrolised or degraded easily [13]. They are used as industrial solvents and are present in many technical products.

Phenoxy acid herbicides can be abundant in LLs and are associated to their disposal in residential areas but their frequency of detection except the MCPP is low [7,20]. Moreover, a variety of pharmaceuticals (i.e. lipid regulators, antiphlogistics, antipyretics, vasodilators, antiepileptics, and repellents) have been identified in LLs showing that degradation of pharmaceuticals is incomplete in landfills [28].

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDFs) usually occur at low concentrations usually in the ng/L level but they are of particular concern because of their high toxicity being usually reported as international toxic equivalents (I-TE) (Table I). However, their occurrence in landfills is related to the waste characteristics (e.g. hazardous, industrial, and sewage) and consequently at several orders of magnitude lower [35].

SAMPLE HANDLING

In general, it is assumed that the sample preservation used for other aqueous matrices applies for leachates but no systematic studies have been carried out on their stability or the storage conditions to avoid organic matter degradation (Table II).

Volatile Contaminants

Usually direct sampling is carried out by collecting the sample directly into a bottle, bailers and in some cases with the aid of a pumping system. The key point is to avoid any headspace in the sampling bottle to minimise the loss of volatile contaminants during transport. This is carried under refrigerated conditions and storage at 4°C or at lower temperatures in glass bottles. Holding time defined by ASTM as "the period of time during which a water sample can be stored after collection and preservation without affecting the accuracy of analysis" is not well defined in case of LL, although a range from 1 or 2 day usually without filtration or pH adjustment is reported (Table II). However, in one paper they report 14 days [31]. Sample filtration under nitrogen pressure has been carried out very seldom [7]. Thiosulphate is added into the sample vial to destroy the residual chlorine [16] or mercury dichloride as a biocide [9]. All-glass vials are preferred for sampling and sample storage avoiding any sample transfer but Teflon-faced screw cap or Teflon-faced septum held on the tube top with a crimp-on aluminium seal are also used (Table II).

In order to find the optimum storage conditions, we have evaluated the stability of VOCs in LL stored under refrigerated conditions (4°C) with different sample stabilisers (i.e. HCl, NaN_3, $CuSO_4$) in all glass tubes without headspace. A decay in all analyte concentrations was always found according to the storage time being more apparent following the second week of sampling. The worst storage conditions were under acid pH because a precipitate was formed during the pH adjustment.

TABLE II Sampling and sample handling for organic contaminant determination landfill leachates according to the analyte type

Analyte	*Sampling technique*	*Storage conditions*	*Storage time* (days)	*References*
Volatile				
TCE	Dual valve bailer or positive displacement valve	Prefiltered (GF/C) 0–5°C	Max. 2 days	[7]
VOC	Peristaltic pump and stored in syringes	Refrigerated	1 day	[31]
VOCs	Bailer-glass bottle transfer. No headspace	Thiosulphate, 4°C	48 h	[16,32]
VOCs (70 compounds)	Pumping peristaltic pump with teflon tubing directly attached to the sandpoint	Stored with ice, $HgCl_2$, *o*-xylene-D_{10} as surrogate	Not specified	[9
VOCs	Not described	Not specified	< 14 days	[30]
Semivolatiles				
Phenols	SS tubing. Glass bottle transfer	Glass bottle Teflon® lined screw caps. Refrigerated	2–7	[11]
PCDDs/PCDFs	Direct collection	Glass flasks, Teflon® lined cap overlain aluminium foil. Refrigerated	–	[21]
Ionic compounds				
MCPP	Submersible pump	Not specified	–	[14]
Phenoxyalkanoic acid herbicides	–	4°C inert atmosphere	–	[20]
Multiple	–	Not specified	Minimum	[13]
Benzene, naphthalene sulphonates	–	10 mL formaldehyde	–	[25]

Another important aspect in the determination of volatile contaminants is the field and laboratory blanks, which is an aspect almost neglected in the published literature. Harkov *et al.* [37] found toluene and benzene at concentrations exceeding 1 μg/L in 50% of the field blanks measured in Tenax-GC cartridges and left for 24 h in the field. They also found chlorinated hydrocarbons in the field blanks but at lower concentrations. Reported procedural blanks are better ranging from below the LOD to 0.13 μg/L [9].

