献给我的老爸老妈, 感谢你们赋予我生命和智慧!

献给我的儿子, 感谢你给予我的欢乐!

献给我的亲人和朋友们,

感谢你们予以我的无私的帮助和支持!

我爱你们!

AN INVESTIGATION OF VOLATILE ORGANIC COMPOUNDS IN LANDFILL GAS

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SUMMARY

Work described in this thesis contains the results on the study of volatile organic compounds (VOCs) in landfill gas from seven landfill sites in the western region of Melbourne, Victoria, Australia.

Sampling methods including sampling with adsorption tubes, tedlar bags and cryogenic trapping were investigated and analytical systems were developed using adsorption tubes with solvent or thermal desorption followed by analysis of VOCs using gas chromatography with mass selective detection (GC/MS).

The abundant VOCs found at all seven landfill sites were n-alkanes, branched chain alkanes, cyclic alkanes, aromatic hydrocarbons and terpenes. The levels and relative abundances of these at all sites were observed and dominant compounds identified. At domestic site F, VOC levels showed a tendency to increase then decline as the waste aged from 3 to 21 years. n-alkane, aromatic hydrocarbons and terpene levels had significantly declined in the older waste that was in the maturation phase of degradation. It is suggested that the behaviour of benzene, toluene and the other aromatics as the waste aged might be due to toluene being the microbial degradation product of other aromatics in young refuse and benzene in older refuse. VOC levels were up to an order of magnitude higher at domestic site E but relative abundances of VOCs were similar at both these sites for waste undergoing methanogenesis. The influence on VOC behaviour from anthropogenic sources at both sites and from young refuse and daily cover material at Site E was addressed. Similar levels and relative abundance of VOCs to those observed for sites E and F were found at prescribed waste site A. The results from this site were surprising given the nature of waste inputs.

The levels and relative abundances of VOCs at domestic sites B, C, D and G could not be explained via waste ages or inputs. Correlations were found with gas extraction rates at these sites where it is suggested air intrusion caused by gas extraction affects the biotic and abiotic processes occurring within a landfill. The VOC behaviour at gas extraction sites was similar to that observed at site F for very old waste in the maturation phase of degradation. Aromatics and terpenes appear to be the most

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affected by gas extraction. The behaviour of VOCs at sites C and G with low extraction rates is more comparable with that observed at sites E and F where the gas escaped passively. It appears that gas extraction favours the production of lower molecular weight compounds as compared to sites from which the gas passively escaped. Industrial waste inputs at sites C and G are also addressed.

DECLARATION

I hereby state that:

- 1. Except where reference is made in the text of the thesis, this thesis contains no material published elsewhere or extracted from a thesis presented by the candidate for another degree or diploma,;
- No other person's work has been used without due acknowledgement, except where due reference is made in the text of the thesis;
- 3. This thesis has not been submitted for the award of any degree or diploma in any other tertiary institution.

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*Names and places have not been disclosed so as to maintain confidentiality.

CHAPTER I **INDRODUCTION**

1.1 Description of Landfills

1.1.1. Landfills in Victoria, Australia

In Victoria, Australia, landfills are licensed by the Victoria Environmental Protection Agency (EPA) according to their solid waste inputs. There are five classifications of solid waste and these are described in Table 1.1. More details about the waste classifications are given in EPA Bulletin 448 (see Appendix A).

Summary of Waste Types		
ТҮРЕ	DESCRIPTION	
FILL MATERIAL	Naturally occurring soil (sand, clay & silt), gravel, rock that has not been used for any industrial process	
SOLID INERT	Demolition material, concrete, bricks, timber, plastic, glass, metals, bitumen, trees, shredded tyres.	
PUTRESCIBLE	Domestic garbage, commercial waste, vegetables, super- market processing, deli, butchers etc., garden clippings / prunings	
LOW LEVEL CONTAMINATED SOIL	Soils	
PRESCRIBED WASTE	Hazardous Wastes.	
* From Appendix A		

TABLE 1.1*

rrom Appendix A

Although there is no formal classification of landfill types in this state three general types can be identified including sanitary, solid / inert and specifically engineered landfills. Sanitary landfills accept putrescible wastes where fill material and low level contaminated soil may be used as daily cover; solid / inert landfills typically accept building material, and specifically engineered landfills accept prescribed waste where again fill material or low level contaminated soil may be used as daily cover. The landfill types found in Victoria include the three individual types described above including landfilling operations accepting more than one type of waste.

Those landfills containing a large proportion of biodegradable organic matter (putrescible), produce large quantities of methane and over the last ten years electricity generation plants have been installed in many metropolitan sanitary landfills in Victoria. Other landfills where the biodegradable organic content is low have not been viable for power generation. For these the landfill gas has been allowed to escape passively or it has been flared.

1.1.2. Reactions Occurring in Landfills

The solid waste landfills receiving putrescible waste can be conceptualised as biochemical reactors, with solid waste and water as the major inputs, and with landfill gas and leachate as the principal outputs. This is shown schematically Figure 1.1



Figure 1.1 Inputs and Outputs of the Landfill Site

Typical sources of putrescible solid waste are listed in Table 1.1 and principle sources of water include water entering the landfill from above such as rain and snow, moisture in the waste and moisture in the cover material.

Solid wastes placed in a sanitary landfill undergo a number of simultaneous and interrelated biotic (biological) and abiotic (chemical and physical) changes. Where the products of these include solid, liquid and gaseous chemicals. The solid products remain within the waste, the gases migrate beyond the waste and the liquid and

soluble materials will, together with infiltrating water, form landfill leachate. Some of the most important reactions occurring within landfills are as follows:

• Biological reactions:

— Microbial conversion of organic content of solid waste to produce landfill gas.

• Chemical reactions:

- Dissolution and suspension of landfill materials and biological conversion products in the liquid percolating through the waste;
- —— Evaporation and vaporization of chemical compounds and water into the evolving landfill gas;
- Sorption of volatile and semivolatile organic compounds into the landfilled material;
- —— Dehalogenation and decomposition of organic compounds;
- ---- Oxidation-reduction reactions affecting metals and the solubility of metal salts.

• Physical changes:

— The settlement caused by consolidation and decomposition of landfilled material.

The processes of waste degradation in landfill sites are still not very clear; there are many possible chemical and microbial pathways⁽¹⁾. However, knowledge of intermediates and end products, and the relevant enzymes present in landfill indicates that the degradation of organic wastes in the landfill sites is approximately the same as the degradation of organic materials in other anaerobic environments.

When deposited within the landfill, oxygen entrapped within voids is rapidly depleted as a result of biological activity. The local environment becomes anaerobic and encourages the growth of anaerobic microorganisms, especially bacteria. Carbon dioxide and methane are produced as a result of anaerobic microbial activity and displace nitrogen remaining from the entrapped air. Eventually a dynamic equilibrium is reached with a gas ratio within the landfill of approximately 60 methane: 40 carbon dioxide⁽¹⁾.

In simple terms then the products of the microbial decomposition in an anaerobic environment of the organic content of solid waste are landfill gas, and the liquid and soluble contributions to leachate. The different types of organic materials (proteins, carbohydrates and lipids) will be decomposed by a variety of reaction pathways all leading to the production of simpler organic compounds⁽¹⁻⁶⁾. A simple reaction for the generation of landfill gas is shown below:



The microbial activity in the landfill releases heat and thus the temperature in the fill rises during the biodegradation stage to about 25 - 45 °C, although temperatures up to 70 °C have been noted⁽⁷⁾.

1.2 Landfill Gas

1.2.1. Landfill Gas Production

Gaseous emissions from a landfill are a result of the processes within the landfill and occur microbiologically. More importantly, the emission can also occur via a physicochemical pathway. Her Majesty's Inspectorate of Pollution⁽⁸⁾ indicates that the microbial decomposition process occurring within a landfill is "... complex and not yet fully understood...". This position is backed by other authors such as El-Fadel *et.al.*⁽⁹⁾ who point out that the current knowledge of gas generation within landfills is derived from experimental models. The point made here is that the process of gas generation is a very complex interaction of microbiological activity, the type of waste initially dumped and the physical conditions occurring within the landfill itself (i.e. temperature, pH etc.). Studies that try to mimic landfill conditions usually involve the use of digesters, lysimeters and test-cells which are usually operated under 'favourable' conditions and don't necessarily reflect the true nature of what is

occurring within the landfill⁽⁹⁾. However, modelling such as this has generally been accepted as the closest possible indication of what actually occurs within a landfill.

There are two main phases of microbial landfill gas generation, an aerobic phase, involving aerobic bacteria, and an anaerobic phase, involving anaerobic bacteria. The aerobic phase occurs first and is highly exothermic but short in duration due to insufficient oxygen (O_2) concentration in the waste⁽⁸⁾. Whether the landfill is covered (clay cover) or not, the major microbial phase occurring within the landfill is an anaerobic one⁽¹⁰⁾.

Abiotic factors also influence the formation of landfill gas and include such parameters as percentage O_2 , H_2 , sulfate ($SO_4^{2^-}$), water, temperature, pH and nutrient concentration. Her Majesty's Inspectorate of Pollution⁽⁸⁾ also highlights that the waste type is a controlling factor in the process. That is, different types of waste will degrade differently on a relative time scale to give varying quantities of evolved gas throughout a landfill's operational lifetime.

The aerobic and anaerobic phases of waste decomposition are described in more detail below:

Immediately after tipping the refuse is aerobic, i.e., air pockets exist in the fill, so the initial decomposition of the waste is via aerobic biological processes. Bacteria do not flourish in dry conditions, so biodegradation starts only when the landfill is moist. The refuse inherently contains moisture but this may be increased due to infiltrating liquid such as rainwater. Once biodegradation has started the oxygen in the waste is soon exhausted and as no replenishment of the free oxygen is available the waste becomes anaerobic. During this initial oxygen depletion stage nitrate and sulfate, which can serve as electron acceptors in biological conversion reactions, are often reduced to nitrogen gas and hydrogen sulfide.

The anaerobic phase of landfill gas generation can be further divided into three stages, an acid formation, and two methane formation stages. Figure 1.2⁽⁸⁾ shows the anaerobic waste degradation processes occurring in landfills.

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Fig. 1.2* Anaerobic Waste Degradation Processes Occurring in Landfills * From Reference 8

The acid formation stage occurs in two steps. The first involves the enzyme-mediated hydrolysis and fermentation of high molecular mass compounds including celluloses (polysaccharides), fats, and proteins by groups of facultative and anaerobic bacteria to produce simple organic materials including salts of acetic acid, propionic acid and pyruvic acid, fatty acids and alcohols with gases including carbon dioxide, hydrogen and ammonia. The simple organic materials produced in this step are used in the metabolism of carbon and energy by the bacteria. In the second step (acetogenic step) fatty acids and other products from the first step are further degraded by acetogenic or acid forming bacteria to acetic acid, carbon dioxide and hydrogen. Leachate pH will drop in the first stage of anaerobic decomposition due to the formation of carboxylic acid and carbon dioxide. The second stage facilitates the establishment of methanogenic (methane forming) bacterial populations where the products of the acid formation stage are finally decomposed producing a gas mixture containing methane and carbon dioxide as major components in the proportion of about 3:2, together with traces of many other components. The third stage is one of steady state gas production. This may last for several decades before gas production rates decline and gas evolution at the landfill is no longer significant^{(8), (10)}.

The timescale for each of the degradation / transformation processes may vary considerably according to the nature of the wastes, landfill management practice, and local environmental conditions. The diverse nature of wastes and the variability of landfill sites and operational practice make it difficult to predict the time of onset and the duration of gas production. Aerobic processes rely on availability of oxygen from the atmosphere. This can be significantly affected by the factors described above. With good compaction and the use of intermediate (daily) cover material it can be expected that aerobic processes will decline within a few days. Thereafter anaerobic processes will predominate and substantial amounts of methane can be expected to be produced within 3 to 12 months of waste deposition. The concentration of methane will gradually increase until it reaches a typical maximum of between 60 to 65 % by volume of the landfill gas after which gas production rates can be expected to plateau, and methane and carbon dioxide may continue to be evolved over several decades after the last deposit of waste, and then decline at a rate depending on site conditions. Figure 1.3⁽⁶⁾ shows the landfill gas composition and production versus time.



Figure 1.3* Landfill Gas Composition and Production Versus Time * From Reference 6

Evidence from very old sites suggests that once the available cellulose is consumed the methanogenic microbial activity reduces and methane and carbon dioxide concentrations gradually decline. This stage of waste degradation is known as the 'maturation phase' (see Fig 1.3) where oxygen levels will begin to rise^{(6), (11)}. Eventually the remaining waste would be regarded, as biologically 'inert' and atmospheric gaseous conditions would be re-established. Gas production may recommence if changes occur at the site, which reactivate microbial activity. This could occur if development occurs on the site or liquid levels within the wastes are allowed to rise by cessation of pumping of leachate.

Additional information on landfill gas production processes can be sourced from various international literatures (12-35).

1.2.2. Factors Influencing Gas Production

Gas production is the result of the biodegradation of the organic content of solid waste, and therefore optimum gas production is dependant upon optimised conditions for the growth of methanogenic bacteria. The main factors affecting gas production include:

- Nature of the waste;
- Moisture content of the fill;
- pH of the fill;
- Temperature of the fill.

The nature of the refuse affects gas production in several ways, and includes such factors as organic content, C-N ratio, particle size, density, trace nutrients and other chemicals.

The quantity and composition of the gas generated in a landfill depends on the types of solid wastes that are decomposing. High gas production rates require a high organic content in the waste. Important here also is the ratio of easily degradable materials to slowly degradable materials. A waste with a large fraction of easily degradable organic material will produce more gas than one that consists largely of inorganic material. Food wastes degrade quite readily, while other materials, such as plastics, rubber, glass and some demolition wastes, are highly resistant to decomposition.

The carbon-nitrogen ratio (C-N ratio) should be around 25:1 or lower for optimum biodegradation. At higher ratios, nutrient deficiency may occur, which will inhibit bacterial activity⁽⁷⁾. If the refuse is pulverized, that is, the particle size is reduced, then microbial activity is increased and this may be reflected in an increased gas production rate, although the number of years for which gas is produced may decrease. Compaction or baling of the refuse, which increases the density of the

landfill, may decrease the rate of water infiltration into the landfill and slows the ability of bacteria to biodegrade the waste. The lack of micronutrients such as sodium, potassium, calcium or magnesium, can retard bacterial growth. In addition the concentration of nutrient salts such as sulphate and nitrate may also be important. If toxic chemicals are present in the landfill biological activity in general and methanogenesis in particular may be inhibited. Methane bacteria can be inhibited by high salt concentrations; for example, 2000 mg/L of calcium can inhibit their activity⁽⁷⁾.

Bacteria do not function well in dry conditions and moisture content of 40 % or higher, based on wet weight of the waste, is desirable for optimal gas production⁽⁷⁾. As leachate control procedures often involve the control and reduction of water entering the fill, the moisture content in a tip may be lower than this value at around 30 % water (wet weight)⁽⁷⁾. There are examples of sites whose gas production is substantial even though the degree of saturation is apparently low. Incoming refuse has an average moisture content of about 25 %, food and garden waste providing the highest moisture input^{(1), (8)}. Thereafter rainfall, surface and groundwater infiltration and the products of waste breakdown can provide additional moisture.

A moist environment is normally associated with high rates of gas production. Liquid movement within sites tends to provide a more even waste moisture content. It also distributes nutrients and bacteria within the mass which can further enhance rates of waste degradation and gas production. The recirculation of leachate, as practiced on some sites, will maintain high moisture contents and provide a source of nutrients and bacteria which will tend to accelerate gas production rates. Extraction of the gas itself can assist this process by drawing moist gases through the fill.

The pH of the fill should be around 7.0 for optimum gas production as methanogenesis proceeds optimally between a pH range of 6.5 to 8.5 and is only inhibited when the pH is outside this range^(6–8). Household waste produces acidic leachate as a consequence of rapid degradation of easily biodegradable material, and unless this is buffered by other wastes it may be responsible for delaying the onset of methane production. Waste streams containing a mix of both biodegradable and 'inert' material are more likely to develop a pH in the optimum range. Thus, for gas production, the presence of significant alkalinity in the fill is desirable in order to act

as a buffer against a low pH. Good pH control is typical of co-disposal landfills but buffering capacity may be lost at mono-disposal landfills.

Microbial activity is affected by temperature and therefore the temperature of the landfill affects gas production. In general the gas production rate increases with tip temperature. The optimum temperature range for maximizing landfill gas generation is between 35 to 45 °C, which is common in deep landfill sites⁽⁸⁾. A dramatic drop in gas production occurs below 10 to 15 °C⁽⁸⁾. In shallow landfill sites variations in production rates may among other factors reflect seasonal changes in ambient temperatures.

These factors influence gas production in different aspects from beginning to end.

1.2.3. Landfill Gas Composition

The principal gases produced from the anaerobic decomposition of biodegradable organic materials present in solid waste are methane, which usually comprises 50 - 60 $\%^{(1), (6-8)}$, followed by carbon dioxide which makes up most of the remaining volume. Other gases produced during biotic conversion reactions include smaller amounts of ammonia (NH₃), hydrogen (H₂), hydrogen sulfide (H₂S) and nitrogen (N₂), and the levels of these vary according to the stage of decomposition^{(6), (11)}. Oxygen from air is also present in small amounts in landfill gas and its level declines in the initial aerobic decomposition of solid waste and rises again when the landfill becomes inert. Other organic compounds present in trace amounts in landfill gas are an assorted array of compounds known as "non-methane organic compounds" (NMOCs) or VOCs, and these usually make up less than 1 % by volume of landfill gas. Trace constituents in landfill gases have two basic sources. They may be brought to the landfill with the incoming waste or they may be produced by biotic and abiotic conversion reactions occurring within the landfill. Trace compounds mixed with the incoming waste are typically in liquid form, but tend to volatilize and become part of landfill gas emissions. Typical classes of VOCs include saturated hydrocarbons, unsaturated hydrocarbons, halogenated compounds, organosulphur compounds, alcohols and others. Typical landfill gas compositions are shown in Table $1.2^{(8)}$.

COMPONENT	% BY VOLUME	
Methane	63.8**	
Carbon dioxide	33.6	
Oxygen	0.16	
Nitrogen	2.4	
Hydrogen	0.05	
Carbon monoxide	0.001	
Ethane	0.005	
Ethene	0.018	
Acetaldehyde	0.005	
Propane	0.002	
Butanes	0.003	
Helium	0.00005	
Higher alkanes	<0.05	
Unsaturated hydrocarbons	0.009	
Halogenated compounds	0.00002	
Hydrogen sulfide	0.00002	
Organosulphur compounds	0.00001	
Alcohols	0.00001	
Others	0.00005	

Table 1.2*Typical Composition of Landfill Gas

* From Reference 8

** The figure for methane reported in this data set is considered high,

A figure of 55 % methane is considered more typical.

More than 100 different volatile organic compounds have been identified as trace components, many of which are known to be toxic or carcinogenic^{(6), (11)}. The presence and concentration of VOCs varies considerably and is related to the landfill, the landfilled waste (waste constituents), the age and extent of waste degradation. The occurrence of significant concentrations of volatile organic compounds in landfill gas is associated with older landfills which accepted industrial and commercial wastes that contained VOCS. In newer landfills where the disposal of hazardous waste has been banned, the concentrations of VOCs in the landfill gas have been extremely low. Organosulphur compounds and esters are found in gases derived from recently deposited wastes from which odours are more obvious. The presence of halogenated hydrocarbons (HHC) in landfill gas is usually due to dumped chemical residues, coolants, propellant agents and chlorinated solvents. Some of these compounds are produced by chemical reactions or by microbial degradation of the waste mass. Table 1.3⁽³⁶⁾ lists typical concentration of trace compounds found in landfill gas at 66 California MSW landfills.

	CONCENT	CONCENTRATION, PPB BY VOLUME		
COMPOUND	MEDIAN	MEAN	MAXIMUM	
Acetone	0	6,838	240,000	
Benzene	932	2,057	39,000	
Carbon dioxide	330,000,000	10,000,000	534,000,000	
Chlorobenzene	0	82	1,640	
Chloroform	0	245	12,000	
1,1-dichloroethane	0	2,801	36,000	
Dichloromethane	1,150	25,694	620,000	
1,1-dichloroethene	0	130	4,000	
Diethylene chloride	0	2,835	20,000	
1,2-trans-dichloroethane	0	36	850	
2,3-dichloropropane	0	0	0	
1,2-dichloropropane	0	0	0	
Ethylene bromide	0	0	0	
Ethylene dichloride	0	59	2,100	
Ethylene oxide	0	0	0	
Ethyl benzene	0	7,334	87,500	
Hydrogen sulfide	0	0	0	
Hydrogen	0	0	4	
Methane	440,000,000	70,000,000	740,000,000	
Nitrogen	12	26	98	
Oxygen	1	2	17	
1,1,2-trichloroethane	0	0	0	
1,1,1-trichloroethane	0	615	14,500	
Trichloroethylene	0	2,079	32,000	
Toluene	8,125	34,907	280,000	
1,1,2,2-tetrachloroethane	0	246	16,000	
Tetrachloroethylene	260	5,244	180,000	
Vinyl chloride	1,150	3,508	32,000	
Methyl ethyl ketone	0	3,092	130,000	
Styrenes	0	1,517	87,000	
Vinyl acetate	0	5,663	240,000	
Xylenes	0	2,651	38,000	

TABLE 1.3*

Typical Concentrations of Trace Compounds Found in Landfill Gas at 66 California MSW Landfills

* From Reference 36

1.2.4. Environmental Impacts of Landfill Gas Emissions

It is suggested that upwards of 95 % of solid waste that is generated, depending on location, is disposed of in landfills globally⁽⁹⁾. This immense 'tonnage' of solid waste can undergo biological, chemical and physical transformations within the landfill producing a gas that is mostly composed of CH_4 and CO_2 with trace concentrations of VOCS. It has been stipulated by El-Fadel *et.al.*⁽⁹⁾ that 1 - 14 L of landfill gas is produced per kilogram of solid waste per year (L/kg/yr.), depending on the abiotic factors of the landfill site.

The accumulation of methane and carbon dioxide in the landfill due to biodegradation of the organic constituents creates a slight gas pressure in the fill. Typical gas pressures are around 2.5 - 5.0 cm of water above atmospheric pressure, although a few reports have indicated higher pressure in isolated pockets. The resulting pressure gradients cause a driving force for the gas to move. Movement of gas due to pressure differences is known as pressure flow, but landfill gas will also migrate due to diffusion flow. This results from the different concentrations of gas in different areas with gas movement from high concentration areas into low concentration areas⁽⁷⁾. Landfill gas can be emitted to the atmosphere either through the clay top cover, particularly if the cover is relatively permeable, directly from uncovered wastes or following the migration through surrounding soil^{(7), (37)}. Fractured or porous subsurface strata may provide the path of least resistance to gas movement. Her Majesty's Inspectorate of Pollution⁽⁸⁾ indicates that this gas migration is governed by factors "... provided by the pressure generated within the site and the pressure gradient with the surrounding strata...". Uncollected gases can migrate through the landfill and be released to the atmosphere from almost anywhere on the surface. They are easily spread through the air to pollute land, water and possibly marine life. The extent of migration poses serious problems for landfill operators because migration cannot be stopped at the operation's boundary. Kjeldsen⁽³⁷⁾ highlights that the current methods to control landfill gas migration (i.e. flaring and electricity generation) are not totally effective. Even when these methods are adopted at a landfill, the uncontrolled migration of landfill gas through the soil can still occur.

It is stressed by authors^{(8), (10)} that 'good landfill practice', will minimize landfill gas migration. Gas control relies upon the creation of paths of least resistance or the use of impermeable barriers. Gas collection may be either passive or active (induced vacuum) or both, where gas wells, vents or gas trenches at the side of the landfill are used for collection. Here gases are collected by a system involving buried pipes after which these gases are then either vented to the atmosphere, burned in flares or used for co-generation. Impermeable barriers can be used to minimise vertical and lateral gas migration. Daily cover material and the landfill cap usually consist of clay soil and helps lateral gas migration by impeding vertical migration. Thus the migrating gas will move to the gas collection system and other evacuated spaces within the landfill^{(8), (10)}. Low permeability fine-grained clay soils are often used as barriers in

landfills in which a high moisture content of the clay retards movement of the landfill gas⁽³⁸⁾. These authors also suggest that gas permeation vertically through the landfill will change depending on water content of the soil. They illustrate that seasonal changes of weather (i.e. precipitation) will affect the permeability of the soil, so that if gas sampling was initiated at the landfill/atmosphere interface the results must take into account the moisture content of the soil as gas permeability is dependent on this moisture parameter. The use of impermeable barriers, whether of clay, bentonite, plastic sheet or cement, for the control of leachate movement have all been used with some success in minimizing lateral gas migration. Gas collection systems must be specifically designed so that the clay top cover (capping) does not cause excess pressure build-up to allow uncontrolled soil migration from the landfill. Even after the landfill has been filled and capped, gas migration can still occur as the site is still microbiologically active for a long time after landfill closure. Figure 1.4⁽⁸⁾ illustrates possible paths for gas migration at a completed or restored site. Her Majesty's Inspectorate of Pollution⁽⁸⁾ indicates that gas migration off-site can occur via underground service ducts (i.e. electricity, telephone, TV and street lighting cable lines), water and gas pipes, sewers and even drains.





Landfill gas emissions affect the air environment both globally and locally in the region immediately surrounding the landfill.

Landfill gas consists mainly of methane and carbon dioxide, and both gases are the cause of the 'greenhouse effect'. Methane is a powerful greenhouse gas with a global warming potential 21 times the effect of the same amount of carbon dioxide, and it contributes significantly to global atmospheric change⁽³⁹⁾. So landfill gas has become significant in the debate over global warming and climate change. Anthropogenic contributions to the greenhouse effect have the potential to damage ecosystems and economies. Although the extent to which climate change will occur due to human activities is uncertain, effects are likely to be intensified by continued increases in emissions.

Methane has been reported to be responsible for about 20 % of recent increases in global warming and landfills are thought to be a major source of methane. In the UK, landfills are the single largest source of methane, contributing an estimated 23 % of total production⁽⁴⁰⁾; with over 1000 sites reported to be producing gas. Globally, it has been estimated that methane from decomposition of municipal solid waste, whether in crude dumps or organized landfills, could account for 7 - 20 % of all anthropogenic methane emissions⁽⁴¹⁾. Recent estimates suggest that landfill emissions of methane could increase more than three-fold over the next 30 years⁽¹⁾. Reducing the amount of organic waste generated and diverting organic material from landfill to onsite mulching, composting and vermiculture are elective options for the mitigation of methane emissions. Following these options, the capture and use of methane for energy recovery provides a means of reducing greenhouse gases and generating a renewable energy source.

In Australia, the waste management sector generates 4 % of Australia's greenhouse gas (GHG) emissions, including 13 % of total methane emissions, mostly from disposal of waste to landfill⁽⁴²⁾. In Victoria, it is estimated that the large Victorian landfills (receiving more than 100,000 tonnes of waste per annum) contribute to almost half (46 %) of the total methane generated. More than half (53 %) of the total methane generated by Victorian landfills is contributed by landfills that are currently

open. Landfills that were closed between 1990 and 1999 contribute approximately 38% of the total methane generated⁽³⁹⁾.

Australia is committed to reducing GHG emissions from the waste sector through a range of measures including waste minimization, reuse and the recovery of gases for energy production.

The environmental impacts of landfill gas emissions in the region immediately surrounding the landfill are mainly related to issues of public health and include the explosive and asphyxiating properties of methane, health hazards associated with the VOCs present in landfill gas and odors.

When methane is present in the air in concentrations between 5 - 15 %, it is explosive⁽⁷⁾. Because only limited amounts of oxygen are present in a landfill when methane concentrations reach this critical level, there is little danger that the landfill will explode. However, methane mixtures in the explosive range can be formed if landfill gas migrates off-site and is mixed with air. Furthermore, landfill gas can asphyxiate a person who enters an enclosure containing it. The migration of gas beyond landfill boundaries has been the cause of a number of hazardous (explosion-related) incidents⁽⁴³⁾ one of the most notable within the UK resulting in destruction of a bungalow at Loscoe in Derbyshire⁽⁴⁴⁾.

On the local level, VOCs in landfill gas perhaps are of greater concern than methane due to the harmful effects of certain VOCs on human health. Certain VOCs are known or suspected human carcinogens and mutagens. Others when combined with nitrogen oxides from other sources such as automobile emissions lead to local production of ozone; a lung irritant. The toxicity of landfill gas depends on the cumulative effect of its constituents⁽⁶⁾.

VOCs in landfill gas originate either from those already existing in the disposed waste or those occurring from microbial action and abiotic degradation. Microbial action and abiotic degradation play a minor role in the emission of VOCs. It is the emission of VOCs originally contained within the waste that predominates and occurs via a physicochemical process. Basically the process is the partitioning of VOCs between phases (i.e. solid-liquid, liquid-gas) that allows, as the waste degrades (or abiotic conditions change), VOCs to enter the gas void within the landfill⁽¹⁰⁾.

U.S. EPA^(45–49) studies into VOCs in landfill gas have demonstrated that VOC emission from a landfill can reach concentrations in the range of $4 \times 10^{-4} - 1 \times 10^{-3}$ kg/m²/day⁽⁹⁾. Eikmann⁽⁵⁰⁾ highlights that residents in the vicinity of a landfill often complain about gaseous odours emitted from these sites. He also explains that local residents are frequently concerned that "...exposure to landfill gas represents not only a potential environmental nuisance but also a serious toxic hazard...".

VOCs in landfill gas can not only contribute to air pollution but may also be responsible for ground water pollution. A number of studies have shown landfill gas migration is the most likely source of VOCs in ground water^(51–52).

Many of the VOCs are responsible for the odour associated with landfill gas and this creates a nuisance, in particular where landfills are located near homes, schools and other public facilities, where individuals can be subjected to the odour. Some components may need to be diluted more than one hundred million times to be below odour threshold values⁽⁵³⁾.

It should be noted that the hazards associated with landfill gas are of immediate concern to site operators and appropriate safety precautions must be taken during site operation. In particular all employees should be aware of the potential danger. Leachate monitoring wells can inadvertently act as gas collection wells and due caution must be taken. VOCs present in landfills pose a threat to workers on landfills due to odour and other effects on health. Harkov *et al.*⁽⁵⁴⁾ found that VOCs levels in ambient air at several landfill sites were in excess of urban background levels. The slow, continuous evolution of gas from the top of a landfill can undoubtedly be a danger particularly if it accumulates in pockets in the site.

As discussed above, the methane produced in landfills may be considered a hazard or a nuisance, however it may also be considered as a resource. The calorific value of pure methane is 37,000 kJ/m³ gas at NTP⁽⁷⁾. As landfill gas is only 55 % methane, and since it may contain moisture or become diluted during collection, its calorific value is usually in the range 16,000 – 20,000 kJ/m³ ⁽⁷⁾. However, this heat value still makes landfill gas a valuable source of energy. Where the collected landfill gas is used for energy recovery this can involve either heating applications (steam-raising via boilers, kiln firing or space heating), or power generation systems where the gas undergoes combustion in specifically designed 'gas-engines'. Where the gas is not utilised for energy production due to low economic viability, either as a result of poor gas quality or insufficient amounts, other means of gas control such as 'flaring' of the landfill gas, or venting without flaring are used. However these methods of gas control are wasteful of the gas produced, whilst the latter is much more harmful to the environment through the release of greenhouse gases, as discussed above. In addition, the analysis of the flared gas from several systems showed low levels (< 10 mg/m³) of components not present in the unburned gas⁽¹¹⁾. These compounds include methyl cyanide, nitromethane, acrolein, ethylene oxide and some alkynes, which must be formed *de novo* in the flaring process⁽¹¹⁾.

The use of landfill gas as an energy resource has been applied to selected large landfills in both Europe and America. Experience is still being gained and much remains to be learnt about the design of gas-collection systems for landfill. Together with the technological problems of the systems is the economics of installing the system compared with the benefit of the gas collected. At present, gas collection is economically viable only on large landfills, but if landfills are designed with gas collection in mind and the tip is operated to maximize gas production, then the economics of installing gas collection systems in a wide range of landfills may become more favourable.

A recent Victorian EPA report concludes that large landfills (receiving more than 100,000 tonnes of waste per annum⁽³⁹⁾) have the greatest potential for generating renewable energy from the capture of methane emissions. These results indicate that emission reduction programs via gas collection and electricity generation from Victorian landfills should focus on the small number (20 out of 521⁽³⁹⁾) of large landfills currently in operation, rather than small landfills.

The impact of some trace constituents on gas collection and control equipment may be significant because landfill gas is water saturated and very corrosive. These properties can affect gas pipes, valves and seals. Her Majesty's Inspectorate of Pollution⁽⁸⁾ indicates that valve selection is quite important because for example, PVC valves are prone to failure at low temperatures at exposed sites during winter (a problem commonly experienced in the Northern Hemisphere). Moisture within the landfill can form a condensate in extraction piping when the gas goes from a temperature of 30 - 40 °C (typical temperature within a landfill) to ambient temperature below zero. This causes functionality (i.e. blockages) and durability (e.g. backpressure) problems of piping around the plant especially during winter periods⁽⁵⁵⁾. The water is usually 'knocked' out using condensate separators. The main reason for removing water from the gas stream is that a moist environment allows the formation of strong acids in the presence of halogenated VOCS.

Stegmann⁽⁵⁶⁾ highlights that fluorinated and chlorinated VOCs can reach concentrations in excess of 200 ppm in young landfills (MSW) and declines to approximately 50 ppm for landfills (MSW) that are greater than three years old (Stegmann⁽⁵⁶⁾). These halogenated VOCs can be converted into strong acids during combustion and may need scrubbing from the landfill gas prior to combustion. The removal of halogenated compounds from the gas stream can occur mainly via absorption processes (eg. HelasorpTM liquid absorbent which removes the VOCs from the gaseous phase to form the absorbate) or by adsorption processes (eg. activated carbon reactors)⁽⁵⁷⁾. Hydrogen Sulfide (H₂S) concentrations in the gas can also cause considerable corrosion as it is converted to H₂SO₄ during combustion⁽⁵⁶⁾. Corrosion problems within a gas engine can be limited by using specifically developed lubricants as well as routinely changing the oil, monitoring pH and metal content of the oil, all of which are likely to indicate possible corrosion problems within the engine.

Since the 1980's volatile siloxanes in landfill gas have been received some attention. During the combustion of landfill gas these siloxanes are converted into microcrystalline silicon dioxide, which contributes to the abrasion of the surfaces within combustion chamber⁽⁵⁸⁻⁶⁰⁾.

Because each landfill is unique depending on the age and contents of the site certain VOCs emitted after combustion may be at concentrations that do not meet health and emission regulation requirements. Henning *et.al.*⁽⁵⁷⁾ describe possible problems that may occur due to high concentrations of some VOCs after combustion:

- Possible emission of polycyclic aromatic hydrocarbons (carcinogenic properties).
- The risk of formation of highly toxic and persistent substances, such as polychlorinated dibenzodioxans (PCDD) and polychlorinated dibenzofurans (PCDF).
- Corrosion by formation of hydrogen chloride and hydrogen fluoride in the combustion chambers of gas engines.
- High chloride and fluoride concentrations in the waste gas from flares and engines.

The combustion process of landfill gas is dependent on the quality of that gas and its suitability as a fuel is primarily dependent on the methane content of the gas. Rettenberger & Schreier⁽⁶¹⁾ highlight that 'trace' VOCs do not influence the combustion process due to their low concentration in landfill gas and combustion is primarily dependent on methane. But they also re-iterate that VOC composition of the exhaust gas must not exceed limits set by standards from existing emission regulations.

Monitoring of VOCs in landfill gas especially in electricity generation is quite important because its effects on gas extraction utilities can have far reaching consequences to the operation of the plant as well to its profitability⁽⁵⁶⁾.

1.2.5. Landfill Gas Monitoring

Environmental monitoring is conducted at sanitary landfills to ensure that no contaminants that may affect public health and the surrounding environment are released from the landfill. The monitoring required might be divided into three
general categories⁽⁶⁾: (1) vadose zone monitoring for gases and liquids, (2) groundwater monitoring, and (3) air quality monitoring. The vadose zone is defined as that zone from the ground surface to where the permanent groundwater is found. Vadose zone monitoring at landfills involves both liquids and gases. Monitoring for liquids in the vadose zone is necessary to detect any leakage of leachate from the bottom of a landfill. Monitoring for gases in the vadose zone is necessary to detect the lateral movement of any landfill gases. Monitoring of the groundwater is necessary to detect changes in water quality that may be caused by the escape of leachate and landfill gases. Air quality monitoring at landfills involves⁽⁶⁾ (1) the monitoring of ambient air quality at and around the landfill site, (2) the monitoring of landfill gases extracted from the landfill, and (3) the monitoring of the offgases from any gas processing or treatment facilities. Ambient air quality is monitored at landfill sites to detect the possible movement of gaseous contaminants from the boundaries of the landfill site. Landfill gas is monitored to assess the composition of the gas and to determine the presence of trace constituents that may pose a health or environmental risk. Monitoring offgases from treatment and energy recovery facilities is done to determine compliance with local air pollution control requirements.

In Victoria, Australia, landfill gas control is part of the operating license and the EPA may require intervention when landfill gases and monitored (methane, VOCs etc.), flared off or used for energy production⁽⁶²⁾.

Landfill gas measurements; be they from deep monitoring boreholes or surface soil measurements, taken at a single point in time reveal little about the gas regime in and around a landfill. It has become clear that a range of environmental factors, including rainfall and atmospheric pressure, affect the production and movement of landfill gas and that measurement at a single point in time cannot account for variations caused by the above. For many landfill sites seasonal trends in gas composition and migration can be detected. In order to begin to understand the 'gas regime' it would be necessary to monitor such sites for at least one year, after which time the analysis of trends in gas composition and flow will be of more value than the individual measurements. Exceptions to this would be when, at a single point in time, the gas composition and flow rate were particularly hazardous⁽¹⁾.

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Several techniques may be used to monitor landfill gas in and around landfill sites⁽⁸⁾. These include:

- a) Surface monitoring;
- b) Sub-surface monitoring (gas probes);
- c) Excavated pits and trenches backfilled around standpipes;
- d) Gas monitoring boreholes or wells; and
- e) The use of leachate wells.

Monitoring using specially constructed boreholes is the preferred method at existing sites. At completed and shallow sites adequate monitoring in the short term may be achieved using excavated pits or trenches. At every site where there is a potential for gas to migrate to development or underground services, monitoring boreholes should be installed at appropriate points outside and between the filled area of the site and any development at risk⁽⁸⁾.

Surface monitoring is carried out to assist in determining the likely presence of gas escapes. Surface monitoring should be used to check the integrity of caps on the waste, as a check on borehole monitoring, to aid the siting of monitoring points, to monitor for the presence of gas during filling and as an indicator of off-site migration⁽⁸⁾.

For sub-surface monitoring, the use of probes driven into waste or strata provides point source monitoring of gas concentrations in the local environment around the probe. Various probes are available, consisting usually of metal tapered tips coupled firstly to short perforated pipe sections and then to longer unperforated metal pipes. They may be driven into soils or wastes usually down to depths of about one to two metres (some have been driven in as far as four metres). They are, therefore, only suitable for measuring gas concentrations near the surface⁽⁸⁾.

Excavated pits and trenches provide a means for monitoring gases in shallow sites. Perforated or slotted plastic tubes (usually around 50 to 80 mm in diameter) are placed within the pit or trench and surrounded with granular medium. The excavation is then backfilled and the surface is sealed eg., with a bentonite or clay cover⁽⁸⁾.

The preferred method for landfill gas monitoring is by using properly designed and constructed boreholes that are dedicated to this function. The boreholes should be installed both inside and outside the fill area of landfills where a risk has been identified. In their simplest form boreholes consist of perforated plastic casing abutting directly to the strata. Sampling from boreholes at locations outside the site can provide data on migration potential at the sampling depth. Information on gas production (at the sampling depth) is obtained from boreholes drilled into the wastes. Boreholes drilled into sites can provide information on gas composition, temperature, pressure, flow rates and on waste composition but will not provide any evidence of lateral migration. To establish the optimum pattern, design and distribution of gas monitoring boreholes specialist advice may be needed⁽⁸⁾.

Where leachate monitoring or extraction wells exist within sites these too may be used for gas monitoring purposes, but only as an additional aid to purpose designed monitoring systems. Where these are covered by the leachate level the measurement may only be of the concentration of the gas in the headspace. Where new sites are being developed, or proposals are under consideration, the design should include the installation of purpose-built gas monitoring boreholes. This will avoid any potential hazards arising from using leachate wells and will ensure reliability of monitoring data⁽⁸⁾.

Further details on landfill gas monitoring, equipment and frequency of monitoring is given in the report of Her Majesty's Inspectorate of Pollution⁽⁸⁾.

1.2.6. VOCs in Landfill Gas

The detrimental effect of migrating landfill gas on the environment and on public health were addressed in Section 1.2.4. The methane present in landfill gas contributes to the green house effect and methane's explosive and asphyxiating properties are of concern in confined spaces. The trace VOCs present in landfill gas are perhaps of greater concern than methane due to the harmful effects of certain VOCs on human health via their contribution to air and water pollution. Not only are some of the compounds responsible for the odour associated with landfill gas they are also suspected human carcinogens and mutagens as well as contributing to local ozone production. VOCs are also detrimental to landfill gas control equipment via corrosion. Air pollution due to VOCs, either present initially or produced in-situ, emitted from control equipment is also of concern to human health. The above concerns over the VOCs present in landfill gas highlights the importance of the monitoring of landfill gas for its VOC content. In a paper by Brosseau and Heitz⁽⁶³⁾ the literature on various aspects of the trace components in landfill gas is reviewed. Included in the review are the formation, nature and origin of the trace components as well as risks posed to human health and the environment. El-Fadel *et al.*⁽⁹⁾ also reviews various aspects of the environmental impacts of solid waste landfilling.

This thesis is principally concerned with the VOCs present in landfill gas from a number of landfills located in the northwest region of Melbourne, Victoria, Australia. In particular the study explores suitable sampling and analytical methodologies and focuses on the major types and levels of VOCs found.

1.3 Literature Review

There is limited literature in scientific journals on VOCs in landfill gas. However there are numerous contributions from conference proceedings and technical reports^(54, 63-84). Since the 1980's a small number of papers have appeared which cover VOCs in landfill gas from America⁽⁸⁵⁻⁸⁶⁾, England⁽⁸⁷⁻⁹²⁾, Finland⁽⁹³⁾, Germany^(58,94-98).

This literature review will include the following:

- A summary of the important papers including brief details on sampling source, VOCs collection and analysis. Types of VOCs found will be highlighted and their relationship to the type and age of waste;
- 2. A summary of the various classes of VOCs found and their relationship to the type and age of waste;
- 3. A survey of the literature giving concentration ranges of various classes of VOCs in landfill gas.

1.3.1. A Summary of Some Important Papers

The sampling and analytical methodologies used for VOCs in landfill gas are the same as those used for sampling and analysis of VOCs in air. Sampling usually involves whole air sampling in bags or canister or pre-concentration using adsorption tubes. Analysis usually involves gas chromatography.

Brookes et al.⁽⁸⁸⁾ and Young et al.⁽⁸⁹⁾ collected undiluted landfill gas samples from probes (modified piezometers) which were driven into the landfill. VOCs were analysed by gas chromatography-mass spectrometry. VOCs were collected on two types of adsorption tubes, Tenax GC (trap at ambient) and Porapak Q (trap at -80 °C) and whole landfill gas was also condensed at -80 °C using methanol and solid CO2. Samples collected on traps were thermally desorbed onto a cryo trap and then flash vaporized onto a SE30 capillary column and a Chromosorb 101 packed column, respectively. Condensate samples were injected directly into various packed columns including Chromosorb 101, Tenax GC and Triton X 100 / KOH. Employing full scan mode the Tenax GC trap / SE30 column provided non-polar VOCs and a general 'finger print' of collected species whereas the Porapak Q trap and condensate samples analysed on the various packed columns provided acidic, basic, neutral and low molecular weight compounds. Selective-ion mass (SIM) monitoring was also used for the analysis of some carboxylic acids and low-molecular weight amines. Calibration procedures involved anisole as internal standard using predetermined relative response factors or direct calibration with appropriate available standards.

Brookes *et al.*⁽⁸⁸⁾ and Young *et al.*⁽⁸⁹⁾ surveyed VOCs in landfill gas from six municipal landfills in the U.K. The landfills received either domestic or industrial waste and some a mixture of domestic, industrial and liquid waste or domestic and liquid waste. The age of the waste at the sampling points varied from 3 weeks to 6 years. At least 100 components were identified including alkanes, alkenes, cyclic compounds, terpenes, aromatic hydrocarbons, chlorinated compounds, organosulphur compounds, alcohols, esters, ethers and other oxygenated compounds including ketones.

They found that mature domestic refuse gave a mixture of mainly hydrocarbons but landfill gas from sites containing freshly deposited domestic refuse or industrial waste showed the presence of a much wider range of compounds. The industrial waste sites were significantly richer in petroleum based hydrocarbons with benzene particularly prevalent at industrial sites where levels were an order of magnitude higher than domestic sites. Concentrations of toluene and xylenes were also higher at industrial sites. Thiols and oxygenated compounds, including alcohols and esters are indicative of fresh refuse in the early stages of decomposition. Low levels of organosulfur compounds and esters found at one site containing 7 month old refuse suggested that age of refuse was not the only factor affecting release of these compounds. Limonene and alkylbenzenes were the most persistent throughout the three domestic sites and their release does not appear to be particularly dependent on the age of the refuse with propylbenzenes found widely in all sites. Increasing levels of higher molecular weight alkylbenzene in domestic sites may be largely due to degradation of larger molecules. Compounds such as halocarbons are present in the deposited waste and organosulfur compounds are decomposition products of the waste, whereas others such as benzene, toluene and vinylchloride appear to be derived from both sources and levels of these may be higher at sites accepting industrial liquid waste. The levels of compounds originating from incoming wastes would be expected to decrease with time, whereas levels of those originating from decomposition processes should reach a maximum at some time after waste deposition. Compounds originating from both sources have a background level at all sites. In sites that accept a wide range of industrial waste considerable variations may occur in VOC levels between different areas of the landfill. More details of the VOCs found at each of the six sites are given below:

In site A the most abundant compounds in domestic refuse of age 5 – 6 years were all hydrocarbons with 8 – 11 C atoms (10 – 137 mg/m³) including $C_1 - C_4$ alkylbenzenes (8 – 138 mg/m³) and terpenes (21 – 63 mg/m³). Solvents, oxygen and sulphur containing compounds were not present to any significant level.

In site B the age of the domestic waste at the sampling point was 7 months but below the depth sampled older waste was deposited. As with site A there were significant levels of $C_8 - C_{11}$ hydrocarbons (85 – 252 mg/m³), $C_1 - C_4$ alkylbenzenes (17.5 – 94 mg/m³) and terpenes (157 – 230 mg/m³). Several oxygenated compounds and organosulfur compounds were now present at appreciable levels and these are indicative of young refuse. Alcohols were the most abundant with propan-2-ol the most abundant at greater than 46 mg/m³. Dimethyl disulfide was present at 4 mg/m³ and benzene 4.2 mg/m³. Esters included ethylacetate (7 mg/m³) and ethylbutanoate (4 mg/m³). Halocarbons were also present including dichlorobenzene (15.5 mg/m³) and trichloroethylene (11 mg/m³).

In site C the age of the domestic waste was 3 weeks and there was no cover material. $C_1 - C_4$ alcohols were in abundance ranging from $17 - 650 \text{ mg/m}^3$. $C_8 - C_{11}$ hydrocarbons, $C_1 - C_4$ alkylbenzenes and terpenes ranged from 12 - 81, 13 - 120 and $33 - 105 \text{ mg/m}^3$ respectively. Esters ranged from $15 - 64 \text{ mg/m}^3$ with the ethylacetate most abundant. In particular concentrations of limonene (105 mg/m³) and propylbenzenes (120 mg/m³) were high and were the most persistent compounds throughout the three domestic sites (A, B and C). Organosulfur compounds were present with methanethiol and dimethyldisulfide present at 87 and 40 mg/m³ respectively.

Site D had received domestic, industrial solids and industrial liquid wastes and the age of the waste at the sampling point was greater than 15 months old. The main differences between site D and sites A, B and C were the presence of more volatile hydrocarbons with $C_6 - C_8$ the most abundant as well as high levels of benzene (114 mg/m³), toluene, xylenes and other industrial solvents. Vinyl chloride was also found and associated with deposited halocarbon solvents. Other possible sources include the degradation of PVC.

Site E had received domestic and industrial liquid wastes and the age of the waste at the sampling point was 6 months with underlying older waste. Alcohols were significant with ethanol at concentration greater than 800 mg/m³ and other alcohols at levels greater than 100 mg/m³. High levels of halocarbons were also present in particular dichloromethane (140 mg/m³) and tetrachloroethylene (350 mg/m³) and these were derived from the liquid waste. Other compounds included vinyl chloride,

benzene, methanethiol, dimethyldisulfide, limonene and low levels of toluene, xylene and hydrocarbons associated with industrial solvents and petroleum waste.

Site F had received industrial wastes and the age of the waste at the sampling point was 5 years. The difference between site F and site A, where the waste was of a similar age, is the presence of petroleum type compounds. There were increased levels of $C_6 - C_8$ hydrocarbons, benzene and volatile hexanes (500 mg/m³). Propylbenzenes levels at 79 mg/m³ were similar to site A and the low levels of terpenes may be due to low levels of vegetation in the deposited waste. Halocarbon levels are also low as these are volatilised within the first 5 years due to high volatility with the most abundant being the least volatile dichlorobenzenes present at 4 mg/m³.

In their work Young et al.⁽⁸⁹⁾ also identified compounds associated with odor and those of toxic significance. Dominant compounds associated with odor include alkylbenzenes, terpenes, in particular limonene, esters, in particular ethylbutanoate, and organosulfur compounds including methanethiol and dimethylsulfide. Alkylbenzenes and limonene along with other hydrocarbons are probably responsible for 'typical' landfill gas smell whereas esters in particular ethylbutanoate are responsible for the 'sweeter' smell of landfill gas from fresh refuse. Organosulfur compounds produce the typical 'bad egg' smell with methanethiol the greatest contributor to odor. It was suggested that the most important odors are common to many sites and are dependent more on the age and decomposition rate than on the nature of the waste. Esters and organosulfur compounds appear to be associated with the early decomposition phase with alkylbenzenes and limonene playing on increasing role in the odor as the more potent former species subside. Longer-term odor appears to be dominated by hydrocarbons. Compounds observed at or above their toxicity thresholds include benzene, C1-C3 alkylbenzenes, halogenated compounds including vinylchloride and tetrachloroethylene and organosulfur compounds including methanethiol and butanethiols. The dilution factors required to bring the above compounds to levels below their odor and toxicity thresholds are 1,000,000 and 100, respectively.

Scott *et al.*⁽⁶⁴⁾ used sampling and analytical protocols similar to those used by Brooks *et al.*⁽⁸⁸⁾. They monitored VOCs from three domestic landfills in the UK over a period of three years after the deposition of the waste. The work identified 136 different components of which 109 were found to be common to all three sites. Classes of compounds found include alkanes, alkenes, cycloalkanes, cycloalkenes, aromatics, halogenated compounds, alcohols, ethers, esters, amines, carboxylic acids and organosulfur compounds.

Alkanes was one of the predominant groups of trace organic compounds found. The distribution in terms of molecular weight was bimodal about compounds containing four carbon atoms and those containing nine carbon atoms. There were high levels of $C_3 - C_5$ and $C_9 - C_{11}$ compounds. It is likely that these two groups of alkanes are produced by different mechanisms in the landfill. The low molecular weight compounds are probably readily volatilized from petroleum products within the waste whereas higher alkanes arise from biochemical reactions and levels of these appear to increase gradually with time as anaerobic degradation of refuse proceeds. Under anaerobic conditions, nonane and decane were the dominant alkanes released. At one of the sites the release of higher molecular weight compounds still occurred well after microbial activity appeared to have terminated suggesting that these types of compounds are being volatilsed directly from materials in the waste and/or that a low degree of activity persists at the site.

The levels of alkenes found at all three sites were generally below those of the corresponding alkanes. Peak levels of alkenes were observed during the early stages of refuse degradation and fell with the onset of methanogenesis. Similar to alkanes, the distribution of alkenes was bimodal except that the higher molecular weight group is favoured and levels of these appear to increase gradually with time as anaerobic degradation of refuse proceeds. Abundant compounds include octene, nonene and decene.

All of the cycloalkanes observed were alkyl substituted cyclopentanes and cyclohexanes and their production is favoured under conditions of reduced anaerobic efficiency. Unsaturated cycloalkenes (terpenes) were consistently found in higher concentrations than cycloalkanes at all three sites. Limonene was the terpene normally found at the highest concentration.

Aromatic compounds were frequently found to be among the most abundant trace components in landfill gas. The level and diversity of aromatic hydrocarbons tended to increase under anaerobic conditions indicating that these compounds are produced as microbial degradation products, as well as direct volatilization from petroleum based materials and solvents discarded with household refuse. The concentration of alkylbenzenes, particularly propylbenzenes and xylenes enhanced following the establishment of anaerobic conditions.

The highest concentrations of organosulfur compounds in landfill gas were found within the first few days following refuse deposition. Organosulfur compounds most probably arise from the degradation of proteinaceous and putrescible fractions of animal and vegetable matter. During the very early phases of refuse degradation methanethiol is observed in relatively high concentration, but levels rapidly decline and dimethyl sulfide and dimethyl disulfide appear to be the principal sulfur containing compounds released during anaerobic degradation.

Relatively high levels of alcohols were observed at all three sites during the days following initial deposition of the refuse. Alcohols were generally low molecular weight compounds in the $C_1 - C_5$ range. During the early phases of refuse degradation ethanol, propan-1-ol and butan-2-ol were common to each site. Alcohols arise particularly from the fermentation of putrescible materials such as fruit and vegetable matter. Levels appear highest under conditions which favour anaerobic activity prior to the development of a substantial methanogenic microbial population.

High levels of esters were produced shortly after refuse deposition with ethyl ethanoate a major component. Other esters, particularly ethyl butanoate and propyl butanoate were common in landfill gas throughout the period of observation. Esters in landfill gas may arise from refuse decomposition products or may be produced from reaction between carboxylic acids and alcohols produced within the landfill. This latter source may explain the absence of carboxylic acids in landfill gas; as these were

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not present above their detection limits. Except for the very low levels of diethyl amine, amines were also not observed above their detection limits and diethyl ether was the only ether found during the course of the study and volatilsed from the waste within the first few days of refuse deposition.

Up to 25 individual halocarbons were identified in landfill gas from the three sites. With the exception of dichlorobenzene, all of the halocarbons were relatively low molecular weight species containing one or two carbon atoms. No bromo or iodo compounds were observed. The halogenated compounds found in landfill gas arise from direct volatilization rather than microbial degradation processes, as they are common components of many household and consumer products. Low molecular weight alkanes and halogenated compounds, particularly those containing fluorine, are emitted at relatively high concentrations during the aerobic activity phase when methane production is low. It is likely that some halocarbons of low molecular weight will be absorbed by refuse. These compounds may be subsequently re-released at rate proportional to the rate of refuse degradation. These compounds may give rise to enhanced rates of corrosion in landfill gas extraction and utilisation equipment when the gas is combusted for the purpose of energy production.

The trace fraction of landfill gas from the three sites essentially comprised of the same organic groups and compounds although the range and relative abundance of individual compounds appeared to be determined by other factors. Inter-site variation in landfill gas trace composition, observed during the course of the study, appeared to be influenced by the individual characteristics of each site and the extent to which these characteristics influence landfill processes. Climate, variations in operational practices and the physical form and location of the wastes deposited are all factors which influence the relative rates of various landfill processes responsible for trace emissions. These dictate, either directly or indirectly, which trace compounds predominate in the vapour / gaseous phase at any particular stage of refuse degradation.

The odour of the landfill gas is dominated by relatively few of the compounds found to exceed their odour thresholds where methanethiol and ethyl butanoate were often among the most odorous components observed. The most odorous emissions from all three sites were observed during the period immediately following the deposition of refuse. A minimum dilution factor of up to 1×10^9 can be required to reduce the level of odorous components below odour thresholds.

Toxic concentrations (levels above Threshold Limit Values) of some organosulfur, organochlorine, alcohols, aromatic and formaldehyde were observed. The maximum dilution of 430 was required to reduce the concentration of the most toxic compound observed (methanethiol) below its individual TLV. Such dilution is usually available above landfill sites.

Assmuth *et al.*⁽⁹³⁾ collected landfill gas samples from probes (PVC wells or piezometers) which were inserted into the landfill. VOCs were collected on TenaxTM adsorption tubes, and analysed via thermal desorption using capillary gas chromatography with flame ionisation detection. Analytical details were referred to a technical report by Kalevi⁽⁹⁹⁾.

These investigators measured VOCs in landfill gas samples from 3 terminated and 1 active municipal landfills in Southern Finland. In all of the sites, codisposal of industrial, hazardous or other special wastes with mixed municipal wastes is reported or assumed to have taken place. The terminated landfills operated for periods ranging from 21 - 31 years and the active landfill had been operating for 36 years. Over 30 trace contaminants were investigated, including halogenated aliphatic hydrocarbons, aromatic hydrocarbons, phenolic compounds and halogenated benzenes.

Compounds found in significantly elevated concentrations included chloromethanes and BTEX compounds (Benzene, Toluene, Ethylbenzene and Xylene). High levels of these were attributed to industrial waste, particularly solvents. Concentration variations between sites were attributed to differences in waste content and site conditions. The levels of aromatic compounds ranged from $1.1 - 445.3 \text{ mg/m}^3$. Halogenated aliphatic hydrocarbons were also persistent at all sites in appreciable levels ranging from $13.01 - 421 \text{ mg/m}^3$. Halogenated benzenes ranged from $0.17 - 0.67 \text{ mg/m}^3$. The concentration of phenolic compounds was less than 0.03 mg/m^3 in all sites. The estimates of dominant contaminant emissions from the study sites were of the order of kg/day where carbon tetrachloride occasionally exceeded toxicity limits and levels of several chloromethanes, chloroethenes and aromatic compounds exceeded urban background levels by up to 100,000 times.

Interestingly, appreciable levels of halogenated aliphatic hydrocarbons were found at all sites even though the age of the fills suggests these volatile compounds are thought to persist for only a few years after waste deposition. Assmuth *et al.*⁽⁹³⁾ point out that volatile halogenated compounds can persist where no gas extraction has occurred and at the four sites studied by Assmuth *et al.*⁽⁹³⁾ gas collection systems had not been installed.

Ward et al.⁽⁸⁹⁾ investigated VOCs in landfill gas and sub-surface gas plume emanating from the landfill by capillary gas chromatograph connected to a mass selective detector. Landfill gas was sampled from a gas venting borehole and plume gas samples from gas probes (hollow soil spike and boreholes). VOCs in gas samples were trapped on adsorbent tubes containing equal amounts of Tenax GR, Haysep Q $(580 \text{ m}^2/\text{g})$ and Carbosieve S-III (550 m²/g). The adsorption tubes allowed a wide range of VOCs to be trapped and the adsorbents were packed in order of increasing adsorption properties thus preventing the high boiling fraction from becoming irreversibly attached to the strongly sorbing material. Samples were thermally desorbed onto a Tenax TA cryogenic trap followed by thermal desorption onto a 5 % phenyldimethylpolysiloxane capillary column. Identification of VOCs was achieved by software comparison with the Wiley / NBS database of mass spectra. Quantitation was achieved using external standards of 11 compounds corresponding to analytes or isomers of analytes in the sampled gas. The detector response was assumed to be the same for the standard and its isomers and, in the absence of data to confirm this, the results of the analysis were regarded as semi-quantitative.

The study analysed VOCs in landfill gas and sub-surface gas plume emanating from a landfill site located in the U.K. The landfill had accepted domestic, dry industrial and commercial wastes deposited between 1982 and 1988, and in 1990 the site was capped and a passive venting system installed. A total of 79 compounds were identified, of which the 44 most abundant compounds were analysed. The range of VOCs found were similar to those in landfills containing predominantly domestic

waste with the most abundant being n-alkanes, branched alkanes, halogenated compounds, cyclic alkanes and aromatic compounds. Other compounds found included alcohols, ketones, esters, alkenes and terpenes. Only two compounds, vinylchloride and dichlorofluoromethane, approached or exceeded toxicity limits outside the landfill.

Halogenated compounds, particularly CFCs were found to be the most mobile and their concentration profiles in the plume suggest that they may have been flushed out of the landfill during its early stages. It was also suggested that the association of halogenated compounds with methane is diagnostic of a landfill source.

Allen et al.⁽⁹²⁾ used adsorption tubes to collect VOCs from landfill gas after which the VOCs were thermally desorbed and analysed by capillary gas chromatography with mass selective detection. Landfill gas was taken from monitoring points on gas extraction systems and a trial gas well which had been installed to assess methane production rates. The adsorption tubes contained a 1:1:1 ratio by volume of the following adsorbents packed in series: Tenax TA (80 / 100 mesh), Chromosorb 102 (80 / 100 mesh), and Carbosieve SIII (60 / 80 mesh). There were arranged in order of increasing adsorptive properties, which enabled a single sample tube to be used to trap VOCs with a wide range of boiling points and volatility. Samples were thermally desorbed onto a Tenax TA cryogenic trap followed by thermal desorption onto a 100 % dimethylpolysiloxane capillary column. Compounds were identified by mass spectral matching to the MS library data and external reference compounds. Quantitation of VOCs was achieved using a 12 component external standard which was introduced into a sampling tube and analysed as were real samples. For those compounds not directly quantified, relative response factors were used. More details on the sampling and analysis protocols were detailed in a previous paper by Allen et al.⁽⁹¹⁾.

These workers studied VOCs in landfill gas from seven municipal landfills in the U.K. At six of the sites gas extraction was underway and these sites had been in operation since 1920, 1984, 1986, 1987, 1990 and 1990 respectively. The other site, where gas extraction had not been undertaken, had been in operation since 1965. The landfills received both domestic and trade waste where the trade waste consisted of

building waste and waste with a similar organic content to that of domestic waste. None of the sites were licensed to accept toxic or industrial waste. Landfill gas samples were collected from gas extraction systems installed at six of the sites and from a trial gas well at the seventh site. Over 140 compounds were identified, of which 90 were present in each of the samples taken. Certain classes of compounds were identified including alkanes, alkenes, alcohols, ketones, chlorinated compounds, cyclic compounds, aromatic compounds, terpenes and esters. They found that the majority of compounds identified were present at all sites but the relative proportions of certain classes varied considerably between sites. These variations were attributed to differences in waste composition and the rates and mechanism of waste decomposition. Exact reasons for variations between sites could not be given as gas sampled was extracted from areas of differing waste ages. Further relevant information on the types of VOCs found is given below.

At two of the sites where gas extraction was conducted, alcohols, esters and ketones were present at levels 2 - 3 orders of magnitude higher than the other sites. Exact reasons for this were not given as the gas sampled was extracted from areas of differing waste ages. However, it was thought that these landfills located in the vicinity of fruit growing districts might have been receiving waste fruit. Other studies indicated that high levels of these compounds were attributed to fresh refuse, putrescible material such as fruit and vegetables, or sites with high gas production rates⁽¹⁰⁰⁻¹⁰²⁾. The levels of alcohols and ketones ranged from $2 - 2069 \text{ mg/m}^3$. Alkanes, aromatic compounds and cyclic compounds were present at appreciable levels at all sites and ranged from 302 - 1543 mg/m³, 94 - 1906 mg/m³ and 80 - 487mg/m³, respectively. Other studies have indicated that the predominance of these types of compounds is usually associated with older refuse⁽¹⁰²⁾. Their persistence at all sites is in accord with these compounds being produced during the waste degradation process, and their levels in the gas are dependant on waste composition and the stage reached in the decomposition process. One of the sites was monitored at monthly intervals for a period of 15 months and the levels of VOCs were reasonably consistent over this period and were directly related to methane levels. Fluctuations were thought to be due to changes in gas extraction rates at the gas well studied, changes in atmospheric pressure and changes to both ambient temperature and the temperature of the landfill itself.

Terpenes were also persistent at all sites in appreciable levels ranging from 35 - 652 mg/m³ where α -pinene and β -pinene accounted for 51 % and 100 %, respectively, of the total terpenes present at each site. They suggested that terpenes are derived from the volatilisation of compounds contained in garden wastes, such as hedge clippings, shrubs, and trees with other potential sources including fragrant household detergents and air fresheners.

Halogenated compounds were also present at all sites and their levels ranged $327 - 1239 \text{ mg/m}^3$. At the seven sites studied by Allen *et al.*⁽⁹²⁾ chlorofluoro compounds (CFCs) accounted for 95 % of the total chlorine measured in the landfill gases. They suggested that CFCs are emitted from the direct volatilisation of compounds present in probable sources such as aerosols, paint remover, dry cleaning agents, dyeing solvents, foam blowing agents, soaps, paint, varnish and refrigerants. They also suggested that CFCs are governed by the composition of the waste and are not influenced by biological decomposition processes. Due to their finite source and volatility CFCs emissions usually occur in the years following waste deposition but Allen *et al.*⁽⁹²⁾ found the highest levels of CFCs in landfill gas from waste in excess of 20 years old and it was thought that this was due to the lack of gas extraction at this site. Variations in CFCs concentrations between sites were attributed to differences are waste composition. At three of the sites the total chlorine content of the gas exceeded levels which were specified as detrimental to gas engine oil (the buffering capacity is reducing) thus increasing the potential for engine corrosion.

Total VOCs emissions from four of the seven sites studied were estimated to be of the order of 10^4 kg/yr. Compounds which exceeded various toxicity limits included chloroethene, toluene, xylene, trimethylbenzenes, tetrachloromethane and dichlorofluoromethane. Allen *et al.*⁽⁹²⁾ point out that their discussion on health risks from VOCs in landfill gas assumes that there are no synergistic or additive effects from the other components present in the gas. Young and Heasman⁽¹⁰¹⁾ indicated that the toxicity of landfill gas depends on the cumulative effect of more than a hundred groups of compounds.

Eklund *et al.*⁽⁸⁵⁾ measured VOCs in landfill gas from a municipal solid waste landfill site in U.S.A. The site began accepting waste in 1948 and up until the time of their study (1998) was currently accepting household garbage. Hazardous waste and medical waste were not currently accepted. Landfill gas samples were taken in Summa polished stainless steel canisters from the headers of the gas extraction system, individual gas extraction wells, passive vents and the landfill surface (flux chamber). Details of sampling and analytical methods were referred to a report by the US EPA⁽¹⁰³⁾ but VOCs analysis basically involved gas chromatography with dual columns and multiple detectors including a flame ionisation detector (FID), a photoionisation detector (PID), and an electrolytic conductivity detector (ELCD). More prevalent VOCs found in all samples included n-alkanes, aromatic compounds, halogenated compounds and terpenes. The landfill gas composition was consistent across all sampling sources even though emission rates for each source were different, indicating that composition does not vary significantly as a function of landfill gas flow rate.

Schweigkofler *et al.*⁽⁵⁸⁾ used evacuated stainless steel canisters (15 L) to directly collect gas samples from two domestic waste disposal landfill sites and two sewage treatment plants. The VOCs were analysed by gas chromatography – mass spectrometry / atomic emission spectroscopy. A defined volume of sample was drawn from the canister and cryogenically trapped at -85 °C. Samples were thermally removed onto a second cryogenic trap (liquid N₂) after which they were thermally displaced onto a dimethylpolysiloxane capillary column. The second trap was used to focus the sample prior to GC and an internal moisture management system was used to minimize the effect of moisture on the chromatography. Simultaneous mass spectrometric and atomic emission spectroscopic detection was used. Mass spectrometry was used for sample identification while atomic emission spectroscopy using four elements specific channels (Si, Cl, S, C) and a 30 component external standard, was used for quantification.

These authors also studied VOCs in biogases from two German domestic waste landfill sites and two sewage treatment plants. More than 80 compounds were identified by MS analysis and the major compounds included $C_5 - C_{12}$ alkanes,

aromatics compounds, terpenes and volatile siloxanes. Oxygenated compounds were also found including alcohols and ketones. Sewage gas was also studied for its VOCs content and contained the same major classes of compounds as landfill gas but at significantly lower levels and more less volatile compounds were observed.

Volatile siloxanes were of particular interest. These are derived from the use of silicoorganic compounds in products such as shampoos, skin creams, toothpaste and others; as well as the possible formation of volatile siloxanes from the degradation, within the landfill, of high molecular weight silicoorganic compounds. These siloxanes are converted into microcrystalline silicon dioxide during combustion of landfill gas and contribute to abrasion of combustion chamber surfaces⁽⁵⁹⁻⁶⁰⁾.

They found that VOC levels in landfill gas from the two sites studied varied considerably. Concentration differences were said to be primarily due to differences in waste composition, the hydrogeological situation of the waste body, and the stage reached in the decomposition process. Other factor, affecting fluctuations in gas composition could be attributed to changes in gas extraction rates and parameters such as gas temperature and atmospheric pressure.

Concentrations of some individual compounds were reported and these are given here for landfill gas where the ranges specified for each class of compounds were determined by addition of the individual compound data. The levels of aromatic compounds ranged from $164.7 - 289.6 \text{ mg/m}^3$. Terpenes were also persistent at all sites in appreciable levels ranging from $19.7 - 102.7 \text{ mg/m}^3$. Alkanes ranged from $48.1 - 67.5 \text{ mg/m}^3$, respectively. Halogenated compounds ranged $7.79 - 18.74 \text{ mg/m}^3$.

