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POTENTIAL SOLUTION TO POLLUTION OF GROUNDWATER BY DIFFUSION OF VOLATILE ORGANIC COMPOUNDS THROUGH THE PRIMARY HDPE GEOMEMBRANE IN COMPOSITE LINING SYSTEMS OF LANDFILLS

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PROJECT REPORT SUMMARY

POTENTIAL SOLUTION TO POLLUTION OF GROUNDWATER BY DIFFUSION OF VOLATILE ORGANIC COMPOUNDS THROUGH THE PRIMARY HDPE GEOMEMBRANE IN COMPOSITE LINING SYSTEMS OF LANDFILLS

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Waste production is not a modern concept. It has always been a byproduct of human beings' use of the earth's natural resources for survival.

The safe and reliable long-term disposal of solid waste residues is an important component of integrated waste management. Solid waste residues are waste components that are not recycled, that remain after processing at a material recovery facility, or that remain after the recovery of energy. Historically, solid waste was placed in depressions in the soil of the earth's crust through a process called landfilling.

In South Africa, most waste produced by households and industries is disposed of on landfill sites. By law, all landfills and waste containment structures are required to have an engineered containment barrier installed that adheres to the minimum standards described in the waste classification and management regulations of the South African National Environmental Management: Waste Act (Act 59 of 2008).

When waste materials in a landfill or any other waste body is exposed to the chemicals and heat generated over time, they produce harmful fluids in the form of leachate or landfill gas that migrate from the landfill towards the liner or capping, and include organic contaminants. These organic contaminants include a group commonly referred to as volatile organic compounds (VOCs) that have been known to migrate to and pollute the underlying groundwater (Prosser & Janechek, 1995).

The High Density Polyethylene (HDPE) Geomembrane is often believed to be the primary barrier to contaminant transport, but the clay component in the composite liner usually controls the rate of transport of VOCs since researchers like Edil (2003) have shown that VOCs diffuse through geomembranes at appreciable rates. Therefore, the effectiveness of modern landfill liner systems in minimising the migration of VOCs merits scrutiny.

The aim of this study was to obtain reliable data on the reduction in diffusion of VOCs through the HDPE geomembranes (GM) component in the composite liner systems of landfills by extracting air through the leakage detection layer or drainage layer of the composite liner. The objective was to undertake tests in three phases:

- Phase 1 aimed to prove that the chosen VOCs diffuse from source to receptor through a GM layer and to compare this to the results obtained from the literature.
- Phase 2 aimed to prove that, even if the separation between the source and receptor consisted of two GMs separated by an air-filled pervious zone, diffusion of the VOCs would still occur from the source to the receptor volumes.
- Phase 3 aimed to prove that, by introducing airflow into the pervious zone between the two GMs, the concentration of VOCs in the receptor volume (due to diffusion through the GM) could be reduced significantly. The testing in this phase also aimed to determine if the rate of air removal would play a role in the diffusive process and the resultant VOC concentrations in the receptor.

Laboratory tests were carried out at the South Campus of the University of Pretoria in South Africa. The tests undertaken were based on the methods used by Prof Kerry Rowe at the Geo-Engineering Centre at the Queens University in Kingston, Canada as demonstrated during a visit to their facility. To undertake these tests it would be required to calculate the Sorption (S_{gf}) and Diffusion (D_g) coefficients for the compound and GM in question. Sorption/Immersion, Diffusion and Weight Gain tests were done to determine the sorption coefficient for the GM and permeant in question. The Diffusion coefficient (D_g) was inferred using the variation in source and receptor concentrations with time (Fick's second law) at the given boundary conditions. This was done using POLLUTEv7®, which solves the one-dimensional contaminant migration equation subject to boundary conditions at the top and bottom of the GM being modelled. The data entry

into POLLUTEv7® includes information such as thickness and density on the layers to be modelled as well as the boundary conditions to be used for modelling.

Phase 1 testing had challenges and limitations but it met its objective of proving that the VOCs in question diffuse from the source, through the 2 mm GM, into the receptor that represents groundwater, at rates that were comparable to those found in literature.

Phase 2 tests took longer to reach equilibrium since the sorption and diffusion process had to take place over two GMs and the 0.8 cm air-filled pervious zone. The temperature under which phase 2 tests were undertaken was higher than that of phase 1 and, as indicated by literature, diffusion occurs faster at elevated temperatures. Undertaking the tests at different temperatures was not on purpose but rather a factor of laboratory conditions and setup. Data on the diffusion across two GMs separated by air, was not readily available to compare the difference that the increased temperature had on the system, but Phase 2 testing successfully met its aim of proving that the diffusion of BTEX and Chloroform takes place from source to receptor across a divide consisting of two 1 mm GMs separated by an air filled pervious zone.

Phase 3 testing showed that, even though the optimal rate of airflow would require additional testing, introducing a flow of air through a pervious zone adjacent to the GM layer in a landfill liner would significantly reduce the concentrations of VOCs in the groundwater beneath landfills and waste containment facilities.

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LIST OF ABBREVIATIONS AND ACRONYMS

BTEX	Benzene, Chloroform, Toluene, Ethylbenzene, Xylene
EVOH	Ethylene Vinyl Alcohol
GC	Gas Chromatograph
GC-FID	Gas Chromatography–Flame Ionisation Detector
GC-MS	Gas Chromatography–Mass Spectrometry
GCL	Geosynthetic Clay Liners
GM	Geomembranes
HDPE	High Density Poly-Ethylene
LDPE	Low Density Poly-Ethylene
LFG	Landfill gas
MS	Mass Spectrometry
MSW	Municipal Solid Waste
POC	Programmed On Column
PSI	Programmed Split/Splitless Injector
USEPA	U.S. Environmental Protection Agency
VOC	Volatile Organic Compounds

CHAPTER 1. INTRODUCTION

1.1 BACKGROUND

Waste production is not a modern concept. It has always been a byproduct of human beings' use of the earth's natural resources for survival. According to the South African National Environmental Management: Waste Amendment Act (Act 26 of 2014), the definition of waste is:

> *"any substance, material or object, that is unwanted, rejected, abandoned, discarded or disposed of, or that is intended or required to be discarded or disposed of, by the holder of that substance, material or object, whether or not such substance, material or object can be re-used, recycled or recovered".*

Until the 1980s, many countries were dumping and disposing of waste in an uncontrolled manner, but by the 1990s many countries started to introduce control measures and regulations for waste disposal. Today, almost all countries have strict regulations and laws on the management and containment of waste.

On a national level in South Africa, waste management is regulated by the Department of Environmental Affairs (DEA). In the 1990s, when active regulation of waste management activities started in South Africa, waste management fell under the then Department of Water Affairs and Forestry, and in its series of documents, referred to in the industry as the Minimum Requirements, it produced a set of guidelines for the industry that is still in use. The Minimum Requirements addressed many aspects of waste management, including a minimum standard for containment barrier design depending on the waste type being disposed of. The Minimum Requirements has since largely been replaced by the National Environmental Management Waste Act (Act 59 of 2008) and its associated Waste Classification and Management Regulations, but portions of the Minimum Requirements documents are still used by industry and authorities.

Most of the waste produced by households and industries in South Africa is disposed of on landfill sites and, under the Waste Act, landfill sites are

categorised into four main classes (Class A, B, C and D) depending on the nature and chemical composition of the waste.

By law, all landfills and waste containment structures are required to have an engineered containment barrier installed that adheres to the minimum standards described in the waste classification and management regulations of the National Environmental Management Waste Act (Act 59 of 2008).

When the waste materials in a landfill or any other waste body are exposed to chemicals and heat that are generated over time, they produce harmful fluids in the form of leachate or landfill gas (LFG). LFG and leachate migrate from a landfill towards the liner or capping, and take organic contaminants with them. These contaminants, commonly referred to as volatile organic compounds (VOC), have been known to migrate to and pollute the underlying groundwater (**Prosser & Janechek, 1995**).

A U.S. Environmental Protection Agency (USEPA) report that characterised landfill leachates from more than 200 Municipal Solid Waste (MSW) landfills found that organic compounds such as Ethylbenzene, Toluene and Benzene were present in over 50% of the leachate samples tested (**USEPA, 2000**) and the professional community at large acknowledges that most, if not all, landfill leachates contain harmful organic compounds.

The advent of new technology has led to many accomplishments in the design and installation of landfill lining systems. Geosynthetic Clay Liners (GCL), an array of geotextiles and various shapes and sizes of High Density Polyethelyne (HDPE) liners extensively contribute to the safe containment of waste. However, there is no such thing as a perfect liner and, with time, VOCs migrate through the intact liner into the groundwater, mainly due to advection and diffusion (**Sangam, 2001**).

1.2 PROBLEM STATEMENT

Most modern landfills and waste containment facilities employ a composite liner system consisting of a geomembrane overlying a compacted clay layer or, more commonly nowadays, a GCL. Because leachate and LFG are produced at these facilities and because they contain VOCs in the gas and liquid phases, it is

conceivable and probable that leachate and LFG could be a source of low-level VOC contamination of groundwater. This is a relatively recent challenge that could have an effect on the way landfills are designed, operated and closed.

The High Density Polyethylene (HDPE) geomembrane is often believed to be the primary barrier to contaminant transport, but the clay component in the composite liner usually controls the rate of VOC transport since researchers like **Edil (2003**) have shown that VOCs diffuse through geomembranes at appreciable rates. Therefore, the effectiveness of modern landfill liner systems to minimise the migration of VOCs effectively merits scrutiny.

The migration of VOCs can cause a number of problems: they can migrate into and contaminate the groundwater, they can be a source of odour problems and they can infiltrate adjacent structures and can cause health risks. These contaminants include organic acids, chlorinated hydrocarbons and numerous other hydrocarbons. The contaminants of greatest concern are typically chlorinated hydrocarbons because many of them are considered a health risk at low concentrations and they are not as easily decomposed in the soil by naturally occurring aerobic bacteria (**Prosser *et. al.*, 1995**). Factors such as liner design, temperature of the liner, concentration of the VOCs in the waste and time of exposure have an influence on the diffusion of VOCs through waste containment barriers.

1.3 OBJECTIVES OF THE STUDY

The aim of this study is to obtain reliable data on the reduction in diffusion of certain VOCs through the HDPE geomembranes (GM) component in composite liner systems of landfills by extracting air through the leakage detection layer or drainage layer of the composite liner.

Various studies show that diffusion and sorption of VOCs increase with the increase of temperature at the landfill liner, and it is believed that with the movement of a fluid through the leakage detection system, the liner could be cooled and the landfill, as a whole, will be cooled, leading to a reduction in VOC diffusion. With the extraction of the fluid, an added benefit should be that some of the VOCs that still diffuse through the composite liner system will be extracted

with the fluid and thus further reduce VOCs in the underlying soil and/or groundwater.

Also, with the extraction of a fluid (if that fluid is liquid) in the composite liner system, the GCL could be hydrated. The benefit of a hydrated GCL is that the hydraulic conductivity is much lower than that of a non-hydrated GCL and it is thus a better-performing containment barrier (**Bouazza & Vangpaisal, 2006**).

The possible hydration (or drying, if the fluid is air) of the GCL component in the composite liner was not investigated as part of this study, which focussed on the possible removal of VOCs that diffuse through the GM layer by passing air through a void in the liner system, which would reduce VOCs in the groundwater.

The objective was to undertake tests in three phases.

- Phase 1 aimed to prove that the chosen VOCs diffuse from source to receptor through a GM layer and to compare to the results obtained in the literature.
- Phase 2 aimed to prove that, even if the separation between the source and receptor consisted of two GMs separated by an air-filled pervious zone, diffusion of the VOCs would still occur from the source to the receptor volumes.
- Phase 3 aimed to prove that, by introducing airflow into the pervious zone between the two GMs, the concentration of VOCs in the receptor volume (due to diffusion through the GM) could be reduced significantly. This phase's testing also aimed to determine if the rate of air removal would play a role in the diffusive process and the resultant VOC concentrations in the receptor.

1.4 SCOPE AND EXTENT OF THE STUDY

For the purposes of this dissertation report, the onsite conditions were replicated in a laboratory using diffusion test cells similar to those used by **Sangam and Rowe (2001)**. Similar diffusion test cells are also used by Prof Rowe at the Queens University in Kingston, Canada, to conduct diffusion tests. As detailed later in this dissertation, the HDPE GM is placed between the closed-off source and receptor volumes to test the diffusion of VOCs from the source concentration

to the receptor concentration. The leakage detection layer in the landfill was simulated by installing a centerpiece between the source and receptor, with an HDPE geomembrane on each side. It was then tested to determine whether the diffusion of VOCs through both the GM layers (as with a composite liner system in a landfill) could be reduced by passing a fluid (in this case, air) through the system.

To conduct this study, tests were initially carried out to determine the diffusion rates of certain VOCs through 1.5-mm thick HDPE and LDPE pipes (to simulate a landfill liner) installed at a hazardous waste leachate dam. Results from the field tests were unreliable for reasons described later in this report. Therefore, diffusion tests were also carried out in the laboratories of the University of Pretoria using 2-mm and 1-mm HDPE GMs and engineered diffusion test cells. All of the GMs used in this study were supplied by Aquatan (Pty) Ltd in South Africa and the diffusion test cells were built by Interlock Systems (Pty) Ltd in Pretoria, South Africa.

This study contains a literature review on work done in the field of VOC diffusion through composite liners (specifically HDPE) at landfills. From the literature study, a research programme was formulated that included an explanation on the construction and testing methods used during the study. The report also contains the test results obtained from the laboratory work and an analysis of the data before reaching a conclusion.

1.5 ORGANIZATION OF THE DISSERTATION

The chapter plan proposed for this dissertation has the following structure:

- **Chapter 1: Introduction** - a short background on landfills and landfill liners in South Africa and the role that advances in the technology of landfill liners play in the sustainability of the science. It also contains the aim and scope of the proposed study.
- **Chapter 2: Literature Review and Theoretical Framework** - the literature obtained and read in preparation for the proposed study. It consists of a theoretical background on landfill and containment liners (specifically HDPE liners) and the diffusion of VOCs through them, as well as previous tests and

studies done on the effect of VOC diffusion through liners into the underlain soil and groundwater.

- **Chapter 3: Research Design and Methodology** - the field and laboratory test methods used during the study and an explanation of the test methodology.
- **Chapter 4: Data Presentation** - test results and data obtained from the tests undertaken in the laboratory.
- **Chapter 5: Data Analysis** - an analysis and discussion of the data obtained.
- **Chapter 6: Conclusions and Recommendations** - takes the literature obtained in Chapter 2, the research design and test methodology of Chapter 3 and the analysed data of Chapters 4 and 5 into consideration to reach conclusions and to make recommendations for further studies on this subject in the future.

CHAPTER 2. LITERATURE REVIEW AND THEORETICAL FRAMEWORK

2.1 INTRODUCTION

Landfill and landfill liner technology has gone through significant developments in recent years. Waste disposal landfills (general and hazardous) have evolved from uncontrolled dumps to highly engineered structures designed to protect the environment and promote environmental sustainability. Liner technology and the relevant regulations that govern them have also evolved from rudimentary compacted clay liners to complex composite engineered lining systems comprising a range of layers such as compacted clay, geosynthetic clay liner, geomembrane, geotextiles.

Early concerns regarding composite liners typically focused on their hydraulic conductivity and their ability to limit advective transport (**Edil, 2003**) but evidence has been presented since then that highlights diffusive transport (i.e., contaminants migration driven by the difference in concentration between the upper and lower sides of the liner) as a dominant mode of transport in well-built liner systems (**McWatters & Rowe, 2009**).

Although HDPE GMs are used for a variety of applications as a barrier for contaminant transport, for the purpose of this study, the only application of HDPE investigated will be that of waste disposal landfill liner.

2.2 WASTE DISPOSAL

The safe and reliable long-term disposal of solid waste residues is an important component of integrated waste management. Solid waste residues are waste components that are not recycled, that remain after processing at a material recovery facility, or that remain after the recovery of energy. Historically, solid waste was placed in depressions in the soil of the earth's crust and this process has since been formalised into a process called sanitary landfilling. Landfills are the physical facilities used for the disposal of residual solid wastes in the surface soils of the earth and have been the most economical and environmentally acceptable method for the disposal of solid wastes (**Tchobanoglous *et al.*,**

1993). Currently, most countries are reducing waste disposal in landfills and are focusing on the alternatives to landfilling, like recycling, recovery and treatment. However, not all wastes can be recycled, treated or recovered, and landfilling will thus remain a critical component of waste management for the foreseeable future.

In South Africa, waste is classified according to the Department of Environmental Affairs' National Environmental Management: Waste Act (59 of 2008): Waste Classification and Management Regulations, as contained in the August 2013 Government Gazette No. 36784. Wastes are categorised into five types (Type 0 to Type 4) depending on the nature and composition of the waste and the total and leachable concentrations of the elements and chemical substances in the waste compared to the total and leachable concentration thresholds in the Waste Act Norms and Standards.

The Waste Act defines hazardous waste as:

> *"any waste that contains organic or inorganic elements or compounds that may, owing to the inherent physical, chemical or toxicological characteristics of that waste, have a detrimental impact on health and the environment".*

Waste can be generated from a wide range of commercial, industrial, agricultural and domestic activities and may be liquid, sludge or solid. These characteristics contribute to the degree of hazard, and are important in the ultimate choice of a safe and environmentally acceptable method of disposal.

In South Africa, landfills are grouped into four classes by the waste types earmarked for disposal (Class A, B, C and D).

- **Class A Landfills** require a minimum of a double composite containment barrier system and are meant for the disposal of hazardous wastes. The Class A landfill liner prescribed in the Waste Classifications and Management Regulations of the Waste Act is presented in **Figure 2.1**.
- **Class B Landfills** require liners that are designed for the disposal of more general waste types and must, as a minimum, contain a single composite lining system.

Waste classified as Type 1 may only be disposed of at a Class A landfill.