Semivolatile and Ionic Contaminants

Sample collection is carried out either directly in the storage bottle by stainless tubing or by using submersible pumps (Table II). Refrigerated containers and the minimisation of transportation time since the sample collection till the laboratory is usually taken as a precaution to avoid sample degradation. However, there is no systematic study to evaluate the holding time for semivolatile organic contaminants in LL. Usually, the same precautions outlined above for volatile contaminants are applied to semivolatiles except a longer holding time and less strict requirement regarding the headspace.

Sample containers used for leachate transportation are usually amber glass with Teflon® lined screw caps. Aluminium foil was used to overlain the sample bottle to avoid any photolabile analyte degradation promoted by sunlight irradiation [21]. In case of aromatic sulphonates determination, formaldehyde is added to the sample keeping it at room temperature [25].

Concentration of phenoxyalkanoic acids found in frozen samples is generally lower than those found in the refrigerated samples [20]. Authors suggest that the freezing process may result in precipitation of mineral phases supersaturated in the leachates (e.g. calcite) with attendant sorption of analytes. However, the concentration of phenoxyalkanoic acids under refrigerated anaerobic conditions and in the darkness did not produce any significant change in concentration of analytes despite TOC decreased 10 fold during the same storage period.

PRECONCENTRATION AND CLEANUP TECHNIQUES

Although surrogate addition before the extraction or preconcentration step is a common practice in environmental analysis, in case of leachate characterisation is rarely used (Table III and IV). It can be particularly critical when the analytical procedure involves multisteps such as in case of semivolatile contaminant determination. The high complexity of leachates and the difficulty to find the proper surrogate according to each analyte class could be the reason.

Volatile Contaminants

Although direct headspace is used for the determination of VCHs and BTEX [12,33,42], a preconcentration technique is required in most of the analytical schemes to reach the LODs required. LLE with pentane has been used several decades ago for the preconcentration of volatiles from aqueous samples [6] but due to the large volume of solvent consumption, it was replaced by Purge and Trap. Tenax® as adsorbent is

TABLE III Preconcentration and cleanup steps for volatile determination

Matrix	*Analyte*	*Surrogates*	*Preconcentration*	*Determination*	*LODs* (μg/L)	*RSDs* (%)	*References*
LL	VCHs	*m*-Chlorofluorobenzene	Purge and trap	GC-MS 4 sector	0.6–3.5	3.6–8.5	[36]
			Pulsed spray and trap	GC-MS	0.002–0.34	4.8–9.7	
			Purge and trap	GC-MS	0.001–0.03	4.3–7.4	
LL	VCHs	Bromotrichloromethane	Distillation closed system	GC-ECD	NR	NR	[17]
LL	VCHs, BTEX	NR	HS, 40°C	GC-MS	NR		[12,33]
LL	TCE and PCE	NR	LLE pentane (950 mL)	GC-ECD	NR	NR	[6]
LL, GW	VOC	NR	Purge and trap (Tenax)	GC-FID, GC-MS GC-FID/Hall	NR	NR	[8,11,13,32] [37]
LL	VOC	NR	Purge and trap (Tenax) Modified sparger unit.	NR	NR	NR	[31]
LL, GW	VOCs (70 analytes)	Surrogate: *o*-xylene-D_{10} I S.: ethylbenzene-D_{10}	Purge and Trap	GC-ITD	0.002–0.093	10	[9]
LL	1,4-Dioxane	1,4-Dioxane-D_4	220 mL, LLE, Na_2SO_4, CH_2Cl_2 (40 + 20 mL), Na_2SO_4, rot. Evap	GC-MS	NR	NR	[13]

LL: Landfill leachate, GW: Groundwater.
NR: Non reported

TABLE IV Preconcentration techniques and clean up in landfill leachates according to analyte