1.3.2. A Summary of the Various Classes of VOCs Found in Landfills

The VOCs found in landfill gas originate from two sources, they are either present in the incoming waste or they are produced during the degradation of the waste. Some compounds originate from both sources. The range of VOCs found in landfill gas from very different sites, including those accepting domestic and both domestic and industrial wastes, is very similar, and includes oxygenated compounds, alkanes, alkenes, cyclic compounds, aromatic compounds, organosulfur compounds, organohalogenated compounds, terpenes and silanes. Compounds such as organosulfur compounds, esters and alcohols are associated with fresh refuse in the early stages of decomposition. The presence of these compounds is associated with the acid formation stage of the decomposition process. The most prevalent compounds in landfill gas which are present from early on and persist right through in the decomposition process are n-alkanes, branched alkanes, aromatic compounds and terpenes. The presence of these compounds alone is indicative of mature refuse. Compounds present in the incoming waste include organohalogenated compounds and these as well as alkanes and aromatic compounds originate from industrial waste. Where gas extraction is taking place, the gas sample represents an average of the VOCs present at the site, and the range of compounds found reflects the different characteristics of the waste, in particular age and composition, across the site. Table 1.4 lists the various classes of VOCs found in landfill gas along with typical compounds, source and other relevant information. The information in Table 1.4 was obtained from literature used to prepare Section 1.3.1.

	TABLE Classes VOCs Found in Landfill Gas	1.4 and Other Relevant Inform	ation
CLASS OF COMPOUNDS	SOME TYPICAL PREDOMINANT COMPOUNDS	SOURCE	OTHER INFORMATION
Oxygenated Compounds			 Levels relatively high from fresh
Alcohols	$C_1 - C_4$ alcohols		retuse and decrease as waste matures
Esters	Ethylacetate, Ethylbutanoate	 Decomposition of fresh refuse or refuse in early 	• Extremely high levels if waste content high in fruit and
Ketones	Acetone	decomposition phases	vegetables due to fermentationSolvents
Ethers	Diisopropylether	 Incoming waste 	• Esters may also be produced from reaction between carboxylic acids and alcohols
n-alkanes and Branched Alkanes	C ₅ - C ₁₂ alkanes, eg. Hexane, Nonane, Dodecane.	Waste decompositionIncoming waste	• C ₈ – C ₁₂ found widely in domestic waste sites
	C ₅ - C ₁₂ branched alkanes, eg. Methylbutane, Methyloctanes, Methyldecanes		 Levels relatively high from mature refuse Elevated levels of C₆ - C₈ from industrial solvent and petroleum waste
Alkenes	C ₆ - C ₁₁ alkenes, eg. Hexene, Nonene, Undecene.	• Waste decomposition	 Found widely in domestic sites Levels below those of corresponding alkanes High molecular weight alkenes
			more abundant

TABLE 1.4 Continued (1)			
CLASS OF COMPOUNDS	SOME TYPICAL PREDOMINAT COMPOUNDS	SOURCE	OTHER INFORMATION
Cyclic Compounds	Cyclohexane, C ₁ – C ₄ Methylcyclohexanes, Propylcyclohexane.	 Waste decomposition Incoming waste 	 Prevalent in domestic sites Levels relatively high from mature refuse Elevated levels from industrial solvent and petroleum waste
Aromatic Compounds	Benzene, Xylenes, Toluene, Ethylbenzene, Trimethylbenzenes, Isopropyltoluene.	 Waste decomposition Incoming waste 	 Levels relatively high from mature refuse Found widely in domestic sites Elevated levels of benzene and BTEX from industrial solvent and petroleum waste
Organosulfur Compounds	Methanethiol, Dimethyl sulfide.	 Decomposition of fresh refuse or refuse in early decomposition phases 	 Levels relatively high from fresh refuse and decrease as waste matures
Terpenes	α-pinene, β-pinene, Camphene, Limonene.	Waste decomposition	 Found widely in domestic sites Derived from garden waste and fragrant household detergents and air fresheners Low levels at industrial sites having received low levels of vegetation

TABLE 1.4 Continued (2)	SOME TYPICAL		
CLASS OF COMPOUNDS	PREDOMINAT COMPOUNDS	SOURCE	OTHER INFORMATION
Organohalogenated Compounds	Chlorofluorocarbons: Chlorodifluoromethane, Dichlorodifluoromethane, Chloroethene (vinyl chloride), Chloroethane, Dichlorofluoromethane, Trichlorofluoromethane, Dichloroethane, Trichloroethene, Trichloroethene, Trichloroethene, Trichloroethene,	• Incoming waste	 Levels expected to decrease early following waste deposition due to volatility Low volatile compounds such as dichlorobenzene may persist dichlorobenzene may persist Vinyl chloride may also be a waste decomposition product ⁽⁹²⁾ Levels of volatile halogenated compounds can persist if no gas extraction Emitted from the direct volatilisation of compounds present in probable sources such as aerosols, paint remover, dry cleaning agents, dyeing solvents, foam blowing agents, soaps, paint, varnish and refrigerants
Silanes	Hexamethyldisiloxane, Octamethyltrisiloxane, Deca-methyltetrasiloxane, Dodecamethylpentasiloxane.	 Incoming waste 	 Derived from silicones, shampoos, skin creams, toothpaste, silicone oils

1.3.3. Factor Affecting the Types and Levels of VOCs Found in Landfill Gas

The range of VOCs is similar across a wide variety of landfill sites but their relative concentrations may differ significantly. Significant variations may also exist between VOCs found in landfill gas taken from different areas of a particular site. Where gas extraction is taking place VOC levels in extracted gas represent an average from across the site. The most important factors influencing the types and levels of VOCs in landfill gas are the stage reached in the waste decomposition process, i.e., the age of the waste and waste composition. Factors which influence the rates of various landfill processes include climate, variations in operating practices, the physical form and the location of the deposited wastes. A number of factors affect methane levels in landfill gas including gas extraction rate, atmospheric pressure, ambient temperature and landfill temperature. These parameters also affect VOC concentrations as they appear to be related to methane concentration.

In general VOC production within a landfill site would be expected to reach a maximum at some time following deposition and then decrease with time as the waste body becomes inert. Compounds produced in the early stage of waste decomposition, such as oxygenated compounds and organosulfur compounds, would be abundant in landfill gas at this stage with their levels decreasing as the waste matures. Compounds such as alkanes, aromatic hydrocarbons and terpenes are persistent throughout the decomposition process and are abundant in landfill gas from mature refuse. Similarly, VOCs present in the incoming waste would also decrease with time as there is a finite source of these. These add to the background levels of VOCs produced from decomposing refuse, in particular elevated levels of hydrocarbons and aromatics indicate petroleum based wastes and solvents. Sites accepting these sorts of waste may show considerable variation in these types of VOCs due to the different levels present in the wide variety of wastes.

The above discussion indicates that it is very difficult to compare VOCs levels in landfill gas taken from different sites or even from different areas of one particular site. Table 1.5 shows the results of VOCs levels in landfill gas from a number of other researchers. No attempt was made to relate types and age of waste or sampling source but rather the Table 1.5 is meant to show levels of VOCs that have been found rather than try to compare levels between researchers. Also, sampling and analytical

	TABLE 1.5 (Total Co	Comparison (oncentrations	of Results Obta of VOCs Quan	ined from Va tified from La	rious Authors andfill Gas)		
	1983	1986	1992	1996	1997	1998	6661
COMPOUND	YOUNG et al. ^a	Scott et al. b	ASSMUTH et al. ^c	WARD et al. ^d	ALLEN et al. ^e	EKLUND et al. ^f	SCHWEIGKO FLER et al. ^g
	(mg/m ³)	(mg/m ³)	(mg/m ³)	(PPMV)	(mg/m ³)	(PPMV)	(mg/m ³)
OXYGENATED COMPOUNDS	BDL * - 1328	BDL - 5198.7		ļ	2 – 2069	6.09	I
ALKANES	328 - 814.1	0.3 - 1737.7	I	82.07	302 - 1543	271.14	48 - 67.5
ALKENES	13 - 167.3	0.1 -304.9	I	I	<0.1 - 36	9.29	Ι
CYCLIC COMPOUNDS	BDL – 5	0.4 - 56.0	I	11.04	80 - 487	I	I
AROMATIC COMPOUNDS	268 - 371.7	0.8 - 552.6	1.1 – 445.3	I	36 - 1906	67.88	164.7 - 289.6
ORGANOSULFUR COMPOUNDS	BDL - 127	BDL – 519.4	I	I	I	I	I
ORGANOHALOGENATED COMPOUNDS	3 – 71	0.2 - 1342.0	0.17 - 421	33.05	259 - 1239	21.59	I
TERPENES	87 - 400	0.3 - 303.4	I	I	35 - 652	43.23	19.7 - 102.7

protocols have not been compared. Details on waste types and age, and sampling and analysis are given in Section 1.3.1.

* BDL - Below Detection Limit

^a - See Reference (89).

b - See Reference (64).
c - See Reference (93).
d - See Reference (90).
e - See Reference (92).
f - See Reference (85).

g – See Reference (58).

1.4 Aims of This Thesis

The main objective of this work was to investigate VOCs in landfill gas from Australian landfill sites as no previous published literature on Australian sites was available. The main aims were:

- 1. to develop sampling and analysis protocols for VOCs in landfill gas, and
- 2. to observe the trends in levels and relative abundance of various VOCs at a number of landfill sites and find correlations with waste age and inputs.

CHAPTER II EXPERIMENTS PREPARATION AND MATERIALS

2.1 Landfill Gas

The landfill gas investigated in this study was taken from seven landfill sites in the western region of Melbourne, Victoria, Australia (see Table 6.1 and 6.2 for landfill sites description and sampling point description, respectively).

2.2 Landfill Gas Sampling Apparatus for Volatile Organic Compounds Collected on Solvent Desorption Adsorption Tubes

2.2.1 Sampling Train

The sampling train used to collect VOCs in landfill gas is shown below in Fig. 2.1. Landfill gas emerging from the landfill bore-hole or well (6) is pumped by the sampling pump (5) through the moisture trap (2). Volatile organic compounds in the dry gas emerging from the moisture trap are collected on adsorption tubes (3). Gas stripped of its VOCs then passes through silica moisture indicator tube (4) before passing through the pump and out to atmosphere. Adsorption tubes, moisture trap, connecting tubing, moisture indicator tube and sampling pump are described in the following sections. The pump flow was set at 200 ml/min and was set after connection to the sampling train to account for flow resistance due to train back pressure. The pump was downstream of the adsorption tubes to avoid contamination of the tubes with pump volatiles. The moisture indicator tube contained SiO₂ which changed color from blue to red if moisture penetrated the moisture trap. It was also placed downstream of the adsorption tube to avoid VOCs being adsorbed on it. For the collection of the minor components in the landfill gas, sealed adsorption tubes were opened, fitted into the sampling train and sampling commenced. Sampling time is discussed in section 3.1.2. When sampling was completed both ends of the adsorption tubes were sealed with the caps provided with the tubes.



Fig. 2.1 The Sampling Train

Samples were kept in the refrigerator if not analyzed on the same day as collection. Sample preparation is described in Section 2.3.

2.2.1.1 Solvent Desorption Adsorption Tubes

Landfill gas was collected on adsorption tubes and collected compounds were desorbed either with carbon disulfide (CS_2) or thermal desorption.

The tubes used in solvent desorption studies are described below and shown Fig. 2.2, and were supplied by SKC. Carbon disulfide (CS_2) was AR. Grade and supplied by Ajax Chemicals. The various tubes include:

- a) Charcoal tubes, Lot 120;
- b) Tenax tubes, Lot 824;
- c) XAD tubes, Lot 816.



Fig. 2.2 Solvent Desorption Adsorption Charcoal Tube

2.2.1.2 Construction of the Moisture Trap

Fig 2.3 (a) & (b) show the construction of the moisture trap. All glass components of the moisture trap were silanised as described in the following section. The polystyrene box containing the moisture trap was a XL 'esky' purchased from K-Mart.



Fig. 2.3 (a) The Construction of The Moisture Trap



Fig. 2.3 (b) The Construction of The Moisture Trap

After sampling, the unit is washed by flushing with hot water for half an hour, following by oven-drying (150 °C) overnight. It was found that this method of cleaning was better than soap or solvent washing as indicated by blank analyses.

2.2.1.3 Silanisation Method

The glass components of the moisture trap were deactivated by the silanisation method described below:

• Rinse with acetone (to remove any manufacturing residues that might interfere with the silanisation).

• Heat at 180 °C for 1 hour (to evaporate polar compounds such as water, alcohols, and amines which could react with the silylation reagents).

• Cool to 50 °C and immediately place in a 5 % solution of dimethyldichlorosilane (DMDCS) preferably in toluene and cover with laboratory stretch film. Soak for 10 minutes (Use caution when removing the glass condensation tubes from the reaction vessel because hydrogen chloride is formed during this reaction).

- Rinse with toluene.
- Place in methanol and soak for 10 minutes.
- Air dry at 25 °C

The silanisation reaction is shown in Fig 2.4.



Fig. 2.4 The Silanisation Reaction

2.2.1.4 Inert Connecting Tubing

The inert tubing placed in the landfill bore hole and used for all connections in the sampling train was $Viton^{\mathbb{R}}$ connecting tubing supplied by Cole-Palmer. Two different size tubings were used in the sampling train and included:

(a). ID 4.8mm, OD 6.4mm, WALL 0.8mm.

(b). ID 6.4mm, OD 8.0mm, WALL 0.8mm.

2.2.1.5 Moisture Indicator Tube

The moisture indicator tube was $15 \text{cm} \times 0.8 \text{cm}$ glass tube containing dried silica with glass wool plugs at each end and is shown in Fig 2.5. The silica changes color from blue to red when exposed to moisture.



Fig. 2.5 The Moisture Indicator Tube

2.2.1.6 Sampling Pump and Sampling Pump Calibration

The sampling pumps are the *Personal Air Sampler* Model: 222-3 and were supplied by SKC. All sampling pumps were calibrated using the *mini-BUCK CALIBRATOR* supplied by A.P. BUCK Inc.. The *mini-BUCK CALIBRATOR* is an electronic bubble flow meter.

The sampling pump was calibrated attached to the sampling train at both the beginning and end at sampling of landfill gas.

2.2.2 Drying Tubes

Sodium sulfate (Na₂SO₄) drying tubes used in initial attempts to remove moisture are described below:

- (a). Commercial Na₂SO₄ drying tube containing 250 mg of Na₂SO₄ supplied by SKC.
- (b). Specially constructed Na_2SO_4 drying tubes were prepared using 15cm \times 0.8cm glass tubing containing dried AR. Grade Na_2SO_4 supplied by Ajax Chemicals.

2.3 Sample Preparation Prior To GC-MS Analysis

VOCs adsorbed on the various adsorption media were desorbed using CS_2 as described in ASTM D3686-95⁽¹⁰⁴⁾. However, 10 ml of CS_2 was used for the 150 mg

adsorbent tubes rather than 1 ml as indicated in the ASTM method in order to produce samples of suitable concentration for GC analysis. The procedures are described below:

The adsorption medium from each adsorption tube was separately transferred into 10 ml glass centrifuge tubes, and 10 ml CS_2 added. A model ST-19 SENTRA vortex shaker was used to agitate solvent and adsorbent for 2 minutes.

For the quantitative analysis, 125 μ l of the above solution was taken, and 20 μ l of each internal standard (see Section 2.4.1) was added, and the solution was diluted to a final volume of 1 ml with CS₂.

2.4 VOCs Standard Solutions For Solvent Desorption of Study

2.4.1 VOCs Standards

VOCs used to prepare standard solutions were supplied by ULTRA Scientific and Sigma-Aldrich. The compounds used in this study are listed below. All solutions were prepared using AR Grade CS_2 supplied by Ajax Chemicals.

- (a). Straight Chain Hydrocarbons: Supplied by ULTRA Scientific.
 n-Hexane, *n*-Heptane, *n*-Octane, *n*-Nonane, *n*-Decane, *n*-Undecane and *n*-Dodecane.
- (b). Cyclic Hydrocarbons: Supplied by ULTRA Scientific.
 Cyclohexane, Methylcyclohexane, 1,2-Dimethylcyclohexane (trans- & cis-),
 1,4-Dimethylcyclohexane, Ethylcyclohexane and iso-Propylcyclohexane.
- (c). Aromatics: Supplied by ULTRA Scientific.
 Benzene, Methylbenzene, 1,2-dimethylbenzene, 1,3-dimethylbenzene,
 1,4-dimethylbenzene, Ethylbenzene, Propylbenzene, 1,2,4-Trimethylbenzene
 and 1,3,5-Trimethylbenzene.

- (d). Terpenes: Supplied by Sigma-Aldrich.
 α-Pinene, β-Pinene and 1-Limonene.
- (e). Deuterated internal standards: Supplied by ULTRA Scientific.
 Ethylbenzene-D₅ (2.010 mg/ml) and Naphthalene-D₈ (1.002 mg/ml),

2.4.2 Standard Solutions Used for Positive Identification

2.4.2.1 Standard Solution for Positive Identification of the Straight Chain, Cyclic and Aromatics Hydrocarbons

A standard solution containing 0.025 μ l/ml each of the straight chain, cyclic and aromatics hydrocarbons listed in Section 2.4.1 (a, b and c) was prepared by adding 20 μ l of each compound into a 10 ml volumetric flask and diluting to a final volume of 10 ml with carbon disulphide (CS₂). A 125 μ l aliquot of this solution was further diluted to a final volume of 10 ml with CS₂. This standard solution was used for positive identification of the straight chain, cyclic and aromatics hydrocarbons.

2.4.2.2 Standard Solution for Positive Identification of the Terpenic Hydrocarbons A standard solution containing 0.025 μ l/ml each of three terpenic hydrocarbons listed in Section 2.4.1 (d) was prepared by adding 20 μ l of each compounds into a 10 ml volumetric flask and diluting to a final volume of 10 ml with carbon disulphide (CS₂). A 125 μ l aliquot of this solution was further diluted to a final volume of 10 ml with CS₂. This standard solution was used for positive identification of the terpenic hydrocarbons.

2.4.3 VOCs Standard Stock Solution for Quantitation

A stock solution containing 0.2 μ l/ml each of the straight chain, cyclic, aromatics and terpenic hydrocarbons listed in Section 2.4.1 (a, b, c, and d) was prepared by adding 20 μ l of each compound into a 10 ml volumetric flask and diluting to a final volume of 10 ml with carbon disulphide (CS₂). This standard solution was stored in a refrigerator. This stock solution was used to prepare calibration solutions for GC analysis.

2.4.4 Standard Solutions

By diluting the stock solution (see Section 2.4.3) with CS_2 , the following standard solutions were prepared:

0.2, 0.1, 0.05, 0.025, 0.0125 and 0.00625 $\,\,\mu l$ of each compound per ml CS_2.

2.4.5 Calibration Solutions

For the quantitation analysis, 960 μ l of each standard solution (see Section 2.4.4) was then taken, and 20 μ l of each internal standard (see Section 2.4.1) was added to give a final volume of 1 ml. The Calibration Solutions prepared were:

0.192, 0.096, 0.048, 0.024, 0.012 and 0.006 μl of each compound per ml $CS_2.$

2.5 GC-MS Conditions For Solvent Desorption Adsorption Tubes

2.5.1 GC-MS Conditions

The gas chromatograph used was a Hewlett-Packard (HP) 5890 series II with a HP 5971 Mass Selective Detector. Injection was performed by a HP 7673 Auto Injector. GC column flow was adjusted at 70 °C GC oven conditions are described in Chapter III. Other GC-MS conditions are described below.

<u>Carrier Gas</u> :	Helium.
Carrier Gas Flow:	0.9 ml/min at 70 °C.
Injection Mode:	Split or splitless depending on VOC concentration in landfill
	and / or sampling time.
Injection Volume:	1 μl
Columns:	Capillary DB-5, 25m \times 0.25mm ID, 0.25 μm film thickness
	(Supplied by J & W)
	Capillary BP-1, 25m \times 0.25mm ID, 0.25 μ m film thickness
	(Supplied by SGE)
	Capillary BP-1, $25m \times 0.25mm$ ID, 1 µm film thickness
	(Supplied by SGE)
Oven Temp:	See Chapter III.

Injection Temp:	Injector 250 °C.	
MS transfer line:	280 °C.	
<u>Solvent delay</u> :	3.0 minutes	
<u>Scan_rate</u> :	1.2 scans/sec.	
<u>Scan range</u> :	40 – 550 amu	
Tuning procedure:	Auto tune	
Mass spectral confirmation: Wiley Mass Spectral Data Base		

2.6 Desorption Method Validation for Solvent Desorption

2.6.1 Preparation of Pure Mixture

A mixture containing nine compounds was prepared by combining 100 μ l each of benzene, cyclohexane, heptane, methylbenzene, ethylbenzene, 1,4-dimethylbenzene, propylbenzene, β -pinene and 1,3,5-trimethylbenzene. The compounds are described in Section 2.4.1.

2.6.2 Preparation of Standard Solution

A standard solution containing 0.0444 μ l of each compound in 5.00 ml CS₂ was prepared as follows. 4.00 μ l of the mixture described in Section 2.6.1 was diluted to 5.00 ml with CS₂. 500 μ l of this solution was further diluted to 5.00 ml with CS₂.

2.6.3 Preparation of Standard Gaseous Mixture

The apparatus used to prepare the standard gaseous mixture is shown in Fig 2.6. To the cap of a 25 L airtight glass container were fixed two hose connectors. A personal sampling pump (Section 2.2.1.6), external to the container, was connected to one hose connector using inert tubing (Section 2.2.1.4). Inert tubing was also used to connect a 5 L Tedlar® bag inside the container, to a 10 L Tedlar® bag outside the container via the other connector. The inert tubing used to connect the 5 L Tedlar® bag was the shortest length possible and a clamp was placed on the inert tubing connecting the 10L Tedlar® bag to the container as close to the connector as possible.



Fig. 2.6 The Apparatus for the Standard Gaseous Mixture Preparation

The procedure used to prepare the standard gaseous mixture was taken from the Victoria EPA standard method⁽¹⁰⁵⁻¹⁰⁶⁾. The procedure ensures that no pump contaminants are introduced into the standard gas mixture as no gas mixture components ever come into contact with the pump. In this procedure a known amount of air is removed from the gas container, consequently the negative pressure produced in the container allows the internal Tedlar[®] bag to fill with an equal amount of gas, so as to balance the internal pressure of the container with the external atmospheric pressure on the container. The procedure involved the following steps.

- 1. The 10 L Tedlar[®] bag is filled with 7 8 L of high purity nitrogen (N₂), connected to the inert tubing and the bag valve opened.
- 2. The clamp is removed and the pump started at a flow rate of 200 ml/min so as to extract air from container.
- 3. After 25 minutes, 5 L air has been extracted from the container, and the pump is stopped.

- 4. After a further 2 minutes when the internal and external container pressures have balanced, the clamp is closed and the 10 L bag removed. The 5 L Tedlar[®] bag plus inert tubing until the clamp now contains 5 L of high purity nitrogen (N₂)
- 5. The container cap is unscrewed and lifted to expose the bag valve. Into the bag is injected 1 μ l or 10 μ l of the mixture described in section 2.6.1, and the cap refitted.
- 6. The bag is left to sit for 6 hours in order for the mixture to evaporate and the gaseous mixture to become homogeneous.
- 7. A charcoal tube is connected to the internal bag via the external inert tubing, i.e., where the 10 L Tedlar[®] bag was initially.
- 8. The pump is connected so as to pump air into the container, the clamp opened, and 2 L of air is introduced into the container at 200 ml/min.
- 9. After 10 minutes, 2 L of gaseous standard has passed through the charcoal tube and the clamp is closed.
- 10. For solvent desorption the charcoal tube is desorbed with 5 ml of CS_2 , as described in section 2.3.

2.7 Landfill Gas Sampling Apparatus for Volatile Organic Compounds Collected on Thermal Desorption Tubes

2.7.1 Sampling Train

The sampling train used to collect VOCs in landfill gas using thermal desorption tubes is shown in Fig. 2.7. The sampling procedure was similar to that described in Section 2.2.1, except that pump flow rates of between 60 and 200 ml/min were used. Pump flow rates and sampling time are discussed in Section 4.1.1. Thermal desorption adsorption tubes are described below and other sampling train components are described in Section 2.2. In Fig 2.7 two thermal desorption tubes are placed in series, where the second tube is used to indicate sample breakthrough. When sampling was completed both ends of the adsorption tubes were sealed with the caps provided with the tubes.


Fig 2.7 The Sampling Train Using Thermal Desorption Tube

2.7.2 Thermal Desorption Adsorption Tubes

The tubes used in thermal desorption are described below and were supplied by Supelco Inc.:

(a): Carbotrap[™] 100; (shown in Fig. 2.8 (a))



Fig. 2.8 (a) Thermal Desorption Tube (Carbotrap[™] 100)

(b): Carbotrap[™] 200 Multi-bed; (shown in Fig. 2.8 (b))



Fig. 2.8 (b) Thermal Desorption Tube (Carbotrap[™] 200 Multi-bed)

(c): Carbotrap[™] 300 Multi-bed; (shown in Fig. 2.8 (c))



Fig. 2.8 (c) Thermal Desorption Tube (Carbotrap[™] 300 Multi-bed)



Fig. 2.8 (d) Thermal Desorption Tube (Tenax TA)

2.7.3 Thermal Desorption Unit (TDU) / GC-MS

A Dynatherm Analytical Instruments Inc. model 890 TDU was used. The gas chromatograph used was a HP 5890 series II with a HP 5971 Mass Selective Detector. Fig 2.9 shows a schematic diagram of the TDU-GCMS setup. The TDU serves as the inlet to the GC column via an inert nickel transfer line, and GC column flow and split flow are adjusted at the TDU. The column used was Capillary BP-1, $25m \times 0.25mm$ ID, 1 µm film thickness supplied by SGE. Column flow and split flow were set at room temperature.



Fig 2.9 Schematic Diagram of the TDU-GCMS

2.7.3.1. TDU and Initial Optimisation for Operation with MSD

When the TDU was first attached to the GC-MS problems obtaining column flow in split mode were encountered. An account of these problems and the solution is given below. Column flow measurements were performed directly from the column outlet using a bubble flow meter supplied by HP.

Fig 2.10⁽¹⁰⁷⁾ shows the carrier gas pathways available with the TDU, where Pathway A is used for sample preparation and tube cleaning, and Pathway B to thermally desorb tube components and transfer them into the GC column. A six port switching valve allows selection of either Pathway A or Pathway B. In sample preparation mode, carrier gas flows through the desorption tube chamber and out through the side port. Sample preparation involves collecting volatiles which originate from samples heated in or injected into the tube chamber onto an adsorption tube placed in the side port. Pathway A is also the pathway used to flush the air present in the thermal desorption tubes prior to thermal desorption. In desorb or heat mode, carrier gas flows through the desorption. In desorb or heat mode, carrier gas flows through the desorption tube chamber and out through the GC column. Pathway B also allows splitting of the desorbed sample, where the split sample can be trapped in an adsorption tube placed in the sample saver chamber for repeat analysis.



Fig 2.10* The Carrier Gas Pathways of the TDU * From Reference 107

Pathway A shows that carrier gas from cylinder (regulator at 60 psi) passes through needle valve V_1 , through the desorption chamber and out through the side port. Open / close switch S_1 allows selection of Pathway A.

Pathway B shows that carrier gas from cylinder (regulator at 60 psi) passes through flow controller V_2 , then through to desorption chamber, column and detector. Diverting switch S_2 allows carrier gas to be diverted to either the flow check port for measurement of system total flow or to the GC column. Open / close switch S_3 allows split / splitless sampling using V_3 to adjust split ratio with split flow measurement at split vent. Sample exiting to split vent via S_3 can also be trapped in adsorption tube placed in the 'sample saver chamber' for repeat analysis. A more detailed description of the operation of the TDU is given in the instrument operating manual.

Flow controller V_2 was initially fitted with a 1 - 7 ml/min flow element, where this was suitable for use with capillary columns operated in splitless mode. As the option of splitting was required, this flow element proved not to be suitable for split operation. With V_2 fully open, total system flow at ≈ 8 ml/min, there was not sufficient column flow even with V_3 slightly open. These adjustments were with the column at room temperature and column flow approached zero as oven temperature was increased.

In order to allow more gas into the system, the flow element was replaced with one offering 5 - 25 ml/min. This flow element is suitable for wide bore capillaries and packed columns, and capillary columns with splitting as an option. We found that with V₂ fully open and total system flow of 25 - 30 ml/min a column flow of 0.6 ml/min was obtainable at room temperature with a 50:1 split ratio. However, when the temperature was increased, column flow decreased and at 150 °C column flow stopped.

In an attempt to allow more gas into the system, the next modification involved the use of a high pressure regulator. This allowed the system inlet pressure to be increased from 60 psi to a maximum of 100 psi. We found that with an inlet pressure of 100 psi and V_2 fully open, the total system flow increased to ≈ 50 ml/min. This allowed the column flow to be adjusted to ≈ 1 ml/min at room temperature and a split ratio of 50:1. When the oven temperature was increased suitable column flow was still obtainable at high temperature, i.e., the operation was similar to normal GC flow rate decrease with temperature programming.

It should be noted that the Pathway B flow rate optimisation described above was conducted with Pathway A closed. Under the conditions used to operate Pathway B, when S₁ was opened the minimum flow through Pathway A (measured at the side port) was ≈ 60 ml/min with V₁ slightly open. For tube conditioning (cleaning), V₁ was adjusted to give a flow of ≈ 120 ml/min measured at the side port. It should also be noted, that the total flow through pathway B of 50 ml/min is in accord with that recommended for optimum desorption efficiency in ASTM D6196-97⁽¹⁰⁸⁾. Further discussion on desorption and cleaning flow rates is given in Section 4.1.3.

2.7.3.2. Direct Injection Via TDU

The TDU has an injection port included in the tube chamber design. An empty 4 mm I.D. glass tube is placed in the tube chamber and liquid or gas samples can be injected directly, via a septum, into the tube chamber.

2.7.3.3. GC-MS and TDU Conditions

GC oven conditions are described in Chapter IV. Thermal Desorption conditions and Other GC-MS conditions are described below.

<u>Carrier Gas</u> :	Helium.
Carrier Gas Flow:	1 ml/min at Room Temp.
Columns:	Capillary BP-1, 25m \times 0.25mm ID, 1 μ m film
	thickness supplied by SGE
Nickel Transfer Line Temp:	250 °C
Desorption Chamber Temp :	Room Temp. \rightarrow 350 °C (\approx 23 Sec.)
	and hold for 5 minutes.
Injection Mode:	Split 50:1 at Room Temp.
Oven Temp:	See Chapter IV.
Cryogenic Fluid:	Liquid CO ₂ .
<u>MS transfer line</u> :	280 °C.
Solvent delay:	See Chapter IV.
Scan rate:	1.2 scans/sec.
Scan range:	40 – 550 amu

Tuning procedure:Auto tuneMass spectral confirmation:Wiley Mass Spectral Data Base

2.8 Desorption Method Validation for Thermal Desorption

2.8.1. Preparation of Pure Mixture

A mixture containing ten pure compounds was prepared by combining 100 μ l each of hexane, benzene, cyclohexane, heptane, methylbenzene, ethylbenzene, 1,4dimethylbenzene, propylbenzene, β -pinene and 1,3,5-trimethylbenzene. The compounds are described in Section 2.4.1.

2.8.2. Preparation of Standard Solution

A standard solution containing 10.00 μ l of each compound in 10 ml CS₂ was prepared as follows. 100 μ l of the mixture described in section 2.8.1 was diluted to 10 ml with CS₂.

2.8.3. Preparation of Standard Gaseous Mixture

The procedure used to prepare the standard gaseous mixture was similar to that described in Section 2.6.3. Steps 1 - 4 were the same as that outlined in Section 2.6.3 and steps 5 - 10 for thermal desorption tubes are described below.

- 5. The container cap is unscrewed and lifted to expose the bag valve. Into the bag is injected 1 μ l or 10 μ l of the mixture described in Section 2.8.1, and the cap replaced.
- 6. The bag is left to sit for 6 hours in order for the mixture to evaporate and the gaseous mixture to become homogeneous.
- A Carbotrap[™] 300 Multi-bed thermal desorption tube is connected to the internal bag via the external inert tubing, i.e., where the 10 L Tedlar[®] bag was initially.
- 8. The pump is connected so as to pump air into the container, the clamp opened, and 50 ml of air is introduced into the container at 100 ml/min.
- 9. After 30 seconds, 50 ml of gaseous standard is passed through the thermal desorption tube and the clamp closed.
- 10. Tubes are desorbed in Thermal Desorption Unit (see Section 2.7.3).

2.9 VOCs Standard Solutions For Thermal Desorption of Study

2.9.1. VOCs Standards

VOCs used to prepare standard solutions were supplied by ULTRA Scientific and Sigma-Aldrich. The compounds used in this study are described in Section 2.4.1. All solutions were prepared using AR Grade CS_2 supplied by Ajax Chemicals.

2.9.2. Preparation of Pure Mixture

A pure mixture containing 26 compounds was prepared by combining 100 μ l each of hexane, benzene, cyclohexane, heptane, methylcyclohexane, methylbenzene, 1,4dimethylcyclohexane, trans-1,2-dimethylcyclohexane, octane, cis-1,2dimethylcyclohexane, ethylcyclohexane, ethylbenzene, 1,2-dimethylbenzene 1,4dimethylbenzene, 1,3-dimethylbenzene, nonane, iso-propylcyclohexane, α -pinene, propylbenzene, 1,2,4-trimethylbenzene, β -pinene, 1,3,5-trimethylbenzene, decane, 1limonene, undecane and dodecane. The compounds are described in Section 2.4.1. For 1,2-dimethylcyclohexane, because the standard material used was a mixture of the cis- and trans- isomers, the amount added in the pure mixture was the sum of both isomers.

2.9.3. Preparation of Standard Gaseous Mixture

The procedure used to prepare the standard gaseous mixture for the quantitation of the thermal desorption study was similar to that described in Section 2.8.3. Other steps were the same as that outlined in Section 2.8.3 except steps 5. Step 5 is described below.

The container cap is unscrewed and lifted to expose the bag valve. Into the bag is injected 1 μl, 2.5μl, 5μl, 7.5μl, 10 μl or 20 μl of the mixture described in section 2.9.2, and the cap replaced.

2.10 Landfill Gas Sampling apparatus for Volatile Organic Compounds Collected in Tedlar[®] Bags

2.10.1. Sampling Train

The sampling train used to collect VOCs from landfill gas by Tedlar[®] bag is shown in Fig. 2.11. Landfill gas emerging from the landfill borehole or well (5) is pumped at 50 ml/min by the sampling pump (3), through the moisture trap (2). Dry landfill gas emerging from the moisture trap passes through the pump then is collected in the Tedlar[®] bag (4). Pump flow rate and sampling time are discussed in Section 5.1.1. Tedlar[®] bags are described below and other sampling train components are described in Section 2.2. Prior to collecting landfill gas in the Tedlar[®] bag, air present in the sampling train is removed by flushing the sampling train with landfill gas for 3 minutes at a flow of 200 ml/min. After sampling Tedlar[®] bags were analysed the same day if possible, if not they were stored away from direct sunlight until ready for analysis.



Fig. 2.11 The Sampling Train Using Tedlar[®] Bag

2.10.2. Tedlar[®] Bag

Tedlar[®] bags were supplied by SKC shown in Fig 2.12.



Fig. 2.12 Tedlar® Bag

2.10.3. Tedlar[®] Bag Cleaning

Tedlar[®] bags were cleaned by flushing with pure nitrogen (N_2) according to the following procedure.

- 1. Open valve and fill bag with nitrogen (N_2) ;
- 2. Squeeze bag until flat to expel nitrogen (N_2) ;
- 3. Repeat steps 1 and 2 five more times;
- 4. Test cleanliness by GC-MS.

2.10.4. Preparation of Pure Mixture

A mixture containing twenty-three compounds was prepared by combining 100 μ l each of hexane, benzene, cyclohexane, heptane, methylcyclohexane, methylbenzene, 1,4-dimethylcyclohexane, trans-1,2-dimethylcyclohexane, octane, cis-1,2-dimethylcyclohexane, ethylcyclohexane, ethylbenzene, 1,2-dimethylbenzene, 1,2-dimethylbenzene, 1,4-dimethylbenzene, 1,3-dimethylbenzene, nonane, iso-propylcyclohexane, propylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, decane, undecane and dodecane. The compounds are described in Section 2.4.1.

2.10.5. Preparation of Standard Gaseous Mixture

The procedure used to prepare the standard gaseous mixture was similar to that described in Section 2.6.3. Steps 1 - 4 were the same as that outlined in Section 2.6.3 and steps 5 - 7 are described below.

- 5. The container cap is unscrewed and lifted to expose the bag valve. Into the bag is injected 1 μ l of the mixture described in section 2.9.4, and the cap screwed back on.
- 6. The bag is left to sit for 6 hours in order for the mixture to evaporate and the gaseous mixture to become homogeneous.
- 7. 1 ml of this gas directly inserted into the injection port with a gas syringe supplied by SGE.

2.10.6. GC-MS Conditions For Sample of Tedlar® Bag

The gas chromatograph used was a Hewlett-Packard (HP) 5890 series II with a Flame Ionization Detector. Gas injection was by a 1 ml gas syringe supplied by SGE inserted directly in the injection port. GC-FID conditions are described below.

<u>Carrier Gas</u> :	Helium.
Carrier Gas Flow:	1 ml/min at Room Temp.
<u>Columns</u> :	Capillary BP-1, 25m \times 0.25mm ID, 1 μ m film thickness
	supplied by SGE
Injection Temp:	Injector 250 °C.
Injection Mode:	Splitless.
Oven Temp:	-20 – 100 °C @ 3 °C/min
	100 – 280 °C @ 20 °C/min.
Cryogenic Fluid:	Liquid CO ₂ .

2.11 Landfill Gas Sampling Apparatus for Volatile Organic Compounds Collected by Cryogenic Trapping

2.11.1. Sampling Train

The sampling train used to collect VOCs from landfill gas by cryogenic trapping is shown in Fig. 2.13. Landfill gas emerging from the landfill borehole or well (6) is pumped by the sampling pump (5), through the moisture trap (2). Dry landfill gas emerging from the moisture trap enters the cryogenic trap where the VOCs present in the landfill gas 'freeze out'. The remaining gaseous components of the landfill gas exit the cryogenic trap, pass through the moisture indicator tube (4) and are expelled into the atmosphere via the pump outlet. The pump flow was set at 200 ml/min and sampling time is discussed in Section 5.3.1. The cryogenic trap is described below and other sampling train components are described in Section 2.2. When sampling was completed both ends of the cryogenic trap were sealed using the plastic caps, and the cryogenic trap was transported back to the laboratory with its coolant still present.

The contents of the cryo trap were kept frozen until sample preparation (See section 2.11.3) in order to avoid losses of volatile components.



Fig. 2.13 The Sampling Train Using Cryogenic Trapping

2.11.2. Cryogenic Trap

The purpose-built cryogenic apparatus is shown in Fig 2.14. The cryogenic trap consisted of four individual 20 ml drechsel bottles connected in series using Viton[®] tubing. The drechsel bottles were housed in a 5 L polystyrene box and the coolant in which the drechsel bottles were immersed was solid carbon dioxide (Dry ice, \approx -78 °C). The Viton[®] tubing is described in Section 2.2.1.4. The drechsel bottles were silanised as described in section 2.2.1.3.



Fig. 2.14 The Purpose-Built Cryogenic Apparatus

2.11.3. Preparation of Landfill Gas Samples for Analysis

Even with up to 3 hours of sampling there was not much visible frozen material in the drechsel bottles. The frozen contents of the cryogenic trap quickly thawed after removal from the coolant and revealed that the initial drechsel bottle contained about 50 μ l of material with the other three successively containing much less than the first. Because the small amount of material was difficult to handle, 2 ml CS₂ was added to each bottle and the contents of each bottle were combined into a single head-space vial and the vial sealed. After shaking for 2 minutes using a vortex shaker the sample was ready for GC analysis. If GC analysis was not possible on the same day the sample was refrigerated until ready for analysis.

2.11.4. GC-MS Conditions For Sample of Cryogenic Trapping

The gas chromatograph used was Hewlett-Packard (HP) 5890 series II with a HP 5971 Mass Selective Detector. Injection was performed by a HP 7673 Auto Injector, where the injection volume was 1 μ l. GC-MS conditions are described below.

Carrier Gas:	Helium.
Carrier Gas Flow:	1 ml/min at Room Temp.
<u>Columns</u> :	Capillary BP-1, 25m X 0.25mm ID, 1 μm film
	thickness supplied by SGE
Injection Temp:	Injector 250 °C.
Injection Mode:	Splitless.
Oven Temp:	-20 – 100 °C @ 3 °C/min
	100 – 280 °C @ 20 °C/min.
Cryogenic Fluid:	Liquid CO ₂ .
MS transfer line:	280 °C.
Solvent delay:	See Chapter V.
Scan rate:	1.2 scans/sec.
<u>Scan range</u> :	40 – 550 amu
Tuning procedure:	Auto tune
Mass spectral confirmation	: Wiley Mass Spectral Data Base

CHAPTER III THE METHODOLOGY AND EXPERIMENTS FOR SOLVENT DESORPTION TECHNIQUE

3.1. Optimisation of Sampling and Gas Chromatographic Separation and Analysis Protocols for Solvent Desorption

The studies reported in this chapter were conducted using landfill gas from leachate well A_{1-1} of landfill site A (see Table 6.1 and 6.2 for landfill sites description and sampling point description, respectively).

The sampling protocol for VOCs in landfill gas was adapted from ASTM D3686- $95^{(104)}$ 'Standard Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)', and involved collection of VOCs on charcoal (coconut shell), Tenax (porous polymers) and XAD-2 (porous polymers) at a pump flow rate of 200 ml/min. The analysis protocol for VOCs in landfill gas was adapted from ASTM D3687- $95^{(109)}$ 'Standard Practice for Analysis of Organic Compound Vapors by the Activated Charcoal Tube Adsorption Method', and involved desorption of collected VOCs using carbon disulfide (CS₂) (Section 2.3) followed by gas chromatographic analysis with mass selective detection (Section 2.5).

3.1.1. Moisture Removal

3.1.1.1. Problems of Sampling and Gas Chromatographic Separation

Traditional air sampling methods to collect VOCs may not be directly suitable for landfill gas because of the high water vapor content of landfill gas. Depending on sampling time and the landfill being investigated, water vapor may condense out in the sampling train. When sampling relatively wet landfill gas, water droplets were clearly visible on the adsorption tubes. It was found that with longer sampling time adsorption capacity was markedly reduced. It is well known that moisture reduces the adsorptive capacity of various adsorption media⁽¹¹⁰⁾. For very wet tubes only trace amounts of compounds were collected.

3.1.1.2. Drying of Landfill Gas

How to remove the water vapor and how to collect the dry gases become an important investigation in its own right. Any method of moisture removal must not affect the integrity of the sample collected.

3.1.1.2.1. Na₂SO₄ Drying Tubes

Initial attempts to remove moisture from the landfill gas involved the use of Na_2SO_4 drying tubes. The testing apparatus used is shown in Fig 3.1; details of sampling train components are given in Section 2.2.1; details of the drying tubes in Section 2.2.2. Landfill gas emerging from the landfill bore hole or well (5) is pumped by the sampling pump (4) at 200 ml/min through the Na_2SO_4 drying tube (2), then through the moisture indicator tube (3) before exiting the pump to atmosphere.



Fig 3.1 The Moisture Testing Apparatus

The aim of this experiment was to measure the water trapping capacity of Na_2SO_4 drying tubes (2). The ability of these tubes to remove moisture was indicated by the change in color of the silica indicator tube (3) from blue to red.

Commercial drying tubes (see Section 2.2.2 (a)) containing 250 mg of Na_2SO_4 proved to be ineffective in removing moisture even for sampling times of 1 hour. The results are shown in Table 3.1. After absorbing considerable moisture the Na_2SO_4 changes appearance from a white crystalline solid to a transparent, wet solid. As the Na_2SO_4 nears this condition the tube begins to block and less gas can pass. Eventually the drying tube completely blocks and no gas can pass.

The Moisture Removing Results Using Na ₂ SO ₄ Drying Tube				
SAMPLING TIME (HOURS)	VOLUME OF GAS PASSED (L)	SILICA INDICATOR TUBE	Na2SO4 ADSORPTION TUBE	RESULTS
0.5	6	NO CHANGE	DRY	SUITABLE
1.0	12	CHANGE	DRY	UNSUITABLE
2.0	24	CHANGE	WET	UNSUITABLE
3.0	36	CHANGE	WET (BLOCKED)	UNSUITABLE

Table 2 1

A similar experiment was performed with purpose built drying tubes (see section 2.2.2 (b)) containing 15 g of Na₂SO₄. These could be used for longer sampling times than the commercial tubes obviously due to the large amount of Na₂SO₄ present. However, the Na₂SO₄ would saturate at the gas entrance end of the tube resulting in tube blockage even though the Na₂SO₄ at the exit end was still dry.

These results showed that these drying tubes could be used for relatively dry landfill gas or for very short sampling time of relatively moist landfill gas.

3.1.1.2.2. The Moisture Trap

Repeated experiments led to an economical and efficient unit for moisture removal from landfill gas. The construction of this apparatus is shown in Fig 2.3 (a) and (b) of Chapter II. All glass components of the moisture trap were silanised (see Section 2.2.1.3) in order to render them inert, i.e., to avoid adsorption of VOCs.

The moisture trap consists of Styrofoam® box filled with salted ice through which a spiral glass tube passes. The spiral glass tube is used to provide a long path length where the moisture has sufficient time to condense. However, the rapid early condensation may allow the condensate to freeze and block the inlet section of the tube. To overcome this, a short convex glass tube is used prior to the spiral tube to collect the initial large quantity of condensate. The capacity of the moisture trap, which is approximately 1 meter long, to remove moisture was tested using a silica gel indicator tube at the outlet end. The sampling train used to test the moisture trap is shown below in Fig 3.2 and details of individual components appear in Section 2.2.1. Landfill gas emerging from the landfill bore hole or well (5) is pumped by the sampling pump (4) through the moisture trap (2), then through the moisture indicator tube (3) before exiting the pump to atmosphere. Using the same landfill gas as that used to test the Na_2SO_4 drying tubes, moisture breakthrough was indicated by the silica changing color from blue to red. The sampling pump was set at 200 ml/min, and sampling times were respectively 0.5, 1, 2 and 3 hours. At the completion of sampling, the silica indicator tubes were examined for moisture. The results (See Table 3.2) showed this method of moisture removal was successful and allowed sampling times of 3 hours or more.



Fig 3.2 The Train Used to Test the Moisture Trap

Table 3.2The Moisture Removing Results Using the Moisture Trap			
SAMPLING TIME (HOURS)	VOLUME OF GAS PASSED (L)	SILICA INDICATOR TUBE	RESULTS
0.5	6	NO CHANGE	SUITABLE
1.0	12	NO CHANGE	SUITABLE
2.0	24	NO CHANGE	SUITABLE
3.0	36	NO CHANGE	SUITABLE

3.1.1.2.3. Testing the Moisture Trap Using Charcoal Tubes

Testing of the moisture trap was conducted in two parts. Firstly VOCs in landfill gas were collected on charcoal adsorption tubes for 1, 2 and 3 hours respectively using a sampling pump flow rate were 200 ml/min. The sampling train is shown in Fig 3.3 and the collection procedure and components are described in section 2.2.1. The moisture indicator tube is connected downstream rather than upstream of the adsorption tube to ensure no VOCs are retained by the SiO₂. The pump is also downstream to ensure no volatiles from the pump can contaminate the adsorption tube. This first test was to show that the moisture trap was indeed effective in removing water vapor and the adsorption capacity of the charcoal tubes would not decrease as sampling time increased. The VOCs collected on the charcoal tubes were desorbed using CS₂ as described in section 2.3. The CS₂ extracts were gas

chromatographed using mass selective detection and the chromatograms are shown in Fig 3.4 (a), (b) & (c). GC-MS conditions on a general-purpose phenylmethylsilicone column (DB5, $25m \times 0.25mmID$, $0.25\mu m$ film thickness) were the same for each sample and shown in figure legends. Refer to 3.1.3 for optimisation of GC conditions. Results show that as sampling time increases so does detector response, and therefore adsorption capacity does not decrease as sampling time of 'dry' landfill gas increases. Optimisation of GC conditions was not conducted at this stage of the study, and the separations achieved are of poor quality.



Fig 3.3 The Sampling Train Used to Test the Moisture Trap



Fig 3.4 (a)

Total Ion Chromatogram Sampled from Landfill Site Using Charcoal Adsorption Tubes for 1 Hour

(The GC-MS conditions were: Carrier Gas: Helium; Injection Mode: Splitless; Temperatures: Injector 250 °C; MS transfer line 280 °C; Solvent delay: 3 min; Scan rate: 1.2 scans/sec; Scan range: 40 – 550 amu; and Mass spectral confirmation: Wiley Mass spectral Data Base.)



To complete the testing of the moisture trap, a 3-hour condensate was analyzed to see if significant amounts of VOCs were being retained by the water. The collected condensate (≈ 0.5 ml) was extracted with an equal volume CS₂ and the extract chromatographed. The result in Fig 3.5 (a) and (b) show the chromatograms of the CS₂ use to extract the condensate and the chromatogram for pure CS₂. As can be seen the only detectable compounds are impurities in the CS₂ solvent. Therefore the moisture trap does not retain, to any significant level, any compounds present in the landfill gas for sampling times of up to 3 hours.



3.1.2. Investigation of Different Adsorption Media and Sampling Time

Sampling time is dependant upon the concentration of VOCs in landfill gas. The volume of gas collected must be large enough to allow easily detectable quantities of VOCs to be collected but the quantity collected must not exceed tube capacity resulting in breakthrough. With the pump set at 200 ml/min, sampling times of 1, 2 and 3 hours were used to collect VOCs in landfill gas on Charcoal, Tenax and XAD-2 adsorption media. Gas collection and sample preparation are described in Section 2.2.1 and 2.3, respectively. The sampling apparatus is shown in Fig 3.3, and the moisture trap is described in section 2.2.1.2.

 CS_2 extracts from the various adsorption media were chromatographed on a general purpose phenylmethylsilicone column (DB5, 25m × 0.25mmID, 0.25µm film thickness) and the total ion chromatograms for gas samples taken on Charcoal, Tenax

and XAD-2 adsorption tubes are shown in Fig 3.6 (a), (b) and (c) for a sampling time of 3 hours. Optimisation of GC conditions was not conducted at this stage of the study, and the separations achieved are of poor quality. Refer to Section 3.1.3 for optimisation of GC conditions.



Total Ion Chromatogram of CS_2 Extract from the Front Part of the Charcoal Adsorption Tube (The GC-MS conditions were shown as Fig 3.4 (a))



Total Ion Chromatogram of CS₂ Extract from the Front Part of the XAD-2 Adsorption Tube (The GC-MS conditions were shown as Fig 3.4 (a))



Total Ion Chromatogram of CS₂ Extract from the Front Part of the Tenax Adsorption Tube (The GC-MS conditions were shown as Fig 3.4 (a))

The chromatograms shown are all similar and indicate that charcoal, Tenax and XAD-2 are able to trap a similar range of compounds. The MS library search for some of VOCs in the sample from Charcoal, Tenax and XAD-2 adsorption tubes are listed in Table 3.3. Compounds listed in Table 3.3 include straight chain hydrocarbons, alkyl aromatics and alkyl cyclohexanes. The compounds listed are those which gave the best visual match between mass spectrum of sample compound and mass spectrum of library compound. The identity of these compounds is confirmed in section 3.3. For dimethylbenzene both 1,2- and 1,4- are listed because the library search results show that 1,2- and 1,4-dimethylbenzene have very similar mass spectra.

COMPOUND Benzene Cyclohexane Heptane Methylcyclohexane Methylbenzene 1,4-Dimethylcyclohexane trans-1,2-Dimethylcyclohexane Octane Ethylcyclohexane Ethylcyclohexane Ithylbenzene 1,2 & 1,4-Dimethylbenzene 1,3-Dimethylbenzene 1,3-Dimethylbenzene I,3-Dimethylbenzene Iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	Some VOCs Collected on Charcoal, Tenax and XAD-2 Adsorption Tubes
Benzene Cyclohexane Heptane Methylcyclohexane 1,4-Dimethylcyclohexane trans-1,2-Dimethylcyclohexane Octane Ethylcyclohexane Ethylbenzene 1,2 & 1,4-Dimethylbenzene 1,3-Dimethylbenzene iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	COMPOUND
Cyclohexane Heptane Methylcyclohexane Methylbenzene 1,4-Dimethylcyclohexane trans-1,2-Dimethylcyclohexane Octane Ethylcyclohexane Ethylbenzene 1,2 & 1,4-Dimethylbenzene 1,3-Dimethylbenzene iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	Benzene
Heptane Methylcyclohexane Methylbenzene 1,4-Dimethylcyclohexane trans-1,2-Dimethylcyclohexane Octane Ethylcyclohexane Ethylbenzene 1,2 & 1,4-Dimethylbenzene 1,3-Dimethylbenzene iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	Cyclohexane
Methylcyclohexane Methylbenzene 1,4-Dimethylcyclohexane trans-1,2-Dimethylcyclohexane Octane Ethylcyclohexane Ethylbenzene 1,2 & 1,4-Dimethylbenzene 1,3-Dimethylbenzene Nonane iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	Heptane
Methylbenzene 1,4-Dimethylcyclohexane trans-1,2-Dimethylcyclohexane Octane Ethylcyclohexane Ethylbenzene 1,2 & 1,4-Dimethylbenzene 1,3-Dimethylbenzene Nonane iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	Methylcyclohexane
1,4-Dimethylcyclohexane trans-1,2-Dimethylcyclohexane Octane Ethylcyclohexane Ethylbenzene 1,2 & 1,4-Dimethylbenzene 1,3-Dimethylbenzene Nonane iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	Methylbenzene
trans-1,2-Dimethylcyclohexane Octane Ethylcyclohexane Ethylbenzene 1,2 & 1,4-Dimethylbenzene 1,3-Dimethylbenzene Nonane iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	1,4-Dimethylcyclohexane
Octane Ethylcyclohexane Ethylbenzene 1,2 & 1,4-Dimethylbenzene 1,3-Dimethylbenzene Nonane iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	trans-1,2-Dimethylcyclohexane
Ethylcyclohexane Ethylbenzene 1,2 & 1,4-Dimethylbenzene 1,3-Dimethylbenzene Nonane iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	Octane
Ethylbenzene 1,2 & 1,4-Dimethylbenzene 1,3-Dimethylbenzene Nonane iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	Ethylcyclohexane
1,2 & 1,4-Dimethylbenzene 1,3-Dimethylbenzene Nonane iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	Ethylbenzene
1,3-Dimethylbenzene Nonane iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	1,2 & 1,4-Dimethylbenzene
Nonane iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	1,3-Dimethylbenzene
iso-Propylcyclohexane Propylbenzene 1,2,4-Trimethylbenzene	Nonane
Propylbenzene 1,2,4-Trimethylbenzene	iso-Propylcyclohexane
1,2,4-Trimethylbenzene	Propylbenzene
	1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene	1,3,5-Trimethylbenzene
Decane	Decane
Undecane	Undecane

 Table 3.3

 Some VOCs Collected on Charcoal, Tenax and XAD-2 Adsorption Tubes

Analysis of the back-up section of the tubes showed that breakthrough occurred after approximately 1 hour of sampling for Tenax and XAD–2, but did not occur for Charcoal even for sampling times of more than 3 hours. Chromatograms of the back section of the Charcoal (3 hours sampling) and XAD–2 (1 hours sampling) adsorption tubes are shown in Fig 3.7 (a) and (b), respectively. Because Charcoal has a much greater adsorption capacity than Tenax and XAD–2, it was used for the further study on VOCs in landfill gas. This greater adsorption capacity allows for longer sampling times and hence a more representative sample of landfill gas to be collected.



(The GC-MS conditions were shown as Fig 3.4 (a))



(The GC-MS conditions were shown as Fig 3.4 (a))

3.1.3. Optimisation of GC Temperature Programme for DB-5 Column

Fig 3.6 (a) in section 3.1.2 shows the chromatogram for VOCs in landfill gas taken on charcoal. The GC conditions had not been fully optimised at this stage but early experimentation with the temperature program showed that reasonable retention and separation could be achieved using the following conditions:

40 °C for 3 minutes, 2 °C/min to 100 °C, 20 °C/min to 280 °C.

The initial 3 minutes hold coincided with the 3 minutes solvent delay for MSD turn on. All components were eluted during the initial temperature ramp after about 22 minutes at a temperature of about 80 °C. The final temperature ramp to 280 °C was included as a thermal flush prior to the next injection being made. Fig 3.6 (a) shows generally poor chromatography over the entire chromatogram. The high total ion counts and peak shapes suggest sample overloading and an immediate improvement in chromatography was obtained by using a 25:1 split injection. This is seen in Fig 3.8 where, because of the sharper peak shapes, the overall separation is much improved. It should be noted that whether or not to use split injection and choice of split ratio will depend on the concentration of VOCs in the landfill gas being sampled and on the sampling time.



Total Ion Chromatogram using Split Injection Mode (Column: Capillary DB-5, 30m X 0.22mm ID, 0.25 μm film thickness. The GC-MS conditions were: Carrier Gas: Helium; Injection Mode: Split (A split ratio of 25:1 was used); Temperatures: Injector 250 °C; MS transfer line 280 °C; Solvent delay: 3 min; Scan rate: 1.2 scans/sec; Scan range: 40 – 550 amu; and Mass spectral confirmation: Wiley Mass spectral Data Base.)

3.1.3.1. Selection of Initial Oven Temperature

The effect of different starting temperatures is shown in Fig 3.9 (a), (b) and (c) for initial temperature of 30 °C, 40 °C, and 50 °C, respectively. In order to help explain the observation, early eluting peaks have been labeled as section X, late eluting peaks as section Z, and those in-between as section Y.



(The other GC-MS conditions were shown as Fig 3.8)



As the initial temperature is decreased from 50 °C to 30 °C there is a significant improvement in the chromatography of compounds eluting in section X. Peaks become narrower allowing for improved separations. This observation can be easily explained by considering the solvent effect. The solvent, carbon disulfide (CS₂), has a boiling point of \approx 46 °C, and at oven temperatures below \approx 46 °C the solvent condenses at the head of the column allowing for volatile compounds to be refocused in the solvent plug at the head of the column. The solvent effect is also responsible for the improved chromatography of compounds eluting in section Y as the initial temperature is decreased from 50 °C to 30 °C.

A decrease in initial temperature appears to have little effect on the chromatography of compounds eluting in section Z. These high boiling compounds enter the column at temperatures well below their boiling points and condense at the head of the column into narrow bands resulting in good chromatography.

Ultimately the room temperature of the laboratory influences the GC starting temperature. Starting temperatures below 35 °C resulted in oven temperature stabilisation times of 30 minutes and longer. Due to the above considerations a starting temperature of 35 °C was chosen for optimisation further studies. A sample chromatogram is shown in Fig 3.10.



3.1.3.2. Selection of Temperature Gradients

The effect of different rates of temperature increase in the first gradient of the temperature programme is shown in Fig 3.11 (a) – (d) for rates of 1, 2, 3 and 4 $^{\circ}$ C/min, respectively.



Fig3.11 (a) Total Ion Chromatogram with Temperature Gradient: 1 °C/min (The other GC-MS conditions were shown as Fig 3.8)



Results show that a rate of change of 1 °C/min produces poor peak shapes of compounds eluting within 25 minutes. The poor peak shape is due to these compounds, after having been refocused in the solvent plug at the head of the column, taking too long to volatilise with the slow temperature ramp. The peak shapes of these

compounds greatly improves as the temperature gradient is increased to 2 °C/min or more. Obviously analysis time shortens as the rate of temperature change increases but resolution decreases. Chromatograms with gradient of 2 °C/min and 3 °C/min in the first step are similar. Good chromatography is observed showing good separation between components and sharp peaks. For further studies, it was decided to choose GC conditions where the rate of temperature change in the first step was 3 °C/min, as analysis times are shorter than the 2 °C/min, case.

3.1.4. Investigation of Column Phase and Thickness

From the result of initial studies, where a moderately polar phenylmethylsilicone column was used, it was found that most of the compounds in the sample are non-polar (see Table 3.3). The use of a non-polar methylsilicone column was therefore investigated so as to observe the chromatographic behavior of the organic compounds present in the landfill gas. Chromatograms are shown in Fig 3.12 (a) and (b) for methylsilicone and phenylmethylsilicone column, respectively. Both columns were of the same dimensions ($25m \times 0.22 \text{ mm ID}$) and both had a 0.25 µm phase thickness.



(The GC-MS conditions were: Carrier Gas: Helium; Injection Mode: Splitless. Temperatures: Injector 250 °C; MS transfer line 280 °C; Solvent delay: 3 min; Scan rate: 1.2 scans/sec; Scan range: 40 – 550 amu; and Mass spectral confirmation: Wiley Mass spectral Data Base.)



Results show that both columns display similar good chromatography but the less polar column gives greater retention. This greater retention allows for extra compounds to be observed very early in the chromatogram. Because of the numerous compounds present in the landfill gas sample, the chromatography displayed poor resolution across the entire separation. To overcome this problem a thicker phase column was used. Fig 3.13 shows the separation on a 1 μ m phase thickness BP-1 column. As can be seen retention is greatly increased and as a result the resolution has improved markedly across the entire separation. Because of the above, the BP1 1 μ m film column was to be used for further studies. It should be noted that the thicker phase allows greater sample capacity and good chromatography; sharp peak shapes with good resolution are still observed in the case of splitless injection.





3.1.5. Optimisation of GC Conditions for BP-1 Column

The above findings show that the GC conditions employed for the BP-1 1 μ m column allowed the separation of compounds with a carbon number 6 and above. In order to retain more volatile compounds the GC starting temperature was lowered from 35 °C to -20 °C using liquid CO₂. The separation of VOCs in landfill gas using a GC starting temperature of -20 °C is shown in Fig 3.26. As can be seen, retention of compounds more volatile than hexane is now possible. Also, the solvent is further retained by comparison with a starting temperature of 35 °C. As a result the solvent delay has increased from 3 minutes to 8.5 minutes. Obviously analysis time has also increased by approximately 12 minutes from the 35 °C starting time.

3.1.6. Summary of Sampling and Analysis protocols for VOCs in Landfill Gas Using Solvent desorption

From the above findings the sampling and gas chromatographic protocols developed for VOCs in landfill gas using adsorption tubes with solvent desorption can be summarized as follows:

- Landfill gas is initially dried by passing through the moisture trap.
- VOCs are collected on charcoal and desorbed using CS₂
- CS₂ extracts are chromatographed on a BP-1 1µm column using the following conditions:

<u>Carrier Gas</u> :	Heliun	n.				
Injection Mode:	Split	or	splitless	depending	on	VOC
	concer	ntratio	on in landfil	l and / or sam	pling	time.
Temperatures:						
Injector:	250 °C	۱ ٠.				
MS transfer line:	280 °C	1 ⁄ •				
Oven:	35 – 1	00 °C	@ 3 °C/mi	n		
	100 -	2 8 0 °	C @ 20 °C/	min		
Cryogenic Fluid:	Liquid	CO ₂				
Solvent delay:	3.0 mi	nutes				

<u>Scan rate</u> :	1.2 scans/sec.
Scan range:	40 – 550 amu
Mass spectral confirmation:	Wiley Mass Spectral Data Base

It should be noted that these conditions are suitable for the separation of compounds with carbon number greater than 6, as the first peak in Fig 3.13 is hexane (identified in Section 3.2.1.2). The separation of compounds with carbon number less than 6 is described in Section 3.3.

3.2 Qualitative and Quantitative Analysis

In this part of the study the gas chromatographic conditions developed in the previous section were used.

3.2.1. Qualitative Analysis

3.2.1.1. Tentative Identification Using Mass Spectral Library

The next part of the study focused on the identification of the VOCs in the landfill gas. Fig 3.14 shows an expanded view, along both the abundance and time scale, of the chromatogram shown in Fig 3.13. The mass spectral data used by the MS software for peak identification is taken at the apex of the peak. Subsequently this data is compared with that in a mass spectral database or library and possible matches are indicated. Using the apex of the peak allows identification of compounds which are not fully resolved because at the apex mass spectral data from adjoining peaks may not contribute substantially. The library search results indicated a total of 112 compounds with quality matching ranging from 9 - 97 %. The quality match is a value representing the probability that the sample compound has been correctly identified as the compound determined by the database search. Values less than 50 mean substantial difference exist between sample and library compound mass spectra and values greater than 90 indicate very good matches. The first step in identifying the VOCs in landfill gas involved visually comparing the spectra of the compounds determined from the Wiley database to be matches of the sample compounds and a suitable match determined. This worked well for sample compounds in high abundance where sample and matching compound mass spectra were very similar and

the quality match was relatively high at about 80 % or greater. For lower abundance compounds, even though high percentage matches may have been achieved, the mass spectra were not similar visually to those matches indicated from the database. This was due to interfering background and, for those compounds which were not fully resolved, interference from ions of adjoining peaks. Background ions occur due to contamination originating from the GC such as column bleed, septum bleed, dirty injector and carrier gas impurities⁽¹¹¹⁾. The problem of interfering background ions can be solved by subtracting background ions from sample compound mass spectra.





Subtraction of background ions can be done automatically by the MS software through the BSB function (Background Subtraction). BSB allows a background mass spectrum to be subtracted from on entire data file, i.e., a point or section on the chromatogram is chosen which contains only baseline and the mass spectrum obtained; this background mass spectrum is then subtracted from every scan comprising the data file, i.e., the entire chromatogram. If was found that for the lower abundance compounds BSB was not particularly useful as the background was not constant throughout the course of the chromatogram. This resulted in either too much background being subtracted in various parts of the chromatogram and vital information being lost or too little background subtracted in other parts of the chromatogram leaving unacceptably high background.

Best results for the lower abundance compounds were obtained when subtraction was performed manually by selecting a baseline point nearest the peak and subtracting this mass spectrum from that taken at the apex of the peak. It was then decided to perform manual subtraction for all compounds in the chromatogram as this generally improved quality matches but more so for the lower abundance compounds. Manual subtraction was performed as indicated in Fig. 3.15, where three typical chromatographic separation situations are shown. The letters used in marking the peaks in Fig. 3.15 are defined as follows. The apex of a peak is denoted 'a', the baseline on either side of a peak as 'b', and the valley between two adjoining peaks as 'v'. The three separation situations in Fig. 3.15 are described below. For each situation the method of subtraction chosen was that which effectively removed interfering ions from the background and adjoining peaks.

Situation A

```
For single peaks: a_1 - b_1 or a_1 - b_2
```

<u>Situation B</u>

For first peak:	$\mathbf{a_l} - \mathbf{b_l} \text{ or } \mathbf{a_l} - \mathbf{v_l}$
For second peak:	$a_2 - v_1 \text{ or } a_2 - b_2$

Situation C

For first peak:	$\mathbf{a}_1 - \mathbf{b}_1$ or $\mathbf{a}_1 - \mathbf{v}_1$
For second peak:	$\mathbf{a}_2 - \mathbf{v}_1 \text{ or } \mathbf{a}_2 - \mathbf{v}_2$
For third peak:	$a_3 - v_2 \text{ or } a_3 - b_2$





Table 3.4 shows the improvement in quality matching after manual background subtraction compared with the initial 'auto' library search. The 'no match' case indicates that the library search did not find a suitable match or sample and matching compound mass spectra were visually dissimilar. The peak at 5.84 minutes has two compounds listed as these co-eluted where the left side of the peak was identified as 2-methylhexane and the right side as 2,3-dimthylpentane. These two compounds do not have a similar mass spectrum. After manual subtraction 104 compounds were

identified where sample and matching compound mass spectra were very similar in all cases.

	Table 3.4			
The Comparison Betwe	The Comparison Between the 'Auto' and 'Manual' Match			
PERCENTAGE OF MATCH	Auto Match	Manual Match		
	Number of Peaks	Number of Peaks		
No Match or visually wrong Match	53	8		
$0 \sim 10\%$	0	0		
$11 \sim 20\%$	0	0		
21~30%	2	0		
31~40%	1	2		
$41 \sim 50\%$	9	-2		
$51 \sim 60\%$	6	7		
61 ~ 70%	6	10		
$71 \sim 80\%$	3	19		
81~90%	15	30		
91 ~100%	17	34		
Total	112	112		

Table 3.5 list the 104 compounds identified in the landfill gas in order of retention time. The 8 peaks where 'no match' was indicated are also listed. Sample and matching compound mass spectra are shown in Appendix B (Part a). The various types of compounds found in the landfill gas include straight chain, branched chain, aromatic, cyclic, terpenic, naphthenic, chloro and alkenyl hydrocarbons. The compounds are listed under the various compounds classes in Table 3.6 (a) – (h). Those compounds typed in bold gave quality matches greater than or equal to 80 %.

