

Odorants and Their Contributions to Overall Odour Emission from a Landfill Leachate

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Abstract: As one of the important odour sources, landfill sites have drawn more and more public attentions. Odour emissions from landfill sites depend on the waste buried, operation activities, running conditions, etc. A study for finding out all possible odorous compounds from a landfill was conducted by analysing of on-site gas phase samples and emission samples from a landfill leachate in Sydney, Australia using thermal desorber – gas chromatography – mass spectrometer (TD-GC-MS) and air server – thermal desorber – gas chromatography – sulfur chemiluminescence detector (AS-TD-GC-SCD). 49 odorants were identified from gas emission samples collected from landfill leachate collection pipes and only 8 odorants were detected from flux hood emission samples of the collected leachate sample. This indicates that more sampling and measurement techniques are always better to acquire all possible pollutants from an unknown odour source. The contributions of these odorants to overall odour emissions were also calculated based on their concentrations and odour thresholds. The top 10 odorants from leachate transportation pipe include methyl mercaptan, ethyl mercaptan, m-xylene, H₂S, CS₂, 1,2,3,4-tetra-methylbenzene, p-xylene, 1,2,4-trimethylbenzene, ethylbenzene and α -pinene. They contributed more than 95% to the odour in the gas accumulated in the leachate collection pipe.

Keywords: odour, odorants, emission, landfill, leachate

1. Introduction

Landfill is still the predominant disposal method to dispose solid industrial and municipal waste in most countries. After moving to a landfill site, piled and buried waste will emit landfill gases because of chemical and biodegradation of the waste under anaerobic condition. Besides greenhouse gases like CH₄ and CO₂, the toxic and health issues of the minor gas components such as volatile organic compounds (VOCs) and volatile sulfur compounds (VSCs) have drawn more and more public attentions. Odour have also become an important issue resulting from increasing number of complaints raised by residents surrounding landfill sites.

Since 1980s, many researchers have tried to specify and quantify composition of emission gases from various landfill sites for disposal of municipal, industrial, construction and demolition, or mixture of different wastes. Table 1 summarised the key investigations that have been reported in past 3 decades and their main observations:

(1) Some of the studies focused only on few specific compounds like reduced sulfur compounds (RSCs): e.g. [1-4], and most of other works paid more attentions on more complicate VOCs such as [5-8], etc.

(2) Investigation sample sources include ambient air, waste gas at different depths, vent well, emissions from cover soil, leachate, etc. Most of samples were collected from the ambient air above the landfill sites or at the boundaries. For ambient air sampling, different sampling heights had been used: 1m [2], 1.5m [9-10], 2m [11], or several different heights [12]. In some studies, even no specification can be found in some of their publications.

(3) Limited gas emission data had reported from the cover soil, landfill waste using dynamic flux hood [13], static flux chamber [4], flux box [14], unspecified hood [5], or wind tunnel [7].

(4) Sampling method varied from researchers to researchers. Generally, gas phase sampling was conducted by using canister [15-16], single or multi-bed sorbent tubes, sampling bags, and liquid trapping.

Liquid trapping was used mainly for NH₃ and H₂S spectrophotometer analysis [17-19]. [20] also used liquid-trapping for sampling of VFAs. Several sorbent tubes had been used: activated carbon or

synthetic carbon+silic gel [17, 21-22], Tenax or Tenax GR [9, 17, 23], Porapak Q [17, 24], Carbotrap 3000 [11], and multi-bed sorbent [5, 13-14, 25-27].

Sampling bags were mainly Tedlar [1-3, 20, 24, 28-32], Nalophan [5, 7-8, 33-34], bioriented polyester [10], or plastic [4] bags.

Other sampling methods used in other studies include diffusive sampler [34], passive sampling [35], and direct sampling to the μ GC-MS in the field [35].

(5) Component separation is almost all done by using gas chromatography (GC) for analysis of VOC and other compounds. However, analytical method differed mainly by the use of different sample processing procedures and detectors.