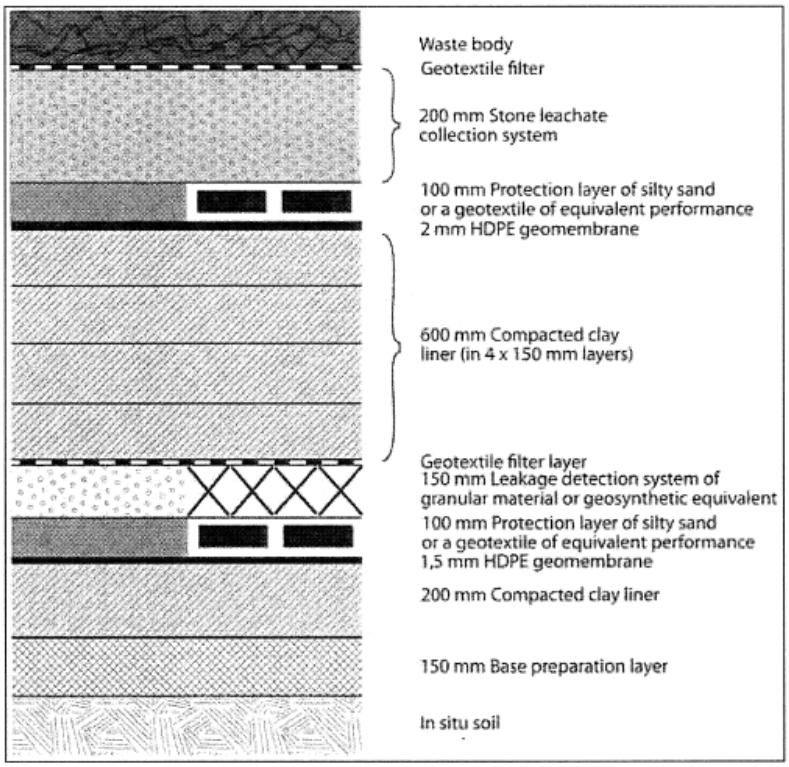


Figure 2.1: Class A (Hazardous) Containment Barrier Design Prescription

The liner detail in **Figure 2.1** is a general minimum standard and every containment facility needs to have its own fit-for-purpose engineered lining system that conforms to the Class of facility it is intended for. The layers can be replaced by other layers of equal or increased performance, and the compacted clay layers are often replaced with a GCL. The leakage detection system made up of granular material can also be replaced by a geosynthetic equivalent such as a cuspated HDPE drainage sheet. A fluid could pass through this layer in order to remove VOCs from the system and cool the liner.

2.3 LEACHATE AND LANDFILL GAS

Leachate is the liquid that results from water percolating through a landfill waste body and landfill gas is the gas that is a result of decomposition of wastes in a landfill. The presence of leachate is mainly due to precipitation falling on the landfill but can also be as a result of the liquids trapped in the waste that were

disposed of on the landfill. The amount of leachate produced is linked to the amount of precipitation around the landfill, the moisture content of the waste disposed, the frequency of dust suppression etc., and landfills in South Africa were classified by, among others, the climatic water balance of the area before changes in the landfill classification systems in 2013/14.

When water percolates through the waste, it promotes and assists the processes of decomposition by bacteria and fungi. These processes release by-products of decomposition and use up any available oxygen, thus creating an anoxic environment. In the process of waste decomposition, the temperature increases and the pH generally decreases, which results in many metal ions dissolving in the developing leachate that, under normal circumstances, would be relatively insoluble at neutral pH. The decomposition processes can also release water, which adds to the volume of leachate.

Leachates of all forms are generally capable of causing oxygen-deprived conditions in watercourses which are a risk to the natural ecology (**Tchobanoglous *et. al.*, 1993**). Leachate composition depends on factors such as:

- the type of waste material put into the landfill (household, industrial, organic or hazardous);
- landfill conditions, including pH, temperature, moisture, age and climate; and
- the characteristics of precipitation entering the landfill.

Modern landfills that can produce significant leachate or that contain waste of a certain predefined type are designed with a leachate management system that prevents most leachate from entering the groundwater. These lining systems comprise various layers, as described in the Waste Regulations.

Landfill liners that are used for leachate management normally comprise compacted clay, HDPE of various thicknesses, Geosynthetic Clay Liners (GCL) and drainage material such as gravel or crushed stone. The leachate that is generated is collected and channeled to a collection point such as a leachate collection pond, from where it can be treated to minimise its effect on the surrounding environment.

However, it is not possible to prevent all leachate from contaminating the groundwater and environmental surrounds because landfill liners could have defects that allow leachate to pass through them and it has been proven that certain volatile organic compounds diffuse through the landfill liner over time and are thus present in the groundwater (**Islam and Rowe, 2009**).

2.4 GROUNDWATER CONTAMINATION

Water is arguably our most precious resource as the lives of all people depend on the availability of clean water. The current global economic and technological growth has an inevitable adverse impact on the quality of water resources. Extensive work is underway to prevent contamination of groundwater, and technology for the treatment of water is improving rapidly, but continual efforts are needed to minimise the contamination of groundwater resources.

Emissions of pollutants to the groundwater are difficult to quantify and are relatively poorly understood. Compounds with high octanol-water partition coefficients are easily absorbed by the soil matrix and tend to be immobile, even in a leaking landfill (**Smith, 1997**). But, some of these compounds are almost completely soluble in the presence of selected solvents, which could produce considerably higher leachate concentrations in landfills than the concentrations found in the original waste being disposed. It is thus the latter tendency and the relatively incomplete understanding of the chemistry and dynamics of leachate that mitigate against any land disposal of highly toxic chemicals (**Smith, 1997**).

The best way to protect the groundwater under or near a landfill or waste containment facility from contamination is to contain the contaminants in the body of the landfill by installing an adequate engineered lining system.

2.5 HIGH DENSITY POLYETHYLENE GEOMEMBRANES

High-density polyethylene (HDPE) is a polyethylene thermoplastic made from petroleum. Known for its large strength to density ratio, HDPE is often used in the production of plastic bottles, corrosion-resistant piping, geomembranes and plastic lumber. HDPE comes in many sizes, shapes and colours and can be used to make many different products. It is also highly recyclable.

HDPE is also widely used for cell liners in sanitary landfills, wherein large sheets of HDPE (normally black) are either extrusion- or wedge-welded together to form a homogeneous chemical-resistant sheet barrier between the waste and the groundwater in order to protect the groundwater from contamination.

By weight, HDPE geomembranes consist of 96% polyethylene resin, 2-3% carbon black and approximately 0.5-1% antioxidants (**Hsuan and Koerner, 1998**). Antioxidants are added to the GM to protect it from oxidative degradation and play a key role in the lifetime of a GM.

2.6 HDPE IN LANDFILL LINERS

Landfill liners are barriers of variable size and thickness that are placed on the excavated surface of landfills and other waste containment structures to prevent the contamination of the surrounding environment. Depending on the type of waste, liners are normally made up of compacted clay, gravel, sand and artificial components such as HDPE, Geosynthetics and GCLs to form a composite lining system. HPDE geomembranes have been widely used in landfill and waste containment barriers due to their high resistance to advective flow of leachate and resistance to chemical attack (**Islam and Rowe, 2009**).

Although the focus of this study is the HDPE geomembrane, in most cases the GM is used as a barrier in conjunction with other layers of a composite lining system that is designed and engineered to be fit for purpose. HDPE GM is an integral part of the composite landfill liner and in South Africa the Department of Environmental Affairs has included HDPE GM in the engineered composite lining system as a prerequisite for the successful application of any waste licence to own or operate a waste disposal facility.

HDPE containment liners are subject to a range of manufacturing and installation specifications that have to be adhered in order to fulfill its purpose of waste containment successfully. The latest (November 2014) GRI-GM13 specifications for the manufacturing of HDPE Geomembranes, as developed by the Geosynthetic Research Institute in the USA, through consultation and review by its member organisations, sets forth a set of minimum physical, mechanical and chemical properties (see **Table 2.1**) that must be met or exceeded by the

geomembrane being manufactured. Although the GRI GM13 specification includes GMs from 0.75 mm thickness to 3.00-mm thickness, this study will focus on the use of 1-mm and 2-mm thick GMs.

Table 2.1: Specifications for Smooth GMs from GRI-GM13

Properties	Test Method	Test Value		Testing Frequency (minimum)
		1 mm	2 mm	
Thickness - mils (min. avg.) lowest individual of 10 values	D5199	nom.(mil) -10%	nom.(mil) -10%	 Per roll
Density (min.)	D1505/D792	0.940g/cc	0.940g/cc	90,000 kg
Tensile Properties (min. avg.) • yield strength • break strength • yield elongation • break elongation	D6693 Type IV	 15 kN/m 27 kN/m 12% 700%	 29 kN/m 53 kN/m 12% 700%	 9,000 kg
Tear Resistance (min. avg.)	D1004	125 N	249 N	20,000 kg
Puncture Resistance (min. avg.)	D4833	320 N	640 N	20,000 kg
Stress Crack Resistance	D5397	500 hr	500hr	Per GRI GM-10
Carbon Black Content - %	D4218	2.0% - 3.0%	2.0% - 3.0%	9,000kg
Oxidative Induction Time (OIT) (min. avg.) (a) Standard OIT — or — (b) High Pressure OIT	 D3895 D5885	 100 min 400 min	 100 min 400 min	 90,000 kg
Oven Aging at 85°C (a) Standard OIT (min. avg.) - % retained after 90 days — or — (b) High Pressure OIT (min. avg.) - % retained after 90 days	D5721 D3895 D5885	 55% 80%	 55% 80%	 Per each formulation
UV Resistance (a) Standard OIT (min. avg.) — or — (b) High Pressure OIT (min. avg.) - % retained after 1600 hrs	D7238 D3895 D5885	 - 50%	 - 50%	Per each formulation

The test methods in **Table 2.1** are standard ASTM test methods for the properties quoted.

HDPE sheets for use in landfill liners are sold in rolls of various sizes and are usually delivered to site by truck. They have to be installed on site by approved contractors under strict supervision of monitoring staff that are experienced in the specifications of the designer and manufacturer.

HDPE GMs remain fit for purpose in landfill liner applications for up to 1,000 years (**Rowe, 2005**), depending on a range of factors such as the period of exposure to active leachate, the height of waste on the liner, the chemical composition of the waste being contained and the temperature of the waste body. The temperature that the HDPE GM is exposed to has a significant impact on the service life of the HDPE and **Rowe (2005)** has shown that GM service life, based on 50% reduction in tensile strength at break, can be between 565 and 900 years when exposed to temperatures not exceeding 20°C, but can reduce to as little as 15-20 years when exposed to temperatures of more than 60°C.

Thus, for an HDPE GM in the landfill liner to be a successful barrier, it needs to be manufactured, installed and monitored according to the specifications given by design engineers and manufactures.

2.7 VOLATILE ORGANIC COMPOUNDS

Volatile Organic Compounds (VOC) are organic chemical compounds that have high enough vapor pressures under normal conditions to significantly vaporise and enter the atmosphere (**Dikshith, 2011**). Many carbon-based molecules, such as aldehydes, ketones and other light hydrocarbons are VOCs. The term may refer both to well-characterised organic compounds and to mixtures of variable composition.

Sometimes, VOCs are released into the environment accidentally, where they can damage soil and groundwater, an example being the landfilling waste and waste-related products in engineered waste disposal landfills equipped with an engineered lining system. VOCs have been shown to diffuse through the lining

systems of landfills resulting in, among other things, groundwater pollution (**Touze-Foltz *et al.*, 2011**).

Methane is the most commonly known VOC and, as a greenhouse gas, is responsible for a considerable amount of environmental pollution. Methane mostly migrates to the surface of landfills and other VOCs such as the aromatic hydrocarbons (Benzene, Chloroform, Toluene, Ethylbenzene, Xylene (BTEX)) commonly found in petroleum products that contribute most to groundwater contamination **(Prosser *et al*, 1995**).

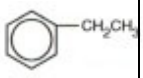
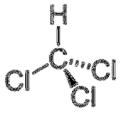
In recent years, the BTEX hydrocarbons have attracted much attention because they constitute one of the most common and serious threats to groundwater reservoirs near contaminated sites. The VOCs used for this study are BTEX (the Xylene being p-Xylene) and Chloroform. These contaminants were selected because they are commonly found in landfill leachates (**Rowe, 2005**). They are also major contributors to groundwater contamination.

Because of their polarity and very soluble characteristics, the BTEXs of petroleum products can enter the soil and groundwater systems and cause serious pollution problems (**Christensen & Elton, 1996**). Exposure to volatile organic compounds in the short and long term can be detrimental to human beings in various ways.

According to the Minnesota Groundwater Association, the United States Environmental Protection Agency (USEPA) is of the opinion that Volatile Organic Compounds from various sourcesare present in one-fifth of the USA's water supplies (**www.mgwa.org**) and in South Africa, the situation is assumed to be similar.

BTEX and Chloroform are flammable, colorless liquids and some additional characteristics are provided in **Table 2.2**.

Table 2.2: BTEX and Chloroform Characteristics as adapted from Christensen & Elton, 1996

	Benzene	Toluene	p-Xylene	Ethyl benzene	Chloroform
Chemical structure					
Chemical formula	C_6H_6	C_7H_8	C_8H_{10}	C_8H_{10}	CHCl3
Molecular weight (g/mol)	78	92	106	106	119.38
Water solubility (mg/l)	1700	515	198	152	80.9
Vapor pressure at 20°C (mmHg)	95.2	28.4	-	9.5	159
Specific density (at 20°C)	0.8787	0.8669	0.8610	0.8670	1.489
Octanol-water partition coeff. (at 20°C) (log K_{ow})	2.13	2.69	3.15	3.15	1.97
Henry's law constant [a] *k* [L (water)/L (air)] at 24°C	0.218	0.258	0.290	0.305	0.37
Polarity	Non-polar	Non-polar	Non-polar	Non-polar	Polar
Biodegradability	Aerobic	Anaerobic /Aerobic	Aerobic	Aerobic	Anaerobic/A erobic
Maximum Contaminant Level (mg/l)	0.005	1.00	10.00	0.7	

[a]**From Mcwatters and Rowe, 2010**

2.8 DIFFUSION THROUGH HDPE

Diffusion is often referred to as molecular diffusion and is a net transport of molecules from a region of higher concentration to one of lower concentration by random molecular motion.

Due to the nature of the material and how it is manufactured, intact HDPE geomembranes do not allow for any advective flow of contaminants through them, hence their widespread use in the containment of water and other liquids, although they allow movement of contaminants through them by means of molecular diffusion (**Rowe, 1998**).

The diffusive movement of contaminants through an intact GM with no faults or holes involves a cooperative rearrangement of the penetrant molecule and the surrounding polymer chain segments. For the penetrant molecule to move into the polymer structure of the HDPE, the process requires the localisation of energy to be available (**Rowe, 1998**). Thus the diffusive motion requires energy and depends on the relative mobility of the penetrant molecules in the waste or leachate and polymer chains in the HDPE. In turn, this will depend on temperature and concentration, the size and shape of the penetrant and the nature of the polymer itself (**Rowe, 1998**).

2.8.1 One Geomembrane Layer

Sangam & Rowe (2001) describe the molecular diffusion of penetrants such as BTEX and Chloroform through an intact GM as a molecular-activated process that occurs in a series of steps following the path of least resistance. For dilute aqueous solutions, as is the case in this study, this involves three steps (**Park and Nibras, 1993**):

1. **Adsorption** (partitioning of contaminant between the inner surface of the GM and medium containing the contaminant.
2. **Diffusion** of the permeant through the GM.
3. **Desorption** (partitioning of the contaminant between the outer surface of the GM and the outer medium).

For water or water-based solutions (as is the case here), the adsorption and desorption processes can be seen as similar and inverted (**Sangam and Rowe, 2001**). In the Keynote Lecture for the 6th International Conference on Geosynthetics held in Atlanta in 1998, **Professor Kerry Rowe** presented a schematic similar to the one shown in **Figure 2.2** to illustrate the diffusive transport of contaminants through a GM. The figure shows partitioning between the concentration in solution and the concentration dissolved in the GM.

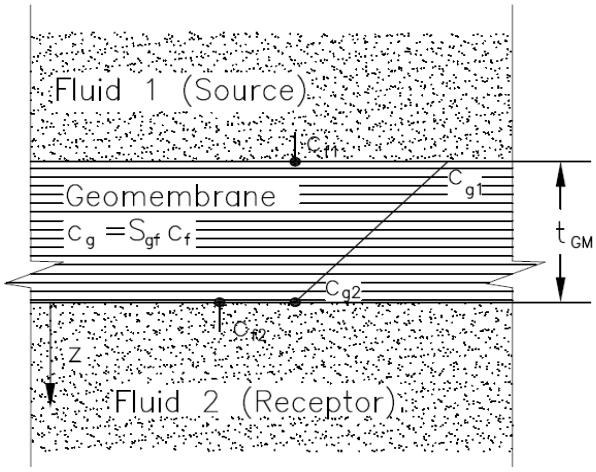


Figure 2.2: Schematic Diagram of Diffusion Through HDPE GM (adapted from Rowe, 1998).

Figure 2.2 illustrates that the process starts with the removal of the molecule from the solution onto the surface of the GM (Step 1: Adsorption). The sorption of the permeant onto the polymer (the HDPE GM) depends on a variety of factors and thus, the extent to which permeant molecules are sorbed and their mode of sorption in a polymer depend upon the activity of the permeant within the polymer at equilibrium (**Muller *et al.*, 1998**). For the simplest case where the permeant does not interact with the polymer (as is the case for a HDPE GM) or at low concentrations (as in landfill leachates), the relationship between the concentration in the fluid and the GM (solid) is given by the Nernst distribution function which takes the linear form shown in **Equation 1** (Henry's law) (**Sangam and Rowe, 2001**):

$$C_g = S_{gf} C_f \qquad \text{(Equation 1)}$$

Where S_{gf} is called a partitioning or sorption coefficient [-] and, in principle, is a constant for the given molecule, fluid, GM and temperature of interest, and C_g and C_f are the concentrations of the permeant in the GM and the fluid respectively.

Although S_{gf} is mostly given as a dimensionless value, it can also be given in units of atm/mol/l since the units are dependent on the units of expressions of the

concentration in the phases. For organic compounds in aqueous solution, like BTEX and/or Chloroform in water, the value of S_{gf} is strongly related to the solubility of the compound of interest in water (**Rowe, 1998**). The lower the solubility in water, the higher the affinity of the GM to attract the compound and thus the higher S_{gf} will be when in aqueous solution (**Rowe, 1998**). Compounds with high solubility thus generally give lower S_{gf} values.