	The 104 Compounds Identified in Order of Retention Time			
PK#	RT	LIBRARY/ID	QUALITY	
1	3.64	Hexane	72	
2	4.33	Methylcyclopentane	76	
3	4.45	2,4-dimethylpentane	76	
4	5.11	Benzene	91	
5	5.46	Cyclohexane	87	
6	5.84	2-methylhexane	81	
7	5.92	2,3-dimethylpentane	87	
8	6.24	3-methylhexane	83	
9	6.54	trans-1,3-dimethylcyclopentane	72	
10	6.69	cis-1,3-dimethylcyclopentane	58	
11	6.81	cis-1,2-dimethylcyclopentane	87	
12	6.90	2,2-dimethylhexane	38	
13	7.53	Heptane	93	
14	8.53	Methylcyclohexane	94	
15	8.71	No match	/	
16	9.15	Ethylcyclopentane	94	
17	9.23	No match	/	
18	9.32	2,4-dimethylhexane	60	

Table 3.5he 104 Compounds Identified in Order of Retention Time

Table 3.5 (Continued)			
PK#	<u>RT</u>	LIBRARY/ID	QUALITY
19	9.60	1,2,4-trimethylcyclopentane	68
20	10.09	3-ethylpentane	59
21	10.27	Methylbenzene	91
22	10.64	2,3-dimethylhexane	80
23	10.94	2-methylheptane	70
24	11.01	4-methylheptane	81
25	11.33	trans-1,4-dimethylcyclohexane	87
26	11.43	trans-1,3-dimethylcyclohexane	80
27	11.67	1,1-dimethylcyclohexane	68
28	11.99	No match	/
29	12.22	trans-1,2-dimethylcyclohexane	81
30	12.38	Tetrachloroethene	98
31	12.51	Octane	90
32	13.54	cis-1,2-dimethylcyclohexane	49
33	13.77	Ethylcyclohexane	90
34	13.99	1,1,3-trimethylcyclohexane	68
35	14.09	No match	/
36	14.49	Ethylbenzene	81
37	14.87	1,2&1,4-dimethylbenzene	97
38	15.11	Octahydropentalene	68
39	15.24	2-methyloctane	83
40	15.52	3-methyloctane	72
41	15.75	1.3-dimethylbenzene	97
42	16.02	trans-1-ethyl-4-methylcyclohexane	87
43	16.11	cis-1-ethyl-4-methylcyclohexane	87
44	16.58	Nonane	91
45	16.38	3.5-dimethylheptene-3	72
45	16.85	cis-1-ethyl-2-methylcyclohexane	58
<u>40</u>	16.00	1-methylethylbenzene	81
/ / 2	17 08	4-ethyloctane	38
40 /0	17.00	1-methylethylcycloheyane	94
77 50	17.21	3_methylbentane	80
51	1727	No match	/
52	17.57	Pronyleyclohevane	94
52	17.37	$() \propto \text{Dipone}$	94
55 5 A	17.04	(-)-u-r mene 2.6 dimethylastana	91
54 55	10.04	2,0-unitenyiociane Dronylhanzena	62
33 57	10.00	riopyiochiculo 3 other 2 mothulhontono	86
50	18.11	S-ethyl-2-methylneptane	Q1
5/	18.20	Campnene	0/
28	18.33	1 ethyl 2 methylbergene	01
59	18.39	1-ethyl-2-methylbenzene	91 01
60	18.58	1,2,4-trimetnyidenzene	71 92
61	18.79	4-metnyinonane	0 <i>3</i> 91
62	18.89	2-methylnonane	03 05
63	19.12	1-β-Pinene	73
64	19.26	trans-1-methyl-4-(1-methylethyl)cyclohexane	87
65	19.44	1,3,5-trimethylbenzene	94
66	19.58	cis-1-methyl-4-(1-methylethyl)cyclohexane	50
67	19.78	1,4-dichlorobenzene	95
68	19.93	2,2,4,6,6-pentamethylheptane	64
69	20.05	Decane	94
70	20.35	1-ethyl-2,4-dimethylbenzene	72
71	20.48	1-methyl-4-(1-methylethyl)benzene	94
72	20.71	1-propenylbenzene	80
73	20.80	1-Limonene	96
74	20.96	5-propylnonane	64
75	21.05	Butylevelohexane	91
Table 3.5 (Continued)

PK#	RT	LIBRARY/ID	OUALITY
76	21.17	3,8-dimethyldecane	72
77	21.22	1,4-diethylbenzene	91
78	21.30	1-methyl-2-propylbenzene	76
79	21.42	Diethylbenzene (Para?)	70
80	21.51	2-ethyl-1,4-dimethylbenzene	91
81	21.77	trans-Decahydronaphthalene	91
82	21.86	5-methyldecane	81
83	21.94	4-methyldecane	83
84	22.06	2-methyldecane	76
85	22.15	1-ethyl-2,4-dimethylbenzene	72
86	22.26	3-methyldecane	87
87	22.34	2-ethyl-1,3-dimethylbenzene	81
88	22.53	3,6-dimethyldecane	64
89	22.69	Undecene-5	72
90	22.88	1-methylbutylbenzene	58
91	22.93	1-methyl-3-(1-methylethyl)benzene	93
92	23.10	Undecane	91
93	23.31	4-ethyl-1,2-dimethylbenzene	93
94	23.4	1,2,3,5-tetramethylbenzene	87
95	23.51	2-methyldecahydronaphthalene	93
96	23.64	3,6-dimethyldecane	81
97	23.93	5-propyldecane	72
98	24.00	2-Methyldecalin (Probably trans)	91
99	24.14	Pentylcyclohexane	72
100	24.22	2,3-dihydro-5-methylindene-1H	87
101	24.32	1-ethyl-3,5-dimethylbenzene	81
102	24.69	No match	/
103	24.81	4-methylundecane	93
104	24.93	2-methylundecane	74
105	25.08	Naphthalene	87
106	25.6	No match	/
107	25.89	Dodecane	91
108	26.31	6-methyldodecane	60
109	27.00	No match	/
110	27.86	6,6-dimethylundecane	59
111	28.08	1-methylnaphthalene	83
112	28.46	2-methylnaphthalene	81

Table 3.6 (a)

PK#	RT	LIBRARY/ID	QUALITY
1	3.64	Hexane	72
13	7.53	Heptane	93
31	12.51	Octane	90
44	16.58	Nonane	91
69	20.05	Decane	94
92	23.1	Undecane	91
107	25.89	Dodecane	91

Table 3.6 (b)Branched Chain Hydrocarbons in the 104 Compounds

 PK#	RT	LIBRARY/ID	QUALITY
3	4.45	2,4-dimethylpentane	76
6	5.84	2-methylhexane	81
7	5.92	2,3-dimethylpentane	87
8	6.24	3-methylhexane	83
12	6.9	2,2-dimethylhexane	38
18	9.32	2,4-dimethylhexane	60
20	10.09	3-ethylpentane	59
22	10.64	2,3-dimethylhexane	80
23	10.94	2-methylheptane	70
24	11.01	4-methylheptane	81
39	15.24	2-methyloctane	83
40	15.52	3-methyloctane	72
48	17.08	4-ethyloctane	38
50	17.27	3-methylheptane	80
54	17.84	2,6-dimethyloctane	91
56	18.11	3-ethyl-2-methylheptane	86
61	18.79	4-methylnonane	83
62	18.89	2-methylnonane	83
68	19.93	2,2,4,6,6-pentamethylheptane	64
74	20.96	5-propylnonane	64
76	21.17	3,8-dimethyldecane	72
82	21.86	5-methyldecane	81
83	21.94	4-methyldecane	83
84	22.06	2-methyldecane	76
86	22.26	3-methyldecane	87
88	22.53	3,6-dimethyldecane	64
96	23.64	4,5-dimethylnonane	81
97	23.93	5-propyldecane	72
103	24.81	4-methylundecane	93
104	24.93	2-methylundecane	74
108	26.31	6-methyldodecane	60
110	27.86	6,6-dimethylundecane	59

PK#	RT	LIBRARY/ID	QUALITY
4	5.11	Benzene	
21	10.27	Methylbenzene	91
36	14.49	Ethylbenzene	81
37	14.87	1,2&1,4-dimethylbenzene	97
41	15.75	1,3-dimethylbenzene	97
47	16.99	1-methylethylbenzene	81
55	18.06	Propylbenzene	62
58	18.33	1-ethyl-3-methylbenzene	94
59	18.39	1-ethyl-2-methylbenzene	91
60	18.58	1,2,4-trimethylbenzene	91
65	19.44	1,3,5-trimethylbenzene	94
70	20.35	1-ethyl-2,4-dimethylbenzene	72
71	20.48	1-methyl-4-(1-methylethyl)benzene	94
72	20. 71	1-propenylbenzene	80
77	21.22	1,4-diethylbenzene	91
78	21.3	1-methyl-2-propylbenzene	76
79	21.42	Diethylbenzene (Para?)	70
80	21.51	2-ethyl-1,4-dimethylbenzene	91
85	22.15	1-ethyl-2,4-dimethylbenzene	72
87	22.34	2-ethyl-1,3-dimethylbenzene	81
90	22.88	1-methylbutylbenzene	58
91	22.93	1-methyl-3-(1-methylethyl)benzene	93
93	23.31	4-ethyl-1,2-dimethylbenzene	93
94	23.4	1,2,3,5-tetramethylbenzene	87
100	24.22	2-butenylbenzene	87
101	24.32	1-ethyl-3,5-dimethylbenzene	81

 Table 3.6 (c)

 Aromatic Chain Hydrocarbons in the 104 Compounds

Table 3.6 (d) vdrocarbons in the 104 Compos

Cyclic Hydrocarbons in the 104 Compounds			
PK#	RT	LIBRARY/ID	QUALITY
2	4.33	Methylcyclopentane	76
5	5.46	Cyclohexane(DOT	87
9	6.54	trans-1,3-dimethylcyclopentane	72
10	6.69	cis-1,3-dimethylcyclopentane	58
11	6.81	cis-1,2-dimethylcyclopentane	87
14	8.53	Methylcyclohexane	94
16	9.15	Ethylcyclopentane	94
19	9.6	1,2,4-trimethylcyclopentane	68
25	11.33	trans-1,4-dimethylcyclohexane	87
26	11.43	trans-1,3-dimethylcyclohexane	80
27	11.67	1,1-dimethylcyclohexane	68
29	12.22	trans-1,2-dimethylcyclohexane	81
32	13.54	cis-1,2-dimethylcyclohexane	49
33	13.77	Ethylcyclohexane	90
34	13.99	1,1,3-trimethylcyclohexane	68
42	16.02	trans-1-ethyl-4-methylcyclohexane	87
43	16.11	cis-1-ethyl-4-methylcyclohexane	87
46	16.85	cis-1-ethyl-2-methylcyclohexane	58
49	17.21	1-methylethylcyclohexane	94
52	17.59	Propylcyclohexane	94
64	19.26	trans-1-methyl-4-(1-methylethyl)cyclohexane	87
66	19.58	cis-1-methyl-4-(1-methylethyl)cyclohexane	50
75	21.05	Butylcyclohexane	91
99	24.14	Pentylcyclohexane	72

Terpenic Hydrocarbons in the 104 Compounds				
PK#	RT	LIBRARY/ID	QUALITY	
53	17.72	(-)-a-Pinene	94	
57	18.2	Camphene	91	
63	19.12	1- β -Pinene	95	
73	20.8	1-Limonene	96	

Table 3.6 (e	e)		
rpenic Hydrocarbons in th	e 104	Com	pounds

Naphthenic Hydrocarbons in the 104 Compounds RT PK# LIBRARY/ID QUALITY 21.77 trans-Decahydronaphthalene 81 91 95 23.51 2-methyldecahydronaphthalene 93 98 24 2-methyldecalin (Probably trans) 91 105 25.08 Naphthalene 87 28.08 1-methylnaphthalene 111 83 112 28.46 2-methylnaphthalene 81

		Chloro Hydrocarbons in the 104 Compounds	
PK#	RT	LIBRARY/ID	QUALITY
30	12.38	Tetrachloroethene	98
67	19.78	1,4-dichlorobenzene	95

Table 3.6 (h)				
		Alkenyl Hydrocarbons in the 104 Compounds		
PK#	RT	LIBRARY/ID	QUALITY	
38	15.11	Octahydropentalene	68	
45	16.74	3,5-dimethylheptene-3	72	
89	22.69	Undecene-5	72	

3.2.1.2 Positive Identification of Straight Chain, Cyclic and Aromatic Hydrocarbons Using Standards

The next part of the study focused on the positive identification of some selected VOCs present in the landfill gas. Selection was based on three factors including what standards were available, compounds representing each class as listed in Tables 3.6 (a) – (h) and abundance in the landfill gas. From the selection process twenty-three VOCs were chosen including straight chain, cyclic and aromatic hydrocarbons. The twenty-three compounds chosen included the majority of the most abundant VOCs present in the landfill gas. The following protocol was used to for positive identification.

- As described in section 3.2.1.1, the best visual match, after interfering ions are subtracted, is chosen.
- The pure compound corresponding to the best match is gas chromatographed in order to establish if retention time is similar to the sample compound.
- The pure compound mass spectrum is visually compared with the mass spectrum of the sample and library matching compound.

Positive identification is indicated when retention times and mass spectra are similar. Results showed that the 'best matches' as determined by the library search were correct in all cases.

Fig 3.16 (a) and (b) show the separation of straight chain, cyclic and aromatic VOCs in landfill gas and the separation of the standard compounds, respectively. Table 3.7 shows the retention time of the VOCs in the sample compared with those of the standard compounds. The compounds are listed under the various compounds classes in Table 3.8.



Fig 3.16 (a) Total Ion Chromatogram from Landfill Gas Sample



Table 3.	7
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The Comparison of Retention Time Between the Sample and Standard					
NO.	COMPOUND	RT OF SAMPLE	RT OF STANDARD		
		(Minutes)	(Minutes)		
1	Hexane	3.62	3.67		
2	Benzene	5.11	5.16		
3	Cyclohexane	5.46	5.48		
4	Heptane	7.53	7.47		
5	Methylcyclohexane	8.54	8.55		
6	Methylbenzene	10.27	10.27		
7	1,4-Dimethylcyclohexane	11.33	11.37		
8	trans-1,2-Dimethylcyclohexane	12.22	12.18		
9	Octane	12.51	12.52		
10	cis-1,2-Dimethylcyclobexane	13.54	13.58		
11	Ethylcyclohexane	13.78	13.79		
12	Ethylbenzene	14.49	14.51		
13	1,2 & 1,4-Dimethylbenzene	14.87	14.89		
14	1,3-Dimethylbenzene	15.75	15.97		
15	Nonane	16.58	16.43		
16	iso-Propylcyclohexane	17.21	17.15		
17	Propylbenzene	18.06	18.03		
18	1,2,4-Trimethylbenzene	18.59	18.57		
19	1,3,5-Trimethylbenzene	19.44	19.46		
20	Decane	20.04	20.03		
21	Undecane	23.10	23.05		
22	Dodecane	25.89	26.05		

The Compounds Listed Under the Various Classes					
STRAIGHT CHAIN	CYCLIC	AROMATICS			
HYDROCARBONS		HIDROCARDONS			
Hexane	Cyclonexane	Benzene			
Heptane	Methylcyclohexane	Methylbenzene			
Octane	trans-1,2-Dimethylcyclohexane	1,2-dimethylbenzene			
Nonane	cis-1,2-Dimethylcyclohexane	1,3-dimethylbenzene			
Decane	1,4-Dimethylcyclohexane	1,4-dimethylbenzene			
Undecane	Ethylcyclohexane	Ethylbenzene			
Dodecane	iso-Propylcyclohexane	Propylbenzene			
		1,2,4-Trimethylbenzene			
		1,3,5-Trimethylbenzene			

Table 3.8 The Compounds Listed Under the Various Classe

Fig 3.17 shows the mass spectra of these compounds in the sample chromatogram, the mass spectra of standard compounds and the mass spectra of compounds from the library match. The mixture of standard compounds used to generate Fig 3.16 (b) was prepared from individual standards, except for 1,2-dimethylcyclohexane which came as a mixture of the cis- and trans- isomers. See Section 2.4.2 for preparation of spectra of cisand trans-1.2mass Although the mixture. standard dimethylcyclohexane are similar, Figs 3.17 (h) and (j), respectively, they differ in the relative abundance of ions. The relative abundance of ions is used in the MS library search protocol, and the cis- and trans- isomers can be distinguished from each other. Therefore it is concluded that peak 8 in Fig 3.16 (b) is the trans- isomer and peak 10 is the cis- isomer.

In the case of dimethylbenzene, when all three isomers were chromatographed individually, 1,3-dimethylbenzene is separated as peak (14) in Fig 3.16 (b), whereas 1,2 and 1,4-dimethylbenzene co-elute as peak (13). Because all three isomers have very similar mass spectra (see Fig 3.17 (m), (n) and (o)), it could not be determined if peak (13) was the 1,2 or 1,4 isomer. As a result, peak (13), represents both 1,2 and 1,4-dimethylbenzene and perhaps both are in fact present in the landfill gas. Table 3.8 lists the twenty-three straight chain, cyclic and aromatic hydrocarbons present in the landfill gas which were positively identified.



Fig 3.17 The Comparison of Mass Spectra from Sample, Standard and Library Match

Fig 3.17 continued



Fig 3.17 continued



Fig 3.17 continued



Fig 3.17 The Comparison of Mass Spectra from Sample, Standard and Library Match

3.2.1.3. Positive Identification of Terpenic Hydrocarbons Using Standards

Fig 3.16 (a) shows that, along with the twenty-three compounds positively identified in section 3.2.1.2, there were three other high abundance compounds present in the landfill gas at approximately 17.7, 19.1 and 20.8 minutes. These terpenic hydrocarbons (see Table 3.6 (e)) were not included in the study described in section 3.2.1.2 because standards were not available at that time. When standards became available, these three compounds were positively identified, using the same protocol described in section 3.2.1.2, as α -Pinene, β -Pinene and 1-Limonene. Fig 3.18 shows the separation of terpenes in the landfill gas. Table 3.9 shows the retention time of terpenes in the sample compared with those of the standard compounds. The preparation of the standard terpene solution is described in Section 2.4.2.2. Fig 3.19 shows the mass spectra of these compounds from the sample, the standard and the library match. Results show that all three terpenes were correctly identified as described in section 3.2.1.2 by the library search.



Table 3.9							
The Cor	The Comparison of Retention Time Between the Sample and Standard						
No	COMPOUND	RT OF SAMPLE	RT OF STANDARD				
		(Minutes)	(Minutes)				
1	α- Pinene	17.72	17.69				
2	β- Pinene	19.12	19.08				
3	1- Limonene	20.80	20.82				



Fig 3.19 The Comparison of Mass Spectra from Sample, Standard and Library Match

3.2.2. Quantitative Analysis of VOCs in Landfill Gas

Over one hundred compounds were present in the landfill gas and quantitative analysis of all VOCs is not practical as standard compounds are required for each VOC. Other workers in this area have approached this problem by using a semiquantitative approach where one standard is used to quantify a number of compounds or compounds in a particular class. Here the detector response is assumed to be the same for the standard and other compounds. Ward⁽⁹⁰⁾ used an eleven compound external standard which represented actual compounds or isomers of compounds in the landfill gas. Similarly, Allen⁽⁹²⁾ used a twelve component external standard where halocarbons were determined with reference to dichloromethane; alcohols to ethanol; substituted aromatics to p-xylene; cyclic compounds to cyclohexane; pinenes to 1limonene; and the alkanes to hexane, heptane, nonane, decane, and dodecane. Young⁽⁸⁹⁾ and Scott⁽⁶⁴⁾ also used a semi-quantitative approach where anisole was used to quantify a number of compounds. In Scott's work it was indicated that the error in using a single standard was thought not to exceed a factor of two.

In this study over sixty VOCs were quantified as follows. The twenty-six compounds positively identified using standards in Section 3.2.1.2 and Section 3.2.1.3 were quantified directly using standard and an internal standard. Other VOCs were semiquantified using standards which represented various compounds in the landfill gas.

3.2.2.1. Quantitative Analysis of Straight Chain, Cyclic, Aromatic and Terpenic Hydrocarbons

The quantitative analysis of straight chain, cyclic and aromatic hydrocarbons positively identified in section 3.2.1.2 and terpenic hydrocarbons positively identified in section 3.2.1.3 was conducted in four parts. Firstly calibration plots were prepared. Secondly, desorption efficiencies were determined. The third part involved the determination of detection limits and finally the VOCs in a landfill gas sample from leachate well (A_{1-1}) of landfill site A (see Table 6.1 and 6.2 for landfill sites description and sampling point description, respectively, Chapter VI) was analysed for the above-mentioned VOCs. The concentrations of these VOCs found in the landfill gas sample will be presented in Section 3.2.2.2 together with those of other VOCs which were semi-quantified.

3.2.2.1.1. Calibration Plots

The large number of VOCs in the landfill gas makes it difficult to find suitable internal standards to use for calibration. Firstly, it would be difficult to find a compound similar to those in the landfill gas, which is not already present in the landfill gas. Secondly, the chromatogram is so cluttered that it is difficult to find a freely eluting internal standard. This problem was readily solved with the aid of deuterated internal standards and the ability of the MS software to selectively extract from the total ion data any specified ion.

Ideally an internal standard should elute close to the compound of interest. Therefore, three deuterated internal standards were sought. Each would cater for a particular section of the chromatogram, for early eluting compounds, late eluting compounds and for compounds eluting in between. However, only two were available, ethylbenzene-D₅ and naphthalene-D₈. Fig 3.20 shows the separation of standards including deuterated internal standards. The preparation of the VOC solution including deuterated internal standards used to generate Fig 3.20 is described in Section 2.4.5, and contains 0.024 μ l/ml CS₂ of each VOC per ml of CS₂. Because a deuterated internal standard for early eluting compounds was not available and naphthalene-D₈ eluted very late in the separation, it was decided to use the mid-range eluting ethylbenzene-D₅ as the internal standard for all compounds.



Fig 3.20 The Separation of Standards Including Deuterated Internal Standards

As mentioned above, the MS software adds an extra level of selectivity as it allows selected ion-chromatograms to be extracted from the total ion data. This feature was used to prepare calibration plots as described below. From the mass spectrum of ethylbenzene-D₅, shown in Fig 3.21, the most abundant ion, m/e = 96, is chosen to extract from the total ion data a chromatogram shown in Fig 3.22. The choice of the most abundant ion is not crucial but does allow for extra sensitivity in the extracted ion chromatogram. Interestingly, only ethylbenzene-D₅ has an ion with m/e = 96. Because ethylbenzene co-elutes with ethylbenzene-D₅, it is important that ethylbenzene does not have an ion with m/e = 96. The mass spectrum of ethylbenzene is shown in Fig 3.23 and as can be seen ethylbenzene and ethylbenzene-D₅ do not share common ions. Calibration plots for the compounds of interest, except for

ethylbenzene, were prepared by plotting peak area response ratio between the compounds of interest in Fig 3.20 (the total ion peak area) and ethylbenzene- D_5 in Fig 3.20 (peak area of m/e = 96) versus mass of compound injected.

This could not be done with ethylbenzene because it co-elutes with ethylbenzene- D_5 . This problem is easily overcome as follows. From the mass spectrum of ethylbenzene, shown in Fig 3.24, the ion with m/e = 91 is chosen from the total ion data and extracted from the total ion data in Fig 3.20 to produced and extracted ion (m/e = 91) chromatogram. This extraction chromatogram is shown in Fig 3.23, and interestingly, other compounds have an ion with m/e = 91, but importantly as mentioned above ethylbenzene and ethylbenzene- D_5 do not share any common ions. Therefore, the calibration for ethylbenzene was prepared by plotting peak area response ratio between ethylbenzene (m/e = 91) and ethylbenzene- D_5 (m/e = 96) versus amount of ethylbenzene injected.



Fig 3.21 Mass Spectrum of Ethylbenzene-D₅



Fig 3.22 Extracted Ion (m/e = 96) Chromatogram of Fig 3.20



Table 3.10 shows concentration and mass data of the solutions used to construct the calibration plots (see Section 2.4.4 for standard solution preparation). Injection mode was splitless with a 1μ l injection volume. The mass injected was calculated as following:

Mass Injected (ng) = 1000 × Solution Concentration (μ l/ml) × Density (mg/ μ l) × Volume Injected (μ l)

In the case of 1,2-dimethylcyclohexane, because the standard material used was a mixture of the cis- and trans- isomers, the calibration plot was prepared using the sum of peak areas for both isomers. In the case of 1,2- and 1,4-dimethylbenzene, because these compounds co-elute, the mass injected is the total for both isomers.

Concentrations of Standard Solutions for the Calibration Plots						
	SOLUTION CONCENTRATION (uL/ML)					
COMPOUND	[0.192]	[0.096]	[0.048]	[0.024]	[0.012]	[0.006]
		MA	SS INJE	CTED (ng)	[]
	M_1	M ₂	M ₃	M ₄ `	^т М ₅	M ₆
Hexane	127	63.4	31.7	15.8	7.92	3.96
Benzene	168	84.1	42.1	21.0	10.5	5.26
Cyclohexane	149	74.7	37.4	18.7	9.34	4.67
Heptane	131	65.6	32.8	16.4	8.20	4.10
Methylcyclohexane	148	73.9	36.9	18.5	9.23	4.62
Methylbenzene	166	83.2	41.6	20.8	10.4	5.20
1,4-Dimethylcyclohexane	150	75.2	37.6	18.8	9.39	4.70
trans-1,2-Dimethylcyclohexane	153	76.4	38.2	19.1	9.56	4.78
Octane	135	67.4	33.7	16.9	8.43	4.22
cis-1,2-Dimethylcyclohexane	149	74.5	37.2	18.6	9.31	4.66
Ethylcyclohexane	151	75.6	37.8	18.9	9.46	4.73
Ethylbenzene	166	83.2	41.6	20.8	10.4	5.20
1,2 & 1,4-dimethylbenzene	169	84.5	42.2	21.1	10.6	5.28
1,3-dimethylbenzene	166	83.0	41.5	20.7	10.4	5.19
Nonane	138	68.9	34.4	17.2	8.61	4.31
iso-Propylcyclohexane	152	76.2	38.1	19.0	9.52	4.76
α-Pinene	165	82.4	41.2	20.6	10.3	5.15
Propylbenzene	166	82.8	41.4	20.7	10.3	5.17
1,2,4-Trimethylbenzene	168	84.1	42.0	21.0	10.5	5.25
β-Pinene	167	83.5	41.7	20.9	10.4	5.22
1,3,5-Trimethylbenzene	166	83.1	41.5	20.8	10.4	5.19
Decane	140	70.1	35.0	17.5	8.76	4.38
1-Limonene	162	80.9	40.4	20.2	10.1	5.05
Undecane	142	71.1	35.5	17.8	8.88	4.44
Dodecane	144	71.9	35.9	18.0	8.98	4.49

Table 3.10 Icentrations of Standard Solutions for the Calibration 1

* Total mass injected for both isomers

Calibration plots are shown in Fig 3.25. The plots include calibration equations and correlation coefficients. All plots were linear with correlation coefficients of 0.999.





Fig 3.25 continued





Fig 3.25 continued





150

100 Mass (ng)

Resp Ratio = 1.17a-002 + Mass Corr Coef = 0.999 Curve Fit: Linear/Origin

50

Fig 3.25 continued



•





Fig 3.25 Calibration Plots for Each Compound

3.2.2.1.2. Solvent Desorption Method Validation

The solvent desorption system, including preparation of standard gaseous mixtures, loading adsorption tubes with standard gases and adsorption tube desorption efficiency, was calibrated against liquid standards injected directly into the gas chromatograph. A number of compounds representing some abundant compounds found in landfill gas, from high boiling to low boiling, were chosen for method heptane, methylbenzene, validation. These included benzene, cyclohexane, 1,3,5β-pinene and ethylbenzene, 1,4-dimethylbenzene, propylbenzene, trimethylbenzene. Method validation of the solvent desorption system included the following steps.

- 1. 5000 ml of a standard gas containing 0.1111 μ l each of compounds including benzene, cyclohexane, heptane, methylbenzene, ethylbenzene, 1,4dimethylbenzene, propylbenzene, β -pinene and 1,3,5-trimethylbenzene was prepared and 2000 ml of this standard gas introduced into a charcoal tube at a flow rate of 200 ml/min. This was the same flow rate used to collect VOCs from landfill gas. The tubes were then refrigerated at 4 °C overnight, again this was the same as the treatment of tubes used to collect landfill gas. See Section 2.6.2 for preparation of standard gas sample. The charcoal tube contained 0.04444 μ l of each compound;
- 2. The charcoal tube was desorbed with 5.00 ml CS_2 , as described in Section 2.3. Total volume of this solution, including desorbed compounds, was 5.0004 ml. From this solution 1.00 µl, which contained 0.0799 nl of mixture or 0.0089 nl of each compound, was gas chromatographed. Splitless injection was used. Peak areas for each compound were recorded (PA₁);
- 3. A standard solution containing 0.04444 μ l of each compound in 5.00 ml CS₂ was prepared (see Section 2.6.2). One micro liter (1.00 μ l) of this standard solution, containing 0.0800 nl of mixture or 0.0089 nl of each compound was gas chromatographed using the splitless mode. Peak areas for each compound were recorded (PA₂);
- 4. The two solutions gas chromatographed in steps 2 and 3 above had only a concentration difference of 0.001%, and were therefore considered to be identical. Recovery (R) of each compound was calculated as follows:

$$R = (PA_1 / PA_2) \times 100\%$$

.

- 5. Recovery studied were also conducted for tube loadings ten times that described above, i.e., the standard gaseous mixture was ten times more concentrated;
- 6. Steps 1-5 were repeated six times in order to determine system precision.

The two tube loadings used covered the range of concentrations of VOCs expected in the landfill gas. Table 3.11 lists tube loading, recoveries (R) and solvent desorption system precision (% relative standard deviations for 6 replicates) for the compounds. As Table 3.11 shows the relative standard deviations for all compounds were found to be below 10 % for low tube loadings and 15 % for high tube loadings.

		Table 3	.11			
Recov	eries and Tub	e Loadir	ngs for E	ach Compoun	ıd	
COMPOUNDS	^a TUBE LOADING (μg)	R (%)	RSD (%)	^b TUBE LOADING (μg)	R (%)	RSD (%)
Benzene	38.96	97.04	5.83	389.6	97.42	12.66
Cyclohexane	34.60	97.66	6.92	346.0	89.96	9.83
Heptane	30.39	90.85	7.49	303.9	95.79	11.98
Methylbenzene	38.53	91.65	9.15	385.3	83.75	13.45
Ethylbenzene	38.53	98.85	2.64	385.3	89.31	10.24
1,4-dimethylbenzene	39.12	97.20	4.52	391.2	81.95	9.69
β-Pinene	38.64	95.93	9.98	386.4	90.32	13.12
Propylbenzene	38.31	100.1	5.46	383.1	88.78	14.12
1,3,5-trimethylbenzene	38.45	96.90	8.97	384.5	78.74	8.33

^aTube Loading = $0.04444 \ \mu l \times density$

^bTube Loading = 0.4444 μ l × density

According to ASTM method D3687-95⁽¹⁰⁹⁾ "Standard Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method", when the desorption efficiency of a chemical is less than 75%, an alternative sampling and analytical method should be considered. Solvent desorption method recovery studies showed that the analytical system recoveries were greater than 75% for all compounds. The recovery studies also showed that the method used to prepare standard gases and load adsorption tubes was also valid.

3.2.2.1.3. Detection Limits

According to National Association of Testing Authorities (NATA) Technical Note $17^{(112)}$ "Format and Content of Test Methods and Procedures for Validation and Verification of Chemical Test Methods", the limit of detection is the concentration of analyte giving a signal-to-noise ratio of 3:1. GC/MS detection limits for the 26 VOCs of interest were determined by dilution of up to 40 times of a stock solution (see Section 2.4.3), containing 0.2 µl of each compound /ml CS₂, until the peak height to

noise ratio was between 2 and 3. For this part of the study an injection split ratio of 25:1 was used. Table 3.12 shows detection limits in terms of solution concentration and mass injected. These values have been adjusted for signal to noise ratio of three. The mass injected was calculated by the formula shown below:

Mass Injected (ng) = $1000 \times [Concentration (\mu l/ml) \times Density (mg/\mu l) \times$ Volume Injected (μ l) × Split Ratio (1/25)]

In the case of 1,2- and 1,4-dimethylbenzene, because these compounds co-elute, detection limit is the total for both compounds.

Detection Limits for the 26 VOCs				
	CONCENTRATION LIMIT	MASS INJECTED		
COMPOUND	$(\mu l/ml) \times 10^3$	(ng)		
Hexane	9.34	0.246		
Benzene	9.85	0.345		
Cyclohexane	9.01	0.280		
Heptane	7.88	0.215		
Methylcyclohexane	10.66	0.328		
Methylbenzene	10.18	0.353		
1,4-Dimethylcyclohexane	18.49	0.579		
trans-1,2-Dimethylcyclohexane	29.41	0.936		
Octane	9.06	0.254		
cis-1,2-Dimethylcyclohexane	7.61	0.236		
Ethylcyclohexane	8.79	0.277		
Ethylbenzene	8.99	0.312		
^a 1,2 & 1,4-Dimethylbenzene	14.38	0.253		
1,3-Dimethylbenzene	7.746	0.267		
Nonane	17.43	0.500		
iso-Propylcyclohexane	12.08	0.383		
a-Pinene	8.28	0.284		
Propylbenzene	5.73	0.197		
1,2,4-Trimethylbenzene	6.04	0.211		
β-Pinene	7.21	0.251		
1,3,5-Trimethylbenzene	4.29	0.148		
Decane	6.47	0.189		
1-Limonene	6.14	0.207		
Undecane	5.66	0.167		
Dodecane	4.53	0.135		

Table 3.12

^a: Total for both compounds.

3.2.2.2 Semi-Quantitative Analysis of Some Other VOCs Present in the Landfill Gas A number of other VOCs were present with an appreciable abundance in the landfill gas and include branched chain alkanes, cyclic alkanes, alkyl aromatics and terpenes. These compounds and other compounds in the same class but present in lower abundances (based on peak area) were quantified as follows. A particular standard used to construct the calibration plots in Section 3.2.2.1.1, where ethylbenzene- D_5 was used as the internal standard, was chosen to represent a number of compounds in the landfill gas. The standards chosen were compounds similar to those being analyzed. From the sample chromatogram the response ratio of the compounds to be quantified were determined relative to ethylbenzene- D_5 and their concentration was determined directly from the standard calibration plot. This procedure assumes that the detector response for the standard and the compounds to be quantified using this standard are the same. The various standards used to quantify a number of other abundant compounds in the landfill gas are listed in Table 3.13. The peak labeled with an asterisk is actually two branched chain alkanes, both with seven carbon atoms, which co-elute (see Section 3.2.1.1). As this is an abundant peak it was quantified using heptane.

COMPOUND	STANDARD USED FOR QUANTITATION	
2-methylhexane*		
2,3-dimethylpentane*	TT	
3-methylhexane	Heptane	
Heptane		
2,3-dimethylhexane		
4-methylheptane	Octane	
3-methylheptane		
2-methyloctane	Nonane	
2,6-dimethyloctane		
3-ethyl-2-methylheptane	Deserve	
4-methylnonane	Decane	
2-methylnonane		
5-methyldecane		
4-methyldecane	Undecane	
3-methyldecane		
3,6-dimethyldecane	Dodecane	
cis-1,2-dimethylcyclopentane	Methylevelohevane	
Ethylcyclopentane		
trans-1,3-dimethylcyclohexane	trans-1,4-dimethylcyclohexane	
trans-1-ethyl-4-methylcyclohexane		
cis-1-ethyl-4-methylcyclohexane		
Propylcyclohexane	1-methylethylcyclohexane	
trans-1-methyl-4-(1-methylethyl)cyclohexane		
Butylcyclohexane		
1-methylethylbenzene		
1-ethyl-3-methylbenzene		
1-ethyl-2-methylbenzene		
1-methyl-4-(1-methylethyl)benzene		
1-propenylbenzene		
1,4-diethylbenzene	Propylbenzene	
2-ethyl-1,4-dimethylbenzene		
2-ethyl-1,3-dimethylbenzene		
1-methyl-3-(1-methylethyl)benzene		
4-ethyl-1,2-dimethylbenzene		
1,2,3,5-tetramethylbenzene		

 Table 3.13

 The List of Standards Used to Quantify Other Compounds in the Landfill Gas

3.2.2.3 Analysis of VOCs in a Landfill Gas Sample

A landfill gas sample taken from leachate well A_{1-1} of landfill site A (see Table 6.1 and 6.2) on the 1st July 1993 was analysed using both direct calibration and semiquantitative calibration as explained in Section 3.2.2.1 and above, respectively. The concentrations of the various VOCs are shown in Table 3.14. Those compounds marked with asterisks have been semi-quantified. It should be noted that the concentration of dimethylbenzene is the total for both the 1,2- and 1,4- isomers.

The Concentrations of Compounds from the Leachate wen A ₁₋₁ of Site A			
COMPOUNDS	<u> </u>		
ALKANES			
Hexane	0.077		
2-methylhexane*	0.072		
2,3-dimethylpentane*	0.088		
3-methylhexane*	0.108		
Heptane	0.215		
2,3-dimethylhexane*	0.044		
4-methylheptane*	0.044		
Octane	0.254		
3-methylheptane*	0.052		
2-methyloctane*	0.200		
Nonane	0.726		
2,6-dimethyloctane*	0.153		
3-ethyl-2-methylheptane*	0.084		
4-methylnonane*	0.189		
2-methylnonane*	0.281		
Decane	0.700		
5-methyldecane*	0.053		
4-methyldecane*	0.066		
3-methyldecane*	0.052		
Undecane	0.290		
3,6-dimethyldecane*	0.032		
Dodecane	0.067		
CYCLIC HYDROCARBONS			
Cyclohexane	0.052		
cis-1,2-dimethylcyclopentane*	0.025		
Methylcyclohexane	0.166		
Ethylcyclopentane*	0.022		
trans-1,4-dimethylcyclohexane	0.383		
trans-1,3-dimethylcyclohexane*	0.108		
trans-1,2-dimethylcyclohexane	0.332		
cis-1,2-dimethylcyclohexane	0.040		
Ethylcyclohexane	0.117		
trans-1-ethyl-4-methylcyclohexane*	0.093		
cis-1-ethyl-4-methylcyclohexane*	0.044		
1-methylethylcyclohexane	0.061		
Propylcyclohexane*	0.134		
trans-1-methyl-4-(1-methylethyl)cyclohexane*	0.036		
Butylcyclohexane*	0.061		

Table 3.14The Concentrations of Compounds from the Leachate Well A11 of Site A

COMPOUNDS	 C (μg/L)
AROMATIC HYDROCARBONS	
Benzene	1.007
Methylbenzene	1.079
Ethylbenzene	0.603
1,2&1,4-dimethylbenzene	0.546
1,3-dimethylbenzene	0.363
1-methylethylbenzene*	0.083
Propylbenzene	0.135
1-ethyl-3-methylbenzene*	0.236
1-ethyl-2-methylbenzene*	0.101
1,2,4-trimethylbenzene	0.292
1,3,5-trimethylbenzene	0.376
1-methyl-4-(1-methylethyl)benzene*	0.166
1-propenylbenzene*	0.100
1,4-diethylbenzene*	0.029
2-ethyl-1,4-dimethylbenzene*	0.076
2-ethyl-1,3-dimethylbenzene*	0.067
1-methyl-3-(1-methylethyl)benzene*	0.027
4-ethyl-1,2-dimethylbenzene*	0.028
1,2,3,5-tetramethylbenzene*	0.032
TERPENIC HYDROCARBONS	
α-Pinene	0.274
B-Pinene	0.255
1-Limonene	0.370

Table 3.14 (continued)The Concentrations of Compounds from the Leachate Well A1-1 of Site A

3.3 Further Optimisation of GC Operating Conditions for BP-1 Column

The GC operating conditions described in Section 3.1.5 were suitable for the separation of hydrocarbons with retention greater than hexane. Using these conditions analytical protocols were successfully developed in Section 3.2.2. In order to retain compounds with retention less than hexane, the GC starting temperature was dropped to -20°C using the liquid CO_2 cryogenic facility incorporated into the Hewlett-Packard (HP) 5890 series II GC. Fig 3.26 shows the separation of VOCs in the landfill gas sample using a starting temperature of -20°C.



Fig. 3.26 The Separation of VOCs in the Sample Using A Starting Temperature of -20°C

As can be seen, other more volatile compounds are now retained and separated before hexane. The lower starting temperature also allows the sample to refocus at the head of the column resulting in sharp chromatographic peaks. Overall, the sub-ambient starting temperature has produced greater retention and sharper peaks, resulting in a better separation than with the ambient starting temperature chromatogram shown in Fig 3.16 (a). The solvent, carbon disulfide, is also retained longer at sub-ambient starting temperature and the tail of the solvent peaks is seen at the start of Fig 3.26.

The compounds eluting before hexane in Fig 3.26 were identified using the MS Wiley database as described in Section 3.2.1.1. Table 3.15 lists the compounds in order of retention time and also indicates the quality match. The mass spectra of sample compounds alongside those from the database can be seen in Appendix B (Part b). There is good similarity, but without retention time matching with standards, identification is only tentative.

	Identified Compounds Eluting Before Hexane					
PK#	RT	LIBRARY/ID	QUALITY			
1	7.03	Pentane	91			
2	9.82	3-methylpentene-1	70			
3	10.10	2,3-dimethylbutane	93			
4	10.41	2-methylpentane	92			
5	11.05	3-methylpentane	90			

Table 3.15 lentified Compounds Eluting Before Hexane

CHAPTER IV THE METHODOLOGY AND EXPERIMENTS FOR THERMAL DESORPTION TECHNIQUE

4.1. Optimisation of Sampling and Gas Chromatographic Separation Protocols for Thermal Desorption

The studies reported in this chapter were conducted using landfill gas from leachate well A_{1-1} of landfill site A (see Table 6.1 and 6.2 for landfill sites description and sampling point description, respectively, Chapter VI). The sampling protocol for VOCs in landfill gas was adapted from ASTM D6196-97⁽¹⁰⁸⁾ 'Standard Practice for Selection of Sorbents and Pumped Sampling / Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air'. VOCs in landfill gas were collected on CarbotrapTM 300 Multi-bed thermal desorption tubes followed by thermal desorption / gas chromatographic analysis with mass selective detection (see Section 2.7.3). The GC column used was the 25m × 0.25mm ID, 1 µm film thickness methylsilicone column also employed for the solvent desorption studies described section 3.1.4.

4.1.1. The Sampling

The sampling train used to collect VOCs in landfill gas using thermal desorption tubes is shown in Fig 4.1. The sampling procedure, except for sampling time which is discussed below, and sampling train components are described in Section 2.7. When sampling relatively wet landfill gas, moisture was clearly visible in the adsorption tubes and therefore the landfill gas was dried before collection. Moisture removal is discussed in section 3.1 and moisture trap construction is described in Section 2.2.



Fig 4.1 The Sampling Train Using Thermal Desorption Tubes

The sampling time is dependant on the concentration of VOCs in the landfill gas. The solvent desorption technique discussed in Chapter III allows for dilution of the collected VOCs in order to avoid overloading in the subsequent GC analysis where a small volume (1 μ l) of the desorbed sample solution (10 ml) is injected. The GC also adds an extra level of dilution by allowing split injection. For thermal desorption, the only method of dilution of the collected VOCs is splitting of desorbed sample at the TDU. The TDU was optimized for use with a set split ratio of 50:1 (see section 2.7.3). Initial studies using thermal desorption tubes indicated that at a pump flow rate of 200 ml/min, short sampling times in the range of 5 – 10 minutes did not produce overloaded chromatograms. In order to obtain a more representative sample of gas, very short sampling times of less than 5 minutes were not employed.

4.1.2. Selection of Adsorbent

ASTM D6196-97⁽¹⁰⁸⁾ provides some guidance in choosing a sorbent for the collection of air-borne volatile organic compounds. Considerations in sorbent selection include analyte volatility and the relative humidity of the air being sampled. Where the analytes present cover a broad range of volatilities, multi-bed sorbent tubes can be used. For atmospheres of up to 95 % humidity, hydrophobic sorbents including porous polymers and graphitized carbon are used. Less hydrophobic sorbents such as pure charcoals and carbonized molecular sieves are suitable for atmospheres with relative humidity in excess of 65 %.

The sorbent tubes available for this study include single bed tubes containing Carbotrap and Tenax sorbents, a dual bed tube containing Carbotrap and Carbosieve sorbents, and triple bed tube containing Carbotrap, Carbotrap C and Carbosieve sorbents. Table 4.1 lists the sorbent properties.

The Properties of Different Sorbents					
SORBENT	MESH SIZE	ТҮРЕ	SURFACE* AREA (m ² /g)	APPLICATION	MAXIMUM DESORPTION TEMP. (°C)
Carbotrap	20/40	Graphitized Carbon Blacks	100	$C_5 - C_{12}$	>400
Carbotrap C	20/40	Graphitized Carbon Blacks	10	$C_{12} - C_{20}$	>400
Carbosieve	60/80	Carbon Molecular Sieves	820	$C_2 - C_5$	400
Tenax	60/80	Porous Polymers	35	$C_5 - C_{26}$	350

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Obtained from SUPELCO product information

Multi-bed sorbent tubes allow the trapping abilities of the individual sorbents to be combined, and Table 4.2 lists the sorbent tubes along with their application range.

The Sorbent tubes and Their Application Range						
SORBENT TUBES*	MATERIALS	APPLICATION RANGE				
Carbotrap™ 100	Carbotrap	$C_5 - C_{12}$				
Carbotrap™ 200	Carbotrap and Carbosieve	$C_2 - C_{12}$				
Carbotrap [™] 300	Carbotrap, Carbotrap C and Carbosieve	$C_2 - C_{20}$				
Tenax	Porous Polymers	$C_{5} - C_{26}$				

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• The tube physical descriptions are given in Section 2.6.2.

The landfill gas under investigation here was the same as that studied by adsorption / solvent desorption in Chapter III, where the VOCs collected ranged from $C_5 - C_{12}$. Table 4.2 shows that any one of the four tubes would be suitable for adsorption / thermal desorption studies as they all were applicable to the expected volatility range of VOCs present in the landfill gas. For thermal desorption studies Carbotrap[™] 300 multi-bed thermal desorption tubes were chosen because they allowed sampling of heavy VOCs with carbon number up to twenty but more importantly allowed sampling of light VOCs with carbon number down to two.

4.1.3. Optimisation of Thermal Desorption

Important considerations for successful thermal desorption include desorption temperature, desorption time, desorption flow rate and clean desorption tubes. According to ASTM D6196-97(108), for tubes of similar dimension and containing similar sized and amounts of adsorbents, Table 4.3 lists the recommended parameters for the three adsorbents in the Carbotrap[™] 300 Multi-bed adsorption tubes. As can be seen, desorption and cleaning temperature and flow rate are the same for all three adsorbents.

IADLE 4.5								
The Three Adsorbents Parameters in Carbotrap [™] 300 Multi-Bed Tube								
	DESORPTION	DESORPTION	CLEANING	CLEANING				
ADSORBENT	TEMP. (°C)	FLOW RATE	TEMP. (°C)	FLOW RATE				
Carbotrap	325 °C	30 ml/min	350 °C	100 ml/min				
Carbotrap C	325 °C	30 ml/min	350 °C	100 ml/min				
Carbosieve	325 °C	<u>30 ml/min</u>	<u>350 °C</u>	100 ml/min				

TABLE 4.3*

* Taken from ASTM D6196-97⁽¹⁰⁸⁾

For optimum desorption efficiency, desorption flow rates should be in the order of 30 to 50 ml/min and desorption time from 5 - 15 minutes. When desorption efficiency is less than 95 %, then desorption parameters should be changed accordingly. For tube cleaning, temperature should be just above the analytical desorption temperature where tubes are cleaned for 10 minutes with carrier gas flow of at least 100 ml/min. Sorbent tube blanks are acceptable when blank peaks are no greater than 10 % of the typical areas of the analytical peaks.

For the current study, Table 4.4 shows the thermal desorption parameters initially trialled for the Carbotrap[™] 300 Multi-bed adsorption tubes.

TABLE 4.4									
The Thermal Desorption Parameters for the Current Study									
DESORP.	DESORP.	DESORP.	CLEANING	CLEANING	CLEANING				
TEMP. (°C)	FLOW RATE	TIME (min)	TEMP. (°C)	FLOW RATE	TIME (min)				
350	50	5	400	120	30				

The desorption conditions proved to be successful as desorption efficiencies were of the order of 95 % (see Section 4.1.4.3). Cleaning conditions were also successful where blank runs showed no chromatographic peaks.

It should be noted that thermal desorption is conducted so that the carrier gas passes through the tube in the reverse direction of sample collection flow. This allows desorbed analytes to quickly exit the tube rather than pass through more adsorbent. Multi-bed tubes are arranged so that during sampling gas passes initially through the least active layer and exits through the most active layer. During desorption, when the flow direction is reversed, desorbed analytes exit the tube by traveling toward the least active sorbent. This is important, as high boiling compounds do not come into contact with the stronger sorbent and therefore can be quickly evacuated from the tube.

Thermal desorption protocol also involves removing the air present in the tubes prior to desorption. This is discussed in Section 4.1.4.2.

4.1.4. Optimisation of Gas Chromatographic Conditions

Initial studies with thermal desorption involved loading a 4 mm I.D. CarbotrapTM 300 Multi-bed adsorption tube (see Section 2.7.2) with a standard gaseous mixture (see Section 2.8.2) containing hexane, benzene, cyclohexane, heptane, methylbenzene, ethylbenzene, 1,2-dimethylbenzene, 1,3-dimethylbenzene, 1,4-dimethylbenzene, propylbenzene and 1,3,5-trimethylbenzene. The tube was thermally desorbed at 350 °C, and the desorbed compounds were then separated on a capillary methylsilicone column (BP-1, 25m × 0.25mm ID, 1 µm film thickness).

4.1.4.1. Sample Refocusing and GC Temperature Programme

The total flow passing through the desorption chamber during desorption is ≈ 50 ml/min and consequently the desorbed sample occupies a volume of several milliliters. In order to avoid broad bands the sample must be refocused before the gas chromatographic separation begins. The two methods of refocusing investigated included transfer of desorbed sample onto a smaller I.D. adsorption tube and cryogenic refocusing.

Smaller I.D. (2 mm) Carbotrap[™] 300 Multi-bed tubes were available to refocus the landfill gas sample collected on 4 mm I.D. tubes. This method of refocusing was not adapted for this study because:

1. The smaller I.D. tubes obviously have a smaller sample capacity and the sample from the 4 mm I.D. tubes could break through. Sampling time for collection of

VOCs on the 4 mm tubes could be shortened, but as discussed in Section 4.1.1 this was not done in order to obtain a more representative sample of landfill gas.

2. Initial trials with 2 mm tubes showed that desorbed samples still produced broad gas chromatographic peaks when ambient starting temperatures were used.

Cryogenic refocusing was used in this study to refocus desorbed samples from the 4 mm I.D. adsorption tubes. Desorbed samples were refocused at sub-ambient temperatures at the head of the gas chromatographic column using liquid CO_2 . Fig 4.2 (a) and (b) show the separation of the desorbed standard sample using ambient and sub-ambient starting temperatures, respectively. Thermal desorption and gas chromatographic condition are shown in the figure legends.



Fig 4.2 (a) The Separation of the Desorbed Standard (Ambient Starting Temperature) [The TDU / GC-MS conditions were: Carrier Gas: Helium; Carry Gas Flow: 1 ml/min at room temp; Injection Mode (TDU): 50 : 1; Desorption Chamber: room temp. → 350 °C and hold for 5 minutes; Nickel transfer line 250 °C; MS transfer line 280 °C; Solvent delay: 2.5 min; Scan rate: 1.2 scans/sec; Scan range: 40 – 550 amu; and Mass spectral confirmation: Wiley Mass spectral Data Base.]



Fig 4.2 (b) The Separation of the Desorbed Standard (Sub-Ambient Starting Temperature) [The other TDU / GC-MS conditions were the same as Fig 4.2(a) except Solvent delay (8.5 min)]
The GC conditions used to generate Fig 4.2 (a) were the optimum conditions developed for the solvent desorption studies in Chapter 3 (see Section 3.1.4) and involved a starting temperature of 35 °C. As can be seen without refocusing broad chromatographic peaks result. When the starting temperature is lowered to -20 °C the desorbed sample refocuses at the head of the column resulting in much narrower peaks and much-improved resolution.

4.1.4.2. Air Purging / Solvent Delay

Fig 4.2 (a) and (b) both employ a solvent delay which may appear unusual when no solvent is employed with thermal desorption. When tubes are initially placed in the thermal desorption chamber they must be flushed of their air with carrier gas prior to thermal desorption. According to ASTM D6196-97⁽¹⁰⁸⁾, the initial air purge involves passage of 10 times the tube volume of carrier gas to completely displace the volume of air in the tube. The 4 mm I.D. tubes used in this study had an internal volume of approximately 1.5 ml and therefore 15 ml of carrier gas is required to remove the air. The workings of the TDU are described in Section 2.7.3.1 and shown in Fig 2.10. The air initially present in the tubes of air was \approx 60 ml/min. At 60 ml/min a flushing time of 15 seconds is required to completely displace the volume of 15 seconds is required to completely displace the volume of 15 seconds is required to completely displace the volume of 15 seconds is required to completely displace the volume of air within the tubes.

Preliminary studies on air purging time revealed that 15 seconds was not sufficient to completely remove air from the thermal desorption tubes. Fig 4.3 shows the desorption of the standard gaseous mixture using an air purge time of 15 seconds and Fig 4.4 is the mass spectrum of the peak eluting at 2.89 minutes. The peak at 2.89 minutes was identified as CO_2 and therefore indicates that air was still present in the adsorption tube prior to GC analysis. Other air components, such as N₂ and O₂, were not seen in the mass spectrum as the mass range for mass spectral data collection was between 40 - 550 amu.



Fig 4.3 The Desorption of the Standard Gaseous Mixture (Air Purge Time: 15 seconds) [The TDU / GC-MS conditions were: Carrier Gas: Helium; Carry Gas Flow: 1 ml/min at room temp; Injection Mode (TDU): 50 : 1; Desorption Chamber: room temp. → 350 °C and hold for 5 minutes; Nickel transfer line 250 °C; MS transfer line 280 °C; Solvent delay: 0 min; Scan rate: 1.2 scans/sec; Scan range: 40 – 550 amu; and Mass spectral confirmation: Wiley Mass spectral Data Base.]



Fig 4.4 The Comparison of Mass Spectrums Between the Peak (RT: 2.89 Minutes) and CO2

In an attempt to completely remove air from the tubes, longer purge times were investigated. Fig 4.5 shows the chromatogram of the standard gaseous mixture using on air purge time of 30 seconds.



Fig 4.5 The Chromatogram of the Standard Gaseous Mixture (Air Purge Time: 30 Seconds) (The GC-MS conditions were shown as Fig 4.3)

This chromatogram revealed the extra purge time removed more air but also resulted in a substantial loss of tube components as indicated by the lower abundance of separated VOCs particularly the more volatile VOCs. This indicated the adsorbed compounds were being lost during air purging. This was proven by analysing an adsorption tube placed in the TDU side port during air purging (15 seconds) of a tube loaded with gaseous standard. Fig 4.6 shows the chromatogram resulting from desorption of the side port tube, and as can be seen the VOCs present indicated that VOCs were lost during air purging. Even with shorter air purging times VOCs were still present in the side port tubes as shown in Fig 4.7 when an air purge time of 8 seconds was used.



Fig 4.6 The Chromatogram from Desorption of the Side Port Tube (The GC-MS conditions were shown as Fig 4.2)



It would perhaps be possible to reduce tube VOCs losses during air purging by lowering the purge carrier gas flow rate but as described in Section 2.7.3.1, flows less than 60 ml/min were not possible. Therefore it was decided to conduct further thermal desorption studies where tube air purging was not performed prior to thermal desorption. This meant that a large plug of air would enter the MS detector and cause the MS detector to halt, and in order to avoid MS detector halting a solvent delay was incorporated in the analysis program. A solvent delay of 1.5 - 2.5 minutes was sufficient to allow the majority of the air to elute prior to MS turn-on.

From the findings above and those in Section 4.1.1 the sampling and gas chromatographic / thermal desorption protocols developed for VOCs in landfill gas using adsorption tubes with thermal desorption can be summarized as follows:

- Landfill gas is initially dried by passing through the moisture trap;
- The sampling times in the range of 5 10 minutes and flow rates of between 60 and 200 ml/min are used;
- VOCs are collected on Carbotrap[™] 300 Multi-bed thermal desorption tubes (see Section 4.1.3) and desorbed using TDU connected to the GC-MS with a Nickel transfer line;

• A Capillary BP-1, 25m × 0.25mm ID, 1 µm film thickness column is used and chromatographic / thermal desorption conditions are described as following:

<u>Carrier Gas</u> :	Helium.
Carrier Gas Flow:	1 ml/min at Room Temp.
Nickel Transfer Line Temp:	250 °C
Desorption Chamber Temp:	Room Temp. \rightarrow 350 °C and hold for 5 minutes.
Injection Mode:	Split 50:1 at Room Temp.
Oven Temp:	-20 – 100 °C @ 3 °C/min
	100 – 280 °C @ 20 °C /min
Cryogenic Fluid:	Liquid CO ₂ .
<u>MS transfer line:</u>	280 °C.
<u>Solvent delay</u> :	1.5 – 2.5 minutes.
<u>Scan rate</u> :	1.2 scans/sec.
<u>Scan range</u> :	40 – 550 amu
Tuning procedure:	Auto tune
Mass spectral confirmation:	Wiley Mass Spectral Data Base

4.1.4.3. Thermal Desorption Method Validation

The method validation of the thermal desorption system includes preparation of standard gaseous mixtures, loading adsorption tubes (CarbotrapTM 300 Multi-bed) with standard gases and adsorption tube desorption efficiency. It was calibrated against liquid standards injected to the empty desorption tube which sits in the chamber of the thermal desorption unit (TDU), and chromatographed. A number of compounds representing some abundant compounds found in landfill gas, from high boiling to low boiling, were chosen for method validation. These included hexane, benzene, cyclohexane, heptane, methylbenzene, ethylbenzene, 1,4-dimethylbenzene, propylbenzene, β -pinene and 1,3,5-trimethylbenzene. The method validation of the thermal desorption system used was similar to the sampling of landfill gas and involved loading the CarbotrapTM 300 Multi-bed thermal desorption tubes with 'gaseous' compounds and this method is described below:

 5000 ml of a standard gas containing 0.1000 μl each of compounds including hexane, benzene, cyclohexane, heptane, methylbenzene, ethylbenzene, 1,4dimethylbenzene, propylbenzene, β -pinene and 1,3,5-trimethylbenzene was prepared and 50 ml of this standard gas introduced into a CarbotrapTM 300 Multi-bed thermal desorption tube at a flow rate of 100 ml/min. This flow rate was typical of that used to collect VOCs from landfill gas. The tubes were then refrigerated at 4 °C overnight, again this was the same as the treatment of tubes used to collect landfill gas. See Section 2.8.3 for preparation of standard gas sample. The CarbotrapTM 300 Multi-bed thermal desorption tube contained 1.000 nl of each compound.

- The Carbotrap[™] 300 Multi-bed tube was desorbed in the Thermal Desorption Unit (See section 2.7.3) and the desorbed sample was gas chromatographed after being split 50:1 at the TDU. Peak areas for each compound were recorded (PA₁).
- 3. A standard solution containing 10.00 μ l of each compound in 10 ml CS₂ was prepared as described in Section 2.8.2. 1 μ l of this standard solution, containing 1.000 nl of each compound, was injected directly into the TDU (see Section 2.7.3.2) and the desorb programme commenced. The desorbed sample was gas chromatographed after being split 50:1 at the TDU. Peak areas for each compound were recorded (PA₂).
- 4. The amount of each compound injected in steps 2 and 3 was identical. The recovery (R) of each compound was calculated as follows:

$R = (PA_1 / PA_2) \times 100\%$

- 5. Recovery studied were also conducted for tube loadings ten times that described above, i.e., the standard gaseous mixture was ten times more concentrated;
- 6. Steps 1 5 were repeated six times in order to determine system precision.

The two tube loadings used covered the range of concentrations of VOCs expected in the landfill gas. Table 4.5 lists tube loading, recoveries (R) and thermal desorption system precision (% relative standard deviations for 6 replicates) for the compounds. As Table 4.5 shows the relative standard deviations for all compounds were found to be below 10 % for both low and high tube loadings.

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		IADLL	4.5			
The Rec	overies And T	ube Loa	ding For	· Each Compo	und	
COMPOUNDS	^a TUBE LOADING (µg)	R (%)	RSD (%)	^b TUBE LOADING (μg)	R (%)	RSD (%)
Hexane	0.660	97.3	7.86	6.60	99.6	5.34
Benzene	0.876	93.4	5.21	8.76	99.7	4.62
Cyclohexane	0.778	92.0	4.95	7.78	94.8	2.94
Heptane	0.683	96.8	6.32	6.83	98.6	5.37
Methylbenzene	0.866	94.9	2.22	8.66	98.6	8.99
Ethylbenzene	0.867	95.4	3.64	8.67	98.3	5.38
1,4-dimethylbenzene	0.880	98.1	8.12	8.80	100.1	6.42
β-Pinene	0.862	95.7	9.32	8.62	98.2	8.75
Propylbenzene	0.869	95.8	4.86	8.69	97. 7	6.19
1,3,5-trimethylbenzene	0.865	93.9	8.31	8.65	96.6	8.21

^aTube Loading = $1.000 \times 10^{-3} \mu l \times density$

^bTube Loading = $1.000 \times 10^{-2} \mu l \times density$

According to ASTM D6196-97⁽¹⁰⁸⁾ 'Standard Practice for Selection of Sorbents and Pumped Sampling / Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air', If the desorption efficiency is less than 95 % change the desorption parameters accordingly. Thermal desorption method shows that at both low and high tube loadings recoveries for all ten compounds are greater than 92 %, with only a small number of compounds exhibiting recoveries less than 95 % at low tube loadings. The recovery studies also showed that the method used to prepare standard gases and load adsorption tubes was also valid.

4.2. Qualitative Analysis

The next part of the study focused on the identification of the VOCs in the landfill gas. In this part of the study landfill gas was sampled using CarbotrapTM 300 Multibed adsorption tubes as described in Section 4.1.1 and 4.1.2, and the thermal desorption / gas chromatographic conditions developed in Section 4.1.3 and 4.1.4 were used. Fig 4.8 shows the separation of VOCs in landfill gas.



4.2.1. Tentative Identification Using Library

Fig 4.9 shows an expanded view, along both the abundance and time scale, of the chromatogram shown in Fig 4.8.

The identification of VOCs, in the landfill gas was similar to that described in section 3.2.1.1, where manual background subtraction was used to remove interfering ions from the background and adjoining peaks. Table 4.6 shows the improvement in quality matching after manual background subtraction compared with the 'auto' library search results. After manual background subtraction 148 compounds were identified and these are listed in Table 4.7 in order of retention time. Sample and matching compound mass spectra were very similar and these are shown in Appendix C. The various types of compounds found in the landfill gas include straight chain, branched chain, aromatic, cyclic, terpenic, naphthenic, chloro and alkenyl hydrocarbons. The compounds are listed under the various compounds classes in Table 4.8 (a) – (h). Those compounds typed in bold gave quality matches greater than or equal to 80 %.