Table 1 Compounds identified from landfill sites

Compounds	Sample Collected	Sources	Sampling Method	Analytical Method	Reference
7 VOCs + DMDS	Diffusive samples	Solid waste treatment plant	Diffusive samplers	TD-GC-MS	[34]
CH ₂ Cl ₂ , C ₂ H ₂ Cl ₂ , C ₂ HCl ₃ , C ₂ Cl ₄ , H ₂ S, CH ₃ SH	Boundaries, 500m away	Landfill sites	Tenax tubes Liquid trapping	TD-GC Spectrophotometer	[18]
68 VOCs, NH ₃ , H ₂ S	Ambient air	Landfill	Nalophan bags + SPME	GC-MS	[19]
22 VOCs	Ambient air (1.5m)	Solid waste treatment plant	Tenax GR tubes	TD-GC-MS	[9]
53 VOCs + 10 VFAs	Soil, water surface (hood)	Landfill	Nalophan + Tenax TA & Carboxen 1000 tubes	TD-GC-MS	[5]
16 VOCs	Ambient air	MSW	Activated carbon tubes	CS ₂ extraction/GC-MS	[21]
More than 80 siloxanes + VOCs	Biogas	Domestic waste disposal sites	Canisters	TD-GC-MS/AED	[36]
Benzene, VCM, PCDD/Fs, DL-PCBs & PAHs	Diffusive surface, point emission	MSW landfill	Nelophan bags + SPME	GC-MS	[33]
19 VOCs	Air	Municipal waste organic fraction treatment plant	Synthetic carbon + silica gel tubes	CS ₂ extraction/GC-MS/HPLC-UV	[22]
63 VOCs	Surface (flux box)	MSW disposal sites	Chromosorb 106 & Carbopack cartridges	TD-GC-MS	[14]
41-66 trace compounds	Ambient air (1.5m)	Landfill for MSW + composting residue	Bioriented polyester bags	Pre-concentrated/GC-MS	[10]
38-66 VOCs	Ambient air (2m)	MSW	Carbotrap 300 tubes	Aerotrap purge and trap concentrator-GC-MS	[11]
H ₂ S + over 100 VOCs	Waste gas (1.0-4.3m deep)	Domestic and industrial waste landfill	Tenax or Porapak Q tubes	GC-MS Spectrophotometer	[17]
VOCs	5 different height of open cells	MSW	Activated carbon tubes	CS ₂ extraction to GC-MS	[12]
140 VOCs	Ambient air	Landfill	Nalophan bags	USEPA TO-15	[7]
Hundreds VOCs with 7 presenting	Ambient air	Landfill area	Tenax & Spherocarb cartridge	TD-GC-MS	[23]

48-66 VOCs	Soil & well gas	Landfill	Glass tubes	SPME/GC-MS	[6]
93 VOCs with 70 positively identified	Ambient air	MSW treatment plants	Tenax TA & Carboxen 1000	TD-GC-MS	[27]
147 VOCs	Laboratory reactor	Real waste sample	Nahophan bag	SPME/GC-MS	[8]
Over 500 compounds	Air	Municipal landfill	Passive sampling Direct sampling	GC-MS μ GC-MS	[35]
100 VOCs	Ambient air	Landfill	Nalophan bags	SPME/GC-MS	[32]
60 VOCs	Closed surface (flux hood)	Landfill	Multi-bed sorbent tubes	TD-GC-MS	[13]
H ₂ S & VOCs	Passive vent, landfill cover, leachate	Landfill	Canister & Tedlar bags	GC/FID/PID/ELCD Jerome	[15]
12 sulfur compounds	Duct	Domestic landfill	Tedlar bag+Porapak Q tube	TD-GC-MS	[24]
3 sulfur compounds	Flux hood sample	Landfill	Glass fiber filters impregnated with mercuric acetate	GC-FID/SCD	[37]
H ₂ S	Cover soil	Construction & demolition debris landfill	Tedlar bags	Jerome	[31]
RSCs, carbonyls, NH ₃ , VOCs, VFAs	Vent	Landfill leachate treatment plant	Tedlar bags DNPH cartridge Liquid trapping Tedlar bag Liquid trapping	TD-GC-MS HPLC-UV UV/VIS TD-GC-MS/FID SPME/TD-GC-FID	[20]
NH ₃ , aromatics, sulfur compounds, oxygenated compounds, amines, fatty acid	Vent system	Landfill	Tedlar bags	SPME/GC-FID, GC-PFPD, HPLC, etc.	[30]
5 sulfur compounds	Active, inactive, covered area	Landfill	Plastic bags	USEPA TO-15	[4]
5 sulfur compounds	Ambient air	Landfill	Tedlar bags	TD-GC-PFPD	[29]

