THE ANALYSIS OF TRACE GAS EMISSIONS FROM LANDFILLS

by

Gletwyn Robert Rubidge

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Promotor: Mr C Labuschagne
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EXECUTIVE SUMMARY

Numerous informal houses have been built on and adjacent to a landfill in iBayi, Port Elizabeth, South Africa, which accepted domestic and industrial waste. Formal housing surrounds most of the site at a greater distance - some 60 m, or further, from the landfill. Both formal and informally housed residents complain of odours, burning eyes, sore throats and headaches - symptoms which they believed were caused by the landfill. The landfill gas and ambient air were analyzed to classify and quantify the VOCs (volatile organic compounds) emitted and then to compare the quantitative data with recognised standards to establish if the residents are at risk. Eighteen target (potentially hazardous) VOCs were quantified. A wide variety of compounds were detected in both the ambient air and landfill gas. The results of the VOC analyses were similar to those of other workers in both the qualitative and quantitative studies. The concentrations of the VOCs were mostly lower than the TLV (threshold limit values) values, but exceeded the MRLs (minimum recommended levels). The combined concentrations of the VOC’s in the ambient air either approached or exceeded the limit values for combined exposure thus indicating that a potential health hazard exists. One third of the VOCs were detected in both the ambient air and the subsurface gas, however, external pollution sources also appear to contribute to the VOC concentrations ambient air. Dangerously high methane concentrations were repeatedly detected in the landfill gas amongst the informal houses. There was a vast improvement in the aesthetic qualities of the landfill since the disposal restriction to accept only domestic refuse and building rubble in July 1997. The ambient air was less odorous and landfill site littered. Fewer informal recyclers were present and their concomitant squabbling over valuables had almost vanished.
The management of the iBayi landfill holds much room for improvement. There is potential for serious injury or even death if no action is taken to remedy the problems at the iBayi landfill. A holistic solution will have to be found to make the landfill a safe neighbour.

Some complementary analyses (such as pH, heavy metal concentrations in the water and sediments etc.) were performed on the leachate and water surrounding the landfill.

**Key Words:** analysis, landfill, methane, pollution, trace gases, volatile organic compounds
CHAPTER 1
MAN, WASTE AND LANDFILLS

1.1 INTRODUCTION

During the last four decades, waste production has increased significantly. The reasons for this increase can be found in the modern lifestyle. The buying of goods has become a ritual - items are consumed, buried, replaced, worn out and discarded at an ever-increasing rate. The end result is the generation of large quantities of useless material, or waste. The current worldwide population explosion (excluding a few developed countries) compounds the problem by reducing the available space where landfills may be sited, while the number of waste producers is ever increasing.

Problems with the disposal of wastes can be traced back to the time when humans first began to congregate in tribes, villages and communities. Since then, waste accumulation has become a part of life. Littering of food and other solid wastes in medieval towns (the practice of throwing wastes into the unpaved streets, roadways and vacant land) led to the breeding of rats, with their attendant fleas carrying bubonic plague. The lack of any plan for the management of solid wastes thus led to a plague epidemic, the Black Death that killed approximately half of the 14th century Europeans.¹

With the advent of plastics, the nature of numerous waste streams (municipal, commercial and industrial) has changed, becoming less biodegradable. Packaged foods such as fast foods or frozen items may reduce food waste in the home, but their packaging contributes considerably to the
volume of municipal waste.

1.2 THE NATURE OF THE PROBLEM

Huge quantities of general waste (municipal, commercial, industrial) are produced annually in the world. For example, 134 million tons of municipal solid waste (MSW) is landfilled every year in the USA alone.\textsuperscript{2} In a 1991 survey, the CSIR estimated that the quantity of solid waste generated in the R.S.A. annually was between 340 and 480 million tons. About 15 million tons of this was MSW.\textsuperscript{3} Considering that the amount of solid waste generated by a person in a day ranges from 0.8 kg for persons with a high income down to 0.2 kg for persons with a low income, it is clear that a single city with a population of 1 million could generate 800 tonnes of MSW per day. This amounts to between 73 000 - 292 000 tons/annum. Since the density of MSW is around 200 kg/m\textsuperscript{3}, a city with an assumed population of 1 million will produce between 365 000 and 1460 000 m\textsuperscript{3} of solid waste annually.\textsuperscript{3} This amounts to about 40 rugby fields piled 6 m high with waste! In practice, however, the volume would be less as the waste is compacted by bulldozers and trucks working on the landfill. Landfills obviously have limited lifetimes, and new sites are required as soon as current sites are spent.

All wastes disposed of by means of landfilling release decomposition products into the atmosphere. The methods of formation of the major components of landfill gas, such as methane and carbon dioxide, are well documented and understood.\textsuperscript{4, 5, 6} Although landfill odours are commonplace and regarded as undesirable, recent concerns have been directed at possible long term health risks associated with these gaseous emissions.\textsuperscript{7}
The migration of landfill gases away from landfill sites can be a serious problem especially where enclosed structures or buildings exist. Methane, the major combustible component of landfill gas, can migrate from landfills and collect in basements or crawl spaces of nearby structures where, if mixed with the correct proportions of air, it can form an explosive gaseous mixture. Pockets of methane mixed with air, upon explosion, may cause injuries, deaths and severe structural damage to buildings. As an example, the US EPA (United States Environmental Protection Agency) has documented nine deaths and 24 serious injuries due to nine different explosions and fires associated with landfill gas over a period of seventeen years.\textsuperscript{8}

Landfill gas from domestic wastes, which have been buried for some time, consists mainly of hydrocarbons and carbon dioxide. A much wider variety of compounds are present in gases from recently buried domestic or industrial wastes. This observation has been explained in terms of the presence of small amounts of oxygen in recently buried wastes which can react with initially-formed degradation products to form a variety of oxygen-containing compounds.

As mentioned earlier, a landfill is potentially dangerous to nearby residents because the possibility exists for methane explosions and asphyxiation. Furthermore, many of the emitted gases are toxic, and hazardous microorganisms may also be present. Two compounds, vinyl chloride and benzene (both known carcinogens), were found in 85\% of 23 Californian municipal landfill sites receiving, in principle, only domestic wastes.\textsuperscript{9} The public are generally not aware of such dangers posed by emissions from a landfill, especially in a developing country such as South Africa.
1.3 SOLID WASTE – ITS NATURE AND TREATMENT

1.3.1 Solid Waste Classification

Solid wastes are classified as domestic waste, commercial waste, industrial waste, waste due to construction and demolition, agricultural waste, institutional waste and miscellaneous waste.\textsuperscript{10}

1.3.1.1 **Domestic waste** is waste produced in the household, and includes garden refuse. Constituents of domestic waste may range from readily decomposable organic materials, \textit{e.g.} potato peels, to relatively non-degradable materials, \textit{e.g.} plastic and concrete.

1.3.1.2 **Commercial waste** is waste produced by commercial establishments such as shops, offices and restaurants. This waste is similar to domestic waste except that it contains a larger percentage of paper.

1.3.1.3 **Industrial waste** is waste produced by industries. The characteristics of this waste will be as varied as the industries themselves, and may range from peach-pips to nuclear waste.

1.3.1.4 **Waste due to demolition and construction** is waste that is generally less decomposable than the first two categories. This type of waste is composed of steel, concrete, wood and other similar materials.

1.3.1.5 **Agricultural waste** forms a significant portion of solid waste. Here, crop and animal wastes are the major contributors. These wastes are often recycled and
reused by the agricultural sector, e.g. by ploughing stalks back into the fields or by using manure on vegetable fields as a fertilizer. Agricultural wastes also contain small amounts of the other classes of waste as agricultural systems are micro systems that are similar to urban areas - farmers also produce household refuse and even small amounts of commercial and medical waste.

1.3.1.6 **Institutional waste** is waste produced by hospitals, prisons, nursing homes, educational facilities, *etc.* These wastes are similar to domestic wastes with the exception that they contain more paper and some hazardous materials such as toxic chemicals and biological wastes.

1.3.1.7 **Miscellaneous waste** is either an assortment of the above classes of waste or a type that is not included amongst these classes.

1.3.2 **Treatment of Waste**

Now that the types of waste have been defined, it is apt to consider methods of waste management. To be effective in treating any problem, the cause should be addressed - this also applies to waste. If there was no waste, there would be no waste associated problems; if there was less waste, there would be less of a waste problem. Douglas\(^{10}\) refers to the four “R’s” which can assist in the management of waste - reduction, recovery, recycle, and reuse.

1.3.2.1 **Reduction:** “Disposal” is a word that exemplifies a modern philosophy that is a major contributor to increased waste production. The producers of “disposables” should undergo compulsory waste education in order to reduce the amount of excess
voluminous materials.

1.3.2.2 **Reuse:** This implies that any item that can serve its purpose more than once should be reused. An example is that of glass COCA-COLA bottles being reused. When a product is designed, *reuse* should be a serious consideration in its design stage.

1.3.2.3 **Recycling:** This involves the reprocessing of waste so that it may be reused. An example is the collection and reprocessing of cardboard or plastic bags. One disadvantage is that the separation of recyclable material from other wastes can become labour intensive and hence costly.

1.3.2.4 **Recovery:** This is a process in which waste is used for some other purpose, for example, utilizing the energy derived from the combustion of waste.

1.3.3 **Methods of Waste Disposal and Waste treatment**

The most commonly employed methods of waste disposal are landfill, incineration and composting. The method of disposal selected by a country will depend on factors such as availability of land, transport infrastructure and economics. Australia, a sparsely populated country, disposes 98% of its waste by landfill while a highly populated country such as Japan landfills only 28% of its waste and incinerates 67%. ¹¹

Solid waste is often treated prior to disposal. The waste can undergo one of the following treatments:

1.3.3.1 **Separation:** This is the process whereby recyclable/reusable materials are extracted
from the rest of the waste prior to landfilling or incineration. In the case of composting, some material may need to be removed so that the quality of the compost produced will be suitable.

1.3.3.2 Compaction: This is usually carried out in order to reduce the volume of waste. Reduced volume facilitates handling and extends the lifespan of landfills.

1.3.3.3 Additions: In order to prepare waste for disposal, various substances may be added to it, for example, water and bacteria are sometimes added to accelerate waste decomposition in landfills. Furthermore, neutralization is required to render acidic waste less hazardous and sodium carbonate, a typical neutralizing agent, may be added in order to achieve this.

1.3.4 Landfill

In the past, waste was dumped into low-lying depressions or holes with little or no engineering to prevent pollution. Waste would occasionally be burnt to reduce its volume. The practice of open dumping had changed little until a few decades ago.\textsuperscript{12}

In landfills, waste is often dumped in cells that are up to five metres deep. At the end of each day, a thin layer of soil, known as daily cover, covers the waste. This reduces odours (caused by the initial decomposition of the waste), prevents scavenging by birds, insects and animals, and curbs wind dispersion of light matter such as plastic bags and paper. In addition, daily cover assists in the reduction of health risks by containing bacteria and germs in the decomposing matter, and also improves the aesthetic quality of the landfill. Daniel\textsuperscript{13} states that the objective of a waste disposal
site is “to contain the waste in a manner that is protective of human health and the environment”. He further suggests, “No liner material is forever impermeable to all chemicals”. One should thus appreciate that the waste will be contained but, inevitably, emissions will occur. If the emissions can be controlled, then their treatment may be facilitated, e.g. the landfill gas may be flared (combusted as it mixes) with air, or the leachate (water that has percolated through the landfill) may be recirculated through the landfill. Flaring assists in the conversion of hazardous substances to potentially less harmful products, e.g. carcinogenic benzene, if burned in an excess of air, is converted to carbon dioxide and water, both of which are more environmentally friendly than benzene itself. Research in the UK\textsuperscript{14} has shown that recycling the leachate reduces its organic strength, especially in the case of volatile organic acids. Spraying leachate onto the surface of a landfill, thereby allowing water to evaporate, may also reduce its volume. Possible problems associated with leachate recirculation include the evaporation of odorous and toxic compounds, and the concentration of species such as chloride, ammonia/ammonium salts and metals. Despite these disadvantages, volume reduction and reduced organic strength may benefit site operations, especially if the site has no nearby communities.