The comparison between the Auto and Mahuar Match				
PERCENTAGE OF MATCH	AUTO MATCH	MANUAL MATCH		
	Number of Peaks	Number of Peaks		
No Match or visually wrong Match	0	0		
0~10%	0	0		
11~20%	1	0		
21~30%	1	0		
31~40%	4	0		
41 ~ 50%	3	2		
51 ~ 60%	15	9		
61 ~ 70%	11	6		
$71 \sim 80\%$	11	17		
81~90%	20	24		
91 ~100%	59	90		
Total	125	148		

Table 4.6The Comparison Between the 'Auto' and 'Manual' Match



Fig 4.9

PK#	RT	LIBRARY/ID	QUALITY
1	3.44	2-methylpropene-1	64
2	5.85	2-methylbutane	91
3	6.89	1,1-dimethylcyclopropane	86
4	7.06	Pentane	90
5	7.49	trans-1,2-dimethylcyclopropane	72
6	8.03	cis-1,2-dimethylcyclopropane	90
7	8.66	2,2-dimethylbutane	83
8	9.78	3-methylpentene-1	72
9	10.12	2,3-dimethylbutane	90
10	10.44	2-methylpentane	91
11	11.09	3-methylpentane	91
12	11.43	Hexene-1	90
13	12.01	Hexane	91
14	12.15	(E)-Hexene-3	76
15	12.26	(E)-Hexene-2	72
16	12.37	2,3-dimethylbutene-2	86
17	12.46	(Z)-3-methylpentene-2	94
18	12.68	(Z)-Hexane-2	90
19	13.09	Methylcyclopentane	90
20	13.45	2,4-dimethylpentane	90
21	14.26	Benzene	91
22	14.61	Cyclohexane	91
23	15.29	2,3-dimethylpentane	83
24	15.67	3-methylhexane	91
25	15.85	trans-1,3-dimethylcyclopentane	91
26	15.97	cis-1,3-dimethylcyclopentane	91
27	16.10	cis-1,2-dimethylcyclopentane	90
28	16.21	2,2,4-trimethylpentane	72
29	16.54	Hexamethyldisiloxane	80
30	16.83	Heptane	91
31	17.20	(Z)-5,5-dimethylhexene-2	90
32	17.42	(Z)-3,4-dimethylpentene-2	91
33	17.59	Methylcyclohexane,	91
34	17.73	1,1,3-trimethylcyclopentane	91
35	18.11	Ethylcyclopentane	94
36	18.25	2,5-dimethylhexane	91
37	18.33	2,4-dimethylhexane	91
38	18.53	1,2,4-trimethylcyclopentane	94
39	18.62	3,3-dimethylhexane	83
40	18.85	1,2,3-trimethylcyclopentane	96
41	18.98	2,3,4-trimethylpentane	9 0
42	19.18	Methylbenzene	94
43	19.49	2,3-dimethylhexane	83
44	19.82	2-methylheptane	91
45	19.87	4-methylheptane	91
46	20.14	trans-1,4-dimethylcyclohexane,	80
47	20.22	trans-1,3-dimethylcyclohexane	94
48	20.32	2,4-dimethylPentanone-3	64
49	20.42	1.1-dimethylcyclohexane	97
50	20.58	trans-1-ethyl-3-methylcyclopentane	93
51	20.68	cis-1-ethyl-3-methylcyclopentane	94
52	20.74	1-ethyl-2-methylcyclopentane	95

 Table 4.7

 The 148 Compounds Identified in Order of Retention Time

LIBRARY/ID **QUALITY** PK# RT 20.95 trans-1,2-dimethylcyclohexane 95 53 Tetrachloroethene 95 21.12 54 87 Octane 55 21.26 72 21.54 propylcyclopentane 56 1,1,3,3-tetramethylcyclopentane 72 57 21.81 2,3,5-trimethylhexane 91 21.91 58 91 cis-1-ethyl-2-methylcyclopentane 59 21.98 22.07 2,2,4-trimethylhexane 72 60 cis-1,2-dimethylcyclohexane 93 22.24 61 Ethylcyclohexane 90 22.48 62 93 1,1,3-trimethylcyclohexane 22.68 63 91 2,5-dimethylheptane 22.80 64 91 Ethylbenzene 23.32 65 91 1,3,5-trimethylcyclohexane 23.39 66 95 1,2&1,4-dimethylbenzene 23.71 67 90 2-methyloctane 68 23.99 87 3-methyloctane 69 24.26 95 1,3-dimethylbenzene 24.53 70 91 trans-1-ethyl-4-methylcyclohexane 71 24.79 cis-1-ethyl-4-methylcyclohexane 91 72 24.87 91 Nonane 73 25.37 74 3,5-dimethylheptene-3 74 25.52 64 cis-1-ethyl-2-methylcyclohexane 75 25.61 91 1-methylethylbenzene 76 25.80 80 Octahydro-2-methylpentalene 77 25.94 94 1-methylethylcyclohexane 78 26.01 72 3-methylheptane 79 26.09 53 Cyclodecane 80 26.19 91 Propylcyclohexane 81 26.44 94 (-)-α-Pinene 26.58 82 93 2,6-dimethyloctane 83 26.72 72 Propylbenzene 26.95 84 83 3-ethyl-2-methylheptane 85 27.00 96 Camphene 27.06 86 95 1-ethyl-3-methylbenzene 87 27.26 95 1-ethyl-2-methylbenzene 88 27.33 80 3,4-dimethyloctane 89 27.50 94 1.2.4-trimethylbenzene 90 27.55 74 4-methylnonane 91 27.75 91 2-methylnonane 92 27.85 80 1-B-Pinene 93 28.10 86 trans-1-methyl-4-(1-methylethyl-)cyclohexane 94 28.23 59 2-ethyl-1,3-dimethylcyclohexane 95 28.35 93 1,3,5-trimethylbenzene 96 28.50 50 cis-1-methyl-4-(1-methylethyl-)cyclohexane 97 28.61 60 1-methyl-3-(2-methylpropyl)cyclopentane 98 28.72 96 1,4-dichlorobenzene 99 28.86 59 2,2,4,6,6-pentamethylheptane 100 28.96 94 Decane 101 29.12 92 δ-3-Carene 102 29.34 90 1,2,3-trimethylbenzene 103 29.47 94 1-methyl-4-(1-methylethyl)benzene 104 29.61 64 1-propenylbenzene 105 29.85

 Table 4.7 (Continued)

PK#	RT	LIBRARY/ID	OUALITY
106	29.96	1-Limonene	94
107	30.09	2,2-dimethyldecane	72
108	30.15	3-methyl-5-propylnonane	59
109	30.22	Butylcyclohexane	91
110	30.35	3,8-dimethyldecane	59
111	30.44	1,4-diethylbenzene	97
112	30.53	1-methyl-2-propylbenzene	90
113	30.67	Diethylbenzene (Para?)	87
114	30.77	2-ethyl-1,4-dimethylbenzene	91
115	31.02	trans-Decahydronaphthalene	97
116	31.13	5-methyldecane	87
117	31.23	4-methyldecane	87
118	31.37	2-methyldecane	94
119	31.44	1-ethyl-2,4-dimethylbenzene	87
120	31.58	3-methyldecane	94
121	31.69	2-ethyl-1,3-dimethylbenzene	81
122	31.90	α-Fenchene	45
123	32.06	Undecene-5	64
124	32.28	l-methylbutylbenzene	53
125	32.37	1-methyl-3-(1-methylethyl)benzene	80
126	32.56	Undecane	94
127	32.80	4-ethyl-1,2-dimethylbenzene	90
128	32.91	1,2,3,5-tetramethylbenzene	94
129	32.99	2-methyldecahydronaphthalene	96
130	33.16	3,6-dimethyldecane	90
131	33.52	2-methyldecalin (probably trans)	96
132	33.70	Pentylcyclohexane,	94
133	33.81	2,3-dihydro-5-methylindene-1H	92
134	33.94	1-ethyl-3,5-dimethylbenzene	72
135	34.02	2,6-dimethylundecane	53
136	34.21	1,1-dimethylpropylbenzene	53
137	34.36	5-methylundecane	92
138	34.49	4-methylundecane	90
139	34.63	2-methylundecane	91
140	34.85	3-methylundecane	78
141	35.12	Spiro[5.5]dodecane	83
142	35.28	Decahydro-2,6-dimethylnaphthalene	86
143	35.40	1-methyl-2-pentylcyclohexane	72
144	35.53	Cyclododecane	49
145	35.75	Dodecane	93
146	36.24	6-methyldodecane	90
147	37.01	4-methylpentylcyclohexane	83
148	38.08	2.6.11-trimethyldodecane	72

Table 47 (Contin ሐ

Table 4.8 (a)Straight Chain Hydrocarbons in the 148 Compounds

PK#	<u></u>		OUALITY
4	7.06	Dentene	
13	12.01		90
30	14.01	Hexane	51
55	10.05	Heptane	91
	21.20	Octane	8/
/3	25.37	Nonane	91
101	29.12	Decane	94
126	32.56	Undecane	94
145	35.75	Dodecane	93

PK#	RT	LIBRARY/ID	
2	5.85	2-methylbutane	QUALITY
7	8.66	2.2-dimethylbutane	91
9	10.12	2.3-dimethylbutane	83
10	10.44	2-methylpentane	90
11	11.09	3-methylnentane	91
20	13.45	2.4-dimethylnentane	91
23	15.29	2.3-dimethylpentane	90
24	15.67	3-methylhexane	83
28	16.21	2,2,4-trimethylpentane	91 72
29	16.54	HexamethylDisiloxane	12
36	18.25	2.5-dimethylhexane	80 01
37	18.33	2,4-dimethylhexane	91
39	18.62	3,3-dimethylhexane	91
41	18.98	2,3,4-trimethylpentane	00
43	19.49	2,3-dimethylhexane	90 83
44	19.82	2-methylheptane	01
45	19.87	4-methylheptane	91
58	21.91	2,3,5-trimethylhexane	91
60	22.07	2,2,4-trimethylhexane	72
64	22.80	2,5-dimethylheptane	91
68	23.99	2-methyloctane	90
69	24.26	3-methyloctane	87
79	26.09	3-methylheptane	72
83	26.72	2,6-dimethyloctane	93
85	27.00	3-ethyl-2-methylheptane	83
89	27.50	3,4-dimethyloctane	80
91	27.75	4-methylnonane	74
92	27.85	2-methylnonane	91
100	28.96	2,2,4,6,6-pentamethylheptane	59
107	30.09	2,2-dimethyldecane	72
108	30.15	3-methyl-5-propylnonane	59
110	30.35	3,8-dimethyldecane	59
110	31.13	5-methyldecane	87
110	31.23	4-methyldecane	87
110	31.37	2-methyldecane	94
120	31.58	3-methyldecane	94
130	33.10	3,6-dimethyldecane	62
125	33.52	2-methyldecalin (probably trans)	96
133	34.02	2,6-dimethylundecane	53
137	34.30	5-methylundecane	92
120	34,49 31 60	4-methylundecane	90
140	34.03 21.95	2-methylundecane	91
140	34.03 35 13	3-methylundecane	78
146	35.12	Spiro[5.5]dodecane	83
1/12	30.24 28 00	6-methyldodecane	90
140	30.08	2,6,11-trimethyldodecane	12

Table 4.8 (b) Branched Chain Hydrocarbons in the 148 Compounds

RT PK# LIBRARY/ID QUALITY 14.26 21 Benzene 91 42 19.18 Methylbenzene 94 65 23.32 Ethylbenzene 91 67 23.71 1,2&1,4-dimethylbenzene 95 70 24.53 1,3-dimethylbenzene 95 76 25.80 1-methylethylBenzene 91 26.95 84 Propylbenzene 72 87 27.26 1-ethyl-3-methylbenzene 95 88 27.33 1-ethyl-2-methylbenzene 95 90 27.55 1,2,4-trimethylbenzene 94 96 28.50 1,3,5-trimethylbenzene 93 103 29.47 1,2,3-trimethylbenzene 90 104 29.61 1-methyl-4-(1-methylethyl)benzene 94 29.85 105 1-propenylbenzene 64 30.44 1,4-diethylbenzene 111 97 30.53 1-methyl-2-propylbenzene 112 90 30.67 Diethylbenzene (Para?) 113 87 114 30.77 2-ethyl-1,4-dimethylbenzene 91 119 31.44 1-ethyl-2,4-dimethylbenzene 87 2-ethyl-1,3-dimethylbenzene 121 31.69 81 124 32.28 1-methylbutylbenzene 53 125 32.37 1-methyl-3-(1-methylethyl)benzene 80 4-ethyl-1,2-dimethylbenzene 127 32.80 90 1,2,3,5-tetramethylbenzene 94 128 32.91 134 33.94 1-ethyl-3,5dimethylbenzene 72 1,1-dimethylpropylbenzene 136 34.21 53

 Table 4.8 (c)

 Aromatic Chain Hydrocarbons in the 148 Compounds

 Table 4.8 (d)

 Cyclic Hydrocarbons in the 148 Compounds

PK#	RT	LIBRARY/ID	
3	6.89	1.1-dimethylcyclopropane	
5	7.49	trans-1.2-dimethylcyclopropane	80
6	8.03	cis-1.2-dimethylcyclopropane	72
19	13.09	Methylcyclopentane	90
22	14.61	Cyclohexane	90
25	15.85	trans-1.3-dimethylcyclopentane	91
26	15.97	cis-1.3-dimethylcyclopentane	91
27	16.10	cis-1.2-dimethylcyclopentane	91
33	17.59	Methylcyclohexane	90
34	17.73	1.1.3-trimethylcyclonentane	91
35	18.11	Ethylcyclopentane	91
38	18.53	1.2.4-trimethylcyclopentane	94
40	18.85	1.2.3-trimethylcyclopentane	94
46	20.14	trans-1.4-dimethylcyclohevane	90
47	20.22	trans-1.3-dimethylcyclohevane	80
49	20.42	1.1-dimethylcycloheyane	94
50	20.58	trans-1-ethyl-3-methylcyclopentane	9/
51	20.68	cis-1-ethyl-3-methylcyclopentane	93
52	20.74	1-ethyl-2-methylcyclopentane	24 05
53	20.95	trans-1.2-dimethylcyclohexane	95
56	21.54	Propylcyclopentane	93 72
57	21.81	1.1.3.3-tetramethylcyclopentane	72
59	21.98	cis-1-ethyl-2-methylcyclopentane.	01
61	22.24	cis-1,2-dimethylcyclohexane	03
62	22.48	Ethylcyclohexane.	90
63	22.68	1,1,3-trimethylcyclohexane	93
66	23.39	1,3,5-trimethylcyclohexane	91
71	24.79	trans-1-ethyl-4-methylcyclohexane	91
72	24.87	cis-1-ethyl-4-methylcyclohexane	91
75	25.61	cis-1-ethyl-2-methylcyclohexane	64
78	26.01	1-methylethylcyclohexane	94
80	26.19	Cyclodecane	53
81	26.44	Propylcyclohexane,	91
94	28.23	trans-1-methyl-4-(1-methylethyl-)cyclohexane	86
95	28.35	2-ethyl-1,3-dimethylcyclohexane	59
97	28.61	cis-1-methyl-4-(1-methylethyl-)cyclohexane	50
98	28.72	1-methyl-3-(2-methylpropyl)cyclopentane	60
109	30.22	Butylcyclohexane	91
132	33.70	Pentylcyclohexane	94
143	35.40	1-methyl-2-pentylcyclohexane	72
144	35.53	Cyclododecane	49
147	37.01	4-methylpentylcyclohexane	83

Table 4.8 (e)

	Ter	penic	Hvd	rocarbon	s in tl	he 148	Com	oounds	
_					•		00444		_

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PK#	RT	LIBRARY/ID	QUALITY
82	26.58	(-)-α-Pinene	94
86	27.06	Camphene	96
93	28.10	1- B -Pinene	80
102	29.34	δ-3-Carene	92
106	29.96	1-Limonene	94
122	31.90	α-Fenchene	45

	Naphtheme Hydrocarbons in the 146 Compounds					
PK#	RT	LIBRARY/ID	QUALITY			
77	25.94	Octahydro-2-methylpentalene	80			
115	31.02	trans-Decahydronaphthalene	97			
129	32.99	Decahydro-2-methylnaphthalene	96			
142	35.28	Decahydro-2,6-dimethylnaphthalene	86			

 Table 4.8 (f)

 Naphthenic Hydrocarbons in the 148 Compounds

Table 4.8 (g)

Chloro Hydrocarbons in the 148 Compounds				
PK#	RT	LIBRARY/ID	QUALITY	
54	21.12	Tetrachloroethene	95	
99	28.86	1,4-dichlorobenzene	96	

Aikenyi Hyutocarbons in the 148 Compounds			
PK#	RT	LIBRARY/ID	QUALITY
1	3.44	2-methylpropene-1	64
8	9.78	3-methylpentene-1	72
12	11.43	1-Hexene	90
14	12.15	(E)-3-Hexene	76
15	12.26	(E)-2-Hexene	72
16	12.37	2,3-dimethylbutene-2	86
17	12.46	(Z)-3-methylpentene-2	94
18	12.68	(Z)-2-hexene	90
31	17.20	(Z)-5,5-dimethylhexene-2	90
32	17.42	(Z)-3,4-dimethylpentene-2	91
48	20.32	2,4-dimethylpentanone-3	64
74	25.52	3,5-dimethylheptene-3	74
123	32.06	Undecene-5	64
133	33.81	2,3-dihydro-5-methylindene-1H	92

Table 4.8 (h)	
Ikenvl Hydrocarbons in the 148 (Compounds

4.2.2. Positive Identification of Straight Chain, Cyclic, Aromatic and Terpenic Hydrocarbons Using Standards

The next part of the study focused on the positive identification of some selected VOCs present in the landfill gas. The protocol used to positively identify various VOCs in the landfill gas was similar to that used for solvent desorption studies in Section 3.2.1.2.

Fig 4.10 (a) and (b) show the separation of various VOCs present in the landfill gas and the separation of the standard compounds respectively. Fig 4.10 (b) shows the chromatogram which was generated by desorbing a CarbotrapTM 300 Multi-bed tube onto which a standard gas mixture had been adsorbed. The standard gas mixture contained 0.238 μ l of each compound in 5 L nitrogen, and 50 ml of this mixture was loaded onto the tube as described in Section 2.8.3. Table 4.9 shows the retention time of the VOCs in the sample compared with those of the standard compounds. Table 4.10 lists the twenty-six straight chain, cyclic, aromatic and terpenic hydrocarbons present in the landfill gas which were positively identified.

Fig 4.11 shows the mass spectra of these compounds in the sample chromatogram, the mass spectra of standard compounds and the mass spectra of compound from the library match. Positive identification was indicated when retention times and mass spectra were similar. Results showed that the 'best matches' as determined by the library search were correct in all cases. A discussion on the cis- and trans- isomers of 1,2-dimethylcyclohexane and the isomers of dimethylbenzene is given in Section 3.2.1.2.







Fig 4.10 (b) Total Ion Chromatogram from Standard Gaseous Mixture

Та	ble	4.9

NO	COMPOUND	RT OF SAMPLE	RT OF STANDARD
NU	COMPOUND	(MINUTES)	(MINUTES)
1	Hexane	12.02	12.01
2	Benzene	14.26	14.19
3	Cyclohexane	14.61	14.59
4	Heptane	16.83	16.80
5	Methylcyclohexane	17.59	17.57
6	Methylbenzene	19.18	19.12
7	1,4-Dimethylcyclohexane	20.14	20.09
8	trans-1,2-Dimethylcyclohexane	20.95	20.94
9	Octane	21.26	21.15
10	cis-1,2-Dimethylcyclohexane	22.24	22.19
11	Ethylcyclohexane	22.48	22.51
12	Ethylbenzene	23.32	23.29
13	1,2 & 1,4-dimethylbenzene	23.71	23.75
14	1,3-dimethylbenzene	24.53	24.54
15	Nonane	25.37	25.38
16	iso-Propylcyclohexane	26.01	26.05
17	a-Pinene	26.58	26.60
18	Propylbenzene	26.95	26.97
19	1,2,4-Trimethylbenzene	27.55	27.58
20	B-Pinene	28.10	28.13
21	1.3.5-Trimethylbenzene	28.50	28.53
22	Decane	29.12	29.18
23	1-Limonene	29.96	29.98
24	Undecane	32.56	32.60
25	Dodecane	35.75	35.79

The Comparison of Retention Time Between the Sample and Standard

The Compounds Listed Under the Various Classes				
STRAIGHT CHAIN HYDROCARBONS	CYCLIC HYDROCARBONS	AROMATICS HYDROCARBONS	TERPENIC HYDROCARBONS	
Hexane	Cyclohexane	Benzene	a-Pinene	
Heptane	Methylcyclohexane	Methylbenzene	β-Pinene	
Octane	trans-1,2-dimethylcyclohexane	1,2-dimethylbenzene	1-Limonene	
Nonane	cis-1,2-dimethylcyclohexane	1,3-dimethylbenzene		
Decane	1,4-dimethylcyclohexane	1,4-dimethylbenzene		
Undecane	Ethylcyclohexane	Ethylbenzene		
Dodecane	iso-propylcyclohexane	Propylbenzene		
		1,2,4-trimethylbenzene		
		1,3,5-trimethylbenzene		

Table 4.10The Compounds Listed Under the Various Classes



Fig 4.11 The Comparison of Mass Spectra from Sample, Standard and Library Match







Fig 4.11 The Comparison of Mass Spectra from Sample, Standard and Library Match

4.3. Quantitative Analysis

Over a hundred compounds were present in the landfill gas and quantitation of each compound with reference to its standard is not practical. As discussed in Section 3.2.2 this problem is overcome by direct quantitation of some compounds and semiquantitation of others. In this study over sixty VOCs were quantified as follows. The twenty-six compounds positively identified using standards in Section 4.2.2 were quantified directly using standard and the calibration plots. Other VOCs were semiquantified using standards which represented various compounds in the landfill gas.

The quantitative analysis of straight chain, cyclic, aromatic and terpenic hydrocarbons positively identified in Section 4.2.2 was conducted in three parts. Firstly, calibration plots were prepared. Secondly, the determination of detection limits and finally the VOCs in a landfill gas sample from leachate well A_{1-1} of landfill site A was analysed for the above-mentioned VOCs. The concentrations of these VOCs found in the landfill gas sample will be presented in Section 4.3.3 together with those of other VOCs which were semi-quantified.

4.3.1. Calibration Plots

It is difficult to use an internal standard method for the quantitative analysis using thermal desorption. Firstly, it would be difficult to add a very small amount of pure compound into the thermal desorption tube containing the sample from the landfill gas. Secondly, even if the pure compound could be added to the thermal desorption tube, some highly volatile components may be lost which the tube in open for the addition. Therefore, for the thermal desorption study, a standard calibration curve was used for the quantitative analysis.

The method of standard calibration curve used was similar to the sampling of landfill gas and involved loading the Carbotrap[™] 300 multi-bed thermal desorption tubes with 'gaseous' compounds and this method is described below.

1. 50 ml of a standard gas containing 0.04000, 0.1000, 0.2000, 0.3000, 0.4000 or 0.8000 µl each of 26 compounds (see Section 2.9.2) in 5000 ml of N₂ was introduced into a CarbotrapTM 300 multi-bed thermal desorption tube at a flow rate of 100 ml/min. This flow rate was typical of that used to collect VOCs from landfill gas. The tubes were then refrigerated at 4 °C overnight, again this was the same as the treatment of tubes used to collect landfill gas. See Section 2.9.3 for preparation of standard gas sample. The CarbotrapTM 300 multi-bed thermal desorption tube contained 0.400, 1.00, 2.00, 3.00, 4.00 or 8.00 nl of each compound.

- 2. The Carbotrap[™] 300 Multi-bed tubes were separately desorbed in the Thermal Desorption Unit (See section 2.7.3) and the desorbed sample was gas chromatographed after being split 50:1 at the TDU. Peak areas for each compound of all solutions were recorded (PA).
- 3. The standard calibration curves were plotted with the peak areas (PA) against the concentrations.

Table 4.11 shows concentration and mass data of the solutions used to construct the calibration plots (See section 2.9.3 for standard gaseous mixture preparation). Injection mode was split 50:1 at the TDU. The mass injected was calculated as follows:

Mass Injected (ng) = C (μ l/ml) × D (mg/ μ l) × VA (ml) × SR (1/50) × 10⁶

C —— Concentration of each compound in the standard gas;
D —— Density of each compound;
VA —— Volume of the standard gas passed through absorption tube;
SR —— Split Ratio at the TDU.

In the case of 1,2-dimethylcyclohexane, because the standard material used was a mixture of the cis- and trans- isomers, the calibration plot was prepared using the sum of peak areas for both isomers. In the case of 1,2- and 1,4-dimethylbenzene, because these compounds co-elute, the mass injected is the total for both isomers.

Concentrations of Standard Solutions for the Calibration Plots						
	SOLUTION CONCENTRATION (µl/ml) X 10 ⁵					
COMPOUND	[16]	[8]	[6]	[4]	[2]	[0.8]
		MA	ASS INJ	ECTED	ng)	[]
	M ₁	M ₂	M ₃	M ₄	⁻ ⁵ M ₅	M ₆
Hexane	106	52.8	39.6	26.4	13.2	5.28
Benzene	140	70.1	52.6	35.1	17.5	7.01
Cyclohexane	125	62.3	46.7	31.1	15.6	6.23
Heptane	109	54.7	41.0	27.3	13.7	5.47
Methylcyclohexane	123	61.6	46.2	30.8	15.4	6.16
Methylbenzene	139	69.4	52.0	34.7	17.3	6.94
1,4-Dimethylcyclohexane	125	62.6	47.0	31.3	15.7	6.26
trans-1,2-Dimethylcyclohexane	127	63.7	47.8	31.9	15.9	6.37
Octane	112	56.2	42.2	28.1	14.1	5.62
cis-1,2-Dimethylcyclohexane	124	62.1	46.6	31.0	15.5	6.21
Ethylcyclohexane	126	63.0	47.3	31.5	15.8	6.30
Ethylbenzene	139	69.4	52.0	34.7	17.3	6.94
1,2 & 1,4-dimethylbenzene	141	70.4	52.8	35.2	17.6	7.04
1,3-dimethylbenzene	138	69.1	51.9	34.6	17.3	6.91
Nonane	115	57.4	43.1	28.7	14.4	5.74
iso-Propylcyclohexane	127	63.5	47.6	31.7	15.9	6.35
a-Pinene	137	68.7	51.5	34.3	17.2	6.87
Propylbenzene	138	69.0	51.7	34.5	17.2	6.90
1,2,4-Trimethylbenzene	140	70.1	52.5	35.0	17.5	7.01
β-Pinene	139	69.6	52.2	34.8	17.4	6.96
1,3,5-Trimethylbenzene	138	69.2	51.9	34.6	17.3	6.92
Decane	117	58.4	43.8	29.2	14.6	5.84
1-Limonene	135	67.4	50.5	33.7	16.8	6.74
Undecane	118	59.2	44.4	29.6	14.8	5.92
Dodecane	120	59.9	44.9	29.9	15.0	5.99

 Table 4.11

 Concentrations of Standard Solutions for the Calibration Plats

(* Total mass injected for both isomers)

Calibration plots are shown in Fig 4.12. The plots include calibration equations and correlation coefficients. All plots were linear with correlation coefficients of 0.999.



Fig 4.12 Calibration Plots for Each Compound

0.006



0.00E+0



MASS INJECTED (ng)

1.40



-

MASS INJECTED (ng)

a obe

.0

40

60



100

120

20

MASS INJECTED (ng)

140 164

0.00

э

40

60

100

50

MASS INJECTED (112)

120

140





Fig 4.12 Calibration Plots for Each Compound

4.3.2. Detection Limits

According to National Association of Testing Authorities (NATA) Technical Note $17^{(112)}$ "Format and Content of Test Methods and Procedures for Validation and Verification of Chemical Test Methods", the limit of detection is the concentration of analyte giving a signal-to-noise ratio of 3:1. TDU-GC/MS detection limits for the twenty-six VOCs of interest were determined by dilution with N₂ of a standard gaseous mixture until the peak height to noise ratio was between 2 and 3. For this part of the study the procedure used to determine detection limits is described below and involved the apparatus described in Section 2.6.3.

- 1. 50 ml of a 5 L standard gaseous mixture containing 0.04 μ l of each VOC per liter of N₂ (prepared as described in Section 2.9.3) was introduced into a thermal desorption tube as described in Section 2.8.3, step 6 – 10. The VOCs were then thermally desorbed and chromatographed using the conditions outlined in Section 4.1.4.2.
- Half of the standard gaseous mixture was expelled into a fumehood by pumping
 2.5 L air into the container.
- 3. The standard gaseous mixture was diluted by introducing N_2 as described in Section 2.6.3, step 1 4 until the volume was again 5 L.
- 4. 50 ml of the diluted standard gaseous mixture was introduced into a thermal desorption tube, after which the VOCs were thermally desorbed and chromatographed.
- 5. The dilution and analysis procedure was repeated until the GC-MS peak height to noise ratio was between 2 and 3.

Table 4.12 shows detection limits in terms of standard gas concentration and mass injected. It should be noted that standard gaseous concentration limit represents that for collection of a 50 ml gas sample. These values have been adjusted for signal to noise ratio of three. The mass injected was calculated by the formula shown below:

Mass Injected (ng) = C (μ l/ml) × D (mg/ μ l) × V (ml) × S (1/50) × 10⁶ (ng/mg)

- C —— Concentration of each compound in the standard gas;
- **D** Density of each compound;
- V Volume of the standard gas passed through absorption tube;
- S —— Split Ratio at the TDU.

In the case of 1,2- and 1,4-dimethylbenzene, because these compounds co-elute, detection limit is the total for both compounds.

Detection Limits for the 26 VOCs				
	CONCENTRATION			
COMPOUND	IN THE	MASS INJECTED		
COMPOUND	STANDARD GAS	(ng)		
	$(\mu l/L) \times 10^3$	(~8)		
Hexane	0.299	0.197		
Benzene	0.335	0.293		
Cyclohexane	0.278	0.216		
Heptane	0.283	0.194		
Methylcyclohexane	0.372	0.286		
Methylbenzene	0.346	0.300		
1,4-Dimethylcyclohexane	0.575	0.450		
trans-1,2-Dimethylcyclohexane	1.087	0.866		
Octane	0.271	0.191		
cis-1,2-Dimethylcyclohexane	0.262	0.203		
Ethylcyclohexane	0.285	0.224		
Ethylbenzene	0.288	0.249		
^a 1,2 & 1,4-dimethylbenzene	0.244	0.215		
1,3-dimethylbenzene	0.278	0.241		
Nonane	0.557	0.400		
iso-Propylcyclohexane	0.391	0.310		
a-Pinene	0.274	0.235		
Propylbenzene	0.189	0.163		
1,2,4-Trimethylbenzene	0.209	0.183		
β-Pinene	0.224	0.195		
1,3,5-Trimethylbenzene	0.146	0.126		
Decane	0.230	0.168		
1-Limonene	0.198	0.167		
Undecane	0.191	0.141		
Dodecane	0.151	0.113		

Table 4.12Detection Limits for the 26 VOC:

^a: Total for both compounds.

4.3.3. Semi-Quantitative Analysis of Some Other VOCs Present in the Landfill Gas

A number of other VOCs were present with an appreciable abundance in the landfill gas and include branched chain alkanes, cyclic alkanes, alkyl aromatics and terpenes. These compounds were quantified as follows. A particular standard used to construct the calibration plots in Section 4.3.1 was chosen to represent a number of compounds in the landfill gas. From the sample chromatogram the peak area of the compounds to be quantified were determined and their concentrations were determined directly from the standard calibration plot. This procedure assumes that the detector response for the standard and the compounds to be quantified are the same. The various standards used to quantify a number of other abundant compounds in the landfill gas are listed in Table 4.13.

COMPOLINDS	STANDADD USED EOD OUA MERITA TION	
2-methylhutane	STATUARD USED FOR QUANTITATION	
Pentane		
2-methylnentane	Hexane	
3-methylpentane		
3-methylhexane	Hantana	
2-methylheptane		
4-methylheptane	Octane	
2,5-dimethylheptane	Nonane	
2-methyloctane		
3-methyloctane		
2,6-dimethyloctane		
3-ethyl-2-methylheptane		
3,4-dimethyloctane	5	
4-methylnonane	Decane	
2-methylnonane		
3-methylnonane		
5-methyldecane	Undecane	
4-methyldecane		
2-methyldecane		
2,2,4,6,6-pentamethylheptane	Dodecane	
Methylcyclopentane	Cyclohexane	
trans-1,3-dimethylcyclohexane	trans 1.4 dimethylayalahayana	
cis-1,3-dimethylcyclohexane		
trans-1-ethyl-4-methylcyclohexane		
cis-1-ethyl-4-methylcyclohexane		
Propylcyclohexane	1-methylethylcyclohexane	
1-methyl-4-(1-methylethyl)cyclohexane		
Butylcyclohexane		
1-methylethylbenzene		
3-ethyl-2-methylbenzene		
1-ethyl-2-methylbenzene		
1-ethyl-4-methylbenzene	Pronylbenzene	
1,2,3-trimethylbenzene	Tropyidenzene	
1-methyl-4-(1-methylethyl)benzene		
1-methyl-2-propylbenzene		
2-ethyl-1,4-dimethylbenzene		
Camphene	α-Pinene	

Table 4.13 The List of Standards Used to Quantify Other Compounds in the Landfill Gas

4.3.4. Analysis of VOCs in a Landfill Gas Sample

A landfill gas sample taken from leachate well A_{1-1} of landfill site A on the 1st July 1997 was analysed using both direct calibration and semi-quantitative calibration as explained in Section 4.1.3 and above, respectively. The concentrations of the various VOCs are shown in Table 4.14. Those compounds marked with asterisks have been semi-quantified. It should be noted that the concentration of dimethylbenzene is the total for both the 1,2- and 1,4- isomers.

COMPOUNDS	С (µg/L)
ALKANES	
2-methylbutane*	BDL ^a
Pentane*	BDL
2-methylpentane*	0.091 - 0.111
3-methylpentane*	0.066 - 0.080
Hexane	0.118 - 0.182
3-methylhexane*	0.181 - 0.357
Heptane	0.275 - 0.539
2-methylheptane*	0.089 - 0.262
4-methylheptane*	0.220 - 0.226
Octane	0.209 - 0.312
2,5-dimethylheptane*	0.104 - 0.480
2-methyloctane*	0.187 - 0.917
3-methyloctane*	0.185 - 0.329
Nonane	0.314 - 0.560
2,6-dimethyloctane*	0.148 - 0.229
3-ethyl-2-methylheptane*	BDL
3,4-dimethyloctane*	BDL
4-methylnonane*	0.079 - 0.227
2-methylnonane*	0.202 - 0.206
3-methylnonane*	BDL
Decane	0.250 - 0.483
5-methyldecane*	0.040 - 0.056
4-methyldecane*	BDL
2-methyldecane*	0.049 - 0.074
Undecane	0.039 - 0.143
2,2,4,6,6-pentamethylheptane*	0.102 - 0.152
Dodecane	0.001 - 0.029
CYCLIC HYDROCARBONS	
Methylcyclopentane*	0.005 - 0.074
Cyclohexane	0.115 - 0.115
Methylcyclohexane	0.217 - 0.460
trans-1,4-dimethylcyclohexane	0.715 - 0.996
trans-1,3-dimethylcyclohexane*	BDL
cis-1,3-dimethylcyclohexane*	BDL
trans-1,2-dimethylcyclohexane	0.656 - 1.122
cis-1,2-dimethylcyclohexane	0.081 - 0.091
Ethylcyclohexane	0.180 - 0.295
trans-1-ethyl-4-methylcyclohexane*	BDL
cis-1-ethyl-4-methylcyclohexane*	0.051 - 0.165
1-methylethylcyclohexane	0.073 - 0.162
Propylcyclohexane*	0.084 - 0.133
1-methyl-4-(1-methylethyl)cyclohexane*	0.037 - 0.119
Butylcyclohexane*	0.049 - 0.091

Table 4.14The Concentrations of Compounds from the Leachate Well A1-1 of Site A

^a: BDL – Below Detection Limit

Table 4.14 (Continued)

COMPOUNDS	C (µg/L)
AROMATIC HYDROCARBONS	
Benzene	1.073 - 1.119
Methylbenzene	0.338 - 0.486
Ethylbenzene	0.569 - 0.586
1,2&1,4-dimethylbenzene	0.317 - 0.366
1,3-dimethylbenzene	0.168 - 0.201
1-methylethylbenzene*	0.067 - 0.320
Propylbenzene	0.218 - 0.250
3-ethyl-2-methylbenzene*	0.093 - 0.297
1-ethyl-2-methylbenzene*	0.116 - 0.247
1-ethyl-4-methylbenzene*	0.075 - 0.148
1,2,4-trimethylbenzene	0.076 - 0.235
1,3,5-trimethylbenzene	0.142 - 0.245
1,2,3-trimethylbenzene*	0.064 - 0.362
1-methyl-4-(1-methylethyl)benzene*	0.098 - 0.102
1-methyl-2-propylbenzene*	0.083 - 0.092
2-ethyl-1,4-dimethylbenzene*	0.053 - 0.101
TERPENIC HYDROCARBONS	
α-Pinene	0.202 - 0.397
Camphene*	BDL
β-Pinene	0.186 - 0.213
1-Limonene	BDL
CHAPTER V METHODOLOGY AND PROCEDURES FOR TEDLAR[®] BAG AND CRYOGENIC TRAPPING TECHNIQUES

The studies reported in this chapter were conducted using landfill gas from leachate well A_{1-1} of landfill site A (see Table 6.1 and 6.2). Section 5.1 describes the collection of landfill gas in Tedlar[®] bags and Section 5.2 describes the cryogenic trapping or 'freezing out' of VOCs from landfill gas.

5.1. Optimisation of Sampling and Gas Chromatographic Separation Protocols for Tedlar[®] Bags

VOCs in landfill gas collected in Tedlar[®] bags were analysed by gas chromatography employing flame ionization detection (see Section 2.10.6). The GC column used was the $25m \times 0.25mm$ ID, 1 µm film thickness methylsilicone column employed for the solvent desorption studies described Section 3.1.4.

5.1.1. The Sampling Train

The sampling train used to collect VOCs in landfill gas using Tedlar[®] bags is shown in Fig 5.1. The sampling procedure, except for sampling time which is discussed below, and sampling train components are described in Section 2.10. When sampling relatively wet landfill gas moisture was clearly visible in the Tedlar[®] bag. Moisture present in the gas during gas chromatographic analysis may interfere with the separation of the VOCs and therefore the landfill gas was dried before collection. The moisture trap is discussed in Section 3.1 and moisture trap construction is described in Section 2.2. The sampling train in Fig 5.1 shows that landfill gas passes through the pump before collection in Tedlar[®] bags. Therefore it is possible that lubricant volatiles from the pump may be introduced into the Tedlar[®] bag. Sampling of pure nitrogen followed by GC-FID analysis showed that no pump contaminants were present in the Tedlar[®] bag. The moisture indicator tube (see Section 2.2.1.5) was not employed for Tedlar[®] bag sampling as the volume of gas collected (5L) was small. Also, if it were to be used it would need to be placed before the Tedlar[®] bag where it would act as an adsorbent and defeat the purpose of its use.



Fig 5.1 The Sampling Train Using Tedlar[®] Bag

The collection of VOCs in landfill gas using Tedlar[®] bags is a 'non-preconcentration' technique and therefore sampling time only determines how much gas is collected. However, sampling time is important where longer sampling times allow a more representative sample of gas to be collected. For the 5 L Tedlar[®] bags using a pump flow rate of 200 ml/min, that typically used when sampling with adsorption tubes, the sampling time would be 25 minutes. In this study a pump flow rate of 50 ml/min was used giving a sampling time of 100 minutes.

5.1.2. Optimisation of Gas Chromatographic Conditions

5.1.2.1. Standard Gaseous Mixture

Initial studies with the Tedlar[®] bag technique involved preparing a standard gaseous mixture containing 23 straight chain, cyclic and aromatic VOCs in nitrogen (see Section 2.10.4 – 2.10.5). One milliliter (1.00 ml) of this gas was injected directly into the GC using a 1 ml gas syringe and the VOCs were then separated on a capillary methylsilicone column (BP-1, $25m \times 0.25mm$ ID, 1 µm film thickness). An initial consideration was splitless or split injection mode. Obviously when sampling landfill gas with relatively low levels of VOCs then splitless injection allows more sample onto the column, therefore, in this study the injection mode was splitless.

5.1.2.2. Sample Refocusing and GC Temperature Programme

The total flow passing through the GC system is ≈ 1 ml/min and consequently the band width of compounds entering the column can not be sharper than the 1 minute injection time unless the gas sample is refocused at the head of the column before the separation begins. Cryogenic refocusing employing liquid CO₂ was used in this study to refocus injected samples from the Tedlar[®] bag at the head of the GC column. Fig 5.2 (a) and (b) show the separation of the standard gas sample using ambient and sub ambient starting temperatures, respectively. The gas chromatographic conditions are shown in the figure legends.



Fig 5.2 (a) The Separation of the Desorbed Standard (Ambient Starting Temperature) [The GC-FID conditions were: Carrier Gas: Helium; Carry Gas Flow: 1 ml/min at room temp; Injection Mode: Splitless; Solvent delay: 0 min.]



Fig 5.2 (b) The Separation of the Desorbed Standard (Sub-Ambient Starting Temperature) [The GC- FID conditions were shown as Fig 5.2 (a)]

Fig 5.2 (a) shows that at ambient temperatures the high boiling late eluting compounds which condense at the head of the column have narrow band widths, but the lower boiling early eluting compounds are extremely broad. When the starting temperature is lowered to -20 °C, Fig 5.2 (b) shows that all compounds are able to

condense at the head of the GC column in a narrow band resulting in sharp chromatographic peaks. Apart from the injection mode the GC conditions used for the tedlar bag study were the same as those used for thermal desorption study.

From the findings above and those in Section 5.1.1 the sampling and gas chromatographic protocols developed for VOCs in landfill gas using Tedlar[®] bag can be summarized as follows:

- Landfill gas is initially dried by passing through the moisture trap;
- Sampling times of up to 100 minutes and flow rate of 50 ml/min are used;
- VOCs are collected in the 5 L Tedlar[®] bag (see Section 2.10.2) and injected directly into the GC using a 1 ml gas syringe;
- A Capillary BP-1, 25m × 0.25mm ID, 1 μm film thickness column is used and chromatographic conditions (GC-FID) are described as following:

<u>Carrier Gas</u> :	Helium.
<u>Carrier Gas Flow</u> :	1 ml/min at Room Temp.
Injection Temp:	Injector 250 °C.
Injection Mode:	Splitless.
Oven Temp:	-20 – 100 °C @ 3 °C/min
	100 – 280 °C @ 20 °C/min.
Cryogenic Fluid:	Liquid CO ₂ .

5.1.3. Qualitative Analysis of Samples Collected Via Tedlar[®] Bag

The next part of the study was the identification of the VOCs in the landfill gas. The collection and chromatographic conditions employed are as in Section 5.1.1 and Section 5.1.2 above. Fig 5.3 shows the separation of VOCs in landfill gas. The GC conditions used for Tedlar[®] bag studies were the same as those used for thermal desorption studies. The GC conditions are shown in the figure legend and the oven program shown in the chromatogram. The large peak eluting at ≈ 2 minutes in Fig 5.3

is more likely due to CH_4 and not CO_2 , the two major components of landfill gas, as the FID detector does not respond to $CO_2^{(113)}$.



5.1.3.1. Positive Identification of Straight Chain, Cyclic and Aromatic Hydrocarbons Using Standards by GC with Flame Ionization Detection

The protocol used to positively identify various VOCs in the landfill gas was comparison of retention times of selected VOCs present in the landfill gas with these of standard compounds

Fig 5.4 (a) and (b) show the separation of various VOCs present in the landfill gas and the separation of the standard compounds respectively. Fig 5.4 (b) shows the chromatogram which was generated by injecting a standard gas mixture (see Section 2.10.5). The standard gas mixture contained 0.455 μ l of each compound in 5 L nitrogen, and 1 ml of this mixture was injected into the injection port using the 1 ml gas syringe.

Table 5.1 shows the retention time of the VOCs in the sample compared with those of the standard compounds. Table 5.2 lists the twenty-three straight chain, cyclic and aromatic hydrocarbons present in the landfill gas which were identified by retention time matching.



[The GC- FID conditions were shown as Fig 5.2 (a)]

	Table 5.1				
<u> </u>	he Comparison of Retention Tin	ne Between the Samp	le and Standard		
NO.	COMPOUND	RT OF SAMPLE (Minutes)	RT OF STANDARD (Minutes)		
1	Hexane	12.02	12.00		
2	Benzene	13.36	13.32		
3	Cyclohexane	13.69	13.67		
4	Heptane	14.97	14.99		
5	Methylcyclohexane	15.57	15.51		
6	Methylbenzene	16.71	16.64		
7	1,4-Dimethylcyclohexane	17.20	17.19		
8	trans-1,2-Dimethylcyclohexane	17.82	17.80		
9	Octane	17.95	17.99		
10	cis-1,2-Dimethylcyclohexane	18.81	18.79		
11	Ethylcyclohexane	18.94	18.96		
12	Ethylbenzene	19.43	19.52		
13	1,2 & 1,4-Dimethylbenzene	19.72	19.80		
14	1,3-Dimethylbenzene	20.31	20.27		
15	Nonane	21.06	21.05		
16	iso-Propylcyclohexane	21.99	21.96		
17	Propylbenzene	22.44	22.41		
18	1,2,4-Trimethylbenzene	23.24	23.19		
19	1,3,5-Trimethylbenzene	23.90	23.93		
20	Decane	24.47	24.63		
21	Undecane	27.96	27.98		
_22	Dodecane	31.46	31.48		

.

<u>1 ne Compounds Listed Under the Various Classes</u>			
STRAIGHT CHAIN	CYCLIC	AROMATICS	
HYDROCARBONS	HYDROCARBONS	HYDROCARBONS	
n-Hexane	Cyclohexane	Benzene	
n-Heptane	Methylcyclohexane	Methylbenzene	
n-Octane	1,4-Dimethylcyclohexane	1,2-Dimethylbenzene	
n-Nonane	trans-1,2-Dimethylcyclohexane	1,3-Dimethylbenzene	
n-Decane	cis-1,2-Dimethylcyclohexane	1,4-Dimethylbenzene	
n-Undecane	Ethylcyclohexane	Ethylbenzene	
n-Dodecane	iso-Propylcyclohexane	Propylbenzene	
		1,2,4-Trimethylbenzene	
		1,3,5-Trimethylbenzene	

 Table 5.2

 The Compounds Listed Under the Various Classes

5.2. Optimisation of Sampling and Gas Chromatographic Separation Protocols for Cryogenic Trapping

VOCs in landfill gas collected by cryogenic trapping were analysed by gas chromatography employing mass selective detection (see Section 2.7.3). The GC column used was the 25m \times 0.25mm ID, 1 µm film thickness methylsilicone column employed for the solvent desorption studies described section 3.1.4.

5.2.1. The Sampling

The sampling train used to collect VOCs in landfill gas using cryogenic trapping is shown in Fig 5.5. The sampling procedure, except for sampling time which is discussed below, and sampling train components are described in Section 2.11. The VOCs present in the landfill gas 'freeze out' in the cryogenic trap, as does the moisture. It is important to dry the gas before passage through the cryogenic trap as eventually ice blocks the trap and prevents further sampling. Moisture removal also aids in the analysis step as only a single organic layer is obtained when the contents of the cryogenic trap are allowed to thaw. This is particularly important as very moist landfill gas produces a large volume of water compared with the organic layer obtained. The moisture trap is discussed in Section 3.1 and moisture trap construction is described in Section 2.2. With a pump flow of 200 ml/min the landfill gas could be sampled for 3 hours or more before the moisture indicator showed that moisture had broken through the sampling train. Even with up to 3 hours of sampling the thawed

contents of the cryogenic trap revealed about 50 μ l of organic condensate in the first drechsel bottle and successively smaller volumes of organic condensate in the other three drechsel bottles.



Fig 5.5 The Sampling Train Using Cryogenic Trapping

5.2.2. Analysis of VOCs in Landfill Gas Using Cryogenic Trapping

The contents of the cryogenic trap were dissolved in CS_2 and 1 μ l of this solution was introduced into the GC. Sample preparation is described in Section 2.11.3. Fig 5.6 shows the separation of a landfill gas sample using the GC conditions employed for the thermal desorption studies. The gas chromatographic conditions are shown in the figure legend and the oven program shown in the chromatogram. The solution used to generate Fig 5.6 was subject to headspace analysis, where 1 ml of headspace, taken with a 1 ml gas syringe, was gas chromatographed. The GC conditions used to generate Fig 5.6 were suitable as the low starting temperature allowed for sample refocusing before separation. Fig 5.7 shows the separation of the components present in the headspace, and as can be seen the headspace profile is similar to that shown in Fig 5.6. Of course, the only difference between the two samples is the levels of VOCs in the headspace are substantially lower than those in the liquid, eventhough the chromatograms indicate that levels are similar. This is easily explained when considering that 1 ml of headspace was injected in the splitless mode, whereas 1 µl of liquid sample was injected with a split ratio of 25:1. Therefore 1 ml of headspace contains similar amounts of VOCs as are present in 1/25 µl of liquid sample. This information can be used to calculate VOCs losses from the liquid sample. For example, if 1 ml of liquid sample is placed in a 2 ml vial, and then 0.004 % of VOCs will be lost to the headspace. This quantity lost is negligible, but does indicate that losses do occur.



Fig 5.6 The Separation of a Landfill Gas Sample

[The GC-MS conditions were: Carrier Gas: Helium; Carry Gas Flow: 1 ml/min at room temp; Injection Mode: Split (A split ratio of 25:1 was used); MS transfer line 280 °C; Solvent delay: 8.5 min; Scan rate: 1.2 scans/sec; Scan range: 40 – 550 amu; and Mass spectral confirmation: Wiley Mass spectral Data Base.]



Fig 5.7 The Separation of the Components Present in the Headspace [The GC-MS conditions were: Carrier Gas: Helium; Carry Gas Flow: 1 ml/min at room temp; Injection Mode: Splitless; MS transfer line 280 °C; Solvent delay: 8.5 min; Scan rate: 1.2 scans/sec; Scan range: 40 – 550 amu; and Mass spectral confirmation: Wiley Mass spectral Data Base.]

5.2.3. Qualitative Analysis of the Sample Collected from the Cryogenic Trap

The identification of VOCs, in the landfill gas was similar to that described in section 3.2.1.1, where manual background subtraction was used to remove interfering ions from the background and adjoining peaks. The compounds identified by MS database matching were similar to those identified by thermal desorption studies and are listed in Table 4.7.

CHAPTER VI VOCS IN LANDFILL GAS FROM SEVEN WASTE DISPOSAL SITES

The results and discussion in this Chapter include the following:

- This researcher's findings on the advantages and disadvantages of the various sampling and analysis techniques employed in this study (Section 6.1);
- The results of the analysis of selected VOCs present in seven landfills located in the western region of Melbourne, Victoria (Section 6.2);

6.1. Discussion of Sampling and Analysis Protocols Investigated in Chapter III, IV and V

This discussion will address all aspects of sampling and analysis and includes the following:

- Moisture removal
- Sampling equipment
- Sampling techniques and the amount of VOCs collected
- Handling, shipment and storage of samples prior to analysis
- Sample preparation and GC analysis
- Types of VOCs collected

6.1.1 Moisture Removal

Some of the landfill gas sampled in this investigation had high relative humidity and in order to avoid problems with moisture in either the sampling or analysis step, all gas was dried before collection of VOCs, and therefore all four methods of VOC collection employed a moisture trap. The moisture trap used is described in Section 2.3.1.2, and proved to be an effective and simple way to dry the landfill gas.

6.1.2 Sampling Equipment

The moisture trap, as discussed above, was an integral part of all four sampling techniques as was the sampling pump. The four sampling methods investigated, differed only in the way in which VOCs were collected. This investigator found that all four methods of VOC collection were simple to apply in the field. The only comment here is that it was much easier to transport adsorbent tubes and Tedlar® bags compared with the cryogenic trap. Since the moisture trap was designed to allow simultaneous collection of four landfill gas samples it would be much easier to transport multiple tubes and bags compared with one very large cryogenic trap capable of multiple sampling, or indeed individual cryogenic traps.

Major differences in the use of the sampling equipment were noticeable only during equipment preparation prior to sampling. The adsorbent tube / solvent extraction method was the most simple and involve the use of a new tube for each sample. In order to avoid 'memory' effects from previous samples, thermal desorption tubes required thermal cleaning between samples and Tedlar[®] bags required nitrogen flushing before reuse. The cryogenic trap also required flushing with hot water before reuse. Cleaning of the thermal desorption tubes was quick and easy, while it was labor intensive for bags, and the cryogenic trap had to be disassembled and reassembled for each sample. The cryogenic trap may also require re-silanising after several uses.

6.1.3 Sampling Techniques and the Amount of VOCs Collected

Ultimately the choice of sampling technique depends on the concentration of VOCs in the landfill gas. The amount of gas collected should allow for easy detection of VOCs.

Tedlar[®] bags allow for whole gas sampling but problems with detection may occur if VOC concentrations in the landfill gas are low. Alternatively, when VOC concentrations are high the limited volume collected in Tedlar[®] bags does not allow an adequate time-averaged sample to be collected. Problems with detection can be overcome by using larger injection volumes while longer time averaged samples can be collected using lower pump flow rates.

When the concentration of VOCs in the landfill gas is low, one of the three preconcentration sampling techniques can be used. With adsorption tubes / solvent desorption sampling, as long as sample breakthrough does not occur, long time averaged samples can be collected. Although the amount of VOCs collected is high, dilution prior to GC analysis is easily performed with the CS_2 solvent.

Long time averaged samples are also possible with cryogenic trapping. In fact, sampling may continue for several hours and is only impeded by moisture breakthrough, water freezing out in the moisture trap or cryogenic coolant evaporation. Dilution with CS_2 solvent is required here as very concentrated samples are collected.

In the case of adsorption tubes / thermal desorption, the amount of VOCs collected is critical as dilution prior to GC analysis is not possible. Dilution here only occurs where the desorbed sample is split at the Thermal Desorption Unit (TDU) and in order that samples and standards are analysed similarly, the amount of VOCs collected needs to be such that the concentrations of the various VOCs falls within the standard calibration range.

6.1.4 Handling, Shipment and Storage of Samples Prior to Analysis

Standard recommended practice, according to ASTM D3687-95⁽¹⁰⁹⁾ 'Standard Practice for Analysis of Organic Compound Vapors by the Activated Charcoal Tube Adsorption Method' and ASTM D6196-97⁽¹⁰⁸⁾ 'Standard Practice for Selection of Sorbents and Pumped Sampling / Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air', was employed in the collection, shipment and storage of adsorption tubes prior to analysis. Tubes were sealed with the appropriate end caps immediately after sampling, kept cool and away from direct sunlight during shipment to the laboratory and refrigerated before analysis. Analysis was always within two days of sampling. Similar good practices were employed with the cryogenic trap where both ends were capped immediately after sampling and the coolant retained during shipment to the laboratory. The Tedlar® bags were kept cool and away from direct sunlight during shipment and analysed as soon as possible, as it has been reported that bags are permeable to various volatile compounds and photodegradation may also occur⁽¹¹⁴⁾.

6.1.5 Sample Preparation and GC Analysis

Samples taken on thermal desorption tubes or in Tedlar® bags require no sample preparation prior to GC analysis whereas sample taken by solvent desorption tubes and cryogenic trapping require treatment with the CS₂ solvent. It would appear that those samples requiring no pre-treatment and therefore no CS₂ solvent peak in the chromatogram would permit the separation of very early eluting compounds. This was not the case because both thermal desorption and Tedlar[®] bag samples display a large early eluting peak. This could not be avoided with Tedlar® bag samples, the peak due to methane (see Section 5.1.3), and CO_2 in the air peak obtained with thermal desorption due to equipment design (see Section 4.1.4.2). Obviously the solvent desorption tube samples require solvent pre-treatment and the concentrated samples collected by cryogenic trapping also require solvent pre-treatment. Therefore, all four methods of sampling produced chromatograms with a very large early eluting peak. Perhaps then, the four different types of samples can be best compared by noting that Tedlar® bag and thermal desorption tube samples which require no sample pretreatment are not subject to volatile losses as compared to solvent desorption tube and cryogenic trapping samples where treatment with CS_2 solvent is required.

Where dilution of the sample is required, this is simple for the solvent desorption tube and cryogenic trapping samples and merely involves more solvent. Volatile losses are again a consideration. Tedlar[®] bag samples can be diluted by transferring a gaseous aliquot into a nitrogen filled Tedlar[®] bag. Thermal desorption samples can be diluted via the split available at the thermal desorption unit, but if samples and standards are to be treated the same, then perhaps sampling time should be such that sample concentration falls within the calibration range.

GC analysis for Tedlar[®] bag and thermal desorption samples required sub-ambient starting temperatures in order to produce sharp early eluting peaks, whereas the liquid samples from solvent desorption tube and cryogenic trapping could be chromatographed with ambient starting temperatures. However, at the ambient starting temperatures, the solvent peak only allowed the separation of compounds eluting after the hexane peak. When sub-ambient starting temperatures are used for all types of sample, compounds eluting before hexane can be separated. Liquid and

gaseous samples displayed good chromatography on the capillary methylsilicone column (BP-1, 25m \times 0.25mm ID, 1 μ m film thickness) with the appropriate operating conditions. This column gave good separation for most of the abundant VOCs present in the landfill gas.

The analysis step should see both samples and standards treated identically and it is here that advantages and disadvantages of the four sampling methods become apparent. The solvent desorption tube and cryogenic trapping methods require solvent pre-treatment prior to analysis and liquid samples are gas chromatographed. For these two methods standards preparation and analysis is simple requiring only dilution of pure liquid standards in solvent and direct syringe injection into the GC. For these two methods, volatile losses during preparation and analysis of samples and standards need to be considered. Analysis of Tedlar[®] bag samples is also simple where a gas sample is injected into the GC using an airtight syringe or gas sampling valve. Preparation of Tedlar® bag standards is also simple and involves injection of liquid standards into a nitrogen filled Tedlar[®] bag or the preparation of a concentrated standard followed by serial dilution where gaseous aliquots are transferred into nitrogen filled Tedlar[®] bags. Thermal desorption samples require no sample pretreatment prior to analysis and this is a distinct advantage. Calibration is by either direct injection of liquid standards into an empty tube or an adsorbent filled tube prior to thermal desorption, or gaseous standards can be pre-concentrated onto an adsorbent filled tube. Preparation of gaseous standards requires more labor and apparatus (pumps, bags, flow meters, etc.), however the advantage of analysis of gaseous standards in parallel with gaseous samples is obvious. There are a number of calibration procedures available for the preparation of gaseous standards⁽¹⁰⁵⁾, but none of these were used in this study.

There are a number of techniques available for the preparation of gaseous standards including static and dynamic methods^(115 - 117). Static techniques involve introducing a known amount of standards into a closed container while dynamic techniques result in a flow of standard gaseous mixture of known concentration. An example of the former includes injection of liquid compounds into a nitrogen filled Tedlar[®] bag and for the latter the use of permeation tubes. Gaseous calibration standards can be

purchased but these are expensive especially if multi-component mixtures, as would be required to analyze the many VOCs in landfill gas, are required. Another problem here is that commercial gaseous mixtures would need to be diluted to produce a calibration series. For the analysis of VOCs in landfill gas, previous workers have used a variety of calibration procedures involving gaseous standards. Brookes *et al.*⁽⁸⁸⁾ and Scott *et al.*⁽⁶⁴⁾ prepared standard atmospheres of VOCs including the internal standard to determine relative response factors. Allen *et al.*⁽⁹²⁾ prepared calibrated thermal desorption tubes by injecting a liquid mixture of standard into a plug of glass wool inserted into the top of the tube while drawing clean air through the tube. Although this technique does not ideally involve a standard gas mixture, it is important to note that standards enters the adsorption tubes as a vapour and thereby mimics the sample. Hodgson *et al.*⁽¹¹⁸⁾ used a similar approach where a liquid mixture was introduced into a helium filled flask after which a gaseous aliquot from the flask was delivered by gas-tight syringe into a flowing helium stream passing through the adsorption tube.

In our laboratories a simple technique has been used to prepare standard gaseous mixtures in Tedlar[®] bags and this is described in Section 2.6.3. Not only was this technique used to prepare standard gaseous mixtures in Tedlar[®] bags, but it was also used to prepare calibrated adsorption tubes (see Section 2.6.3, 2.8.3 and 2.9.3) and dilute Tedlar[®] bag standards (see Section 4.3.2). We found this technique of preparing standard gaseous mixtures simple and versatile. SKC⁽¹¹⁹⁾ report that accurate gas volumes can not be determined by this technique, unless some kind of flow calibration device is fitted in line, and that the volume can be only estimated based on pump flow and run time. Method validation of solvent desorption (see Section 3.2.2.1.2) and thermal desorption (see Section 4.1.4.3) analytical systems gave excellent recoveries with good precision, demonstrating that this technique of preparing standard gaseous mixtures was analytically valid.

The last point to consider with respect to type of sample collected and standards used, involves storage time prior to analysis. Sample and calibrated adsorption tubes, calibrated either by liquid compounds or gaseous mixtures can be refrigerated for a considerable length of time prior to analysis, whereas Tedlar[®] bags need to be analysed quickly as these are permeable and volatile losses may occur. In this study it

was standard practice to analyze all samples and standards soon after collection or preparation (within one day).

6.1.6 Types of VOCs Collected

All four methods of sample collection displayed similar chromatograms where $C_5 - C_{12}$ hydrocarbons were collected. The landfill gas studies in Chapter III, IV and V was taken from a leachate well A_{1-1} of landfill site A (see Table 6.1 and 6.2). The most abundant VOCs present included straight chain, cyclic, aromatic and terpenic hydrocarbons, and some of these were positively identified by retention time matching with standards and mass spectral comparison with standards. Other hydrocarbons identified only by MS library matching included branched chain alkanes, naphthenic, olefinic, and chlorinated hydrocarbons. Of these, the branched chain were the most abundant with traces of olefinic and naphthenic hydrocarbons present. List of compounds is given in Table 4.7, Section 4.2.1.

Only two chlorinated hydrocarbons were identified by MS library matching, and both were of relatively low abundance. Other chlorinated hydrocarbons and in particular more volatile ones were not observed. Other landfill gas studies have shown that chlorinated hydrocarbons and organosulfur hydrocarbons are present in landfill gas (see Chapter I). These were not observed here as GC conditions were not optimised for these compounds. These compounds may also be present in trace amounts making detection difficult. Organohalogen and organosulfur compounds were investigated in a separate study conducted in our laboratories⁽¹²⁰⁾.

6.2. Trace VOCs in Seven Landfills in the Western Region of Melbourne, Victoria

In this section the sampling and analysis protocols developed in Chapter III and Chapter IV were used to study selected trace VOCs present in seven landfills located in the western region of Melbourne, Victoria, Australia. Here VOCs were trapped on Carbotrap 300 Multi-bed thermal desorption tubes and the VOCs were analysed by thermal desorption / GC-MS. Quantitation for over 60 VOCs was by direct calibration versus standards or indirectly using standards representing various groups of VOCs. The latter calibration method gives results which can be considered as semiquantitative. Calibration procedures are described in Section 4.3.1 and 4.3.3.

As described in Chapter III, the most abundant trace VOCs were straight chain, branched chain, cyclic, aromatic and terpenic hydrocarbons, and GC conditions were optimised for the separation of these compounds. Interestingly, as described later in this chapter, these five classes of compounds were also the most abundant VOCs present in the other landfills studied.

A summary of the seven landfills studied is given in Table 6.1 and sampling points (emission source) are described in Table 6.2.

	Summary of Seven Landfill Sites Studied				
SITE	SITE	FILLING	WASTE	GAS END USE	
T JCH A	Blue Stone guarry	DALL	Liquid wastes	None	
Landiii A	Basin		solid/inert,	None	
		1071 1097	putrescible, and		
<u>Section 1</u> (\mathbf{A}_1)		19/1 - 190/	low level		
		1071 1002	contaminated,		
<u>Section 2</u> (A_2)		19/1 – 1992	prescribed soli		
	O Duit	1000 2007*	Demestic and	Electricity.	
Landfill B	Quarry Basin	1990 - 2006*	solid inert waste	generation system	
			John mert waste	was installed in	
				1993	
Landfill C	Quarry Basin	1985 - 1990	Domestic and	Electricity	
			solid inert waste	was installed in	
				1993	
Landfill D	Quarry Basin		Domestic and	Electricity	
			solid inert waste	generation system	
Section 1 (D ₁)		1984 - 2000		1993	
				~~~~	
Section 2 (D ₂ )		1984 - 2001			
-					
Landfill E	<b>Basalt Basin</b>		Council waste	None at time of	
			and low level	study, electricity	
Section 1 (E ₁ )		1990 - 1995	soil	was installed in	
				2001	
Section $2^*$ (E ₂ )		1995 - 2004**			
Landfill F			Domestic waste	None	
			including		
Section 1 $(\mathbf{F}_1)$	Above ground fill	1976 - 1981	degradable		
			garbage (31%),		
Section 2 (F ₂ )	Above ground fill	1981 – 1986	moderately		
	-		garbage (47%),		
Section 3 (F ₁ )	Above ground fill	1986 - 1992	and inert		
<u> </u>	0		garbage (2270)		
Section 4 (F.)	Quarry infill	1992 — 1994			
(- 4)					
Landfill G	Above ground fill	1979 - 2009**	Domestic waste,	Electricity	
_anann G	U U		hazardous	generation system	
			substances, and	was installed in 1992	
			invustriai waste		

Table 6.1

* New rubbish overlying old rubbish; ** Estimated completion date.

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	Table 6.2Sampling Points	
LANDFILL	SAMPLING POINTS (EMISSION SOURCE)	GAS PRESSURE
Α	Leachate well and passive vent	Passive
В	Gas extraction pipe line	Under vacuum
С	Gas extraction pipe line	Under vacuum
D	Gas extraction pipe line	Under vacuum
E	Testing probe*	Passive
F	LFG probe**	Passive
G	Gas extraction pipe line	Under vacuum

* These test probes (90 mm diameter, made of high density polyethylene) will become a part of final gas collection system.

** These test probes ( $40 \sim 50$  mm diameter PVC pipe) used for methane generation study.

#### 6.2.1 Sampling and Analysis Protocols

The study of VOCs in landfill gas from seven landfills in the western region of Melbourne was conducted in 1997. Sampling and analysis protocols are summarized below.

#### Sampling:

- Two samples were taken within a week for each sampling point;
- Sampling times ranged from 5 10 minutes at pump flow rates of 60 200 ml/min;
- Landfill gas is initially dried by passing through the moisture trap (See Section 2.2.1.2);
- VOCs in landfill gas are collected on Carbotrap 300 Multi-bed thermal desorption tubes and thermally desorbed (see Section 2.7.2 & Section 2.7.3);

#### Analysis:

Calibration plots were prepared by loading 50 ml of the standard gaseous mixture containing 0.04000 to 0.8000 µl each of 26 compounds (see Section 2.9.2) into the Carbotrap[™] 300 Multi-bed thermal desorption tubes (See Section 4.3.1);

• The Calibration Solutions were run once every week prior to the analysis of the two weekly samples. The following conditions were used:

<u>Carrier Gas</u> :	Helium.
Carrier Gas Flow:	1 ml/min at Room Temp.
Nickel Transfer Line Temp:	250 °C
<b>Desorption Chamber Temp:</b>	Room Temp. $\rightarrow$ 350 °C and hold for 5 minutes.
Injection Mode:	Split 50:1 at Room Temp.
Oven Temp:	-20 – 100 °C @ 3 °C/min
	100 – 280 °C @ 20 °C /min
Cryogenic Fluid:	Liquid CO ₂ .
MS transfer line:	280 °C.
Solvent delay:	1.5 – 2.5 minutes.
Scan rate:	1.2 scans/sec.
Scan range:	40 – 550 amu
Tuning procedure:	Auto tune
Mass spectral confirmation:	Wiley Mass Spectral Data Base

- Calibration plots for 26 compounds including straight chain, cyclic, aromatic and terpenic hydrocarbons were prepared individually (see Section 4.3.1);
- The concentrations of the individual compounds were determined from the calibration plots;
- Other straight chain, branched chain, cyclic, aromatic and terpenic hydrocarbons were semi-quantified by using reference compounds used to prepare calibration plots above (see Section 4.3.3);
- No correction was made for desorption efficiency as method validation gave recoveries greater than 90 % (see Section 4.1.4.3);
- Method validation gave recoveries greater than 90 % and precision (n = 6) of less than 10 % (see Section 4.1.4.3);

- The 26 compounds used to prepare calibration plots were positively identified in the landfill gas by retention time matching with standards and mass spectral matching with standards and mass spectral library (see Section 4.2.2);
- Other compounds analysed were tentatively identified by mass spectral library and mass sample spectral matching (see Section 4.2.1);
- For 1,2-dimethylcyclohexane, because the standard material used was a mixture of the cis- and trans- isomers, the calibration plot was prepared using the sum of peak areas for both isomers (see Section 4.3.1);
- For 1,2- and 1,4-dimethylbenzene, because these compounds co-elute, the mass injected is the total for both isomers (see Section 4.3.1);
- The concentration of 2-methylhexane and 2,3-dimethylpentane is the total for both compounds as these co-elute (see Section 4.2.1).

#### 6.2.2 Results and Discussion for VOCs in Seven Landfills

The most abundant compounds, based on peak height comparison amongst GC peaks, found in landfill gas from all landfill sites include straight chain, branched chain, cyclic, aromatic and terpenic hydrocarbons. This finding is consistent with other studies where these groups of compounds were also found to be the most prevalent in landfill gas right throughout the waste degradation process^(64, 85, 88, 89, 90, 92, 93, 58).

In this section the VOCs in landfill gas results for the various landfills will be discussed as follows:

Landfill F will be discussed first. The four sections of this domestic waste site had waste ranging from 3 – 21 years and trends in VOC production with age of waste can be established. Sampling was via landfill probes and variability between sampling points (emission source) can be observed (results presented in Section 6.2.2.1);

- Landfill E will be discussed second. This was also a domestic waste site and sampling was via landfill probes. Results from this site could be compared with site F and variability between sampling points can be observed (results presented in Section 6.2.2.1);
- Landfill A will be discussed third. This site is a Prescribed Waste landfill whereas all the others are domestic waste landfills. Results for site A will be compared with the domestic sites E and F to observe differences (results presented in Section 6.2.2.2).
- Domestic landfills B, C, D, and G will be discussed last and together because all four sites employ gas extraction for electricity generation and landfill gas samples were taken from the extraction system. These samples represent an average of the VOC population in each landfill thus allowing good comparison between the four sites (results presented in Section 6.2.2.3);

#### 6.2.2.1 Landfills F and E

Details of domestic waste landfills F and E are given in Table 6.1, Section 6.2. At the time of the study there was no gas extraction at either site but a landfill gas study was underway and landfill gas probes had been constructed.

Site F had received domestic waste and an assessment of waste proportions found the waste to consist of 31% rapidly degradable garbage, 47% moderately degradable garbage, and 22% inert garbage. Site F consists of four sections ( $F_1$ ,  $F_2$ ,  $F_3$  and  $F_4$ ), where sections  $F_1$ ,  $F_2$  and  $F_3$  are primarily above ground landfills and section  $F_4$  is a landfilled quarry hole. Landfill gas testing probes were installed in particular areas of each section. Landfill gas samples were taken from two areas of section  $F_2$  ( $F_{2A}$  and  $F_{2B}$ ), three areas of section  $F_3$  ( $F_{3A}$ ,  $F_{3B}$  and  $F_{3C}$ ). In total at site F fourteen probes were sampled, two in section  $F_1$  ( $F_{1-1}$  and  $F_{1-2}$ ), four in section  $F_{2A}$  ( $F_{2A-1}$ ,  $F_{2A-2}$ ,  $F_{2A-3}$  and  $F_{2A-4}$ ), two in section  $F_{2B}$  ( $F_{2B-1}$  and  $F_{2B-2}$ ), two in section  $F_3$  ( $F_{3A-1}$  and  $F_{3A-2}$ ), one in section  $F_{3B}$  ( $F_{3B-1}$ ), one in section  $F_{3C}$  ( $F_{3C-1}$ ), and two in section  $F_4$  ( $F_{4-1}$  and  $F_{4-2}$ ). Table 6.3⁽¹²¹⁾ details each of the four areas of site F including filling dates, average

depth and landfill gas testing probe depths, Table 6.3 also lists the age of the waste in each section at the time of study in 1997.

Table 6.3       Details of Landfill F					
SECTION & AREAS	FILLING DATE	AVERAGE DEPTH (M) TO MAX.	NO. OF SAMPLING PROBE	PROBES DEPTH (m)	AGE OF WASTE AT TIME OF STUDY (year)
Section 1 (F ₁ )	1976 – 1981	4 - 7	F ₁₋₁ F ₁₋₂	6.0 3.0	16 - 21
Section 2 (F ₂ )					
			F _{2A-1}	9.0	
Area 1 (F _{2A} )		12 - 16	F _{2A-2}	3.0	
× 2A/	1981 – 1986		F _{2A-3}	3.0	11 – 16
			F _{2A-4}	3.0	
Area 2 (F _{2B} )		3 - 7	F _{2B-1}	3.0	
			¹ 2B-2	3.0	
Section 3 (F ₃ )					
Area 1 (F)		6 9	F _{3A-1}	3.0	
Area 1 (1 ⁻ 3A)	1986 – 1992	0-8	F _{3A-2}	3.0	5 11
Area 2 (F _{3B} )		7 - 10	F _{3B-1}	3.0	5-11
Area 3 (F _{3C} )		4 – 10	F _{3C-1}	3.0	
	1007 1004		F ₄₋₁	9.0	
Section 4 $(F_4)$	1774 - 1794	10.3 – 11.6	F ₄₋₂	3.0	3 – 5

Landfill F is a 'dry landfill', meaning that all putrescible wastes are placed above the natural water table and the landfill cells are closed and capped to prevent infiltration of rainwater. The drilling returns were generally noted to be moist, but not significantly wet. For site F, results of the landfill gas evaluation study in 1995⁽¹²¹⁾ found that methane and carbon dioxide levels were highest at the more recently completed sections three and four as compared with the earlier completed sections one and two. This indicated that the waste was in the methanogenic phase of the landfill gas cycle in sections three and four whereas in sections one and two the waste had probably reached the maturation phase of gas production.

Site E began receiving waste in 1990 and a landfill gas feasibility study focused on two sections of the site. Site E, section 1 ( $E_1$ ) commenced filling with council waste

and solid / inert waste in 1990 and ceased filling in 1995. In this section six 19 m deep probes were constructed. Section 2 ( $E_2$ ) began filling with council waste in 1990 and in 1995 began accepting low level contaminated soil (contaminated with heavy metals and hydrocarbons) as daily cover. In section  $E_2$  the landfilling practice was to segregate putrescible and solid / inert waste. In 1997 at the time of this study this section had ceased accepting waste and had been capped with soil. In this section four 12 m test probes were constructed where the bottom 6 m was inserted into pre-1995 waste and the top 6 m into post-1995 waste. From the above information, at the time of the study the waste in site  $E_1$  was between two and seven years old and that in site  $E_2$  was between a few months to seven years old. Landfill gas samples were taken from two sections of site E ( $E_1$  and  $E_2$ ). In total at Site E eight probes were sampled, six in Site  $E_1$  ( $E_{1-1}$ ,  $E_{1-2}$ ,  $E_{1-3}$ ,  $E_{1-4}$ ,  $E_{1-5}$ , and  $E_{1-6}$ ), two in site  $E_2$  ( $E_{2-1}$  and  $E_{2-2}$ ). Table 6.4 lists various information for site E.

Table 6.4 Details of Landfill E				
SECTION & AREAS	FILLING DATE	NO. OF SAMPLING PROBE	PROBES DEPTH (m)	AGE OF WASTE AT TIME OF STUDY (year)
Section 1 (E ₁ )	1990 – 1995	$E_{1-1}$ $E_{1-2}$ $E_{1-3}$ $E_{1-4}$ $E_{1-5}$ $E_{1-6}$	19	2 – 7
Section 2 (E ₂ )	1990 - 1997	E ₂₋₁ E ₂₋₂	12*	Few months – 2 years

* Bottom 6 m in pre-1995 waste; and top 6 m in post-1995 waste

The results of the studies⁽¹²²⁾ showed that at both sites the landfill gas contained sufficient methane for commercial use. Gas extraction commenced at site E in 2001. Landfill gas samples at both sites were collected from the landfill testing probes and thus it would be possible to observe variation between sampling points at each site. Fig 6.1 - 6.2 shows typical GC traces for VOCs in landfill gas from sites F and E. As can be seen the GC fingerprints for both sites are very similar.



Over 120 different VOCs were present in landfill gas from each site. Table 6.5 lists all the compounds in order of retention time. Table 6.6 (a) – (h) list the compounds under the various classes of compounds. The various classes found include straight chain, branched chain, cyclic, aromatic, terpenic, olefinic, naphthenic, chlorinated, esteric and alcoholic hydrocarbons. Of these the most abundant based on peak heights, included straight chain, branched chain, cyclic, aromatic and terpenic hydrocarbons. From this group of compounds some straight chain, cyclic, aromatic and terpenic compounds were positively identified by retention time matching and mass spectral matching (as described in Section 3.2.1 of Chapter III) with standard compounds. Other abundant compounds from these classes and branched chain compounds were only tentatively identified by mass spectral matching with the library search. Other classes of compounds were found at low abundance and were also only tentatively identified by mass spectral matching with the library search. Those compounds typed in bold gave quality matches with the mass spectral library greater than or equal to 80 %.