Analytes	*Preconcentration*	*Fractionation or clean up*	*Recovery* (%)	*Determination*	*LOD* ($\mu g/L^{-1}$)	*RSD* (%)	*References*
Chlorinated pesticides	SPME, PDMS 100 μm	–	–	GC-ECD	0.067	< 20	[38]
Alkylphosphates	LLE, CH_2Cl_2 (200 + 100 mL) Kuderna-Danish	–	–	GC-FPD	NR*	NR	[13]
Phthalates	40 mL, LLE, hexane (5 mL), NaCl (10 g)	–	–		NR	NR	[13]
Semivolatiles	1L, 150 g NaCl, LLE CH_2Cl_2 (100 + 50 mL), Na_2SO_4, Kuderna-Danish,	Silica gel (5% H_2O, 3 fractions)	–	GC-MS, IS (perdeuterated PAHs)	NR	NR	[13]
PCDDs/PCDFs	Liquid phase: (1L) CH_2Cl_2 (2 × 200 mL) Filter: Soxhlet toluene (16 h), evap., reconstitut. C_6H_{14}, H_2SO_4, LLE (2 × 100 mL),	H_2SO_4 treat. Alumina/silica column (EPA 1613).	45–97	GC-HRMS	NR	NR	[39]
PCDDs/PCDFs	Solid: toluene/ethanol (1:1), Soxhlet, 24 h Liquid: LLE toluene	Conc. H_2SO_4 in silica gel, activ. carbon, Activa. alumina	> 60% all congeners	GC-HRMS	10	NR	[21]
Benzene and naphthalene sulphonates	SPE (Envi-Carb)	–	24–87%	LC-ESI-MS	0.6–4.4	1.1–5.1	[25]
Multiple analytes	LLE extraction	Acid–Base partitioning 4 fractions	NR	GC-ECD GC-MS	NR	NR	[40]
Multiple analytes	(1) 2 L, LLE CH_2Cl_2, (1 × 200 mL, 2 × 50 mL)	Acid–Base partitioning (4-fractions)	NR	GC-MS	NR	NR	[34]
Phenoxyalkanoic herbicides	pH = 10, LLE 2 × 100 mL CH_2Cl_2, Na_2SO_4, pH = 1, LLE 3 × 150 mL MTBE, Na_2SO_4, Kuderna-Danish, BF_3–MeOH Continuous LLE, pH = 8	Acid–Base partitioning (3 fractions)	92–106%	GC-MS	1–2	10	[20]

*NR: Non reported

the most commonly used nowadays because its low moisture sorption and high sample capacity [8,9,11,13,31]. However, foaming formation during the purging step can lead to trap contamination and deactivation being common problems encountered when a conventional equipment is used in complex matrices such as LL. Chichester-Constable and coworkers [31] have modified a commercially available sparking unit to improve its efficiency in case of dirty leachates with high particle content. They found a frequent clogging in the glass frit due to the presence of iron hydroxide and particles occurring in the samples. The highest abundances were obtained with a modified sparger device without frit providing 1.5 times more abundance than a commercial unit. Lee *et al.* [36] have compared a conventional purge-and-trap concentrator with a pulsed system that allows lower LODs in leachate samples (Fig. 1). Reported recoveries for *o*-xylene-D_{10} as surrogate in groundwater was 70 ± 13 ($n = 42$). However, similar data for LL is missing.

Distillation has been used for concentration and cleanup of volatile contaminants in leachates [17]. The limitation of that analytical procedure is the time required to complete the process that is increasing with the decrease of the Henry constant of the analyte. For instance, if a complete distillation can be accomplished in 2 h for chlorinated ethanes and ethenes, for chloronitrobenzene even after 6 h only the 40% is removed from the aqueous sample. Enrichment factors from 5 to 9 can be obtained.