It may be difficult to decide on the proper location of a landfill since a number of conditions must be satisfied for a landfill to be economically and environmentally viable. Some factors that affect the location of a landfill are the proximity to the waste source and population, the infrastructure, climate, geological conditions and availability of building materials such as clay, daily cover and gravel. The likelihood of all these factors being favourable for a specified location is small, and hence some compromise is usually required.
Landfill sites have increasingly become a target of environmental pressure groups because of pollution resulting from leachate and landfill gas emissions. The concerns of these groups are that the production of leachate may contaminate both surface water and ground water, and that gaseous emissions occurring from the landfill may contribute to the greenhouse effect (due to CO₂ and CH₄ production). Also certain toxic and/or odorous trace gases may be released.

Variables that are likely to affect gaseous emissions from landfills are atmospheric pressure, temperature and the nature of the landfill, e.g. moisture content, type of refuse, permeability of top-cover, etc. Lin et al.¹⁵ developed a model to describe pollution from landfills. They found that variables such as transport of species, partitioning among phases, degradation/reaction of species and mass transfer all affect the emission rates.

A landfill exists in iBayi, a suburb of Port Elizabeth that was suspected of causing pollution, which adversely affected the health of the iBayi residents living near the landfill. If it is true that these residents were being affected by the pollution that originated from the landfill, then the Bill of Rights is not protecting the environmental rights of these people. The said Bill of Rights is contained in Chapter 2 of the Constitution of the Republic of South Africa, Act 108 of 1996, Section 24(a)¹⁶ and states that “everyone has the right to an environment that is not harmful to their health or well being”. One of the aims of this study was to determine the nature and extent of the VOC (volatile organic compounds) pollution at the iBayi landfill.
1.3.4.1 Phases of Refuse Decomposition in Landfills

In a typical sample of municipal refuse, one is likely to find paper, garden refuse, metal, plastic, food, glass, textiles, leather, wood, and a host of other items. When these types of waste are combined and allowed to stand for some time, a gas is eventually produced consisting of mostly methane and carbon dioxide. Gaseous substances such as hydrogen sulphide, and volatile organic compounds such as benzene, toluene and hexane, also form but to a much lesser extent.\textsuperscript{17} The total combined percentage of released trace gases, \textit{i.e.} gases other than carbon dioxide and methane, may not even exceed 1\% of the total volume of gas produced. Brosseau and Heitz\textsuperscript{18} reported total trace gas percentages of between 0.7\% and 5\%, while O’Leary and Walsh\textsuperscript{19} found typical values of around 0.5\%. Though toxic trace gases are present in relatively small amounts, they are still considered a potential danger due to the accumulative effects of long-term exposure.

The major source of methane production is the degradation cellulose and hemi-cellulose. These two constituents account for 91\% of the methane that is produced by the refuse. The mechanism of methane production is as follows:

\[
\text{Biological Polymers (s)} \xrightarrow{\text{hydrolytic and fermentative organisms}} H_2 (g) + CO_2 (g) + CH_3CO_2^- \\
\xrightarrow{\text{acetophyllic and hydrogenophyllic methanogens}} CH_4 + CO_2
\]
The decomposition of municipal waste may be divided into four stages, and these are discussed below:

- **The aerobic stage**
  This stage is characterised by large amounts of carbon dioxide being released initially, followed by a gradual decrease as the supply of oxygen trapped in the landfill is used up by microbial activity. This stage is short-lived as oxygen ingress into the site is slow due to the positive pressure within the site caused by gas generation.

- **The anaerobic stage**
  During this stage, the pH of the waste drops due to the production of carboxylic acids in the decomposing refuse. Accumulation of carboxylic acids is the result of sugar fermentation. The concentration of methanogenic microorganisms increases thereby augmenting the rate of methane production, while the carbon dioxide emissions are reduced.

- **The accelerated methane stage**
  Microorganism concentrations continue to increase during this stage, resulting in an increasing rate of methane production. The pH begins to increase as the microorganisms convert carboxylic acids into methane and carbon dioxide.

- **The decelerated methane stage**
  The pH of the waste continues to rise as carboxylic acids are consumed by microbial activity. Cellulose and hemi-cellulose are decomposed in this stage, resulting in a noticeable volume reduction of the waste as compared to the first three stages. The total amount of gas produced reduces and the ratio of carbon dioxide to methane remains at approximately 4:6.
It should be noted that none of the above stages would at any time be truly representative of the entire landfill. Typically, waste is filled into “cells” separated by layers of clay that constitute the cell walls. Since cells are formed sequentially as waste is landfilled over an extended time period, different cells will be at different decomposition stages at any given time during the lifetime of the landfill. Factors such as moisture content and temperature have an influence on the rate of waste decomposition within the landfill. Methane production generally increases with temperature and moisture content. Too high a temperature, however, would result in the destruction of microorganisms and, consequently, a decrease in the rate of waste decomposition.

As the waste decomposes and generates gas, its volume reduces. Gas generation rates of 10-20 liters/kg/year have been reported for municipal wastes. Depending on the type of waste and degree of compaction of the waste, settling or consolidation will reduce the waste volume by 15-20% or more during the lifespan (typically 30 years or longer) of the landfill. In poorly compacted wastes, settlements of up to 50% have been observed. Volume reduction can lead to cracking as one section of the site settles more than another. Varying waste densities, for example by mixing building rubble with household waste, can facilitate the occurrence of cracking. Cracks may act as conduits through which landfill gases may move out of the site. During periods of low atmospheric pressure, increased gas migration will occur because of the pressure gradient. The potential for asphyxiation, explosion and ingress of trace gases are likely to increase to a maximum a few years after the deposition of the waste. This is due to the fact that gas decomposition reaches a peak during the latter part of the “accelerated methane production” stage.
1.3.4.2 Leachate

Water percolating through the landfill will dissolve both inorganic and organic substances that are present in the waste. This water collects at the bottom of the site and may form streams or pools at the base of the landfill. The leachate is often dark in colour and odorous. Factors that affect the constitution of the leachate are the type and age of the waste, the climate, the availability of oxygen, the rate of water infiltration and the geological design of the site.

1.3.4.3 Constituents of Landfill Gas and Leachate

Brosseau et al established that landfill gas consists of the following major components: methane, carbon dioxide, hydrogen, hydrogen sulphide and carbon monoxide.\(^\text{18}\) The minor components that can be found in trace concentrations in landfill gas are hydrocarbons (both aliphatic and aromatic), carboxylic acids, chlorinated compounds, natural hydrocarbons, esters, sulphur compounds, aldehydes, ketones, phenols and anhydrides.\(^\text{22}\)

Leachate will contain any soluble or slightly soluble substances that can be leached from the waste. Many organic substances are only slightly soluble in water, but may still dissolve to a sufficient degree to pose a threat to life forms that make use of the contaminated water.

Typical analyses\(^\text{14}\) that can be performed on the leachate to gauge its potential impact on the environment include pH, BOD (biological oxygen demand) and COD (chemical oxygen demand), as well as analyses for sulphates, chlorides, nitrates, nitrites, and total phosphorus, sodium, potassium,
ammonium, heavy metals and organic halides.

1.4 TOXICOLOGICAL ASPECTS OF GASEOUS EMISSIONS FROM THE IBAYI LANDFILL

1.4.1 Introduction

This section will begin with some pertinent physiological data selected from *The Encyclopaedia of Occupational Health and Safety*, thereafter various effects produced on humans by toxic volatile organic compounds will be discussed. The aforementioned reference was used to compile Table 1.3, a summary of adverse affects produced by compounds that were detected at the iBayi landfill. Numerous toxic and non-toxic compounds have been detected at landfills, including the iBayi site. Research since 1991 has reinforced concerns over the scope of the problems posed to human health and ecological systems by endocrine-disrupting (hormone disrupting) chemicals. New evidence is especially worrisome because it underscores the exquisite sensitivity of the developing nervous system to chemical perturbations (disturbances) that result in functional abnormalities. The full range of substances interfering with natural endocrine modulation of neural and behavioural development cannot be entirely defined at present, however, compounds shown to have endocrine effects include dioxins, PCBs, phenolics, phthalates and many pesticides. Any compound mimicking or antagonising actions of, or altering levels of, neuro-transmitters, hormones, and growth factors in the developing brain are potentially in this group. Phenol and phthalates were detected at the iBayi landfill in the qualitative study of this research.
Families are living on and around the iBayi landfill, these people are potential receptors and may adversely be affected by toxic emissions from the landfill. Ndlovu\textsuperscript{22} detected phthalates at the iBayi landfill. They are used extensively in plasticizers for soft PVC as well as in the production of lacquers, polyamides, insect repellents, lubricants and host of other uses.\textsuperscript{14} The developing brain [of humans and animals] exhibits a specific and often narrow windows during which exposure to endocrine disruptors can produce permanent changes in its structure and functions. The unborn children of the iBayi landfill residents are included as potential receptors to endocrine affecting chemicals.

Considering the presence of toxic compounds in air at the iBayi landfill let us consider some points of the body reference of man by consulting Table 1.1.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Adult Male</th>
<th>Adult Female</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of total body</td>
<td>70 kg</td>
<td>58 kg</td>
</tr>
<tr>
<td>Surface area of body</td>
<td>18 000 cm(^2)</td>
<td>16 000 cm(^2)</td>
</tr>
<tr>
<td>Surface area of alveoli</td>
<td>72 m(^2)</td>
<td>66 m(^2)</td>
</tr>
<tr>
<td>Total lung capacity</td>
<td>5.6 L</td>
<td>4.4 L</td>
</tr>
<tr>
<td>Total volume of air breathed in 24 hours</td>
<td>23 000 L</td>
<td>21 000 L</td>
</tr>
</tbody>
</table>

The 72 m\(^2\) surface area is equivalent to 8.5 X 8.5 m room floor, a large surface upon which a gas molecule may contact the lung wall and be ingested.
1.4.2 Exposure Pathways

In order to evaluate the potential human exposure to hazardous substances and their health related effects, the exposure pathways need to be investigated. An exposure pathway (the course a chemical takes from the source to the receptor) includes the components shown in Table 1.2.

<table>
<thead>
<tr>
<th>source</th>
<th>landfill, fire, etc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>transport media</td>
<td>air, groundwater, dust etc.</td>
</tr>
<tr>
<td>exposure point</td>
<td>food source, water well, etc.</td>
</tr>
<tr>
<td>route of exposure</td>
<td>ingestion, inhalation, etc.</td>
</tr>
<tr>
<td>receptor population</td>
<td>families, schoolchildren, animals, etc.</td>
</tr>
</tbody>
</table>

The above table depicts, in a step-wise manner, the cradle to grave path followed by pollutants. Various important variables are emphasized. At the iBayi site the primary pollutant source is the landfill itself, but exhaust emissions, airborne pollutants from local industry and residential areas and water bourne pollutants (in the streams on the east and west side of the landfill) should not be overlooked. Transport media identified are air, groundwater, surface water, dust, and animal sources (livestock). Exposure points are as variable as the exposed organism is mobile and
located *e.g.* a person may be exposed to trace gases in his bed while sleeping in a dwelling located on the landfill. Routes of exposure may be: ingestion, inhalation, and adsorption onto and through the skin. Receptor populations are fairly high at the landfill as is to be expected in informal settlements.

Domestic livestock (chickens, pigs, goats and milk producing cows) feed on the vegetable organic matter dumped at the landfill. The inhabitants of the site use these animals and their products as food sources. If the meat, eggs or milk were to become contaminated, health hazard could be posed by ingestion of bio-accumulated compounds. The site has extensive vehicular traffic that creates dust that may be inhaled by people living and scavenging there. Gaseous pollutants from the landfill may contaminate the air and produce odours that are unpleasant and possibly toxic.