The 125 Compounds Identified in Order of Referition Time			
<u>No.</u>	RT	Library/ID	Quality
1	3.78	Butane	50
2	5.98	2-methylbutane	86
3	6.95	Pentene-2	80
4	7.14	Pentane	80
5	8.08	Dichloromethane	58
6	8.67	2,2-dimethylbutane	56
7	10.11	2,3-dimethylbutane	86
8	10.41	2-methylpentane	91
9	11.05	3-methylpentane	90
10	11.56	1,2-dichloroethene	94
11	11.95	Hexane	83
12	13.02	Methylcyclopentane	90
13	13.39	2,4-dimethylpentane	86
14	14.23	Benzene	87
15	14.55	Cyclohexane	91
16	15.20	2,3-dimethylpentane	53
17	15.57	3-methylhexane	87
18	15.76	trans-1,3-dimethylcyclopentane	72
19	15.89	cis-1,3-dimethylcyclopentane	83
20	16.02	Trichloroethene	50
21	16.13	2,2,4-trimethylpentane	72
22	16.74	Heptane	87
23	17.32	3,4-dimethylpentene-2	87
24	17.50	Methylcyclohexane	91
25	17.65	1,1,3-trimethylcyclopentane	78
26	18.03	Ethylcyclopentane	95
27	18.17	2,5-dimethylhexane	91
28	18.25	2,4-dimethylhexane	91
29	18.44	1,2,4-trimethylcyclopentane	91
30	18.51	3,3-dimethylhexane	59
31	18.76	1,2,3-trimethylcyclopentane	95
32	18.90	2,3,4-trimethylpentane	90
33	19.11	Methylbenzene	91
34	19.41	2,3-dimethylhexane	78
35	19.73	2-methylheptane	91
36	19.78	4-methylheptane	80
37	20.04	trans-1,4-dimethylcyclohexane	89
38	20.13	trans-1,3-dimethylcyclohexane	91
39	20.34	1,1-dimethylcyclohexane	91
40	20.50	trans-1-ethyl-3-methylcyclopentane	92
41	20.65	1-ethyl-2-methylcyclopentane	95
42	20.86	trans-1,2-dimethylcyclohexane	91
43	21.03	Tetrachloroethene	97
44	21.20	Octane	92

Table 6.5The 123 Compounds Identified in Order of Retention Time

Table 6.5 (Continued)

No.	RT	Library/ID	Quality
45	21.46	Propylcyclopentane	72
46	21.83	2,3,5-trimethylhexane	90
47	21.99	2,2,4-trimethylhexane	72
48	22.16	cis-1,2-dimethylcyclohexane	47
49	22.39	Ethylcyclohexane	90
50	22.60	1,1,3-trimethylcyclohexane	91
51	22.72	2,5-dimethylheptane	64
52	22.86	1,2-Dichlorooctane	59
53	23.24	Ethylbenzene	83
54	23.30	1,3,5-trimethylcyclohexane	91
55	23.61	1,2&1,4-dimethylbenzene	93
56	23.74	Octahydropentalene	53
57	23.92	2-methyloctane	91
58	24.21	3-methyloctane	93
59	24.49	1,3-dimethylbenzene	94
60	24.72	trans-1-ethyl-4-methylcyclohexane	80
61	24.80	cis-1-ethyl-4-methylcyclohexane	64
62	25.31	Nonane	91
63	25.45	3,5-dimethylheptene-3	64
64	25.55	cis-1-ethyl-2-methylcyclohexane	74
65	25.73	1-methylethylbenzene	91
66	25.87	Octahydro-2-methylpentalene	49
67	25.95	1-methylethylcyclohexane	81
68	26.04	3-methylheptane	53
69	26.12	7-methyloctyne-3	43
70	26.39	Propylcyclohexane	91
71	26.57	α-Pinene	90
72	26.67	2,6-dimethyloctane	90
73	26.91	propylbenzene	81
74	27.02	Camphene	<b>9</b> 7
75	27.21	1-ethyl-2-methylbenzene	90
76	27.45	3,4-dimethyloctane	/8
77	27.49	1,2,4-trimethylbenzene	97
78	27.70	4-methylnonane	83
79	27.81	2-methylnonane	81
80	28.05	β-Pinene	89
81	28.18	1-methyl-4-(1-methylethyl)cyclonexane	40
82	28.46	1,3,5-trimethylbenzene	93 67
83	28.56	6,6-(D2)menth-2-ene	02
84	28.82	1,2-dichlorobenzene	56
85	28.95	2,2,4,6,6-pentamethylneptane	95
86	29.10	Decane	83
87	29.31	o-Carene-3	03
88	29,43	I-etnyl-4-metnylbenzene	94
89	29.64	1-methyl-4-(1-methylethyl)benzene	76
90	29.96		95
91	30.05	1-metnyi-4-(1-metnyiid)cyclonexane	90
92	30.20	Butyicycionexane	50
93	30.32	5,8-CHINEURY ICECANE	95
94	<b>30.41</b>	1,4-diethylbenzene	49
95	30.50	Disthulhonzene	74
96	30.64	LACHTYLUCHZCHC	93
97	30.73	1-etnyl-3,3-almetnylbenzene	94
98	30.99	trans-decanydronaphthalene	

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	Table 0.5 (Continued)				
No.	RT	Library/ID	Ouality		
99	31.09	5-methyldecane	72		
100	31.19	4-methyldecane	86		
101	31.32	2-methyldecane	91		
102	31.40	2,6,8-trimethyldecane	46		
103	31.54	3-methyldecane	78		
104	31.66	2-ethyl-1,3-dimethylbenzene	81		
105	31.86	a-Terpinene	93		
106	32.02	1-methyl-3-propylcyclohexane	59		
107	32.15	Undecene-5	38		
108	32.26	l-methylbutylbenzene	53		
109	32.34	l-methyl-3-(1-methylethyl)benzene	76		
110	32.53	Undecane	91		
111	32.77	4-ethyl-1,2-dimethylbenzene	92		
112	32.89	1,2,3,5-tetramethylbenzene	94		
113	32.95	Decahydro-2-methylnaphthalene	97		
114	33.13	3,6-dimethyldecane	64		
115	33.47	2-methyldecalin (probably trans)	47		
116	33.68	Pentylcyclohexane	76		
117	33.93	1-ethyl-3,5-dimethylbenzene	76		
118	34.36	5-methylundecane	97		
119	34.48	4-methylundecane	74		
120	34.62	2-methylundecane	83		
121	34.84	3-methylundecane	87		
122	35.76	Dodecane	91		
123	36.27	3.6-dimethylundecane	83		

Table 6.5 (Continued)

Table 6.6 (a)Straight Chain Hydrocarbons in the 123 Compounds

No.	RT	Library/ID	Quality
1	3.78	Butane	50
4	7.14	Pentane	80
11	11.95	Hexane	83
22	16.74	Heptane	87
44	21.2	Octane	92
62	25.31	Nonane	91
86	29.1	Decane	95
110	32.53	Undecane	91
122	35.76	Dodecane	91

No.	RT	Library/ID	Quality
2	5.98	2-methylbutane	86
6	8.67	2,2-dimethylbutane	56
7	10.11	2,3-dimethylbutane	86
8	10.41	2-methylpentane	91
9	11.05	3-methylpentane	90
13	13.39	2,4-dimethylpentane	86
16	15.2	2,3-dimethylpentane	53
17	15.57	3-methylhexane	87
21	16.13	2,2,4-trimethylpentane	72
27	18.17	2,5-dimethylhexane	91
28	18.25	2,4-dimethylhexane	91
30	18.51	3,3-dimethylhexane	59
32	18.9	2,3,4-trimethylpentane	90
34	19.41	2,3-dimethylhexane	78
35	19.73	2-methylheptane	91
36	19.78	4-methylheptane	80
46	21.83	2,3,5-trimethylhexane	90
47	21.99	2,2,4-trimethylhexane	72
51	22.72	2,5-dimethylheptane	64
57	23.92	2-methyloctane	91
58	24.21	3-methyloctane	93
68	26.04	3-methylheptane	53
72	26.67	2,6-dimethyloctane	90
76	27.45	3,4-dimethyloctane	78
78	27.7	4-methylnonane	83
79	27.81	2-methylnonane	81
85	28.95	2,2,4,6,6-pentamethylheptane	56
93	30.32	3,8-dimethyldecane	50
95	30.5	3,7-dimethylnonane	49
99	31.09	5-methyldecane	72
100	31.19	4-methyldecane	86
101	31.32	2-methyldecane	91
102	31.4	2,6,8-trimethyldecane	46
103	31.54	3-methyldecane	78
114	33.13	3,6-dimethyldecane	64
115	33.47	2-methyldecalin	47
116	33.68	Pentylcyclohexane	76
118	34.36	5-methylundecane	97
119	34.48	4-methylundecane	74
120	34.62	2-methylundecane	83
121	34.84	3-methylundecane	87
123	36.27	3,6-dimethylundecane	83

Table 6.6 (b)Branched Chain Hydrocarbons in the 123 Compounds

No.	RT	Library/ID	Quality
14	14.23	Benzene	87
33	19.11	Methylbenzene	91
53	23.24	Ethylbenzene	83
55	23.61	1,2&1,4-dimethylbenzene	93
59	24.49	1,3-dimethylbenzene	94
65	25.73	1-methylethylbenzene	91
73	26.91	propylbenzene	81
75	27.21	1-ethyl-2-methylbenzene	90
77	27.49	1,2,4-trimethylbenzene	97
82	28.46	1,3,5-trimethylbenzene	93
88	29.43	1-ethyl-4-methylbenzene	93
89	29.64	1-methyl-4-(1-methylethyl)benzene	94
94	30.41	1,4-diethylbenzene	95
96	30.64	Diethylbenzene	74
97	30.73	1-ethyl-3,5-dimethylbenzene	93
104	31.66	2-ethyl-1,3-dimethylbenzene	81
108	32.26	1-methylbutylbenzene	53
109	32.34	1-methyl-3-(1-methylethyl)benzene	76
111	32.77	4-ethyl-1,2-dimethylbenzene	92
112	32.89	1,2,3,5-tetramethylbenzene	94
117	33.93	1-ethyl-3,5-dimethylbenzene	76

Table 6.6 (c)Aromatic Hydrocarbons in the 123 Compounds

Table 6.6 (d)Cyclic Hydrocarbons in the 123 Compounds

No.	RT	Library/ID	Ouality
12	13.02	Methylcyclopentane	<u></u> 90
15	14.55	Cyclohexane	91
18	15.76	trans-1,3-dimethylcyclopentane	72
19	15.89	cis-1,3-dimethylcyclopentane	83
24	17.5	Methylcyclohexane	91
25	17.65	1,1,3-trimethylcyclopentane	78
26	18.03	Ethylcyclopentane	95
29	18.44	1,2,4-trimethylcyclopentane	91
31	18.76	1,2,3-trimethylcyclopentane	95
37	20.04	trans-1,4-dimethylcyclohexane	89
38	20.13	trans-1,3-dimethylcyclohexane	91
39	20.34	1,1-dimethylcyclohexane	91
40	20.5	trans-1-ethyl-3-methylcyclopentane	92
41	20.65	1-ethyl-2-methylcyclopentane	95
42	20.86	trans-1,2-dimethylcyclohexane	91
45	21.46	Propylcyclopentane	72
48	22.16	cis-1,2-dimethylcyclohexane	47
49	22.39	Ethylcyclohexane	90
50	22.6	1,1,3-trimethylcyclohexane	91
54	23.3	1,3,5-trimethylcyclohexane	91
60	24.72	trans-1-ethyl-4-methylcyclohexane	80
<b>6</b> 1	24.8	cis-1-ethyl-4-methylcyclohexane	64
64	25.55	cis-1-ethyl-2-methylcyclohexane	74
67	25.95	1-methylethylcyclohexane	81
70	26.39	Propylcyclohexane	91
81	28.18	1-methyl-4-(1-methylethyl)cyclohexane	46
91	30.05	1-methyl-4-(1-methylid)cyclohexane	95
92	30.2	Butylcyclohexane	90
106	32.02	1-methyl-3-propylcyclohexane	59
116	33.68	Pentylcyclohexane	76

Table 6.6 (e)

Terpenic Hydrocarbons in the 123 Compounds

No.	RT	Library/ID	Quality
71	26.57	α-Pinene	90
74	27.02	Camphene	97
80	28.05	β-Pinene	89
87	29.31	δ-Carene-3	83
90	29.96	Limonene-1	76
105	31.86	α-Terpinene	93

Table 6.6 (f)

Naphthenic Hydrocarbons in the 123 Compounds

No.	RT	Library/ID	Quality
56	23.74	Octahydropentalene	53
66	25.87	Octahydro-2-methylpentalene	49
<b>98</b>	30.99	trans-decahydronaphthalene	94
113	32.95	Decahydro-2-methylnaphthalene	97

Chloro Hydrocarbons in the 125 Compounds								
RT	Library/ID	Quality						
8.08	Dichloromethane	58						
11.56	1,2-dichloroethene	94						
16.02	Trichloroethene	50						
21.03	Tetrachloroethene	97						
22.86	1,2-Dichlorooctane	59						
28.82	1,2-dichlorobenzene	96						
	RT           8.08           11.56           16.02           21.03           22.86           28.82	RTLibrary/ID8.08Dichloromethane11.561,2-dichloroethene16.02Trichloroethene21.03Tetrachloroethene22.861,2-Dichlorooctane28.821,2-dichlorobenzene						

Table 6.6 (g)Chloro Hydrocarbons in the 123 Compounds

Table 6.6 (h)Alkenyl Hydrocarbons in the 123 Compounds

No.	RT	Library/ID	Quality
3	6.95	Pentene-2	80
23	17.32	3,4-dimethylpentene-2	87
63	25.45	3,5-dimethylheptene-3	64
69	26.12	7-methyloctyne-3	43
83	28.56	6,6-(D2)menth-2-ene	62
107	32.15	Undecene-5	38

Over 70 VOCs were quantified either directly or indirectly as described in Section 4.1.3 and 4.3.3, respectively. Table 6.7 lists those compounds which were quantified in the landfill gas with compounds marked with an asterisk indirectly quantified. Table 6.8 shows the standard compound used for indirect quantification.

NAME OF COMPOUNDS	NAME OF COMPOUNDS
<b>BRANCHED CHAIN HYDROCARBONS</b>	CYCLIC HYDROCARBONS
2-methylbutane*	Methylcyclopentane*
2-methylpentane*	Cyclohexane
3-methylpentane*	Methylcyclohexane
Hexane	trans-1,4-dimethylcyclohexane
2-methylhexane*	cis-1,3-dimethylcyclohexane *
2,3-dimethylpentane*	trans-1,2-dimethylcyclohexane
3-methylhexane *	cis-1,2-dimethylcyclohexane
Heptane	Ethylcyclohexane
2,3,4-trimethylpentane*	1,1,3-trimethylcyclohexane*
2-methylheptane*	trans-1-ethyl-4-methylcyclohexane*
4-methylheptane*	cis-1-ethyl-4-methylcyclohexane*
Octane	1-methylethylcyclohexane
2,4-dimethylhexane*	Propylcyclohexane*
2,5-dimethylheptane*	1-methyl-4-(1-methylethyl)cyclohexane*
2,6-dimethylheptane*	Butylcyclohexane*
2-methyloctane*	
3-methyloctane*	AROMATIC HYDROCARBONS
1,1,3-trimethylhexane*	
Nonane	Benzene
2,5-dimethyloctane*	Methylbenzene
2,6-dimethyloctane*	Ethylbenzene
3-ethyl-2-methylheptane*	1,2&1,4-dimethylbenzene
3,4-dimethyloctane*	1,3-dimethylbenzene
4-methylnonane*	1-methylethylbenzene*
2-methylnonane*	Propylbenzene
3-methylnonane*	1-ethyl-2-methylbenzene*
Decane	1-ethyl-4-methylbenzene*
5-methyldecane*	1,2,4-trimethylbenzene
4-methyldecane*	1,3,5-trimethylbenzene
2-methyldecane*	1-methyl-4-(1-methylethyl)benzene*
3-methyldecane*	1-methyl-2-propylbenzene*
4-methyldecane*	2-ethyl-1,4-dimethylbenzene*
Undecane	
2,2,4,6,6-pentamethylheptane*	TERPENIC HYDROCARBONS
3,8-dimethyldecane*	α-Pinene
Dodecane	Camphene*
Tridecane*	β-Pinene
	δ-3-Carene
STRAIGHT CHAIN HYDROCARBONS	1-Limonene
Pentane*	

Table 6.7The Compounds Quantified in Sites E and F

COMPOUNDS	STANDARD USED FOR OUANTITATION
2-methylbutane	
Pentane	
2-methylpentane	Hexane
3-methylpentane	
2-methylhexane	
2,3-dimethylpentane	Heptane
3-methylhexane	
2,3,4-trimethylpentane	
2-methylheptane	
4-methylheptane	2
2,4-dimethylhexane	Octane
2,5-dimethylheptane	
2,6-dimethylheptane	
2-methyloctane	
3-methyloctane	Nonane
1,1,3-trimethylhexane	
2,5-dimethyloctane	
2,6-dimethyloctane	
3-ethyl-2-methylheptane	
3,4-dimethyloctane	Decane
4-methylnonane	
2-methylnonane	
3-methylnonane	
5-methyldecane	
4-methyldecane	
2-methyldecane	Undecane
3-methyldecane	
4-methyldecane	
2,2,4,6,6-pentamethylheptane	
3,8-dimethyldecane	Dodecane
Tridecane	
Methylcyclopentane	Cyclohexane
cis-1,3-dimethylcyclohexane	trans-1,4-dimethylcyclohexane
1,1,3-trimethylcyclohexane	
trans-1-ethyl-4-methylcyclohexane	
cis-1-ethyl-4-methylcyclohexane	1 methylethyleyeleheyene
Propylcyclohexane	1-methylethyleyclonexane
1-methyl-4-(1-methylethyl)cyclohexane	
Butylcyclohexane	
1-methylethylbenzene	
1-ethyl-2-methylbenzene	
1-ethyl-4-methylbenzene	Dronylhonzono
1-methyl-4-(1-methylethyl)benzene	rropymenzene
1-methyl-2-propylbenzene	
2-ethyl-1,3-dimethylbenzene	
Camphene	α-Pinene

 Table 6.8

 The Standard Compound Used for Indirect Quantification

The classes of VOCs found are typical of those found by other workers (Section 1.3, Chapter I), and discussion on VOCs found in landfill gas from landfills E and F will be based on the following:

- Discussion of those straight chain, cyclic, aromatic and terpenic hydrocarbons which were positively identified and were also directly quantified as these were amongst the most abundant VOCs found. Other compounds from these four classes which were tentatively identified and indirectly quantified will be included in the discussion. These may be prevalent at all sites or present in appreciable amounts and can help in finding correlations between sites or sampling points or help in drawing conclusions in general. It should be noted that all of those compounds which were tentatively identified gave extremely good mass spectral matches including both quality match and visual match;
- Discussion will include branched chain hydrocarbons because of their number and abundance. Although they were only tentatively identified, the spectral matches, both quality match and visual match, were extremely good. Analysis of these compounds was semi-quantitative;
- The remaining groups of compounds were present in relatively small amounts and will not help in making comparisons between the different landfills. Also, these compounds were only tentatively identified and mass spectral matching was variable. Discussion here will focus on chlorinated compounds giving good mass spectral matching, both quality and visual, as these have been identified as relevant compounds in landfill gas by other workers. These will be discussed in Section 6.2.2.4.

#### 6.2.2.1.1 Landfill F

#### 6.2.2.1.1.1 n-Alkanes – Positively Identified and Directly Quantified

n-alkane levels at landfill F are shown in Table 6.9. The two samples taken at each sampling point are represented by S1 and S2. Total levels ranged from  $0.024 - 0.714 \mu g/L$  at section  $F_1$ ,  $0.652 - 1.860 \mu g/L$  at section  $F_2$ ,  $0.212 - 1.469 \mu g/L$  at section  $F_3$  and  $0.412 - 0.943 \mu g/L$  at section  $F_4$ . Table 6.10 shows average total levels of n-alkanes at each section of site F. Average total alkane levels at section  $F_1$ ,  $F_2$ ,  $F_3$  and  $F_4$  were 0.304  $\mu g/L \pm 100.3$  %, 0.966  $\mu g/L \pm 43.1$  %, 0.853  $\mu g/L \pm 51.0$  % and 0.610  $\mu g/L \pm 40.5$  %, respectively. The relative standard deviations appear to be high but this is expected. As discussed in Section 1.3.3 the concentration of VOCs in landfill

gas depends on a number of factors including waste age, degree of degradation, waste composition, landfilling practices, climate and physical form of the waste. Therefore, it was not expected that each sampling point at each section of site F should yield data with little variation. Considering the above it is fair to say that intrasection variations for each section of site F were not significant.

Quantined from Site F										
(ug/L)	<b>F</b> ₁₋₁		<b>F</b> ₁₋₂		F _{2A-1}		F _{2A-2}		<b>F</b> _{2A-3}	
(46,6)	S1	S2	<b>S1</b>	S2	<b>S</b> 1	S2	<b>S</b> 1	S2	<u>S1</u>	S2
Hexane	0.017	0.137	0.001	0.078	0.039	0.040	0.030	0.081	0.045	0.038
Heptane	0.021	0.198	0.007	0.053	0.098	0.109	0.117	0.319	0.094	0.065
Octane	0.019	0.140	0.005	0.033	0.092	0.102	0.096	0.271	0.140	0.104
Nonane	0.020	0.158	0.007	0.057	0.180	0.200	0.272	0.582	0.443	0.351
Decane	0.039	0.044	0.003	0.026	0.164	0.183	0.204	0.417	0.275	0.206
Undecane	0.015	0.036	BDL	0.050	0.070	0.078	0.029	0.136	0.099	0.039
Dodecane	BDL	BDL	BDL	0.050	0.011	0.012	0.003	0.052	0.014	0.003
Total (µg/L)	0.130	0.714	0.024	0.347	0.654	0.723	0.751	1.859	1.111	0.806

Table 6.9The Levels of n-Alkanes Directly Quantified from Site F

Table 6.9 (Continued)The Levels of n-Alkanes Directly Quantified from Site F

(ug/L)	<b>F</b> _{2A-4}		F _{2B-1}		<b>F</b> _{2B-2}		<b>F</b> _{3A-1}		<b>F</b> _{3A-2}	
(µg/L)	S1	<b>S2</b>	<b>S</b> 1	<b>S2</b>	<b>S</b> 1	S2	S1	S2	<b>S</b> 1	S2
Hexane	0.129	0.058	0.068	0.043	0.034	0.074	0.043	0.025	0.058	0.020
Heptane	0.255	0.126	0.128	0.054	0.094	0.205	0.164	0.085	0.070	0.036
Octane	0.199	0.091	0.107	0.044	0.075	0.197	0.153	0.076	0.067	0.040
Nonane	0.406	0.172	0.239	0.145	0.218	0.433	0.387	0.262	0.151	0.065
Decane	0.375	0.152	0.229	0.131	0.237	0.356	0.425	0.270	0.085	0.033
Undecane	0.130	0.047	0.145	0.046	0.039	0.077	0.170	0.093	0.011	0.013
Dodecane	0.015	0.005	0.091	0.007	0.005	0.003	0.107	0.043	0.002	0.007
Total (µg/L)	1.509	0.652	1.007	0.470	0.702	1.346	1.450	0.853	0.444	0.212

Table 6.9 (Continued)The Levels of n-Alkanes Directly Quantified from Site F

					2						
(μg/L)	F _{3B-1}		F _{3C-1}		<b>F</b> ₄₋₁		<b>F</b> ₄₋₂				
	<b>S1</b>	<b>S2</b>	S1	S2	S1	S2	S1	S2			
Hexane	0.150	0.085	0.178	0.068	0.013	0.028	0.027	0.058			
Heptane	0.405	0.220	0.214	0.190	0.053	0.067	0.073	0.256			
Octane	0.315	0.152	0.095	0.092	0.089	0.047	0.057	0.136			
Nonane	0.329	0.177	0.161	0.168	0.272	0.123	0.096	0.258			
Decane	0.201	0.103	0.156	0.124	0.130	0.130	0.078	0.187			
Undecane	0.055	0.028	0.047	0.120	0.077	0.034	0.053	0.042			
Dodecane	0.014	0.008	0.008	BDL	BDL	0.005	0.027	0.005			
Total (µg/L)	1.469	0.773	0.860	0.764	0.651	0.434	0.412	0.943			
AVG (µg/L)	F ₄	F ₃	F ₂	<b>F</b> ₁							
--------------	----------------	-----------------	-----------------	-----------------------	--	--	--	--	--	--	--
Hexane	0.031 ± 59.8 %	0.079 ± 73.2 %	0.057 ± 49.9 %	0.058 ± 106.4 %							
Heptane	0.112 ± 85.7 %	0.173 ± 67.4 %	0.139 ± 57.7 %	0.070 ± 125.4 %							
Octane	0.082 ± 48.6 %	0.124 ± 70.0 %	0.127 ± 51.0 %	0.049 ± 125.2 %							
Nonane	0.187 ± 48.2 %	0.212 ± 49.7 %	0.303 ± 45.3 %	0.060 ± 113.2 %							
Decane	0.131 ± 34.0 %	0.175 ± 71.5 %	0.244 ± 38.2 %	0.028 ± 65.1 %							
Undecane	0.051 ± 36.3 %	0.067 ± 84.2 %	0.078 ± 52.7 %	0.025 ± 87.8 %							
Dodecane	0.014 ± 76.3 %	0.024 ± 153.0 %	0.018 ± 144.4 %	0.012 ± 200.0 %							
Total (µg/L)	0.610 ± 40.5 %	0.853 ± 51.0 %	0.966 ± 43.1 %	0.304 ± 100.3 %							

Table 6.10Average Total Levels of n-Alkanes from Site F

Considering the age of the waste and stage of degradation at each section of site F, the results suggest that the total n-alkane levels increase as the waste enters more advanced stages of methanogenesis and then decline as the waste enters the maturation stage of waste degradation. This is clearly seen in Fig. 6.3 where average total levels at each section of site F are shown.



Fig 6.3 Average Total Levels of Directly Quantified n-Alkanes at Site F

Fig 6.4 shows average total individual n-alkane levels at site F. These results reveal that  $C_7 - C_{10}$  n-alkanes are the abundant compounds in waste ranging from 3 – 11 years and as the waste ages to 16 years levels of  $C_9$  and  $C_{10}$  increase significantly, while levels of  $C_7$  and  $C_8$  decline slightly. Levels of  $C_6$ ,  $C_{11}$  and  $C_{12}$  follow a similar

trend to  $C_7$  and  $C_8$  as the waste ages from 3 – 16 years. In very old waste (16 – 21 years) levels of  $C_7 - C_{11}$  have declined dramatically. Levels of  $C_6$  and  $C_{12}$  remain fairly constant throughout the waste decomposition process.



What is also interesting about the trend shown in Fig 6.4, is that it followed that of methane generation as waste proceeds through active methanogenesis and then enters the maturation phase of waste degradation where gas generation diminishes (see Fig 1.3). This indicates that n-alkane levels in landfill gas are directly related to methane production. Allen *et al.*⁽⁹²⁾ also found that VOCs in landfill appeared to be directly related to the levels of methane.

Our findings agree with those of other workers. Young *et al.*⁽⁸⁹⁾ found  $C_8 - C_{11}$  n-alkanes were dominant in gas from five to six years old domestic refuse with decane the most abundant and octane the least. However, Young *et al.*⁽⁸⁹⁾ also found that nonane, decane and undecane dominated in gas from refuse three weeks to seven months old. The three week old refuse produced insignificant levels of methane (0.05 % was reported). Schweigkofler *et al.*⁽⁹⁰⁾ also found  $C_9 - C_{11}$  n-alkanes to be more abundant than  $C_8$  and  $C_{12}$  n-alkanes in domestic landfill sites. Scott *et al.*⁽⁶⁴⁾ also

reported that nonane and decane were the dominant alkanes released under anaerobic conditions. Eklund *et al.*⁽⁸⁵⁾ found that  $C_9 - C_{11}$  n-alkanes were dominant in landfill gas extracted from a fifty year old operating site, which was receiving household garbage. On the other hand, Ward *et al.*⁽⁹⁰⁾ found that for nine years old domestic waste  $C_6 - C_8$  n-alkanes were more abundant that  $C_9$  and  $C_{10}$  with octane the most abundant.

Our results show that  $C_7$  and  $C_{10}$  are abundant right through the methanogenic phase of waste degradation (waste 3 – 16 years old) and their abundance declines during the maturation phase of waste degradation. During the maturation phase (>16 years), the abundances of  $C_6 - C_9$  n-alkanes are comparable, as are those of  $C_{10} - C_{12}$ .

Table 6.11 shows the average gas composition with respect to n-alkanes at each section of site F. This data was generated by calculating the percentage of total individual levels in total n-alkane levels. As can be seen the gas composition is fairly constant for waste undergoing methanogenesis (age 3 – 16 years) where nonane and decane account for approximately 50 % of total n-alkanes. Gas composition changes for waste in the maturation phase of waste degradation, where the percentages of C₉ and particularly C₁₀ have declined while contributions from C₆ have increased.

The Avera	The Average Gas Composition of n-Alkanes at Each Section of Site F											
%	F ₄	F ₃	<b>F</b> ₂	F ₁								
Hexane	5.2	9.2	5.9	19.3								
Heptane	18.4	20.3	14.4	23.0								
Octane	13.5	14.5	13.1	16.2								
Nonane	30.7	24.9	31.4	19.9								
Decane	21.5	20.5	25.3	9.3								
Undecane	8.4	7.9	8.1	8.2								
Dodecane	2.3	2.8	1.9	4.1								
TOTAL	100.0	100.0	100.0	100.0								

Table 6 11

6.2.2.1.1.2 **n-Alkanes** – Tentatively Identified and Indirectly Quantified

The levels of other straight chain hydrocarbons found in landfill gas in site F are found in Table 6.12. Pentane was only observed at two sampling points, point  $F_{1-2}$  and  $F_{2B-1}$ . Interestingly it was the most abundant n-alkane at site  $F_{1-2}$ . This was surprising

as the waste here was > 16 years old and if pentane was present in the deposited waste its volatility suggests it would have volatilised much earlier. Perhaps conditions at sampling point  $F_{1-2}$  favoured its production via microbial degradation of waste. When pentane results were combined with those of other alkanes, its contribution to gas composition was 10 % and 0.5 % at section  $F_1$  and  $F_2$ , respectively.

The Levels of n-Alkanes Indirectly Quantified from Sites F										
(ug/I)	F	1-2	<b>F</b> _{2B-1}							
(µg/L)	S1	S1	S2	S2						
Pentane	0.013	0.012	0.051	0.112						

Table 6 17

## 6.2.2.1.1.3 Branched Chain Alkanes – Tentatively Identified and Indirectly

#### Quantified

The levels of various branched chain alkanes at site F are shown in Table 6.13. Total branched chain alkane levels at site F ranged from 0.137-1.789  $\mu$ g/L at section F₁,  $0.339 - 3.408 \ \mu g/L$  at section F₂,  $0.346 - 2.386 \ \mu g/L$  at section F₃,  $0.125 - 0.261 \ \mu g/L$ at section F₄. Table 6.14 shows average total branched chain alkane levels, and average total levels of individual groups of branched chain alkanes at site F. Average total branched chain alkane levels at section  $F_1$ ,  $F_2$ ,  $F_3$  and  $F_4$  were 1.013  $\mu$ g/L  $\pm$  70.3 %, 1.383  $\mu$ g/L ± 73.1 %, 1.060  $\mu$ g/L ± 70.0 % and 0.213  $\mu$ g/L ± 29.6 %, respectively. Overall, intrasection variations at each section of site F were not significant.

[	(1)		-1	<b>F</b> ₁	-2	F ₂	A-1	<b>F</b> ₂	A-2	F _{2A}	-3
	(µg/L)	<b>S1</b>	S2	<b>S</b> 1	S2	<b>S1</b>	S2	<b>S1</b>	S2	<b>S1</b>	S2
C ₅	2-methylbutane	/**	/	0.015	0.084	0.034	0.044	/	/	/	/
l	Total C5	/	/	0.015	0.084	0.034	0.044	/	/	/	/
C	2-methylpentane	0.013	0.057	0.005	0.068	0.030	0.040	0.022	0.029	/	/
C ₆	3-methylpentane	0.011	0.049	0.005	0.058	0.053	0.059	0.006	0.034	/	/
	Total C6	0.024	0.105	0.010	0.126	0.083	0.099	0.028	0.063	/	/
C ₇	*2-methylhexane & 2,3-dimethylpentane	0.195	0.047	0.017	0.223	0.092	0.034	0.018	0.051	/	/
	3-methylhexane	0.030	0.125	0.009	0.128	0.059	0.053	0.021	0.058	/	/
	Total C7	0.225	0.172	0.026	0.351	0.151	0.088	0.039	0.109	/	/
	2,2-dimethylhexane	0.028	0.075	0.005	0.073	/	/	/	/	/	/
	2,3,4-trimethylpentane	0.018	0.045	/	/	/	/	/	/	/	/
C ₈	2-methylheptane	0.010	0.045	0.000	0.000	0.057	0.069	0.017	0.063	0.016	0.135
	4-methylheptane	/	/	/	/	/	/	/	/	/	/
	2,4-dimethylhexane	/	1	/	/	1	/	/	/	0.015	0.153
	Total C8	0.056	0.164	0.005	0.073	0.057	0.069	0.017	0.063	0.031	0.288
	2,5-dimethylheptane	0.020	0.061	0.005	0.073	0.051	0.102	0.051	0.073	0.018	0.143
	2,6-dimethylheptane	/	/	/	/	/	/	/	/	0.050	0.192
C,	2-methyloctane	0.009	0.070	0.006	0.024	0.098	0.108	0.017	0.106	0.000	0.000
	3-methyloctane	0.021	0.078	0.008	0.061	0.106	0.518	0.007	0.096	0.043	0.351
	1,1,3-trimethylhexane	/	/	0.005	0.113	/	/	/	/	0.021	0.405
	Total C9	0.050	0.209	0.023	0.271	0.255	0.728	0.075	0.275	0.132	1.091
	2,5-dimethyloctane	/	/	0.007	0.050	/	/	/	/	1	1
	2,6-dimethyloctane	0.023	0.075	0.007	0.126	0.085	0.093	0.055	0.080	0.037	0.223
	3-ethyl-2-methylheptane	0.044	0.092	0.010	0.172	/	/	/	/	0.048	0.247
C ₁₀	3,4-dimethyloctane	1	/	/	/	/	/	0.053	0.067	0.040	0.213
	4-methylnonane	1	/	/	/	/	/	/	/	0.031	0.152
	2-methylnonane	0.082	0.159	/	/	/	/	/	/	0.042	0.049
	3-methylnonane	1	/	/	/	1	/	/	/	0.034	0.039
	Total C10	0.148	0.326	0.024	0.348	0.085	0.093	0.108	0.147	0.232	0.923
	5-methyldecane	0.029	0.043	/	/	/	/	/	/	: /	/
	4-methyldecane	0.130	0.138	0.009	0.061	0.086	0.089	0.029	0.055	/	/
<b>C</b> ₁₁	2-methyldecane	0.043	0.059	0.002	0.079	0.145	0.224	0.043	0.207	/	/
	3-methyldecane	0.035	0.046	0.005	0.090	/	1	/	/	/	/
	4-methyldecane	/	/	0.004	0.079	/	1	/	/	/	/
	Total C11	0.236	0.285	0.021	0.309	0.231	0.313	0.072	0.262	/	/
	2,2,4,6,6- pentamethylheptane	0.031	0.037	0.007	0.086	0.151	0.160	/	1	0.045	0.088
C ₁₂	3,8-dimethyldecane	0.022	0.035	0.002	0.046	0.066	0.074	/	/	/	/
	Total C12	0.053	0.072	0.009	0.132	0.217	0.234	/	/	0.045	0.088
C ₁₃	Tridecane	1	_/	0.004	0.095	/	/	<u> </u> /	/		
	Total	0.794	1.336	5 0.137	1.789	1.113	1.668	0.339	0.919	0.440	2.390

Table 6.13 The levels of Branched Chain Alkanes Indirectly Quantified at site F

* The concentration of 2-methylhexane & 2,3-dimethylpentane is the total for both as these co-elute; ** negligible levels.

	(µg/L)	F ₂	A-4	F ₂	B-1	F ₂	B-2	F ₃	A-1	F ₃	4-2
		<b>S1</b>	S2	<b>S1</b>	S2	S1	S2	S1	S2	S1	S2
C ₅	2-methylbutane	0.058	0.100	0.023	0.044	/	/	/	/	/	/
	Total C5	0.058	0.100	0.023	0.044	/	/	/	/	/	/
C	2-methylpentane	/	/	0.010	0.057	/	/	/	/	0.007	0.035
C ₆	3-methylpentane	0.092	0.167	0.022	0.133	/	/	/	/	0.006	0.032
	Total C6	0.092	0.167	0.032	0.190	/	/	/	/	0.013	0.067
C ₇	*2-methylhexane & 2,3-dimethylpentane	0.175	0.224	0.022	0.133	0.044	0.063	/	/	/	/
	3-methylhexane	0.139	0.291	0.013	0.101	0.027	0.039	/	/	/	/
	Total C7	0.314	0.515	0.035	0.234	0.071	0.103	/	/	/	/
	2,2-dimethylhexane	/	/	/	/	/	/	/	/	0.011	0.027
	2,3,4-trimethylpentane	/	/	/	/	/	/	/	/	/	/
C ₈	2-methylheptane	0.064	0.145	0.011	0.098	0.036	0.040	/	/	0.018	0.037
	4-methylheptane	/	/	/	/	/	/	/	/	0.023	0.028
	2,4-dimethylhexane	/	/	/	/	/	/	/	/	/	/
	Total C8	0.064	0.145	0.011	0.098	0.036	0.040	/	/	0.052	0.092
	2,5-dimethylheptane	/	/	/	/	0.022	0.046	0.048	0.067	0.018	0.025
	2,6-dimethylheptane	0.074	0.111	/	/	/	/	/	/	/	/
C9	2-methyloctane	0.135	0.239	0.023	0.151	0.053	0.133	0.081	0.528	0.028	0.063
	3-methyloctane	0.137	0.210	0.027	0.189	0.047	0.184	0.095	0.194	0.016	0.042
	1,1,3-trimethylhexane	0.217	0.280	/	/	/	/	/	/	/	/
	Total C9	0.563	0.840	0.050	0.340	0.122	0.363	0.224	0.789	0.062	0.130
	2,5-dimethyloctane	/	/	/	/	/	/	/	/	/	/
	2,6-dimethyloctane	1	/	0.027	0.151	0.024	0.044	/	/	/	/
	3-ethyl-2-methylheptane	1	/	0.032	0.151	/	/	/	/	0.025	0.045
C ₁₀	3,4-dimethyloctane	0.137	0.231	0.029	0.178	0.053	0.069	/	/	0.007	0.025
	4-methylnonane	0.348	0.530	0.026	0.162	0.097	0.176	0.049	0.164	0.023	0.034
	2-methylnonane	1	/	0.018	0.181	0.050	0.091	0.073	0.112	0.008	0.034
	3-methylnonane	1	/	/	/	/	/	/	1	/	/
	Total C10	0.485	0.761	0.132	0.823	0.224	0.380	0.122	0.276	0.063	0.138
	5-methyldecane	0.079	0.190	0.022	0.157	/	/	/	/	/	1
	4-methyldecane	0.149	0.336	/	/	/	/	/	/	/	/
C ₁₁	2-methyldecane	0.156	0.245	/	/	/	/	1	/	/	/
	3-methyldecane	0.067	0.109	0.018	0.131	/	/	1	/	/	/
	4-methyldecane	/	/	/	/	/	/	1	/	/	/
	Total C11	0.451	0.880	0.040	0.288	/	/	/	/	/	/
	2,2,4,6,6- pentamethylheptane	1	/	0.019	0.139	0.037	0.050	/	/	/	/
C ₁₂	3,8-dimethyldecane	1	/	0.012	0.355	1		/	/	/	/
	Total C12	0.000	0.000	0.031	0.494	0.037	0.050	0.000	0.000	0.000	0.000
C ₁₃	Tridecane	/	/	/	/	/	/	/	_/	/	/
	Total	2.027	3.408	0.354	2.511	0.490	0.936	0.346	1.065	0.190	0.427

 Table 6.13 (Continued)

 The levels of Branched Chain Alkanes Indirectly Quantified at site F

	(µg/L)	F ₃	B-1	F _{3C-1}		<b>F</b> ₄₋₁		<b>F</b> ₄₋₂	
		S1	S2	S1	S2	S1	S2	S1	<u>52</u>
C ₅	2-methylbutane	/	/	/	/	1	/	/	/
	Total C5	1	/	/	/	1	/	/	/
C,	2-methylpentane	1	/	0.044	0.073	0.013	0.077	0.019	0.036
- 0	3-methylpentane	1	1	0.040	0.065	1	/	/	/
	Total C6	0.000	0.000	0.084	0.138	0.013	0.077	0.019	0.036
C ₇	*2-methylhexane & 2,3-dimethylpentane	0.273	0.345	0.193	0.280	1	/	0.091	0.051
	3-methylhexane	0.202	0.254	0.101	0.182	/	1	0.074	0.040
	Total C7	0.475	0.598	0.294	0.461	/	1	0.165	0.091
	2,2-dimethylhexane	0.114	0.143	/	/	1	/	/	/
	2,3,4-trimethylpentane	0.093	0.109	0.085	0.100	/	/	/	/
C ₈	2-methylheptane	0.201	0.240	/	/	1	1	/	/
	4-methylheptane	1	1	/	/	1	1	/	1
	2,4-dimethylhexane	1	1	0.025	0.030	/	/	/	/
	Total C8	0.408	0.492	0.110	0.130	/	/	/	/
	2,5-dimethylheptane	0.077	0.091	/	/	1	/	/	/
	2,6-dimethylheptane	1	/	0.043	0.050	1	/	/	/
C ₉	2-methyloctane	0.178	0.217	0.053	0.072	0.051	0.092	0.043	0.049
	3-methyloctane	0.156	0.180	0.066	0.068	1	/	0.034	0.034
	1,1,3-trimethylhexane	1	/	/	/	1	/	/	/
	Total C9	0.411	0.488	0.162	0.190	0.051	0.092	0.077	0.083
	2,5-dimethyloctane	1	1	/	1	/	/	/	/
	2,6-dimethyloctane	0.079	0.386	0.228	0.390	1	/	/	/
	3-ethyl-2-methylheptane	1	/	0.062	0.076	1	/	/	/
C ₁₀	3,4-dimethyloctane	1	1	/	/	/	/	/	/
	4-methylnonane	0.108	0.221	0.043	0.075	0.061	0.087		
	2-methylnonane	0.062	0.201	0.036	0.047	1	/	/	/
	3-methylnonane	/	/	/	1	/	/	/	/
	Total C10	0.249	0.808	0.369	0.588	0.061	0.087	0.000	0.000
	5-methyldecane	/	/	/	/	/	/	/	1,
	4-methyldecane	/	/	/	/	1	/	/	/
C ₁₁	2-methyldecane	/	1	/	/	/	/	/	/
	3-methyldecane	/	/	/	/	/	/	/	1
	4-methyldecane	1	/	/	/	/	/	/	1
	Total C11	/	/	/	/	1	/	/	/
C ₁ ,	2,2,4,6,6- pentamethylheptane	/	/	/	/	/	/	/	/
12	3,8-dimethyldecane	/	/	/	/	/	/	/	/
	Total C12	/	/	/	/	/	/	/	/
C ₁₃	Tridecane	/	/	/	/	/	/	/	/
	Total	1.543	2.386	1.019	1.507	0.125	0.256	0.261	0.210

# Table 6.13 (Continued) The levels of Branched Chain Alkanes Indirectly Quantified at site F

11verage rotar	Bevels of Branes		tes at Each Seet	IUL UI SILE I
COMPOUNDS	F ₄	F ₃	F ₂	F ₁
Total C5	/	1	0.025 ± 127.0 %	0.025 ± 162.9 %
Total C6	0.036 ± 79.6 %	0.038 ± 139.3 %	0.063 ± 104.7 %	0.066 ± 87.1 %
Total C7	0.064 ± 124.7 %	0.229 ± 112.7 %	0.138 ± 109.1 %	0.194 ± 69.5 %
Total C8	1	0.161 ± 116.0 %	0.077 ± 99.0 %	0.075 ± 88.8 %
Total C9	0.076 ± 23.3 %	0.307 ± 78.7 %	0.403 ± 82.8 %	0.138 ± 87.3 %
Total C10	0.037 ± 119.0 %	0.327 ± 78.3 %	0.366 ± 84.5 %	0.212 ± 72.6 %
Total C11	1	1	0.211 ± 123.6 %	0.213 ± 61.8 %
Total C12	1	1	0.100 ± 148.6 %	0.067 ± 76.5 %
Total C13	1	1	1	0.025 ± 189.2 %
Total	0.213 ± 29.6 %	1.060 ± 70.0 %	1.383 ± 73.1 %	1.013 ± 70.3 %

 Table 6.14

 Average Total Levels of Branched Chain Alkanes at Each Section of Site F

Fig 6.5 shows average total levels of each group of branched chain alkanes at site F, where n-alkane data (including pentane) is also shown for comparison. As can be seen the branched chain alkane results are similar to those for n-alkanes showing that the branched chain alkane levels increase as the waste ages from 3 - 16 years then levels drop off slightly as the waste ages beyond 16 years old. Similar to n-alkane results, branched chain alkane levels follow that of methane generation where levels decline as the waste enters the maturation phase of waste degradation. However unlike n-alkane trends which decrease noticeably in the maturation phase of waste degradation, branched chain alkane levels are higher in gas from the aged waste than in the younger refuse.



Fig. 6.5 Average Total Levels of Branched Chain Alkanes at Site F

Fig. 6.5 also shows total branched chain alkane levels compared with n-alkanes in young refuse (3 - 5 years) are significantly lower. Similar levels of branched chain alkanes to those of n-alkanes are found for refuse 5 - 16 years old. As the waste ages beyond 16 years, n-alkane levels decline dramatically, whereas branched chain alkane levels decline slightly. Overall the trends suggest that the mechanisms responsible for the generation and release of n-alkanes are similar to those of branched chain alkanes.

Average total levels of each group of branched chain alkanes at site F are shown in Fig 6.6.  $C_9$  and  $C_{10}$  branched chain alkanes are the abundant compounds right throughout the waste degradation process. Their levels increase as the waste ages from 3 – 16 years after which levels decline as the waste further matures. The trend for  $C_7$  and  $C_8$  branched chain alkanes is different in that levels increase as the waste ages from 3 – 11 years, after which levels drop and remain fairly constant as the waste ages. Different again is the behavior of  $C_5$ ,  $C_6$ ,  $C_{11}$  and  $C_{12}$  branched chain alkanes. Their levels are low (some below detection limit) in waste of ages 3 – 11 years after which levels increase as the waste ages and remain fairly constant until the maturation phase of waste degradation. In very old waste (11 – 21 years) levels of  $C_7$ ,  $C_{10}$  and  $C_{11}$  are very similar and  $C_{13}$  branched chain alkanes begin to appear..



Fig. 6.6 Average Levels of Each Group of Branched Chain Alkanes at Site F

The above trends are clearly seen when the gas composition with respect to branched chain alkanes, shown in Table 6.15, is considered. For waste undergoing methanogenesis  $C_9$  and  $C_{10}$  branched chain alkanes account for approximately 50 % of total branched chain alkanes and decline to approximately 30 % for waste in the maturation phase of waste degradation. The abundance of  $C_{11}$  branched chain alkanes, at approximately 20 %, only become significant in mature waste older than 11 years. Unlike n-alkane results, it appears  $C_{11}$  branched chain alkanes become dominant in the older refuse.  $C_7$  branched chain alkanes are also abundant where they account for 30 - 10 % of total branched chain alkanes as the waste ages from 3 - 16 years, after which there abundance increase to approximately 20 % in mature refuse.

	at Each Section of Site F												
%	F ₄	F ₃	F ₂	F ₁									
Total C5	/	/	1.8	2.4									
Total C6	17.0	3.6	4.5	6.5									
Total C7	30.1	21.6	10.0	19.1									
Total C8	0.0	15.1	5.5	7.4									
Total C9	35.6	28.9	29.1	13.6									
Total C10	17.4	30.8	26.5	20.9									
Total C11	1	/	15.3	21.0									
Total C12	. /	/	7.2	6.6									
Total C13	1	1	1	2.5									
TOTAL	100.0	100.0	100.0	100.0									

 Table 6.15

 The Average Gas Composition of Branched Chain Alkanes

The similarity in behavior between the individual branched chain alkane groups and corresponding n-alkane is further proof that similar landfill processes are responsible for their production.

The range of branched chain alkanes observed in Table 6.15 also shows that the methyl derivatives of n-alkanes were the dominant branched chain alkanes. Ward *et al.*⁽⁹⁰⁾ also found that methyl alkanes were the dominant branched chain alkanes in 3 - 9 years old domestic waste.

#### 6.2.2.1.1.4 Cyclic Alkanes – Positively Identified and Directly Quantified

The levels of various cyclic alkanes at site F are shown in Table 6.16. Total levels ranged from  $0.094 - 1.840 \ \mu\text{g/L}$  at section  $F_1$ ,  $0.306 - 1.488 \ \mu\text{g/L}$  at section  $F_2$ ,  $0.300 - 2.030 \ \mu\text{g/L}$  at section  $F_3$ ,  $0.264 - 0.777 \ \mu\text{g/L}$  at section  $F_4$ . Table 6.17 shows average total levels of cyclic alkanes at each section of site F. Average total cyclic alkane levels at section  $F_1$ ,  $F_2$ ,  $F_3$  and  $F_4$  were 0.724  $\mu\text{g/L} \pm 105.8 \%$ , 0.809  $\mu\text{g/L} \pm 46.5 \%$ , 0.918  $\mu\text{g/L} \pm 61.7 \%$  and 0.544  $\mu\text{g/L} \pm 45.6 \%$ . These results show that intrasection variation at site F were not significant.

(ug/L)	<b>F</b> ₁₋₁		<b>F</b> ₁₋₂		F_2A-1		<b>F</b> _{2A-2}		<b>F</b> _{2A-3}	
(P6, 2)	S1	S2	<b>S1</b>	S2	S1	S2	S1	S2	<b>S</b> 1	S2
Cyclohexane	0.060	0.240	0.014	0.052	0.057	0.075	0.036	0.122	0.050	0.044
Methylcyclohexane	0.068	0.212	0.013	0.038	0.062	0.080	0.064	0.186	0.072	0.050
trans-1,4-dimethylcyclohexane	0.144	0.622	0.026	0.119	0.262	0.302	0.142	0.132	0.319	0.043
trans-1,2-dimethylcyclohexane	0.155	0.518	0.028	0.170	0.204	0.238	0.194	0.592	0.286	0.195
cis-1,2-dimethylcyclohexane	0.016	0.068	0.003	0.031	0.018	0.031	0.011	0.103	0.044	0.000
Ethylcyclohexane	0.035	0.134	0.007	0.036	0.059	0.077	0.061	0.185	0.126	0.083
1-methylethylcyclohexane	0.021	0.047	0.004	0.018	0.028	0.020	0.029	0.065	0.040	0.037
Total (µg/L)	0.499	1.840	0.094	0.463	0.692	0.824	0.537	1.386	0.937	0.451

Table 6.16The Levels of Cyclic Alkanes Directly Quantified from Sites F

Table 6.16 (Continued)The Levels of Cyclic Alkanes Directly Quantified from Sites F

(ug/I )	F _{2A-4}		F _{2B-1}		<b>F</b> _{2B-2}		<b>F</b> _{3A-1}		<b>F</b> _{3A-2}	
(µg/ £)	<b>S1</b>	S2	S1	S2	<b>S</b> 1	S2	S1	S2	S1	S2
Cyclohexane	0.200	0.085	0.108	0.046	0.045	0.104	0.098	0.051	0.060	0.032
Methylcyclohexane	0.162	0.078	0.087	0.047	0.079	0.191	0.078	0.050	0.056	0.037
trans-1,4-dimethylcyclohexane	0.521	0.043	0.306	0.026	0.170	0.119	0.254	0.062	0.106	0.015
trans-1,2-dimethylcyclohexane	0.418	0.178	0.382	0.117	0.168	0.379	0.418	0.276	0.108	0.150
cis-1,2-dimethylcyclohexane	0.000	0.000	0.076	0.000	0.007	0.000	0.087	0.047	0.005	0.019
Ethylcyclohexane	0.141	0.071	0.101	0.046	0.042	0.094	0.099	0.063	0.021	0.031
1-methylethylcyclohexane	0.046	0.022	0.037	0.025	0.052	0.064	0.027	0.018	0.017	0.015
Total (µg/L)	1.488	0.476	1.098	0.306	0.563	0.951	1.059	0.567	0.372	0.300

Table 6.16 (Continued)The Levels of Cyclic Alkanes Directly Quantified from Sites F

	F _{3B-1}		F _{3C-1}		<b>F</b> ₄₋₁		F ₄₋₂	
(µg/L)	S1	<b>S2</b>	<b>S1</b>	S2	<b>S</b> 1	<b>S2</b>	S1	S2
Cyclohexane	0.268	0.176	0.175	0.174	0.036	0.019	0.049	0.114
Methylcyclohexane	0.243	0.142	0.121	0.126	0.040	0.018	0.045	0.117
trans-1,4-dimethylcyclohexane	0.598	0.467	0.261	0.066	0.168	0.051	0.098	0.238
trans-1,2-dimethylcyclohexane	0.734	0.445	0.231	0.352	0.451	0.150	0.165	0.177
cis-1,2-dimethylcyclohexane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethylcyclohexane	0.153	0.088	0.060	0.068	0.045	0.013	0.039	0.062
1-methylethylcyclohexane	0.034	0.020	0.024	0.022	0.037	0.013	0.012	0.020
Total (µg/L)	2.030	1.337	0.871	0.808	0.777	0.264	0.409	0.728

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(µg/L)	F ₄	F ₃	F ₂	<b>F</b> ₁
Cyclohexane	0.055 ± 76.0 %	0.129 ± 63.2 %	0.081 ± 58.3 %	0.091 ± 110.3 %
Methylcyclohexane	0.055 ± 78.0 %	0.107 ± 63.4 %	0.096 ± 53.9 %	0.083 ± 107.9 %
trans-1,4-dimethylcyclohexane	0.139 ± 59.1 %	0.228 ± 92.0 %	0.199 ± 74.0 %	0.228 ± 117.5 %
trans-1,2-dimethylcyclohexane	0.236 ± 61.0 %	0.339 ± 58.8 %	0.279 ± 49.3 %	0.218 ± 96.5 %
cis-1,2-dimethylcyclohexane	/	0.020 ± 160.8 %	0.024 ± 140.7 %	0.030 ± 95.4 %
Ethylcyclohexane	0.040 ± 50.4 %	0.073 ± 57.0 %	0.091 ± 46.6 %	0.053 ± 105.8 %
1-methylethylcyclohexane	0.020 ± 56.6 %	0.022 ± 28.3 %	0.039 ± 39.6 %	0.023 ± 79.5 %
TOTAL	0.544 ± 45.6 %	0.918 ± 61.7 %	0.809 ± 46.5 %	0.724 ± 105.8 %

Table 6.17Average Total Levels of Cyclic Alkanes at Each Section of Site F

Fig 6.7 shows average total cyclic alkane levels at site F, where n-alkane and branched chain alkane levels have been included to allow comparison. The behavior of cyclic alkanes during the waste degradation process is slightly different from the other alkanes. Total cyclic alkane levels increase as the waste age increases beyond 5 years then decline only slightly through until the waste enters the maturation phase of waste degradation process not differing by more than a factor of 3. The similarity in behavior between the n-alkanes, branched chain alkanes and cyclic alkanes again indicates that similar landfill processes are responsible for their production. As was mentioned for n-alkane and branched chain alkanes, the trend of cyclic alkanes follows that of methane generation where cyclic alkane levels increase during active methanogenesis then decline as the waste enters the maturation phase. Similar to branched chain alkane levels, levels of cyclic alkanes are higher in gas from the very old waste in the maturation phase of waste degradation than levels in the younger refuse.



Fig. 6.7 Average Total Levels of Cyclic Alkanes at Site F

Total average individual cyclic alkane levels at site F are shown in Fig 6.8. Trans-1,2dimethylcyclohexane and trans-1,4-dimethylcyclohexane are the most abundant cyclic alkanes throughout the waste decomposition process. The next most abundant compounds were cyclohexane, methylcyclohexane and ethylcyclohexane. The other two cyclic alkanes, 1-methylethylcyclohexane and cis-1,2-dimethylcyclohexane were the least abundant. Levels of the abundant cyclic alkanes increase as the waste ages to about 11 years, then slightly decline as the waste ages to 21 years.



These results concur with other studies which show that cyclohexanes are the most abundant and common cyclic alkanes found in landfill gas. However these results differ on which cyclohexanes are the most abundant. Ward et al.⁽⁹⁰⁾ found that for 3 - 19 years old domestic waste methylcyclohexane was present at slightly higher levels than cyclohexane, and both compounds were present at levels an order of magnitude dimethylcyclohexanes, trimethylcyclohexanes higher and than tetramethylcyclohexanes. Similarly, Allen et al.⁽⁹²⁾ found that methylcyclohexane and cyclohexane were more abundant than dimethylcyclohexane, and interestingly significant levels of trimethylcyclohexanes were present. However, Allen's results represent an average of landfill gas from seven landfills of differing waste inputs and ages. Scott et al.⁽⁶⁴⁾ reported that low levels of cyclopentanes and cyclohexanes were observed and the data suggested that their production is favored under conditions of reduced anaerobic efficiency. This agrees with Young et al.⁽⁸⁹⁾ where only low levels of propylcyclohexanes were observed in landfill gas from domestic waste ranging from seven months to 5-6 years of age.

Our results across the age range 3 - 21 years show that trans-1,2- and 1,4dimethylcyclohexane are the most abundant cyclic alkanes by at least a factor of 2 compared with cyclohexane, methylcyclohexane and ethylcyclohexane. Table 6.18 shows the average gas composition with respect to cyclic alkanes at each section of site F. Interestingly the gas composition remains fairly constant throughout the waste degradation process. As can be seen trans-1,2-dimethylcyclohexane and trans-1,4-dimethylcyclohexane account for approximately 60 % of cyclic alkanes, with cyclohexane and methylcyclohexane and ethylcyclohexane about 30 %.

The Average Gas Con	position of	Cyclic Alkanes	at Each Secti	<u>on of Site F</u>
%	F4	<b>F</b> ₃	F ₂	$\mathbf{F}_{1}$
Cyclohexane	10.0	14.1	10.0	12.6
Methylcyclohexane	10.1	11.6	11.9	11.4
trans-1,4-dimethylcyclohexane	25.5	24.9	24.6	31.5
trans-1,2-dimethylcyclohexane	43.3	37.0	34.5	30.0
cis-1,2-dimethylcyclohexane	/	2.1	3.0	4.1
Ethylcyclohexane	7.3	7.9	11.2	7.3
1-methylethylcyclohexane	3.7	2.4	4.8	3.1
TOTAL	100.0	100.0	100.0	100.0

Table 6.18The Average Gas Composition of Cyclic Alkanes at Each Section of Site F

6.2.2.1.1.5 Cyclic Alkanes - Tentatively Identified and Indirectly Quantified

Levels of other cyclic hydrocarbons found at site F are shown in Table 6.19. Average total levels are shown in Table 6.20. These were 0.183  $\mu$ g/L ± 60.7 %, 0.168  $\mu$ g/L ± 89.8 %, 0.259  $\mu$ g/L ± 122.6 % and 0.156  $\mu$ g/L ± 126.5 % at sections F₁, F₂, F₃ and F₄, respectively. These cyclic hydrocarbons contributed significantly to total cyclic hydrocarbons levels at site F. This is shown in Fig 6.9, where overall total cyclic hydrocarbon levels at site F are shown alongside those of overall total n-alkane and branched chain alkane. Trends observed in Fig 6.7 are still maintained in Fig 6.9. Overall total cyclic alkane levels were obtained by combining results in Table 6.16 and 6.19. These are shown in Table 6.21, where cyclic alkanes have been grouped as methylcyclopentane (C₁), C₂-cyclopentanes, cyclohexanes, C₁-cyclohexanes, C₂-cyclohexanes and C₄-cyclohexanes.

(µơ/[.)	<b>F</b> ₁₋₁		F	<b>F</b> ₁₋₂		<b>F</b> _{2A-1}		<b>F</b> _{2A-2}		A-3
(µg/2)	S1	S2	<b>S</b> 1	<b>S2</b>	S1	S2	<b>S1</b>	S2	S1	S2
Methylcyclopentane	0.063	0.019	0.007	0.073	/	/	/	1	/	/
cis-1,3-dimethylcyclohexane	0.088	0.144	0.002	0.033	1	/	/	/	/	/
1,1,3-trimethylcyclohexane	1	1	/	/	/	/	0.046	0.047	/	1
trans-1-ethyl-4- methylcyclohexane	1	1	0.004	0.072	/	1	/	/	0.015	0.089
cis-1-ethyl-4- methylcyclohexane	0.045	0.023	/	1	1	1	/	/	0.009	0.050
Propylcyclohexane	0.050	0.018	0.005	0.045	0.063	0.051	0.160	0.043	0.025	0.278
1-methyl-4- (1-methylethyl)cyclohexane	1	/	0.002	0.040	0.044	0.033	0.050	0.277	/	/
Butylcyclohexane	1	/	/	/	0.033	0.029	/	/	0.015	0.084
Total (μg/L)	0.246	0.204	0.021	0.263	0.139	0.113	0.256	0.366	0.064	0.502

Table 6.19The Levels of Cyclic Alkanes Indirectly Quantified from Sites F

Table 6.19 (Continued)The Levels of Cyclic Alkanes Indirectly Quantified from Sites F

(µg/L)	F _{2A-4}		<b>F</b> _{2B-1}		<b>F</b> _{2B-2}		F _{3A-1}		F _{3A-2}	
(µg/L)	<b>S1</b>	S2	<b>S</b> 1	<b>S2</b>	S1	S2	S1	<b>S2</b>	S1	<b>S2</b>
Methylcyclopentane	/	/	/	/	/	/	/	/	0.038	0.015
cis-1,3-dimethylcyclohexane	/	/	/	/	/	/	/	/	0.019	0.007
1,1,3-trimethylcyclohexane	/	/	/	/	0.143	0.143	/	/	/	/
trans-1-ethyl-4- methylcyclohexane	/	/	0.012	0.088	/	/	0.035	0.164	/	/
cis-1-ethyl-4- methylcyclohexane	/	/	/	/	/	/	0.034	0.076	/	1
Propylcyclohexane	/	/	0.019	0.119	0.035	0.015	/	/	0.016	0.013
1-methyl-4- (1-methylethyl)cyclohexane	/	/	/	1	/	/	0.031	0.201	/	/
Butylcyclohexane	/	/	/	/	/	/	0.030	0.580	/	1
Total (µg/L)	/	/	0.031	0.208	0.179	0.158	0.131	1.022	0.073	0.035

## Table 6.19 (Continued)

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The Levels of Cyclic Alkanes	Indirectly	<b>Ouantified</b>	from Sites F
		· · · · · · · · · · · · · · · · · · ·	

	F ₃	B-1	F ₃	F _{3C-1}		4-1	F ₄₋₂	
(µg/L)	<u>S1</u>	S2	<u>\$1</u>	S2	S1	S2	<b>S</b> 1	S2
Methylcyclopentane	/	/	0.034	0.052	/	/	0.035	0.024
cis-1,3-dimethylcyclohexane	/	/	/	/	/	/	/	/
1,1,3-trimethylcyclohexane	/	/	0.041	0.049	/	/	/	/
trans-1-ethyl-4- methylcyclohexane	1	1	/	/	/	1	/	/
cis-1-ethyl-4- methylcyclohexane	/	/	0.041	0.050	/	/	/	/
Propylcyclohexane	/	/	0.030	0.039	/	/	/	/
1-methyl-4- (1-methylethyl)cyclohexane	0.063	0.076	/	/	/	1	0.024	0.025
Butylcyclohexane	0.068	0.088	0.040	0.022	0.029	0.450	0.017	0.019
 Total (μg/L)	0.132	0.164	0.111	0.112	0.029	0.450	0.041	0.044

 Table 6.20

 Total Levels of Cyclic Alkanes Indirectly Quantified at Each Section of Site F

(µg/L)	F ₄	F ₃	F ₂	<b>F</b> ₁
Methylcyclopentane	0.015 ± 120.0 %	0.017 ± 121.6 %	1	0.041 ± 79.6 %
cis-1,3-dimethylcyclohexane	1	0.015 ± 137.7 %	1	0.067 ± 93.9 %
1,1,3-trimethylcyclohexane	1	0.011 ± 186.3 %	0.032 ± 174.4 %	1
trans-1-ethyl-4- methylcyclohexane	1	0.034 ± 165.6 %	0.017 ± 199.4 %	0.019 ± 185.6 %
cis-1-ethyl-4- methylcyclohexane	0.012 ± 115.6 %	0.031 ± 114.7 %	0.005 ± 291.4 %	0.017 ± 127.1 %
Propylcyclohexane	0.129 ± 166.2 %	0.031 ± 104.0 %	0.067 ± 121.6 %	0.029 ± 74.2 %
1-methyl-4- (1-methylethyl)cyclohexane	1	0.029 ± 242.2 %	0.034 ± 234.6 %	0.011 ± 185.8 %
Butylcyclohexane	1	0.092 ± 217.6 %	0.013 ± 189.1 %	1
Total (µg/L)	0.156 ± 126.5 %	0.259 ± 122.6 %	0.168 ± 89.8 %	0.183 ± 60.7 %



Figure 6.10 shows average levels of grouped cycloalkanes at site F. As can be seen  $C_2$ -alkyl cyclohexanes are the most abundant cyclic alkanes right throughout the waste degradation process. The next most abundant again for the entire waste degradation process are  $C_3$ -alkylcyclohexanes. These results are further highlighted by considering the gas composition, shown in Table 6.22. As can be seen at site F for waste undergoing methanogenesis right throughout until the maturation phase,  $C_2$ -alkylcyclohexanes account for 60 % of total cycloalkanes,  $C_3$ -alkylcycloalkanes account for up to 20 % and cyclohexanes and methylcyclohexanes contribute approx

10 % each. It should be noted that for  $C_2$ -alkylcyclohexanes, trans-1,2dimethylcyclohexane and trans-1,4-dimethylcyclohexane are the predominant compounds, whereas, the abundance of  $C_3$ -alkylcycloalkanes is made up of small contributions from a number of compounds.

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(μg/L)	F_4	F ₃	F ₂	F ₁
C1-cyclopentane	0.015 ± 120.0 %	0.017 ± 121.6 %	1	0.041 ± 79.6 %
C2-cyclopentane	1	0.015 ± 137.7 %	1	0.067 ± 93.9 %
Cyclohexane	0.055 ± 76.0 %	0.129 ± 63.2 %	0.081 ± 58.3 %	0.091 ± 110.3 %
C1-cyclohexane	0.055 ± 78.0 %	0.107 ± 63.4 %	0.096 ± 53.9 %	0.083 ± 107.9 %
C2-cyclohexane	0.415 ± 48.0 %	0.660 ± 65.2 %	0.593 ± 49.1 %	0.528 ± 106.1 %
C3-cyclohexane	0.161 ± 124.6 %	0.129 ± 59.6 %	0.160 ± 76.6 %	0.088 ± 60.9 %
C4-cyclohexane	/	0.121 ± 222.8 %	0.047 ± 168.9 %	0.011 ± 185.8 %
TOTAL (µg/L)	0.700 ± 21.3 %	1.178 ± 50.8 %	0.977 ± 37.6 %	0.908 ± 89.5 %

Table 6.21Average Levels of Total Grouped Cyclic Alkanes at Each Section Site F



Fig. 6.10 Average Levels of Grouped Cyclic Alkanes at Site F

	at Each Section of She r											
%	F ₄	F ₃	F ₂	<b>F</b> ₁								
C1-cyclopentane	2.1	1.5	0.0	4.5								
C2-cyclopentane	1	1.2	0.0	7.4								
Cyclohexane	7.8	11.0	8.3	10.1								
C1-cyclohexane	7.9	9.0	9.9	9.1								
C2-cyclohexane	59.2	56.1	60.7	58.1								
C3-cyclohexane	23.0	11.0	16.3	9.7								
C4-cyclohexane	/	10.2	4.8	1.2								
TOTAL	100.0	100.0	100.0	100.0								

Table 6.22The Average Groups Gas Composition of Cyclic Alkanes<br/>at Each Section of Site F

6.2.2.1.1.6 Aromatic Hydrocarbons – Positively Identified and Directly Quantified Positively identified and directly quantified aromatic hydrocarbons at site F are shown in Table 6.23. Totals ranged from  $0.025 - 0.256 \ \mu g/L$  at section F₁,  $0.348 - 5.041 \ \mu g/L$  at section F₂,  $0.174 - 2447 \ \mu g/L$  at section F₃ and  $0.914 - 1.853 \ \mu g/L$  at section F₄. Average total levels of aromatic hydrocarbons are shown in Table 6.24 and were  $0.126 \ \mu g/L \pm 87.3 \ \%, 1.927 \ \mu g/L \pm 61.7 \ \%, 1.345 \ \mu g/L \pm 57.6 \ \%$  and  $1.434 \ \mu g/L \pm 33.7 \ \%$  at section F₁, F₂, F₃ and F₄, respectively. Overall intrasection variations at each section of site F were not significant.