Sulfur compounds	Landfill gas, soil vapore, ambient air	Landfill	Tedlar bags	Jerome, purge & trap concentrator/GC-MS	[3]
5 RSCs	Vent pipes	MSW	Tedlar bags	TD-GC-PFPD	[1]
5 RSCs	Vent pipes	4 landfill sites	Tedlar bags	TD-GC-PFPD	[28]
4 RSCs	Ambient air (1m)	2 landfill sites	Tedlar bags	TD-GC-PFPD	[2]
VOCs	Leachate	Industrial landfill	SPE/SPME	GC-MS, LC-MS, NMR, LC- NMR	[38]
Over 200 compounds with 35 priority pollutants	Leachate	MSW	Multi-bed carbotrap tubes	TD-GC-MS	[26]
VOCs + inorganic compounds	Leachate + suspended particles	Landfill sites	Solvent extraction	HPLC/GC-MS/FID	[39]
180 VOCs (22 quantified)	Seepage, leakage	Landfill leachate	Solvent extraction	GC-FID/ECD GC-MS	[36]
11 predominant VOCs	Leachate	Landfill	Liquid-liquid extraction	GC-MS	[40]
45 organic compounds	Leachate	Municipal landfill	Solvent extraction	GC-MS	[41]

The most often used detector for VOC analysis is mass spectrometer (MS), which made GC-MS the basic configuration for VOC analysis. Pulsed flame photometric detector (PFPD) was used for analysis of sulfur compounds [1-2, 28-29]. Other detectors include FID (flame ionization detector), PID (photoionisation detector), ELCD (electrolytic conductivity detector), ECD (electron capture detector), AED (atomic emission detector), SCD (sulfur chemiluminescence detector), UV (UV detector) were also used in some studies.

In these studies, most of the sample processing procedures utilised thermal desorber (TD) when canisters, bags, or sorbent tubes samples were collected. So, the most frequently used instrument combination is TD-GC-MS [5, 9, 13-14, 16, 23-25, 27, 34]. In some cases when bag samples were collected, solid phase microextraction (SPME) technique was employed for GC-MS sample processing [6, 8, 19, 30, 32-33]. [20] also used SPME to absorb VFAs from head space of liquid-trapping samples.

(6) H₂S was also measured directly or indirectly (sampled to the bag before the measurement) by using Jerome gold film analyzer [3, 15, 31] in the field.

(7) No leachate emission data had reported although leachate composition was reported after HPLC/GC-MS/FID analysis [39], SPE/SPME/GC-MS, LC-MS, NMR, LC-NMR analysis [38], or GC-MS analysis after liquid-liquid extraction [36, 40-41].

(8) VOCs and sulfur compounds were two major groups of compounds investigated. The number of detected compounds varied quite significantly from one publication to another not just because of the differences between landfill sites, but also because of what the investigators focused on, and the sampling and analytical techniques available for using during their investigation.

(9) Odorous compounds were specially spotted in some of the studies. [42] summarised the top 15 odorous compounds present in landfill gas (Table 2). NH₃ was measured by some researchers [19, 43]. As odorous compounds, H₂S and/or up to 14 other sulfur compounds from landfill sites were reported by [3, 8, 17, 19, 24, 28-29, 31, 34, 37, 43-44]. Apart from 7 sulfides (DMDS, CS₂, methyl propyl disulfide, allyl mercaptan, DMTS, allyl methyl sulfide, 1-propene-1-methylthio), 2 nitrides (trimethylamine and 2-methyl pyridine) were also thought to be the main odour emission contributors [8].

Some of the VOCs and VFAs were also thought to cause the annoying odour at the landfill sites: alkylbenzene, terpenes and limonene [11]; 2-butanone, α -pinene, tetrachloroethylenen, β -pinene, limonene, phenol and benzoic acid [34]; acetic acid, 2,3-butanedione, ethyl acetate, α -pinene, and limonene [9]; acetic acid and n-butyraldehyde [30], methyl butyrate, ethyl butyrate, propionate, butyric acid, limonene, and butan-2-ol [44]; esters and ethyl butanoate [17]; aldehydes, ketones, and esters [5]; toluene, styrene, xylene, methyl ethyl ketone, methyl isobutyl ketone, butyl acetate, isobutyl alcohol, propionic acid, butyric acid, isovaleric acid, and valeric acid [20].