Headspace-SPME is another method that can be used for the characterisation of the volatile contaminants in leachates since the fibre is not directly exposed to the sample. Some applications have also been reported in case of semivolatiles such as the organochlorine pesticides [38] and chlorophenols [19] in LL and lipids [41] in distillates from LL. Some selectivity can be achieved depending on the composition

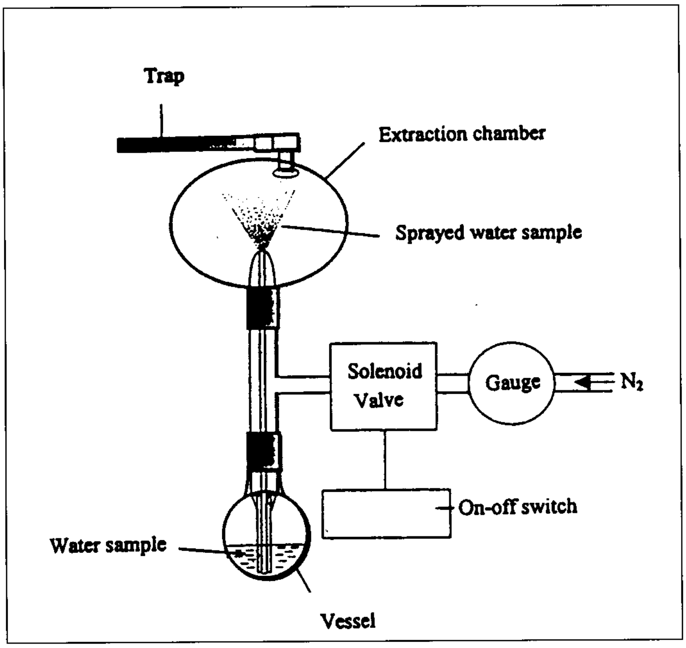

FIGURE 1 Pulsed spray-and-trap system. Reprinted with permission from Elsevier Science from reference [36].

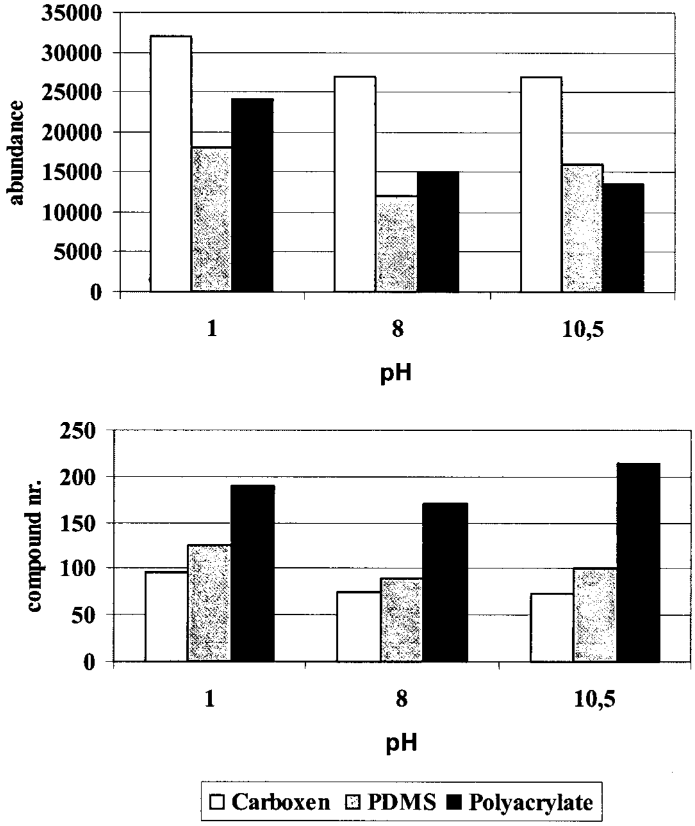

FIGURE 2 Evaluation of the SPME selectivity and concentration capacity according with fibre composition and sample pH.

of the polymer and the predominant extraction mechanism involved (Fig. 2). The highest K' of VOCs was obtained with the Carboxen fibre but with the polyacrylate, a larger number of analytes were preconcentrated independently of sample pH. This fact is consistent with the adsorption mechanism of Carboxen and only the smaller size analytes can be preconcentrated whereas polyacrylate is not selective.

The determination of dioxane in leachates has been carried by LLE with dichloromethane followed by rotary evaporation [13]. Perdeuterated-1,4-dioxane standard is used as surrogate for this particular determination allowing the recovery calculation of the analytical procedure. Over-evaporation can be critical in terms of poor analyte recoveries.