									<u> </u>	
(u <b>ʊ/l</b> .)	<b>F</b> ₁₋₁		<b>F</b> ₁₋₂		F _{2A-1}		<b>F</b> _{2A-2}		<b>F</b> _{2A-3}	
(¤ga)	<b>S1</b>	S2	<b>S</b> 1	S2	<b>S</b> 1	S2	<b>S</b> 1	S2	S1	S2
Benzene	0.004	0.085	0.018	0.120	0.572	0.646	0.429	1.871	0.479	0.290
Methylbenzene	0.021	0.095	0.011	0.039	0.145	0.173	0.293	1.392	0.342	0.244
Ethylbenzene	BDL	BDL	0.003	0.022	0.212	0.246	0.157	0.442	0.307	0.351
1,2&1,4-dimethylbenzene	BDL	BDL	0.003	0.019	0.112	0.135	0.124	0.331	0.149	0.263
1,3-dimethylbenzene	BDL	BDL	0.003	0.024	0.118	0.142	0.140	0.350	0.249	0.169
Propylbenzene	BDL	BDL	BDL	BDL	0.086	0.107	0.065	0.190	0.169	0.108
1,2,4-trimethylbenzene	BDL	BDL	BDL	BDL	0.108	0.131	0.041	0.198	0.245	0.103
1,3,5-trimethylbenzene	BDL	BDL	0.006	0.031	0.135	0.161	0.071	0.267	0.226	0.087
Total (µg/L)	0.025	0.180	0.044	0.256	1.487	1.741	1.321	5.041	2.166	1.616

Table 6.23The Levels of Aromatic Hydrocarbons Directly Quantified from Sites F

 Table 6.23 (Continued)

The Levels of Aromatic Hydrocarbons Directly Quantified from Sites F

 (μg/L)	F _{2A-4}		F ₂	<b>F</b> _{2B-1}		F _{2B-2}		F _{3A-1}		F _{3A-2}	
(µg/L)	S1	S2	S1	S2	<b>S</b> 1	S2	<b>S</b> 1	<b>S2</b>	<b>S1</b>	S2	
Benzene	1.209	0.612	0.306	0.034	0.470	1.040	0.264	0.165	0.114	0.021	
Methylbenzene	0.265	0.121	0.196	0.046	0.115	0.299	0.545	0.604	0.219	0.038	
Ethylbenzene	0.245	0.142	0.237	0.050	0.101	0.195	0.298	0.300	0.062	0.016	
1,2&1,4-dimethylbenzene	0.199	0.098	0.117	0.055	0.074	0.173	0.210	0.247	0.065	0.020	
1,3-dimethylbenzene	0.172	0.081	0.127	0.035	0.081	0.190	0.229	0.217	0.047	0.018	
Propylbenzene	0.266	0.084	0.208	0.000	0.074	0.150	0.145	0.075	0.035	0.000	
1,2,4-trimethylbenzene	0.228	0.064	0.145	0.053	0.059	0.228	0.163	0.126	0.034	0.035	
1,3,5-trimethylbenzene	0.366	0.133	0.168	0.075	0.129	0.242	0.204	0.155	0.043	0.025	
Total (µg/L)	2.950	1.335	1.502	0.348	1.102	2.517	2.058	1.889	0.619	0.174	

Table 6.23 (Continued)

The Levels of Aromatic H	ydrocarbons Dir	rectly Quantified from Sites F
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( )	<b>F</b> _{3B-1}		F _{3C-1}		<b>F</b> ₄₋₁		<b>F</b> ₄₋₂	
(µg/L)	<u>S1</u>	S2	<b>S1</b>	S2	S1	S2	S1	S2
Benzene	0.477	0.350	0.114	0.168	0.158	0.070	0.134	0.224
Methylbenzene	0.881	0.372	0.372	0.399	0.500	0.237	0.480	0.974
Ethylbenzene	0.305	0.181	0.112	0.083	0.351	0.103	0.120	0.162
1,2&1,4-dimethylbenzene	0.241	0.151	0.155	0.137	0.220	0.124	0.132	0.187
1,3-dimethylbenzene	0.188	0.114	0.167	0.121	0.277	0.225	0.085	0.106
Propylbenzene	0.113	0.061	0.058	0.000	0.111	0.017	0.049	0.063
1,2,4-trimethylbenzene	0.108	0.063	0.074	0.097	0.168	0.053	0.069	0.032
1,3,5-trimethylbenzene	0.184	0.117	0.054	0.000	0.053	0.085	0.063	0.105
Total (µg/L)	2.497	1.408	1.108	1.007	1.837	0.914	1.133	1.853

(μg/L)	F ₄	F ₃	F ₂	<b>F</b> ₁
Benzene	0.146 ± 43.4 %	0.209 ± 70.3 %	0.663 ± 74.7 %	0.057 ± 96.4 %
Methylbenzene	0.548 ± 56.3 %	0.429 ± 59.3 %	0.303 ± 117.1 %	0.042 ± 90.0 %
Ethylbenzene	0.184 ± 62.1 %	0.170 ± 69.6 %	0.224 ± 48.5 %	0.006 ± 166.4 %
1,2&1,4-dimethylbenzene	0.166 ± 27.6 %	0.153 ± 52.6 %	0.152 ± 52.1 %	0.006 ± 162.9 %
1,3-dimethylbenzene	0.173 ± 53.5 %	0.138 ± 55.9 %	0.155 ± 53.9 %	0.007 ± 172.6 %
Propylbenzene	0.060 ± 64.8 %	0.061 ± 83.6 %	0.126 ± 58.3 %	1
1,2,4-trimethylbenzene	0.080 ± 75.0 %	0.088 ± 51.1 %	0.133 ± 56.0 %	1
1,3,5-trimethylbenzene	0.077 ± 30.4 %	0.098 ± 79.2 %	0.172 ± 51.6 %	0.009 ± 161.5 %
Total (μg/L)	1.434 ± 33.7 %	1.345 ± 57.6 %	1.927 ± 61.7 %	0.126 ± 87.3 %

Table 6.24Average Total Levels of Aromatic Hydrocarbons at Each Section of Site F

Average total levels of aromatic hydrocarbons at site F are shown in Figure 6.11, alongside those of other VOC (overall totals) to allow comparison. The first obvious observation is that aromatic hydrocarbons are more abundant in waste undergoing methanogenesis (waste 3 - 1 6 years old), after which levels decline significantly (by a factor of 15) as the waste enters the maturation phase of decomposition. They go from the most abundant in the early years (0 - 15 years) to the least abundant VOCs beyond 15 years. The behavior of aromatic hydrocarbons is similar to that of n-alkanes and branched chain alkanes in that levels rise as the waste ages to 16 years, then decline as the wastes further ages. However, aromatic hydrocarbon levels are similar in waste 3 - 11 years of age.



Fig. 6.11 Average Total Levels of Aromatic Hydrocarbons at Site F

It should be noted that the impact on aromatic levels from petroleum based materials and solvents discarded with household waste has not been considered. However, levels from anthropogenic sources, as there is a finite source of these, would be expected to decline over time as the waste ages. The increase in aromatic hydrocarbon levels in waste 11 - 16 years old indicates that aromatic hydrocarbons are being produced from microbial degradation of waste. This is further supported by the fact that the behavior of aromatic hydrocarbons, like that of alkanes, followed that of methane generation during the waste degradation process. Similar to n-alkanes, aromatic hydrocarbon levels in very old waste are lower, with aromatic hydrocarbon levels significantly lower, than levels in young refuse. The slightly elevated levels of aromatic hydrocarbons in waste 3 - 5 years may have some contribution from anthropogenic sources.

Figure 6.12 shows the average total individual aromatic hydrocarbon levels at site F, it is here that some striking observations are made. Aromatic hydrocarbon levels, except toluene, are fairly constant in waste 3 - 11 years old. Levels of these rise as the waste ages to 16 years, however, the rise in benzene levels is dramatic. Toluene behavior is completely different to that of other aromatic hydrocarbons. Toluene is significantly the most abundant aromatic hydrocarbon in waste 3 - 11 years of age and its levels decline gradually as the waste ages to 16 years old. As wastes enters the maturation phase of degradation (> 16 years), all aromatic hydrocarbon levels decrease dramatically. The behavior of toluene levels points to anthropogenic sources of this compound. Scott et al.⁽⁶⁴⁾ found that toluene was the most abundant compound observed during the first few days of waste degradation probably from direct volatilization. If in fact there is a significant contribution to toluene levels from anthropogenic sources, then Figure 6.12 shows that this contribution can persist for many years after waste deposition. Another likely explanation for the behavior of toluene and benzene may be than benzene is the product from the microbial degradation of toluene during methanogenesis. This would explain the dramatic fall and rise of toluene and benzene, respectively, as the waste ages. The high initial levels of toluene may be due to it being the main product of microbial degradation of other alkylbenzenes in very young refuse.



Fig. 6.12 Average Levels of Individual Aromatic Hydrocarbons at Site F

Table 6.25 shows the average gas composition with respect to aromatic hydrocarbons at each section at site F. As can be seen benzene and toluene account for approximately 50 % of total aromatic hydrocarbons in gas undergoing methanogenesis. During this phase ethyl benzene and xylenes are also significant contributors to gas composition. In the low levels of aromatic hydrocarbons left at the maturation phase of waste degradation benzene and toluene account for approximately 80 % of total aromatic hydrocarbons. Overall BTEX compounds are the major contributors to gas composition.

%	F ₄	F ₃	F ₂	F ₁
Benzene	10.2	15.5	34.4	45.1
Methylbenzene	38.2	31.9	15.7	32.9
Ethylbenzene	12.8	12.6	11.6	5.0
1,2&1,4-dimethylbenzene	11.6	11.4	7.9	4.5
1,3-dimethylbenzene	12.1	10.2	8.0	5.4
Propylbenzene	4.2	4.5	6.5	1
1,2,4-trimethylbenzene	5.6	6.5	6.9	1
1,3,5-trimethylbenzene	5.4	7.3	8.9	7.2
TOTAL	100.0	100.0	100.0	100.0

Table 6.25The Average Gas Composition of Aromatic Hydrocarbonsat Each Section of Site F

#### 6.2.2.1.1.7 Aromatic Hydrocarbons - Tentatively Identified and Indirectly

#### Quantified

Levels of other aromatics found at site F are shown in Table 6.26, and average total levels are shown in Table 6.27. Total average levels of these at sections  $F_1$ ,  $F_2$ ,  $F_3$  and  $F_4$  were 0.012 µg/L ± 189.1 %, 0.280 µg/L ± 80.6 %, 0.278 µg/L ± 70.1 % and 0.701 µg/L ± 158.8 %. These other aromatics are  $C_3$  and  $C_4$ -alkylbenzenes and contribute significantly to total levels at site F, particularly section  $F_4$ . These compounds include 1-ethyl-4-methylbenzene and 1-methyl-4-(1-methylethyl)benzene. This is shown in Fig 6.13, where overall aromatic hydrocarbon levels at site F are shown alongside those of overall total levels of other VOCs studied thus far. Trends observed in Fig 6.11 are still maintained in Fig 6.13. Overall aromatic hydrocarbon levels were obtained by combining results in Table 6.23 and 6.26. These are shown in Table 6.28, where aromatics are grouped as Benzene, Toluene ( $C_1$ ),  $C_2$ -alkyl benzenes,  $C_3$ -alkyl benzenes.

							-			
(ug/I)	F ₁₋₁		F	<b>F</b> ₁₋₂		<b>F</b> _{2A-1}		<b>F</b> _{2A-2}		A-3
(μg/L)	<b>S1</b>	S2	<b>S1</b>	S2	S1	S2	<b>S1</b>	S2	S1	S2
1-methylethylbenzene	/	/	/	/	0.037	0.045	/	/	0.01	0.062
1-ethyl-2-methylbenzene	/	/	/	/	0.071	0.106	0.05	0.113	/	1
1-ethyl-4-methylbenzene	/	/	/	1	0.031	0.043	/	1	0.026	0.11
1-methyl-4- (1-methylethyl)benzene	1	1	0.002	0.046	1	1	0.065	0.093	0.017	0.632
1-methyl-2-propylbenzene	1	/	/	/	1	1	1	1	0.019	0.073
2-ethyl-1,3-dimethylbenzene	1	/	/	/	0.095	0.163	/	/	/	/
Total (μg/L)	/	/	0.002	0.046	0.234	0.357	0.115	0.206	0.072	0.877

Table 6.26The Levels of Aromatic Hydrocarbons Indirectly Quantified from Sites F

## Table 6.26 (Continued)

The Levels of Aromatic Hydrocarbons Indirectly Quantified from Sites F

(ug/[)	F _{2A-4}		<b>F</b> _{2B-1}		<b>F</b> _{2B-2}		<b>F</b> _{3A-1}		F _{3A-2}	
(µg/L)	<b>S1</b>	S2	<b>S</b> 1	<b>S2</b>	<b>S</b> 1	<b>S2</b>	<b>S1</b>	S2	<b>S1</b>	S2
1-methylethylbenzene	1	/	/	1	0.024	0.045	1	/	/	1
1-ethyl-2-methylbenzene	1	1	0.013	0.11	0.028	0.057	0.068	0.082	/	1
1-ethyl-4-methylbenzene	0.073	0.173	/	1	0.015	0.042	0.042	0.142	0.019	0.027
1-methyl-4- (1-methylethyl)benzene	0.175	0.317	0.018	0.17	0.103	0.133	0.122	0.247	0.028	0.145
1-methyl-2-propylbenzene	1	1	/	1	/	1	0.039	0.085	/	/
2-ethyl-1,3-dimethylbenzene	1	/	/	/	/	1	/	/	/	/
Total (μg/L)	0.248	0.49	0.031	0.28	0.17	0.277	0.271	0.556	0.047	0.172

Table 6.26 (Continued)The Levels of Aromatic Hydrocarbons Indirectly Quantified from Sites F

	F _{3B-1}		F ₃	F _{3C-1}		4-1	F ₄₋₂	
(µg/L)	<u>S1</u>	S2	<b>S1</b>	S2	<b>S</b> 1	S2	<b>S1</b>	S2
1-methylethylbenzene	0.07	0.078	/	/	0.086	0.267	/	/
1-ethyl-2-methylbenzene	/	/	/	/	0.049	0.128	/	/
l-ethyl-4-methylbenzene	0.092	0.094	/	/	0.039	0.9	0.021	0.043
1-methyl-4- (1-methylethyl)benzene	0.289	0.316	0.096	0.146	0.123	1.069	0.032	0.048
1-methyl-2-propylbenzene	/	1	/	/	1	/	/	/
2-ethyl-1,3-dimethylbenzene	/	1	/	/	/	/	_/	/
 Total (μg/L)	0.451	0.488	0.096	0.146	0.297	2.364	0.053	0.091

(µg/L)	F	<b>F</b> ₃	F ₂	<b>F</b> ₁	
1-methylethylbenzene	0.088 ± 142.6 %	0.019 ± 185.5 %	0.019 ± 123.5 %		
1-ethyl-2-methylbenzene	0.044 ± 136.5 %	0.019 ± 186.2 %	0.046 ± 99.7 %	1	
1-ethyl-4-methylbenzene	0.251 ± 172.7 %	0.052 ± 99.4 %	0.043 ± 124.0 %	1	
1-methyl-4-(1-methylethyl)benzene	0.318 ± 157.9 %	0.174 ± 57.8 %	0.144 ± 124.9 %	0.012 ± 189.1 %	
1-methyi-2-propylbenzene	1	0.016 ± 201.4 %	0.008 ± 277.7 %	1	
2-ethyl-1,3-dimethylbenzene	/	/	0.022 ± 243.1 %	1	
Total (µg/L)	0.701 ± 158.8 %	0.278 ± 70.1 %	0.280 ± 80.6 %	0.012 ± 189.1 %	

 Table 6.27

 Average Total Levels of Other Aromatic Hydrocarbons at Each Section of Site F



 Table 6.28

 Average Total Group Levels of Aromatic Hydrocarbons at Each Section of Site F

(μg/L)	F ₄	F ₃	F ₂	<b>F</b> ₁
Benzene	0.146 ± 43.4 %	0.209 ± 70.3 %	0.663 ± 74.7 %	0.057 ± 96.4 %
C ₁ -Alkylbenzene	0.548 ± 56.3 %	0.429 ± 59.3 %	0.303 ± 117.1 %	0.042 ± 90.0 %
C ₂ -Alkylbenzene	0.523 ± 42.8 %	0.461 ± 58.4 %	0.531 ± 49.1 %	0.019 ± 167.5 %
C ₃ -Alkylbenzene	0.601 ± 28.3 %	0.336 ± 58.6 %	0.538 ± 64.6 %	0.009 ± 85.5 %
C ₄ -Alkylbenzene	0.318 ± 157.9 %	0.189 ± 58.5 %	0.173 ± 107.2 %	0.012 ± 189.1 %
Total (µg/L)	2.135 ± 26.3 %	1.623 ± 56.6 %	2.207 ± 62.9 %	0.138 ± 88.0 %

Figure 6.14 shows average total levels of benzene, toluene,  $C_2$ -alkylbenzenes,  $C_3$ -alkylbenzenes and  $C_4$ -alkylbenzenes at site F. When the data is viewed in this way, compared with Figure 6.12, some interesting trends are observed.  $C_1 - C_4$ -

alkylbenzene levels decrease as the waste ages to 11 years. As the waste further ages to 16 years the behavior of  $C_1 - C_4$ -alkylbenzenes changes. Toluene levels continue to decline,  $C_2$  and  $C_4$  levels remain fairly constant and  $C_3$  levels increase. Similar to toluene trends described earlier, these results suggest the initial levels of  $C_2 - C_4$ alkylbenzenes may have some contributions from anthropogenic sources and these are depleted as the waste ages to 11 years. As the waste ages beyond 11 years aromatic hydrocarbon levels, particularly benzene and  $C_3$ -alkylbenzene, rise due to microbial degradation of waste. As mentioned previously the dramatic rise in benzene levels as the waste ages to 16 years may be that it is final product from the microbial degradation of  $C_1 - C_4$ -alkylbenzenes.



Fig. 6.14 Average Total Levels of Each Group of Aromatic Hydrocarbons at Site F

The gas composition shown in Table 6.29 further highlights the trends of the various groups of aromatic hydrocarbons. In waste 3 - 11 years of age  $C_1 - C_3$  abundances are comparable and account for approximately 80 % of total aromatic hydrocarbons, and benzene is the least abundant. As the waste ages to 16 years,  $C_1 - C_3$  abundances drop to approximately 60 % and benzene rise to 30 %.  $C_4$ -alkylbenzene levels are the lowest beyond 5 years waste age.

%	$\mathbf{F}_4$	F ₃	F ₂	<b>F</b> ₁
Benzene	6.9	12.9	30.0	41.1
C ₁ -Alkylbenzene	25.6	26.4	13.7	30.0
C ₂ -Alkylbenzene	24.5	28.4	24.0	13.6
C ₃ -Alkylbenzene	28.1	20.7	24.4	6.6
C ₄ -Alkylbenzene	14.9	11.7	7.8	8.7
TOTAL	100	100	100	100

Table 6.29The Average Groups Gas Composition of Aromatic Hydrocarbons<br/>at Each Section of Site F

Young et al.⁽⁸⁹⁾ found that in landfill gas from domestic sites where the waste ranged in age from three weeks to 5 - 6 years, propylbenzenes and butylbenzenes were usually the most abundant aromatic compounds, with appreciable levels of xylenes, ethylbenzene and toluene. Propylbenzene was one of the most persistent compounds across the three domestic sites and its release appeared not to be dependent on the age of the refuse. Benzene was by far the least abundant. Our results for  $C_1 - C_3$ alkylbenzenes agree with Young et al.⁽⁸⁹⁾ as these were abundant aromatics throughout the methanogenic phase of waste degradation, however C4-alkylbenzenes were not abundant. We also found benzene to be the least abundant aromatic hydrocarbon in younger refuse (3 - 5 years). Allen et al.⁽⁹²⁾, results from the study of seven landfills of varying waste age and similar inputs, showed that appreciable levels of  $C_1 - C_4$  benzenes were present. However levels of benzene were extremely low. Like Allen et  $al^{(92)}$ , we found appreciable levels of  $C_1 - C_4$  alkylbenzenes but in contrast benzene levels were comparable to other aromatic groups and were the most abundant in later stages of methanogenesis. Other workers also found benzene to be the least abundant, for example, Eklund et al.(85) found that, compared with other aromatic hydrocarbons, benzene was the least and toluene the most abundant in landfill gas from municipal solid waste of varying ages. Other aromatics found include xylenes, trimethylbenzenes, butylbenzenes, propylbenzenes, ethyltoluenes, diethyltoluenes and benzenes. Similarly Schweigkofler et al. (58) found benzene to be the least abundant aromatic compound in landfill gas from two domestic sites. Levels of xylenes, toluene, ethylbenzene, trimethylbenzenes and isopropyltoluene were an order of magnitude higher. Our results also concur with those of Scott et al.⁽⁶⁴⁾ who found that as anaerobic conditions were established the concentration of alkylbenzenes, particularly  $C_3$  and xylenes, became significant. We also found that toluene became significant as anaerobic conditions were established (3 – 5 years) and has been mentioned that contributions to toluene levels may have come from anthropogenic sources or microbial degradation of other alkylbenzenes.

#### 6.2.2.1.1.8 Terpenes – Positively Identified and Directly Quantified

Terpenes levels found at site F are shown in Table 6.30. Total levels at site F, ranged from  $0.001 - 0.035 \ \mu g/L$ ,  $0.462 - 3.980 \ \mu g/L$  at section F₂,  $0.154 - 2.548 \ \mu g/L$  at section F₃ and  $0.789 - 2.768 \ \mu g/L$  at section F₄. Table 6.31 shows average levels of terpene at each section of site F, and these were  $0.009 \ \mu g/L \pm 191.4 \ \% 1.320 \ \mu g/L \pm 84.3 \ \% 1.085 \ \mu g/L \pm 75.6 \ \%$  and  $1.821 \ \mu g/L \pm 48.8 \ \%$  at section F₁, F₂, F₃ and F₄ respectively. Similar to other VOC results at site F, intrasection variations at each section of the site F for terpenes were not significant.

Table 6.30The Levels of Terpenes Directly Quantified from Sites F

(μg/L)	<b>F</b> ₁₋₁		F ₁₋₂		<b>F</b> _{2A-1}		<b>F</b> _{2A-2}		<b>F</b> _{2A-3}	
	<b>S1</b>	S2	S1	S2	S1	S2	S1	S2	S1	S2
a-Pinene	BDL	BDL	0.001	0.035	0.190	0.222	0.775	0.534	1.251	0.291
β-Pinene	BDL	BDL	BDL	BDL	0.094	0.115	0.256	0.312	0.469	0.105
Limonene-1	BDL	BDL	BDL	BDL	0.187	0.219	1.309	1.116	2.260	0.300
Total (μg/L)	BDL	BDL	0.001	0.035	0.471	0.556	2.340	1.962	3.980	0.695

Table 6.30 (Continued)The Levels of Terpenes Directly Quantified from Sites F

(ug/I)	F _{2A-4}		F ₂	F _{2B-1}		<b>F</b> _{2B-2}		F _{3A-1}		<b>F</b> _{3A-2}	
(µg/L)	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	
a-Pinene	0.464	0.333	0.457	0.076	0.414	0.208	0.916	0.666	0.169	0.064	
β-Pinene	0.168	0.109	0.430	0.076	0.144	0.156	0.464	0.254	0.050	0.039	
Limonene-1	1.016	0.019	1.205	0.125	0.288	0.148	1.168	1.098	0.146	0.050	
Total (µg/L)	1.648	0.462	2.092	0.278	0.846	0.512	2.548	2.018	0.364	0.154	

Table 6.30 (Continued)The Levels of Terpenes Directly Quantified from Sites F

(ug/I)	F ₃	F _{3B-1}		<b>F</b> _{3C-1}		F ₄₋₁		F ₄₋₂	
(µg/L)	S1	S2	<b>S1</b>	S2	S1	S2	<b>S</b> 1	S2	
a-Pinene	0.259	0.167	0.589	0.345	0.948	0.244	0.818	0.496	
β-Pinene	0.104	0.079	0.166	0.111	0.972	0.108	0.200	0.153	
Limonene-1	0.768	0.623	0.262	0.122	0.849	0.437	1.296	0.762	
Total (μg/L)	1.131	0.869	1.016	0.577	2.768	0.789	2.314	1.412	

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(µg/L)	<b>F</b>	F ₃	F ₂	F ₁
a-Pinene	0.626 ± 50.7 %	0.397 ± 74.8 %	0.435 ± 73.1 %	0.009 ± 191.4 %
β-Pinene	0.358 ± 114.6 %	0.158 ± 89.2 %	0.203 ± 66.2 %	/
Limonene-1	0.836 ± 42.4 %	0.530 ± 84.8 %	0.683 ± 101.2 %	/
Total (µg/L)	1.821 ± 48.8 %	1.085 ± 75.6 %	1.320 ± 84.3 %	0.009 ± 191.4 %

 Table 6.31

 Average Total Levels of Terpenes at Each Section of Site F

Total average levels of terpenes at site F are shown in Figure 6.15, alongside other VOC levels (overall) for comparison. As can be seen terpenes are the second most abundant class of VOC, next to aromatic hydrocarbons in younger refuse (3 - 5 years). In waste 5 - 16 years old terpene levels are comparable to those of alkanes. Similar to aromatic hydrocarbons their levels begin high then decline as the waste ages to 11 years, after which levels slightly rise in waste 16 years old. In very old waste negligible terpenes are present. Again, similar to aromatic hydrocarbons, high initial levels may be due to anthropogenic sources. Allen *et al.*⁽⁹²⁾ suggested potential sources of terpenes include fragrant household detergents and air fresheners. However it is likely that easily degradable wastes such as garden waste may also be a large contributor. Negligible levels of terpene in very old waste indicate that biodegradable sources of terpene have been depleted. Similar to other VOCs studied at site F, terpene trends followed that of methane generation where levels are similar during methanogenesis and in very old waste in the maturation phase of degradation, terpene levels decline significantly.



Figure 6.16 shows average total individual terpene levels at site F. Limonene is clearly the most abundant terpene throughout the methanogenic phase of waste degradation. Levels of all three terpenes show a similar trend, where levels begin high and decline as the waste ages to 11 years after which they rise, but not to initial levels, before they are completely depleted in waste in the maturation phase of waste degradation.

Similar to other studies^(58, 64, 85, 89, 90, 92)  $\alpha$ - Pinene and limonene were the dominant terpenes found in landfill gas. Young *et al.*⁽⁸⁹⁾ found that limonene was one of the most persistent VOCs in landfill gas from three domestic sites. Limonene levels when compared with other terpenes were higher in three weeks, and seven months old refuse, but in 5 – 6 years old refuse limonene levels were lower than other terpenes. Similar results were found by Allen *et al.*⁽⁹²⁾ where in landfill gas from seven waste disposal sites, all containing waste at least six year old waste at the time of the study,  $\alpha$ - and  $\beta$ -pinene accounted for between 51 % and 100 % of total terpenes. On the other hand Scott *et al.*⁽⁶⁴⁾ observed that limonene was normally found at the highest concentration while Eklund *et al.*⁽⁸⁵⁾ found limonene was five times more abundant than  $\alpha$ -pinene and the abundance of  $\beta$ -Pinene was lower by (at least) a factor of 10. Schweigkofler *et al.*⁽⁵⁸⁾ also found limonene to be slightly more abundant than  $\alpha$ -

pinene. Our results show that limonene was the most abundant terpene in waste 3 - 16 years old undergoing methanogenesis. This is further highlighted in Table 6.32, where average gas composition at site F with respect to terpene is shown in Table 6.32. Section F₁, will not be considered as only traces of  $\alpha$ -pinene were found here. At sections F₂ to F₄ where the waste age was 3 - 16 years and in advanced stages of methanogenesis, terpene abundances in the gas were almost identical. Limonene,  $\alpha$ -pinene and  $\beta$ -pinene accounted for approx. 50 %, 35 % and 15 %, respectively.



<b>Table 6.32</b>
The Average Gas Composition of Terpenes at Each Section of Site F

%	F ₄	F ₃	F ₂	F ₁
a-Pinene	34.4	36.6	32.9	100.0
β-Pinene	19.7	14.6	15.4	1
Limonene-1	45.9	48.8	51.7	/
TOTAL	100.0	100.0	100.0	100.0

6.2.2.1.1.9 Terpenes - Tentatively Identified and Indirectly Quantified

Levels of other terpenic hydrocarbons found at site F are shown in Table 6.33. At section  $F_1$  camphene levels were comparable with those of  $\alpha$ -pinene and at section  $F_2$  and  $F_3$  camphene was the least abundant terpene. At section  $F_4$ , carene was observed

and even though not abundant its levels were significant. Schweigkofler *et al.*⁽⁵⁸⁾ also found camphene in landfill gas from two domestic sites but its levels were significantly lower than limonene and  $\alpha$ -pinene,.

Table 6.33The Levels of Terpenes Indirectly Quantified from Sites F

(	F	1-1	<b>F</b>	-2	<b>F</b> ₂	4-1	<b>F</b> ₂	4-2	F ₂	A-3
(µg/L)	S1	S2	<u>S1</u>	S2	<b>S1</b>	S2	S1	S2	<b>S</b> 1	
Camphene	/	/	0.004	0.065	0.037	0.053	0.016	0.019	0.018	0.206
δ-Carene-3	/	/	/	/	/	1	1	1	/	/

Table 6.33 (Continued)The Levels of Terpenes Indirectly Quantified from Sites F

(ug/I_)	F ₂	A-4	F ₂	B-1	<b>F</b> ₂	B-2	<b>F</b> ₃	A-1	F ₃	A-2
(µg/L)	S1	S2	S1	S2	S1	S2	<b>S</b> 1	S2	<b>S</b> 1	S2
Camphene	0.062	0.354	0.011	0.275	0.016	0.077	0.045	0.193	1	1
δ-Carene-3	/	/	1	/	/	1	1	/	1	1

Table 6.33 (Continued)The Levels of Terpenes Indirectly Quantified from Sites F

(μg/L)	F ₃	B-1	F ₃	C-1	F.	4-1	F	4-2
	S1	S2	S1	S2	S1	S2	S1	S2
Camphene	1	/	0.038	0.040	1	1	1	1
δ-Carene-3	/	/	/	/	0.147	0.366	1	/

#### 6.2.2.1.2 Landfill E

## 6.2.2.1.2.1 n-Alkanes - Positively Identified and Directly Quantified

n-alkane levels at site E are show in Table 6.34 and total levels ranged from 4.843 – 13.079  $\mu$ g/L at section E₁ and 8.002 – 11.265  $\mu$ g/L at section E₂. Average total n-alkane levels are shown in Table 6.35 and were 8.305  $\mu$ g/L ± 34.4 % at section E₁ and 9.510  $\mu$ g/L ± 14.6 % at section E₂. Intrasection variations at site E were not significant. Levels of n-alkanes at site E were an order of magnitude higher than at site F for waste of similar ages. This is not surprising as levels of VOCs found in landfill depend on a number of factors, as was discussed in Section 1.3.3.

	I HV D		1 Miller	Directly	Zuantin	cu nom )	She E	
(ug/L)	E	1-1	E	1-2	E	1-3	E	1-4
(µg/L)	S1	<b>S2</b>	<b>S1</b>	S2	<b>S1</b>	S2	S1	S2
Hexane	0.161	0.153	0.835	0.844	0.326	0.219	0.094	0.140
Heptane	0.788	0.732	2.257	2.508	1.259	0.804	0.291	0.443
Octane	1.073	0.895	1.246	1.385	1.258	1.043	0.349	0.504
Nonane	2.821	2.196	2.840	3.155	2.897	2.615	2.924	2.060
Decane	1.967	1.415	2.703	3.004	2.072	2.026	2.851	3.672
Undecane	0.459	0.258	1.130	1.456	1.039	0.744	0.749	0.993
Dodecane	BDL	BDL	0.656	0.728	BDL	BDL	0.009	0.022
Total (µg/L)	7.269	5.649	11.667	13.079	8.853	7.451	7.266	7.833

 Table 6.34

 The Levels of n-Alkanes Directly Quantified from Site E

Table 6.34 (*Continued*) The Levels of n-Alkanes Directly Quantified from Site E

					<u> </u>			
(ug/I)	Ε	1-5	E	1-6	E	2-1	E	2-2
(µg/L)	S1	S2	<b>S1</b>	<b>S2</b>	S1	S2	S1	S2
Hexane	0.212	0.066	0.140	0.263	0.644	0.736	0.431	0.496
Heptane	0.785	0.294	0.638	0.899	2.442	2.713	2.045	2.272
Octane	0.966	0.414	0.505	0.740	0.950	1.056	1.018	1.131
Nonane	4.815	1.927	1.899	2.515	2.269	2.522	2.589	2.876
Decane	4.954	1.658	1.355	1.848	1.377	1.530	1.539	1.710
Undecane	1.335	0.591	0.394	0.892	0.292	0.345	1.256	1.706
Dodecane	BDL	BDL	0.052	0.440	0.027	0.030	0.965	1.072
Total (µg/L)	13.068	4.950	4.984	7.598	8.003	8.932	9.843	11.265

Average Iutar	Levels of II-Alkanes at Lach	Section of Site E
(µg/L)	E ₁	E ₂
Hexane	0.288 ± 92.9 %	0.577 ± 24.0 %
Heptane	0.975 ± 73.0 %	2.368 ± 11.9 %
Octane	0.865 ± 41.3 %	1.039 ± 7.3 %
Nonane	2.722 ± 28.8 %	2.564 ± 9.7 %
Decane	2.46 ± 42.6 %	1.539 ± 8.9 %
Undecane	0.837 ± 44.7 %	0.900 ± 77.4 %
Dodecane	0.159 ± 175.4 %	0.524 ± 109.4 %
Total (µg/L)	8.305 ± 34.4 %	9.510 ± 14.6 %

Table 6.35 Average Total Levels of n-Alkanes at Each Section of Site F

Total average n-alkane levels at site E are shown in Figure 6.17 and as can be seen, the levels are similar. Remembering that the age of waste at sections  $E_1$  and  $E_2$  ranged from 2 – 7 years and a few months – 7 years respectively, the slightly higher levels of n-alkane at section  $E_2$  indicates that there is little contribution to n-alkane levels from the fresher waste (a few months – 2 years). This is consistent with n-alkane results for site F, where levels increased as the waste entered later stages of methanogenesis. (see Figure 6.3). Also, there appears to be no impact on n-alkane levels from the daily cover material (soil contaminated with metal and hydrocarbons) at section  $E_2$ .



Fig 6.17 Average Total Levels of n-Alkanes at Each Section of Site E
Figure 6.18 shows the average total individual n-alkane levels at site E. The results here can be related to those for n-alkane at site F (see Figure 6.4). At site F,  $C_7$ ,  $C_9$ and  $C_{10}$  are the most abundant n-alkanes during the methanogenic phase of waste degradation (3 – 16 years old). For waste 3 –11 years old, nonane was the most abundant, followed by similar levels of  $C_7$  and  $C_{10}$ . The next abundant compound is octane followed by comparable levels of  $C_6$  and  $C_{11}$  and dodecane is the least abundant. These exact same trends are seen at site E where the waste age was from a few months – 7 years and actively producing methane. The high levels of heptane at section  $E_2$  can be best explained by considering that it is one of the abundant compounds produced during methanogenesis and can be expected to be found in levels comparable to nonane and decane. There does not appear to be any major contribution to heptane levels from anthropogenic sources or the cover material at site  $E_2$ .



Table 6.36 shows the gas composition with respect to n-alkanes at site E. The gas composition at each section of site E is fairly consistent, except for abundances of  $C_7$  and  $C_{10}$ . Overall  $C_7$ ,  $C_9$  and  $C_{10}$  account for approximately 70 % of total n-alkanes.

The Gas Composi	tion of n-Alkanes at Each Se	ction of Site E
%	E ₁	E ₂
Hexane	3.5	6.1
Heptane	11.7	24.9
Octane	10.4	10.9
Nonane	32.8	27.0
Decane	29.6	16.2
Undecane	10.1	9.46
Dodecane	1.9	5.5
TOTAL	100.0	100.0

Table 6.36The Gas Composition of n-Alkanes at Each Section of Site E

Comparison with gas composition at site F (Table 6.11) shows that the gas at section  $E_1$  (waste 2 – 7 years old) is similar to section  $F_2$  (waste 11 – 16 years old). However, gas at section  $E_2$  (waste a few months – 7 years old) is similar to sections  $F_3$  (5 – 11 years old). Overall the composition at site E resembles the waste 5 – 16 years old at site F in the methanogenic phase of waste degradation. This again indicates that there is minor contribution to n-alkanes from the fresh refuse and also indicated that the waste at section  $E_1$  may be in further stages of methanogenesis than section  $E_2$ .

Our results for waste undergoing methanogenesis at sites E and F were very consistent where  $C_8 - C_{11}$  n-alkanes, particularly  $C_7$ ,  $C_9$  and  $C_{10}$ , were the abundant n-alkanes. These results concur with those of Young *et al.*⁽⁸⁹⁾ and Eklund *et al.*⁽⁸⁵⁾ where  $C_8 - C_{11}$  alkanes were the most abundant in older refuse and also with Scott *et al.*⁽⁶⁴⁾, where  $C_9$  and  $C_{10}$  were the dominant alkanes released under anaerobic conditions. Schweigkofler *et al.*⁽⁹⁰⁾ also found  $C_9 - C_{11}$  alkanes to be the abundant n-alkanes in domestic sites. We also found heptane to be an abundant n-alkane in waste undergoing methanogenesis. Although, levels of n-alkanes were an order of magnitude higher than site F, n-alkane trends were similar.

#### 6.2.2.1.2.2 n-Alkanes - Tentatively Identified and Indirectly Quantified

Other tentatively identified and indirectly quantified n-alkanes found in landfill gas from site E are shown in Table 6.37.

11	I he Levels of h-Alkanes hun eery Quantineu from Site E									
$E_{1-1}$			E	1-3	E	1-4				
(µg/L)	g/L) S1 S2		<b>S1</b>	S2	<b>S</b> 1	S2	<b>S</b> 1	S2		
Pentane	0.245	0.327	0.270	0.449	0.381	0.554	0.063	0.091		

Table 6.37The Levels of n-Alkanes Indirectly Quantified from Site E

Table 6.37 (*Continued*) The Levels of n-Alkanes Indirectly Quantified from Site F.

				an oong	2			
	E	1-5	E	1-6	E	2-1	E	2-2
(µg/L)	S1	S2	<b>S</b> 1	S2	S1	S2	S1	S2
Pentane	0.056	0.205	/	/	0.295	0.373	0.233	0.363

Table 6.38 shows pentane levels at site E where average total levels at sections  $E_1$  and  $E_2$  were 0.220 µg/L ± 83.2 % and 0.316 µg/L ± 20.6 %. At site E, pentane levels are significant compared with site F for waste of similar ages. This may suggest that there are contributions to pentane levels at site E from anthropogenic sources. At section  $E_2$  these contributions could come from the fresher refuse (a few months – 2 years) or the daily cover material, but, at section  $E_1$  the pentane levels are not so easily explained. However the pentane levels at site E are not surprising as n-alkane levels at site E are an order of magnitude higher than site F. Therefore it is safe to say that pentane is being produced from the microbial degradation of waste.

These levels did not impact greatly on total n-alkane levels. This is further highlighted in Table 6.39 where pentane has been added to the gas composition data, and as can be seen gas composition as compared to Table 6.36 has not been affected.

 Table 6.38

 Average Total Levels of Pentane at Each Section of Site E

(μg/L)	E ₁	E ₂
Pentane	0.220 ± 83.2 %	0.316 ± 20.6 %

%	$\mathbf{E}_{1}$	E ₂
Pentane	2.6	3.2
Hexane	3.4	5.9
Heptane	11.4	24.1
Octane	10.1	10.6
Nonane	31.9	26.1
Decane	28.9	15.7
Undecane	9.8	9.2
Dodecane	1.9	5.3
TOTAL	100.0	100.0

Table 6.39The Gas Composition of Total n-Alkanes at Each Section of Site E

# 6.2.2.1.2.3 Branched Chain Alkanes - Tentatively Identified and Indirectly Quantified

The levels of branched chain alkanes at site E are shown in Table 6.40 and total levels ranged from  $1.089 - 9.646 \ \mu g/L$  at section  $E_1$ , and  $4.736 - 10.610 \ \mu g/L$  at section  $E_2$ . Average totals levels of branched chain alkane groups are shown in Table 6.41 and were  $4.914 \ \mu g/L \pm 47.2 \ \%$  at section  $E_1$ , and  $7.658 \ \mu g/L \pm 32.3 \ \%$  at section  $E_2$ . Intrasection variations at each section of site E were not significant. Similar to n-alkane results, levels of branched chain alkanes for wastes of similar ages, were up to an order of magnitude higher at site E than site F.

(μg/L)		E	-1	E	E1-2		1-3	E1-4	
		S1	S2	<b>S</b> 1	S2	S1	S2	<b>S1</b>	S2
C5	2-methylbutane	0.254	0.342	0.269	0.308	0.277	0.420	0.108	0.122
	Total C5	0.254	0.342	0.269	0.308	0.277	0.420	0.108	0.122
C6	2-methylpentane	/**	/	0.441	0.560	/	/	0.141	0.211
	Total C6	/	/	0.441	0.560	/	/	0.141	0.211
C ₇	*2-methylhexane & 2,3-dimethylpentane	0.377	0.371	1.466	1.878	0.374	0.551	0.266	0.270
	3-methylhexane	0.258	0.283	1.110	1.421	0.272	0.412	0.128	0.183
	Total C7	0.635	0.654	2.576	3.299	0.646	0.963	0.394	0.453
C.	2,3-dimethylhexane	/	/	0.371	0.440	/	/	/	/
C8	2-methylheptane	0.229	0.381	0.500	0.502	0.253	0.474	/	/
	Total C8	0.229	0.381	0.871	0.942	0.253	0.474	/	/
C	2-methyloctane	0.862	0.955	1.311	1.434	0.928	1.017	0.719	1.003
C9	3-methyloctane	0.879	1.085	1.103	1.411	0.763	0.863	0.720	1.042
	Total C9	1.741	2.040	2.414	2.845	1.691	1.880	1.439	2.045
	2,6-dimethyloctane	0.623	0.931	/	/	0.538	0.590	/	/
<b>C</b> 10	4-methylnonane	0.567	0.797	0.859	0.971	0.578	0.589	1.069	1.430
	2-methylnonane	0.500	1.015	0.652	0.721	0.523	0.662	0.998	1.799
	Total C10	1.690	2.743	1.511	1.692	1.639	1.841	2.067	3.229
<b>C</b> 12	2,2,4,6,6- pentamethylheptane	/	/	/	/	/	/	0.336	0.522
	Total C12	/	/	/	/	/	/	0.336	0.522
	TOTAL	4.549	6.16	8.082	9.646	4.506	5.578	4.485	6.582

**Table 6.40** The Levels of Branched Chain Alkanes Indirectly Quantified from Site E

* The concentration of 2-methylhexane & 2,3-dimethylpentane is the total for both as these co-elute. ** negligible levels.

		J Canada and Andrea							
	(ug/L)	E	1-5	<u> </u>	E1-6		2-1	E	2-2
		<u>\$1</u>	<u>S2</u>	<u>\$1</u>	S2	<b>S1</b>	S2	<b>S1</b>	S2
<b>C</b> 5	2-methylbutane	0.093	0.384	/	/	0.79	0.866	0.361	0.517
	Total C5	0.093	0.384	/	/	0.79	0.87	0.361	0.517
<b>C</b> 6	2-methylpentane	1	/	/	/	0.589	0.686	0.256	0.338
	Total C6	1	/	/	/	0.589	0.69	0.256	0.338
C7	*2-methylhexane & 2,3-dimethylpentane	/	/	/	/	1.477	1.687	0.593	0.958
	3-methylhexane	1	/	/	/	1.287	1.471	0.464	0.75
	Total C7	1	/	/	/	1.287	1.47	0.464	0.75
C.	2,3-dimethylhexane	1	/	/	/	0.233	0.361	/	/
C8	2-methylheptane	/	1	/	/	0.235	0.262	/	/
	Total C8	/	1	/	/	0.468	0.623	/	/
C.	2-methyloctane	/	/	0.176	0.243	0.536	0.63	0.441	0.567
C9	3-methyloctane	/	/	0.497	0.747	0.797	1.042	0.869	1.206
	Total C9	/	/	0.673	0.990	1.333	1.672	1.310	1.773
	2,6-dimethyloctane	0.445	1.306	0.41	0.62	0.94	0.962	0.791	1.045
<b>C</b> 10	4-methylnonane	1	/	/	/	0.818	0.957	/	/
	2-methylnonane	0.551	1.946	0.378	1.098	0.979	1.052	0.534	0.629
	Total C10	0.996	3.252	0.788	1.718	2.737	2.971	1.325	1.674
<b>C</b> 12	2,2,4,6,6- pentamethylheptane	/	/	0.305	0.996	0.61	0.631	0.427	0.582
	Total C12	/	/	0.305	0.996	0.610	0.630	0.427	0.582
	TOTAL	1.089	3.636	1.766	3.704	9.291	10.61	4.736	6.592

 Table 6.40 (Continued)

 The Levels of Branched Chain Alkanes Indirectly Quantified from Site E

 Table 6.41

 Average Total Levels of Branched Chain Alkanes at Each Section of Site E

The star bereis of Dranched Chain Annunes at Each Section of Site E							
(μg/L)	E ₁	E ₂					
C5-Branched Chain Alkanes	0.258 ± 44.9 %	0.634 ± 37.2 %					
C6-Branched Chain Alkanes	0.338 ± 57.8 %	0.467 ± 43.5 %					
C7-Branched Chain Alkanes	0.802 ± 132.1 %	2.172 ± 44.3 %					
<b>C8-Branched Chain Alkanes</b>	0.916 ± 74.9 %	0.668 ± 30.3 %					
C9-Branched Chain Alkanes	1.786 ± 37.9 %	2.357 ± 23.3 %					
C10-Branched Chain Alkanes	0.904 ± 55.9 %	0.799 ± 32.0 %					
C12-Branched Chain Alkanes	0.540 ± 59.1 %	0.563 ± 16.5 %					
Total (µg/L)	4.914 ± 47.2 %	7.658 ± 32.3 %					

Total average branched chain alkane levels at site E is shown in Figure 6.19 alongside those of n-alkanes (including pentane). At both sections of site E, branched chain alkane levels were lower than n-alkane and this trend was also observed in refuse of similar age at site F (3 – 5 years at section  $F_4$ , a few months – 7 years at site E). Similar total branched chain alkane levels at sections  $E_1$  and  $E_2$  also indicates that

there was not any major contribution to branched chain alkane levels from the younger refuse (a few months – 2 years) or daily cover material at section  $E_2$ .



Figure 6.19 Average Total Levels of Branched Chain Alkane at Site E

Figure 6.20 shows the total individual branched chain alkane group levels at site E. Similar to n-alkane results at site F,  $C_7 - C_{10}$  branched chain alkanes are abundant where  $C_9$  is always the most abundant.  $C_8 - C_{12}$  levels at each section were comparable where  $C_5 - C_7$  levels, particularly  $C_7$ , were higher at section  $E_2$ . Section  $E_2$  contained the younger refuse (a few months – 2 years) and perhaps these higher levels  $C_5 - C_7$  branched chain alkanes are due to the younger refuse. The difference in levels of  $C_5$  and  $C_7$  at section  $E_1$  and  $F_2$  do not indicate any major contribution due to direct volatilization from anthropogenic sources or as was mentioned for n-alkanes, the waste in section  $E_1$  may be in further stages of methanogenesis than section  $E_2$ . This is because at site F,  $C_5$  and  $C_6$  branched chain alkane levels increase in older waste (11 – 16 years). Overall, trends observed at site E are similar to branched chain alkane trends at site F, eventhough levels differed by an order of magnitude, where during methanogenesis  $C_7 - C_{10}$  branched chain alkanes were the abundant branched chain alkanes with  $C_9$  and  $C_{10}$  usually the most abundant.



Fig. 6.20 Average Total Levels of Grouped Branched Chain Alkanes at Site E

Table 6.42 shows the gas composition at site E. As can be seen the greatest contribution is from the  $C_7 - C_{10}$  branched chain alkanes, which account for approximately 80 % of total branched chain alkane levels. C9 is the major contributor accounting for approximately 35 % of the total.

The Gas Composition of at Each	The Gas Composition of Group Branched Chain Alkanes at Each Section of Site E							
%	E	E ₂						
C5-Branched Chain Alkanes	4.4	8.3						
C6-Branched Chain Alkanes	6.9	6.1						
C7-Branched Chain Alkanes	16.3	28.4						
C8-Branched Chain Alkanes	18.6	8.7						
C9-Branched Chain Alkanes	36.3	30.8						
C10-Branched Chain Alkanes	18.4	10.4						
C12-Branched Chain Alkanes	11.0	7.3						
TOTAL	100.0	100.0						

Table 6.42

Our results suggest that for mature refuse actively producing methane,  $C_7 - C_{10}$ branched chain alkanes are the abundant branched chain alkanes. Another interesting observation is that methyl substituted n-alkanes are the major source of branched

chain alkanes. Our results did not suggest any particular contribution from the contaminated soil at section  $E_2$ .

# 6.2.2.1.2.4 Cyclic Alkanes - Positively Identified and Directly Quantified

The levels of various cyclic alkanes at site E are shown in Table 6.43 where total levels ranged from  $1.726 - 7.678 \ \mu g/L$  at section E₁, and  $7.336 - 11.333 \ \mu g/L$  at section E₂. Average total levels are shown in Table 6.44 and were  $4.552 \ \mu g/L \pm 46.1$ % at section E₁ and  $9.235 \ \mu g/L \pm 19.3$ % at section E₂. These results show that intrasection variation were not significant. Similar to other alkane results, levels of cyclic alkanes at site E were an order of magnitude higher than at section F₄ of site F for waste of similar ages.

I ne Levels of C	yene A	ikanes	Directi	y Quan	tified f	rom Si	te E	
(ug/L)	E ₁₋₁		E ₁₋₂		E	1-3	E ₁₋₄	
(µg, b)	S1	S2	<u>S1</u>	S2	<b>S</b> 1	S2	S1	S2
Cyclohexane	0.347	0.370	1.477	1.641	0.931	0.538	0.351	0.210
Methylcyclohexane	0.575	0.505	1.404	1.560	0.695	0.505	0.199	0.298
trans-1,4-dimethylcyclohexane	1.855	0.158	0.480	0.544	1.938	0.270	0.616	0.112
trans-1,2-dimethylcyclohexane	1.388	1.490	2.590	2.878	2.395	1.694	0.616	0.734
cis-1,2-dimethylcyclohexane	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ethylcyclohexane	0.576	0.495	0.616	0.685	0.601	0.440	0.328	0.453
1-methylethylcyclohexane	0.248	0.211	0.323	0.370	0.360	0.234	0.276	0.359
Total (µg/L)	4.989	3.229	6.890	7.678	6.919	3.681	2.386	2.165

 Table 6.43

 The Levels of Cyclic Alkanes Directly Quantified from Site E

Table 6.43 (Continued)The Levels of Cyclic Alkanes Directly Quantified from Site E

	я Т		; F		F		F	
(µg/L)		1-5		1-6		2-1		2-2
	S1	S2	<b>S1</b>	S2	S1	S2	<b>S</b> 1	S2
Cyclohexane	1.045	0.337	0.443	1.068	1.228	1.465	1.107	1.230
Methylcyclohexane	0.598	0.201	0.421	0.569	1.362	1.514	1.240	1.577
trans-1,4-dimethylcyclohexane	1.384	0.072	1.034	1.733	2.426	2.696	2.739	3.044
trans-1,2-dimethylcyclohexane	1.724	0.714	0.674	1.736	1.518	1.687	3.736	4.151
cis-1,2-dimethylcyclohexane	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ethylcyclohexane	0.646	0.246	0.264	0.476	0.587	0.652	0.825	0.916
1-methylethylcyclohexane	0.694	0.155	0.144	0.306	0.213	0.248	0.364	0.415
Total (µg/L)	6.091	1.726	2.980	5.888	7.336	8.262	10.010	11.333

Average Total Levels of Cyclic Alkanes at Each Section of Site E							
(µg/L)	<b>E</b> ₁	E ₂					
Cyclohexane	0.730 ± 66.7 %	1.257 ± 11.9 %					
Methylcyclohexane	0.627 ± 68.5 %	1.423 ± 10.7 %					
trans-1,4-dimethylcyclohexane	0.850 ± 83.5 %	2.726 ± 9.3 %					
trans-1,2-dimethylcyclohexane	1.553 ± 50.2 %	2.773 ± 49.2 %					
cis-1,2-dimethylcyclohexane	/	1					
Ethylcyclohexane	0.486 ± 30.3 %	0.745 ± 20.4 %					
1-methylethylcyclohexane	$0.307 \pm 47.0$ %	0.310 ± 30.6 %					
Total (μg/L)	4.552 ± 46.1 %	9.235 ± 19.3 %					

 Table 6.44

 Average Total Levels of Cyclic Alkanes at Each Section of Site E

Total average cyclic alkane levels at site E are shown in Figure 6.21 alongside those of other alkanes. Cyclic alkane levels were comparable with those of other alkanes at site E and this is consistent with results from site F (Figure 6.7) for waste of a similar age (3 - 11 years). Cyclic alkane levels at section  $E_2$  were higher than at section  $E_1$ , and this may be due to direct volatilization from anthropogenic sources, including daily cover material, as well as contributions from the younger refuse (a few months – 2 years) at section  $E_2$ .



Fig. 6.22 shows total individual cyclic alkane levels at site E. As described above, total cyclic alkane levels were higher at section  $E_2$  and this is clearly seen in Figure

6.21. Even though levels were different at each section of site E trends in levels of cyclic alkanes were similar. That is, at each section of site E trans-1, 2-dimethylcyclohexane and trans-1,4-dimethylcyclohexane were the most abundant compounds followed by comparable levels of cyclohexane and methylcyclohexane. The next abundant cyclic alkanes, ethylcyclohexane and 1-methylethylcyclohexane were at comparable levels at both sections of site E. These findings agree well with cyclic alkane results from site F (see Figure 6.8) where this order of abundances was observed for waste undergoing methanogenesis.



Fig. 6.22 Average Individual Levels of Cyclic Alkanes at Site E

Table 6.45 shows the gas composition from site E and it is fairly consistent at both sections, except for the abundances of trans-1,4-dimethylcyclohexane at section  $E_2$ . Overall, trans-1,2-dimethylcyclohexane and trans-1,4-dimethylcyclohexane account for > 50% of total cyclic alkane levels at site E, and methylcyclohexane and cyclohexane for approximately 30 %. Similar results were observed in gas composition at site F for waste undergoing methanogenesis.

The Gas Composition of Cyclic Alkanes at Each Section of Site E						
%	E ₁	E ₂				
Cyclohexane	16.0	13.6				
Methylcyclohexane	13.8	15.4				
trans-1,4-dimethylcyclohexane	18.7	29.5				
trans-1,2-dimethylcyclohexane	34.1	30.0				
cis-1,2-dimethylcyclohexane	/	/				
Ethylcyclohexane	10.7	8.07				
1-methylethylcyclohexane	6.74	3.36				
Total	100.0	100.0				

Table 6.45The Gas Composition of Cyclic Alkanes at Each Section of Site E

6.2.2.1.2.5 Cyclic Alkanes - Tentatively Identified and Indirectly Quantified

Levels of other cyclic hydrocarbons found at site E are shown in Table 6.46. Average total levels are shown in Table 6.47. These were 1.196  $\mu$ g/L ± 51.6 % at sections E₁ and 1.816  $\mu$ g/L ± 34.5 % at sections E₂, respectively. These cyclic hydrocarbons contributed significantly to total cyclic hydrocarbons levels at site E. This is shown in Fig 6.23. Overall total cyclic alkane levels at site E are shown alongside those of overall total n-alkane and branched chain alkane. Trends observed in Fig 6.21 are still maintained in Fig 6.9. Overall total cyclic alkane levels were obtained by combining results in Table 6.43 and Table 6.46. These are shown in Table 6.48 where cyclic alkanes have been grouped as methylcyclopentane (C₁), C₂-cyclopentanes, cyclohexanes, C₁-cyclohexanes, C₂-cyclohexanes, C₃-cyclohexanes and C₄-cyclohexanes.

(ug/L)	E ₁₋₁		E ₁₋₂		E ₁₋₃		<b>E</b> ₁₋₄		
(µg, =)	S1	S2	<u>S1</u>	S2	S1	S2	S1	S2	
Methylcyclopentane	/	/	0.663	0.629	0.153	0.183	0.112	0.075	
cis-1,3-dimethylcyclopentane	/	/	/	/	/	1	0.198	0.137	
trans-1-ethyl-4-methylcyclohexane	0.367	0.460	0.465	0.414	0.320	0.311	0.559	0.367	
cis-1-ethyl-4-methylcyclohexane	/	1	0.251	0.366	/	1	0.285	0.140	
Propylcyclohexane	0.403	0.530	0.522	0.475	0.386	0.258	0.903	0.394	
1-methyl-4- (1-methylethyl)cyclohexane	/	/	/	/	/	/	0.302	0.203	
Total (µg/L)	0.771	0.990	1.901	1.884	0.859	0.752	2.360	1.317	

Table 6.46The Levels of Cyclic Alkanes Indirectly Quantified from Site E

Table 6.46 (Continued)The Levels of Cyclic Alkanes Indirectly Quantified from Site E

(ug/L)	E ₁₋₅		E ₁₋₆		E ₂₋₁		E ₂₋₂	
(µg/L)	S1	S2	S1	S2	S1	S2	S1	S2
Methylcyclopentane	1	/	/	/	0.594	0.910	0.424	0.611
cis-1,3-dimethylcyclopentane	1	/	/	/	0.353	0.505	/	1
trans-1-ethyl-4-methylcyclohexane	0.209	0.596	0.322	0.204	0.459	0.571	0.325	0.353
cis-1-ethyl-4-methylcyclohexane	1	/	/	/	0.229	0.190	/	1
Propylcyclohexane	0.321	0.697	0.321	0.221	0.379	0.420	0.411	0.531
1-methyl-4- (1-methylethyl)cyclohexane	1	/	/	/	1	/	/	/
Total (µg/L)	0.530	1.293	0.642	0.424	2.014	2.596	1.160	1.494

**Table 6.47** 

## Total Levels of Cyclic Alkanes Indirectly Quantified at Each Section of Site E

(μg/L)	E ₁	E ₂
Methylcyclopentane	0.182 ± 132.5 %	0.635 ± 31.9 %
cis-1,3-dimethylcyclopentane	0.034 ± 198.5 %	0.214 ± 119.0 %
trans-1-ethyl-4-methylcyclohexane	0.377 ± 32.6 %	0.427 ± 26.3 %
cis-1-ethyl-4-methylcyclohexane	0.104 ± 131.7 %	0.209 ± 13.3 %
Propylcyclohexane	$0.45 \pm 43.0$ %	0.435 ± 15.2 %
1-methyl-4-(1-methylethyl)cyclohexane	0.05 ± 199.1 %	_/
Total (µg/L)	1.196 ± 51.6 %	1.816 ± 34.5 %



Table 6.48

Average Levels of Total Grou	ned Cyclic Alkanes	at Fach Section of Site F
interage Devels of Total Orou	peu cyche Aikanes	at Lach Section of She E

(µg/L)	E	E ₂
C1-Cyclopentane	0.151 ± 159.0 %	0.635 ± 31.9 %
C2-Cyclopentane	0.028 ± 238.2 %	0.214 ± 119.0 %
Cyclohexane	$0.730 \pm 66.7 \%$	1.257 ± 11.9 %
C1-Cyclohexanes	0.627 ± 68.5 %	1.423 ± 10.7 %
C2- Cyclohexanes	2.888 ± 44.8 %	6.244 ± 27.7 %
C3- Cyclohexanes	1.229 ± 31.5 %	1.277 ± 10.6 %
C4- Cyclohexanes	0.042 ± 238.9 %	/
Total (µg/L)	5.696 ± 37.9 %	11.051 ± 12.9 %

Figure 6.24 shows average levels of grouped cycloalkanes at site E. Similar to cycloalkane results for site F,  $C_2$ -cyclohexanes were the most abundant compounds in waste undergoing methanogenesis. Also similar to site F is the next group of abundant cycloalkanes are cyclohexanes, methylcyclohexanes and  $C_3$ -cyclohexanes. The higher levels of  $C_1$ - and  $C_2$ -cyclopentanes at site E compared to site F, is due to cyclic alkane levels being higher, by a factor of up to 10, at site E. At site E, cyclopentanes are still amongst the least abundant cyclic alkanes. The trends observed for cyclic alkanes at site E, were similar to site F, eventhough levels at site E were an order of magnitude higher.



Figure 6.24 Average Levels of Grouped Cyclic Alkanes at Site E

Table 6.49 shows the gas composition at site E. For waste undergoing methanogenesis  $C_2$ -alkylcyclohexanes account for 50 – 60 % of total cycloalkanes. The abundance of cyclohexane, methylcyclohexane and  $C_3$ -alkylcycloalkanes are similar at site E. However the lower abundance of  $C_3$ -alkylcycloalkanes at section  $E_2$ , is caused by the higher levels of other abundant cycloalkanes at this site. Overall, gas composition at site E and F for waste undergoing methanogenesis is very similar.

The Average Groups Gas Composition of Cyclic Alkanes at Each Section of Site E					
%	E ₁	E ₂			
C1-Cyclopentane	2.7	5.7			
C2-Cyclopentane	0.5	1.9			
Cyclohexane	12.8	11.4			
C1-Cyclohexanes	11.0	12.9			
C2- Cyclohexanes	50.7	56.5			
C3- Cyclohexanes	21.6	11.6			
C4- Cyclohexanes	0.7	/			
TOTAL	100.0	100.0			

Table 6 49

6.2.2.1.2.6 Aromatic Hydrocarbons - Positively Identified and Directly Quantified Levels of various aromatic hydrocarbon compounds at site E are shown in Table 6.50, and ranged from  $8.795 - 18.409 \ \mu g/L$  at section E₁, and  $7.270 - 18.593 \ \mu g/L$  at section E₂. Average total levels at site E are shown in Table 6.51 and were 11.82  $\mu g/L$  $\pm 30.9$  % at section E₁ and 12.72  $\mu g/L \pm 43.5$  % at section E₂. Intrasection variations were not significant. Similar to alkane results, levels of aromatic hydrocarbons at site E were an order of magnitude higher than at site F, for waste of similar ages.

Average total levels of aromatic hydrocarbons at site E are shown in Figure 6.25 alongside total overall levels alkanes at site E. Aromatic hydrocarbons are significantly more abundant than alkanes at site E, and are similar finding was also observed at site F. Similar levels of aromatic hydrocarbons at section  $E_1$  and  $E_2$  indicate there is no major contribution from the daily cover material used at section  $E_2$ . Results for aromatic hydrocarbons for site F, shown in Figure 6.11, showed that high aromatic hydrocarbon levels in 3 - 5 year old waste declined as the waste aged to 5 - 11 years, and this may be indicative of aromatic hydrocarbon losses from direct volatilization in the younger refuse. The similar levels of aromatic hydrocarbon set both sections of site E indicate there are minor contributions to aromatic hydrocarbon levels from the younger refuse at section  $E_2$ .

								, <b>L</b>
(ug/L)	E ₁₋₁		E ₁₋₂		E ₁₋₃		E ₁₋₄	
(µg/L)	S1	S2	S1	S2	S1	S2	<b>S1</b>	S2
Benzene	0.550	0.600	1.098	1.320	1.807	1.136	0.152	0.234
Methylbenzene	1.627	1.432	1.379	1.733	5.716	1.680	1.794	1.812
Ethylbenzene	2.008	1.467	2.508	2.987	2.375	0.933	0.875	1.552
1,2&1,4-dimethylbenzene	2.364	1.810	1.468	1.831	2.219	1.514	1.079	1.423
1,3-dimethylbenzene	2.352	1.700	2.047	2.474	2.156	2.423	0.903	1.398
Propylbenzene	0.888	0.645	1.261	1.601	0.928	0.824	0.929	1.499
1,2,4-trimethylbenzene	0.864	0.631	1.875	2.283	0.758	0.966	1.028	1.390
1,3,5-trimethylbenzene	0.907	0.510	1.997	2.219	0.968	0.977	1.325	1.756
Total (μg/L)	11.561	8.795	13.633	16.448	16.927	10.452	8.086	11.065

Table 6.50The Levels of Aromatic Hydrocarbons Directly Quantified from Site E

Table 6.50 (Continued)

The Levels of Aromatic Hydrocarbons Directly Quantified from Site E

					* ~			
(u=1)	E ₁₋₅		E ₁₋₆		E ₂₋₁		E ₂₋₂	
(µg/L)	S1	S2	S1	S2	S1	S2	S1	S2
Benzene	1.080	0.424	0.300	1.020	0.837	0.950	2.782	3.191
Methylbenzene	2.009	1.951	3.317	1.433	1.753	2.047	2.474	2.788
Ethylbenzene	2.947	1.384	1.344	1.567	0.870	0.987	2.221	2.568
1,2&1,4-dimethylbenzene	2.934	1.416	1.226	1.370	1.135	1.461	1.637	1.839
1,3-dimethylbenzene	2.103	1.045	1.013	1.388	0.896	1.006	2.693	3.001
Propylbenzene	1.928	0.736	0.473	0.771	0.541	0.651	1.399	1.654
1,2,4-trimethylbenzene	2.520	0.764	0.240	0.574	0.699	0.886	1.108	1.331
1,3,5-trimethylbenzene	2.887	0.956	0.688	1.091	0.538	0.798	1.908	2.220
Total (µg/L)	18.409	8.676	8.599	9.214	7.270	8.788	16.223	18.593

**Table 6.51** 

Average Total Levels of Aromatic Hydrocarbons at Each Section of Site E

 (μg/L)	E	E ₂
Benzene	0.81 ± 62.8 %	1.94 ± 62.9 %
Methylbenzene	2.157 ± 57.1 %	2.266 ± 20.2 %
Ethylbenzene	1.829 ± 39.7 %	1.662 ± 51.7 %
1,2&1,4-dimethylbenzene	1.721 ± 31.4 %	1.518 ± 19.6 %
1,3-dimethylbenzene	1.75 ± 33.3 %	1.899 ± 58.1 %
Propylbenzene	1.04 ± 42.0 %	1.062 ± 51.7 %
1,2,4-trimethylbenzene	1.158 ± 61.7 %	$1.006 \pm 27.2$ %
1,3,5-trimethylbenzene	1.357 ± 52.4 %	$1.366 \pm 60.2$ %
Total (µg/L)	11.82 ± 30.9 %	12.72 ± 43.5 %



Figure 6.26 shows the average total individual aromatic hydrocarbon levels at site E. As can be seen levels of each compound were similar at both sections of site E, except for the difference in benzene levels. This may indicate a contribution from the daily cover material and direct volatilization from the younger refuse (a few months – 2 years) at section  $E_2$ . Another explanation for the higher benzene levels at section  $E_2$ , may be that the older underlying refuse has entered more advanced stages of methanogenesis, and as Figure 6.12 shows, benzene levels increase in the older waste. Overall, the difference in benzene levels between section  $E_2$  and  $E_2$  is not significant enough indicate major contributions from anthropogenic sources or older waste. When compared with site F, where toluene levels were elevated, site E toluene levels were not significantly elevated relative to other aromatic hydrocarbons.



Figure 6.26 Average Individual Levels of Aromatic Hydrocarbons at Site E

Overall, considering the high abundance of toluene at site F, the abundance of aromatic hydrocarbon compounds at site E are similar to site F for waste at a similar age or stage of waste degradation, where BTEX compounds, are the most abundant aromatic hydrocarbon compounds. This is further highlighted by the gas composition shown in Table 6.52, where BTEX compounds account for approximately 70 % of total aromatic hydrocarbons.

The Average Gas Co at E	The Average Gas Composition of Aromatic Hydrocarbons at Each Section of Site E						
0/	E1	E2					
Benzene	6.9	15.3					
Methylbenzene	18.2	17.8					
Ethylbenzene	15.5	13.1					
1,2&1,4-dimethylbenzene	14.6	11.9					
1,3-dimethylbenzene	14.8	14.9					
Propylbenzene	8.8	8.3					
1,2,4-trimethylbenzene	9.8	7.9					
1,3,5-trimethylbenzene	11.5	10.7					
Total	100.0	100.0					

**Table 6.52** 

# 6.2.2.1.2.7 Aromatic Hydrocarbons - Tentatively Identified and Indirectly

### Quantified

Levels of other aromatics found at site E are shown in Table 6.53, and average total levels are shown in Table 6.54. Total average levels of these at sections  $E_1$  and  $E_2$  were 2.644 µg/L ± 49.9 % and 1.834 µg/L ± 40.6 %. These other aromatics are C₃ and C₄-alkylbenzenes and contribute significantly to total levels at site E. Similar to site F, significant contributors included 1-ethyl-2-methylbenzene and 1-methyl-4-(1-methylethyl)benzene.

Table 6.53The Levels of Aromatic Hydrocarbons Indirectly Quantified from Site E

(ug/[_)	E ₁₋₁		E ₁₋₂		E ₁₋₃		E ₁₋₄	
(µg/L)	<b>S1</b>	S2	S1	S2	S1	S2	S1	S2
1-methylethylbenzene	/	1	0.380	0.431	0.356	0.346	0.427	0.300
1-ethyl-2-methylbenzene	0.357	0.912	1.374	1.552	0.752	0.672	0.746	0.521
1-ethyl-4-methylbenzene	/	/	0.474	0.462	0.342	0.320	0.334	0.223
1-methyl-4- (1-methylethyl)benzene	0.328	0.632	1.194	1.262	0.491	0.449	2.721	2.386
1-methyl-2-propylbenzene	1	/	0.419	0.495	/	/	/	/
2-ethyl-1,4-dimethylbenzene	/	/	0.330	0.411	/	/	/	/
Total (µg/L)	0.685	1.545	4.170	4.612	1.941	1.788	4.229	3.430

Table 6.53 (Continued)The Levels of Aromatic Hydrocarbons Indirectly Quantified from Site E

					<u> </u>			
(	E ₁₋₅		<b>E</b> ₁₋₆		E ₂₋₁		E ₂₋₂	
(µg/L)	S1	S2	S1	S2	S1	S2	S1	S2
1-methylethylbenzene	0.194	0.506	/	/	/	/	0.273	0.265
1-ethyl-2-methylbenzene	0.914	1.278	0.425	0.461	0.416	0.408	0.795	0.714
1-ethyl-4-methylbenzene	/	/	0.340	0.188	/	/	/	/
1-methyl-4- (1-methylethyl)benzene	0.817	2.064	1.201	0.945	/	/	/	/
1-methyl-2-propylbenzene	1	/	/	/	/	/	/	/
2-ethyl-1,4-dimethylbenzene	/	/	/	/	0.805	0.781	1.198	1.683
Total (µg/L)	1.925	3.847	1.966	1.594	1.221	1.188	2.266	2.662

<u></u>		
(μg/L)	E	E ₂
1-methylethylbenzene	$0.245 \pm 80.0$ %	0.135 ± 115.5 %
1-ethyl-3-methylbenzene	0.830 ± 47.2 %	0.583 ± 34.4 %
1-ethyl-2-methylbenzene	$0.224 \pm 82.0$ %	1
1-methyl-4-(1-methylethyl)benzene	1.207 ± 65.3 %	1
1-methyl-2-propylbenzene	0.076 ± 234.5 %	1
2-ethyl-1,4-dimethylbenzene	0.062 ± 235.2 %	1.117 ± 37.9 %
Total (µg/L)	2.644 ± 49.9 %	1.834 ± 40.6 %

Table 6.54 Average Total Levels of Aromatic Hydrocarbons Indirectly Quantified at Each Section of Site E

Overall total levels of aromatic hydrocarbons at site E are shown in Fig 6.27 alongside those of overall total levels of alkanes. Trends observed in Fig 6.25 are still maintained in Fig 6.27. Overall total aromatic hydrocarbon levels were obtained by combining results in Table 6.50 and Table 6.53. These are shown in Table 6.55 where aromatic hydrocarbons are grouped as benzene,  $C_1$ -alkylbenzenes,  $C_2$ -alkylbenzenes,  $C_3$ -alkylbenzenes and  $C_4$ -alkylbenzenes.