1.4.3 Hazards Presented by Gases and Trace Gases at Municipal Landfill Sites

The numerous gases and trace gases found at municipal landfill sites are frequently a cause of concern. They present various hazards ranging from the explosiveness of methane mixed with air to foul odours. Some of the potential problems which may arise due to landfill gas are discussed below:

1.4.3.1 Toxicity of Trace Gases

Numerous trace gases emitted from municipal landfills are known to be toxic, inducing acute or
chronic effects on human health. The toxicity may also depend on the cumulative effect of the gases. Repeated small doses of toxic compounds may not show any visible symptom, however, little is known of long term exposure to small amounts of toxic compounds.

1.4.3.2 Carcinogenicity/Mutagenicity of Trace Gases

Trace gases such as benzene and vinyl chloride may bring about a carcinogenic response. Unlike the aforementioned two substances, other aromatic hydrocarbons have irritant and narcotic properties. The toxic and carcinogenic effects of trace gases, released by municipal landfills, are dependent on the degree of exposure (absolute concentrations and duration of exposure). Products of incomplete combustion are associated with increased lung cancer risks. Fires at the iBayi landfill produce thick black smoke indicating incomplete combustion, such smoke has been reported to contain carcinogenic fumes (benzopyrenes and dioxins).

1.4.3.3 Trace Gases Resulting from Combustion at Municipal Landfill Sites

Gaseous pollutants can be emitted from municipal landfill sites as a result of controlled combustion (flaring) and uncontrolled combustion of organic matter and landfill gas. Recycling operations, at the iBayi landfill involve the burning of plastic coated copper wire is burned to remove the plastic, this activity produces large amounts of black smoke. Brosseau and Heitz reported that polychlorinated dibenzodioxins and dibenzofurans are readily formed in incinerators with an available source of chlorine. Should the temperature of the fire used by the informal recycler be hot enough it could form the above mentioned compounds. Chlorine could be supplied by the polyvinyl chloride coating on the wire that is burned at a landfill. High PCB
(polychlorinated biphenyls) concentrations were reported in a spontaneous landfill fire by
Ruokojarvi and co-workers. The iBayi landfill often has persistent fires that smoulder away
for extended periods of time. The author has directly observed such fires as well having been
informed of earlier fires by residents of the site.

1.4.3.4 Subsurface Gas Migration

A potential hazard at a municipal landfill site is the sub-surface migration of landfill gases via
cracks to residences close to the landfill. The migration may occur via cracks formed as a result
of gas pressure or via porous soil. Examples of potential hazards from the subsurface migration
of various gasses include:

- CO₂ - nausea, dizziness, headaches and suffocation;
- CH₄ - nausea, headaches, vomiting, explosion in air at levels between 5 and 15% v/v,
  asphyxiation at high concentration;
- Trace gasses - some are toxic and carcinogenic, e.g. such as vinyl chloride and benzene,
  while others such as limonene, xylene, substituted benzenes and dimethylsulphide could
  produce odours. The aforementioned compounds were all detected at the iBayi landfill
  in both this research and that of Ndlovu in 1996. Other substances that produce odours
  are organosulphur compounds, esters, organic acids, hydrocarbons and alcohols. Woods
  and Porter, as cited by Brosseau and Heitz, reported vinyl chloride levels 3-5 times
  higher than set standards, in houses close to a municipal landfill in California.

Table 1.3 lists the harmful effects that may be caused by the compounds that were detected at the
iBayi landfill, it was compiled from data selected from the *Encyclopaedia of Occupational Health and Safety.*

### Table 1.3 Harmful affects that may be caused by gases selected organic compounds

<table>
<thead>
<tr>
<th>Compound/Group Formed</th>
<th>Harmful Effects</th>
<th>Possible Source/Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>aliphatic hydrocarbons C1 - C15 saturated</td>
<td>Methane-asphyxiant. These hydrocarbons generally slightly affect humans. Acute effects such as narcosis and in-coordination are produced only by high concentrations of these compounds. The shorter the chain length the less toxic. Generally of low toxicity.</td>
<td>fuels, lubricants, solvents, starting materials for organic synthesis, welding, metal cutting.</td>
</tr>
<tr>
<td>unsaturated aliphatic hydrocarbons</td>
<td>narcotic, irritant properties increase with increasing molecular mass.</td>
<td>starting materials for synthesis.</td>
</tr>
<tr>
<td>benzene</td>
<td>inhalation - outer, chronic poisoning skin contact - dermatitis cancer - 15-60% of inhaled benzene in metabolised forming benzene epoxide which reacts with proteins and nucleic acids.</td>
<td>solvent - adhesives, fuel, reagent, paint.</td>
</tr>
<tr>
<td>halogenated aliphatic hydrocarbons</td>
<td>depression of the central nervous system, narcosis, headache, nausea, headache.</td>
<td>solvents, degreasers, aerosols, dry-cleaning.</td>
</tr>
<tr>
<td>ketones</td>
<td>eye irritation, throat irritation, headache, trachea irritation, nausea, dermatitis</td>
<td>solvents for plastics, artificial silk, explosives, perfumes, pharmaceuticals, waxes, fats</td>
</tr>
<tr>
<td>acetone, methyl ethyl ketone, isobutyl ketone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substance</td>
<td>Health Effects</td>
<td>Uses</td>
</tr>
<tr>
<td>------------------------</td>
<td>--------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Haemolytic anaemia, hepatitis and renal disorders, dermatitis optic neuritis.</td>
<td>Mothballs-plastic, wood preservation, starting material for organic synthesis.</td>
</tr>
<tr>
<td>Diethyl phthalate</td>
<td>Absorbed through skin. Slight toxicity.</td>
<td>Softening PVC, lacquers, insect repellants, and other minor uses.</td>
</tr>
<tr>
<td>Styrene</td>
<td>Irritation of mucous membranes, toxic hepatitis, reduced arterial pressure.</td>
<td>Product of pyrolysis of organic matter polymers.</td>
</tr>
<tr>
<td>Toluene</td>
<td>Dermatitis, asthma, bronchitis.</td>
<td>Epoxy resin emission, solvent.</td>
</tr>
<tr>
<td>Xylene</td>
<td>Narcosis, fatigue, dizziness, shivering, dyspnea, nausea, headache.</td>
<td>Thinner, varnishes, narcotic, fuel, printing-ink solvent.</td>
</tr>
</tbody>
</table>

1.5 ORIGIN AND SCOPE OF THE INVESTIGATION

21
1.5.1 History of the iBayi landfill

The landfill in iBayi is located in a salt pan. The salt pan began being used as a refuse dump in about 1970. In the course of time, the salt pan was used to dump a variety of wastes including industrial, commercial, building, institutional and residential wastes. Some unemployed people, initially arriving in Port Elizabeth in search of work, began informally recycling metals, plastics and cardboard obtained from the site. They built informal houses close to the landfill because of the living with which it provided them, and building materials and food for humans and animals could be procured from the waste. Numerous informal houses have since been built on the older part of the landfill. Formal housing surrounds most of the site at a greater distance, some 60 m or further from the landfill. Appendices 1 and 2 depict the site layout and location, while Appendices 8 & 9 contain photographs of the landfill.

The iBayi landfill has accepted domestic, commercial and industrial waste, but due to the lack of control of incoming waste and the absence of a boundary fence, it is probable that the dumping of other wastes may have occurred. During mid 1997, the municipality restricted the type of waste that waste producers were allowed to dispose of at the landfill to only building rubble and municipal waste, but this could not be enforced.

At present, the waste is not covered daily with a thin layer of soil. Low-density materials are therefore carried by the wind into the neighborhood. The lack of daily cover also attracts birds, insects, rodents, stray domestic animals and even impoverished people - a situation which is not
conducive to good health. As mentioned previously, random, informal recycling is rife, and the recyclers have been seen fighting amongst themselves in their quest to gather the most recyclable materials. Fires are made at random on the landfill for warmth, cooking and other purposes - fuels range from tyres and plastic to grass and cardboard. Furthermore, storm water drains currently feed “ponds” at the base of the landfill. These “ponds” are also shown in Appendix 1. Leachate from the landfill may contaminate the ponds that may contaminate the local groundwater. Domestic animals that drink from may accumulate toxins that may reach humans higher up the food chain.

1.5.2 Origin of the Investigation

The Community Environmental Network (CEN) in the iBayi suburb of Port Elizabeth had received complaints from residents in the vicinity of a landfill in the suburb. The CEN approached the PE Technikon for assistance to investigate the complaints and ascertain their causes. Meetings were held with the street committees of the areas surrounding the landfill to discuss the problems experienced by the residents. Residents complained of bad odors, sore throats, burning eyes, increased sickness, flies, mosquitoes, rats, a leaking sewer, dust, noise, fires on the landfill, and litter. It was decided that the PE Technikon would conduct an initial qualitative study to determine if the landfill gas and the ambient air at the iBayi landfill was significantly hazardous to these residents.
1.5.3 Specific Objectives of this Study

With the problems highlighted above in mind, it is now apt to consider the objectives of this study. These objectives are:

► to identify the major types of VOC’s (volatile organic compounds) emitted from the landfill;

► to quantify selected VOC’s in the ambient air and the subsurface gas;

► to compare the concentrations of selected VOC’s found in the ambient air with those found in sub-surface samples;

► to compare all quantitative data with recognized standards to establish if the residents of the landfill are at risk;

► to compile a document containing a literature review on aspects concerning waste, waste management and disposal, and dangers/problems arising as a result of mismanagement of landfills;

► to supply a report (a copy of this thesis) to the appropriate authorities to make them aware of any significant results obtained in this study which may assist in
avoiding potential accidents and reducing health risks at the iBayi site.
CHAPTER 2

SAMPLING AND EXPERIMENTAL METHODS

2.1 INTRODUCTION

This chapter describes the methods and the equipment used to collect and analyze gaseous volatile organic compounds (VOC’s) at the iBay landfill. VOC’s may be present in air samples at concentrations below the detection limit of most gas chromatographs. In such cases, pre-concentration can be used to bring the concentration of the analyte within the detection limit of the gas chromatograph. This is achieved by discarding the sample matrix (air) whilst retaining the analyte. Pre-concentration methods were evaluated for use during this investigation.

Since volatile organic compounds are found in varying concentrations in air, their method of sampling is largely determined by the expected concentration of the VOC’s and the sensitivity of the analytical method being used. If the VOC’s are present in high concentrations, no pre-concentration is required and the sample can be analyzed directly. If, however, the sample is very dilute it will need to be pre-concentrated by one of the following means:

♦ Trapping by adsorption
♦ Cold Trapping
♦ Solvent trapping
2.2 METHODS OF PRE-CENTRATION

2.2.1 Adsorption

A compound with a polarity similar to the surface of a solid or liquid can be adsorbed onto that surface. The ability of the adsorbent to trap VOC’s is dependent on its surface area, polarity and dimensions. Adsorption is defined as “the existence of a higher concentration of any particular substance at the surface of a liquid (or solid) than is present in the bulk of the medium”. An increase in pressure and/or decrease of temperature results in increased adsorption of a gas/vapor onto a solid. The reverse is also true: a decrease in pressure and/or increase in temperature reduces the degree of adsorption of a gas/vapor onto a solid. Adsorption may also be performed in solution by passing a liquid over a solid adsorbent such as silica gel or charcoal.