The process ends with desorption (Step 3: Desorption), which is similar to adsorption and, for an aqueous solution in contact with a HDPE GM, it can be assumed that the above equation (**Equation 1)** also holds true, meaning the partitioning coefficient for adsorption and desorption of BTEX and Chloroform in aqueous solutions are equal (**Sangam and Rowe, 2001**).

The diffusion process in the GM happens between the adsorption and desorption processes and can be explained by Fick's first law:

$$f = -D_g \frac{\partial c_g}{\partial_z} \qquad \text{(Equation 2)}$$

Where f is the rate of transfer per unit area [$ML^{-2}T^{-1}$] (typically mg per m^2 per second), D_g is the Diffusion coefficient in the GM [L^2T^{-1}] (typically m^2 per second), C_g is the concentration of the substance that is diffusing and z is the direction parallel to the direction of the diffusion (typically the thickness of the GM).

∂_c / ∂_z is thus the concentration gradient and in transient state, allowing for the conservation of mass, the governing differential equation is given by Fick's Second Law (**Rowe, 1998**):

$$\frac{\partial c_g}{\partial_t} = D_g \frac{\partial^2 c_g}{\partial z^2} \qquad \text{(Equation 3)}$$

This equation needs to be solved for the appropriate boundary and initial conditions to obtain the Diffusion coefficient of the solution/GM system at equilibrium.

To measure the concentration change in the GM when doing diffusion tests is difficult so it is useful to express the diffusion equations in terms of the concentration in adjacent solutions (**Sangam and Rowe, 2001**). **Equation 1** gives the relationship between the concentrations in the GM and the adjacent fluid. **Equation 2** gives the flux (diffusion) within the GM, so substituting **Equation 1** into **Equation 2** gives the flux on one side of the GM to a similar fluid on the other side of a GM (**Rowe, 1998**).

$$f = -D_g \frac{dc_g}{d_z} = -S_{gf} D_g \frac{dc_f}{d_z} = -P_g \frac{dc_f}{d_z} \qquad \text{(Equation 4)}$$

Where $P_g = S_{gf} D_g$ (**Equation 5**)

P_g gives the relationship between the Diffusion coefficient and the Sorption coefficient and is referred to in polymer literature as the Permeability Coefficient (**Sangam *et al*, 2001**). This permeability coefficient (P_g) should not be confused with the soil mechanics term *coefficient of permeability*, which more often is called the hydraulic conductivity, or the intrinsic permeability of a porous medium. It has nothing to do with Darcy's law or the flow through the open voids within porous media, but accounts for the effects of both diffusion and partitioning.

Based on **Equation 5**, the mass flux across a GM of thickness t_{GM} is given by:

$$f = S_{gf} D_g \frac{\Delta c_f}{t_{GM}} \qquad \text{(Equation 6)}$$

Where $S_{gf}D_g$ can be replaced by P_g (**Equation 5**) and where Δc_f is the difference in concentration in the fluid on either side of the GM (c_{f1} and c_{f2} in **Figure 2.2**).

In general, the concentration change in the source is predominantly controlled by S_{gf} while the concentration change in the receptor is predominantly controlled by P_g (**Sangam and Rowe, 2005**). This makes sense since the higher the value of S_{gf} the more of the contaminant will sorb onto the GM leaving less concentration

in the Source, and the higher the value of *Pg* the more permeable the GM is resulting in a higher concentration in the Receptor.

The purpose is thus to determine the S_{gf} and D_g (and thus P_g) values of the system in question and compare them to the values found in the literature, before trying to prove that VOCs can be extracted successfully through a pervious zone in the liner system.

2.8.2 Two Geomembrane layers

For the purpose of this study, it is the intention to draw air through a pervious zone in the liner system, thereby removing VOCs that would have contaminated the groundwater. This is simulated by separating the source and receptor volumes using two HDPE GMs with an air void between them, as shown in **Figure 2.3** (which is adapted from **Rowe's** figure (see **Figure 2.2**):

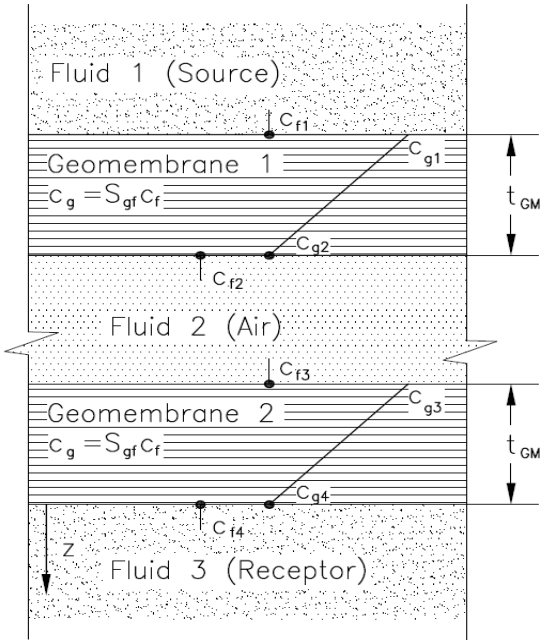


Figure 2.3: Schematic Diagram of Diffusion through Two HDPE GMs Separated by an Air Void

The two GMs will be identical and the theory applied for the calculation of the Sorption and Diffusion coefficients will remain. A study by **McWatters and Rowe (2009)** investigated the transport of VOCs (BTEX) through GMs from both aqueous and vapour phases and found that:

"diffusive transport of VOC contaminants through geomembranes in a simulated landfill environment is identical despite the phase they originated from, simplifying the analysis of contaminant transport".

This principle would be adopted in the work for this dissertation study, indicating that diffusive transport should still occur across a system similar to the description in **Figure 2.3**.

2.8.3 Coefficients in Diffusion Process

Sorption Coefficient

S_{gf} is the Henry's coefficient, and is also called a Solubility, Sorption or Partitioning coefficient (**Rowe, 1998**). It is the ratio of the concentration of the chemical in the GM at equilibrium to the concentration of the chemical in the solution in contact with the GM (**Park *et. al.*, 1993**). S_{gf} is most often unitless and, when doing diffusion tests where the concentration of contaminants in the source and receptor is monitored over time, can be calculated using **Equation 7** and can then be used to infer the diffusion coefficient (D_g) using POLLUTE®, as described later in this dissertation.

Diffusion Coefficient

The Diffusion coefficient (D_g), or so-called diffusivity, has the dimensions of [length^2 time^{-1}], which result from the underlying kinetic theory. It is a proportionally constant between the molar flux due to molecular diffusion and the gradient in the concentration of the species (or the driving force for diffusion). Generally, it is prescribed for a given pair of species, but for a multi-component system, it is prescribed for each pair of species in the system.

The higher the diffusivity (of one substance with respect to another), the faster they diffuse into each other; thus the higher the diffusion coefficient of the VOC in question, given a certain GM and concentration profile, the faster diffusion will occur through the GM into the underlying groundwater or vadose zone under landfills and waste containment facilities.

2.8.4 Calculation of the Sorption and Diffusion Coefficients

Starting with the Sorption coefficient S_{gf} which is a unitless coefficient linked to the solution/GM system in question, each fluid, permeant and polymer combination will thus have its own sorption coefficient value. When the flux across one GM is investigated, the S_{gf} value can be determined in various ways, as described by **Rowe (1998)** and **Sangam *et. al.,* (2001)**. For VOCs, however, the best method is the diffusion test method, which is the diffusion from solution on one side of the GM to solution on the other side and monitoring the change in concentration in the source and receptor over time until equilibrium is reached (no significant change in the concentrations in the source and receptor volumes). The value for S_{gf} is then calculated using the following equation (**Rowe, 1998*)***:

$$S_{gf} = \frac{C_{fo}V_s - C_{fF}(V_s+V_r) - \Sigma V_i C_i}{At_{GM}C_{fF}} \qquad \text{(Equation 7)}$$

Where:

c_{fo}	Is the initial concentration of fluid in the source reservoir [ML^{-3}]
V_s, V_r	Are the volumes of the source and receptor reservoirs [L^3]
C_{fF}	Is the final equilibrium concentration in the source and receptor reservoirs [ML^{-3}]
$\Sigma V_i C_i$	Is the mass removed by sampling events [M] (V_i and c_i being the volume and concentration removed at each sampling event)
A	Is the area of the GM through which diffusion occurs [L^2]
t_{GM}	Is the thickness of the GM [L]

S_{gf} can also be calculated by doing either of two forms of immersion tests. One way is weight gain method where immerse a piece of GM is immersed in the leachate solution and the weighed at determined intervals to measure the weight gain until equilibrium.

This method for determining the sorption coefficient is faster than alternative test methods but each chemical needs to be examined separately. It is suitable for pure solvents but is generally not the first choice of method when working with VOCs since the possibility of errors due to losses during weighing is high.

The increase in mass of a GM immersed in the fluid of interest is monitored from an initial value of m_0 until reaching equilibrium at m_∞. Once the masses are all measured, a plot is made of $(m_t - m_0) / (m_\infty - m_0)$ VS $\sqrt{t}$ where m_t is the mass at a given time and t is the time. The coefficient S_{gf} is then calculated using the equation:

$$S_{gf} = \left(\rho_g / C_{Ff}\right)\left((m_\infty / m_0) - 1\right) \qquad \textbf{(Equation 8)}$$

Where:

ρ_g = Geomembrane Density

C_{Ff} = Final equilibrium fluid concentration

The other method of immersion testing is the sorption test method where the GM is immersed in the leachate solution and samples of the leachate solution are extracted at given intervals and the concentrations are measured with a Gas Chromatograph until equilibrium. **Equation 9** is then used to determine S_{gf}.

$$S_{gf} = \frac{(C_{fo}V_{f0} - C_{fF}V_{fF})\rho_g}{M_g C_{fF}} \qquad \textbf{(Equation 9)}$$

Where C_{fo} and C_{fF} are the initial and final concentrations of the solution, respectively, V_{f0} and V_{fF} are the initial and final volumes of the solution, respectively, ρ_g is the GM density and M_g is the initial mass of the GM.

Theoretically, immersion tests or diffusion tests to calculate S_{gf} will have the same result if all the parameters can be controlled, but under the normal variation

in laboratory conditions, this is unlikely. When using the same GM and VOC in question, the values for S_{gf} obtained through sorption tests can be used to infer the diffusion coefficient using POLLUTEv7®. However, equilibrium will be reached faster using the immersion test since the GM is surrounded by the leachate solution, thereby allowing sorption from all sides.

The Diffusion coefficient (D_g) is then inferred by using **Equation 3** and the variation in source and receptor concentrations with time (Fick's second law) at the given boundary conditions. This is done using POLLUTEv7®, which solves the one-dimensional contaminant migration equation subject to boundary conditions at the top and bottom of the GM being modelled (**Sangam *et. al.*, 2005**). There are three possible top boundary conditions: zero flux, constant concentration, and finite mass.

The top boundary is the point of contact between the source and the GM. The bottom boundary (the point of contact between the GM and receptor) may be zero flux, constant concentration, fixed outflow or infinite thickness, depending on the conditions.

2.8.5 Experimentally Determined Diffusion and Partition Coefficients from Literature

Values of the Sorption coefficient S_{gf} and the Diffusion coefficient D_g, based on the literature are summarised in **Table 2.3**. Only values for BTEX (with the X being p-Xylene) and Chloroform using 1 mm or 2 mm GMs are given since they are the VOCs and GMs used in this study.

Table 2.3: Sorption and Diffusion Coefficients from Literature (D_g in m^2/s)

Source	Notes	Benzene		Toluene		Ethylbenzene		P-Xylene		Chloroform	
		S_{gf}	D_g	S_{gf}	D_g	S_{gf}	D_g	S_{gf}	D_g	S_{gf}	D_g
Mueller *et. al.* (1998)	1 mm GM using diffusion and immersion tests			160	$0.2x10^{-12}$			556		0.134	$5.9x10^{-12}$
Prasad *et. al.* (1994)	1 mm GM using immersion method	57.2	$0.04x10^{-12}$	192	$0.51x10^{-12}$			498			
Sangam and Rowe (2001)	2 mm GM	30	$3.5x10^{-13}$	100	$3.0x10^{-13}$	285	$1.8x10^{-13}$	347	$1.7x10^{-13}$		
KP Chao *et. al.* (2007)	1 mm GM at 25°C	9.69	$5.3x10^{-12}$	10.35	$6.1x10^{-12}$	10.2	$4.5x10^{-12}$			9.61	$5.1x10^{-11}$
Luber (1992)	2 mm GM using Stainless steel permeation cells at 25°C										$1.7x10^{-11}$
Touze-Foltz *et. al.* (2011)	2 mm GM Diffusion tests at 22°C	51	$0.3x10^{-12}$	193							
Park & Nibras (1993)	2 mm GM Diffusion tests at 22°C			150				310			
Haxo & Lahey (1988)	2 mm GM	54		137				376			

The values in **Table 2.3** should be used with caution since they are dependent on factors such as temperature, concentration, the chemical composition of the containment source, polymer crystallinity and additives. Therefore, **Rowe (1998)** urges that published values should only be used as an initial guide and should not replace experimentally determined values for the specific GM and system in question.

2.9 POLLUTEv7® SOFTWARE

POLLUTEv7® (POLLUTE) is software that can be used to provide fast, accurate, and comprehensive contaminant migration analysis capabilities. It was first developed by R.K. Rowe and J.R. Booker in 2004. The Copyright belongs to GAEA Technologies Ltd in Canada. This program implements a one-and-a-half dimensional solution to the advection-dispersion equation (**Equation 3**).

Given the sorption coefficient normally derived from sorption or diffusion tests, the results for concentrations determined at different times are coupled with model specific boundary conditions to allow POLLUTE to infer diffusion (and partition) coefficients by fitting a theoretical solution of the diffusion equation to the data measured.

The program allows the modelling of the boundary conditions and layer data for any unique liner design to determine the flux across the system.

2.10 FACTORS INFLUENCING DIFFUSION OF VOCS

2.10.1 Temperature

Sorption, Diffusion and Permeation coefficients show an increase with an increase in Temperature (**Aminabhavi and Naik, 1998**) and the temperature dependence of the coefficients can be described by the following Arrhenius relationships, according to **Sangam *et. al.*, 2001**:

$$D_g = D_{g0} e^{\frac{-E_d}{RT}}, \qquad \textbf{(Equation 10)}$$

$$S_{gf} = S_{gf0} e^{\frac{-\Delta H_S}{RT}}, \qquad \textbf{(Equation 11)}$$

$$P_g = P_{g0} e^{\frac{-E_p}{RT}}, \qquad \textbf{(Equation 12)}$$

Where E_d and E_p are the activation energies for Permeation and Diffusion, which are laboratory-calculated values defined as the minimum energy required to start the process (usually given in kilojoules per mol). ΔH_s is the heat of the solution of the penetrant in the polymer (***Sangam et. al., 2001***), R is the gas constant and T is temperature.

Aminabhawi *et. al.* (1998*)* calculated the Activation energy values and *ΔHs* for a range of organic liquids and HDPE, although it is not clear whether it was for pure chemicals or aqueous solutions. The relevant values for the BTEX chemicals used in this study (obtained from **Aminabhawi *et. al.* (1998))** are shown in **Table 2.4**.

Table 2.4: Activation Energies and Heat Values for Certain VOCs

Compound	E_d (kJ/mol)	E_p (kJ/mol)	ΔHs (kJ/mol)
Benzene	30.9±2.3	47.6±0.2	16.7±2.4
Toluene	32.3±5.9	48.5±4.4	16.2±1.5
p-Xylene	33.1±5.4	48.4±3.5	15.3±1.9

The diffusion tests for the study by ***Aminabhawi et. al. (1998)*** took place at three different temperatures and for the applicable compounds of interest the influence on sorption and diffusion coefficients are given in **Table 2.5**.

Table 2.5: Effect of Temperature on the Sorption and Diffusion Coefficients

Compound	Sorption Coefficient (mol%)			Diffusion Coefficient (10^7 cm^3/sec)		
	25°C	50°C	70°C	25°C	50°C	70°C
Benzene	0.12	0.18	0.30	0.64	1.84	3.22
Toluene	0.11	0.17	0.26	0.68	2.40	3.62
p-Xylene	0.10	0.15	0.22	0.64	2.28	3.60

Temperature thus plays a significant role in the tempo or rate of diffusion because energy is required for diffusion to take place. Diffusion, and particularly the diffusion of VOCs through HDPE, occurs faster in higher temperatures and diffusion and permeation coefficients thus show an increase with increasing temperature (**Aminabhavi *et. al.*, 1998**).

The long-term performance of HDPE GMs depend on the selection of suitable material, appropriate protection of the GM from mechanical damage and stress concentrations, the chemistry of the contacting fluid and the temperature of materials / liquids in contact with the liner. According to **Rowe (2005)**, chemical ageing has three distinct stages:

- Stage 1: depletion of antioxidants.
- Stage 2: induction time to the onset of polymer degradation.
- Stage 3: degradation of the polymer to decrease some property (or properties) to an arbitrary level (for example, to 50% of the original value).

From the laboratory work undertaken by **Rowe (2005**), the service lives of HDPE GMs at different temperatures were estimated (see **Table 2.6**).

Rowe (2005) indicates that even with an effective leachate collection system and negligible leachate mound, the liner temperature can be expected to reach 30-40℃ for normal municipal landfill operations. With recirculation of leachate, the liner temperature increases faster than under normal operating conditions, and may be expected to be 40-45℃. Temperatures on the liner can also increase depending on the type of waste in the landfill, like the 80-110℃ reported by **Jafari, Stark and Rowe (2014)** at a monofill landfill containing Aluminum Production Wastes.

Table 2.6: Estimated HDPE GM Service Life Based on 50% Reduction in Tensile Strength at Break for Different Temperatures (Rowe, 2005)

Temperature (℃)	**Service Life (Years)**
20	565 - 900
30	205 - 315
35	130 - 190
40	80 - 120
50	35 - 50
60	15 - 20

The studies done in preparation of this dissertation had three stages of laboratory testing and were undertaken in ambient laboratory temperatures at the University of Pretoria. These temperatures ranged from 18°C to about 34°C, depending on the season.