Table 2 Most odorous compounds present in landfill gas [42]

Rank	Odour Importance	by Hurst et al 2005	by Parker et al 2002
1		Methanethiol	Hydrogen sulfide
2		Ethyl butanoate	Methanethiol
3		Ethanethiol	Butanoic acid
4		Dimethyl sulfide	Ethanal
5		Dimethyl disulfide	Carbon disulfide
6		Diethyl sulfide	Ethyl butanoate
7		Butanoic acid	1-propanethiol
8		Hydrogen sulfide	Dimethyl disulfide
9		1,1-dichloroethane	Ethanethiol
10		Diethyl ether	1-pentene
11		Propan-1-ol	Dimethyl sulfide
12		Methyl butanoate	1-butanethiol
13		Pentanethiols	Propanoic acid
14		Propyl propanoate	Butyl ethanoate
15		Propyl benzenes	Butanal

(10) From the leachate, only [26] specified odour contributors that included aromatic hydrocarbons, ketones, alcohols, sulfur containing compounds, pyridines, pyrazines, carvone, cyclic esters, and dioxolans.

In this study, odorants emitted from the leachate of a municipal waste landfill site were investigated. The landfill site is located west of Sydney, Australia. It occupies approximately 31 ha and 16 ha are currently used for waste burial, recycling stockpiling material and front entrance customer service facilities. The site commenced in service from 1950's and expected to provide 15-20 years of landfilling capacity based on current disposal rates. It currently receives around 45,000 tons of municipal waste a year. The emission gas from the leachate transport pipe and emission gas from the leachate surface were sampled for TD-GC-MS and air server-TD-GC-SCD analysis. Based on the identified compounds, and their odour threshold (OT) values, contributions of the key odorants were calculated and ranked.

2. Methodology

2.1 Sample collection

Field sampling activities included fugitive gas emission samples collected from the liquid aeration return pipe stretching out above the leachate dam; and liquid sample collected from the leachate storage dam.

2.1.1 Fugitive gas sampling

Fugitive gas samples were collected for VOC and VSC analysis. The samples were collected from the leachate aeration liquid nozzle of the liquid aeration return pipe stretching out above the leachate dam.

VOC samples were collected on-site using reconditioned Tenax TA sorbent tubes (Marks International). These samples were collected near the nozzle of the liquid aeration return pipe stretching out above the leachate dam. Calibrated sampling pumps (SKC AirChek 2000) were used to draw the gas phase stream through the sorbent tubes (collection rate 100 mL/min; duration 10 min; sample volume 1 L). VOC samples were collected in duplicates, each of which had two tubes connected in series to confirm if there is any potential breakthrough of analytes absorbed to the first sampling tube.

VSC samples were collected in duplicate into 5 L Tedlar™ bags utilising a lung sampler (collection rate 2.5 L/min).

2.1.2 Leachate and its emission sampling

A 5 L composite leachate sample was collected from the leachate storage dam into an amber glass bottle with no headspace. The sample bottle was kept refrigerated before the emission test. It was used to collect emission samples as the leachate dam was not safely accessible for emission sampling using flux hood chamber [48] or portable wind tunnel [49] surface source sampling device.

The emission simulation test of the leachate was conducted using a flux hood chamber in compliance with Australian Standard method [50]. This method was also approved by the Department of Environment and Conservation for sampling emissions from a surface area [51]. Prior to sampling, the flux hood chamber was seated on the leachate surface and purged with high purity nitrogen gas for 30 min at the flow rate of 5 L/min before the sampling. Duplicate bag samples (5L Tedlar™) were collected using a lung sampler (collection rate 2.5 L/min) for VSC analysis. Duplicate Tenax TA sorbent tube samples were also collected (collection rate 100 mL/min for duration of 30 min with total sampling volume of 3 L) for VOC analysis.

2.2 Analyses of VOCs and VSCs

Sorbent tube analysis was performed using an Ultra autosampler equipped thermal desorber (TD, Ultra + Unity II Markes International, UK) – gas chromatograph – mass spectrometer (GC-MS, 7890A GC + 5975C Agilent Technologies) system. The thermal desorber was fitted with a general purpose graphitised carbon analyte focussing trap (U-T11GPC-2S, Markes International UK); the gas chromatograph was fitted with a low polarity DB-VRX (Agilent Technologies) capillary column (30m × 0.25mm × 1.4µm) for analyte separation; GC carrier gas was ultra high purity helium (1.8 mL/min).