The adsorbents used during this investigation were placed in deactivated (silanized) glass tubes, and kept in place by means deactivated glass wool plugs (Figure 2.1). To trap compounds of various polarities, a multiple adsorbent train can be used, e.g. silica gel to trap polar compounds and charcoal to trap non-polar compounds. An ideal adsorbent will trap and retain the compounds of interest for the entire sampling period, and allow complete adsorption of all solutes from the fluid. The adsorbed compounds may be desorbed from the adsorption tubes by thermal desorption, or solvent extraction.
2.2.2 Cold Trapping

Cold trapping involves cooling a stream of air so that the analyte/s condense in a vessel that may be closed to contain the sample until analysis. A common method involves passing the gaseous sample matrix through a “U” tube that is immersed in a beaker of coolant. The “U” tube is usually filled with inert packing material such as glass beads to aid condensation. The choice of coolant depends on the boiling point of the analyte/s – very volatile substances require low temperatures to facilitate condensation, and in this case, dry ice (solid carbon dioxide) or liquid nitrogen may be used as coolant. In the case of a less volatile analyte, ordinary ice or ice-salt mixtures may suffice.

2.2.3 Solvent Trapping

Solvent trapping involves passing the gaseous matrix containing the analyte/s through a
small volume of solvent that readily dissolves the analyte/s. Preconcentration is also achieved in this way, the degree of which depends on the ratio of the volumes of matrix to trapping solvent. The use of volatile solvents may require that the solvent be cooled to prevent its loss through evaporation into the gaseous sample matrix.

2.3 CANISTER SAMPLING (WHOLE AIR COLLECTION)

Another method of sampling gases is to collect a sample by pumping it into a canister where it may be stored under pressure, and aliquots may be tapped off as needed. Teflon sample bags are the low-pressure version of the canister. Such bags are fitted with valves that allow the bag to be refilled, sampled from by using a syringe, or completely evacuated. The advantage of canisters and sample bags over tube sampling is that multiple injections may be performed. The advantage of direct pre-concentration, however, is lost.

There are a number of disadvantages associated with this method of sampling. Canisters are made of metals such as stainless steel, and some sample components may adsorb onto the metal walls of the canister. Furthermore, samples being stored under pressure may react, thus altering the constitution of the original sample. Canisters are more costly than adsorption tubes and require a pump (with inert surfaces on working parts which come into contact with the sample) that can generate pressures of a few atmospheres; while adsorption tubes do not demand as strong a pump. Also, non-volatile components may condense within a canister and be partially excluded from the analysis.
2.4 DESORPTION METHODS

Once a sample has been separated from its matrix by adsorption, it must be desorbed from the adsorbent for analysis. Two commonly applied methods of desorption are discussed in this section.

2.4.1 THERMAL DESORPTION

This method of desorption utilizes the principle that the extent and strength of adsorption onto a particular surface reduces as temperature rises. Samples can thus be collected at low temperatures (the degree and strength of adsorption is high at low temperatures) and then desorbed at higher temperatures (either *ex situ* or *in situ* from the analytical instrument). It is essential that adsorbents be thermally stable to minimize background contamination during quantification. The rate at which compounds are desorbed (or released) should be rapid so as to reduce analysis time and to effect efficient separation especially if the chromatographic analyses are at lower temperatures. It has been empirically observed by the present author that slow desorption (or slow heating of the adsorbent tube) results in peak broadening.

2.4.1.1 Disadvantages of Thermal Desorption

► *Decomposition of unstable analytes*

A disadvantage of thermal desorption is that thermally unstable compounds may decompose at high desorption temperatures. This disadvantage is offset by the fact that one can achieve very low method detection limits when the whole sample is desorbed onto the column. Analyst skill, however, has to be greater for whole tube desorptions compared with ordinary injections through a septum. Special
desorption units can be used for this purpose but the costs of these units can be prohibitive.

► **No replication**

Another disadvantage of thermal desorption is that replicate analyses cannot be performed as the whole sample is transferred to the gas chromatograph. Replication by sampling simultaneously can be used to determine reproducibility, but additional equipment would be required to collect additional samples at each sampling site. Changes in the landfill gas composition (typically ranging from 15 - 27% of the mean)\(^{29}\) can affect sequentially collected samples, making this approach less desirable.

► **Production of artifact species**

A further disadvantage is that collected compounds may react during desorption (or adsorption) and result in formation of artifact species.

### 2.4.1.2 Advantages of Thermal Desorption

► **Enhanced detection limits**

Thermal desorption has the advantage of pre-concentration thus method detection limits may be reduced even though the instrumental sensitivity remains unchanged.

► **Matrix separation**

When a sample is collected by adsorption much of the matrix, *i.e.* water vapour and air, discarded – leaving a less complex mixture to be separated by the gas chromatograph.
2.4.2 Solvent Desorption

A solvent will dissolve an adsorbed substance from the adsorbent if its polarity is suitable. One should thus consider the polarity of the analytes when selecting a solvent for desorption. Complete desorption may require repeated aliquots of solvent to quantitatively remove the analytes from the adsorbent.

The most frequently used desorption liquid is carbon disulphide, which may be used for desorption of aliphatic, aromatic and chlorinated hydrocarbons, as well as ketones. Its use is exemplified in the National Institute Of Safety and Health (NIOSH) methods 1500, 1501, 1003 and 1300.

2.4.2.1 Disadvantages of Solvent Desorption

► Solvent contamination

Analytes may be present as impurities in desorption solvents, e.g. carbon disulphide used during this investigation was found to contain trace amounts of benzene. Positive errors may be made if a contaminated solvent is used without incorporating a correction factor. In other words, “solvent blank” checks need to be performed to correct for the presence of trace contaminants in the desorption solvent.

► Analyte dilution

Analyte dilution occurs during the desorption process, and analytes present in low concentrations may be diluted to below the detection limit of the analytical instrument.
**Loss of volatiles**

When a volatile solvent such as dichloromethane is used, it may adsorb onto the surface of the adsorbent, release energy, and lead to heating or even boiling of the solvent. Loss of volatiles may thus occur. This heating effect can be overcome by cooling the solvent and the tubes prior to desorption. Tubes may be cooled by folding a tinfoil icepack around the tube for about a minute prior to adding the desorption solvent.

### 2.4.2.2 Advantages of Solvent Desorption

- Solvent standards are much more readily available than gas standards, the latter having to be specifically manufactured and calibrated at great cost.

- Repeated injections may be done if an outlier is suspected or if an error is made in the analysis. Thermal desorption would require that a whole new sample has to be collected. Since a sample is not necessarily analysed on the same day as it was collected, and conditions (such as temperature and atmospheric pressure) at the landfill may change and hence affect the rates of VOC emissions, the constituents of this new sample may differ from the original leading to different results.

### 2.5 ADSORBENTS FOR ADSORPTIVE TRAPPING

This section will describe the common adsorbents used for VOC collection. The three adsorbents used in this research are described first followed by a discussion of various adsorbents.
2.5.1 Adsorbents Used in the VOC Analyses at the iBayi Landfill

The three adsorbents (Table 2.1) used were obtained from “ANATECH” (Durban - South Africa) and manufactured by “SUPELCO”. (The catalogue numbers are also given for each product.)

Table 2.1 Adsorbents used for iBayi VOC’s

<table>
<thead>
<tr>
<th>NAME</th>
<th>Carbotrap C</th>
<th>Carbosieve S-111</th>
<th>Tennax TA</th>
</tr>
</thead>
<tbody>
<tr>
<td>PARTICLE SIZE</td>
<td>20/40 mesh</td>
<td>60/80 mesh</td>
<td>60/80 mesh</td>
</tr>
<tr>
<td>SURFACE AREA</td>
<td>10 m²/g</td>
<td>820 m²/g</td>
<td>35 m²/g</td>
</tr>
<tr>
<td>CATALOGUE NUMBER</td>
<td>2-0309</td>
<td>1-0/84</td>
<td>1-1982</td>
</tr>
</tbody>
</table>

**Carbotrap C:** This product is graphitized carbon black that is ideal for trapping a wide range of airborne organic compounds, ranging from C₄ - C₅ hydrocarbons to polychlorinated biphenyl compounds and other large molecules. Carbotrap C is thermally stable (manufactured at over 2000°C) and hydrophobic (prevents sample displacement by water). One can thus desorb samples at high temperatures with minimal bleed, and samples may be collected in humid conditions.³⁵

**Carbosieve S-111 molecular sieves:** The large surface area and small pore size (15 – 40Å) make Carbosieve S-111 an excellent adsorbent for trapping small airborne molecules, such as chloromethane. The upper temperature limit for desorption is approximately 400°C.

**Tennax TA:** Tennax TA is a porous, polymeric material based on 2,6-diphenylene oxide. It is especially suited to trapping volatile and semi-volatile compounds ranging from C₅ to C₁₂ compounds. The upper temperature limit for desorption is approximately 350°C.
2.5.2 Activated Carbon

Activated carbon is prepared by treating charcoal or other carbonaceous materials such as nutshells, coal, peat, etc. with hot steam (typically 800-1000°C). Alternately, chemical activation of uncarbonized materials such as peat or sawdust is induced at 400-1000°C using dehydrating agents such as phosphoric acid or zinc chloride. Activated carbons may have a surface area of 1500 m²/gram. Coconut shell charcoal is commonly used for non-polar VOC adsorption. A disadvantage of activated carbon is that large molecules can be irreversibly adsorbed.

2.5.2.2 Siliceous Compounds

Molecular sieves and silica gel are used to adsorb polar compounds. A drawback of these compounds is that they are hydrophilic and may become saturated in humid conditions.

2.5.2.3 Porous Polymeric Adsorbents

Non-polar, hydrophobic organic polymers have been developed for the sampling of organic compounds. Two commonly used adsorbents are Tennax and Amberlite XAD-2, made of poly(2,6-diphenylene oxide) and poly-aromatic resin respectively. Tennax GC is used for volatile compounds while Amberlite XAD-2 is applied for semi-volatile compounds.

2.5.2.4 Reactive/Colorimetric Adsorbents

This type of tube is filled with a coated granular material. The coating is a substance that will react with a single pollutant and stain the inside of the tube as the sample is drawn through the tube. The length of the stain or the intensity of its colour is proportional to the
concentration of the pollutant. Disadvantages of colorimetric tubes is that they substance-specific and cannot be used as a general adsorbent.

2.6 SAMPLING PROCEDURES

2.6.1 Preparation of Adsorption Tubes – Identification of Selected VOC’s

Sampling tubes were prepared by loading 100 mg of Tennax TA between two silanized glass wool plugs in a glass tube, 78 mm long and with a 4.8 mm i.d. (6 mm o.d). These specific tube dimensions were chosen so as to allow the tube to be fitted directly into the Hewlett Packard 5890 gas chromatographic injection port where desorption could be carried out directly onto the column. This method was chosen in order to allow the detection of as many compounds as possible. The ends of the tubes were sealed with custom-made Teflon end caps before and after sampling. The caps were made by cutting 50 mm strips of Teflon tubing, with 5 mm i.d. and 1.5 mm thick walls, and folding the ends over to seal the tube. Galvanized wire (1.5 mm thickness) was tied around the fold to keep it sealed.

2.6.2 Preparation of Adsorption Tubes – Quantification of Selected VOC’s

Quantitative analyses were performed in order to determine the concentrations of specific high priority pollutants, i.e. those considered to be most toxic. The types of compounds that were analysed for were aromatics such as benzene and toluene, as well as halogenated VOC’s such as chloroform and perchloroethylene.

Sampling was performed in a similar manner as described for the qualitative study, with
the exception of the following modifications: the sample tubes used were made of borosilicate glass, 200 mm in length (3 mm i.d., 5 mm o.d.) with a tapered end (to allow solvent desorption into narrow-necked receiving tubes). The intake end was tapered in a Bunsen flame to facilitate solvent desorption into narrow-necked vials. The tube was filled with 300 mg of Carbotrap C (20/40 mesh) - between two silanized glass wool plugs, followed by 200 mg of Carbosieve S-111 and a third glass wool plug to keep the adsorption train in place. When a tube containing more than one of the above adsorbents is used, samples are adsorbed in a weak (Carbotrap C) to strong (Carbosieve S-111) adsorption train. Desorption is performed in the reverse direction. This methodology prevents large molecules from being permanently adsorbed onto strong adsorbents that would result in some loss. Longer sampling tubes were used to minimize breakthrough (non-retention of VOC’s due to too short a length of adsorbent). Each tube was marked using a vibrograver to aid differentiation and identification.