Although HDPE GM liners in landfill applications have a shorter lifespan when exposed to the prolonged effects of an elevated temperature, and although diffusion occurs across a GM faster in higher temperatures, the laboratory temperatures in which the work for this study was carried out should not have a major effect on the outcomes of the results. It is, however, noted that values for S_{gf} and D_g can be expected to be slightly higher than the values found in literature when tests were conducted in South African Summer conditions of about 33°C.

2.10.2 Age

Islam and Rowe (2009) tested the permeation of BTEX through GMs aged in the laboratory at 85°C for 32 months and found that the diffusion and partitioning coefficients decreased with increased aging. The coefficient decrease was in the order of 36-62% and the associated increase in crystallinity during the 32 month aging period was 38-54% and 48-61% in the two GMs tested. Since the diffusion of organic compounds occurs through the amorphous region of the semi-crystalline GM, the GM crystallinity is a factor in the diffusion process.

As the crystallinity increases the amorphous zone decreases and a higher activation energy is required to drive the diffusion process. Thus, the decrease in coefficients is directly related to the increase in GM crystallinity during aging. Apart from the GM thickness (as is apparent from the Diffusion equation) of the GM and the temperature, the GM crystallinity change also plays a role in the rate of diffusion.

GMs used in the preparation of this dissertation were stored in laboratory conditions for the duration of the experimental work. The storage time (less than 32 months) and temperature (not more than 34°C) would thus not have a major effect on the crystallinity of the GM and the possible effects of HDPE aging were thus not considered.

2.11 POSSIBLE SOLUTIONS TO DIFFUSION OF VOCS THROUGH HDPE

2.11.1 Surface Fluorination

Sangam *et. al.*, (2005) and **Rowe, Mukonoki and Lindsay (2011)** studied the possibility of improving the effectiveness of a GM with regard to the permeation of organic contaminants by means of fluorination. This entailed applying a very thin (2.5 µm) layer of fluorine to the surface of the GM, as is commonly done in the polyolefin container industry to improve the shelf-life storage of hydrocarbon fluids (**Sangam *et. al.*, 2005**). Both studies found that although the fluorination makes little to no difference to the physical properties of the GM, it increased its resistance to the permeation of BTEX penetrants by about a factor of 2.4 at 22°C. They further found that the hydrophobic contaminants are most affected by the fluorination due its effect on octanol water partitioning coefficient and hence works best for aromatic hydrocarbons like BTEX.

The sorption coefficient remained effectively the same for sorption and desorption tests but the diffusion coefficient decreased depending on the thickness of the fluorinated layer. Thus, fluorinating the surfaces of GM liners in landfills could increase the effectiveness of the GM as a barrier to organic contaminants.

2.11.2 EVOH Co-extrusion

Co-extrusion is an extrusion process used to obtain a product that combines two textures, so that one material is extruded and continuously filled with another to form a single product.

McWatters and Rowe (2014) investigated the diffusion of Toluene and TCE through Ethylene Vinyl Alcohol (EVOH) coextruded GMs and showed that diffusion tests of Toluene through a co-extruded LLDPE/EVOH/LLDPE geomembrane at 23°C had not yet reached equilibrium after a testing period of 6.5 years. Even though LLDPE was used and not HDPE, as in this dissertation, it shows how effective the GM co-extrusion with EVOH could be to prevent groundwater contamination by diffusion of VOCs.

2.11.3 Aquatan Enhanced Barrier System

The temperature effect on liner longevity is well known and this led GM and geotextile manufacturers to discover new ways to mitigate these negative effects. Aquatan Lining Systems is a South African geomembrane supplier that developed a concept that involves drawing a fluid under negative pressure through a pervious zone adjacent to the barrier so that the fluid could be used to cool the primary composite lining and adjacent drainage systems, and to introduce moisture to the GCL beneath the overlying geomembrane for its hydration (after placement of a normal load and prior to the risk of its exposure to leachate). The fluid (gaseous, liquid or two-phase mixture) passing through the pervious zone would also maintain the leak detection system at a low-to-zero concentration of VOCs, thus preventing their further diffusion into the adjacent environment **(Meyer, Meyer & Gundle, 2015)**. Aquatan calls it the Enhanced Barrier System™ (shown in **Figure 2.4**).

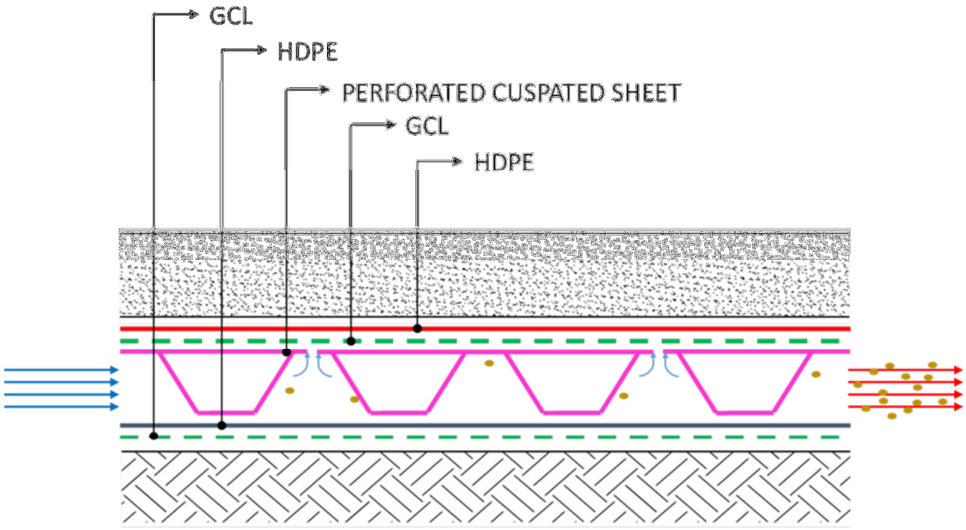


Figure 2.4: Aquatan's Enhanced Barrier System™ (Meyer *et. al.*, 2015)

This concept formed the basis of the work done for this dissertation with the focus being on the diffusion through HDPE and possible removal of VOCs only. This dissertation did not look into the impact on other layers in the liner system or at the possible cooling and hydration effects of the fluid passing through the

system. Since this system requires constant pumping there will have to be an analysis on the long-term sustainability and economic feasibility of the system but this study did not focus on that.

2.12 CONCLUSIONS

- The literature shows that in recent times much has been done to protect the groundwater and other surrounding receptors from possible harm due to the effects of disposal of waste at landfills. Liners have developed from basic compacted soil liners to intricate composite lining systems incorporating the latest technology.
- Several authors confirmed that VOCs are present in landfill leachates and that they are harmful to, among other things, the groundwater under and surrounding landfills and waste containment facilities. It was also confirmed that these compounds can permeate landfill liners by means of diffusion and that diffusion takes place faster at higher temperatures. The literature shows that it is not only temperature that affects the rate of diffusion and that the difference in the sorption and diffusion coefficients found in the literature is a result of factors such as concentrations, chemical composition of containment source, polymer crystallinity and additives.
- It was confirmed that the HDPE liner in a composite landfill lining system is the primary barrier to prevent contaminant transport through the liner but that even HDPE can be penetrated and breached by the diffusion of VOCs, and that this needs to be further investigated to find a possible solution.

CHAPTER 3. RESEARCH DESIGN AND METHODOLOGY

3.1 INTRODUCTION

The aim of the experimental setup required for the study was to investigate the diffusion of the VOCs, BTEX and Chloroform, through the HDPE geomembrane section of a composite liner in a landfill, and to then investigate the possibility of passing a fluid (air) through a pervious zone adjacent to the GM barrier to measure the possible reduction in VOCs in the receptor volume that represents the groundwater beneath landfills.

In applying this technology, it could be possible that the fluid be a liquid passed through under a negative pressure to simultaneously hydrate the GCL component and cool down the liner. The negative pressure is important in order to prevent the introduction of oxygen to the waste body through a possible discontinuity in the base geomembrane that could increase the risk of spontaneous combustion (**Meyer *et. al.*, 2015**). However, more studies are required to confirm this.

For the purpose of this dissertation, the fluid used was ambient laboratory air and investigations into GCL hydration; effect of liner cooling, and possible spontaneous combustion did not form part of this work. The only focus was on the HDPE GM and the diffusion of VOCs.

3.2 BACKGROUND

To obtain the aim of this study, field tests and laboratory diffusion and sorption tests were undertaken. When the author became involved in the project, some field work had already been done by Mr K Legge and Aquatan Linings at a leachate dam of the Holfontein Hazardous Waste Landfill near Springs in Gauteng, South Africa and these tests were continued under this study. Results from the field tests and the laboratory test would then be used to reach a conclusion.

For the laboratory tests, a successful application for funding was submitted to the National Research Foundation's THRIP scheme. Funding for the laboratory work was also provided in part by Aquatan (Pty) Ltd and AECOM SA (Pty) Ltd.

From an analysis of the data collected, the following hypotheses were tested:

H0: The extraction of air through a pervious zone in the composite landfill liner does not reduce the concentration of VOCs in the groundwater beneath landfills that are present due to the diffusion of VOCs through the HDPE GM in the composite liner.

H1: The extraction of air through a pervious zone in the composite landfill liner reduces the concentration of VOCs in the groundwater beneath landfills that are present due to the diffusion of VOCs through the HDPE GM in the composite liner.

3.3 FIELD TESTS

For a Class A landfill facility capable of accepting most hazardous waste types, the Department of Environmental Affairs prescribes a minimum of a double composite liner system consisting of a leachate collection system and leakage detection system. Although the regulations were different at the time of construction of the leachate dam used for the field testing, the facility had a similar liner configuration with a double composite liner. HDPE and LDPE pipes were then installed on the liner of the leachate ponds.

Since previous studies (see **Chapter 2**) show that VOC transport through composite landfill liners can occur by diffusion, the VOCs at the leachate dam in question should diffuse through the outer wall of the pipes and be present in unknown quantities in the pipe. Tests were carried out at pre-determined times by analysing the gas inside the pipes. The gaseous sample was pumped from the pipe and passed through a three-bed solid sorbent tube connected to the pump unit. The sorbent tubes were designed to retain a wide variety of volatile organic substances.

The amount of certain VOCs in the air sample from the pipes was determined and compared to a control and to the amount of the particular VOCs in ambient air to estimate the rate of diffusion of the VOC through the pipe wall.

3.3.1 Field Test Setup

The initial aim of the study was to replace the leakage detection system in the composite liner with a cuspated HDPE drainage layer similar to the Hi-Drain product manufactured by Aquatan, and then to extract the fluid through this layer to determine the VOC reduction.

The Holfontein Hazardous Waste Disposal Site (managed by Enviroserv (Pty) Ltd) agreed to the use of one of its hazardous waste leachate dams for this study. Because the dam was already in use, meaning that the liner had already been installed without the cuspated drainage layer or fluid extraction equipment, it was not possible to recreate the complete composite liner at the leachate dam as planned.

Thus, hollow 100-mm diameter, 1.5-mm wall thickness, Poly-Ethylene pipes were installed on top of the current lagoon liner to simulate a leachate drainage layer as part of a composite liner and measure the VOC reduction in the pipes over time with extraction of air through the pipes. The three pipes (one Low Density Poly-Ethylene (LDPE) and two High Density Poly-Ethylene (HDPE)) pipes were inserted as shown in **Figure 3.1**.

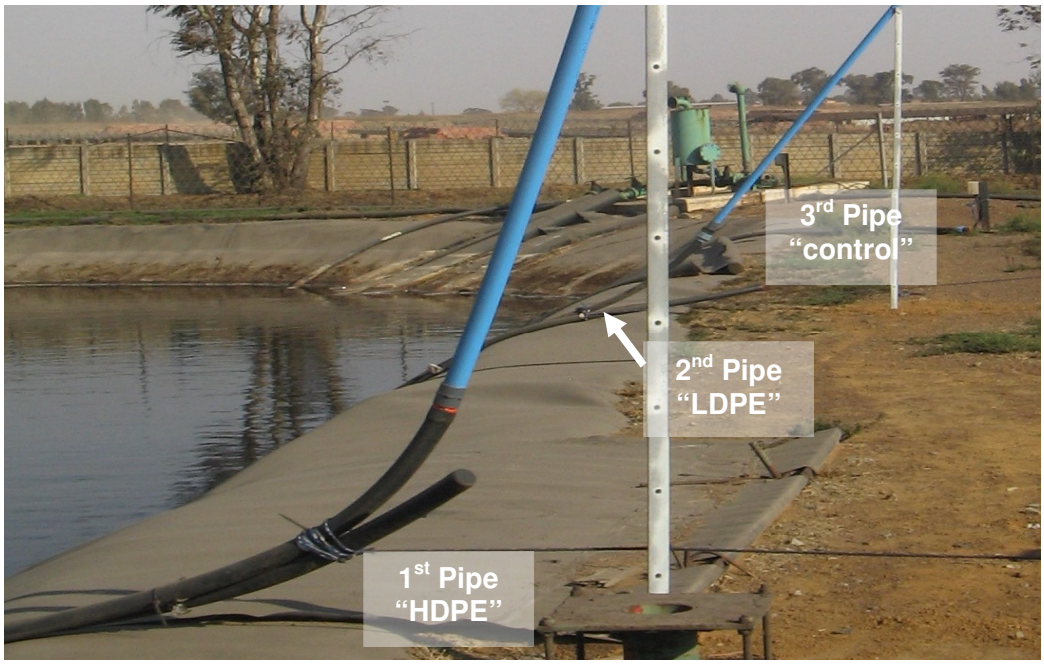


Figure 3.1: Pipe Layout at Leachate Dam for Field Tests

The three polyethylene pipes were placed in parallel along the breadth of the dam (east to west), with their ends protruding on opposite sides of the dam. On the eastern bank of the dam, the ends of the middle pipe and northern pipe (first and second pipes) were connected to an extraction fan that pulled ambient air through the pipes at a constant flow rate. The ends of these two pipes on the western bank of the leachate dam served as inlets for the ambient air flowing through the pipes. The intakes were raised to approximately three meters above ground level through an extension of PVC pipe (see **Figure 3.1**).

The third pipe, closest to the southern end of the dam, was closed off from the atmosphere, based on a theory that that any VOCs that could diffuse through a standard high density polyethylene (HDPE) liner, used in the construction of leachate dams and landfills, would also diffuse and accumulate in this pipe and would be available for sampling. In comparison, it was expected that very little VOCs would be present in the first two pipes (one HDPE and one LDPE) connected to the extractor fan, as the constant flow of ambient air would flush out any accumulated VOCs that had diffused into these pipes from the leachate.

The closed-off, third pipe (HDPE) on the southern end of the dam was labelled ‘Control’ and the pipe in the middle and the one closer to the northern side were labelled ‘LDPE’ and ‘HDPE’, respectively.

The measured parameters included the air quality inside the pipes at certain time periods and were compared to proven diffusion rates of certain VOCs through HDPE GMs.

3.3.2 Tested VOCs

The VOCs tested during the field tests were Toluene, Perchloroethelyne, n-Butylacetate, Ethyl benzene, Xylene, Propyl Benzene, 1,2,3-Trimethylbenzene, 1,2,4-Trimethylbenzene and Naphthalene. They were selected based on their relatively high detection frequency in contaminated environments such as landfill leachate, as well as for their reasonably broad range of solubilities and molecular weights.

Infotox (Pty) Ltd took four sets of samples on site, one each from the three pipes and one background sample, and sent them to the CSIR Consulting and Analytical Services Laboratory in Pretoria for analysis. The background sample

was collected to determine the concentrations of VOCs in the ambient air sucked into the two open polyethylene pipes. The Background Sample was collected at approximately two meters above ground level. The samples were analysed by gas chromatography–mass spectrometry (GC-MS) for the set of organic compounds identified.

3.3.3 Results and Conclusions

- A full report is available on the methodology and results of the field tests. The report by Infotox is titled: *Enviroserv (Pty) Ltd - Holfontein Leachate Dam Number 3 - VOC Removal System Investigation - Measurement of Volatile Organic Substances - Summary Report: 015-2009 Rev 2.0 - Prepared for Aquatan (Pty) Ltd by N Potgieter MSc (Chemistry) Pr Sci Nat (Environmental Science).*
- The results indicated that the composition of the Control Sample (the closed pipe) with regard to the target compounds is largely similar to that of the HDPE, LDPE and Background air samples. This was largely because most of the target compounds can be found in ambient air and are commonly present in the vicinity of industrial areas, refueling stations and busy highways, as reported by Infotox in the report quoted above. However, concentrations of benzene and chloroform, which were the two most volatile of the target compounds, were higher in the control sample compared to concentrations in the HDPE and LDPE samples.
- These results appear to indicate that ventilation of the HDPE and LDPE polyethylene pipes could significantly reduce the concentrations of the compounds that may have diffused into the pipes from the surrounding leachate in the dam. However, as concluded by Infotox, it is difficult to attribute the observed concentrations of hydrocarbons in the control sample conclusively to diffusion from the leachate without a more complete understanding of the composition of the contents of the leachate dam and the mechanism of transport through the polyethylene membrane.
- Due to the uncertainties in the conclusions that could be derived from the results of the field tests, field testing was aborted and the focus shifted to tests in the laboratory where a more controlled environment was possible.

3.4 LABORATORY TESTS

Laboratory tests were carried out at the South Campus of the University of Pretoria in South Africa. The tests undertaken were based on the methods used by Prof Kerry Rowes at the Geo-Engineering Centre at the Queens University in Kingston, Canada as demonstrated during a visit to their facility. The aim was to first prove that the chosen VOCs (BTEX and Chloroform) do diffuse through the HDPE GM as well as two GMs separated by an air filled pervious zone, and then to move into a possible method of preventing this. To undertake these tests it would be required to calculate the Sorption (S_{gf}) and Diffusion (D_g) coefficients for the compound and GM in question and the methods used to evaluate diffusion and partitioning (sorption) coefficients can be classified in two categories according to **Sangam and Rowe (2001)**. These categories are immersion/sorption methods and permeation/diffusion methods. The main difference being the way the HDPE GM is in contact with the permeant during the test as is described in detail in this chapter of the dissertation.