GC oven temperature was programmed initially setup at 50°C for 2 min then increased to 200°C with an increment of 15°C/min and held for 3 min. Analyte speciation was performed by the mass selective detector operating in continuous scan mode (35-335 m/z); NIST02 and NIST11 libraries were used for spectra matching and compound identification. Gas phase TO-17 standard (from Air Liquid) was used for calibration and quantification of some compounds, and all other compounds were quantified based on their peak area against toluene calibration factor.

VSC bag samples were analysed on the same day of the field sampling. Sample bags were directly sampled by an air server (AS, Markes International) coupled to a thermal desorber (TD) Unity (Markes International) and analysed by gas chromatograph (GC, Agilent Technologies) coupled to a sulfur chemiluminescence detector (SCD, Agilent Technologies). The thermal desorber was fitted with a sulfur specific carbon molecular sieve analyte focussing trap (U-T6SUL-2S, Markes International UK). A DB-VRX column (30m×0.25mm×1.4 μm) was used for GC separation, initially starting at 37°C held for 3 minutes; the temperature was increased at 15°C/min up to 225°C and held for 2 minutes. The flow rate of the carrier gas (ultrahigh purity helium) was set as 1.5 mL/min. The sulfur compounds determined by TD-GC-SCD system include carbonyl sulfide, hydrogen sulfide, methyl mercaptan, ethyl mercaptan, dimethyl sulfide, carbon disulfide, 2-methyl-2-propanthiol, ethyl methyl sulfide, 2-butanehiol, 1-butanethiol, dimethyl disulfide, ethyl methyl sulfide, diethyl disulfide, and dimethyl trisulfide. Their quantifications were based on high-purity individual liquid standards purchased from Sigma-Aldrich, Arkema Inc. or SAFC Supply Solutions using the dynamic injection sample preparation method [52].

2.3 Calculation of odour emission contribution

Based on the measurements, odour unit factor was calculated for all quantifiable components using the equation (1)

$$OUF_i = C_i / OT_i \quad (1)$$

where OUF_i is the odour unit factor of an odourant; C_i is concentration (mg/m³); OT_i is the odour threshold concentration (mg/m³).

Contribution of an odorant to total odours can be calculated as

$$c_i = OUF_i / \sum OUF_i \cdot 100\% \quad (2)$$

where c_i is the contribution of an odorant to total odour.

3. Results and Discussion

3.1 Identified odorants

Over 130 VOCs and VSCs were detected from the gas samples collected from the leachate pipe; among which at least 49 of them are documented odorants (Table 3). These compounds are mainly hydrocarbons (29), sulfur compounds (15), halogenalkanes (2), and oxygenated hydrocarbons (3).

Table 4 lists odorants found in the flux hood emission samples of collected leachate sample. Comparing with the field gas sample results (Table 3), it can be seen that much less odorous compounds were identified. The reason for this may be: (1) some of odorants had mostly evaporated after the leachate was stored in the leachate dam for a period of time; (2) the leachate in the dam had been diluted by rain water; (3) most of odorants had low evaporation ability or they were trapped in the liquid phase when the emission test was carried out; (4) field gas sample may also include landfill gases that appear unusually in the leachate.

Almost all of these odorous VOCs were detected by many of previous researchers from the landfill gases although not all of them had been mentioned to be odorous.

In total, 17 sulfur compounds were detected from field gas samples, of which 14 VSCs (only 12 were listed in Table 3 because ethyl methyl disulfide and diethyl disulfide had not been quantified as

they only showed small peaks) were detected by TD-GC-SCD method and 3 more (sulfur dioxide, 1-propanethiol and 2-propanethiol) were detected by TD-GC-MS.

Apart from the common sulfur compounds like H₂S, methyl mercaptan, dimethyl sulfide (DMS), CS₂, and dimethyl disulfide (DMDS) reported by other researches, this study also detected other VSCs with very limited reports such as carbonyl sulfide by [2, 24]; ethyl mercaptan, 2-methyl-2-propanethiol, 2-butanethiol by [2]; 2-butanethiol by [2, 27]; 1-butanethiol by [24, 42]; DES by [4]; DMTS by [8, 30]. Ethyl methyl disulfide could be firstly detected from landfill as it was not on the listed sulfur compounds detected in previous studies. This may be because GC-SCD is the extremely powerful tool to characterise and quantify a wide range of low-level sulfur species in gaseous streams [53].