End caps for the tubes were prepared by drawing ordinary glass rods in a Bunsen flame so that they fit the 3 mm i.d. tubing with a little room to spare. Teflon tape was wound around the glass to ensure a tight fit that would seal the tubes to prevent ingestion of VOC’s or the escape of adsorbed compounds. Teflon tape was wound tightly around the capped ends of the adsorption tubes as a further precaution.

All adsorbent tubes were thermally pre-treated (activated) by heating at 250°C for 3 hours in a stream (30 mL/minute) of pure nitrogen. This step both activates and cleans the adsorption tubes of any remaining compounds that might still be bound to the packing. Tubes were tested for complete desorption by re-insertion into the gas chromatographic
injector after this heating period, and no carry-over analyte peaks were detected.

2.6.3 Evaluation of Sampling Tubes - Breakthrough Tests

Breakthrough tests were carried out by spiking glass wool fixed in a 5 mm i.d. glass tube connected to the front of the first adsorption tube with 50 μL of a standard (made up in methanol) that was 1000 ppm (mg/L) in the following compounds:

- acetone
- acetaldehyde
- allyl chloride
- benzene
- butylbenzene
- carbon disulphide
- carbon tetrachloride
- chloroform
- cyclohexane
- chlorobenzene
- dichloromethane
- ethyl acetate
- hexane
- toluene
- trichloroethylene
- tetrachloroethylene
- tetrahydrofuran
- xylene

All the compounds used in the standard were of AR-grade. Various flow-rates were used to check for breakthrough. Breakthrough only occurred at flow rates greater than 80 mL/minute after 90 minutes.

2.6.4 Evaluation of Carbon Disulphide Solvent Desorption Efficiency

The desorption efficiency of the carbon disulphide solvent was determined as follows:

1. The following apparatus was set up: three tubes, in-series, were linked using Tygon tubing. The first tube contained only glass wool, while the second and third tubes were adsorption tubes used for qualitative trace gas analyses. A volume of 2.50 μL of a 100 μg/mL VOC (obtained from SUPELCO, Bellefonte, USA standard) was injected into the front tube containing the glass wool.
3. The VOC’s were evaporated with a stream of pure dry nitrogen flowing at 40 mL/minute at room temperature. The evaporation time was 120 minutes.

4. The adsorption tubes were desorbed with carbon disulphide (triplicate flushes using 0.300, 0.300 and 0.400 mL of carbon disulphide, respectively).

5. The remaining carbon disulphide was allowed to evaporate in a stream of nitrogen at room temperature for 10 minutes.

6. The two adsorption tubes (placed after the tube used to evaporate the VOC standard) were placed in the gas chromatograph in order to thermally desorb any adsorbed material that remained. The results of this test showed that no analytes remained except for a small amount of benzene which was likely to have been introduced via the solvent as a contaminant - it was thus assumed that the desorption efficiency would be suitable for this method.

2.6.5 Collection of Ambient Air Samples

Qualitative analyses

Sample volumes of up to 30 L were collected at 200 mL/minute for the qualitative analyses. Teflon tubing of 5 mm i.d. was used to transport the sample from ‘head height’ to the cooled adsorption tube in an icebox. After completion of sampling, the tubes were stored in ice inside a polystyrene cooler box.

Samples were collected 1.5 – 1.8 m above the soil in order to simulate the position of air being breathed by a standing person in the standing position. Gas flow rates during sampling were measured by using a Gillian “Gilibrator” primary flow calibrator.
(PN#800268) fitted with a bubble generator (PND800286), capable of measuring flows between 20 mL - 6 L per minute. A Gillian “Aircon 2” high volume air sampler pump, fitted with a needle valve to allow flow control, was used for sampling. Meteorological conditions, namely temperature, wind direction and approximate velocity, were noted on each sampling trip. Two “in series” tubes were used, the back one as a breakthrough tube to collect any substances that did not get adsorbed in the front tube due to adsorbent saturation. The sampling apparatus is shown in Figure 2.2.

Figure 2.2 Ambient air sampling

**Quantitative analyses**

Ambient air samples for quantification were collected at a flow rate of at 60-120 mL/minute. Higher flow rates (±200 mL/minute) were used during the sampling of ambient air samples so as to sample larger volumes of air. VOC’s were expected to be
present in lower concentrations in ambient air than in sub-surface air as suggested by a comparison of corresponding peak areas in the chromatograms during the qualitative study. Flow rate calibrations were carried out before sampling using a packed tube similar to the actual sampling tubes to simulate the resistance of the packing, thus maintaining the same flow rate for the sample. Sampling times ranged from 80 to 120 minutes. Tubes were capped immediately after sampling was complete.

As tests indicated that breakthrough does not occur at the flow rates and sampling times with the shorter sampling tubes used in the qualitative study, it was not unreasonable to assume that no breakthrough would occur when using the longer sampling tubes.

Blank samples were treated a similar routine to the samples, with the exception that air was drawn through them with the pump; the blank tubes were capped during “sampling time” to prevent diffusion of VOC’s into the tube from the surrounding air.

2.6.6 Collection of Sub-surface Samples

Sub-surface samples were taken from within the landfill. Holes were made in the landfill by percussion drilling using a 4 kg hammer and a 2 m steel pole (diameter = 50 mm) sharpened at one end. A crossbar was welded 10 cm from the top to facilitate extraction by upward blows of the hammer. The depth of the holes ranged from 1.0 - 1.5 m. Samples were collected as deep as possible within the holes by inserting a 5 mm i.d. Teflon tube into the hole. Samples were drawn up the tube and through the adsorbent (chilled as described for ambient air sampling in Section 2.6.5). Occasionally, especially
after heavy rains, it was required that the samples be taken shallower in the holes as leachate collected in the hole and its level would gradually rise.

The holes were covered during sampling by packing bricks around the tube to prevent mixing of external landfill gas and air down in the bottom of the holes. Fortunately, a positive pressure was always present within the holes, as evidenced by bubbling of the leachate.

After the sample collection was complete, the tubes were capped to prevent loss of volatiles and/or adsorption of extraneous contaminants. The sub-surface sampling method for the qualitative study is illustrated in Figure 2.3.

Flow rates were approximately 20 mL/minute, and while sampling times approximately 90 minutes. Exact flow rates and sampling times were recorded. Adsorption tubes were covered in aluminium foil, and stored at low temperatures (0°C or less) until analysis.

The manufacturers of the adsorbents (Carbotrap C and Carbosieve S-111) claimed that samples could be collected at ambient temperatures due to the strength (adsorptive capacity) of these substances.
During the quantitative sampling periods, the sampling apparatus used was similar to that shown in Figure 2.3 except that the cooler box was omitted and the aluminium foil-covered adsorption tube was fitted to the air intake end of the tube connected to the sampling pump. Flow rate calibrations were carried out before sampling using a packed tube similar to the actual sampling tubes to simulate the resistance of the packing. Sampling times ranged from 80 to 120 minutes. Flow rates were maintained at between 40
and 60 mL/minute for the sub-surface samples where VOC’s were expected to be present in higher concentrations than in the ambient air.

In order to prevent loss of VOC’s, sample tubes were stored in a deep-freeze until analysis, this being carried out as soon as possible after sampling.

2.7 DESORPTION PROCEDURES

In this research, qualitative analyses were performed by whole tube desorption while solvent desorption was used for quantitative analyses. The procedures are outlined below in the next two subsections.

2.7.1 Thermal Desorption – Qualitative Analyses

Samples were removed from cold storage and allowed to warm to room temperature. The gas chromatograph was prepared for analysis. The gas chromatographic insert tube was removed and the carrier gas turned off. The adsorption tube was inserted in this position, the insert cover was replaced, the carrier gas flow was restored, and the temperature programs for the oven and the injector were initiated (Table 2.2). Once the analysis was complete the injector was rapidly cooled by running a small stream of liquid nitrogen into an orifice made in the glass wool insulation surrounding. Injector-cooling time was reduced from about 5 to 12 minutes in this way.

2.7.2 Solvent Desorption – Quantitative Analyses

Desorptions were done using the solvent extraction method as illustrated in Figure 2.4. Carbon disulphide was selected as the solvent for desorption since it dissolves and elutes
all the VOC’s of interest.\textsuperscript{34} It has a low boiling point (46.3°C) and a high vapour pressure (360 mm Hg/6800 Pa at 25°C).\textsuperscript{38} (WARNING: The use of carbon disulphide should be restricted to well ventilated spaces to prevent poisoning). Methanol and dichloromethane were also tested as desorption solvents but were found to give poor chromatographic separation by interfering with the chromatographic process – these tended to temporarily function as undesirable polar stationary phases in the column prior to reaching their boiling points. Desorptions were performed in a room fitted with a strong extractor fan able to remove carbon disulphide vapours.

The carbon disulphide (1.00 mL) was injected into the tubes in 100 μL aliquots using a microsyringe. Three to four aliquots were added to each tube before the solvent was displaced from the tube by applying a positive air pressure (induced by squeezing a plastic bulb that fitted the tube closely). Vials (2.5 mL) were used to collect the extractions were and sealed with a Teflon coated seal held in place by a screw-on lid.
2.8 ANALYTICAL PROCEDURES

2.8.1 Identification of VOC’s

A Hewlett Packard 5890 series II gas chromatograph, fitted with a mass selective detector (Hewlett Packard 5972), was used for analyses. A Supelco BP 5 capillary column suitable for the analysis of a wide range of compounds (medium polarity stationary phase) was used. The low starting temperature (-10°C) was chosen to allow very volatile species (such as propane) to separate while less volatile species were cold-trapped at the front of the column. The carrier gas, helium, was switched off prior to the removal of the injector insert and switched on again once the adsorption tube had been inserted - in this way, sample loss to the atmosphere was minimized. The oven was cooled with either CO₂ or liquid N₂. When using CO₂, the cryogenic inlet on the GC-oven was used, while liquid nitrogen was placed in a custom-built aluminium foil bath directly into the oven. The oven fan was turned off when the baths were filled, and started again once the door was closed - the oven would reach sub-zero temperatures within three to four minutes. The final oven temperature of 200°C was chosen to ensure desorption of non-volatile compounds. Table 2.2 lists the gas chromatographic settings used for the qualitative analyses.
Table 2.2 Instrument parameters for qualitative analysis of VOCs at the iBayi landfill site

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Injector:</strong></td>
<td></td>
</tr>
<tr>
<td>initial temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>initial hold time</td>
<td>none</td>
</tr>
<tr>
<td>heating rate</td>
<td>300°C/minute</td>
</tr>
<tr>
<td>final temperature</td>
<td>220°C</td>
</tr>
<tr>
<td>final hold time</td>
<td>50 minutes</td>
</tr>
<tr>
<td><strong>Column:</strong></td>
<td></td>
</tr>
<tr>
<td>initial temperature</td>
<td>-10°C</td>
</tr>
<tr>
<td>initial hold time</td>
<td>2 minutes</td>
</tr>
<tr>
<td>heating rate</td>
<td>4°C/minute</td>
</tr>
<tr>
<td>final temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>final hold time</td>
<td>10 minutes</td>
</tr>
<tr>
<td><strong>Total run time</strong></td>
<td>64.5 minutes</td>
</tr>
<tr>
<td><strong>Column length</strong></td>
<td>30 m</td>
</tr>
<tr>
<td><strong>Column diameter</strong></td>
<td>0.25 mm</td>
</tr>
<tr>
<td><strong>Stationary phase thickness</strong></td>
<td>0.25 μm</td>
</tr>
<tr>
<td><strong>Carrier gas</strong></td>
<td>He</td>
</tr>
<tr>
<td><strong>Carrier flow</strong></td>
<td>1.1 mL/minute</td>
</tr>
<tr>
<td><strong>Linear velocity (carrier)</strong></td>
<td>38.0 cm/second</td>
</tr>
<tr>
<td><strong>Inlet pressure</strong></td>
<td>8.8 psi</td>
</tr>
<tr>
<td><strong>Detector Settings:</strong></td>
<td></td>
</tr>
<tr>
<td>Low mass</td>
<td>20 AMU(for 10 minutes)</td>
</tr>
<tr>
<td>High mass</td>
<td>200 AMU(for 10 minutes)</td>
</tr>
<tr>
<td>Low mass</td>
<td>30 AMU(after 10 minutes)</td>
</tr>
<tr>
<td>High mass</td>
<td>300 AMU(after 10 minutes)</td>
</tr>
<tr>
<td>Temperature</td>
<td>300°C</td>
</tr>
</tbody>
</table>

*Lower masses (atomic mass units) were scanned early in the run to detect the more volatile compounds; higher masses were then scanned to detect molecular ions of the higher molecular mass compounds which eluted later.*
2.8.2 Quantification of Selected VOCs

The instrument parameters (for the Hewlett Packard 5890 gas chromatograph and its 5790 mass selective detector) used for the quantitative determination of VOC’s are listed in Table 2.3.