3.5 SORPTION/IMMERSION TESTS

Sorption/Immersion tests are done to determine the sorption coefficient (S_{gf}) for the GM and permeant in question. The coefficient is defined as the ratio of the concentration of the chemical in the GM at equilibrium to the concentration of the chemical in the solution in contact with the GM (**Park et al, 1993)**. S_{gf} is normally unitless and can be calculated from **Equation 9** when using an immersion test method or **Equation 7** when using the diffusion test method where concentrations of compounds in the solution in contact with the GM are monitored over time until equilibrium is reached.

Alternatively the S_{gf} can be calculated by doing weight gain tests (**Equation 8**) where a piece of GM of a known weight is immersed in the compound in question and weighed at given intervals until the weight does not significantly increase for different weightings. All three methods were used for this study in order to compare results.

3.5.1 Methodology (Sorption Tests)

Sorption tests were done using glass vials with sampling caps, about 80-mm high and 50-mm diameter (see **Figure 3.2**). Glass sorption cells are similar in shape and size to the glass sorption cells used by **Sangam *et. al.* (2001)**. Tests were done on the 2-mm GM using methanol as a medium for the BTEX solution and tests were done on both the 1-mm and 2-mm GM using an aqueous solution containing BTEX and Chloroform.

Methanol tests were done in triplicate with two control cells containing no GM in order to measure the losses to the glass, sampling cap and sampling process. The aqueous tests were done in duplicate for both the 1-mm and the 2-mm GMs and two control cells were included.

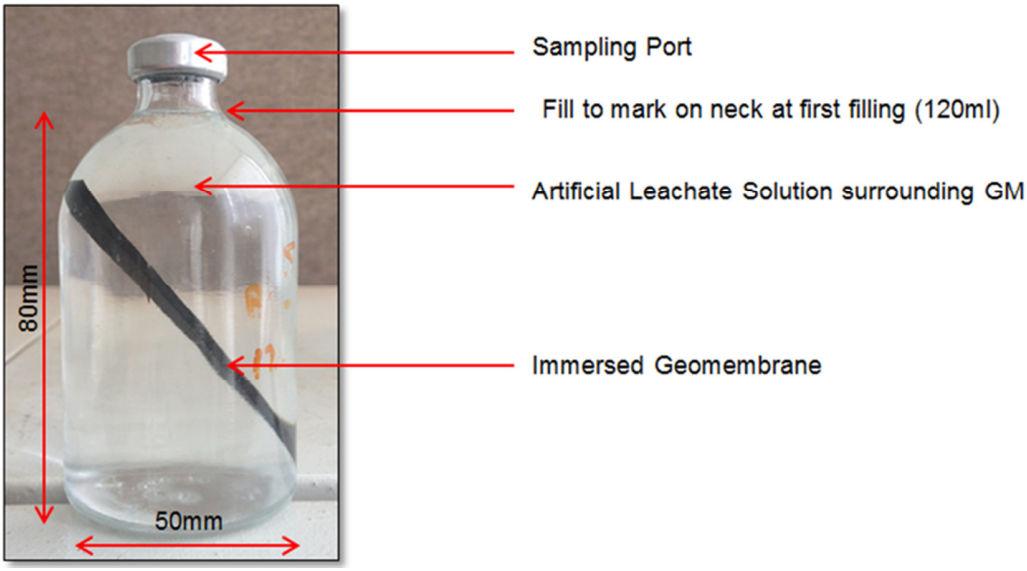


Figure 3.2: Sorption Test Cell

Sorption and diffusion tests were initially done using methanol as a medium and although the VOCs diffused through the GM, the methanol diffusion tests were replaced by aqueous tests to better replicate the actual landfilling conditions. The methodology and results of methanol Sorption tests are included in this dissertation to enable an analysis and comparison to the aqueous tests results.

Filling and Sampling Procedure

When filling the sorption test cells, the following procedure was followed.

1. Ensure the vials are clean and dry.
2. Cut the pieces of HDPE GM (about 1 cm by 5 cm) and weigh it using an electronic scale with sensitivity of 0.01 mg to obtain the initial mass of the GMs.
3. Fill all the vials up to the mark on the bottle neck with deionised water.
4. Make up a leachate (BTEX and Chloroform) solution with theoretical initial concentration of 2 mg/l using the method described in this chapter.
5. Place the GMs in the allocated vials and clamp the vials shut by placing the septa containing cap over the vials.
6. Using a gas-tight laboratory syringe, remove the required amount of water from the vials and replace with volume of leachate solution.
7. Sample immediately to obtain day 0 concentrations.

The cap of the test vial was completely sealed and clamped over the vial, made of aluminum and covered with parafilm when not sampling to ensure that the cap was not a sink for the sorption.

Due to the small volume of air between the solution and the cap of the vials, there would thus be mass transferred to the head space, as per Henry's law, and control tests were thus essential to assess losses. The control vials were identical to the test vials except that they contained no GM.

Gentle vibration using a vibrating table (ensuring the fluid did not touch the top cap) was introduced to maintain uniform concentration in the fluid.

Every time a sample was taken, the headspace increased with the volume of sample so it was important to replicate the sampling procedure every time. This included replicating the distance the needle was inserted into the vials each time.

Experiments were performed at room temperature in the laboratory (24 ± 2^{o}C) and for the methanol tests, 1 ml samples were taken at days 0, 14, 21, 44 and 62. For the aqueous tests, 1 ml samples were taken at days 0, 2, 5, 12 and 21. Samples were placed into glass Gas Chromatograph (GC) sampling vials for testing in the GC (GC-MS).

The concentrations of contaminants were monitored until the equilibrium concentration was reached. The system was deemed to be in equilibrium if no significant attributable change in concentrations occurred for consecutive

sampling events. Due to the high solubilities of the contaminants in methanol, the S_{gf} values were expected to be much lower than that of aqueous solutions due to the slower sorption characteristics of VOCs in methanol. In other words, it was expected that it would be more difficult for the VOCs to remove themselves from methanol solution in order to sorb onto the GM.

Also, the methanol solution would take much longer to reach equilibrium and there would also be a difference in time to equilibrium expected for the 1 mm and 2 mm GMs due to the difference in thickness.

The sorption coefficient of each contaminant was calculated using **Equation 9**.

Leachate Makeup

The synthetic leachates used in the sorption vials were made up in the lab using laboratory grade BTEX and Chloroform made by SAAR Chem-Trade (Pvt) Ltd with selected properties (adapted from **Rowe *et. al.* 2001**), given in **Table 3.1**:

Table 3.1: Selected Properties of VOCs Used

Chemicals	Density (g/cm^3)	Aqueous Solubility[a] (mg/l)	Log K_{ow} [b]	Molecular Weight (g/mol)	Henry's constant[c] *k* (l water/l air)
Benzene	0.876	1780	2.13	78.11	0.218
Toluene	0.870	515	2.79	92.14	0.258
Ethylbenzene	0.867	152	3.13	106.17	0.305
p-Xylene	0.870	156	3.18	106.17	0.290
Chloroform	1.484	8000	1.97	119.38	0.304

[a] at 20°c
[b] n-octanol/water coefficient
[c] from Mcwatters & Rowe (2009), at 24°c

The initial solution concentrations for the contaminants was 2mg/l and although sorption tests are often conducted at different solution concentrations in order to develop an isotherm, this was not for this study. For the aqueous sorption tests, a 100 µl of each VOC was mixed with 100 ml of Methanol to create a stock solution because BTEX and Chloroform are not easily dissolved in water but can be dissolved by organic solvents like methanol, which dissolves in water.

Using the relationship $C_1V_1 = C_2V_2$ where C_1 and V_1 is the volume and concentration of the test vial and C_2 and V_2 the concentration and volume of the stock solution, it was determined how much liquid needed to be removed from

the test vials and replaced with stock solution to arrive at the desired initial BTEX and Chloroform concentration of 2 mg/l. Details are given in **Table 3.2**

Table 3.2: Sorption Leachate Solution Makeup (Stock Solution 100ml)

VOC	Density (g/cm^3)	Solubility (mg/l)	1ml thus contains (mg)	100µl thus contains (g)	Stock solution thus contains (mg/l)	Thus, V_2 in ml
Benzene	0.88	1780	877.0	0.087	877.0	0.34
Toluene	0.87	515	866.9	0.086	866.9	0.35
Ethylbenzene	0.87	152	866.5	0.086	866.5	0.35
p-Xylene	0.86	156	861.0	0.086	861.0	0.35
Chloroform	1.48	9300	1483.0	0.148	1483.0	0.20

3.5.2 Weight Gain Test Methodology

The 1-mm and 2-mm HDPE GM samples were cut into rectangular 1 cm x 3 cm shapes (10 for each thickness). The dry samples were weighed to obtain their M_0 weights using an electronic scale with sensitivity of 0.01 mg and were immersed in cylindrical 13 ml glass vials filled with BTEX and Chloroform (each in its own jar) that can be sealed using an airtight lid. The tests were carried out in duplicate for BTEX and Chloroform.

The time of final filling was recorded and noted as time 0. Weight gain was recorded at 10 minutes, 30 minutes, 45 minutes, 180 minutes, 250 minutes, 360 minutes and 1440 minutes (24 Hours) for the 1 mm GM and at 30 minutes, 50 minutes, 90 minutes, 190 minutes, 280 minutes, 370 minutes and 1440 minutes for the 2 mm GM. The ambient temperature in the lab was 17°C at the time of the experiment.

For weighing, the sample was taken out of the bottle and its surface dried on a paper towel for several seconds before weighing. Immediately after weighing, the sample was immersed in the solution and the cap was replaced. This procedure took 45-65 seconds. Depending on the difference in volatility of the VOCs, the weight of samples had a minimum readable value that varied between 0.01 mg

and 0.1 mg. It was also assumed that the weight loss during measurement was negligible. The Sorption coefficient (S_{gf}) was calculated using **Equation 8**.

3.6 DIFFUSION TESTS

Diffusion tests were done following the examples given in the work by **Rowe (2009)** to determine the rate of diffusion of the VOCs through the GM by measuring the change in concentrations of solutions on either side of the GM. Diffusion tests were carried out in three phases.

- **Phase 1 – Diffusion tests using one GM:** This test would replicate work already done by others in order to prove that by using the equipment and laboratory setup for this project, diffusion would take place across a 2 mm intact HDPE GM separating a source and receptor volume (see **Figure 2.2**) of a diffusion test cell made up as described in this chapter. All phase 1 work was done in laboratory temperatures ranging from 18-28°C.
- **Phase 2 – Diffusion tests using two GMs:** The second phase of testing replicated the first, with the 2 mm GM being replaced by 2 x 1 mm GMs separated by a 0.8 cm gap filled with air to replicate the top and bottom of an HDPE cuspated leakage detection system. The purpose was to prove that diffusion would take place across both GMs (separated by air in the pervious zone as shown on **Figure 2.3**) and still reach groundwater beneath the liner system. The two GMs are assumed identical and when there is no flow through the system the VOC concentration in the water above and below the GMs will reach equilibrium with the concentration of the VOC in the air layer, resulting in the S_{gf}, and D_g values being the same for the two GMs. Phase 2 and 3 testing took place in a different room to phase 1 testing and the temperature in the lab where phase 2 and 3 tests were undertaken ranged from 30-34°C.
- **Phase 3 – Extraction of air:** The third phase replicated phase 2, with air being extracted through the gap between the two GMs to represent the flow of a fluid through the leakage detection system of a landfill liner. The purpose

was to prove that by removing the air between the two GMs at regular intervals, the VOCs would be removed from the system and would not reach the groundwater. The two GMs were assumed identical, but since there would now be a flow of air through the gap between the two GMs, the concentration profile would change resulting in a change of flux, which could result in a change in the D_g values of the two GMs. At dilute concentrations of BTEX there should theoretically be no concentration dependence of D_g but each GM will probably have its own D_g value due to the difference in concentration gradients. For the purpose of this study, it was assumed that the sorption coefficient (S_{gf}) for GM1 and GM2 would be equal.

3.6.1 Methodology

Diffusion Test Cell

To perform the diffusion tests correctly, diffusion test cells were required since results would require verification from literature. Stainless steel, which has been used by several investigators to examine the diffusion of BTEX compounds (**Sangam & Rowe, 2001)** was used to manufacture the diffusion cells and the cells were designed to replicate the diffusion test cells used by **Professor Rowe** at the Queens University in Kingston, Canada. The test cells were made in South Africa by Interlock Systems and had the dimensions and properties shown in **Figure 3.3**:

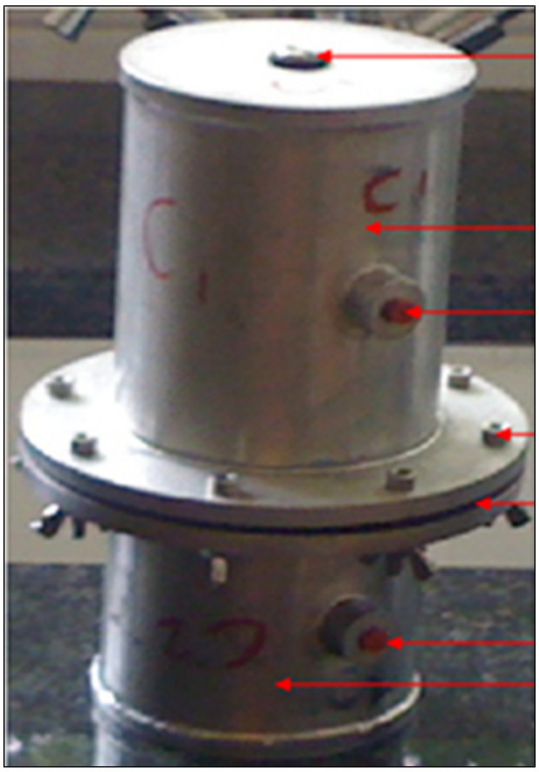


Figure 3.3: Diffusion Test Cell

Five cells were made so that tests could be done in triplicate with one control cell and one blank cell to measure losses and outside influences. For phases one and two of testing, the cells were marked A to E and Cells A, B and C were used for diffusion testing. Cell D was set up in the same manner as A, B and C, but contained no VOCs so that it could be determined whether outside factors had any influence on the concentrations in the cells.

Cell E was made up with a synthetic leachate with the same concentrations of BTEX and Chloroform as the source cells of A, B and C but Cell E contained no GMs so that the losses due to sorption or the like, to the gaskets, septums or stainless steel could be measured. From bottom to top in **Figure 3.3**, the Diffusion tests cells details are described below.

- Receptor Reservoir: 70 mm high with a 70 mm diameter (about 0.27 liters), flanged and open at the top. The receptor reservoir represented the groundwater beneath lined landfill facilities and was filled with deionized water at the start of testing. The Receptor reservoir also had a small

magnetic stirrer bar that would ensure proper mixing of the solution when placed on magnetic tables.

- Sampling port with septum: The rubber septum was firmly lodged into the sampling port so that a needle could be used to extract solution samples from the receptor reservoir with minimal losses. During testing, the sampling ports were covered with a rubber seal and clamped shut to further reduce losses. A similar sampling was added to the source reservoir.
- Gaskets: Gaskets were inserted above and below the GM in the flanged sections to ensure the system sealed properly. The gaskets were made from Viton since it studies by **Rowe (1998, 2009)** proved that Viton has a very high chemical resistance and that VOCs do not sorb to the Viton as easily as to other compounds, thus reducing losses.
- Locking Mechanism: To lock the system together, the flanges had holes though which bolts were fastened by wingnuts using pliers and an Allen key.
- Geomembrane: The Geomembranes used for this work were supplied by Aquatan Lining Systems (Pty) Ltd. For phase one testing a 2 mm thick GM was used, and a 1 mm thick GM was used for phases two and three testing. The GM was cut into a circle by hand to fit exactly into the depressions in the flanges of the source and receptor cells so that a full intimate contact between the source/receptor solution and the GM could be maintained.
- Source Reservoir: 120 mm high with a 70 mm diameter (about 0.385 liters), flanged and open to the bottom. The source reservoir represented the leachate in a lined landfill and was filled with a prepared synthetic leachate solution using the filling port. The Source reservoir also included a small magnetic stirrer bar that would be used to ensure proper mixing of the solution when placed on magnetic tables.
- Filling port: The source reservoir included a filling port to ensure that the reservoirs could be completely filled once the test cell was assembled. The filling procedure is described later in this report. The filling port was sealed off with a screw and rubber o-ring to ensure a tight seal with minimal losses.

- Centerpiece (Phases 2 and 3 testing): For phases 2 and 3 testing, a centerpiece was inserted between the source and receptor reservoirs. GMs (1 mm thick) were placed directly below and above the centerpiece and the centerpiece replicated the pervious zone in the liner system through which a fluid would be passed to remove VOCs that diffused through the top GM. The centerpiece was 0.8 cm high and had holes aligned so it fit perfectly between the flanges of the source and receptor reservoirs. It had a hole on the sides though which air could be passed and the holes could be blocked off with screws if they were not required. The centerpiece had two diagonal plates (**Figure 3.4**) through the center with holes in them so that air that passed though could be evenly spread across the whole pervious zone and not concentrated through the center.

Figure 3.4: Centerpiece of Diffusion Test Cell

Filling Procedures

When filling the diffusion test cells for Phase 1 testing, the following procedure was followed.

1. Ensure test cells are clean and dry.
2. Insert septa into sampling ports, ensuring they are as gas tight as possible.

3. For Test Cells A, B, C and D, place receptor volume on table, place gaskets and fill with deionised water until meniscus forms, ensuring it is completely full.
4. Insert magnetic stirrer bar into receptor volumes of cells.
5. Place 2 mm HDPE GM disk onto gasket and place another stirrer bar onto HDPE GM disk so that the source and receptor volumes of the test cell both have a stirrer bar.
6. Place another gasket onto the HDPE GM.
7. Place receptor reservoir on top, aligning the holes in the flanges and fasten tightly using Allen key and pliers (for wing nuts).
8. Assemble Test Cell E by placing gasket, but with no HDPE GM.
9. Connect a tube to the tank of deionised water and insert the other part of the tube into a funnel that fits into the hole of the filling port on the cell. Open the tap on the tank and close it when water escapes from the top of the filling port, which indicates it is completely full. Close the hole in the filling port with a screw and o ring. Repeat this step to fill all cells.
10. Secure with clamps over nozzles.
11. Place on magnetic tables until sampling, ensuring that the test cells are placed on their sides to enable complete contact between the solutions in the source and receptor volumes and the GMs.