Table 3 Odorants identified in gas phase field samples

Rank	Compound	Formula	MW	Odour Description [*]	OT		Concentration (mg/m ³)	Odour Contribution (%)
					ppm ^[45]	mg/m ³ ^[46]		
1	Methyl mercaptan	CH ₃ SH	48.11	Rotten cabbage	0.00007		0.0156	29.29
2	Ethyl mercaptan	C ₂ H ₅ SH	62.13	Leek, onion odour	0.0000087		0.0013	15.19
3	<i>m</i> -xylene	C ₈ H ₁₀	106.17	Sweet, aromatic	0.041		8.8859	12.89
4	Hydrogen sulfide	H ₂ S	34.08	Rotten egg	0.00041		0.0257	11.61
5	Carbon disulfide	CS ₂	76.14	Sweetish aromatic	0.21		24.601	9.72
6	1,2,3,4-tetra-methyl-benzene	C ₁₀ H ₁₄	134.22	Aromatic	0.0011		0.1272	5.44
7	<i>p</i> -xylene	C ₈ H ₁₀	106.17	Sweet	0.058		4.0263	4.13
8	1,2,4-trimethyl benzene	C ₉ H ₁₂	120.19	Aromatic	0.12		7.3886	3.23
9	Ethylbenzene	C ₈ H ₁₀	106.17	Aromatic, gasoline type	0.17		6.0946	2.13
10	α -pinene	C ₁₀ H ₁₆	136.24	Herbal, terpenic	0.018		0.807	2.08
11	Carbonyl sulfide	COS	60.08	Distinct sulfide smell	0.055		0.6884	1.32
12	Toluene	C ₇ H ₈	92.14	Sweet, pungent	0.33		4.0797	0.85

13	Methyl cyclohexane	C ₇ H ₁₄	98.19	Petroleum-like	0.15	1.377	0.59
14	Heptane	C ₇ H ₁₆	100.20	Gasoline-like	0.67	2.9604	0.28
15	1,3,5-trimethylbenzene	C ₉ H ₁₂	120.19	Distinctive, aromatic	0.17	0.8941	0.28
16	2-methylheptane	C ₈ H ₁₈	114.23	Natural gas odour	0.11	0.4849	0.24
17	Decane	C ₁₀ H ₂₂	142.29	Petrolic odour	0.62	3.2479	0.23
18	Nonane	C ₉ H ₂₀	128.26	Petrolic odour	2.2	6.1924	0.14
19	Octane	C ₈ H ₁₈	114.23	Gasoline-like	1.7	2.1731	0.09
20	3-methylhexane	C ₇ H ₁₆	100.20	Petrolic odour	0.84	0.8938	0.07
21	Undecane	C ₁₁ H ₂₄	156.31	Petrolic odour	0.87	1.3541	0.06
22	Dodecane	C ₁₂ H ₂₆	170.34	Petrolic odour	0.11	0.1192	0.04
23	Hexane	C ₆ H ₁₄	86.18	Petrolic, gasoline-like	1.5	0.779	0.04
24	Benzene	C ₆ H ₆	78.11	Sweet, solvent	2.7	0.9719	0.03
25	Methylcyclopentane	C ₆ H ₁₂	84.16	Sweetish gasoline-line	1.7	0.5073	0.02
26	3-methylpentane	C ₇ H ₁₆	100.20	Not available	0.37	0.0932	0.02
27	3-methylheptane	C ₈ H ₁₈	114.23	Petrolic odour	1.5	0.4216	0.02
28	1-pentane	C ₅ H ₁₀	70.13	Gasoline-like, hydrocarbon odour	0.1	0.0097	0.01
29	2-methylpentane	C ₆ H ₁₄	86.18	Gasoline-like	7	0.4770	<0.01
30	Sulfur dioxide	SO ₂	64.07	Burnt match	0.87	0.0314	<0.01