Semivolatile and Ionic Contaminants

LLE by using dichloromethane or hexane has been the method of choice for semivolatiles in leachates for this matrix. If LLE is carried out at different pHs, it allows a fractionation based on acid–base properties of analytes (i.e. neutral, acid-strong or weak-basic) [20,34,40]. Further fractionation of the neutral fraction can be accomplished by column chromatography yielding to fractions of increasing polarity [13]. The large solvent volume used in LLE can be a source of blank problems or analyte losses by evaporation during the concentration step. Kuderna-Danish can overcome the latter but still the large solvent volume leads to a time consuming evaporation process. Emulsion formation is another frequent problem encountered in LLE at extreme pHs necessary to extract phenoxyalkanoic acid herbicides [20,44]. The use of a continuous liquid–liquid extractor at lower pHs improved the emulsion formation. SPE or direct SPME immersion could be useful but the colloidal fraction occurring in leachates may difficult the filtration and/or extraction process. A combination of centrifugation and/or filtration becomes imperative before SPE [25] to speed up the extraction process as well as the use of filtre aid to increase the filtration surface. Another alternative for the extraction of LL was to adsorb the sample on a XAD-4 resin under stirring for 15 min, then the adsorbent was transferred to a column chromatography and eluted with a mixture of methanol–acetone [45]. A variety of carboxylic acids, ketones, amines and amides were identified by GC-MS by using this extraction procedure.

Moreover, matrix effects can be relevant in SPME of leachates affecting the sensitivity of detection. Humic acids and surfactants affect the extraction efficiency. The matrix not only hampers the diffusion of chlorophenols to the coating but also inhibit their absorption on it [16]. Authors suggest that these effects could be overcome by the extension of the extraction time or alternatively by using surrogates of the same characteristics that the analytes.

Benzene and naphthalene sulphonates from leachates can be extracted with activated carbon SPE cartridges [25]. Recoveries ranging from 24 to 87% have been reported depending on the analyte substituents.

FINAL DETERMINATION (GC-MS, LC-MS, LC-NMR)

GC-MS and Related GC Techniques

These are the most widely used techniques for the determination of volatile and semivolatile organic contaminants in LLs (Tables III and IV). In general, electronic impact with a quadrupolar analyser is used except for the determination of PCDD/Fs that is usually carried out by high resolution MS at 10 000. ^{13}C-labelled congeners are the internal standards of choice. Detection limits range of 10 pg/L for liquids and 0.5 pg/g for solids [21]. Alternatively, ion trap GC-MS-MS has also been used for the determination of volatile organochlorine compounds. It allows higher selectivity but some sensitivity is lost compared with the conventional GC-MS [19]. On the other hand, perdeuterated PAHs are used in the GC-MS determination of the neutral fraction despite PAHs are not a major class of contaminants in licensed landfills where no combustion process occurs.

In addition to MS, several systems combined with GC have been used for the determination of different analyte classes in leachates. FID, ECD, FPD, PID, and Hall electroconductivity have been used for hydrocarbons, alkylphosphates and chlorinated compound quantitation previous identification by GC-MS (Table IV). The relatively low cost bench-top GC-MS has increased its utilisation for both qualitative and quantitative applications. FPD in the phosphorus mode has been used for the determination of alkylphosphates and ECD for organochlorine pesticides.

Quantification limits in the range of 2–15 ng/L and 100 ng/L respectively, have been achieved.

Although the GC determination is usually carried out by using free analytes, phenoxyalkanoic acid herbicides demand a derivatisation step prior to GC determination. Methyl and pentafluorobenzyl derivatives have been used for this purpose [20].

External standard calibration is the most common calibration but the internal standard is getting increasingly used. Isotopic dilution using perdeuterated or ^{13}C standards are the method of choice for GC-MS in terms of precision. Standard addition has been also employed when matrix effects are expected.