Test Cells A, B, C and D were thus theoretically completely similar after filling. Water would be removed from the source reservoirs of Cells A, B and C and replaced with a synthetic leachate solution as described in this chapter.

When filling the test cells for Phases 2 and 3 testing, the following procedure was followed.

1. Make sure test cells are clean and dry;
2. Insert septa into sampling ports making sure that they are as gas tight as possible;
3. For Test Cells A, B, C and D - Place receptor volume on table, place gaskets and fill with deionized water until meniscus forms ensuring it is completely full;
4. Insert magnetic stirrer bar into receptor volumes of cells;

5. Place 1 mm HDPE GM disk onto gasket and place centerpiece on 1mm HDPE GM;
6. Place another gasket onto the centerpiece and place the second 1mm HDPE GM on top the gasket with a stirrer bar on the GM;
7. Place receptor reservoir on top, aligning the holes in the flanges and fasten tightly using allen key and pliers (for wing nuts);
8. Assemble Test Cell E by placing gaskets and centerpiece but with no HDPE GM;
9. Fill all cells with deionized water through filling port ensuring that they are completely full then close hole in filling port with screw and o ring;
10. Secure with clamps over nozzles;
11. Place on magnetic tables until sampling, making sure that the test cells are placed on their sides. This ensures complete contact between the solutions in the source and receptor volumes and the GMs.

3.6.1.3 Leachate Make Up

The synthetic leachates in the Source reservoirs for each phase of testing were made up as follows:

Phase 1:

1 ml (1,000 µl) of water was extracted from source compartments of Cells A, B, C and E using a 500 µl syringe and discarded. Then 100 µl (microliter) each of Benzene, Toluene, Ethylbenzene, p-Xylene and Chloroform was mixed with 500 µl of methanol and injected into the source volumes of cells A,B,C and E to replace the 1 ml of water that was removed. The chemicals were diluted in methanol before being injected into the cells so that they were kept in solution until mixed with the water in the cell. This would assist in ensuring a proper mix of the VOCs in the source cell.

Table 3.3: Phase 1 Diffusion Testing Leachate Make Up

VOC	Density (g/cm^3)	Solubility (mg/l)	1ml thus contains (mg)	100µl thus contains (g)	Stock solution thus contains (mg/l)	Thus, V_2 in ml
Benzene	0.88	1780	877.0	0.088	87 700	208.3
Toluene	0.87	515	866.9	0.087	86 690	205.9
Ethylbenzene	0.87	152	866.5	0.087	86 650	205.8
p-Xylene	0.86	156	861.0	0.086	86 100	204.5
Chloroform	1.48	9300	1483.0	0.148	148 300	352.3

When using the relationship $C_1V_1 = C_2V_2$ where C_1 and V_1 is the volume and concentration of the test vial and C_2 and V_2 the concentration and volume of the stock solution, it can be determined how much liquid needed to be removed from the test vials and replaced with stock solution to arrive at the desired initial BTEX and Chloroform concentrations.

This method was not accurately followed during make up of phase 1 leachate, which resulted in the initial concentrations in the source cells being much higher than the desired 10 mg/l**.** For Ethylbenzene and p-Xylene, the concentrations in the source were (theoretically) even higher than the maximum solubilities of the compounds, which was not desirable. The results obtained were also not temperature corrected and the implications of this are discussed during the analysis of results in later chapters.

Also, on the day of phase one filling, chloroform had not been delivered to the lab so the day zero setup was done without Chloroform, using the rationale above. Chloroform was added when it arrived five days later. This created challenges, which are discussed in **Chapter 5** of this dissertation.

Phase 2:

50 µl was extracted from source cells of cell A, B, C and E. 5 µl each of BTEX and Chloroform was mixed with 25 µl of methanol and injected into source volumes of cells A, B, C and E to replace the 50 µl removed.

Cell E which contained no GM but included the centerpiece had a larger volume. For Cell E, 9 µl of each VOC (45 µl) was mixed into 45 µl methanol (90 µl) and injected so that the initial concentrations were similar to the other cells.

Table 3.4: Phase 2 Diffusion Testing Leachate Make Up

VOC	Density (g/cm^3)	Solubility (mg/l)	1ml thus contains (mg)	5µl thus contains (g)	Stock solution thus contains (mg/l)	Thus, V_2 in ml
Benzene	0.88	1780	877.0	$8.8x10^{-5}$	$8.7x10^{5}$	104.157
Toluene	0.87	515	866.9	$8.7x10^{-5}$	$8.7x10^{5}$	12.957
Ethylbenzene	0.87	152	866.5	$8.7x10^{-5}$	$8.7x10^{5}$	102.910
p-Xylene	0.86	156	861.0	$8.6x10^{-5}$	$8.6x10^{5}$	102.257
Chloroform	1.48	9300	1483.0	$1.5x10^{-4}$	$1.5x10^{6}$	176.128

The initial concentrations for phase 2 tests were lower than for phase 1 testing by a factor of about 10 to compare more easily with literature. As shown later in this dissertation, the actual day zero recorded concentrations in the source cells of the phase 2 diffusion test cells were much lower than the theoretical concentrations using the rationale above. This could be attributed to the high error probability when mixing synthetic leachate from five VOCs using microliters in a single syringe.

Phase 3:

For the phase three diffusion tests a 100 ul of each VOC was mixed with 100 ml of Methanol to create a stock solution with concentrations given in **Table 3.5**.

Table 3.5: Phase 3 Diffusion testing leachate make up

VOC	Density (g/cm^3)	Solubility (mg/l)	1ml thus contains (mg)	100ul thus contains (g)	Stock solution thus contains (mg/l)	Thus, V_2 in ml
Benzene	0.88	1780	877.0	0.088	877.00	4.80
Toluene	0.87	515	866.9	0.087	866.90	4.86
Ethylbenzene	0.87	152	866.5	0.087	866.50	4.86
p-Xylene	0.86	156	861.0	0.086	861.00	4.89
Chloroform	1.48	9300	1483.0	0.148	1483.00	2.84

Using the equation $C_1V_1 = C_2V_2$ where C_1 and V_1 is the volume and concentration of the test vial and C_2 and V_2 the concentration and volume of the stock solution, it was determined how much liquid needed to be removed from the test vials and

replaced with stock solution to arrive at the desired initial BTEX and Chloroform concentration of 10 mg/l. This volume is represented as V_2 in the above table.

Sampling Procedures

When samples were taken for diffusion testing, the following procedure was followed:

1. Remove the test cell from the magnetic table and remove the clamps.
2. Mark the GC sample vials with the corresponding compartment: 1 for source and 2 for receptor, so if the sample is taken from the receptor volume of Cell B, mark the GC vial B2 with a permanent marker.
3. Take 1 ml samples through the septum in the sampling ports using a 500 µl needle. (That was the only needle available so two 500 µl samples were injected into the GC sample vial).
4. Clamp the GC vial shut immediately and place aside.
5. Inject 1 ml of deionised water back into the cell volume using the 500 ul needle to ensure the test cells stayed full with no air pockets for the VOCs to sorb to.
6. Replace the clamps over the sampling ports and place the cell back on the stirrer.
7. Repeat for all cells requiring testing and take to the GC lab immediately after sampling for analysis in order to reduce losses;
8. Time from first sample to last is approximately 5-8 minutes.

Phase 3 Extraction Method

For the phase 1 diffusion tests, the source and receptor cells were separated only by the HDPE GM and the increase in concentration over time in the receptor cell was monitored. During phase 2, a centerpiece was added to introduce the pervious zone into the liner system. The centerpiece was separated from the source and receptor reservoirs by HDPE GMs so that the configuration was Source-GM-Pervious Zone-GM-Receptor. The centerpiece has a hole on each side (see **Figure 3.4**) and during phase 2 testing these holes were plugged using screws and thread-seal tape to ensure a tight seal (**Figure 3.5**). During phase-

two testing the system was thus completely blocked off with no flow of air in the pervious zone between the two GMs.

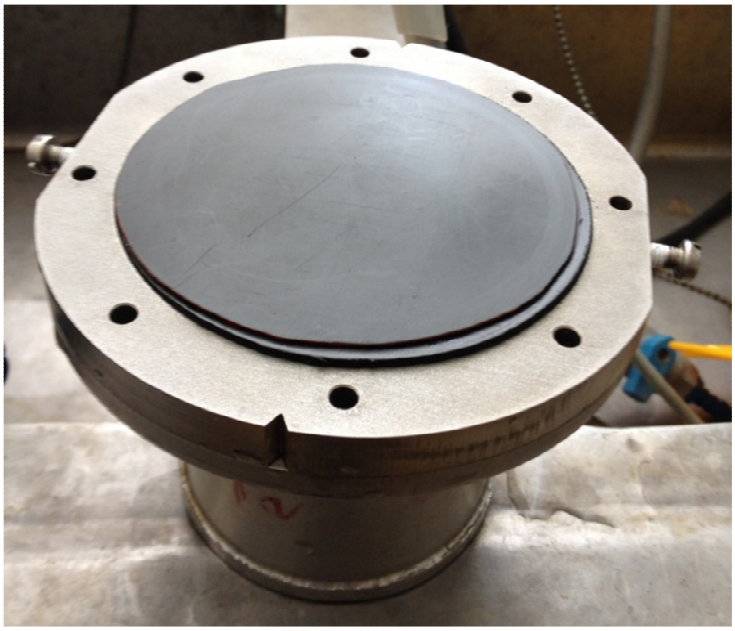


Figure 3.5: Centerpiece Air Extraction Holes Sealed with Screws and Tape (Top GM Already Placed Over Centerpiece)

During phase 3 testing the holes in the centerpiece were used to introduce air flow to the system. Using the five test cells (A to E), different air flow rates were introduced in four of the cells, leaving one cell permanently closed as for phase 2 testing in order to provide a control. Cell A was the control and airflow was not introduced to it so a comparison with phase 2 tests would be possible. In Cell B the air pervious zone between the GMs was replaced by clean ambient laboratory air once every 24 hours. In Cell C, the air was replaced once every 72 hours and in Cell D once every 7 days.

One of the cells had a minor leak at first filling and was not used as the fifth cell for phase 3 testing. One of the two screws was removed from the fifth cell and it was left upright with the source at the top on the counter next to the other four cells.

Figure 3.6 describes how airflow was introduced to the cells during phase 3 testing. Airflow through the pervious zone in the liner was mimicked by opening the screws on both ends of the centerpiece (picture 1 and 2 of **Figure 3.6**) and

inserting the tip of a plastic 60 ml syringe in to the hole (picture 3). Air was sucked through the system by quickly pulling the plunger through the full barrel of the syringe so that it came out the barrel top (pictures 3 to 6 of **Figure 3.6**). This process was repeated twice every time. The full barrel of the 60 ml syringe had a volume of about 80 ml and The pervious zone volume between the two GMs was about 38 ml. By using this procedure, a volume of at least twice the air volume in the pervious zone was extracted through the system every time to ensure complete replacement of the air in the system.

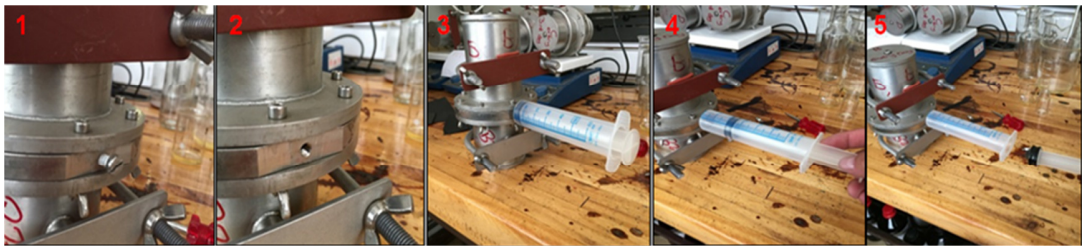


Figure 3.6: Process of Airflow in Cells for Phase 3 Testing

Sorption coefficient using diffusion tests

In addition to the sorption test and weight gain methods described earlier, the S_{gf} value was also obtained from the diffusion test using **Equation 7** after the completion of Diffusion tests at equilibrium.

3.7 METHODOLOGY FOR CALCULATION OF DIFFUSION COEFFICIENT

The Diffusion coefficient (D_g) was inferred using **Equation 3** and the variation in source and receptor concentrations with time (Fick's second law) at the given boundary conditions. This was done using POLLUTE, which solves the one-dimensional contaminant migration equation subject to boundary conditions at the top and bottom of the GM being modelled (**Sangam *et. al.*, 2005**).

The data entry into POLLUTE includes information such as thickness and density on the layers to be modelled as well as the boundary conditions to be used for modelling.

3.7.1 Phase 1 Diffusion Testing

For diffusion models in phase 1 testing there were three layers for which layer-data had to be provided (receptor, GM and source). The maximum depth requested by POLLUTE is the total depth of these three and for ease of modelling the source and receptor depths were modelled as a very thin layer in order to represent the boundary conditions above and below the GM.

The boundary conditions used for modelling were Finite Mass at the top (source) and Fixed Outflow Velocity at the bottom (receptor). Finite Mass was used as the top boundary condition since there was no addition of contaminant to the source and the concentration in the source decreased with time. The Fixed Outflow Velocity boundary condition was used at the receptor boundary to model it as an aquifer with a thickness equal to the height of the receptor (7 cm). This could be done because the stirrer bars in the test cell ensured good mixing in the receptor volume and the cross-sectional area of receptor was the same as the exposed area of the GM. Since the 1 ml samples that were taken were very small with respect to the receptor volume (270 ml), the outflow velocity used was zero.

As there was sorption of the contaminants onto the GM, the Passive Sink option under the Special Features of POLLUTE was used to allow the inclusion of a phase change with depth into the models in order to model sorption. For phase 1 testing, the modeling only allowed for one phase change interval, which was the GM separating the source and receptor volumes. The Phase Parameter input is the S_{gf} value calculated using the methods described in this Chapter.

Once all the data was entered, the value of the diffusion coefficient in the layer data entry field of the GM layer was changed until the output graph visually replicated the data obtained from laboratory results as accurately as possible. The ultimate value of the Coefficient of Hydraulic Dispersivity used, is the Diffusion coefficient (D_g) for the GM system in question.

3.7.2 Phase 2 Diffusion Testing

For Phase 2, nine layers were used for modelling since the test cells had two 1 mm GMs separated by the air void with the source and receptor above and below the GMs.

The layers from top to bottom were: Source layer, 1 mm GM layer with a very thin water layer above and below it. The thin water layers had a S_{gf} = 1 and a high diffusion coefficient to replicate a thin layer of condensation on the bottom of the GM so that modeling could be done with equal adsorption and desorption coefficients . That was followed by the air void layer and another GM layer with thin water layers above and below it and, finally, the receptor layer.

The boundary conditions used for modelling were the same as for phase 1, with Finite Mass at the top (source) and Fixed Outflow Velocity at the bottom (receptor).

The modeling of the passive sink was slightly more involved for Phase 2 testing. Since there was sorption of the contaminants onto the GM, then desorption into the thin water layer (which is included to prevent having to change the S_{gf} value in the modelling) going into the air layer, then adsorption onto the second GM and then desorption again, the Passive Sink option under the Special Features of POLLUTE was used and included seven intervals for all layers in the model except for the source and receptor layers. The four thin water layers above and below the GMs were modelled as having a phase parameter (S_{gf}) of 1 (as were the source and receptor layers). The GMs had the S_{gf} with respect to water as calculated doing Sorption/Diffusion tests and the air layer between the two GMs had a phase parameter (S_{gf}) in air with respect to water (Henry's Constant) as given in **Table 2.2**.

In the layer data entry field, the D_g values for the air layer of BTEX, given in **Table 3.6**, were taken from the work done by Tucker and Nelken in 1982, as represented by **Mcwatters & Rowe (2010)** and the D_g value for Chloroform was taken from the work done by **Larson (1964)**. The D_g for the air layer was 10^4 larger than that for water.

Table 3.6: Values of Diffusion Coefficient (Dg) used in the Air Layer of Phase 2 and 3 Test Modelling

VOC	Coefficient of Diffusion in Air (m^2/s)
Benzene	9.6×10^{-6}
Toluene	8.5×10^{-6}
Ethylbenzene	7.7×10^{-6}
p-Xylene	7.7×10^{-6}
Chloroform	9.04×10^{-6}

Once the data was entered, the value of the Coefficient of Hydraulic Dispersivity (diffusion coefficient) in the layer data entry field of the GMs was changed (D_{gGM1} = Dg_{GM2}) until the output graph most accurately replicated the data obtained from laboratory results. The ultimate value of the Coefficient of Hydraulic Dispersivity used, is then the Diffusion coefficient (D_g) for the GM system in question.

3.7.3 Phase 3 Diffusion Testing

For phase 3, nine layers were used for modelling, as for phase 2. The boundary conditions used for modelling were the same as for phase 2 with Finite Mass at the top (source) and Fixed Outflow Velocity at the bottom (receptor).

The modelling of the passive sink changed slightly from that in phase 2 since there was now an extraction of air through the pervious zone between the two GMs. This was modelled by adding a Rate of Removal value into the passive sink data set corresponding to the air layer. For Cell B, the rate of removal was 0.8 cm/day since the volume of the 0.8 cm high centerpiece was replaced by ambient laboratory air once per day. For Cell C, where extraction took place once every 72 hours, the rate of removal was 0.2667 cm/day and for Cell D (extraction once every week) the rate of removal was 0.1143 cm/day.

In the layer data entry field, the D_g values for the air layer were as for Phase 2 but the D_g values for the GMs changed since the concentration profile below the first GM and above the second GM differed due to the extraction of air through the system.