Table 2.3 Instrument parameters for quantitative analysis of VOCs at the iBayi landfill site.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injector: initial temperature</td>
<td>220°C</td>
</tr>
<tr>
<td>Column: initial temperature</td>
<td></td>
</tr>
<tr>
<td>initial hold time</td>
<td>40°C</td>
</tr>
<tr>
<td>heating rate</td>
<td>1 minute</td>
</tr>
<tr>
<td>final temperature</td>
<td>5°C/minute</td>
</tr>
<tr>
<td>final hold time</td>
<td>220°C</td>
</tr>
<tr>
<td></td>
<td>1 minute</td>
</tr>
<tr>
<td>Total run time</td>
<td>38 minutes</td>
</tr>
<tr>
<td>Column length</td>
<td>30 m</td>
</tr>
<tr>
<td>Column diameter</td>
<td>0.25 mm</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He</td>
</tr>
<tr>
<td>Stationary phase thickness</td>
<td>0.25 μm</td>
</tr>
<tr>
<td>Carrier flow</td>
<td>1.1 mL/minute</td>
</tr>
<tr>
<td>Linear velocity (carrier)</td>
<td>38.0 cm/second</td>
</tr>
<tr>
<td>Inlet pressure</td>
<td>8.8 psi</td>
</tr>
<tr>
<td>Detector Settings:</td>
<td></td>
</tr>
<tr>
<td>Low mass</td>
<td>20 AMU(for 10 minutes)</td>
</tr>
<tr>
<td>High mass</td>
<td>200 AMU(for 10 minutes)</td>
</tr>
<tr>
<td>Low mass</td>
<td>30 AMU(after 10 minutes)</td>
</tr>
<tr>
<td>High mass</td>
<td>300 AMU(after 10 minutes)</td>
</tr>
<tr>
<td>Temperature</td>
<td>300 °C</td>
</tr>
</tbody>
</table>
Total ion chromatograms were generated and these were manipulated further using the Hewlett Packard software (MSD Productivity Chemstation Software Revision B.01.00. and Wiley 6th Edition Mass Spectral Library: HP Product G1035A). Each analyte produced numerous mass/charge (m/z) peaks, some having a greater abundance than others. Better analytical sensitivity (and selectivity) was obtained when the area of most abundant peaks rather than the total ion peak area was used in the analysis. The peaks were plotted as m/z intensity (relative to the base peak) versus time. Table 2.4 lists the analytes and the corresponding m/z value selected for quantification.

Table 2.4 The m/z values and the retention times for each analyte

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (minutes)</th>
<th>Base Peak (AMU/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.42</td>
<td>78</td>
</tr>
<tr>
<td>2-Chloro-1,1-difluoroethene</td>
<td>1.67</td>
<td>96</td>
</tr>
<tr>
<td>Dichloropropane</td>
<td>2.06</td>
<td>39</td>
</tr>
<tr>
<td>Methylbenzene</td>
<td>2.34</td>
<td>65</td>
</tr>
<tr>
<td>Dichloropropene</td>
<td>2.69</td>
<td>75</td>
</tr>
<tr>
<td>1,1,2-Tetrachloroethane</td>
<td>3.87</td>
<td>131</td>
</tr>
<tr>
<td>Xylene*</td>
<td>4.07</td>
<td>106</td>
</tr>
<tr>
<td>Xylene*</td>
<td>4.22</td>
<td>106</td>
</tr>
<tr>
<td>Styrene</td>
<td>4.64</td>
<td>51</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>5.12</td>
<td>83</td>
</tr>
<tr>
<td>1,3-Dichloropropene</td>
<td>5.25</td>
<td>75</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>5.5</td>
<td>177</td>
</tr>
<tr>
<td>Trimethylbenzene*</td>
<td>6.41</td>
<td>120</td>
</tr>
<tr>
<td>Trimethylbenzene*</td>
<td>7</td>
<td>120</td>
</tr>
<tr>
<td>1-Methyl-4-methyl ethyl benzene</td>
<td>7.87</td>
<td>119</td>
</tr>
<tr>
<td>Butylbenzene</td>
<td>8.72</td>
<td>91</td>
</tr>
<tr>
<td>Trichlorobenzene*</td>
<td>12</td>
<td>180</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>12.14</td>
<td>128</td>
</tr>
<tr>
<td>Trichlorobenzene*</td>
<td>12.96</td>
<td>180</td>
</tr>
<tr>
<td>Hexachloro-1,3-butadiene</td>
<td>13.11</td>
<td>225</td>
</tr>
</tbody>
</table>

* Isomers that the mass spectrometer could not differentiate between
2.8.3 Methane Analyses

Methane production may vary according to the age of the waste cells that are constructed on the iBayi landfill (Section 1.3.4.1). Sixteen methane measurements were made in two series of eight determinations each. An Exotector G624p methane meter was used for the methane analyses.

2.8.3.1 Principle of Operation of the Methane Meter

For the lower explosive limit (LEL) range of 0 – 5% methane (by volume), the sample is pumped into a combustion chamber where catalytic combustion occurs (if the sample contains combustible components). The combustion chamber houses two sensors. The first sensor consists of a catalytically active metal coil surrounding an inert support. The combustible components of the sample burn resulting in a temperature change that is sensed by a second, inert sensor. The temperature change due to the combustion results in a proportional change in the electrical resistance of a Wheatstone bridge circuit. The signal is amplified and indicates the relative percentage of methane on the instrument readout.

Other combustible gases may contribute to the methane signal. Methane measurements are thus subject to errors depending on the relative amounts of other combustible gases in the sample.

For the high methane range (0 – 100%), the methane monitor uses the principle of thermal conductivity. The instrument houses two thermal conductivity sensors: a reference sensor
in a sealed air-filled chamber and a sample sensor over which a stream of the sample is pumped. Both sensors are heated to a working temperature, and the passage of the sample over the sample sensor causes it to cool down or heat up depending on its thermal conductivity. The temperature difference between the two sensors depends on the nature of the gaseous constituents of the sample and their relative abundances.

Certain gases have positive thermal conductivities relative to air (e.g. methane and hydrogen), while other gases have negative thermal conductivities (e.g. propane, butane and ethane). Such differences in thermal conductivities may result in errors in the methane reading. For example, consider the response of the methane meter to a mixture of propane and methane in air. The methane will contribute to a positive reading, but the propane will reduce that reading. Carbon dioxide, a gas frequently found in landfill gas in considerable amounts, causes a negative error in methane measurements. The manufacturers of the G 624 p Exotector claim that the negative signal behavior of the meter has been markedly reduced compared to other sensors – typically one could expect an error of 2 – 4% when a gaseous sample containing 50% methane and 10% carbon dioxide is read with the G 624 p Exotector.

Oxygen deficiencies of less than 5% in the LEL range lead to inaccurate results as the stoichiometric amount of oxygen to allow complete catalytic combustion is not available.

Another source of errors in the LEL range is catalytic poisons. Sulphur, lead or silicon compounds tend to reduce signals. Significant concentrations of halogenated compounds have a corrosive effect on the sensor as acids form during the combustion of halogenated
organic compounds.

Samples were taken by inserting the probe of the meter into the hole drilled for VOC sampling. Holes were evenly spaced over the old and newer sections of the site including the residential area on the landfill. The Exotector has two sensitivity ranges: *LEL* (*lower explosive limit*) is used for measurements of less than 5% methane (measures to two decimal places of 1 percent) while the higher range *HEL* (*higher explosive limit*) of 15-100% measures no decimal.

### 2.8.3.2 Calibration of the Methane Meter

The blank (air) setting was set to zero with air in the sample chamber on both the *LEL* and *HEL* ranges. Calibrations were performed by adjusting the calibration screw (if needed) while pumping standard test gases: 0.4% methane, 2% methane and 100% methane.

### 2.8.4 Column Performance and Reproducibility

Resolution describes the ability of the column to separate two compounds. Two cases of value in this research are well separated and poorly separated peaks. The resolution was calculated for well-separated peaks (styrene and tetrachloroethane), and poorly separated peaks (benzene and dichloropropene). The former yielded a resolution of 1.81 while the latter gave a value of 0.24. A resolution of 1.5 is considered satisfactory with the peaks being only 0.3% merged. The resolution of 1.81 is good while that of benzene and dichloropropene is very poor as the peaks are co-eluting. Co-eluting peaks may still be resolved by select ion monitoring (SIM) mass spectrometry. The most abundant high mass
ion/s should be used to avoid interferences.\textsuperscript{39} An advantage of using SIM is that a 10-100 fold improvement in detection limits is realized. The 30 m capillary column used for VOC quantification was tested for its efficiency as described by N, the number of theoretical plates per meter of column. The formula\textsuperscript{41} used to calculate N is as follows: $N = 16\left(\frac{T_R}{W}\right)^2$, where $T_R$ is the retention time of the compound and $W$ is the peak width at base. The column showed 3520 plates per meter when tested by the manufacturers using pentadecane to calculate the efficiency. If 3520 plates per meter is taken as 100%, then calculating the efficiency using tetrachloroethane and styrene in the 100 mg/L VOC standard used for calibration gave efficiencies of 105% and 79%. The column was thus working effectively for these two compounds. Dichloropropene, on the other hand, only showed 5% efficiency. The poorer the efficiency, the wider and flatter the peaks, and thus the chances of a multi-component separation are reduced. Higher temperatures improve efficiency - dichloropropene eluted in 2.5 minutes when the oven was only 47.5°C, thus explaining its poor efficiency.

Standard deviation ($s$) for five standard injections was 12.2% based on trimethylbenzene. The standard deviation was calculated using the degrees of freedom (N-1) rather than the number of observations (N) to eliminate bias when determining $s$ for small sets of data.\textsuperscript{42} The standard deviation for desorption and analysis was 14.9%.
CHAPTER 4

SUMMARY AND RECOMMENDATIONS

4.1 INTRODUCTION

In this chapter a brief discussion of the history of the iBayi landfill site is given together with a summary of the main findings of the VOC analyses. In addition, the results of complementary heavy metal analyses of the leachate (or pond-waters) and soil, together with additional analyses (pH, COD and electrical conductivity) of the leachate are also given. The current status of the iBayi landfill is then compared to the “Minimum Standards for Waste Disposal by Landfill”56 a guide to landfill management. Lastly, recommendations to the administrators of the landfill site are presented.

4.2 HISTORY AND CURRENT STATUS OF THE LANDFILL

In the early years, before leachate problems were well understood, waste was dumped into low-lying depressions and holes. During 1974, a saltpan in the iBayi area was used as a waste-dump. This poorly chosen, low-lying area where water collects, eventually became a landfill. It was receiving an estimated 600 tonnes of waste per day in 1996.