LC Hyphenated Techniques

These techniques have been rarely used for the characterisation of leachates because of the great complexity of this matrix. Benzene and naphthalene sulphonic acids have been determined by LC-ESI reaching detection limits of 0.6–4.4 µg/L and 10–190 ng/L for leachates and groundwater, respectively, depending on the analyte [46].

As mentioned in the former section, mecoprop is a common herbicide found in leachates and groundwater downstream because its high water solubility and low tendency to adsorb to humic substances [47]. As in case of many chiral compounds only one of the enantiomeric forms is biologically active. The possibility to resolve the racemic mixture by LC-MS with a chiral stationary phase allowed the resolution of enantiomers and to evaluate the enantioselective degradation of the (*S*)-mecoprop in the leachate plume [43].

LC-NMR provides high structural information, which is of particular advantage in non-target analysis. However, due to the low analyte concentration in environmental samples and the limited sensitivity of NMR, LC-NMR is precluded to ^{1}H-NMR [48]. The technique is complementary to MS allowing the identification of isomers and a combination of both techniques has been applied to the identification of aromatic carboxylic acids in industrial LLs [49].

FUTURE DEVELOPMENTS

In situ measurements is one of the areas that need to be developed for landfill pollution control because conventional analytical methods can lead to volatile losses during sampling and transport. Thermal extraction cone penetrometry gas chromatography mass spectrometry [50] allows the determination of PCBs, PAHs, chlorinated pesticides, and explosives in subsurface wet or dried soils down to 30 m depth. Further development is needed to obtain accurate data comparable to conventional analytical techniques because concentrations of contaminants are underestimated from 5 to 40% depending on the contaminant type. Optical sensors based on IR spectroscopy combined with IR fibres may allow field measurements of different chemical classes of contaminants but still the main problem is their sensitivity and the signal depletion in accordance with the distance from the source to the detector. The use of a heading sensor with coated polymers could allow a significant improvement in sensitivity but the used polymers must be transparent to the wavelength where analytes absorb the IR irradiation [51].

SPME using proper surrogates is one of the most reliable analytical technique for the determination of VOCs in LLs but the main limitation is the limited capacity of adsorption fibres which may lead to a narrow linearity range in the calibration plots. Headspace stirring bar sorptive extraction could overcome some of the SPME limitations because a large amount of stationary phase is used although limited in terms of stationary phase composition. Matrix solid-phase dispersion seems more feasible than conventional SPE for semivolatile determination in LL because the high matrix complexity. Passive sampling techniques appears to be the method of choice for the preconcentration of semivolatiles deploying semipermeable membranes devices (SPMDs) or related systems in the piezometers or monitoring wells to evaluate landfill plume attenuation.

Emerging classes of contaminants occurring in LL need to be updated particularly those that may migrate and contaminate groundwater. Preliminary reports have shown the occurrence of pharmaceuticals in urban LL [28]. Further research is needed to ascertain the significance of this finding. Bioassay-directed fractionation [52] appears to be an interesting approach to identify the contaminants responsible for the toxicity in landfill plumes.

ACRONYMS

BDF	Bioassay-Directed Fractionation
BOD	Biological Oxygen Demand
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
COD	Chemical Oxygen Demand
Dichlorprop	2-(2,4-Dichlorophenoxy)propionic acid
DOC	Dissolved Organic Carbon
EC	Electroconductivity
ESI	Electrospray Ionisation
LLE	Liquid–Liquid Extraction
LC	Liquid Chromatography
MCPA	4-Chloro-(2-methylphenoxy)acetic acid
Mecoprop	2-(4-Chloro-2-methylphenoxy)propionic acid
MSPD	Matrix Solid-Phase Dispersion
P and T	Purge and Trap
PCE	Tetrachloroethylene
PID	Photoionisation Detector
PD	Perdeuterated
PDMS	Polydimethylsiloxane
PFBBr	Pentafluorobenzylbromide
SPE	Solid-Phase Extraction
SPME	Solid-Phase Micro-Extraction
TCE	Trichloroethylene
TOC	Total Organic Carbon
VCHs	Volatile Chlorinated Hydrocarbons
VOCs	Volatile Organic compounds

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