Fig 6.27 Average levels of Total Aromatic Hydrocarbons at Site E

	at Each Section of Site E	
 (μg/L)	E	E ₂
Benzene	0.810 ± 62.8 %	1.940 ± 62.9 %
C1-Alkylbenzene	2.157 ± 57.1 %	2.266 ± 20.2 %
C2-Alkylbenzene	5.300 ± 30.6 %	5.079 ± 44.0 %
C3-Alkylbenzene	4.854 ± 45.4 %	4.152 ± 47.6 %
C4-Alkylbenzene	1.345 ± 63.6 %	1.117 ± 37.9 %
 Total (μg/L)	14.467 ± 27.4 %	14.553 ± 43.1 %

Table 6.55 Average Total Group Levels of Aromatic Hydrocarbons at Each Section of Site F

Figure 6.28 shows that the abundant groups of aromatic hydrocarbons at site E were  $C_1 - C_3$  alkylbenzenes for waste undergoing methanogenesis. Benzene and  $C_4$ -alkyl benzene were of lower abundances. These results are in accord with those of site F where, for waste at a similar age (3 – 11 years), similar trends were observed (see Figure 6.14). The higher abundance of toluene at site F was previously explained.



Fig. 6.28 Average Levels of Grouped Aromatic Hydrocarbons at Site E

Other studies have shown  $C_1 - C_4$  alkylbenzenes to be the most abundant aromatics in landfill gas from domestic waste. Young *et al.*⁽⁸⁹⁾ found that  $C_1 - C_4$  alkylbenzenes were dominant and benzene the least in gas from domestic waste ranging from 3 weeks to 5 – 6 years old. Allen *et al.*⁽⁹²⁾ also found gas from domestic / trade waste of

varying ages to produce appreciable levels of  $C_1 - C_4$  alkylbenzenes with low levels of benzene. Schweigkofler *et al.*⁽⁵⁸⁾ also observed similar trends from two domestic sites and Scott *et al.*⁽⁶⁴⁾ found that alkylbenzenes particularly  $C_3$  and xylene become significant as anaerobic conditions were established.

Our results concur with findings of other researchers in that  $C_2$ - and  $C_3$ -alkylbenzenes are dominant compounds, however, we found that levels of benzene, toluene and  $C_4$ - alkylbenzenes were comparable. Also,  $C_2$ - and  $C_3$ -alkylbenzene levels were only a factor of 2 – 5 times greater than the other aromatic hydrocarbons.

Table 6.56 shows the gas composition at site E. As can be seen, except for higher abundances of benzene at section  $E_2$ , gas composition was similar at both sites. A noticeable difference in gas composition at site E and waste of similar age at section  $F_3$  and  $F_4$  of site F was the lower abundance of toluene and higher abundance of  $C_2$ -and  $C_3$ -alkylbenzenes.

at Lo	ach Section of Site E	
%	E ₁	E ₂
Benzene	5.6	13.3
C1-Alkylbenzene	14.9	15.6
C2-Alkylbenzene	36.6	34.9
C3-Alkylbenzene	33.6	28.5
C4-Alkylbenzene	9.3	7.7
Total	100.0	100.0

Table 6.56 The Average Groups Gas Composition of Aromatic Hydrocarbons at Each Section of Site E

#### 6.2.2.1.2.8 Terpenes - Positively Identified and Directly Quantified

The levels of various terpenes found in landfill gas from site E are shown the Table 6.57. Total levels of section  $E_1$  ranged from  $4.643 - 10.830 \ \mu g/L$  and section  $E_2$  from  $4.643 - 9.116 \ \mu g/L$ . Average total levels of terpenes at site E are shown in Table 6.58 and were 7.072  $\ \mu g/L \pm 29.7 \ \%$  at section  $E_1$  and 6.78  $\ \mu g/L \pm 30.7 \ \%$  at section  $E_2$ . Similar to other VOCs studies thus far, terpene levels at site E were higher than site F. Unlike the other VOCs though, terpene levels at site E were only approximately 2

times higher than site F. These results shows there are no significant intrasite differences in terpene levels at site E.

 Table 6.57

 The Levels of Terpenes Directly Quantified from Site E

	E	1-1	E	1-2	E	1-3	E	1-4
(µg/L)	<u></u>	S2	S1	S2	S1	S2	S1	S2
α-Pinene	4.016	4.410	3.438	1.673	3.837	2.887	1.689	2.265
β-Pinene	1.399	1.681	0.878	1.387	1.093	1.051	1.064	1.414
Limonene-1	3.463	4.740	3.775	2.322	1.710	3.026	1.890	4.525
Total (µg/L)	8.878	10.830	8.092	5.382	6.640	6.964	4.643	8.204

 Table 6.57 (Continued)

 The Levels of Terpenes Directly Quantified from Site E

	E	E ₁₋₅		E ₁₋₆		E ₂₋₁		E ₂₋₂	
(µg/L)	S1	S2	S1	S2	S1	S2	S1	S2	
α-Pinene	3.837	1.619	2.887	2.915	1.689	1.977	2.165	2.517	
β-Pinene	1.093	0.658	1.051	1.592	1.064	1.282	1.314	1.571	
Limonene-1	1.710	0.668	3.026	4.170	1.890	2.200	4.425	5.028	
Total (µg/L)	6.640	2.946	6.964	8.677	4.643	5.458	7.904	9.116	

Table 6.58

Average Total Lev	els of Terpenes at Each Se	ection of Site E
(µg/L)	E ₁	E ₂
α-Pinene	2.956 ± 33.1 %	2.087 ± 16.6 %
β-Pinene	1.197 ± 25.0 %	1.308 ± 15.9 %
Limonene-1	2.919 ± 43.7 %	3.385 ± 46.5 %
Total (μg/L)	7.072 ± 29.7 %	6.78 ± 30.7 %

Average total levels of terpenes at site E are shown in Figure 6.29 alongside total overall levels of other VOCs. Similar to site F for waste in the methanogenic phase of degradation, terpene levels were comparable with those of other alkanes, but relative levels of terpenes compared with other VOCs were lower, by a factor of approximately 2, at site E. Terpene levels at both sections of site E were very similar and this indicated that there was no contribution to terpene levels from the younger refuse (a few months – 2 years) at section  $E_2$ .



Figure 6.29 Average Total Levels of Terpenes at Site E

Figure 6.30 shows average total individual terpene levels at site E, where similar levels of individual terpenes were observed at both sections of site E. As can be seen, limonene and  $\alpha$ -pinene are the abundant compounds with lower levels of  $\beta$ -pinene. The gas composition shown in Table 6.59 shows that limonene and  $\alpha$ -pinene account for approximately 80 % of total terpenes at site E. The gas composition at site E was in accord with that at section F₃ and F₄ for waste of a similar age.

Unlike Allen *et al.*⁽⁹²⁾ and Scott *et al.*⁽⁶⁴⁾ who found  $\alpha$ -pinene and limonene respectively to be the dominant compounds. Our results suggest that for domestic waste actively producing methane, both  $\alpha$ -pinene and limonene are the abundant terpenes with low levels of  $\beta$ -pinene.



Figure 6.30 Average Individual Levels of Terpenes at Site E

The Average Gas Co	Table 6.59omposition of Terpenes at E	Cach Section of Site E
%	E ₁	E ₂
α-Pinene	41.8	30.8
β-Pinene	16.9	19.3
Limonene-1	41.3	49.9
Total	100.0	100.0

6.2.2.1.2.9 **Terpenes -** Tentatively Identified and Indirectly Quantified

The levels of other terpenes found in landfill gas in site E are found in Table 6.60. Interestingly only section  $E_1$  shows the presence of other terpenes including camphene and carene. Both of these were present in appreciable amounts with camphene the most prevalent, and carene was only observed at sampling point  $E_{1-2}$ . When camphene results are combined with those of other terpenes, its contribution to gas composition was approximately 7 %. Gas composition is shown in Table 6.61.

	MC LICICI		peneo and		awarre			
(µg/L)	E	1-1	E	1-2	E	1-3	E	1-4
	S1	S2	S1	S2	<b>S</b> 1	S2	<b>S1</b>	S2
Camphene	/	/	0.508	0.537	/	1	0.943	1.289
δ-Carene-3	1	1	0.407	0.468	/	/	/	/

Table 6.60The Levels of Terpenes Indirectly Quantified from Site E

Table 6.60 (Continued)The Levels of Terpenes Indirectly Quantified from Site E

		••••P	• • • • • • •					
(μg/L)	E ₁	E ₁₋₅ E ₁₋₆		1-6	E ₂₋₁		E ₂₋₂	
	S1	S2	S1	S2	<b>S1</b>	S2	S1	S2
Camphene	0.471	1.255	0.521	0.788	/	/	/	/
δ–Carene–3	/	/	1	1	/	1	/	1

Table 6.61

The Average Gas Composition of Total Terpenes at Each Section of Site E

%	E ₁	E ₂
a-Pinene	38.9	30.8
β-Pinene	15.8	19.3
Limonene-1	38.4	49.9
Camphene	6.9	/
Total %	100.0	100.0

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#### 6.2.2.2 Landfill A

Site A is a prescribed waste site and began operations in 1971. The wastes received included uncompacted solids, non-putrescible industrial waste and industrial liquid waste. Liquid wastes were landfilled by pouring them into craters constructed in the solid waste. Leachate removal and treatment have been practiced throughout the landfill's life. Leachate treatment involved oil separation, aeration and lime neutralization after which it was discharged to sewer. Landfill gas samples were taken from two sections of site A, section 1 (A₁) and section 2 (A₂). Information from site operators indicated that both sections of site A had received liquid wastes. At section A₁ gas samples were taken from three leachate wells, A₂₋₁, A₂₋₂ and A₂₋₃. Fig 4.8 (see Section 4.2 Chapter IV) shows a typical GC trace for landfill A. Table 4.7 (see Section 4.21 Chapter IV) lists all the compounds in order of retention time and Table 4.8(a) – (h) shows the compounds under the various compound classes.

Over 70 VOCs were quantified either directly or indirectly as described in Section 4.1.3 and 4.3.3, respectively. Table 4.14 lists those compounds which were quantified in the landfill gas, where compounds marked with an asterisk were indirectly quantified. Table 4.13 shows the standard compound used for indirect quantification.

#### 6.2.2.2.1 n-Alkanes - Positively Identified and Directly Quantified

The levels of various n-alkanes found in landfill gas from site A are shown in Table 6.62. Total levels at section  $A_1$  ranged from  $1.406 - 2.054 \ \mu g/L$  and  $0.112 - 0.413 \ \mu g/L$  at section  $A_2$ . Average total levels are shown in Table 6.63 and are  $1.773 \ \mu g/L \pm 17.7 \ \%$  at section  $A_1$  and  $0.233 \ \mu g/L \pm 48.3 \ \%$  at section  $A_2$ . Intrasection variations at section  $A_1$  were small considering sampling points were different, i.e., a passive vent and a leachate well. Both of these released gas passively suggesting that other variables, such as flow rate, did not have any significant impact on levels released. Overall, intrasection variations at site A were not significant.

									<u> </u>	-
(uơ/L)	A	1-1	A ₁₋₂		A ₂₋₁		A ₂₋₂		A ₂₋₃	
(µ6, 2)	<b>S1</b>	S2	<u>S1</u>	<b>S2</b>	<b>S</b> 1	<b>S2</b>	S1	S2	<b>S</b> 1	S2
Hexane	0.118	0.183	0.227	0.184	0.018	0.019	0.031	0.015	0.007	0.008
Heptane	0.539	0.275	0.428	0.350	0.032	0.032	0.059	0.028	0.019	0.023
Octane	0.312	0.209	0.294	0.272	0.026	0.028	0.047	0.023	0.012	0.022
Nonane	0.560	0.315	0.412	0.287	0.067	0.072	0.108	0.040	0.039	0.070
Decane	0.484	0.251	0.288	0.233	0.082	0.092	0.114	0.016	0.028	0.059
Undecane	0.040	0.144	0.345	0.287	0.034	0.035	0.047	0.003	0.007	0.017
Dodecane	0.001	0.029	0.019	0.005	0.006	0.006	0.008	BDL	BDL	BDL
Total (µg/L)	2.054	1.406	2.012	1.620	0.266	0.283	0.413	0.126	0.112	0.198

Table 6.62The Levels of n-Alkanes Directly Quantified from Site A

Table 6.63

Average Total Levels of n-Alkanes Directly Quantified at Each Section of Sites A

(µg/L)	A ₁	A ₂
Hexane	0.178 ± 25.1 %	0.016 ± 53.1 %
Heptane	0.398 ± 28.3 %	0.032 ± 43.3 %
Octane	0.272 ± 16.4 %	0.026 ± 44.3 %
Nonane	0.393 ± 31.4 %	0.066 ± 38.3 %
Decane	0.314 ± 36.8 %	0.065 ± 57.8 %
Undecane	0.204 ±67.8 %	0.024 ± 74.4 %
Dodecane	0.014 ± 95.1 %	0.003 ± 111.8 %
Total (µg/L)	1.773 ± 17.7 %	0.233 ± 48.3 %

Total levels at site A are shown in Figure 6.31, and can be seen where levels at section  $A_1$ , were approximately 8 times greater than those at section  $A_2$ . The waste at the two sections of site A was of a similar age and therefore waste age cannot account for the difference in levels. However, being a prescribed waste facility these intrasite differences may be easily explained considering the diverse nature of all the waste at site A. However, what is even more surprising is that the levels of n-alkanes found at site A are comparable with those at the domestic waste sites studied. Given the nature of site A it was expected that gas from this site would most certainly contain high levels (compared to domestic sites) of VOCs. This finding will be further discussed when other VOCs at site A have been reviewed.



Figure 6.31 Average Total Levels of n-Alkanes at Site A

Figure 6.32 shows average total individual n-alkane levels at site A, where it is clear that levels at section  $A_1$  are considerably higher. Another surprising finding is that relative amounts are similar to those found at domestic waste sites. Again considering the diverse nature of waste accepted at site A, this was not expected. The gas composition is shown in Table 6.64, and when compared to site F, it is more typical of domestic rubbish in the methanogenic phase of waste degradation. At both sections of site A nonane and decane accounted for approx. 50 % of total alkanes. Gas compositions are comparable at section  $A_1$  and section  $F_3$  and sections  $A_2$  and sections  $A_2$  and section  $E_1$ .



Figure 6.32 Average Individual Levels of n-Alkanes at Site A

Table 6.64								
The Average Gas Composition of n-Alkanes Directly Quantified								
at Each Section of Site A								

%	A ₁	A ₂
Hexane	10.0	7.0
Heptane	22.5	13.8
Octane	15.3	11.2
Nonane	22.2	28.3
Decane	17.7	28.0
Undecane	11.5	10.2
Dodecane	0.8	1.4
TOTAL	100.0	100.0

#### 6.2.2.2.2 n-Alkanes - Tentatively Identified and Indirectly Quantified

Pentane levels are shown in Table 6.65. Pentane was found only at sampling points  $A_{2-1}$  and  $A_{2-2}$ . Interestingly at sampling point  $A_{2-1}$  it was the most abundant n-alkane, but at sampling point  $A_{2-2}$  it was one of the least abundant n-alkanes. Pentane levels at these two sampling points of section  $A_2$  differed by a factor of 10. Again, the diverse nature of the waste may be the cause. The significance of pentane levels can be seen when it is included in the gas composition of section  $A_2$ , and compared to that in Table 6.66. As can be seen at section  $A_2$  pentane accounts for 15% of total alkanes.

Pentane was also found at similar abundance at section  $F_1$  where the waste age was 16 - 21 years. Interestingly, the waste at section  $A_2$  was of a similar age (5 - 26 years old).

,	The Le	vels of	n-Alka	nes Ind	lirectly (	Quanti	ified fro	m Sites	Α	
(μ <u>g</u> /L)	A ₁₋₁ A ₁₋₂		1-2	A ₂₋₁		A ₂₋₂		A ₂₋₃		
	<b>S1</b>	<b>S2</b>	<b>S1</b>	S2	<b>S</b> 1	S2	S1	S2	<b>S1</b>	S2
Pentane	/	/	/	/	0.099	0.123	0.009	0.020	/	/

Table 6 65

The Average Gas Composition of Total n-Alkanes at Each Section of Site A							
%	$\mathbf{A}_{1}$	A ₂					
Pentane	0.0	15.3					
Hexane	10.0	5.9					
Heptane	22.5	11.7					
Octane	15.3	9.5					
Nonane	22.2	24.0					
Decane	17.7	23.7					
Undecane	11.5	8.6					
Dodecane	0.8	1.2					
TOTAL	100.0	100.0					

# Table 6 66

# 6.2.2.2.3 Branched Chain Alkanes - Tentatively Identified and Indirectly

#### Quantified

The levels of branched chain alkanes found in landfill gas at site A are shown in Table 6.67. Total levels at section A₁ ranged from 1.388 – 3.806  $\mu$ g/L and 0.150 – 0.395  $\mu$ g/L at section A₂. Average total levels is shown in Table 6.68 and at section A₁, were 2.185  $\mu$ g/L ± 51.3 % and 0.217  $\mu$ g/L ± 44.7 % at section A₂. Intrasection variations at site A were not significant.

	(ug/L)		(ug/L)		A ₁₋₂		A ₂₋₁		A ₂₋₂		A ₂₋₃	
	(µg/L)	<b>S1</b>	S2	S1	S2	S1	S2	S1	S2	<b>S1</b>	<u>52</u>	
C5	2-methylbutane	/**	/	/	1	0.098	0.132	0.021	0.006	/	/	
	Total C5	1	/	/	1	0.098	0.132	0.021	0.006	/	/	
<b>C</b> 6	2-methylpentane	0.111	0.092	/	1	/	/	0.017	0.008	/	/	
CU	3-methylpentane	0.081	0.066	/	/	1	/	0.012	0.006	· · /	/	
	Total C6	0.192	0.158	/	/	1	/	0.029	0.013	/	/	
C7	*2-methylhexane & 2,3-dimethylpentane	0.115	0.295	/	/	/	/	/	/	/	/	
	3-methylhexane	0.357	0.181	0.196	0.229	/	/	0.030	0.014	0.019	0.014	
	Total C7	0.472	0.476	0.196	0.229	1	/	0.030	0.014	0.019	0.014	
	2-methylheptane	0.262	0.089	/	/	/	/	0.019	0.009	/	1	
C8	4-methylheptane	0.220	0.227	0.148	0.162	/	/	/	/	/	/	
	Total C8	0.483	0.316	0.148	0.162	/	/	0.019	0.009	/	/	
	2,5-dimethylheptane	0.481	0.105	0.160	0.176	1	/	0.016	0.008	/	/	
С9	2-methyloctane	0.918	0.188	/	/	0.020	0.018	0.035	0.015	0.020	0.012	
	3-methyloctane	0.330	0.185	0.337	0.376	0.015	0.014	0.029	0.014	0.018	0.013	
	Total C9	1.728	0.478	0.496	0.551	0.035	0.031	0.080	0.036	0.039	0.025	
	2,6-dimethyloctane	0.229	0.148	/	/	0.017	0.015	0.030	0.011	0.022	0.013	
	3-ethyl-2-methylheptane	1	/	/	/	/	/	0.043	0.013	0.035	0.016	
C10	3,4-dimethyloctane	1	/	/	/	0.012	0.011	0.022	0.010	0.018	0.015	
C10	4-methylnonane	0.228	0.080	0.299	0.340	1	/	0.023	0.009	0.018	0.009	
	2-methylnonane	0.207	0.203	/	/	/	/	0.028	0.009	0.020	0.011	
	3-methylnonane	/	/	/	/	/	/	0.038	0.010	/	/	
	Total C10	0.664	0.431	0.299	0.340	0.029	0.026	0.183	0.062	0.113	0.063	
	5-methyldecane	0.041	0.056	/	/	/	/	/	/	0.011	0.003	
C11	4-methyldecane	1	/	0.131	0.075	0.005	0.018	/	/	/	/	
	2-methyldecane	0.075	0.049	0.117	0.123	0.017	0.016	/	/	/	/	
	Total C11	0.116	0.106	0.248	0.198	0.023	0.034	0.000	0.000	0.011	0.003	
C12	2,2,4,6,6- pentamethylheptane	0.152	0.102	/	/	0.020	0.017	0.032	0.009	0.019	0.011	
	Total C12	0.152	0.102	/	/	0.020	0.017	0.032	0.009	0.019	0.011	
	TOTAL	3.806	2.066	1.388	1.481	0.204	0.239	0.395	0.150	0.200	0.116	

**Table 6.67** The Levels of Branched Chain Alkanes Indirectly Quantified from Site A

* The concentration of 2-methylhexane & 2,3-dimethylpentane is the total for both as these co-elute; ** negligible levels.

(μg/L)	A ₁	A ₂
C5-Branched Chain Alkanes	0.000	0.043 ± 133.6 %
C6-Branched Chain Alkanes	0.087 ± 116.5 %	0.007 ± 170.1 %
C7-Branched Chain Alkanes	$0.343 \pm 44.2$ %	0.013 ± 90.2 %
C8-Branched Chain Alkanes	0.277 ± 56.4 %	0.005 ± 168.9 %
C9-Branched Chain Alkanes	0.813 ± 75.1 %	0.041 ± 47.9 %
C10-Branched Chain Alkanes	0.433 ± 37.6 %	0.079 ± 75.3 %
C11-Branched Chain Alkanes	0.167 ± 40.8 %	0.012 ± 118.9 %
C12-Branched Chain Alkanes	0.064 ± 119.8 %	0.018 ± 46.6 %
Total (µg/L)	2.185 ± 51.3 %	0.217 ± 44.7 %

Table 6.68Average Levels of grouped Branched Chain Alkanes at Each Section of Site A

Total branched chain alkane levels are shown in Figure 6.33 alongside those of nalkanes (including pentane). As can be seen branched chain alkane levels were significantly higher at section  $A_1$ , by a factor of about 10. Again, the diverse nature of the waste may be the cause. Figure 6.33 also shows that n-alkane and branched chain alkane levels at each section of site A, were similar. As mentioned for the n-alkanes results the low levels of branched chain alkanes were not expected, and these were similar to levels of branched chain alkanes found in the domestic sites. The similarity in n-alkane and branched chain alkane levels is also similar to trends found in domestic waste sites.



Figure 6.33 Average Total Levels of Branched Chain Alkanes at Site A

Figure 6.34 shows total individual branched chain alkane group levels at site A. As was found for n-alkanes branched chain alkane trends resembled those of domestic waste sites where  $C_9$  and  $C_{10}$  compounds were abundant. This is further highlighted when gas composition, shown in Table 6.69, is considered.  $C_9$  and  $C_{10}$  branched chain alkanes accounted for approximately 50 % of total branched chain alkanes. Higher abundances of  $C_{10}$  branched chain alkanes than  $C_9$  were observed for very old waste at site F and a similar trend was observed at section  $A_2$ . Similar branched chain alkane trends at section  $A_1$  were found at site F for waste in advanced stages of methanogenesis. Interestingly, the abundances of  $C_5$  branched chain alkane was considerable at section  $A_2$  (approximately 20 %) and a similar result was found for pentane at section  $A_2$  (approximately 15 %). Also, pentane and  $C_5$  branched chain alkane trends at site F, and this is consistent with n-alkane and branched chain alkane trends at site A resembling that of mature domestic waste.



Figure 6.34 Average Individual Levels of Branched Chain Alkanes at Site A

at Each Section of Site A							
%	A	A					
C5-Branched Chain Alkanes	0.0	19.7					
C6-Branched Chain Alkanes	4.0	3.2					
C7-Branched Chain Alkanes	15.7	5.9					
<b>C8-Branched Chain Alkanes</b>	12.7	2.1					
C9-Branched Chain Alkanes	37.2	18.9					
C10-Branched Chain Alkanes	19.8	36.5					
C11-Branched Chain Alkanes	7.6	5.4					
C12-Branched Chain Alkanes	2.9	8.2					
Total	100.0	100.0					

Table 6.69The Average Gas Composition of Grouped Branched Chain Alkanes<br/>at Each Section of Site A

## 6.2.2.2.4 Cyclic Alkanes - Positively Identified and Directly Quantified

The levels of cyclic hydrocarbons found in landfill gas from site A are shown in Table 6.70. Total levels at section  $A_1$ , ranged from  $1.934 - 3.233 \ \mu g/L$  and at section  $A_2$  from  $0.086 - 0.323 \ \mu g/L$ . Average total levels are shown in Table 6.71 and are 2.376  $\mu g/L \pm 24.8$  % at section  $A_1$  and  $0.191 \ \mu g/L \pm 41.0$  % at section  $A_2$ . Intrasection variations were not significant. Similar to n-alkane and branched chain alkane results, levels of cyclic alkanes were higher at section  $A_1$ , by a factor of approximately 12 times, than at section  $A_2$ .

									-	
(µg/L)	A ₁₋₁		A ₁₋₂		A ₂₋₁		A ₂₋₂		A ₂₋₃	
	S1	S2	S1	<b>S2</b>	S1	<b>S2</b>	S1	S2	S1	S2
Cyclohexane	0.115	0.115	0.165	0.109	0.013	0.013	0.021	0.010	0.009	0.009
Methylcyclohexane	0.218	0.460	0.260	0.226	0.020	0.019	0.046	0.024	0.016	0.011
trans-1,4-dimethylcyclohexane	0.715	0.997	0.671	0.578	0.067	0.062	0.107	0.068	0.053	0.025
trans-1,2-dimethylcyclohexane	0.656	1.123	0.729	0.624	0.043	0.039	0.087	0.045	0.044	0.024
cis-1,2-dimethylcyclohexane	0.092	0.081	0.145	0.118	0.046	0.042	0.024	0.011	0.007	0.005
Ethylcyclohexane	0.180	0.295	0.199	0.177	0.014	0.013	0.027	0.013	0.017	0.008
1-methylethylcyclohexane	0.073	0.163	0.117	0.103	0.007	0.006	0.011	0.005	0.009	0.005
Total (µg/L)	2.049	3.234	2.286	1.934	0.210	0.195	0.324	0.176	0.155	0.086

Table 6.70The Levels of Cyclic Alkanes Directly Quantified from Site A
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(µg/L)	A ₁	A ₂
Cyclohexane	0.126 ± 20.6 %	0.013 ±36.7 %
Methylcyclohexane	0.291 ± 39.3 %	0.023 ± 52.9 %
trans-1,4-dimethylcyclohexane	0.740 ± 24.3 %	0.064 ±42.1 %
trans-1,2-dimethylcyclohexane	0.783 ± 29.5 %	0.047 ±45.2 %
cis-1,2-dimethylcyclohexane	0.109 ± 26.3 %	0.023 ± 80.3 %
Ethylcyclohexane	0.213 ± 26.3 %	0.015 ± 41.1 %
1-methylethylcyclohexane	0.114 ± 32.7 %	0.007 ± 35.7 %
Total (µg/L)	2.376 ± 24.8 %	0.191 ± 41.0 %

 Table 6.71

 Average Levels of Cyclic Alkanes Directly Quantified at Each Section of Site A

Total cyclic alkane levels at site A are shown in Figure 6.35 alongside those of nalkanes and branched chain alkanes. Cyclic alkane levels were similar to those of other alkanes at site A. This result is similar to that observed for levels of these VOCs of domestic waste sites. As mentioned previously for the other alkanes at site A, higher levels of cyclic alkanes were expected at the prescribed waste site. Again total levels of cyclic hydrocarbons at section  $A_1$  were significantly higher than at section  $A_2$ . There were little intrasection variations in total cyclic hydrocarbon levels at each section of site A.



Figure 6.35 Average Total Levels of Cyclic Alkanes at Site A

Figure 6.36 shows individual cyclic alkane levels at site A. Like previous VOC studies at this site, trends in relative amounts of compounds were similar to that found at domestic waste sites. The gas composition is shown in Table 6.72. As can be seen gas composition at both sections of site A was similar, where trans-1,2- and trans-1,4- dimethylcyclohexane accounted for approx. 60 % of total cyclic alkanes at site A. Similar results were observed for the cyclic alkane gas composition at sites E and F (see Table 6.18 and Table 6.45). At site F trans-1,2 and 1,4 dimethylcyclohexane were abundant throughout the waste decomposition process. What is noticeable about the gas composition in Table 6.7, is the abundance of cis-1,2-dimethylcyclohexane. At the domestic sites studies this compound was only found in domestic waste at site F and its abundance increased as the waste matured.



Figure 6.36 Average Individual Levels of Cyclic Alkanes at Site A

A ₁	A ₂
5.3	6.6
12.3	11.9
31.2	33.3
32.9	24.6
4.6	11.8
8.9	8.0
4.8	3.7
100.0	100.0
	A ₁ 5.3 12.3 31.2 32.9 4.6 8.9 4.8 100.0

Table 6.72The Average Gas Composition of Cyclic Alkanes Directly Quantified<br/>at Each Section of Site A

6.2.2.2.5 Cyclic Alkanes - Tentatively Identified and Indirectly Quantified

The levels of other cyclic hydrocarbons found in landfill gas from site A are shown in Table 6.73. Total levels at section  $A_1$  ranged from  $0.229 - 1.178 \ \mu g/L$  and  $0.016 - 0.104 \ \mu g/L$  at section  $A_2$ . Average total levels of these other cyclic alkanes are shown in Table 6.74, and they were  $0.692 \pm 57.2$  % at section  $A_1$ , and  $0.045 \pm 73.6$  % at section  $A_2$ . These other cyclic alkanes contributed significantly to total levels of cyclic alkanes at site A. High levels of trans-1,3-dimethylcyclohexane at sampling point  $A_{1-2}$  are contribute significantly to total levels of other cyclic hydrocarbons at section  $A_1$ . It is present in levels comparable to the abundant trans-1,2- and 1,4-dimethylcyclohexane at this site. Interestingly, this cyclic alkane was not observed at the domestic waste sites E and F.

A₂₋₁ A₂₋₃ A₁₋₂ A₂₋₂ A₁₋₁  $(\mu g/L)$ **S1 S2 S1 S2 S1 S2 S1 S2 S1 S2** 0.006 0.075 1 1 1 0.008 0.015 1 Methylcyclopentane 1 1 1 / 0.299 0.652 1 1 0.012 0.023 1 1 trans-1,3-dimethylcyclohexane cis-1,3-dimethylcyclohexane 1 0.013 0.025 1 1 1 1 trans-1-ethyl-4-methylcyclohexane / / 0.095 0.11 0.007 0.008 0.008 0.016 0.007 0.012 0.004 0.009 0.004 0.052 0.166 0.065 0.072 0.007 cis-1-ethyl-4-methylcyclohexane 1 1 0.009 0.01 0.006 0.016 0.007 0.015 Propylcyclohexane 0.084 0.133 0.13 0.14 1-methyl-4-0.038 0.119 0.073 0.08 0.004 0.009 1 1 1 (1-methylethyl)cyclohexane 1 0.005 0.009 0.049 0.092 0.115 0.123 1 Butylcyclohexane 1 1 TOTAL 0.229 0.584 0.777 1.178 0.016 0.019 0.050 0.104 0.027 0.052

Table 6.73The Levels of Cyclic Alkanes Indirectly Quantified from Sites A

(μg/Ľ)	A	A
Methylcyclopentane	0.020 ± 181.6 %	0.004 ± 167.3 %
trans-1,3-dimethylcyclohexane	0.238 ± 130.4 %	0.006 ± 166.6 %
cis-1,3-dimethylcyclohexane	/	0.006 ± 166.7 %
trans-1-ethyl-4-methylcyclohexane	0.051 ± 116.1 %	0.010 ± 37.9 %
cis-1-ethyl-4-methylcyclohexane	0.089 ± 58.5 %	0.004 ± 90.6 %
Propylcyclohexane	0.122 ± 21.0 %	0.011 ± 37.8 %
1-methyl-4-(1-methylethyl)cyclohexane	0.077 ± 43.2 %	0.002 ± 168.8 %
Butylcyclohexane	0.095 ± 34.9 %	0.002 ± 167.7 %
Total (µg/L)	0.692 ± 57.2 %	0.045 ± 73.6 %

Table 6.74 Average Levels of Cyclic Alkanes Indirectly Quantified at Each Section of Site A

When total average levels in Table 6.70 and Table 6.73 are combined, overall total levels at site A are obtained. These are shown in Table 6.75, where compounds have been grouped. As can be seen C₂-cyclohexanes are significantly more abundant than other cyclic alkanes. The gas composition, shown in Table 6.76, further illustrates this. C₂-cyclohexane accounted for more than 60 % of total group levels. The gas composition at sections A₁ and A₂, is very similar and resembles that at section  $F_2$  and  $F_1$  for 16 – 21 year old domestic waste.

Average Levels of Grouped Cyclic Alkanes at Each Section of Site A				
(µg/L)	A ₁	A ₂		
Methylcyclopentane	$0.020 \pm 181.6$ %	0.004 ± 167.3 %		
Cyclohexane	0.126 ± 20.6 %	0.013 ± 36.7 %		
Methylcyclohexane	0.291 ± 39.3 %	$0.023 \pm 52.9 \%$		
C2-cyclohexanes	2.082 ± 16.9 %	0.160 ± 43.3 %		
C3-cyclohexanes	$0.376 \pm 30.2$ %	0.031 ± 28.8 %		
C4-cyclohexanes	0.172 ± 33.4 %	0.004 ± 168.2 %		
Total (μg/L)	3.068 ± 20.5 %	$0.235 \pm 35.0$ %		

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Table 6.75Average Levels of Grouped Cyclic Alkanes at Each Section of Site A

at Di	den beetion of blie A	
%	A ₁	A ₂
Methylcyclopentane	0.7	1.6
Cyclohexane	4.1	5.4
Methylcyclohexane	9.5	9.7
C2-cyclohexanes	67.9	68.1
C3-cyclohexanes	12.3	13.3
C4-cyclohexanes	5.6	1.9
TOTAL	100.0	100.0

Table 6.76 The Average Gas Composition of Grouped Cyclic Alkanes at Each Section of Site A

6.2.2.2.6 Aromatic Hydrocarbons - Positively Identified and Directly Quantified

The levels of aromatic hydrocarbons found in landfill gas from site A are shown in Table 6.77. Total levels at section  $A_1$  ranged from  $3.196 - 7.372 \ \mu g/L$  and  $0.169 - 1.239 \ \mu g/L$  at section  $A_2$ . Average total levels at section  $A_1$  and at section  $A_2$  are shown in Table 6.78, they were 5.075  $\mu g/L \pm 43.2$  % and 0.668  $\mu g/L \pm 64.6$  %. Intrasection variations were not significant. As was found for alkanes, aromatic hydrocarbon levels at section  $A_1$ , were higher, by a factor of approximately 8, than section  $A_2$ .

The Levels of Aromatic Hydrocarbons Directly Quantified from Site A										
(µg/L)	A ₁₋₁		Α	A ₁₋₂		A ₂₋₁		A ₂₋₂		2-3
	S1	S2	S1	S2	S1	S2	<b>S1</b>	S2	S1	<b>S2</b>
Benzene	1.119	1.073	2.008	1.232	0.427	0.501	0.251	0.127	0.031	0.083
Methylbenzene	0.486	0.339	1.370	1.416	0.208	0.247	0.172	0.061	0.043	0.070
Ethylbenzene	0.586	0.569	0.910	0.979	0.181	0.229	0.155	0.041	0.031	0.135
1,2&1,4-dimethylbenzene	0.367	0.317	0.474	0.478	0.088	0.116	0.091	0.020	0.021	0.079
1,3-dimethylbenzene	0.169	0.202	0.954	0.968	0.042	0.052	0.054	0.011	0.013	0.032
Propylbenzene	0.251	0.219	0.440	0.391	0.021	0.024	0.033	0.002	0.014	0.015
1,2,4-trimethylbenzene	0.077	0.235	0.530	0.489	0.027	0.032	0.043	BDL	0.006	0.034
1,3,5-trimethylbenzene	0.142	0.245	0.686	0.578	0.030	0.038	0.037	BDL	0.011	0.029
Total (µg/L)	3.197	3.198	7.373	6.531	1.024	1.240	0.835	0.262	0.170	0.478

Table 6.77The Levels of Aromatic Hydrocarbons Directly Quantified from Site A

(μg/L)	$\overline{\mathbf{A}_1}$	A ₂
Benzene	1.358 ± 32.3 %	0.237 ± 81.2 %
Methylbenzene	0.903 ± 63.1 %	0.133 ± 64.8 %
Ethylbenzene	0.761 ± 28.1 %	0.129 ± 60.9 %
1,2&1,4-dimethylbenzene	0.409 ± 19.5 %	0.069 ± 57.4 %
1,3-dimethylbenzene	0.573 ± 78.2 %	0.034 ± 54.7 %
Propylbenzene	$0.325 \pm 32.9 \%$	0.018 ± 58.1 %
1,2,4-trimethylbenzene	$0.333 \pm 64.6$ %	0.023 ± 71.8 %
1,3,5-trimethylbenzene	0.413 ± 63.1 %	0.024 ± 63.5 %
Total (µg/L)	5.075 ± 43.2 %	0.668 ± 64.6 %

Table 6.78Average Levels of Aromatic Hydrocarbons Directly Quantified<br/>at Each Section of Site A

Figure 6.37 shows total aromatic hydrocarbon levels and alkane (overall total) levels at site A. Aromatic hydrocarbon levels at each section of site A were higher than alkanes. A similar observation was made at the domestic waste sites studied. As mentioned previously for alkanes, these levels of aromatic hydrocarbons, similar to levels at domestic sites, were lower than expected.



Figure 6.37 Average Total Levels of Aromatic Hydrocarbons at Site A

Figure 6.38 shows individual levels at site A. Relative levels were similar to those found at site F for domestic waste in advanced stages of methanogenesis. This is further highlighted by the gas composition, shown in Table 6.79. The gas composition

was similar at both sections of site A and was similar to the gas composition found at sections  $F_2$  and  $F_1$  (Table 6.25) for domestic waste 16 - 21 years old.



Figure 6.38 Average Individual Levels of Aromatic Hydrocarbons at Site A

#### **Table 6.79**

The Average Gas Composition of Aromatic Hydrocarbons Directly Quantified at Each Section of Site A

%	A ₁	A ₂
Benzene	26.8	35.4
Methylbenzene	17.8	20.0
Ethylbenzene	15.0	19.3
1,2&1,4-dimethylbenzene	8.1	10.4
1,3-dimethylbenzene	11.3	5.1
Propylbenzene	6.4	2.7
1,2,4-trimethylbenzene	6.6	3.5
1,3,5-trimethylbenzene	8.1	3.6
TOTAL	100.0	100.0

6.2.2.2.7 Aromatic Hydrocarbons - Tentatively Identified and Indirectly Quantified The levels of other aromatic compounds found at site A are shown in Table 6.80. Total levels at section  $A_1$  ranged from  $0.652 - 1.672 \mu g/L$  and  $0.004 - 0.069 \mu g/L$  at section  $A_2$ . Average total levels of these other aromatic hydrocarbons were  $1.285 \pm 35.5$  % at section  $A_1$ , and  $0.030 \pm 86.5$  % at section  $A_2$ , and are shown in Table 6.81. The levels of these other aromatic hydrocarbons did contribute significantly to total levels at section  $A_1$ , but not at section  $A_2$ .

		<u> </u>								
(ug/I)	A ₁₋₁		A ₁₋₂		A ₂₋₁		A ₂₋₂		A ₂₋₃	
(µg/L)	<b>S1</b>	S2	S1	S2	<b>S1</b>	S2	<b>S</b> 1	S2	<b>S1</b>	S2
1-methylethylbenzene	0.067	0.321	0.208	0.21	0.008	0.011	0.004	0.015	0.002	0.009
3-ethyl-2-methylbenzene	0.094	0.297	/	/	1	/	/	1	/	/
1-ethyl-2-methylbenzene	0.116	0.248	0.464	0.466	0.015	0.02	/	1	0.004	0.014
1-ethyl-4-methylbenzene	0.076	0.149	0.176	0.346	0.008	0.011	/	/	0.003	0.01
1,2,3-trimethylbenzene	0.065	0.362	/	/	1	1	/	/	/	/
1-methyl-4- (1-methylethyl)benzene	0.098	0.102	0.111	0.22	0.011	0.016	/	/	/	1
1-methyl-2-propylbenzene	0.083	0.092	0.189	0.196	0.009	0.012	/	/	/	/
2-ethyl-1,4-dimethylbenzene	0.053	0.101	0.115	0.116	1	/	/	/	/	/
Total (µg/L)	0.652	1.672	1.262	1.554	0.05	0.069	0.004	0.015	0.008	0.033

Table 6.80The Levels of Aromatic Hydrocarbons Indirectly Quantified from Sites A

Table 6.81Total Levels of Aromatic Hydrocarbons Indirectly Quantified<br/>at Each Section of Site A

(μg/L)	A ₁	A ₂
1-methylethylbenzene	0.201 ± 51.6 %	0.008 ± 57.0 %
3-ethyl-2-methylbenzene	0.098 ± 143.4 %	1
1-ethyl-2-methylbenzene	0.324 ± 53.1 %	$0.009 \pm 98.9$ %
1-ethyl-4-methylbenzene	0.186 ± 61.4 %	0.005 ± 93.0 %
1,2,3-trimethylbenzene	0.107 ± 162.0 %	/
1-methyl-4-(1-methylethyl)benzene	0.133 ± 44.0 %	0.004 ± 159.5 %
1-methyl-2-propylbenzene	0.140 ± 43.4 %	0.003 ± 157.5 %
2-ethyl-1,4-dimethylbenzene	0.096 ± 30.6 %	/
Total (µg/L)	1.285 ± 35.5 %	0.030 ± 86.5 %

When total average levels in Table 6.77 and Table 6.80 are combined, overall total levels at site A are obtained. These are shown in Table 6.82, where compounds have been grouped. The gas composition is shown in Table 6.83. Again, there are similarities with gas from domestic refuse, in particular gas at site E. The noticeable differences being the greater abundances of benzene at both sections  $A_1$  and  $A_2$ , and the lower abundances of  $C_3$  – alkylbenzene at section  $A_2$ . However, given the nature of section  $A_1$ , these differences are not unexpected.

Average Levels of Grouped Aromatic Hydrocarbons at Each Section of Site A				
(µg/L)	A ₁	A ₂		
Benzene	1.358 ± 32.3 %	0.237 ± 81.2 %		
Methylbenzene	$0.903 \pm 63.1$ %	0.133 ± 64.8 %		
C2-Alkylbenzenes	1.743 ± 42.3 %	0.232 ± 58.3 %		
C3-Alkylbenzenes	1.987 ± 38.2 %	0.088 ± 54.7 %		
C4-Alkylbenzenes	0.369 ± 35.7 %	0.008 ± 158.5 %		
Total (μg/L)	6.360 ± 37.1 %	0.698 ± 64.6 %		

Table 6.82Average Levels of Grouped Aromatic Hydrocarbons at Each Section of Site A

Ta	ble	6.83	,

The Average Gas Composition of Grouped Aromatic Hydrocarbons at Each Section of Site A

A ₁	A ₂
21.4	33.9
14.2	19.1
27.4	33.3
31.2	12.6
5.8	1.1
100.0	100.0
	A1           21.4           14.2           27.4           31.2           5.8           100.0

#### 6.2.2.2.8 Terpenes - Positively Identified and Directly Quantified

The levels of various terpenes found in landfill gas from site A are shown in Table 6.84. Total levels at section  $A_1$  ranged from  $0.388 - 1.868 \ \mu g/L$  and  $0.042 - 0.142 \ \mu g/L$  at section  $A_2$ . Average total levels at site A shown in Table 6.85 were 1.135  $\ \mu g/L \pm 65.5 \ \%$  at section  $A_1$ , and  $0.103 \ \mu g/L \pm 35.2 \ \%$  at section  $A_2$ . Similar to other VOCs at site A, intrasection variations were not significant and terpene levels were 10 times higher at section  $A_1$ .

1	The Levels of Terpenes Directly Quantined it on site									
	A ₁₋₁		A ₁₋₂		A	A		A ₂₋₂		2-3
(µg/L)	<b>S1</b>	S2	<b>S</b> 1	S2	S1	S2	S1	S2	<b>S</b> 1	S2
a-Pinene	0.397	0.202	0.612	0.683	0.040	0.035	0.023	0.060	0.065	0.068
β-Pinene	0.213	0.186	0.383	0.432	0.028	0.025	0.011	0.039	0.021	0.036
Limonene-1	BDL	BDL	0.676	0.753	0.032	0.029	0.009	0.043	0.021	0.035
Total (µg/L)	0.610	0.389	1.672	1.869	0.099	0.090	0.043	0.142	0.107	0.138

 Table 6.84

 The Levels of Terpenes Directly Quantified from Site A

Average Levels of T	erpenes Directly Quantified	at Each Section of Site A
(µg/L)	A	A ₂
α-Pinene	0.474 ± 46.0 %	0.048 ± 37.8 %
β-Pinene	$0.304 \pm 40.2$ %	0.027 ± 38.1 %
Limonene-1	0.357 ± 115.8 %	$0.028 \pm 42.2$ %
Total (µg/L)	1.135 ± 65.5 %	0.103 ± 35.2 %

 Table 6.85

 Average Levels of Terpenes Directly Quantified at Each Section of Site A

Figure 6.39 shows total average terpene levels at site A, including overall total levels of other VOCs. Terpenes are the least abundant compounds at site A, and given the waste inputs this is not surprising. At the domestic sites studied, terpenes were amongst the abundant groups of VOCs in landfill gas. Low levels of terpenes compared to other VOCs were only observed very old domestic refuse at site F.



Figure 6.39 Average Total Levels of Terpenes at Site A

Figure 6.40 shows individual terpene levels at site A. Similar to the domestic sites studied,  $\alpha$ -pinene,  $\beta$ -pinene and limonene were the major terpenes found. Gas composition is shown in Table 6.86.  $\alpha$ -pinene is the most abundant terpene (approximately 45 %), followed by comparable levels of  $\beta$ -pinene (approximately 25%) and limonene (approximately 30 %). This is different to the trends at domestic sites studied, where limonene was usually the most abundant terpene (approximately

50 %), followed by  $\alpha$ -pinene (approximately 35 %), then  $\beta$ -pinene (approximately 15%).



Figure 6.40 Average Individual Levels of Terpenes at Site A

# Table 6.86The Average Gas Composition of Terpenes Directly Quantified<br/>at Each Section of Site A

%	A ₁	A ₂			
α-Pinene	41.7	46.8			
β-Pinene	26.8	26.0			
Limonene-1	31.5	27.2			
Total %	100.0	100.0			

#### 6.2.2.2.9 Terpenes - Tentatively Identified and Indirectly Quantified

As shown in Table 6.87, camphene was also found at two sampling points of section  $A_2$ , but its levels were not significant. Gas composition, where camphene is included, is shown in Table 6.88. As can be seen, camphene accounts for only approximately 5% of total terpenes at section  $A_2$ .

 (μg/L)	A	1-1	A	1-2	A	2-1	A	2-2	A	2-3
	S1	S2	<b>S</b> 1	S2	S1	S2	<b>S1</b>	S2	<b>S</b> 1	S2
Camphene	/	1	/	/	/	1	0.006	0.013	0.009	0.011

Table 6.87The Levels of Terpenes Indirectly Quantified from Sites A

Table 6.88

The Average Gas Co	mposition of Terpenes at Ea	ch Section of Site A
%	A ₁	A ₂
α-Pinene	41.7	44.1
β-Pinene	26.8	24.5
Limonene-1	31.5	25.6
Camphene	0.0	5.8
Total %	100.0	100.0

#### 6.2.2.3 Landfills B, C, D and G

Details of landfills B, C, D and G are given in Table 6.1, Section 6.2. All four sites had received domestic waste and commercial waste and landfills C and G had also received industrial waste. Table 6.89 shows the average waste inputs into each site. Information gathered from landfill operators indicated that waste segregation was generally not practiced at these sites⁽¹⁰⁵⁾. Gas extraction began at all four sites in the early 1990's. All four sites were actively producing methane and landfill gas samples were taken from the extraction system and thus the VOCs collected represented an average of those present at each site. Landfill D was divided into two areas, site D1 and D2, and landfill gas from the extraction system was sampled individually from each area. It should be noted that at the time of study gas was being extracted from all areas (old and new) of each site, i.e., areas that had ceased receiving waste and that were still receiving waste.

The Average Waste Inputs into Landfills B, C, D and G						
LANDFILL	DOMESTIC WASTE (%)	COMMERCIAL WASTE (%)	INDUSTRIAL WASTE (%)	INERT WASTE (%)		
Site B						
1978 - 1983	40	25	1	35		
1984 - 1989	/	/	/	100		
1990 - 1997	17	44	1	37		
Site C	30	20	20	30		
Site <b>D</b> ₁	37	23	/	40		
Site D ₂	37	23		40		
Site G	30	/	28	42		

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Discussions with on-site gas extraction operators revealed a standard practice for construction of the gas extraction system⁽¹⁰⁵⁾. The main points of the practice include:

- Disused landfills and completed capped sections of operating landfills are • vertically drilled;
- Where filling continuing, if possible, horizontal extraction pipes are inserted into a lift. When the cell is complete vertical drilling takes place;

- Horizontal extraction pipes can be inserted into a lift containing waste only two weeks old. Horizontal pipes may also be needed to control gas migration when odours concern nearby residents;
- When or if horizontal or vertical pipes are laid depends on a number of factors including logistics, economics and availability of construction crew;
- The majority of the gas being extracted is coming from waste well into the methanogenic phase of decomposition;
- The same practice applies to sites B, C, D and G;
- Peak methane levels are achieved approximately six months after capping each cell.

The above information is important as it indicates that the gas being sampled may be coming from waste as fresh as two weeks old, but that the majority of gas is coming from waste which has entered the methanogenic phase of waste degradation. Table 6.90 shows the age of the waste at the time of this study, where it is assumed that horizontal pipes have been laid into lifts receiving waste.

Table 6.90           The Age of the Waste from Sites B, C, D ₁ , D ₂ and G at the Time of This Study				
LANDFILL	AGE OF WASTE			
Site B	2 Weeks – 19 years old			
Site C	7-12 years old			
Site D ₁	9-13 years old			
Site D ₂	2 Weeks – 6 years old			
Site G	2 Weeks – 21 years old			

The GC fingerprints for all five sites were similar except for the relative abundance of some compounds. Fig 6.41 - 6.45 show the GC traces for landfills B, C, D₁, D₂ and G.

















35.00

Time

Over a hundred different VOCs were present in landfill gas from each site. Table 6.91 lists all the compounds in order of retention time and Table 6.92 (a) – (j) list the compounds under the various classes of compounds. The various classes found include straight chain, branched chain, cyclic, aromatic, terpenic, olefinic, naphthenic, chlorinated, esteric and alcoholic hydrocarbons. Of these the most abundant, based on peak heights, included straight chain, branched chain, cyclic, aromatic and terpenic hydrocarbons. From this group of compounds some straight chain, cyclic, aromatic and terpenic and terpenic compounds were positively identified by retention time matching and mass spectral matching (as described in Section 3.2.1 of Chapter III) with standard compounds. Other abundant compounds from these classes and branched chain

compounds were tentatively identified by mass spectral matching with the mass spectral library search. The other various classes of compounds found were not abundant and were also only tentatively identified by mass spectral matching with the library search.

No.	RT	LIBRARY/ID	QUALITY
1	2.97	Chloroethene	72
2	3.23	Butane	72
3	5.88	2-methylbutane	91
4	6.91	Pentene-2	86
5	7.08	Pentane	86
6	8.09	dichloromethane	90
7	8.68	2.2-dimethylbutane	72
8	10.15	2.3-dimethylbutane	86
9	10.45	2-methylpentane	91
10	11.01	Butanone-2	80
11	11.11	3-methylpentane	87
12	11.60	1.2-dichloroethene-(Z)	91
13	12.00	Hexane	91
14	12.36	Ethyl acetate	80
15	12.69	Tetrahydrofuran	86
16	13.12	Methylcyclopentane	90
17	13.46	2.4-dimethylpentane	91
18	14.27	Benzene	91
19	14.65	Cyclohexane	91
20	15 29	2.3-dimethylpentane	68
20	15.68	3-methylbexane	87
21	15.80	trans-1.3-dimethylcyclopentane	91
23	15.99	cis-1.3-dimethylcyclopentane	94
23	16.12	Trichloroethene	94
25	16.24	2.2.4-trimethylpentane	72
25	16.57	Hexamethyldisiloxane	90
20	16.86	Hentane	91
28	16.98	Propylacetate	78
20	17.61	Methylcyclohexane	95
30	17.01	1.1.3-trimethylcyclopentane	90
31	17.87	4-methylpentanone-2	90
32	18.15	Ethylcyclopentane	93
32	18.29	2.5-dimethylbexane	91
34	18.36	2.4-dimethylhexane	95
35	18.56	1.2.4-trimethylcyclopentane	91
36	18.50	3.3-dimethylhexane	86
37	18.89	1.2.3-trimethylovclopentane	94
38	10.02	2 3 4-trimethylpentane	90
30	19.08	Methylbenzene	90
39 40	19.50	2 3_dimethylbeyane	81
40	19.33	2,5-uniterrymexane	93
41	19.04	2-methylheptane	90
42	19.90 20.16	trans_1 A-dimethylovelohevane	71
43 AA	20.10	trans 1 3-dimethylovalahavana	94
44 15	20.23	2 A-dimethylpentanone-3	72
43	20.30	2,4-uniculyipentanone-5	94
40	20.40	1,1-uincuryicycionexanc 1_ethyl_3_methylovalanentane	93
<del>4</del> /	20.02		

Table 6.91The 111 Compounds Identified in Order of Retention Time

# Table 6.91 (Continued)

No.	RT	LIBRARY/ID	QUALITY
48	20.73	Ethyl butanoic acid ester	93
49	20.99	trans-1,2-dimethylcyclohexane	97
50	21.16	Tetrachloroethene	98
51	21.30	Octane	90
52	22.10	2,2,4-trimethylhexane	72
53	22.28	cis-1.2-dimethylcyclohexane	80
54	22.50	Ethylcyclohexane	94
55	22.72	1.1.3-trimethylcyclohexane	94
56	22.82	2.5-dimethylheptane	74
57	22.98	2-ethylhexyl acetate	47
58	23.30	Ethylbenzene	91
59	23.38	1.3.5-trimethylcyclohexane	86
60	23.70	1.3&1.4-dimethylbenzene	96
61	23.83	Octahydropentalene	71
62	24 00	2-methyloctane	87
63	24.00	3-methyloctane	90
64	24.20	2-butyloctanol-1	47
65	24.55	1.2-dimethylbenzene	97
66	24.33	trans-1-ethyl-4-methylcyclohexane	72
67	24.77	cis-1-ethyl-4-methylcyclohexane	87
68	25.41	Nonane	94
60	25.41	3 5-dimethylbeptene-3	64
70	25.54	cis-1-ethyl-2-methylcyclohexane	74
70	25.05	1-methylethylbenzene	90
71	25.02	Octahydro-2-methylpentalene	62
72	25.97	1-methylethylcyclohexane	93
73	20.04	3-methyleptane	72
74	20.12	7-methyloctyne-3	35
75	20.22	Propylcycloheyane	94
70	20.40	a-Pinene	95
70	20.05	2 6-dimethyloctane	91
/ð 70	20.73	Propylbenzene	65
/9	27.01	Camphene	98
8U 91	27.10	1_ethyl_3_methylbenzene	95
81	27.20	1_ethyl-2-methylbenzene	93
82	27.55	3 4-dimethyloctane	64
83	27.31	1.2.4-trimethylbenzene	95
84	27.50	A-methylnonane	87
85	27.70	2-methylnonane	83
80	27.85	R- Pinene	96
8/	28.11	1 methyl 4 (1 methylethyl)cyclohexane	87
88	28.24	1 3 5 trimethylbenzene	93
89	28.48	aio 1 mothyl 4 (1 methylethyl-)cyclohexane	62
90	28.61	2.2.4.6. 6-pentamethylbentane	72
91	28.97	2,2,4,0,0-pentamentymeptane	95
92	29.14	S Corono 3	95
93	29.36	o-Carene-5	25
94	29.51	(- respinence	97
95	29.64	I-metnyl-4-(I-metnyletilyl)benzene	58
96	29.86		95
97	29.98		94
98	30.08	1-meinyl-4-(1-meinyliu)cyclonexene	00
99	30.24	Dutyicycionexane	50
100	30.36	3,8-aimethylaecane	6/
101	30.52	3, /-dimethylnonane	12
102	30.79	1-ethyl-3,5-dimethylbenzene	43
103	30.96	Sabinene	/0
104	31.03	trans-decahydronaphthalene	93

No.	RT	LIBRARY/ID	QUALITY			
105	31.14	5-methyldecane	72			
106	31.25	4-methyldecane	87			
107	31.38	2-methyldecane	90			
108	31.46	2,6,8-trimethyldecane	59			
109	31.60	3-methyldecane	90			
110	31.91	Undecene-5	52			
111	32.56	Undecane	94			

Table 6.91 (Continued)

Table 6.92 (a)

Straight Chain Hydrocarbons in the 111 Compounds				
NO.	RT	LIBRARY/ID	QUALITY	
2	3.23	Butane	72	
5	7.08	Pentane	86	
13	12.00	Hexane	91	
27	16.86	Heptane	91	
51	21.30	Octane	90	
68	25.41	Nonane	94	
92	29.14	Decane	95	
111	32.56	Undecane	94	

Table 6.92 (b)

Branched	Chain H	vdrocarbons	in the	111	Compounds
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NO.		LIBRARY/ID	QUALITY
3	5.88	2-methylbutane	91
7	8.68	2,2-dimethylbutane	72
8	10.15	2,3-dimethylbutane	86
9	10.45	2-methylpentane	91
11	11.11	3-methylpentane	87
17	13.46	2,4-dimethylpentane	91
20	15.29	2,3-dimethylpentane	68
21	15.68	3-methylhexane	87
25	16.24	2,2,4-trimethylpentane	72
33	18.29	2,5-dimethylhexane	91
34	18.36	2,4-dimethylhexane	95
36	18.64	3,3-dimethylhexane	86
38	19.08	2,3,4-trimethylpentane	90
40	19.53	2,3-dimethylhexane	81
41	19.84	2-methylheptane	93
42	19.90	4-methylheptane	90
52	22.10	2,2,4-trimethylhexane	72
56	22.82	2,5-dimethylheptane	74
62	24.00	2-methyloctane	87
63	24.28	3-methyloctane	90
74	26.12	3-methylheptane	72
78	26.73	2,6-dimethyloctane	91
83	27.51	3,4-dimethyloctane	64
85	27.76	4-methylnonane	87
86	27.85	2-methylnonane	83
91	28.97	2,2,4,6,6-pentamethylheptane	72
100	30.36	3,8-dimethyldecane	50
101	30.52	3,7-dimethylnonane	64
105	31.14	5-methyldecane	72
106	31.25	4-methyldecane	87
107	31.38	2-methyldecane	90
108	31.46	2,6,8-trimethyldecane	59
109	31.60	3-methyldecane	90

			5
NO.	RT	LIBRARY/ID	QUALITY
18	14.27	Benzene	91
39	19.30	Methylbenzene	90
58	23.30	Ethylbenzene	91
60	23.70	1,3&1,4-dimethylbenzene	96
65	24.55	1,2-dimethylbenzene	97
71	25.82	1-methylethylbenzene	90
79	27.01	Propylbenzene	65
81	27.26	1-ethyl-3-methylbenzene	95
82	27.33	1-ethyl-2-methylbenzene	93
84	27.56	1,2,4-trimethylbenzene	95
89	28.48	1,3,5-trimethylbenzene	93
95	29.64	1-methyl-4-(1-methylethyl)benzene	97
102	30.79	1-ethyl-3,5-dimethylbenzene	43

Table 6.92 (c)Aromatic Chain Hydrocarbons in the 111 Compounds

Table 6.92 (d)Cyclic Hydrocarbons in the 111 Compounds

NO.	RT	LIBRARY/ID	QUALITY
16	13.12	Methylcyclopentane	90
19	14.65	Cyclohexane	91
22	15.87	trans-1,3-dimethylcyclopentane	91
23	15.99	cis-1,3-dimethylcyclopentane	94
29	17.61	Methylcyclohexane	95
30	17.76	1,1,3-trimethylcyclopentane	90
32	18.15	Ethylcyclopentane	93
35	18.56	1,2,4-trimethylcyclopentane	91
37	18.89	1,2,3-trimethylcyclopentane	94
43	20.16	trans-1,4-dimethylcyclohexane	71
44	20.25	trans-1,3-dimethylcyclohexane	94
46	20.46	1,1-dimethylcyclohexane	94
47	20.62	1-ethyl-3-methylcyclopentane	93
49	20.99	trans-1,2-dimethylcyclohexane	97
53	22.28	cis-1,2-dimethylcyclohexane	80
54	22.50	Ethylcyclohexane	94
55	22.72	1,1,3-trimethylcyclohexane	94
59	23.38	1,3,5-trimethylcyclohexane	86
66	24.79	trans-1-ethyl-4-methylcyclohexane	72
67	24.89	cis-1-ethyl-4-methylcyclohexane	87
70	25.65	cis-1-ethyl-2-methylcyclohexane	74
73	26.04	1-methylethylcyclohexane	93
76	26.46	Propylcyclohexane	94
88	28.24	1-methyl-4-(1-methylethyl)cyclohexane	87
90	28.61	cis-1-methyl-4-(1-methylethyl-)cyclohexane	62
98	30.08	1-methyl-4-(1-methylid)cyclohexene	94
99	30.24	butylcyclohexane	90

Table 6.92 (e)

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Terpenic Hydrocarb	ons in the 111	Compounds

NO.	RT	LIBRARY/ID	QUALITY
77	26.65	α-Pinene	95
80	27.10	Camphene	98
87	28.11	β-Pinene	96
93	29.36	δ-Carene-3	95
94	29.51	a-Terpinene	25
97	29.98	Limonene-1	95
103	30.96	Sabinene	70

	Naphthenic Hydrocarbons in the 111 Compounds		
NO.	RT	LIBRARY/ID	QUALITY
72	25.97	Octahydro-2-methylpentalene	62
104	31.03	trans-decahydronaphthalene	93

Table 6.92 (f)

# Table 6.92 (g)

Culoro Hydrocarbous in the 111 Compounds			
NO.	RT	LIBRARY/ID	QUALITY
1	2.97	Chloroethene	72
6	8.09	Dichloromethane	90
12	11.60	1,2-dichloroethene-(Z)	91
15	12.69	Tetrahydrofuran	86
24	16.12	Trichloroethene	94
50	21.16	Tetrachloroethene	98

#### Table 6.92 (h)

	Alkenyl Hydrocarbons in the 111 Compounds		
NO.	RT	LIBRARY/ID	QUALITY
4	6.91	Pentene-2	86
110	31.91	Undecene-5	52

#### Table 6.92 (i)

NO.	RT	LIBRARY/ID	QUALITY
14	12.36	Ethyl acetate	80
28	16.98	Propyl acetate	78
48	20.73	Ethyl butanoic acid ester	93
57	22.98	2-ethylhexyl acetate	47

Table 6.92 (j) Alcohols & Ketones in the 111 Compounds

	71100	nois de litetones in the III compounds	
NO.	RT	LIBRARY/ID	QUALITY
10	11.01	Butanone-2	80
31	17.87	4-methylpentanone-2	90
45	20.36	2,4-dimethylpentanone-3	72
64	24.44	2-butyloctanol-1	47
96	29.86	Octadecenal-7	58

Over 60 VOCs were quantified either directly or indirectly as described in Section 4.1.3 and 4.3.3, respectively. Table 6.93 lists those compounds which were quantified in the landfill gas, where compounds marked with an asterisks were indirectly quantified. Table 6.94 shows the standard compound used for indirect quantification.

Table 6.93The Compounds Quantified in Sites B, C, D1, D2 and G

COMPOUNDS	COMPOUNDS
ALKANES	CYCLIC HYDROCARBONS
2-methylbutane*	Methylcyclopentane*
Pentane*	Cyclohexane
2,3-dimethylbutane*	Methylcyclohexane
2-methylpentane*	trans-1,4-dimethylcyclohexane
3-methylpentane*	cis-1,3-dimethylcyclohexane*
Hexane	trans-1,2-dimethylcyclohexane
2,4-dimethylpentane*	cis-1,2-dimethylcyclohexane
2-methylhexane	Ethylcyclohexane
2,3-dimethylpentane	trans-1-ethyl-4-methylcyclohexane*
3-methylhexane*	1-methylethylcyclohexane
Heptane	Propylcyclohexane*
2,2,4-trimethylpentane*	1-methyl-4-(1-methylethyl)cyclohexane
2,4-dimethylhexane*	
2,3,4-trimethylpentane*	AROMATIC HYDROCARBONS
2,3-dimethylhexane*	Benzene
2-methylheptane*	Methylbenzene
4-methylheptane*	Ethylbenzene
Octane	1,2&1,4-dimethylbenzene
2-methyloctane*	1,3-dimethylbenzene
3-methyloctane*	1-methylethylbenzene*
Nonane	Propylbenzene
2,6-dimethyloctane*	1-ethyl-4-methylbenzene*
4-methylnonane*	1,2,4-trimethylbenzene
2-methylnonane*	1,3,5-trimethylbenzene
Decane	1-methyl-4-(1-methylethyl)benzene*
Undecane	
2,2,4,6,6-pentamethylheptane*	TERPENIC HYDROCARBONS
Dodecane	α-Pinene
	Camphene*
	β-Pinene
	1-Limonene

COMPOUNDS	STANDARD USED FOR OUANTITATION
Pentane	
2-methylbutane	
2,3-dimethylbutane	Hexane
2-methylpentane	
3-methylpentane	
2,4-dimethylpentane	
2-methylhexane	TT
2,3-dimethylpentane	Heptane
3-methylhexane	
2,2,4-trimethylpentane	
2,4-dimethylhexane	
2,3,4-trimethylpentane	Ostora
2,3-dimethylhexane	Octane
2-methylheptane	
4-methylheptane	
2-methyloctane	Nonono
3-methyloctane	Nollalle
2,6-dimethyloctane	
4-methylnonane	Decane
2-methylnonane	
2,2,4,6,6-pentamethylheptane	Dodecane
Methylcyclopentane	Cyclohexane
cis-1,3-dimethylcyclopentane	trans-1,4-dimethylcyclohexane
trans-1-ethyl-4-methylcyclohexane	
Propylcyclohexane	1-methylethylcyclohexane
1-methyl-4-(1-methylethyl)cyclohexane	
1-methylethylbenzene	
1-ethyl-4-methylbenzene	Propylbenzene
1-methyl-4-(1-methylethyl)benzene	
Camphene	α-Pinene

 Table 6.94

 The Standard Compound Used for Indirect Quantification

The classes of VOCs found are typical of those found by other workers (Section 1.3, Chapter I), and discussion on VOCs found in landfill gas from landfills B, C,  $D_1$ ,  $D_2$  and G will be based on the description in Section 6.2.2.1.

Only two samples were taken from the gas extraction system at these sites, and therefore no statistics will be applied to the data. The relative amounts of particular compounds were similar in each sample, indicating that the gas composition was fairly constant, even though compound levels in each sample may have been different.

#### 6.2.2.3.1 n-Alkanes - Positively Identified and Directly Quantified

The levels of n-alkane at sites B, C,  $D_1$ ,  $D_2$  and G are shown in Table 6.95. Levels at sites B,  $D_1$  and  $D_2$  were similar ranging from  $0.338 - 1.238 \mu g/L$ . Higher levels were

observed at sites C and G, and ranged from  $1.595 - 2.404 \ \mu g/L$ . The n-alkane levels at these sites were typical of those observed at site F ( $0.213 - 1.383 \ \mu g/L$ ).

	2 and 3 and 4 shes b, c, b ₁ , b ₂ and 6									U
(µg/L)	SITE B		SITE C		SITE D ₁		SITE D ₂		SITE G	
	<u>S1</u>	S2	<u>S1</u>	S2	S1	S2	S1	S2	<b>S</b> 1	S2
Hexane	0.132	0.364	0.341	0.285	0.213	0.234	0.170	0.142	0.382	0.358
Heptane	0.170	0.622	0.322	0.289	0.283	0.340	0.728	0.346	0.706	0.623
Octane	0.027	0.193	0.226	0.227	0.123	0.155	0.202	0.115	0.282	0.234
Nonane	0.007	0.041	0.515	0.468	0.043	0.055	0.097	0.113	0.426	0.305
Decane	0.002	0.011	0.503	0.458	BDL	0.014	0.013	0.007	0.099	0.076
Undecane	BDL	0.007	0.302	0.129	BDL	BDL	BDL	BDL	BDL	BDL
Dodecane	BDL	BDL	0.194	0.007	BDL	BDL	BDL	BDL	BDL	BDL
Total (µg/L)	0.338	1.238	2.404	1.864	0.662	0.798	1.210	0.722	1.894	1.595

Table 6.95The Levels of n-Alkanes Directly Quantified at Sites B, C, D1, D2 and G

Total average levels are shown in Table 6.96. Figure 6.46 shows total average alkane levels at each site. Interestingly, sites C and G also accepted industrial waste (see Table 6.3), and there may be some contribution to n-alkane levels at these two sites. Levels at sites C and G were about a factor of 2 higher than the other sites.

Table 6.96
The Total Average Levels of n-Alkanes Directly Quantified
at Sites B, C, D ₁ , D ₂ and G

		, ,	1, 2		
(μg/L)	SITE B	SITE C	SITE D ₁	SITE D ₂	SITE G
Hexane	0.248	0.313	0.223	0.156	0.370
Heptane	0.396	0.306	0.312	0.537	0.664
Octane	0.110	0.227	0.139	0.158	0.258
Nonane	0.024	0.492	0.049	0.105	0.365
Decane	0.007	0.481	0.007	0.010	0.088
Undecane	0.004	0.215	0.000	0.000	0.000
Dodecane	0.000	0.101	0.000	0.000	0.000
Total (µg/L)	0.788	2.134	0.730	0.966	1.745

in gas composition at sites C and section  $F_2 - F_4$  of site F for waste aged 7 – 12 years and 3 – 16 years old respectively, but even here, hexane abundance at site C is higher.