The expansion of the landfill between 1981 and 1995 can be approximated by comparing the 1995 (solid lines) and the 1981 (dashed lines) of the 20, 25 and 30 m contours in Appendix 2. Several shallow ponds and marsh areas exist in the low-lying areas (>20m). The sources of these
ponds are primarily through groundwater seepage and via streams, one of which flows in from the south-west, and the other from the south-east. The stream on the south-western side flows in through the industrial areas of Struandale, a suburb of Port Elizabeth that houses various industries. The author has observed oil floating on the surface of this stream regularly, which might have originated from the industrial area. The slip face of the active dumping area is some 300 m in length and 8 –10 m in height (April 1997). The active portion of the site is illustrated in Appendix 2.

4.2.1 Relation to Nearby Communities

Formal and informal housing surrounds the site. The formal housing is located on the south-eastern, eastern and north-eastern sides of the landfill. The nearest formal houses are some sixty metres away from the landfill to the east.

Informal housing surrounds the landfill, starting from the south-east, clockwise around to the northwest. The informal housing is located on, immediately adjacent to, and near the landfill. Photographs in Appendix show these houses.

The designation G:L:B+ describes this landfill ("G" represents general waste, "L"- large landfill, “B”-significant leachate production.). General waste is defined as follows: “General waste is a generic term applied to all urban waste that is produced within the domain of local authorities. It comprises building rubble, garden, domestic, commercial and general dry industrial wastes. It may also contain small quantities of hazardous substances dispersed within it, for example lead acid batteries, insecticides, weed killers and medical waste discarded on domestic and
commercial premises. The “B” classification (significant leachate production) is due to the selection of the site - it is located in a salt pan into which water drains both naturally and from a blocked sewerage pipe. (Appendix 2 shows the topographic contours).

4.3 SUMMARY OF VOC ANALYSIS

4.3.1 VOC’s in the Ambient Air and the Landfill Gas at the iBayi Landfill

A wide variety of compounds were detected in both the ambient air and the landfill gas of the iBayi landfill. The predominant types of compounds were hydrocarbons. Aromatic hydrocarbons, aliphatic hydrocarbons, natural hydrocarbons, ketones, and chlorinated hydrocarbons were common to both the ambient air and the sub-surface samples. Aldehydes and benzoic acid were found in the ambient air but not in the landfill gas. Long chain fatty acids were present in the landfill gas but not in the ambient air.

Methane concentrations in the landfill gas at the iBayi site ranged from 4 and 63%. A total number of 16 sub-surface samples were analyzed yielding a mean methane concentration of 28%. A significant number of samples were collected amongst and in the informal dwellings to the south-east of the active dumping area in order to assess the potential danger of methane explosions amongst or in dwellings. The possibility of methane explosions in the future cannot be excluded.

4.3.2 Quantification of Selected VOC’s

Eighteen compounds were analyzed for, six in the ambient air and twelve in the landfill gas. The
average concentration of the compounds quantified in the landfill gas was found to be about 2.7 times greater than in the ambient air. The sums of the fractions of the maximum recommended levels (MRL’s) and the threshold limit values (TLV’s) of the VOC’s quantified averaged 65.42 and 0.95 respectively. The possibility of harmful exposure to combined VOC’s in the ambient air would be considered safe if the MRL fraction was unity or less. Equal to and above a TLV sum of unity, a person breathing that air can experience harmful affects from those VOC’s. A fraction of 0.95 means that the air is 5% from being potentially harmful. When taking the 95% confidence limit (based on the average analytical precision - Section 3.5.1) into account the combined TLV fraction may well exceed unity. Considering that the MRL fraction is thoroughly exceeded and that the TLV fraction may also be exceeded, the air may be considered potentially harmful, especially on calm days of low atmospheric pressure. Table 4.1 presents the averages of the concentrations of the compounds that were analyzed for in the ambient air and the sub-surface gas along with their TLV’s and MRL’s.

Commented [b1]: How far did you get with establishing some confidence limits on your analyses. If you could determine those, we might find that the confidence levels may in fact exceed the “safe” level.
Table 4.1  TLV & MRL values for compounds quantified at the iBayi landfill together with the average concentration of these compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Subsurface</th>
<th>Ambient Air</th>
<th>TLV</th>
<th>OSHA</th>
<th>acute</th>
<th>int.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/m³</td>
<td>ppm (v/v)</td>
<td>mg/m³</td>
<td>ppm (v/v)</td>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>benzene</td>
<td>25399.59</td>
<td>7961.76</td>
<td>Nd</td>
<td>nd</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2-chloro-1,1-difluoroethene</td>
<td>273.62</td>
<td>50.33</td>
<td>Nd</td>
<td>nd</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>dichloropropene</td>
<td>1287.84</td>
<td>266.87</td>
<td>Nd</td>
<td>nd</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>methyl benzene</td>
<td>523.44</td>
<td>138.87</td>
<td>78.05</td>
<td>20.74</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>dichloropropene</td>
<td>nd</td>
<td>nd</td>
<td>Nd</td>
<td>nd</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,1,1,2-tetrachloroethane</td>
<td>171.99</td>
<td>26.98</td>
<td>Nd</td>
<td>nd</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>xylene</td>
<td>70.1</td>
<td>16.17</td>
<td>99.8</td>
<td>23.05</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>styrene</td>
<td>65.99</td>
<td>13.64</td>
<td>62.16</td>
<td>12.88</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>1,1,2,2-tetrachloroethane</td>
<td>31.54</td>
<td>4.95</td>
<td>Nd</td>
<td>nd</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>1,3-dichloropropene</td>
<td>nd</td>
<td>nd</td>
<td>Nd</td>
<td>nd</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>bromobenzene</td>
<td>nd</td>
<td>nd</td>
<td>Nd</td>
<td>nd</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>trimethylbenzene</td>
<td>nd</td>
<td>nd</td>
<td>Nd</td>
<td>nd</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>trimethylbenzene</td>
<td>25.21</td>
<td>5.13</td>
<td>6.09</td>
<td>1.24</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>1-methyl-4-(methylthyl benzene)</td>
<td>nd</td>
<td>nd</td>
<td>Nd</td>
<td>nd</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>trichlorobenzene</td>
<td>76.94</td>
<td>10.37</td>
<td>Nd</td>
<td>nd</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>naphthalene</td>
<td>149.75</td>
<td>28.52</td>
<td>Nd</td>
<td>nd</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>trichlorobenzene</td>
<td>13.07</td>
<td>1.76</td>
<td>6.56</td>
<td>1.11</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>hexachlorobutadiene</td>
<td>nd</td>
<td>nd</td>
<td>Nd</td>
<td>nd</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

"-" indicates that no TLV or MRL was given, “nd” indicates that the compound was not detected
4.4 METAL ANALYSES AND LEACHATE PARAMETERS

To make the study more complete, the leachate and pond-waters were analysed for heavy metals and some other relevant parameters that could shed some light on the degree contamination of the water at the landfill. It should be stated here that this study was not meant to be a complete investigation of the contamination of the soil and leachate, but simply to obtain some idea of the level of contamination so that responsible recommendations can be give. Soil and pond sediments were also analysed for heavy metals as it has contact with water and may also be contaminated. Table 4.2 compares the leachate parameters and heavy metal concentrations of the iBayi landfills leachates and pond-waters with the range of these parameters found at other landfills.

<table>
<thead>
<tr>
<th>Leachate Parameter</th>
<th>iBayi</th>
<th>Other Landfills</th>
<th>TLV*</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.1</td>
<td>5.2-8.0</td>
<td>5.5 - 7.5</td>
</tr>
<tr>
<td>COD, mg/l</td>
<td>4450</td>
<td>229-40000</td>
<td>30</td>
</tr>
<tr>
<td>Conductivity, mS/m</td>
<td>3316</td>
<td>198-15300</td>
<td>250</td>
</tr>
<tr>
<td>Cd, mg/l</td>
<td>nd</td>
<td>0.005-0.02</td>
<td>0.004-0.015</td>
</tr>
<tr>
<td>Hg, mg/l</td>
<td>nd</td>
<td>&lt;0.0001-0.001</td>
<td>0.000005-0.0003</td>
</tr>
<tr>
<td>Pb, mg/l</td>
<td>0.017</td>
<td>&lt;0.04-0.087</td>
<td>0.01-0.15</td>
</tr>
<tr>
<td>Cr, mg/l</td>
<td>0.002</td>
<td>&lt;0.02-0.28</td>
<td>0.001-0.1</td>
</tr>
<tr>
<td>Ni, mg/l</td>
<td>0.008</td>
<td>0.05-0.17</td>
<td>0.04</td>
</tr>
<tr>
<td>Zn, mg/l</td>
<td>nd</td>
<td>&lt;0.05-5.6</td>
<td>0.3</td>
</tr>
<tr>
<td>benzene, µg/l</td>
<td>19500</td>
<td>&lt;1.1-7370</td>
<td>5000</td>
</tr>
<tr>
<td>toluene, µg/l</td>
<td>500</td>
<td>&lt;5-100 000</td>
<td>5000</td>
</tr>
</tbody>
</table>

* In some instances, a range of TLV values is given rather than a single value as some variance exists between values recommended by different organizations
The soil or sediment heavy metal concentrations of the iBayi landfill are compared to local river sediment metal levels in Table 4.3.

<table>
<thead>
<tr>
<th>Metal</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>iBayi</td>
<td>77</td>
<td>27</td>
<td>30</td>
<td>4.1</td>
<td>375</td>
<td>352</td>
<td>28.8</td>
<td>76</td>
<td>196</td>
</tr>
<tr>
<td>Buffalo river</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.5-30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4-28</td>
<td>5-63</td>
</tr>
<tr>
<td>Sunday s river</td>
<td>-</td>
<td>0.019-0.093</td>
<td>17.2-64.7</td>
<td>0.8-20.4</td>
<td>-</td>
<td>100-621</td>
<td>5.8-26.8</td>
<td>0.7-24.6</td>
<td>6.1-78.6</td>
</tr>
<tr>
<td>TLV (ppm)</td>
<td>2-10</td>
<td>0.8-3</td>
<td>100-600</td>
<td>36-200</td>
<td>0.3-14</td>
<td>-</td>
<td>-</td>
<td>85-530</td>
<td>200-500</td>
</tr>
</tbody>
</table>

Of all the values determined, the concentration of Hg is the most disturbing. A typical rate of soil ingestion by humans is 60 mg/day; during a year 21.92 g of soil will be thus ingested. Therefore the amount of Hg (at 375 mg/kg) that will be ingested with that soil per annum is 8.22 mg. Considering the cumulative nature of Hg in the human body, these results indicate a real health hazard. It should also be pointed out that the daily ingestion rate may well exceed 60 mg/day in informal housing since such houses are not as well sealed from the external environment as more formally structured houses.

Particulate matter emissions may originate from handling of materials and exposed surface areas at landfills. The iBayi landfill has a large, flat, raised surface that is exposed to wind. The author has experienced strong winds at the landfill on some sampling days; the dust was sufficiently unpleasant on such days and so less windy days had to be selected on which to
collect samples. Trucks and earth-moving equipment generate large amounts of dust especially on the dirt entrance road. Open waste piles are an additional source of dust.