31	Dimethyl sulfide	C ₂ H ₆ S	62.13	Cabbage, sulfurous	0.003	0.0001	<0.01
32	4-methyl-heptane	C ₈ H ₁₈	114.23	Gasoline-like	1.7	0.0910	<0.01
33	4-octane	C ₈ H ₁₆	112.21	Gasoline-like	1.7	0.0672	<0.01
34	Dimethyl disulfide	C ₂ H ₆ S ₂	94.20	Cabbage, sulfurous	0.0022	0.00007	<0.01
35	3-methyl-pentane	C ₆ H ₁₄	86.18	Gasoline-like	8.9	0.1851	<0.01
36	Tetra-hydrofuran	C ₄ H ₈ O	72.11	Ether-like	30 ^[47]	0.0061	<0.01
37	2,2-dimethyl-butane	C ₆ H ₁₄	86.18	Gasoline-like	20	0.0045	<0.01
38	2-butanethiol	C ₄ H ₁₀ S	90.19	Heavy skunk, foul sulfur	0.007	0.311636	<0.01
39	2-methyl-2-propanthiol	C ₄ H ₁₀ S	90.19	Skunk	0.00009	0.001	<0.01
40	2-propanethiol	C ₃ H ₈ S	76.16	Cabbage-like	0.0081	0.0468	<0.01
41	Butane	C ₄ H ₁₀	58.12	Gasoline-like	1200	0.0155	<0.01
42	Dimethyl trisulfide	C ₂ H ₆ S ₃	126.26	Rotten cabbage	0.00006	0.00013	<0.01
43	1-propanethiol	C ₃ H ₈ S	76.16	Cabbage-like	0.018	0.0233	<0.01
44	1-butanethiol	C ₄ H ₁₀ S	90.19	Skunk	0.003	0.0002	<0.01
45	Ethyl methyl sulfide	C ₃ H ₈ S	76.16	Sulfurous odour	0.042	0.002	<0.01
46	1,7,7-trimethyl-bicyclo[2,2,1]-heptan-2-one	C ₁₀ H ₁₆ O	152.24	Fragrant and penetratin g	2.84	0.1109	<0.01

47	1,2-dichloro-ethene	C ₂ H ₄ Cl ₂	96.94	Acrid, chloroform-like	25	0.1437	<0.01
48	1,1,1-trichloro-ethene	C ₂ H ₃ Cl ₃	133.40	Sweet, chloroform-like	5.3	0.0264	<0.01
49	2,5-dimethyl-furan	C ₆ H ₈ O	96.13	Aromatic caustic odour	100	0.0647	<0.01

* Odour descriptors were summarised based on references [54-56]

Table 4 Odorants from the leachate using flux hood sampling

Rank	Compound	Formula	MW	Odour Descriptor	OT ppm ^[45]	Concentration (mg/m ³)	Odour Contribution (%)
1	Hydrogen sulfide	H ₂ S	34.08	Rotten egg	0.00041	0.0006	94.56
2	Carbonyl sulfide	COS	60.08	Distinct sulfide smell	0.055	0.0031	2.06
3	<i>m</i> -xylene	C ₈ H ₁₀	106.17	Sweet, aromatic	0.041	0.004	2.04
4	<i>p</i> -xylene	C ₈ H ₁₀	106.17	Sweet	0.058	0.0016	0.58
5	1,2,4-trimethyl benzene	C ₉ H ₁₂	120.19	Aromatic	0.12	0.0021	0.31
6	Ethylbenzene	C ₈ H ₁₀	106.17	Aromatic, gasoline type	0.17	0.0018	0.22
7	Toluene	C ₇ H ₈	92.14	Sweet, pungent	0.33	0.0031	0.22
8	Tetra-hydrofuran	C ₄ H ₈ O	72.11	Similar to acetone	30 ^[47]	0.0053	0.01

3.2 Contributions of key odorants

49 odorants from emission gas samples collected from landfill leachate collection pipe and 8 odorants from flux hood emission samples of the collected leachate sample were identified. Their contributions to the overall odour were determined based on their odour unit factors calculated from their concentrations and odour thresholds. The top 10 odorants are methyl mercaptan, ethyl mercaptan, *m*-xylene, H₂S, CS₂, 1,2,3,4-tetra-methylbenzene, *p*-xylene, 1,2,4-trimethylbenzene, ethylbenzene and α -pinene, which contributed more than 95% odour in the gas accumulated in the leachate collection pipe.

It may also need to remember that the calculation here was carried out on the basis of these assumption and facts:

- The key odorants investigated are only these compounds and contributions from other compounds are ignorable;
- The contributions of these odorants are additive to overall odour. Possibility of synergic or antagonistic as [57] found between these odorous compounds did not take into account because it is really hard to determine if the same function still exist when so many of different odorous compounds combine together.
- Available odour thresholds (even from different references) of these compounds are trustable and comparable. In order to avoid possible inconsistency and ensure reliability, most of OT values (Table 3 and Table 4) were quoted from [45] as they were obtained using the same triangular bag method.