Figure 6.47 Average Individual Levels of n-Alkanes at Sites B, C, D₁, D₂ and G

	at Sites B, C, D ₁ , D ₂ and G										
%	SITE B	SITE C	SITE D ₁	SITE D ₂	SITE G						
Hexane	31.5	14.7	30.6	16.1	21.2						
Heptane	50.2	14.3	42.7	55.6	38.1						
Octane	13.9	10.6	19.1	16.4	14.8						
Nonane	3.1	23.0	6.7	10.9	20.9						
Decane	0.9	22.5	1.0	1.0	5.0						
Undecane	0.4	10.1	0.0	0.0	0.0						
Dodecane	0.0	4.7	0.0	0.0	0.0						
Total	100.0	100.0	100.0	100.0	100.0						

Table 6.97 The Average Gas Composition of n-Alkanes Directly Quantified at Sites B, C, D₁, D₂ and G

Our attention was drawn to the apparent differences between relative abundances of n-alkanes at landfills where gas extraction was conducted compared with landfills where the gas escaped passively. This idea will be pursued as the other groups of VOCs are studied at sites B, C,  $D_1$ ,  $D_2$  and G.

A closer look at the results reveals that the n-alkanes most influenced by gas extraction are C₆, C₇, C₉, C₁₀, C₁₁ and C₁₂. The observations are:

- Gas extraction produces landfill gas more abundant in hexane and heptane and less abundant in nonane, and particularly decane, than landfill gas which passively escapes.
- Octane, with levels around 15 %, appears not to be affected by the gas extraction. Its abundance is relatively constant right throughout the waste decomposition process at site F, where similar abundances are found at site E, and similar abundances at the gas extraction sites B, C,  $D_1$ ,  $D_2$  and G.
- Negligible abundances of undecane and dodecane are observed at gas extraction sites.

The exception to the above observations is site C, however when gas extraction rates are considered some interesting correlations are found. Gas extraction rates are shown in Table 6.98.

Gas Extraction	Flow Rates Using for Sites B, C, D ₁ , D ₂ and G
LANDFILL	GAS EXTRACTION AVERAGE RATE (m ³ /Houre)
Site B	2200
Site C	700 - 1100
Site D ₁	1450
Site D ₂	1450
Site G	600 - 1000

Table ( 00

It appears that as gas extraction increases, the deviation in n-alkane abundances from that found in passive landfill gas increases. Alternately expressed, as pumping rate decreases the behaviour of n-alkanes approaches that expected in passive landfill gas. Site C and site G with the lowest pumping rates approach the n-alkane behaviour found for passive domestic waste sites. At site C and G, nonane and decane combined accounted for approximately 45 % and 25 %, respectively, of total n-alkanes. At sites  $D_1$  and  $D_2$  where the pumping rate is higher, nonane and decane combined account for approximately 8 % and 12 % respectively. At site B with the highest pumping rate, nonane and decane combined account for approximately 4 % of total n-alkane. While relative abundances of nonane and decane decrease as the pumping rate increase, the relative abundances of hexane and heptane increase. At sites C and G, hexane and heptane combined account for approximately 30 % and 60 % of total n-alkanes. At sites D₁ and D₂, hexane and heptane combined account for approximately 70 % of total n-alkanes at both sites. At site B with the highest pumping rate, hexane and heptane combined account for approximately 80 % of total n-alkanes.

The above findings, as mentioned previously could not he explained by waste inputs or waste ages. Even direct volatilisation from young refuse seems unlikely, as site C and D₁ no longer accept waste. One possible explanation is the effect of air infiltration into the landfill as the gas is extracted. Those sites with the higher flow rates, will have higher rates of air infiltration. When this assumption was checked with gas extraction site operators it was not substantiated. They indicated that pumping rates were determined by gas quality (methane) and that higher pumping rates did not necessarily mean more air entered the sites, as the sites (site cover and gas wells) were well sealed. The average amount of oxygen in the gas from all sites was less than  $1\%^{(105)}$ .

If the percentage of oxygen in the gas is low and fairly constant at each site our result suggests that the rate at which the gas is pumped has an effect on the physical, chemical and biological processes occurring within a landfill. Allen *et al.*⁽⁹²⁾ also suggested that the rates of gas extraction will directly affect the levels of VOCs observed, which in turn accounted for differences observed in landfill gas composition between sites. However, to assess the magnitude of this effect further work was required. The small amount of air (O₂) present in the gas due to air infiltration should not be overlooked, as the rate of O₂ moving through the waste is determined by the gas pumping rate. It is interesting to note that the n-alkane trends found at sites B, C, D₁, D₂ and G are similar to those observed at sections F₄ of site F, where the waste (16 – 21 years old) was in the maturation phase of waste degradation. It is toward the end of the active methanogenesis phase that air begins to enter the landfill.^{(6), (119)} (see Fig 1.3).

#### 6.2.2.3.2 n-Alkanes - Tentatively Identified and Indirectly Quantified

Pentane levels at sites B, C,  $D_1$ ,  $D_2$  and G are shown in Table 6.99. Pentane contributed significantly to n-alkane levels at these sites, as can be seen in Figure 6.48 and Table 6.100, where the gas composition is shown. Such high abundances of pentane were not observed at sites E and F.

Table 6.99
The Levels of n-Alkanes Indirectly Quantified at Sites B, C, D₁, D₂ and G

(μg/L)	SIT	FE B SIT		E C SIT		E D ₁	SITE D ₂		SITE G	
	<b>S1</b>	S2	<b>S</b> 1	S2	<b>S</b> 1	S2	<b>S</b> 1	S2	<b>S1</b>	S2
Pentane	0.050	0.139	0.040	0.045	0.050	0.053	/	1	0.153	0.166



Fig 6.48 Average Total levels of Total n-Alkanes and the n-Alkanes Directed Quantified at Sites B, C, D₁, D₂ and G

0	-			/ / / 1	, 7
	Site B	Site C	Site <b>D</b> ₁	Site D ₂	Site G
(µg/L)	%	%	%	%	%
Pentane	10.7	1.9	6.6	0.0	8.4
Hexane	28.1	14.4	28.6	16.1	19.4
Heptane	44.8	14.1	39.9	55.6	34.9
Octane	12.5	10.4	17.8	16.4	13.5
Nonane	2.7	22.6	6.3	10.9	19.2
Decane	0.8	22.1	0.9	1.0	4.6
Undecane	0.4	9.9	0.0	0.0	0.0
Dodecane	0.0	4.6	0.0	0.0	0.0
Total (µg/L)	100.0	100.0	100.0	100.0	100.0

Table 6.100 The Average Gas Composition of Total n-Alkanes at Sites B, C, D₁, D, and G

Overall, the n-alkane results suggest that the conditions imposed in a landfill site by gas extraction and air infiltration favour the production of  $C_5 - C_7$  n-alkanes over  $C_9 - C_{12}$  n-alkanes. It appears the production of  $C_8$  is unaffected by either type of gas removal.

# 6.2.2.3.3 Branched Chain Alkanes - Tentatively Identified and Indirectly Quantified

Levels of branched chain alkanes for site B, C, D₁, D₂ and G are shown in Table 6.101, and ranged from 0.887 – 2.020  $\mu$ g/L at sites B, D₁ and D₂, and 2.510 – 3.533  $\mu$ g/L at sites C and G. Similar to n-alkane results, branched chain alkane levels were higher at sites C and G. Overall, branched chain alkane levels at all five sites were similar to those observed at site F (0.213 – 1.383  $\mu$ g/L). The higher branched chain alkane levels at sites C and G (about a factor of 2 as compared with the other sites) may indicate contributions from industrial waste accepted at these two sites.

		0.70				2					
	(µg/L)		<u>E B</u>		<u>E C</u>	SIT	$\mathbf{E} \mathbf{D}_1$	SIT	ED ₂	SIT	EG
		<u>S1</u>	S2	<u>S1</u>	<u>S2</u>	<b>S</b> 1	S2	S1	<b>S2</b>	<b>S</b> 1	<b>S</b> 2
C ₅	2-methylbutane	0.241	0.226	0.044	0.040	0.049	0.040	0.025	0.033	0.246	0.236
	Total of C ₅	0.241	0.226	0.044	0.040	0.049	0.040	0.025	0.033	0.246	0.236
	2,3-dimethylbutane	/**	/	0.036	0.045	/	1	/	1	/	1
C ₆	2-methylpentane	0.238	0.083	0.176	0.167	0.141	0.121	0.058	0.083	0.233	0.258
	3-methylpentane	0.345	0.112	0.176	0.165	0.104	0.104	0.059	0.065	0.233	0.211
	Total of C ₆	0.583	0.195	0.388	0.378	0.244	0.225	0.116	0.148	0.466	0.469
	2,4-dimethylpentane	/	/	0.061	0.084	1	/	/	/	0.097	0.182
<b>C</b> ₇	*2-methylhexane & 2,3-dimethylpentane	0.473	0.153	0.388	0.487	0.291	0.247	0.334	0.307	0.600	0.553
	3-methylhexane	0.355	0.117	0.170	0.189	0.160	0.140	0.180	0.243	0.449	0.486
	Total of C ₇	0.829	0.270	0.619	0.760	0.451	0.387	0.513	0.550	1.146	1.220
	2,2,4-trimethylpentane	1	/	0.050	0.075	0.123	0.106	1	/	0.201	0.251
	2,4-dimethylhexane	0.061	0.015	0.040	0.062	0.040	0.034	0.027	0.035	0.079	0.098
C	2,3,4-trimethylpentane	0.092	0.072	0.035	0.058	0.050	0.044	1	/	0.090	0.126
℃8	2,3-dimethylhexane	/	/	0.049	0.103	/	/	1	/	0.069	0.151
	2-methylheptane	0.138	0.049	0.114	0.214	0.118	0.106	0.096	0.114	0.113	0.245
	4-methylheptane	0.075	0.060	0.064	0.335	0.201	0.181	0.120	0.172	1	1
	Total of C ₈	0.367	0.196	0.352	0.849	0.531	0.471	0.243	0.321	0.551	0.871
	2-methyloctane	/	/	0.211	0.248	1	/	0.058	0.049	0.121	0.187
C ₉	3-methyloctane	/	/	0.196	0.270	/	/	0.053	0.044	0.119	0.223
	2,6-dimethyloctane	/	/	0.227	0.220	/	/	/	/	/	1
	Total of C ₉	/	/	0.633	0.738	/	/	0.111	0.093	0.240	0.410
C	4-methylnonane	/	/	0.173	0.225	/	/	/	1	/	/
$C_{10}$	2-methylnonane	/	1	0.157	0.339	/	/	/	/	/	/
	Total of C ₁₀	/	/	0.330	0.564	/	/	/	/	1	/
C ₁₂	2,2,4,6,6- pentamethylheptane	/	/	0.144	0.205	/	/	/	/	/	/
	Total of C ₁₂ (µg/L)	/	/	0.144	0.205	/	/	/	/	1	/
	TOTAL	2.020	0.887	2.510	3.533	1.275	1.122	1.009	1.146	2.649	3.206

Table 6.12 The Levels of Branched Chain Alkanes Indirectly Quantified from Sites B, C, D₁, D₂ and G

* The concentration of 2-methylhexane & 2,3-dimethylpentane is the total for both as these co-elute;
** negligible levels.

Total average levels are shown in Table 6.102. Fig 6.49 shows total average branched chain alkane levels at each site alongside those of n-alkanes (including pentane). At all sites branched chain alkane levels were comparable with n-alkane levels, and this was similar to results at site F and E for waste undergoing methanogenesis. Again branched chain alkane levels were higher at site C and G.

from Sites B, C, D ₁ , D ₂ and G									
(µg/L)	Site B	Site C	Site D ₁	Site D ₂	Site G				
C5-Branched Chain Alkanes	0.234	0.042	0.045	0.029	0.241				
C6-Branched Chain Alkanes	0.389	0.383	0.234	0.132	0.468				
<b>C7-Branched Chain Alkanes</b>	0.236	0.251	0.150	0.212	0.607				
<b>C8-Branched Chain Alkanes</b>	0.281	0.601	0.501	0.282	0.711				
C9-Branched Chain Alkanes	0.000	0.462	0.000	0.102	0.325				
C10-Branched Chain Alkanes	0.000	0.447	0.000	0.000	0.000				
C12-Branched Chain Alkanes	0.000	0.174	0.000	0.000	0.000				
Total (μg/L)	1.140	2.360	0.930	0.757	2.352				

 Table 6.102

 Average Total Levels of grouped Branched Chain Alkanes



Fig. 6.49 Average Total Levels of Branched Chain Alkanes at Sites B, C, D₁, D₂ and G

Individual levels of group branched chain alkanes are shown in Fig 6.50. Similar to nalkane results at these sites, the abundant branched chain alkane groups were different from those found at sites E and F for domestic refuse undergoing methanogenesis and of similar ages. Again, only site C had branched chain alkane distributions similar to that at sites E and F. This is further highlighted when the gas composition, shown in Table 6.103, is considered. At sections  $F_1$  and  $F_2$  (waste age 11 – 16 years) of site F,  $C_9 - C_{11}$  branched chain alkanes accounted for approximately 60 % of total branched chain alkanes and at sections  $F_3$  and  $F_4$  (waste age 3 – 11 years) of site F,  $C_9$  and  $C_{10}$ accounted for approximately 60 %. At sections  $E_1$  and  $E_2$  of site E,  $C_8 - C_{10}$  branched chain alkanes accounted for approximately 80 % and 60 %, respectively, where  $C_8$  branched chain alkane accounted for approximately 20 % and 10 % respectively. Of the gas extraction sites, only site C had similar branched chain alkane abundances where  $C_8 - C_{10}$  branched chain alkanes accounted for approximately 60 % of total branched chain alkanes, with  $C_8$  being the most abundant group. Also,  $C_{10}$  branched chain alkanes were only observed at site C. At sites B, C, D₁, D₂ and G, C₆ - C₈ branched chain alkanes accounted for approximately 80 %, 50 %, 90 %, 80 % and 70%, respectively. Also interesting is that appreciable abundances of C₅ branched chain alkanes are also observed at sites B and G. These were found to be one of the least abundant groups at sites E and F. A similar observation was made with the n-alkane results, where pentane abundances also increased at the gas extraction sites.



Fig. 6.50 Average Individual Levels of Branched Chain Alkanes at Sites B, C, D₁, D₂ and G

$\mathbf{H} \mathbf{G} \mathbf{H} \mathbf{G} \mathbf{G} \mathbf{G} \mathbf{G} \mathbf{G} \mathbf{G} \mathbf{G} G$									
%	Site B	Site C	Site D ₁	Site D ₂	Site G				
C5-Branched Chain Alkanes	20.5	1.8	4.8	3.8	10.3				
C6-Branched Chain Alkanes	34.1	16.2	25.2	17.5	19.9				
C7-Branched Chain Alkanes	20.7	10.7	16.1	28.0	25.8				
C8-Branched Chain Alkanes	24.7	25.5	53.9	37.2	30.2				
C9-Branched Chain Alkanes	0.0	19.6	0.0	13.5	13.8				
C10-Branched Chain Alkanes	0.0	18.9	0.0	0.0	0.0				
C12-Branched Chain Alkanes	0.0	7.4	0.0	0.0	0.0				
TOTAL	100.0	100.0	100.0	100.0	100.0				

Table 6.103The Average Gas Composition of Grouped Branched Chain Alkanes<br/>from Sites B, C, D, D, and G

Overall, our results suggest that the change in conditions imposed in a landfill site by gas extraction and air infiltration favor the production of  $C_5 - C_8$  branched chain alkanes, as compared to  $C_9 - C_{11}$  branched chain alkanes found in passive landfills.

#### 6.2.2.3.4 Cyclic Alkanes - Positively Identified and Directly Quantified

The levels of cyclic alkane results for sites B, C, D₁, D₂ and G are shown in Table 6.104, and ranged from  $0.448 - 1.970 \ \mu g/L$  at sites B, D₁ and D₂, and  $1.900 - 2.883 \ \mu g/L$  at sites C and G. Like previous alkane results for these sites, levels of cyclic alkanes were highest (by about a factor of 2) at sites C and G, and again there may be contributions from the industrial waste accepted at these sites. Overall levels of cyclic alkanes at these sites were significantly higher than levels observed at site F (0.544 - 0.918 \ \mu g/L, Table 6.17).

from Sites B, C, D₁, D₂ and G SITE D₁ SITE D, SITE G SITE B SITE C  $(\mu g/L)$ S2 **S2 S1 S1 S1 S1 S2 S2 S1 S2** 0.361 0.337 0.171 0.236 0.371 0.173 0.305 0.245 0.279 0.104 Cyclohexane 0.256 0.450 0.204 0.365 0.326 0.208 0.225 0.211 0.098 0.379 Methylcyclohexane 0.057 0.922 0.808 0.427 0.519 0.675 0.792 0.766 0.142 0.727 trans-1,4-dimethylcyclohexane 0.987 0.748 0.265 0.431 0.388 0.203 0.708 0.440 0.093 0.454 trans-1,2-dimethylcyclohexane BDL cis-1,2-dimethylcyclohexane 0.048 0.178 0.158 0.062 0.078 0.159 0.133 0.049 0.009 0.072 Ethylcyclohexane 0.070 0.053 BDL 0.007 0.009 0.056 BDL BDL 0.078 1-methylethylcyclohexane 0.001 2.883 2.429 1.970 0.695 0.448 1.937 2.191 1.900 1.122 1.505 Total (µg/L)

Table 6.104 The Levels of Cyclic Alkanes Directly Quantified from Sites B. C. D. D. and G

Total average levels are shown in Table 6.105. Fig 6.51 shows total average cyclic alkane levels at each site, alongside those of other alkanes. As can be seen levels of all classes of alkanes at each site are comparable, and a similar observation was made at sites E and F.

(μg/L)	Site B	Site C	Site <b>D</b> ₁	Site D ₂	Site G			
Cyclohexane	0.204	0.262	0.204	0.272	0.349			
Methylcyclohexane	0.238	0.216	0.234	0.327	0.345			
trans-1,4-dimethylcyclohexane	0.435	0.779	0.473	0.366	0.865			
trans-1,2-dimethylcyclohexane	0.274	0.574	0.348	0.296	0.867			
cis-1,2-dimethylcyclohexane	0.000	0.000	0.000	0.000	0.000			
Ethylcyclohexane	0.041	0.146	0.056	0.063	0.168			
1-methylethylcyclohexane	0.000	0.067	0.000	0.008	0.062			
Total (µg/L)	1.192	2.045	1.314	1.333	2.656			

Table 6.105Average Levels of Cyclic Alkanes Directly Quantifiedfrom Sites B, C, D1, D2 and G



Fig. 6.51 Average Total Levels of Cyclic Alkanes at Sites B, C, D₁, D₂ and G

Individual levels of cyclic alkanes are shown in Fig 6.52. As can be seen trans-1,2and trans-1,4-dimethylcyclohexane are the abundant compounds followed by cyclohexane and methylcyclohexane. This was similar to sites E and F for domestic waste undergoing methanogenesis. This is further highlighted in Table 6.106 where gas composition is shown. At sites B, C, D₁, D₂ and G, trans-1,2- and trans-1,4dimethylcyclohexane accounted for approximately 50 - 65 % of total cyclic alkanes with cyclohexane and methylcyclohexane accounting for approximately 25 - 45 %. Similar observations were made at sites E and F. Unlike n-alkane and branched chain alkane results, it appears cyclic alkanes abundances are unaffected by gas extraction.



Fig. 6.52 Average Individual Levels of Cyclic Alkanes at Site B, C, D₁, D₂ and G

The Average Gas Composition of Cyclic Alkanes Directly Quantified from Sites B, C, D ₁ , D ₂ and G											
%	Site B	Site C	Site D ₁	Site D ₂	Site G						
Cyclohexane	17.1	12.8	15.5	20.4	13.1						
Methylcyclohexane	20.0	10.6	17.8	24.5	13.0						
trans-1,4-dimethylcyclohexane	36.5	38.1	36.0	27.5	32.6						
trans-1,2-dimethylcyclohexane	22.9	28.1	26.5	22.2	32.7						
cis-1,2-dimethylcyclohexane	0.0	0.0	0.0	0.0	0.0						
Ethylcyclohexane	3.4	7.1	4.2	4.7	6.3						
1-methylethylcyclohexane	0.0	3.3	0.0	0.6	2.3						
TOTAL	100.0	100.0	100.0	100.0	100.0						

**Table 6.106** 

### 6.2.2.3.5 Cyclic Alkanes - Tentatively Identified and Indirectly Quantified

Levels of other cyclic alkanes found at sites B, C, D₁, D₂ and G are shown in Table 6.107. These other cyclic alkanes contributed significantly to total cyclic alkane levels at these sites. This is shown in Fig 6.53 where total overall cyclic alkane levels are shown alongside those of overall total n-alkanes and branched chain alkanes. Trends observed in Fig 6.51 are still maintained in Fig 6.9. Overall total cyclic alkane levels were obtained by combining results in Table 6.104 and Table 6.107. These are shown in Table 6.108 where cyclic alkanes have been grouped as methylcyclopentane (C₁), C₂-cyclopentanes, cyclohexanes, C₁-cyclohexanes, C₂-cyclohexanes, C₃-cyclohexanes and C₄-cyclohexanes.

Table 6.107The Levels of Cyclic Alkanes Indirectly Quantifiedfrom Sites B, C, D1, D2 and G

(μg/L)	SITE B		SITE C		SITE D ₁		SITE D ₂		SITE G	
	<b>S1</b>	<b>S2</b>	<b>S1</b>	<b>S2</b>	<b>S1</b>	<b>S2</b>	<b>S1</b>	<b>S2</b>	<b>S1</b>	S2
Methylcyclopentane	0.231	0.082	0.240	0.249	0.159	0.150	0.083	0.110	0.2656	0.312
cis-1,3-dimethylcyclopentane	0.074	0.020	0.038	0.045	0.037	0.035	0.041	0.052	1	1
trans-1-ethyl-4- methylcyclohexane	1	1	0.014	0.100	1	1	1	1	1	1
Propylcyclohexane	1	/	0.071	0.056	1	/	/	/	1	/
1-methyl-4- (1-methylethyl)cyclohexane	/	1	0.120	0.187	1	1	/	1	/	1
Total (µg/L)	0.305	0.102	0.483	0.637	0.196	0.185	0.124	0.162	0.266	0.312



Fig. 6.53 Average Total levels of Total Cyclic Alkanes at Sites B, C, D₁, D₂ and G
Fig 6.54 shows average levels of grouped cyclic alkanes at sites B, C,  $D_1$ ,  $D_2$  and G. As can be seen C₂-cyclohexanes are the most abundant cyclic alkanes at all sites. The gas composition is shown in Table 6.109. It is here that some differences between the passive sites, E and F, and the gas extraction sites, B, C, D₁, D₂ and G are shown. The abundance of  $C_2$ -cyclohexanes is > 50 % at all sites while the abundance of  $C_3$ cyclohexanes, which ranged from 10 - 20 % at sites E and F, is extremely low at the gas extraction sites. The highest abundance of C3-cyclohexanes was approximately 7% at site C, but even at this site where the cyclic alkane behavior resembled that found at sites E and F, the abundance of C3-cyclohexanes was much lower. Cyclohexane and methylcyclohexane abundances also appear higher at the gas extraction sites as do the abundances of methylcyclopentane. At sites C and G, with the lower gas pumping rates, cyclohexane and methylcyclohexane accounted for approximately 20 % of total cyclic alkanes. This was similar to their abundances at sites E and F. However, at sites B,  $D_1$  and  $D_2$ , where the gas pumping rate was higher, their abundances ranged from approximately 30 - 40 %. Methylcyclopentane abundances were lower than approximately 6 % at site E and F, but ranged from 6 -11 % at the gas extraction sites.

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(μg/L)	Site B	Site C	Site D ₁	Site D ₂	Site G		
C1-Cyclopentane	0.157	0.245	0.155	0.096	0.289		
C2-Cyclopentane	0.047	0.041	0.036	0.047	0.000		
Cyclohexane	0.204	0.262	0.204	0.272	0.349		
C1-Cyclohexane	0.238	0.216	0.234	0.327	0.345		
C2-Cyclohexanes	0.749	1.499	0.876	0.725	1.900		
C3-Cyclohexanes	0.000	0.188	0.000	0.008	0.062		
C4-Cyclohexanes	0.000	0.154	0.000	0.000	0.000		
Total (µg/L)	1.396	2.605	1.504	1.476	2.945		

Table 6.108Average Levels of Grouped Cyclic Alkanes from Sites B, C, D1, D2 and G



Fig. 6.54 Average Levels of Grouped Cyclic Alkanes at Sites B, C,  $D_1$ ,  $D_2$  and G

	from Sites B, C, D ₁ , D ₂ and G											
%	Site B	Site C	Site D ₁	Site D ₂	Site G							
C1-Cyclopentane	11.2	9.4	10.3	6.5	9.8							
C2-Cyclopentane	3.4	1.6	2.4	3.2	0.0							
Cyclohexane	14.6	10.1	13.5	18.5	11.8							
C1-Cyclohexane	17.1	8.3	15.5	22.2	11.7							
C2-Cyclohexanes	53.7	57.5	58.3	49.1	64.5							
C3-Cyclohexanes	0.0	7.2	0.0	0.6	2.1							
C4-Cyclohexanes	0.0	5.9	0.0	0.0	0.0							
TOTAL	100.0	100.0	100.0	100.0	100.0							

Table 6.109 The Average Gas Composition of Grouped Cyclic Alkanes from Sites B, C, D₁, D₂ and G

Overall our results suggest that the change in landfill conditions caused by gas extraction and air infiltration favour the production of methylcyclohexane, cyclohexane and methylcyclopentane.  $C_2$ -cyclohexane abundances remain fairly constant in both types of gas and the production of  $C_3$ -cyclohexanes is not favoured in 'gas extraction' sites.

6.2.2.3.6 Aromatic Hydrocarbons - Positively Identified and Directly Quantified Levels of aromatic hydrocarbon results for sites B, C, D₁, D₂ and G are show in Table 6.110 and ranged from  $0.102 - 0.859 \ \mu g/L$  at sites B, C, D₁ and D₂, and 2.915 - 3.594  $\mu$ g/L at sites C and G. As was observed for alkanes, levels of aromatic hydrocarbons are higher at sites C and G, and The difference in levels between sites C and G and the other sites was substantial (about a factor of 8) and this suggests that there may be contributions from industrial wastes at these two sites.

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(ng/L)	SITE B		SIT	SITE C		SITE D ₁		SITE D ₂		SITE G		
(µg/L)	S1	<b>S2</b>	S1	S2	S1	S2	S1	S2	<b>S</b> 1	S2		
Benzene	0.068	0.410	0.388	0.202	0.127	0.230	0.231	0.118	1.613	1.846		
Methylbenzene	0.022	0.263	0.778	0.757	0.187	0.234	0.541	0.492	0.953	1.255		
Ethylbenzene	0.004	0.017	0.736	0.628	BDL	BDL	0.046	0.026	0.087	0.125		
1,2&1,4-dimethylbenzene	0.004	0.022	0.507	0.466	BDL	BDL	0.023	0.027	0.081	0.113		
1,3-dimethylbenzene	0.002	BDL	0.337	0.212	BDL	BDL	0.018	0.015	0.083	0.114		
Propylbenzene	BDL	BDL	0.228	0.187	BDL	BDL	BDL	BDL	BDL	BDL		
1,2,4-trimethylbenzene	BDL	0.008	0.276	0.198	BDL	0.011	BDL	BDL	BDL	BDL		
1,3,5-trimethylbenzene	0.001	0.013	0.344	0.257	BDL	0.018	BDL	BDL	0.098	0.131		
Total (μg/L)	0.102	0.733	3.594	2.908	0.313	0.492	0.859	0.679	2.915	3.584		

Table 6.110 The Levels of Aromatic Hydrocarbons Directly Quantified from Sites B. C. D. D. and G

Total average aromatic hydrocarbon levels are shown in Table 6.111. Fig 6.55 shows total average aromatic hydrocarbon levels at each site alongside those of overall total alkanes. Interestingly, aromatic hydrocarbon levels were lower than alkane levels at sites B, D₁ and D₂, but higher at sites C and G. Sites C and G received industrial waste and as mentioned previously this may be the reason for the higher levels at these two sites. It may also be that lower gas extraction rates at these sites is responsible for increased aromatic hydrocarbon levels. At sites E and F for domestic waste undergoing methanogenesis, aromatic hydrocarbon levels were higher than that of other VOCs. Only at section  $F_1$  of site F where the very old waste (16 – 21 years) was in the maturation phase of waste degradation had aromatic hydrocarbon levels dropped significantly below those of other VOCs (Fig 6.11). It is also in this maturation phase that air intrusion occurs. It was at site C and G that gas extraction rates were lower than sites B, D1 and D2. As was mentioned previously sites with lower gas extraction rates behave more like passive sites, whereas the sites with the higher gas extraction rates behave differently to passive sites. Sites B, D1 and D2 have very low levels of aromatic hydrocarbons similar to that observed at section  $F_1$  of site F.

Tom Sites D, C, D ₁ , D ₂ and G										
(μg/L)	Site B	Site C	Site D ₁	Site D ₂	Site G					
Benzene	0.239	0.295	0.178	0.175	1.730					
Methylbenzene	0.143	0.767	0.210	0.516	1.104					
Ethylbenzene	0.011	0.682	0.000	0.036	0.106					
1,2&1,4-dimethylbenzene	0.013	0.487	0.000	0.025	0.097					
1,3-dimethylbenzene	0.001	0.275	0.000	0.017	0.098					
Propylbenzene	0.000	0.207	0.000	0.000	0.000					
1,2,4-trimethylbenzene	0.004	0.237	0.005	0.000	0.000					
1,3,5-trimethylbenzene	0.007	0.300	0.009	0.000	0.114					
Total (µg/L)	0.417	3.251	0.403	0.769	3.250					

Table 6.111 Average Levels of Aromatic Hydrocarbons Directly Quantified from Sites B, C, D, D, and G



Fig. 6.55 Average Total Levels of Aromatic Hydrocarbons at Sites B, C, D₁, D₂ and G

Individual levels of aromatic hydrocarbons are shown in Fig 6.56 and it is here that the above conclusions gather more support. All gas extraction sites, except C have gas containing only benzene and toluene. This is further highlighted in Table 6.112 where the gas composition is shown. As can be seen at sites B, D₁, D₂ and G, benzene and toluene account for approximately 90 % of total aromatic hydrocarbons. This behavior was again observed at section  $F_1$  of site F for very old waste in the maturation phase of waste degradation where benzene and toluene also accounted for approximately 80 % of total aromatic hydrocarbons (Table 6.25). It must be emphasized again that the above findings cannot be explained via waste inputs or ages at these 'gas extraction' sites.



Fig. 6.56 Average Levels of Individual Aromatic Hydrocarbons at Sites B, C, D₁, D₂ and G

Table 6.112The Average Gas Composition of Aromatic Hydrocarbons Directly Quantified<br/>from of Sites B, C, D1, D2 and G

%	Site B	Site C	Site D ₁	Site D ₂	Site G
Benzene	57.3	9.1	44.3	22.7	53.2
Methylbenzene	34.2	23.6	52.2	67.2	34.0
Ethylbenzene	2.5	21.0	0.0	4.7	3.3
1,2&1,4-dimethylbenzene	3.1	15.0	0.0	3.3	3.0
1,3-dimethylbenzene	0.3	8.5	0.0	2.2	3.0
Propylbenzene	0.0	6.4	0.0	0.0	0.0
1,2,4-trimethylbenzene	0.9	7.3	1.3	0.0	0.0
1,3,5-trimethylbenzene	1.6	9.2	2.2	0.0	3.5
TOTAL	100.0	100.0	100.0	100.0	100.0

6.2.2.3.7 Aromatic Hydrocarbons - Tentatively Identified and Indirectly Quantified Levels of other aromatic hydrocarbons found at sites B, C,  $D_1$ ,  $D_2$  and G are shown in Table 6.113. As can be seen, only at site C were other aromatic hydrocarbons present. These other aromatic hydrocarbons contributed significantly (about 15 %) to total aromatic hydrocarbons at site C. Fig 6.57 shows the levels of grouped aromatic hydrocarbons at sites B, C,  $D_1$ ,  $D_2$  and G, where the contribution from other aromatic hydrocarbons at site C has been included. The gas composition is shown in Table 6.114.

Table 6.113The Levels of Aromatic Hydrocarbons Indirectly Quantified<br/>from Sites B, C, D1, D2 and G

(ug/L)	SITE B		SITE C		SITE D ₁		SITE D ₂		SITE G	
(#6, 2)	<b>S1</b>	S2	<b>S1</b>	<b>S2</b>	<b>S</b> 1	S2	<b>S</b> 1	S2	<b>S</b> 1	S2
1-methylethylbenzene	1	/	0.084	0.117	1	1	1	1	1	/
1-ethyi-4-methylbenzene	1	1	0.088	0.201	1	1	1	1	1	1
1-methyl-4- (1-methylethyl)benzene	/	/	0.239	0.381	/	1	1	1	1	1



Fig. 6.57 Average Levels of Grouped of Aromatic Hydrocarbons at Sites B, C, D₁, D₂ and G

Table 6.114
The Average Levels & Gas Composition of Grouped Aromatic Hydrocarbons
from Sites B, C, D ₁ , D ₂ and G

(ug/I)	Site B Site C		Site D ₁	Site D ₂	Site G						
(µg/L)	%	%	%	%	%						
Benzene	57.3	7.8	44.3	22.7	53.2						
Methylbenzene	34.2	20.2	52.2	67.2	34.0						
C2-Alkylbenzenes	5.9	37.9	0.0	10.1	9.3						
C3-Alkylbenzenes	2.5	26.0	3.6	0.0	3.5						
C4-Alkylbenzenes	0.0	8.1	0.0	0.0	0.0						
Total (µg/L)	100.0	100.0	100.0	100.0	100.0						

As can be seen benzene and toluene are still dominant accounting for approximately 90% of total aromatic hydrocarbon levels at sites B,  $D_1$ ,  $D_2$  and G. Site C had aromatic hydrocarbon abundances similar to those observed at site E and F. Very interesting is the very low abundance of C₂-alkylbenzenes at sites B,  $D_1$ ,  $D_2$  and G, where these aromatic hydrocarbons were the most abundant at sites E and F for waste undergoing active methanogenesis. A similar observation was made with C₃-alkylbenzene results where the production of these was not favored in gas extraction sites. The abundance of C₂ – C₃-alkylbenzenes at sites B,  $D_1$ ,  $D_2$  and G was also more comparable with that found in very old waste in the maturation phase of waste degradation. Also, C₄-alkylbenzenes were only found at site C.

Overall, our results suggest that the conditions imposed on a landfill by gas extraction favour the production of benzene and toluene. The production of  $C_2 - C_4$ -alkylbenzenes is not favored at gas extraction sites. It should be noted that although gas extraction sites favor the production of benzene and toluene, levels released are comparable with those released at the passive sites E and F.

#### 6.2.2.3.8 Terpenes - Positively Identified and Directly Quantified

Terpene results for sites B, C, D₁, D₂ and G are shown in Table 6.115 and Total average levels are shown in Table 6.116. Fig 6.58 shows the total average terpene levels at each site along side overall total levels of other VOCs. Terpene levels were higher at site C and G as were other VOCs at these two sites, and terpenes were the least abundant VOCs at all sites. Overall terpene levels were extremely low compared with sites E and F, where terpenes were the most abundant VOCs. Only at section  $F_1$  of site F in very old waste (16 – 21 years) in the maturation phase of methanogenesis were terpenes the least abundant. As was explained for other VOCs at sites B, C, D₁, D₂ and G, the behavior of the 'gas extraction' sites does not resemble that of passive sites, during methanogenesis. The behavior of the 'gas extraction' sites is similar to section  $F_1$  of site F, where waste is in the maturation phase of waste degradation and air intrusion occurs.

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(µg/L)	SITE B		SITE C		SITE D ₁		SITE D ₂		SITE G	
	<b>S1</b>	S2	<b>S1</b>	<b>S2</b>	S1	<b>S2</b>	<b>S1</b>	S2	<b>S1</b>	S2
a-Pinene	0.002	0.072	0.397	0.408	0.051	0.059	0.122	0.170	0.286	0.401
β-Pinene	BDL	BDL	0.195	0.247	0.004	BDL	0.013	0.024	0.108	0.148
Limonene-1	BDL	BDL	0.282	0.377	BDL	0.014	BDL	BDL	BDL	BDL
Total (µg/L)	0.002	0.072	0.874	1.032	0.054	0.074	0.135	0.194	0.394	0.549

Table 6.115The Levels of Terpenes Directly Quantified from Sites B, C, D1, D2 and G

Table 6.116 Average Levels of Terpenes Directly Quantified at Sites B, C, D₁, D₂ and G

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(µg/L)	Site B	Site C	Site D ₁	Site D ₂	Site G		
α-Pinene	0.037	0.403	0.055	0.146	0.343		
β-Pinene	0.000	0.221	0.002	0.019	0.128		
Limonene-1	0.000	0.330	0.007	0.000	0.000		
Total (µg/L)	0.037	0.953	0.064	0.165	0.471		



Fig. 6.58 Average Total Levels of Terpenes at Sites B, C, D₁, D₂ and G

Individual levels of terpene are shown in Fig 6.59 and gas composition is shown in Table 6.117. Only site C had terpene abundances similar to sites E and F for waste undergoing methanogenesis. Here  $\alpha$ -pinene and limonene abundances were comparable and accounted for approximately 75 % of the total terpenes. However, limonene abundances were slightly lower and  $\beta$ -pinene abundances slightly higher

than sites E and F. At sites B,  $D_1$ ,  $D_2$  and G,  $\alpha$ -pinene accounts for 100 %, 86 %, 89% and 73 % of total terpenes, respectively. Again this result is similar to that observed at section  $F_1$  of site F, where for very old waste where only traces of  $\alpha$ -pinene were found. Limonene was not found at sites B, D₂ and G. As mentioned previously for other VOCs at the gas extraction sites, terpene trends could not be explained by waste inputs or ages.



Fig. 6.60 Average Levels of Individual Terpenes at Sites B, C,  $D_1$ ,  $D_2$  and G

The Average Levels & Gas Composition of Terpenes from Sites B, C, D ₁ , D ₂ and G										
%	Site B	Site C	Site D ₁	Site D ₂	Site G					
α-Pinene	100.0	42.3	85.8	88.7	72.8					
β-Pinene	0.0	23.2	2.9	11.3	27.2					
Limonene-1	0.0	34.6	11.3	0.0	0.0					
TOTAL	( 100.0	100.0	100.0	100.0	100.0					

**Table 6.117** 

#### 6.2.2.3.9 Terpenes - Tentatively Identified and Indirectly Quantified

The only other terpene found was camphene at site C, see Table 6.118, where its levels were significant and accounted for 11.5 % of total terpenes at this site (see Table 6.119).

	· 1										
(µg/L)	SIT	ЪВ	SITE C		SITE D ₁		SITE D ₂		SITE G		
	<b>S1</b>	<b>S2</b>	S1	<b>S2</b>	<b>S1</b>	<b>S2</b>	S1	<b>S2</b>	<b>S</b> 1	S2	
Camphene	/	/	0.102	0.145	1	1	1	1	1	1	

Table 6.118The Levels of Terpenes Indirectly Quantified from Sites B, C, D1, D2 and G

Table 6.119 The Average Levels & Gas Composition of Terpenes from Sites B, C, D₁, D₂ and G

(ug/L)	Site B	Site C	Site D ₁	Site D ₂	Site G
(µg/L)	%	%	%	%	%
α-Pinene	100.0	37.4	85.8	88.7	72.8
β-Pinene	0.0	20.5	2.9	11.3	27.2
Limonene-1	0.0	30.6	11.3	0.0	0.0
Camphene	0.0	11.5	0.0	0.0	0.0
Total (µg/L)	100.0	100.0	100.0	100.0	100.0

Overall, terpene results have followed those of other VOCs at the gas extraction sites where terpene behavior is different from that observed at passive sites. Only site C, with the low gas extraction rate had terpene trends similar to that of passive sites

Our results suggest that the conditions imposed on a landfill by gas extraction do not favour the production of large amounts of terpenes. For the low levels of terpenes produced,  $\alpha$ -pinene is the predominant terpene.

#### 6.2.2.4 Other VOCs at Sites A – F

#### **Chlorinated Compounds**

A number of chlorinated compounds were found in landfill gas at Sites A-G. These are shown in Table 6.120. GC-MS conditions were not optimised for chlorinated compounds and in a separate study⁽¹²⁰⁾ where chromatographic conditions were optimised for chlorinated compounds these were identified using retention time matching with standards.

Table 6.120         Chlorinated Compounds in Landfill Gas at Sites A-G					
COMPOUND	COMPOUND				
Chloroethene	Tetrachloroethene				
Dichloromethane	1,2-Dichlorooctane				
1,2-Dichloroethene	1,2-Dichlorobenzene				
Trichloroethene					

The types of chlorinated compounds found in landfill gas at these sites are similar to those found in other studies ^{(58, 64, 85, 89, 90, 92).} Sources of these includes industrial solvents and many household and consumer products.

#### 6.2.2.5 Conclusion

Landfill F provided the opportunity to observe the behaviour of VOCs in landfill gas from domestic waste ranging in age from 3 - 21 years. A previous gas evaluation study had found the waste to be undergoing active methanogenesis where the older waste was in the maturation phase of degradation. Overall the levels of VOCs investigated, including n-alkanes, branched chain alkanes, cyclic alkanes, aromatic hydrocarbons and terpenes followed closely the methane generation curve over the lifetime of a landfill. The levels of VOCs at landfill F show a tendency to increase as the waste aged to 16 years after which levels decreased as the waste aged to 21 years. Aromatic hydrocarbon and terpene levels were high in the younger refuse indicating they are actively produced during this phase of waste degradation or there may be contributions from anthropogenic sources. Terpene levels declined slowly as the waste aged to 16 years whereas aromatic hydrocarbon levels remained fairly constant. The decline in levels for waste in the maturation phase of waste degradation was significant for n-alkanes, aromatics and terpenes but not so for branched chain alkanes and cyclic alkanes where levels were higher still than those in the younger refuse. These results suggest that branched chain and cyclic alkanes are the abundant compounds produced in gas from waste in the maturation phase of degradation. The behavior of aromatic hydrocarbons was peculiar and it was thought that anthropogenic sources were responsible since toluene levels were significantly higher than other aromatics in the youngest refuse. However while the levels of other aromatic hydrocarbons remained fairly constant as the waste aged to 16 years the levels of toluene decrease whereas the levels of benzene increased significantly. This finding suggested that microbial sources were at play where benzene was the product of microbial degradation of toluene. The high toluene levels in the younger refuse suggest that during this phase of waste degradation, toluene may be the main product from the microbial degradation of other alkylbenzenes. Interestingly, in the oldest waste the small amount of aromatic hydrocarbon compounds are mainly benzene and toluene.

Landfill E contains two sections where the waste age was 2 - 7 years and a few months - 7 years. Methane was actively being produced from both. The section with the younger refuse also contained low level contaminated soil as daily cover material. Levels of all VOCs were similar at both sections which indicated there was no major

contribution to levels from the younger refuse or daily cover material. At site E, VOC levels were an order of magnitude higher than at site F for wastes of similar ages. It is thought that the reason may be due to site E being a quarry infill compared with site F which is an above ground landfill. The gas evaluation study at landfill F found it to be a 'dry landfill' due to it being above ground. If site E contains more moisture than Site F then conditions are more favorable for gas production at Site E and VOC levels have been found to be directly related to gas production. Interestingly, gas utilization at site F. Although VOC levels were different at both sites, the gas composition was similar at both sites for waste undergoing methanogenesis.

Landfill A is a Prescribed Waste site emitting low quality gas and produced surprising VOC results. Firstly VOC levels were similar to those found at the domestic sites E and F and this was surprising given that site A had accepted industrial solid and liquid wastes. It was anticipated that particular types of VOCs, such as alkanes and aromatic hydrocarbons would be found in higher levels than domestic sites. The low levels of terpenes at site A were in accord with the types of non-putrescible waste accepted. The two sections studied at site A had waste of similar ages and the differences in levels was obviously due to the heterogeneous nature of waste inputs and gas produced. The second surprising find from site A, given the nature of waste input, was that the gas composition was similar at both sections and bore some resemblance to that found at the domestic Sites E and F. It is thought that leachate removal from the site along with gas emission has over time depleted this site of its anthropogenic VOC content. The site now behaves similarly to a domestic site where the remaining degradable material is undergoing methanogenesis.

Landfills B, C,  $D_1$ ,  $D_2$  and G are domestic waste sites where sites C and G had also received industrial waste. The waste at these sites varied in age and all sites employed gas extraction. VOC levels were higher at sites C and G and this was attributed to their industrial waste inputs. What was most surprising about these sites was that the relative abundances of particular VOCs could not be explained via waste age or inputs. However, correlations were found with gas extraction rates. It appeared that as the gas extraction rate increased the relative abundances deviated from those that had been observed in domestic sites from which the gas escaped passively. The results suggested that the production of lower molecular weight species was favoured at gas extraction sites. Not only did the relative abundance of various VOCs change with gas extraction, it appeared levels were influenced as well. At sites B,  $D_1$  and  $D_2$  where gas extraction was highest aromatic hydrocarbons and terpenes were the least abundant VOCs. Terpenes were also the least abundant VOCs at sites C and G where lower gas extraction rates were employed. Levels of these VOCs were comparable to others at sites E and F where the gas escaped passively. The influence of gas extraction on relative abundances and levels of VOCs produced results comparable with results from the gas passively emitted from the waste in the maturation phase of waste degradation. It is in this phase of waste degradation that air intrusion occurs into the landfill. It is suggested that the small amount of air drawn into the landfill as gas is being extracted influences the biotic and abiotic processes occurring in the landfill.

For domestic waste undergoing methanogenesis the abundant VOCs in gas passively escaping the sites were as follows.  $C_7 - C_{11}$  n-alkanes were abundant compounds with  $C_9$  and  $C_{10}$  usually the most abundant with  $C_7$  occasionally found in comparable abundances.  $C_7 - C_{10}$  were the abundant branched chain alkanes with  $C_9$  usually the most abundant.  $C_2$ -cyclohexanes were significantly the most abundant cyclic alkanes. Other abundant compounds included cyclohexane, methylcyclohexane and  $C_3$ -cyclohexanes but these can vary from site to site. Appreciable amounts of  $C_4$ -cyclohexanes can sometimes be found. Benzene and  $C_1 - C_4$ -alkylbenzenes were the abundant in younger refuse and benzene in older refuse.  $C_4$ -alkylbenzene abundance was appreciable in younger refuse. Terpenes comprised mainly of limonene,  $\alpha$ -pinene and  $\beta$ -pinene, where the former two were the most abundant.

For landfill gas escaping passively from waste in the maturation phase the abundant VOCs were as follows.  $C_6 - C_9$  n-alkanes were abundant.  $C_7 - C_{11}$  branched alkanes were abundant where  $C_8$  was the lowest.  $C_2$ -cyclohexanes were again significantly the most abundant, with comparable abundances of  $C_2$ -cyclopentanes, cyclohexane,

methyl cyclohexane and C₃-cyclohexanes. Benzene, toluene and C₂-alkylbenzenes were abundant with C₂-alkylbenzenes the lowest. Traces of  $\alpha$ -pinene were found.

For domestic waste undergoing methanogenesis the abundant VOCs in gas extracted from the sites were as follows.  $C_6 - C_8$  n-alkanes where  $C_6$  and  $C_7$  are the most abundant.  $C_6 - C_9$  branched chain alkanes were abundant where  $C_8$  was usually the most abundant.  $C_2$ -cyclohexanes were significantly the most abundant followed by comparable abundances of methylcyclopentane, cyclohexane and methylcyclohexane. Benzene and toluene were the most abundant aromatic compounds.  $\alpha$ -pinene is the dominant terpene. It should be noted that variations to the above occur with changes in gas extraction rates.

The VOC levels found in this study are presented alongside those of other authors in Table 6.121. No attempt was made to relate types and age of waste or sampling source. As can be seen the levels of VOCs found in landfill gas from Australian sites is typical of levels found internationally.

Table 6.122 list dominant compounds which can be found in landfill gas from the Australian sites studies. These are similar to dominant compounds found by other workers.

TABLE 6.121 Comparison of Results Obtained from This study with Those Published by Other Authors (Total Concentrations of VOCs Quantified from Landfill Gas)

		THIS WORK		1983	1986	1992	1996	1997	1998	1999
COMPOUND	SITES E & F	SITE A	SITES B, D ₁ , D ₂ & G	YOUNG et al. ^a	SCOTT et al. ^b	ASSMUTH et al. ^c	WARD et al. d	ALLEN et al. ^c	EKLUND et al. ^f	SCHWEIGK OFLER et al. ⁸
	(mg/m ³ )	(mg/m ³ )	(mg/m ³ )	(mg/m ³ )	(mg/m ³ )	(mg/m ³ )	(PPMV)	(mg/m ³ )	(VMAJ)	(mg/m ³ )
OXYGENATED COMPOUNDS	I		1	BDL - 1328	BDL - 5198	3	1	2 - 2069	6.09	}
ALKANES	0.16-22.52*	0.28 - 5.86*	1.94 - 5.40	328 - 814.1	0.3 - 1737.7	I	82.07	302 - 1543	271.14	48 - 67.5
ALKENES	* * *	I	I	13 - 167.3	0.1 -304.9	I	ł	<0.1 - 36	9.29	1
CYCLIC COMPOUNDS	0.12-12.83	0.139 - 3.82	1.40 - 2.95	BDL** - 5	0.4 - 56.0	I	11.04	80 - 487	I	1
AROMATIC COMPOUNDS	0.05 - 21.26	0.277 - 8.63	0.40 - 3.25	268 - 371.7	0.8 - 552.6	1.1 - 445.3	1	36 - 1906	67.88	164.7 - 289.6
ORGANOSULFUR COMPOUNDS	I	I	I	BDL - 127	BDL - 519.4	1	ł	I	I	1
ORGANOHALOGENATED COMPOUNDS	I	I	I	3 – 71	0.2 - 1342.0	0.17 - 421	33.05	259 - 1239	21.59	I
TERPENES	BDL - 10.83	0.09 - 1.87	3.95 - 12.69	87 - 400	0.3 - 303.4	ł	1	35 - 652	43.23	19.7 - 102.7

* Total of n-alkanes and branched chain alkanes; ** BDL - Below Detection Limit; *** Not analyzed for or concentrations not quoted.

^a - See Reference (89).

b – See Reference (64).

c - See Reference (93).

d – See Reference (90).

e – See Reference (92).

f – See Reference (85).

^g – Sce Reference (58).

NAME OF COMPOUNDS	NAME OF COMPOUNDS
BRANCHED CHAIN HYDROCARBONS	CYCLIC HYDROCARBONS
2-methylbutane	Methylcyclopentane
2-methylpentane	Cyclohexane
3-methylpentane	Methylcyclohexane
Hexane	trans-1,4-dimethylcyclohexane
2-methylhexane	cis-1,3-dimethylcyclohexane
2,3-dimethylpentane	trans-1,2-dimethylcyclohexane
3-methylhexane	cis-1,2-dimethylcyclohexane
Heptane	Ethylcyclohexane
2,3,4-trimethylpentane	1,1,3-trimethylcyclohexane
2-methylheptane	trans-1-ethyl-4-methylcyclohexane
4-methylheptane	cis-1-ethyl-4-methylcyclohexane
Octane	1-methylethylcyclohexane
2,4-dimethylhexane	Propylcyclohexane
2,5-dimethylheptane	1-methyl-4-(1-methylethyl)cyclohexane
2,6-dimethylheptane	Butylcyclohexane
2-methyloctane	
3-methyloctane	AROMATIC HYDROCARBONS
1,1,3-trimethylhexane	
Nonane	Benzene
2,5-dimethyloctane	Methylbenzene
2,6-dimethyloctaлe	Ethylbenzene
3-ethyl-2-methylheptane	1,2&1,4-dimethylbenzene
3,4-dimethyloctane	1,3-dimethylbenzene
4-methylnonane	1-methylethylbenzene
2-methylnonane	Propylbenzene
3-methylnonane	1-ethyl-2-methylbenzene
Decane	1-ethyl-4-methylbenzene
5-methyldecane	1,2,4-trimethylbenzene
4-methyldecane	1,3,5-trimethylbenzene
2-methyldecane	1-methyl-4-(1-methylethyl)benzene
3-methyldecane	1-methyl-2-propylbenzene
4-methyldecane	2-ethyl-1,4-dimethylbenzene
Undecane	
2,2,4,6,6-pentamethylheptane	TERPENIC HYDROCARBONS
3,8-dimethyldecane	α-Pinene
Dodecane	Camphene
Tridecane	β-Pinene
	δ-3-Carene
STRAIGHT CHAIN HYDROCARBONS	1-Limonene
Pentane	

Table 6.122The Dominant Compounds found in Landfill Gas

.

#### 6.2.2.6 Further Studies

There are many avenues for further studies on VOCs in landfill gas that have arisen from this work. The relationship between methane levels and VOC levels needs further investigation at sites that passively emit gas as well as sites where the gas is extracted. In particular the relationship between gas extraction rates and VOC levels and relative abundances requires further work. Included here should be an investigation into the effects on biotic and abiotic processes caused by gas extraction and air intrusion.

The behaviour of benzene and toluene along with the other aromatics as waste ages proved to be an interesting finding and further work is required here to unlock this mystery. Continuing work on the behaviour of all VOCs in landfill gas should prove an interesting venture for potential researchers in this area.

Future studies should also focus on the sampling and analysis of other VOCs including organohalogen, organosulfur, alkenic and oxygenated compounds. These provide further insite into waste inputs and degradation processes occurring in landfills. Attention should be directed to the quantitation step, where class specific relative response factors will permit easier quantitation of the large array of VOCs found in landfill gas.

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# **APPENDIX** A

# PA Bulletin From ATION ATION FROM ATION FROM

### **CLASSIFICATION OF WASTES**

#### Publication448

#### 1. INTRODUCTION

The Environment Protection Authority is responsible for ensuring the proper storage, transport, treatment and disposal of waste in Victoria. This bulletin deals with the wastes which are taken off-site for treatment and disposal. It does not address wastes normally disposed of to sewer including trade waste. Wastes can be classified as one of five types (Table 1) to determine EPA requirements and to choose an appropriate management option.

September 1995

	Summary		
ТҮРЕ	DESCRIEPTION	EPA REQUIREMENTS FOR OFFSITE TREATMENT/DISPOSAL	MANAGEMZNT OPTIONS
FILL MATERIAL	soil (sand, clay & silt), gravel, rock; contamination levels must be less than listed in Table 2.	<ul> <li>No licence required, however disposal must not give rise to any offsite impact</li> </ul>	<ul> <li>Fill material needs (site filling/levelling)</li> <li>Landfill</li> </ul>
SOLID INERT	demolition material, concrete, bricks, timber, plastic, glass, metals, bitumen, trees, shredded tyres.	<ul> <li>Non-municipal landfills must be licensed</li> <li>When disposing to municipal landfill serving &gt; 5000 persons site must be licensed</li> </ul>	<ul><li> Re-use,</li><li> Recycling</li><li> Landfill</li></ul>
PUTRESCIBLE	domestic garbage, commercial waste, vegetables, supermarket processing, deli, butchers etc., garden clippings/prunings	<ul> <li>Non-municipal landfills must be licensed</li> <li>When disposing to municipal landfill serving &gt; 5000 persons site must be licensed</li> </ul>	<ul> <li>Composting</li> <li>Landfill</li> <li>Stock food²</li> <li>Incineration</li> </ul>
LOW LEVEL CONTAMINATED SOIL	Soils with contamination levels and elutdable fractions less than set out in Table 3	<ul> <li>Disposal to licensed site</li> <li>Letter of agreement from EPA prior to transport and disposal.</li> </ul>	<ul> <li>On-site remediation</li> <li>Off-site remediation</li> <li>Landfill</li> </ul>
PRESCRIBED WASTE	Listed in the Prescribed Waste Regulations and Table 4	<ul> <li>Disposal to licensed site¹</li> <li>EPA Transport certificate system must be used.</li> <li>Vehicles must hold EPA permit (some exceptions apply).</li> </ul>	Various treatment and disposal methods depending on waste eg: • Physico-chemical • Incineration • Biological • Immobilization • Landfill for solids or residues ³

**TABLE 1**Summary Of Waste Types

1 Sites must be licensed to receive the particular type of waste.

2 Some commercial waste may be suitable as stock food. The Department of Agriculture can provide advice.

3 Note that liquid wastes are not permitted in landfills.

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With all wastes it is desirable that the Waste Management Hierarchy set out in the industrial Waste Management Policy (Waste Minimisation) is followed. This hierarchy is:

Waste avoidance and/or waste reduction Waste reuse, recycling and reclamation Waste treatment Waste disposal

#### 2. WASTE TYPES

#### 2.1 Fill material

This classification consists of soil (being clay, silt sand), gravel and rock, all being naturally occurring materials. Contaminant levels must be below those specified in Table 2, otherwise the material must be classified as either low level contaminated soil, or prescribed waste.

EPA has no restriction on where fill material may be disposed although councils may have other requirements. The deposit of fill material must not result in any offsite impact on surface or groundwaters.

The industry refers to fill material as "clean fill". Fill material may contain contaminants above background levels and may not be suitable for all uses. Fill material is generally suitable for use within an urban environment but care needs to be taken in an agricultural environment based on an assessment of contaminant levels and intended use.

#### 2.2 Solid Inert Waste

Solid inert wane is defined in the State Environment Protection Policy (Sitting and Management of Landfills receiving Municipal Waste) as hard waste and dry vegetative material which has negligible activity or effect on the environment. This is the least hazardous category of the wastes which EPA controls.

Landfills licensed by EPA to accept Solid Inert waste usually have less stringent operating and monitoring requirements than other landfills, and do not normally have the same associated problems.

Re-use and recycle options should be closely examined for this type of waste, as in many cases solid inert waste, such as building materials, can be re-used.

#### 2.3 Putrescible Waste

Putrescible waste is defined in the abovementioned Landfill State Environment Protection Policy (SEPP) as waste able to be decomposed by bacterial action. Because of this property, a significant amount of putrescible type waste can usually be composted.

Putrescible waste is the most common form of waste, as practically all households produce some amount of domestic garbage. Also included in this category are food wastes from industrial or commercial sources such as restaurants, food markets, supermarkets, butchers, etc.

Problems associated with putrescible waste landfills often include: vermin, seagulls, dust, odour, flies and other insects, fires, litter, surface and groundwater contamination by leachate. As such the design and operating requirements for a putrescible waste landfill are generally more stringent than for a site accepting solid inert waste only.

#### 2.4 Low Level Contaminated Soil

Levels of contaminants in the soil and in the elutriable fraction must be less than the limits set out in Table 3 (and greater than the limits set out in Table 2) for soil to be included in this category.

Low level contaminated soil may be disposed of at a landfill licensed to accept it. Before low level contaminated soil is transported off-site a letter of agreement must be obtained from EPA. The letter of agreement gives permission to transport a given volume of soil from a particular location to a specified landfill and must be carried with the load and shown to the landfill operator. Before issuing a letter of agreement for disposal of the soil, EPA will need to be satisfied that the levels of contaminants in the soil and in the elutriable fraction are less than those in Table 3 by means of a technical report which includes NATA endorsed analytical results verifying the level of contamination. Transport certificates are not required to handle this type of waste and should not be used. Vehicles transporting the contaminated soil do not require an EPA Waste Transport Permit. All loads should be covered to prevent wind blown loss.

Leaks or spills of contaminated material to the environment must be prevented.

Figure 1 shows the decision tree for the disposal of contaminated soils.



#### 2.5 Prescribed Waste

Prescribed waste is the most hazardous category of waste. If not managed properly, these wastes may pose a threat to the life or health of living organisms due to their toxic properties. Other wastes in this category may pose a threat to the safety of humans or equipment due to explosive, reactive or corrosive properties. Prescribed wastes are listed in the Environment Protection (Prescribed Waste) Regulation 1987 as amended (see Table 4 for listing). The only prescribed waste of domestic origin is grease trap waste. All others are of industrial origin.

The range of waste within each prescribed

industrial waste type (eg organic solvents) may be very wide. Written advice should be sought from EPA if doubt exists as to whether or not a waste is prescribed under the regulations.

Contaminated soil which exceeds the limits in Table 3 may require treatment before being disposed of as a prescribed waste to landfill.

All prescribed industrial waste must be transported in accordance with the Environment Protection (Transport) Regulations 1987 which requires the use of transport certificates for each load of waste. Vehicles used to transport prescribed wastes must hold an EPA Waste Transport Permit unless the vehicle is exempt.

Because of the hazardous nature of prescribed wastes, strong emphasis should be placed on reducing the amount of waste at the source. Certain organic solvents and waste oils may be recycled or reclaimed, and some may be suitable for biological treatment. A significant proportion of liquid wastes can be discharged to sewer after appropriate treatment, with the permission of the local sewerage authority. Note that the disposal of liquid wastes to landfill is not permitted.

With all forms of waste treatment, however, there are usually residues which require, landfill. Often such residues need to be immobilised by solidification into blocks to prevent leaching of contaminants into surface and groundwater.

The design and operating requirements for prescribed waste sites are the most stringent of any landfill type. In particular, a prescribed waste landfill would normally require a clay and geotextile liner, leachate collection, and monitoring of leachate, groundwater and landfill gas. In some cases, gas collection and utilisation would be required.

Most prescribed waste will need to be analysed before disposal to landfill to determine compliance with levels specified in the site's EPA licence. The elutriation test method approved by the Authority is the US EPA Toxicity Characteristic Leaching Procedure [TCLP] Test (Method 1311)¹. If the waste does not meet the acceptance criteria further treatment and stabilisation will be required.

#### 2.6 Other Wastes

There are certain wastes and waste types which warrant mention here:

Asbestos wastes: The transport and disposal of Asbestos wastes needs to be carried out under strictly controlled conditions. EPA has produced a separate guideline (Publication 364) regarding these wastes. Asbestos waste from domestic origin is not a prescribed waste. However, sites disposing of any asbestos waste need to be licensed for this purpose.

Mining and extractive industry wastes include a range of wastes (overburden, rock, tailings) with varying contamination levels. Sites used for the deposit of waste not in accordance with the Extractive Industries Act 1966 or the Mineral Resources Development Act 1990 require a licence.

Scheduled Wastes (formally known as Intractable Wastes) are wastes which cannot be treated within Australia using current treatment technology. Examples of these are polychlorinated bi-phenyls (PCBS) organochlorine pesticides and hexachlorobenzene. In the past, such wastes have been stored for transport overseas to a high temperature incinerator, however these arrangements are no longer permitted. New treatment technologies are currently being developed and treatment of some of these wastes within Australia is possible. Contact EPA for further advice.

**Priority Wastes** are listed in the Industrial Waste Management Policy (Waste Minimisation) and consist of the most hazardous of the prescribed wastes, such as some heavy metals, PCBs and certain chlorinated hydrocarbons. Also included are ozone depleting substances and photochemically reactive substances which pose other environmental problems. Priority wastes must be minimised at the source using Best Available Technology (BAT).

Note that this publication replaces information bulletin WM91/01 "Off-site Disposal of Contaminated Soil" and Publication 448 dated may 1995.

¹ Method 131 1, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, SW-846, 3rd ed, USEPA, 1992

#### TABLE 2

Maximum concentrations of

#### TABLE 3

Maximum contaminant concentrations and elutriable fractions allowed in soil to be disposed of as Low Level

contaminants allowed in soil to be disposed of as Fill material		fractions allowed in soil to be disposed of as Low Level Contaminated Soil.		
Contaminant	Maximum	Contaminant	Maximum	Elutriable
	Concentration		Concentration	Fraction
	(total) mg/kg		(total) mg/kg	(pH 5.0 extract)
	dry weight		dry weight	g/m ³
Arsenic	30	Arsenic	300	5.0
Cadmium	5	Cadmium	50	0.5
Chromium	250	Chromium	2500	5.0
Copper	100	Copper	1000	10
Cobalt	50	Cobalt	500	-
Lead	300	Lead	3000	5.0
Mercury	2	Mercury	20	0.1
Molybdenum	40	Molybdenum	400	-
Nickel	100	Nickel	1000	-
Tin	50	Tin	500	-
Selenium	10	Selenium	100	1.0
Zinc	500	Zinc	5000	50
Cyanide	50	Cyanide	500	10
Fluoride	450	Fluoride	4500	150
Phenols	1	Phenols	10	-
Monocyclic	7	Monocyclic	70	-
Aromatic		Aromatic		
Hydrocarbons		Hydrocarbons		
Polycyclic	20	Polycyclic	200	-
Aromatic		Aromatic		
Hydrocarbons		Hydrocarbons		
Total Petroleum	100	Total Petroleum	1000	-
Hydrocarbons		Hydrocarbons		
$(C_6 \text{ to } C_9)$		$(C_6 \text{ to } C_9)$		
Total Petroleum	1000	Total Petroleum	10000	-
Hydrocarbons		Hydrocarbons		
(>C ₉ )		(>C ₉ )		
Organochlorine	1	Organochlorine	10	-
Compounds		Compounds		

#### **TABLE 4**

Prescribed Waste List

#### DOMESTIC ORIGLN

Grease interceptor trap effluent and residues

#### INDUSTRIAL ORIGIN

Abattoir effluent Acids and acidic solutions Adhesives (excluding solid inert polymeric materials) Alkalis and alkaline solutions Animal effluent Antimony and antimony compounds Arsenic and arsenic compounds Asbestos (all chemical forms) Azides Barium and barium compounds Beryllium and beryllium compounds Biocides Boiler blowdown sludge Boron and boron compounds Cadmium and cadmium compounds Caustic solutions Chlorates Chromium compounds Containers and bags containing hazardous compounds Copper compounds Detergents Distillation residues Dyes Electroplating effluent and residues Filter backwash waters Filter cake sludges and residues Fish processing residues Fly ash Food processing effluent Grease interceptor trap effluent and residues Heat treatment salts

Heterocyclic organic compounds containing oxygen, nitrogen or sulphur Hydrocarbons and their oxygen, nitrogen or sulphur compounds Immobilised waste Industrial plant washdown waters Ink Infectious substances Inorganic cyanides and cyanide complexes Inorganic halogen containing compounds Inorganic sulphur containing compounds Isocyanate compounds (excluding solid inert polymeric materials) Laboratory chemicals Lead compounds Lime neutralised sludges Lime sludges Materials or equipment contaminated with infectious substances Mercaptans Mercury and its compounds and equipment containing mercury Metal finishing effluent and residues Methacrylate compounds (excluding solid inert polymeric materials) Nickel compounds Oils Oil interceptor sludges Oil water emulsions Oil water mixes Organic halogen compounds (excluding solid inert polymeric materials) Organic solvents Oxidising agents Paint sludges and residues Perchlorates Peroxides Pesticides Pharmaceutical substances

Phenolic compounds (excluding solid inert polymeric materials) Phosphorus and its compounds Pickling liquors Polychlorinated biphenyls and related materials and equipment containing polychlorinated biphenyls and related materials Polymeric lattices Poultry processing and effluent Reactive chemicals Reducing agents Resins (excluding solid inert polymeric materials) Saline effluent and residues Scallop processing residues Selenium and selenium compounds Silver and silver compounds Solvent recovery residues Surfactants Tallow Tannery effluent and residues Tars and tarry residues Tellurium and tellurium compounds Textile effluent and residues Thallium and thallium compounds Timber preservative effluent and residues Treatment plant sludge and residues (excluding sewage and septic sludges and residues) Triple interceptor trap effluent and residues Vanadium and vanadium compounds Vegetable oils Waste-carrying vehicle washdown waters Wool scouring effluents and residues Zinc compounds Waste other than that already specified, which poses an environmental threat.

#### **FURTHER READING**

- EPA Publication 387 "Industrial Waste Strategy (A Summary Of Industrial Waste Regulations)"
- EPA Publication 388 "Industrial Waste Strategy (Responsibilities For Industrial Waste Management)"
- EPA Information Bulletin WM8/88 "Treatment, Recycling, Stabilisation and Disposal Facilities for Prescribed Waste".
- EPA Information Bulletin 395 "Instructions for Completion of Transport Certificates".
- EPA Publication 364 "The Transport and Disposal of Asbestos"
- Environment Protection (Prescribed Waste) Regulations 1987 as amended.
- Environment Protection (Transport) Regulations 1987
- State Environment Protection Policy (Sitting and Management of Landfills Receiving Municipal Wastes).
- Industrial Waste Management Policy (Waste Minimisation).

# **APPENDIX B**

## (Part a)

THE MASS SPECTRUMS OF 112 COMPOUNDS IDENTIFIED FROM REAL SAMPLE DESORBED WITH CS₂




























#### (Part b)

### THE MASS SPECTRUMS OF 5 COMPOUNDS ELUTING BEFORE HEXANE IDENTIFIED FROM REAL SAMPLE DESORBED WITH CS $_{\rm 2}$



(5). 3-METHYLPENTANE

# **APPENDIX C**

THE MASS SPECTRUMS OF 148 COMPOUNDS IDENTIFIED FROM REAL SAMPLE ANALIZED WITH THERMAL DESORPTION TUBE



(7). 2,2-dimethylbutane











(25). trans-1,3-dimethylcyclopentane



(27). cis-1,2-dimethylcyclopentane





(28). 2,2-dimethylhexane









(51). cis-1-ethyl-3-methylcyclopentane

(52). 1-ethyl-2-methylcyclopentane









(62). Ethylcyclohexane







(79). 3-methylheptane

(80). Cyclodecane









(103). 1,2,3-trimethylbenzene

(104). 1-methyl-4-(1-methylethyl)benzene













# **APPENDIX D**

#### LIST OF PAPERS PRESENTED IN THE CONFERENCE
- L. Yang, T. Fatosh, A., D. Caridi and G. Hamilton, Volatile Organic Compounds in Landfill Gas, Australian International Symposium on Analytical Science, Melbourne Convention Center, Melbourne, Australia (1999).
- L. Yang, D. Caridi, G. Hamilton, R. J. Casey and R. Spokas, Hydrocarbons in Landfill Gas: Sampling and analysis, The Royal Australian Chemical Institute's 10th National Convention Adelaide Convention Center, South Australia (1995).

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