Table 4.3 also shows a comparison of the metal concentrations in the local river sediments compared to those of the iBayi ponds along with their respective TLV’s. The concentrations of Pb and Zn in the iBayi pond sediments exceed the metal concentrations in local rivers by a factor of three, but they approximate the TLV’s. Cadmium concentrations in the sediments exceeded the TLV by a factor of approximately three while exceeding the local river concentrations by a factor of 290. Mercury was 27 times more abundant in the sediment than its maximum TLV permits, but no data was available on the local river sediments. Cr and Mn metal concentrations in the sediment were similar to local river Cr and Mn levels. The Cr and Cu levels were the only metals that were found in concentrations well below their TLV’s. In general, the heavy metal concentrations in the sediments at the iBayi landfill are significantly higher than the corresponding concentrations found in the sediments of the Sundays river and the Buffalo river. The metal concentrations in the sediments at the iBayi landfill are between 2 and 3 times higher than those reported by Talbot for the Buffalo river, and between 4 and 100 times higher than background levels for the Eastern Cape estuaries. Talbot also claims that the Papenkuils river sediments (the Papenkuils river is near Port Elizabeth) have similar levels of Cu, Pb and Zn.

### 4.5 BACTERIAL ANALYSES

Samples were taken from the streams and ponds that are located around the iBayi landfill. Appendix 7 shows the location of each sampling point. The results of the bacterial analyses are
presented in Table 4.4.

Table 4.4   Results of bacterial analyses from waters surrounding the iBayi landfill

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Faecal coli / 100 ml</th>
<th>Guideline value</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>15 000</td>
<td>0</td>
</tr>
<tr>
<td>B2</td>
<td>5800</td>
<td>0</td>
</tr>
<tr>
<td>B3</td>
<td>250</td>
<td>0</td>
</tr>
<tr>
<td>B4</td>
<td>1600</td>
<td>0</td>
</tr>
<tr>
<td>B5</td>
<td>&gt;150 000</td>
<td>0</td>
</tr>
</tbody>
</table>

The guideline bacteria levels are well exceeded, especially in Sample 5 taken near a sewerage leak. Sample B1 is predictably lower; yet still a high level, as it was taken from a pond downstream of the sewerage leak. On the western side, Sample B4 was taken near informal houses that had no sewerage network in order to remove the sewerage, thus some contamination of the water is expected.

4.6  MINIMUM REQUIREMENTS FOR LANDFILL OPERATION

4.6.1  Signposting and Access

Signs in the appropriate official languages must be erected in the vicinity of the landfill, indicating the route and distance to the landfill site from the nearest main roads. Suitable signs must also be erected on-site, to direct vehicle drivers appropriately and to control speed. A general notice board must be erected at the site entrance. This must be in the appropriate official languages, stating the names, addresses and telephone numbers of the Permit Holder and the
Responsible Person, hours of operation, tariffs and an emergency telephone number. The type of waste to be accepted must be clearly indicated.

The iBayi landfill site has only recently acquired signs designating the types of waste to be disposed of since its “closure” in mid 1997. These signs are no longer clearly visible as they have been damaged (April 1999).

Unsurfaced roads must be regularly graded and watered to control dust. The roads at the iBayi landfill are not surfaced and no dust control measures are implemented despite the close proximity of residents.

4.6.2 Controls

Waste acceptance at “G” sites requires that it be inspected to confirm its character as General.

Vehicle access in a site must be limited to a single controlled entrance to prevent the unauthorised entry and illegal dumping of waste on site. The site entrance must comprise a lockable gate which should be manned during hours of operation. At medium, large and hazardous waste sites, additional security is required after operating hours.

All sites must have the portion of the site currently in use adequately fenced and secured.

The above three requirements are not met at the iBayi landfill.
4.6.3 Security

Primarily for the purpose of protecting public health and safety, illegal scavenging and illegal residence construction should be discouraged at all waste disposal sites.

In this aspect, the iBayi site fails dismally with illegal informal housing and squatting being prevalent on the site.

4.6.4 Operating Plan

Everything pertaining to the operation of the landfill should be included in the operating plan, which is subject to regular update.

4.7 RESOURCES

4.7.1 Infrastructure

Large sites would typically have services such as water, sewerage, electricity, telephones, security as well as infrastructure such as weigh-bridges and site offices.

4.7.2 Equipment

Larger sites would have a combination of purpose-built landfill compactors, bulldozers, loaders and trucks to transport material. The iBayi site has a bulldozer, but daily cover is not applied each day. The bulldozer is periodically out of use.
4.7.3 **Staff**

A G:L:B+ site requires a landfill manager with a post-matric qualification to be the responsible person. Sufficient qualified staff and backup are required to ensure that the minimum requirements relating to operation are met.

4.8 **LANDFILL OPERATION**

4.8.1 **Principles**

Waste must be compacted and covered at the end of each day’s operations. The minimum thickness of compacted soil should be 150 mm.

4.8.2 **Methods of landfilling: General Waste**

The standard cell method, in which a cell of compacted waste is formed and is covered at the end of each day, is recommended. “End Tipping” is the method whereby waste is pushed over the edge of an advancing face. This is not permitted on a normal landfill because it results in minimal compaction, slope instability and many other problems. The iBayi site uses this approach combined with periodic covering of cells.

4.8.3 **Final Cover**

This must conform to the thickness and the cover design for the specific class of landfill. For G:L:B+ sites, the waste body must be covered by 450 mm compacted clayey soil (in 3 x 150 mm layers). Above this layer, 200 mm of topsoil is to be placed.
4.8.4 Other Elements of Operation

4.8.4.1 Control of Nuisances

**Burning of waste** is prohibited at all landfills. **Accidental fires** must be extinguished immediately. Regular fires have broken out at the iBayi landfill, and numerous waste recyclers make their own fires by burning wood and tyres for warmth or cooking and burning plastic off copper wire for recycling purposes. Smouldering fires usually persist for long periods.

Since the waste regulation in July 1997, fewer fires have been observed.

**Litter** must be contained within the site where it is subjected to high winds; moveable litter fences are a minimum requirement. The iBayi landfill is windswept and has no litter fences to contain wind-blown litter. The result is extensive relocation of plastic bags and other light items.

**Odours** must be combated by good cover applications and maintenance. If landfill gas produces the odour, it should be properly engineered and flared to alleviate odour problems.

The iBayi landfill produced foul odours prior to its restriction to accept only building rubble and garden refuse. This was primarily due to poor or no application of daily cover - rotting waste would remain uncovered for extended periods of time.

**Dust and noise** levels should be reduced. All equipment on site must conform to local authority by-laws concerning noise levels and hours of operation. Dust producing surfaces must be watered to reduce nuisance to workers and users of the facility.
Disease and vermin should be combated. It is a minimum requirement that landfill sites be kept free of vermin. Appropriate measures must be taken to eliminate or minimise these vectors such as rats or flies. The iBayi site suffers poorly in this regard: flies are prevalent - attracted by animal manure and uncovered waste, mosquitoes breed in the ponds at the base of the site. Local residents complain bitterly about the mosquito problem.

Up-slope run off must be diverted away from the waste to prevent water contamination and to minimise leachate generation.

The ponds at the iBayi site were fed from the southeast by a blocked sewerage pipe. On the west side, a storm water drain runs to the toe of the landfill where ponds form. The potential for groundwater contamination is thus augmented. Clean, uncontaminated run-off water must not be permitted to mix with, and increase the volume of, contaminated water. Here again, the improper management of the iBayi landfill allows mixing of runoff with polluted water at the toe of the landfill.

4.8.4.2 Leachate and gas management

In G:L:B+ sites, significant leachate is generated and leachate management is mandatory. The iBayi landfill has no leachate management system.

4.8.4.3 Rehabilitation

Progressive rehabilitation by means of establishment of vegetation is a minimum requirement.
This should commence on all areas where no further waste deposition will take place. Final slopes should not be steeper than 1 in 2.5 to discourage erosion. Establishment of vegetation has not been carried out; instead, the establishment of informal housing has taken place. Some final slopes on the landfill are a lot steeper than 1 in 2.5 with resultant erosion.

4.9 ADDITIONAL COMMENTS ON RECOMMENDATIONS

This section is based on the authors’ knowledge of landfills, waste and the iBayi landfill.

As a first option, the informal houses on the landfill should be relocated, as they should never have been built there in the first place. The relocation may be costly and difficult as some of these residents have lived there for over six years. Additionally, water, electricity and sewerage services were provided for the residents living on the landfill. As the landfill ages the volume of the waste can be expected to decrease as micro-organisms convert some of it into gaseous products. The reduction of the volume is likely to lead to the formation of cracks which could occur under a dwelling and leading to methane explosion, asphyxiation or “in-door air pollution”.

Should relocation not be possible, the landfill gas should be vented off amongst the informal houses that have been built on the site thereby reducing the pressure within the landfill and reducing the likelihood of landfill gas entering the dwellings. Sufficient wells should be put in place to vent most of the gas. The wells should have vent pipes that are connected to allow flaring of the gas. An education program for the residents would prove invaluable as they could be alerted to the dangers involved and the merits of leaving the venting system intact.
A responsible member of the community should be elected as the “responsible person” who may then report any new developments to officials. This person should be educated in the “minimum requirements for landfills” so that he may work with the officials to achieve an optimum solution. A checklist of all outstanding minimum requirements should be drawn up, prioritised and strived for. The work required should be done by people who live in the area to make the people more responsible to improving the living conditions in the area.

A clay-lined leachate dam should be built a little north of the current slip-face of the landfill so that the leachate may be contained and thus prevent unnecessary groundwater contamination. The leachate could be circulated through the section of the landfill that is not populated to enhance decomposition of the waste.

The landfill gas, ambient air, leachate and groundwater should be periodically analysed to keep track of priority contaminant levels in case of a sudden increase that may threaten the residents’ health.

Strict monitoring (keeping of a logbook) of waste type and quantities entering the landfill should be encouraged to prevent any hazardous materials being disposed of at this site. Sturdy entrance gates should be erected.
REFERENCES


47. Association for Toxic Substances and Disease Registry, (Internet site: 
http://www.atsdr.cdc.gov/99list.html, [contains the 1997 list and the 1999 updated list]).


Appendix 1  The Situation of the iBayi Landfill

- 20 m contour 1995
- Boundary of landfill
- Formal housing
- Informal housing
- Wetlands and ponds
- Active dumping area
- Roads
- Power lines

New Brighton

Kwaford sports stadium

Algoa College of Education
Appendix 2  A Map Showing the 1995 Contours and the Extent of the Landfill

1995

- 40 m
- 35 m
- 30 m
- 25 m
- 20 m
- 17.5 m
- 15 m

current slip face ~25 m

extent of landfill area

active working area

wetlands and ponds
Appendix 3  CH₄ Sampling Sites at the iBayi Landfill

![Map of iBayi Landfill with sampling sites labeled G1 to G18 and marked as wetlands and ponds, active dump area, and access road. The map includes coordinates 20m (1981) and 25m (1981).]
Appendix 4  VOC sampling sites for Ambient air and Sub-surface samples (H = sub-surface gas, A = ambient air)
Appendix 5  Location of the Sediment/Soil Sampling Sites at the iBayi Landfill

![Map of the iBayi Landfill showing the location of sediment/soil sampling sites, wetlands, and active dump areas. The map includes markers for S1, S2, S3, S4, S5, and S6, with a legend indicating wetlands and ponds, and an active dump area. The map also notes the access road and a scale of 500 m.]
Appendix 6   Location of Water Sampling Sites for Bacteria Analyses

- Wetlands
- Ponds
- Active dump area

Map showing locations B1, B2, B3, B4, B5, Sewerage Leak, and W6.
Appendix 6 Location of Water Sampling Sites (VOC & Metal Determinations)

- W1
- W2
- W3
- W4
- W5
- W6

- Wetlands
- Active dump area
- Access road
Appendix 7  Location of Water Sampling Sites for Bacteria Analyses

[Map showing various locations labeled B1, B2, B3, B4, B5, and B6, with areas marked as wetlands and ponds, active dump area, and sewerage leak.]

Wetlands and ponds
Active dump area
Sewerage Leak
Access road

B1
B2
B3
B4
B5
W6

20 (1981)
20
Appendix 8  Pictures of the iBayi Landfill

A northeast view from the slipface – note the ponds at the toe of the landfill.

A northerly view from the active dumping area. (note that the dwellings on the left are on an old section of fill)