3.3 Sampling and analytical method assessment based on the investigation results

For VOCs sampling and analysis, significant (>10%) breakthrough of the analytes in the second sampling tube was found despite a relatively low sample volume being collected (1 L). Figure 1 illustrates a pair of series sorbent tubes; the upper trace representing the front (first exposed to the sample stream) and the lower trace representing the back (second tube in series) tube. Both chromatograms are displayed on identical axes; despite the apparently low concentrations in the back (second tube in series) tube, the magnitude is significant. This tells us that more sampling options should be considered and managed properly when sampling from an unknown source in case of under-estimation or over-estimation of investigation sources.

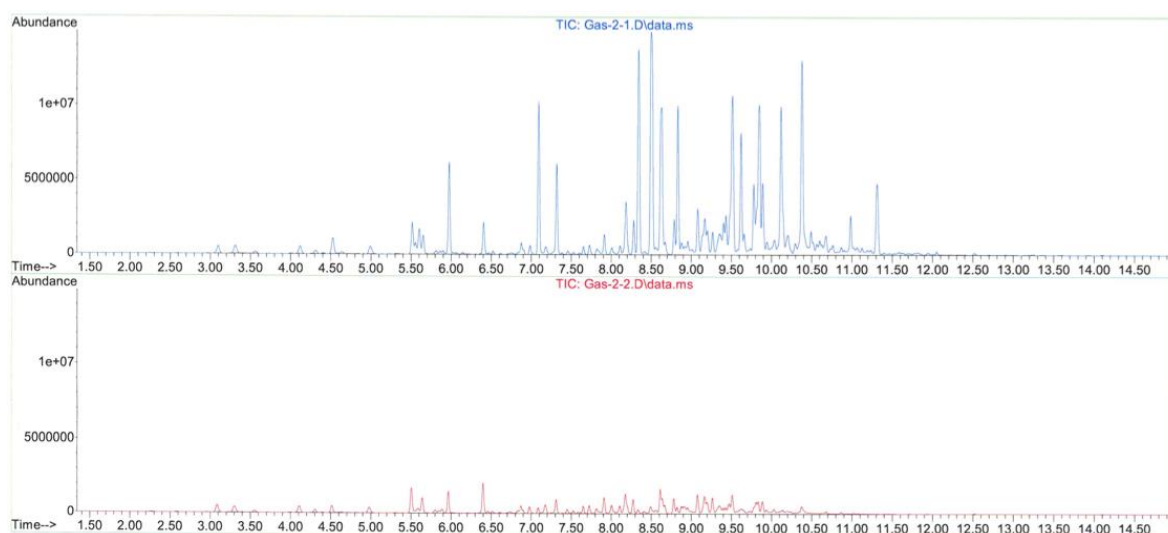


Figure 1 Total ion chromatograms from gas phase field samples

The results of the chemical speciation that have been performed on the gas samples collected on-site and the emission from the leachate collected indicate that the VOC and VSC emissions associated with the fugitive landfill gas were significantly greater than those from the leachate. This may also indicate that emissions from leachate are much complicate and different sampling and analytical method may give quiet different results.

As the differences between the Table 3 and Table 4 shows, different sampling and analytical methods may find quite different emission results. This also indicates that more sampling and measurement techniques are always better to be employed for finding all possible pollutants from an unknown pollution source.

4. Conclusions

Over 130 VOCs and VSCs were detected from the leachate emission of a landfill site in Sydney, Australia. 49 of them from landfill leachate collection pipe and 8 of them from flux hood emission were found to be odorous. The contributions of these odorants to overall odour emissions were also

calculated based on their concentrations and odour thresholds. The top 10 odorants from leachate transportation pipe include methyl mercaptan, ethyl mercaptan, m-xylene, H₂S, CS₂, 1,2,3,4-tetramethylbenzene, p-xylene, 1,2,4-trimethylbenzene, ethylbenzene and α -pinene. They contributed more than 95% of the odour in the gas accumulated in the leachate collection pipe. Different results of different sampling and analytical methods indicates that more sampling and measurement techniques are always better for determination of the all possible pollutants from an unknown pollution source.

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