Once the data was entered, the values of the Coefficient of Hydraulic Dispersivity (diffusion coefficient) in the layer data entry field of the GMs were changed (D_{gGM1}

> Dg_{GM2}) until the output graph most accurately replicated the data obtained from laboratory results. The ultimate value of the Coefficient of Hydraulic Dispersivity used, is then the Diffusion coefficient (D_g) for the GM system in question.

3.8 GAS CHROMATOGRAPH

The analytical method for analysing the samples for sorption and diffusion testing was done using the Gas Chromatograph of the University of Pretoria.

3.8.1 Instrumentation

Analyses were performed using a PerkinElmer Gas Chromatography (GC) system comprising a Clarus 600 GC-FID (Flame Ionisation Detector), and a Clarus 600 T Mass Spectrometer (MS) (PerkinElmer, South Africa division).

The GC system injector consists of a split/splitless injector (CHP), a temperature programmed split/splitless injector (PSI), and a temperature programmed on column injector (POC). Sample injection was achieved by a multi-mode autosampler comprising an 82-vial multi injection automated rack, using a 50 µL syringe. The chemical separation component was the Elite 5MS GC system capillary column (30 m, 250 µm) from PerkinElmer. Carrier gas was Helium (He) of 99.999% purity and applied at a flow rate of 1 mL/min.

MS interface has an Electron Ioniser (EI), a high performance mass analyser, and a detector consisting of a dynode, phosphor plate and photomultiplier tube. Instrument is ultra-tuned weekly to optimise parameters and mass calibrated quarterly.

The chemical detention for most of the diffusion and sorption testing was conducted using FID which has a higher limit of detection (upper micro-grams towards milli-grams). During phase three testing under airflow conditions, increment changes in concentrations observed in the receptor volume were expected to range to much lower detection levels, beyond the capability of FID under the current instrument method. Mass Scpectroscopy (MS) has much improved detection capacity to FID and when venturing to lower micro-grams towards nano-grams concentrations, there is higher confidence in MS lower

mass resolution detection, especially when fractional differences in concentration determination were expected. For this reason, testing was moved from FID to MS during phase 3 testing.

3.8.2 Instrument settings

1 ml Samples were placed in GC sampling vials and sample volumes of 0.5 µL were injected into the GC system operating at a fast injection speed, injection port temperature was set at 250˚C. The column oven program was initiated at 35˚C (not held) → ramped at 10˚C per minute until 200˚C. Carrier gas split flow of 65 mL/min and a flow rate of 1 mL/min. The MS method was operated using Electron Ionisation (EI+) mode, centroid data setting. Scan duration was set at 0.3 seconds and inter scan delay was 0.2 seconds. FID water operated at heater temperature of 300˚C, airflow and hydrogen (H_2, 99.999 %) settings of 450 ml and 45 ml.

3.9 CHALLENGES AND LIMITATIONS

During the course of the laboratory work required for this study, a number of challenges were encountered which led to minor adjustments in laboratory setups and design methodologies. This section mentions and describes the challenges. The implications and influences of these challenges on the results and outcome of the study are discussed in Chapters 4 and 5 of this dissertation.

Initial concentration makeup for phase 1 and 2

During the test cell setup for phase 1 and 2 diffusion testing, the methodology used for making up the initial concentrations of BTEX and Chloroform in the source cell was different to the methodology used in phase 3. Earlier sections of this dissertation describe the leachate make-up methodology and from there it is clear that the targeted initial concentrations in the source cell were not always reached.

For phase 1, initial concentrations of some compounds were even higher than the maximum solubilities of those compounds, although the main the purpose of

the experiment, which was to prove diffusion through an intact HDPE GM into the receptor, was still achieved.

Late Chloroform introduction in phase 1

During the initial setup for phase 1 testing, chloroform was not available in the laboratory so it was not initially added to the source volume of the diffusion test cells. When the Chloroform arrived five days later, it was added to the source volume. This meant that day 0 concentrations excluded Chloroform and that there would effectively be a new initial concentration for the leachate in the source cell with the addition of Chloroform since the interaction within the source cell between the VOCs changed. However, this only had a minor influence on the main purpose of the experiment but the effects of the situation are worth analysing.

Sample Needle and Septum

When sampling for the diffusion tests, the GC required that a 1 ml sample be taken since the samples were first placed in GC vials and not introduced to the GC through direct injection, and the GC vials had to be filled to a certain level for the GC needle to comfortably reach the sample. The septum in the sampling ports of the diffusion test cell was small and, to reduce damage, a thin needle was used, as is typically used in laboratory work. The syringe was a 500 µl syringe which meant that it had to be filled twice to produce the required 1 ml sample. Since the 1 ml sample was replaced in the source / receptor reservoirs by deionised water, the effect was that the septum would be punctured four times to take one sample. Although the septums were designed for sample-taking using needles, the possibility of losses increased with increased puncturing of the septum. To reduce the possibility of losses, the septums were covered by clamping the sampling ports shut. Also, analysis of the control cell would give an indication of losses incurred and this was considered in the calculation of the coefficients.

Time between sampling and GC testing

Being in a laboratory environment, control over the coinciding of the GC availability and sample taking was sometimes challenging, especially in the early stages of the study. The time between sampling and testing was, in some cases, more than 3 hours. Although the samples were kept in a 4°C cold room during these times, the ideal situation was always to test the samples almost immediately after sampling to ensure minimisation of losses.

Magnetic stirrer

The magnetic stirrer bar placed inside the source and receptor reservoirs of the diffusion test cell was there to enable mixing of the liquid in the cell to ensure a uniform concentration in the compartment. This was done so that the sample taken would be representative of the concentration in the reservoir. The magnetic plate and stirrer bar setup was tested at first filling but, due to the construction of the cell, it did not have intimate contact with the magnetic plate at all times. Also, since the cells were made of stainless steel, mixing could not be observed. The possibility thus exists that continuous stirring of the test cells did not always take place. To assist with the uniformity of concentration during sampling, the cells were thoroughly shaken for at least 30 seconds before samples were taken. During phase 3 testing, the cells were shaken daily since air had to be extracted from at least one cell every day.

Temperature fluctuations

Experiments could not always take place at a controlled temperature of 22°C ± 2°C since constant temperature rooms at the University of Pretoria laboratory were not always available. However, the temperatures at which experiments took place were recorded and their observed effect on results (if any) is discussed in Chapter 5 of this dissertation.

3.10 CONCLUSION

- The laboratory setup used for the experiments of this study replicated the methods used by Professor Rowe at Queens University in Kingston Canada. The methodologies followed in the experiments required to calculate the sorption and diffusion coefficients for the three phases of testing was based on methods used in literature and the laboratory conditions were that of the University of Pretoria (South Campus) in Pretoria.
- Sorption and diffusion tests would be done to calculate the required sorption (S_{gf}) and diffusion coefficients (D_g) required to reach conclusions on the hypotheses of this dissertation. Chapter 4 contains the results obtained during testing and experiments described in Chapter 3.

CHAPTER 4. DATA PRESENTATION

4.1 INTRODUCTION

This chapter presents the data gathered through the tests and experiments, which were undertaken based on theory from the literature review of Chapter 2 and following the methodologies described in Chapter 3. This includes sorption and diffusion tests required to test the hypothesis of the study.

As shown in Chapter 3, the results from the field tests will not be further analysed and this chapter will thus present data from laboratory tests only.

4.2 SORPTION TESTS FOR SORPTION COEFFICIENT CALCULATION

Sorption tests were undertaken to determine the Sorption coefficient (S_{gf}) of the pollutant and GM in question and was done using both the immersion, diffusion and weight gain methods. For the immersion method, sorption tests were undertaken using methanol and aqueous solution as medium.

4.2.1 Methanol Sorption

Sorption tests using methanol as medium were conducted using the methodology described in Chapter 3. The tests were conducted in triplicate and the measured concentrations are given in **Table 4.1**.

Table 4.1: Methanol Sorption Test Concentrations at Given Times

VOC	Test Nr.	Measured Concentrations in mg/l				
		Day 0	Day 14	Day 21	Day 44	Day 62
Benzene	S1	2.127	1.316	1.391	1.436	1.344
	S2	2.135	2.094	2.074	1.978	1.881
	S3	2.217	2.142	2.136	2.153	2.082
Toluene	S1	2.192	1.881	1.863	1.775	1.727
	S2	2.245	2.320	2.320	2.260	2.151
	S3	3.240	2.355	2.322	2.256	2.094
Ethylbenzene	S1	1.596	1.533	1.675	1.653	1.614
	S2	2.475	2.046	2.061	1.833	1.836
	S3	3.310	1.765	1.985	1.879	1.871

p-Xylene	S1	3.845	3.421	3.458	3.257	3.286
	S2	4.678	4.265	4.301	4.041	4.005
	S3	5.599	4.135	4.364	4.046	4.037
Control Cells						
Benzene	C1	2.217	2.434	2.445	2.487	2.323
	C2	2.217	2.464	2.448	2.487	2.241
Toluene	C1	3.240	3.360	3.354	3.263	3.064
	C2	3.240	3.365	3.338	3.263	3.192
Ethylbenzene	C1	3.310	2.345	2.223	2.832	2.661
	C2	3.310	2.819	2.867	2.832	2.961
p-Xylene	C1	5.599	5.261	5.138	5.254	5.122
	C2	5.599	5.138	5.270	5.254	5.178

The results show that concentrations in the control cells were fairly constant throughout, indicating very little loss, and the S_{gf} values shown in **Table 4.2** were calculated using the methodology described in Chapter 3.

Table 4.2: Calculated S_{gf} Values for Methanol Sorption Tests

VOC	S_{gf} Values			
	S1	**S2**	**S3**	**Average**
Benzene	5.34	1.39	0.74	2.49
Toluene	2.62	0.64	4.35	2.54
Ethylbenzene	0.19	3.16	6.02	3.12
p-Xylene	1.76	1.67	3.15	2.19

4.2.2 Aqueous Sorption

Sorption tests using deionized water as medium were conducted using the methodology described in Chapter 3. The tests were conducted in triplicate at laboratory temperatures of 23°C ± 2°C and the measured concentrations are given in **Table 4.3**.

Table 4.3: Aqua Sorption Test Concentrations at Given Times

1mm GM		Measured Concentrations in mg/l				
		Day 0	**Day 2**	**Day 5**	**Day 12**	**Day 21**
Benzene	S1	6.946	0.595	1.801	1.200	0.766
	S2	1.004	0.470	0.562	0.375	0.806
Toluene	S1	7.236	0.451	1.185	0.634	0.223
	S2	0.661	0.359	0.373	0.268	0.016
Ethylbenzene	S1	7.718	0.291	0.602	0.381	0.034
	S2	1.120	0.223	0.181	0.122	0.034
p-Xylene	S1	7.800	0.249	0.552	0.396	0.020
	S2	1.100	0.195	0.154	0.127	0.111
Chloroform	S1	13.892	4.413	4.177	1.565	1.262
	S2	2.223	1.186	1.407	1.055	1.393
2mm GM						
		Day 0	**Day 2**	**Day 5**	**Day 12**	**Day 21**
Benzene	S1	0.644	0.607	0.447	0.298	0.078
	S2	0.698	0.608	0.575	0.383	0.449
Toluene	S1	0.589	0.466	0.244	0.245	0.001
	S2	0.694	0.427	0.349	0.315	0.047
Ethylbenzene	S1	0.627	0.308	0.125	0.127	0.001
	S2	0.706	0.287	0.193	0.152	0.003
p-Xylene	S1	0.646	0.256	0.073	0.099	0.001
	S2	0.735	0.227	0.143	0.131	0.001
Chloroform	S1	1.309	1.51	1.126	0.845	0.114
	S2	1.443	1.109	1.381	1.041	0.905
Control Cells						
		Day 0	**Day 2**	**Day 5**	**Day 12**	**Day 21**
Benzene	C1	0.971	1.510	0.61	0.412	0.298
	C2	0.542	2.082	0.610	0.406	0.340
Toluene	C1	0.996	1.301	0.491	0.725	0.056
	C2	0.574	1.953	0.560	2.043	0.109
Ethylbenzene	C1	1.076	1.096	0.370	0.459	0.016
	C2	0.609	1.770	0.460	1.475	0.049
p-Xylene	C1	1.075	1.014	0.334	0.465	0.011
	C2	0.580	1.716	0.434	1.600	0.027
Chloroform	C1	1.968	2.820	1.185	1.065	0.393
	C2	1.212	1.401	1.382	1.041	0.564

The results from the control cells indicated significant losses because of the sampling process or as a result of sorption onto the glass or vial caps, and the uncorrected and corrected (after accounting for the losses) S_{gf} values for both the 1mm and 2mm HDPE GMs are shown in **Table 4.4**.

Table 4.4: Calculated S_{gf} values for aqua sorption tests

1mm GM	***S_{gf}* Values (Uncorrected)**			***S_{gf}* Values (Corrected)**		
	S1	**S2**	**Avg.**	**S1**	**S2**	**Avg.**
Benzene	115	3.8	59	54	1.8	27.8
Toluene	448	557	502	55	68	61.9
Ethylbenzene	3140	436	1788	153	21	87.2
p-Xylene	5369	121	2745	156	3.5	80.2
Chloroform	143	8.6	75	47	2.9	25.1
2mm GM	***S_{gf}* Values (Uncorrected)**			***S_{gf}* Values (Corrected)**		
	S1	**S2**	**Avg.**	**S1**	**S2**	**Avg.**
Benzene	55.7	4.5	30.1	26.0	2.09	14.1
Toluene	3117	105	1610	383	12.9	198
Ethylbenzene	11679	1694	6686	569	82.6	326
p-Xylene	3950	3089	3519	115	90.2	103
Chloroform	80.9	4.8	42.8	26.9	1.6	14.2

4.3 WEIGHT GAIN METHOD FOR SORPTION COEFFICIENT CALCULATION

Sorption tests were also conducted using the weight gain method described in Chapter 3. Although the weight gain method is prone to error when using VOCs it was done to see if any comparisons could be derived. The recorded weights obtained during testing using the 1 mm and 2 mm HDPE GM is given in **Tables 4.5** and **4.6**.

Table 4.5: Weights Recorded at Given intervals for 1 mm GM

1 mm GM	Dry Weight (m_0)	Weights (mg) at given Time (minutes)						
Sample		10	30	45	180	250	360	1440
Benzene A	387.48	388.60	391.26	392.82	396.50	399.15	402.20	416.05
Benzene B	379.18	380.50	382.85	384.41	388.11	390.41	393.56	407.03
Ethylbenzene A	364.88	367.01	368.22	369.49	372.38	374.41	376.80	391.20
Ethylbenzene B	419.64	421.50	423.26	424.72	427.80	430.11	432.66	449.60
Toluene A	411.29	414.01	416.03	418.08	422.72	426.20	430.51	444.60
Toluene B	390.23	392.92	394.80	396.80	401.22	404.61	408.85	421.58
p-Xylene A	315.08	317.02	319.08	320.61	324.02	326.96	330.51	341.50
p-Xylene B	357.76	360.24	362.32	364.12	368.29	371.88	375.96	388.61
Chloroform A	425.57	430.90	434.25	437.60	445.30	451.30	459.09	482.61
Chloroform B	444.75	451.06	454.25	457.35	466.24	472.61	481.41	505.11

Table 4.6: Weights Recorded at Given Intervals for 2 mm GM

2 mm GM	Dry Weight (m_0)	Weights (mg) at given Time (minutes)						
Sample		30	50	90	190	280	370	1440
Benzene A	793.08	797.50	799.13	801.20	805.70	808.80	812.31	840.21
Benzene B	724.34	728.30	730.14	731.90	736.01	739.01	742.22	767.91
Ethylbenzene A	648.08	651.34	652.67	654.30	657.18	659.50	661.91	680.81
Ethylbenzene B	737.11	741.12	742.40	743.90	747.20	749.74	752.50	772.98
Toluene A	644.70	648.60	650.71	652.40	657.29	660.54	663.98	692.98
Toluene B	641.43	645.17	647.52	649.56	653.97	657.18	660.65	689.47
p-Xylene A	696.07	702.02	703.42	705.32	709.86	713.50	717.80	749.91
p-Xylene B	669.23	674.75	676.22	678.55	683.20	686.90	690.74	722.80
Chloroform A	761.85	770.69	773.57	777.54	786.35	792.28	799.11	854.10
Chloroform B	705.10	713.10	716.14	719.90	728.34	733.99	739.90	792.71

Using the data in **Tables 4.5** and **4.6** and the methodology in Chapter 3, the S_{gf} values were calculated and shown in **Table 4.7.**

Table 4.7: S_{gf} Values using Weight Gain Method for 1 mm and 2 mm HDPE GM

	S_{gf} Values for 1mm GM		
VOC	**Sample A**	**Sample B**	**Avg.**
Benzene	69.3	69.0	69.2
Toluene	76.1	75.5	75.8
Ethylbenzene	67.8	67.1	67.5
p-Xylene	78.8	81.1	79.9
Chloroform	126	128	126.8
	S_{gf} Values for 2mm GM		
VOC	**Sample A**	**Sample B**	**Avg.**
Benzene	55.9	56.5	56.2
Toluene	70.3	70.4	70.4
Ethylbenzene	47.4	45.7	46.6
p-Xylene	72.7	75.2	73.9
Chloroform	113	116	115

4.3.1 Sorption Coefficient Calculation from Diffusion Tests

As discussed in Chapters 2 and 3, the sorption coefficient S_{gf} can also be determined from the results of the diffusion tests using **Equation 7**. The results of the Diffusion tests will be presented in this chapter but selected Phase 1 results (one 2 mm GM) are given in **Tables 4.8** to **4.11** to indicate how the S_{gf} values were calculated.

Phase 2 and 3 diffusion tests were not used for calculation of the sorption coefficient since the introduction of the centerpiece filled with air containing an unknown initial concentration of VOC would not allow the rationale followed in **Equation 7** to be used. Therefore, the sorption coefficients obtained doing sorption/immersion tests were used in the modeling of phase 2 and 3.

Table 4.8: Calculation of S_{gf} from Diffusion Test Results of Benzene

	Mass in mg contained in each 1 ml sample removed per cell						
	A2	**B2**	**C2**	**A1**	**B1**	**C1**	
Day 0	0	0	0	0.187482	0.187482	0.187482	
Day 3	0	0	0	0.168700	0.197600	0.148000	
Day 8	0.001599	0.000164	0.000789	0.071460	0.097800	0.093600	
Day 15	0.023500	0.016500	0.016500	0.070500	0.071000	0.063000	
Day 22	0.058200	0.028400	0.021200	0.047900	0.054000	0.055900	
Day 36	0.07000	0.064200	0.093600	0.047000	0.054800	0.050100	
	Calculation of S_{gf} using Equation 7						
	A2	**B2**	**C2**	**A1**	**B1**	**C1**	**UNITS**
C_{fo}	0.19	0.19	0.19	0.19	0.19	0.19	**mg/cm^3**
C_{fF}	0.04	0.04	0.05	0.04	0.04	0.05	**mg/cm^3**
V_s	384.85	384.85	384.85	384.85	384.85	384.85	**cm^3**
V_r	269.39	269.39	269.39	269.39	269.39	269.39	**cm^3**
A	38.48	38.48	38.48	38.48	38.48	38.48	**cm^2**
t_{GM}	0.2	0.2	0.2	0.2	0.2	0.2	**cm**
$\Sigma V_i C_i$	0.15	0.11	0.13	0.59	0.66	0.59	**mg**
S_{gf}	131.6	128.1	91.4	130.3	126.4	90.27	
			Avg.	**116.4**			

Table 4.9: Calculation of S_{gf} from Diffusion Test Results of Toluene

	Mass in mg contained in each 1 ml sample removed per cell						
	A2	**B2**	**C2**	**A1**	**B1**	**C1**	
Day 0	0	0	0	0.185323	0.185323	0.185323	
Day 3	0	0	0	0.165000	0.196100	0.146600	
Day 8	0.000978	0.000089	0.000468	0.038700	0.062850	0.063450	
Day 15	0.035700	0.027000	0.028000	0.047300	0.041700	0.039100	
Day 22	0.066700	0.034400	0.028600	0.035100	0.035000	0.035400	
Day 36	0.065700	0.055900	0.073300	0.037800	0.037300	0.035100	
	Calculation of S_{gf} using Equation 7						
	A2	**B2**	**C2**	**A1**	**B1**	**C1**	**UNITS**
C_{fo}	0.19	0.19	0.19	0.19	0.19	0.19	**mg/cm^3**
C_{fF}	0.04	0.03	0.04	0.04	0.03	0.04	**mg/cm^3**
V_s	384.85	384.85	384.85	384.85	384.85	384.85	**cm^3**
V_r	269.39	269.39	269.39	269.39	269.39	269.39	**cm^3**
A	38.48	38.48	38.48	38.48	38.48	38.48	**cm^2**
t_{GM}	0.2	0.2	0.2	0.2	0.2	0.2	**cm**
$\Sigma V_i C_i$	0.17	0.11	0.13	0.51	0.56	0.50	**mg**
S_{gf}	178.6	207.9	166.8	177.3	206.1	165.5	
			Avg.	**183.7**			

Table 4.10: Calculation of S_{gf} from Diffusion Test Results of Ethylbenzene

	Mass in mg contained in each 1ml sample removed per cell						
	A2	**B2**	**C2**	**A1**	**B1**	**C1**	
Day 0	0	0	0	0.18532	0.18532	0.18532	
Day 3	0	0	0	0.16500	0.19610	0.14660	
Day 8	0	0	0	0.03870	0.06285	0.06345	
Day 15	0.0081	0.0066	0.0071	0.04730	0.04170	0.03910	
Day 22	0.0194	0.0085	0.0068	0.03510	0.03500	0.03540	
Day 36	0.0189	0.0163	0.0265	0.03780	0.03730	0.03510	
	Calculation of S_{gf} using Equation 7						
	A2	**B2**	**C2**	**A1**	**B1**	**C1**	**UNITS**
C_{fo}	0.19	0.19	0.19	0.19	0.19	0.19	**mg/cm^3**
C_{fF}	0.02	0.02	0.02	0.02	0.02	0.02	**mg/cm^3**
V_s	384.8451	384.8451	384.8451	384.8451	384.8451	384.845	**cm^3**
V_r	269.3916	269.3916	269.3916	269.3916	269.3916	269.391	**cm^3**
A	38.48	38.48	38.48	38.48	38.48	38.48	**cm^2**
t_{GM}	0.2	0.2	0.2	0.2	0.2	0.2	**cm**
$\Sigma V_i C_i$	0.046	0.031	0.040	0.509	0.558	0.505	**mg**
S_{gf}	396.9	424.9	358.7	393.9	421.2	355.8	
			Avg.	**391.9**			

Table 4.11: Calculation of S_{gf} from Diffusion Test Results of p-Xylene

	Mass in mg contained in each 1ml sample removed per cell						
	A2	**B2**	**C2**	**A1**	**B1**	**C1**	
Day 0	0	0	0	0.1404	0.1404	0.1404	
Day 3	0	0	0	0.0773	0.0913	0.0814	
Day 8	0	0	0	0.0579	0.0639	0.0645	
Day 15	0.0408	0.0399	0.0410	0.0411	0.0406	0.0402	
Day 22	0.0442	0.0404	0.0395	0.0394	0.0402	0.0402	
Day 36	0.0449	0.0431	0.0482	0.0399	0.0408	0.0405	
	Calculation of S_{gf} using Equation 7						
	A2	**B2**	**C2**	**A1**	**B1**	**C1**	**UNITS**
C_{fo}	0.14	0.14	0.14	0.14	0.14	0.19	**mg/cm^3**
C_{fF}	0.03	0.03	0.03	0.03	0.03	0.03	**mg/cm^3**
V_s	384.845	384.845	384.845	384.845	384.845	384.845	**cm^3**
V_r	269.392	269.392	269.392	269.392	269.392	269.392	**cm^3**
A	38.48	38.48	38.48	38.48	38.48	38.48	**cm^2**
t_{GM}	0.2	0.2	0.2	0.2	0.2	0.2	**cm**
$\Sigma V_i C_i$	0.129	0.123	0.128	0.39	0.417	0.407	**mg**
S_{gf}	178.1	181.0	166.6	176.8	179.5	245.9	
			Avg.	**188.0**			

4.4 SUMMARY OF SORPTION COEFFICIENT CALCULATIONS

The aim of the sorption tests was to determine the sorption coefficient S_{gf} for the GM and compound in question. Tests were conducted at the start of the study using methanol as a medium and although the final chosen medium for the study was aqua solutions it was decided to include the results of methanol sorption tests so that comparisons could be made. **Table 4.12** summarizes the averaged and corrected S_{gf} values obtained using the different test methods and the results of the sorption and diffusion tests will be analyzed in Chapter 5 of this dissertation.

Table 4.12: Summary of S_{gf} Values Obtained Using Different Test Methods

VOC	Methanol Sorption		Aqua Sorption		Weight Gain		Diffusion Test	
	1mm	2mm	1mm	2mm	1mm	2mm	1mm	2mm
Benzene	-	2.49	27.8	14.1	69.2	56.2	-	116
Toluene	-	2.54	61.9	198	75.8	70.4	-	183
Ethylbenzene	-	3.12	87.2	326	67.5	46.6	-	391
p-Xylene	-	2.19	80.2	102	79.9	73.9	-	188
Chloroform	-	-	25.1	14.2	126	115	-	-

4.5 CONCENTRATIONS FROM DIFFUSION TESTS

Diffusion tests were carried out in three phases (see Chapter 3).

- Phase 1 measured the change in concentration over time of BTEX and Chloroform in the source and receptor compartments of diffusion cells. The source and receptor compartments were separated by a 2 mm HDPE GM.
- Phase 2 tests used 2 x 1 mm HDPE GMs and a pervious zone filled with air separating the source and receptor compartments.
- Phase 3 replicated phase 2 testing and introduced the extraction of air through the pervious zone between the two 1 mm GMs.

4.5.1 Phase 1 – Diffusion tests using one GM

Graphical Representation of results

Tests were conducted in triplicate (Cells A, B and C) with a control cell (Cell E) and a blank cell (Cell D) to measure losses and possible outside influences. Concentrations in the source and receptor cells were measured on days 0, 3, 8, 15 and 22. Concentrations were averaged and plotted (initial concentration over measured concentration) against time for the source **Figure 4.1** and receptor **Figure 4.2** volumes. The concentrations measured in Cell E were also plotted (initial concentration over measured concentration) against time and are shown in **Figure 4.3.**

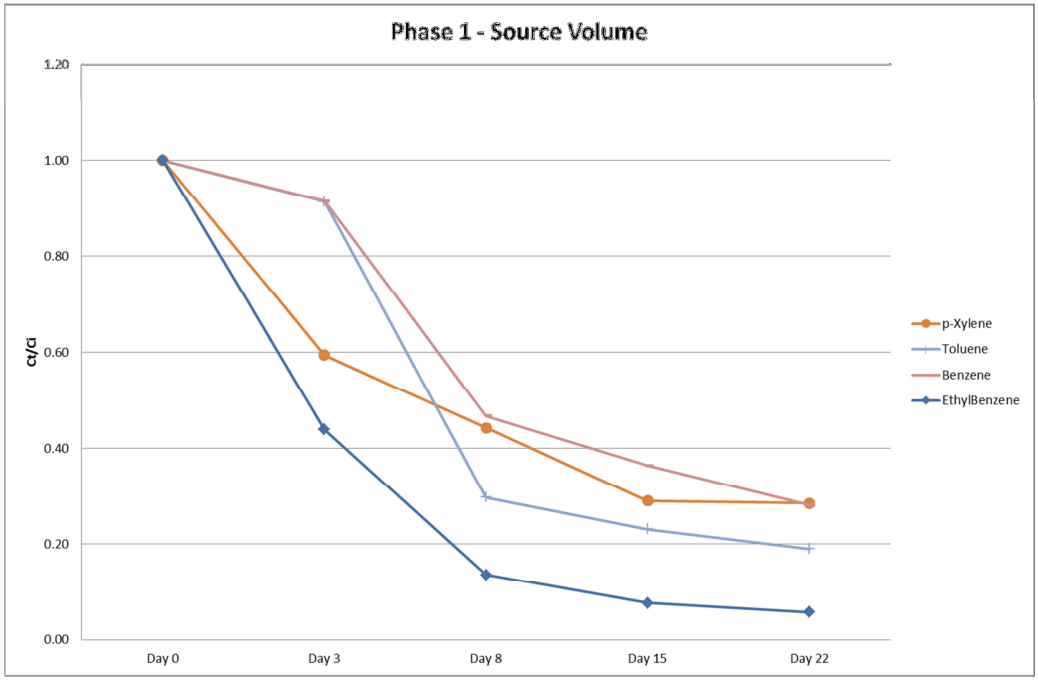


Figure 4.1: Phase 1 – Source Volume Graph

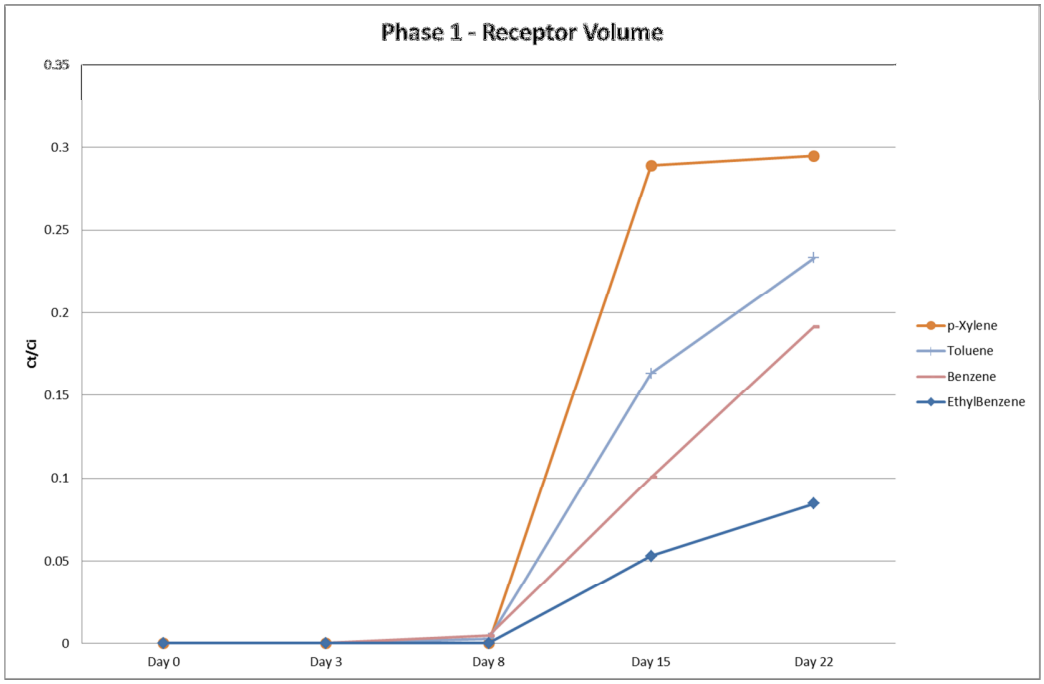


Figure 4.2: Phase 1 – Receptor Volume Graph

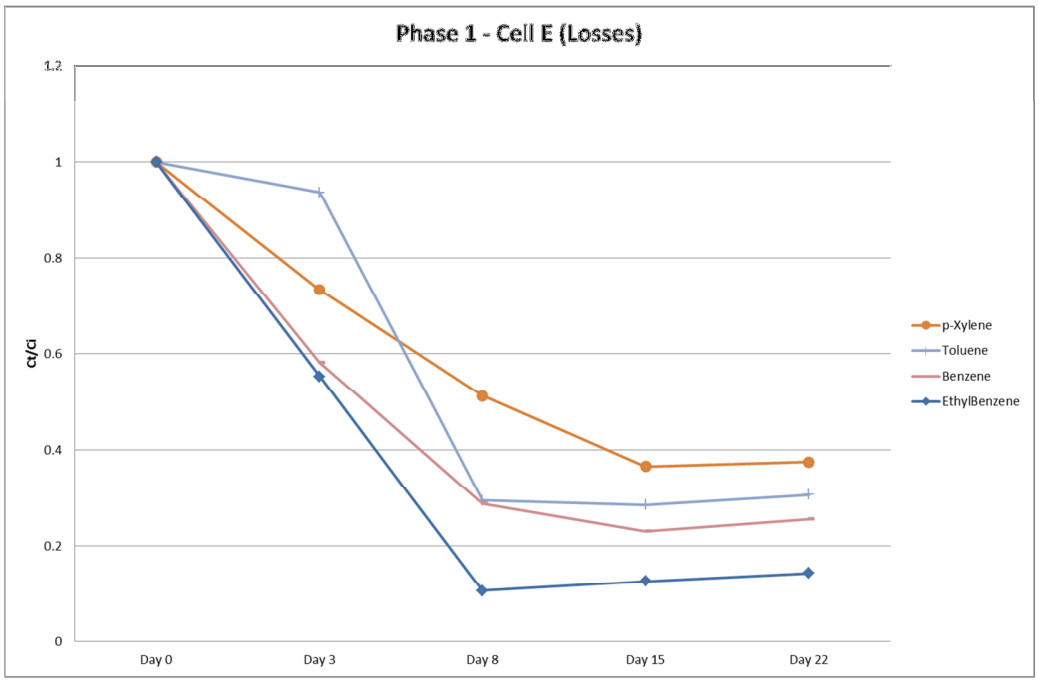


Figure 4.3: Phase 1 – Cell E - Losses

Calculation of Diffusion Coefficient

As described in preceding chapters the calculation of the Diffusion coefficient D_g was done using the computer program POLLUTE. The concentration versus time output graphs that POLLUTE then produces if the methodologies described in Chapter 3 were correctly followed, were combined with the actual laboratory test results and is shown on **Figures 4.4** to **4.7** for phase 1 testing.

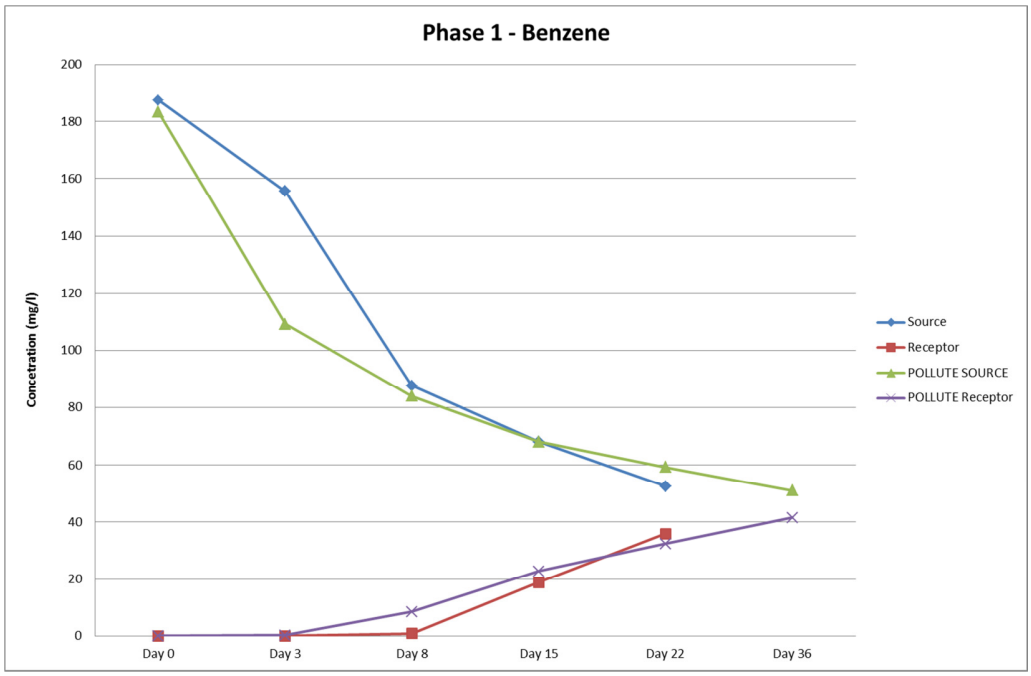


Figure 4.4: Combined Output Graph for Benzene

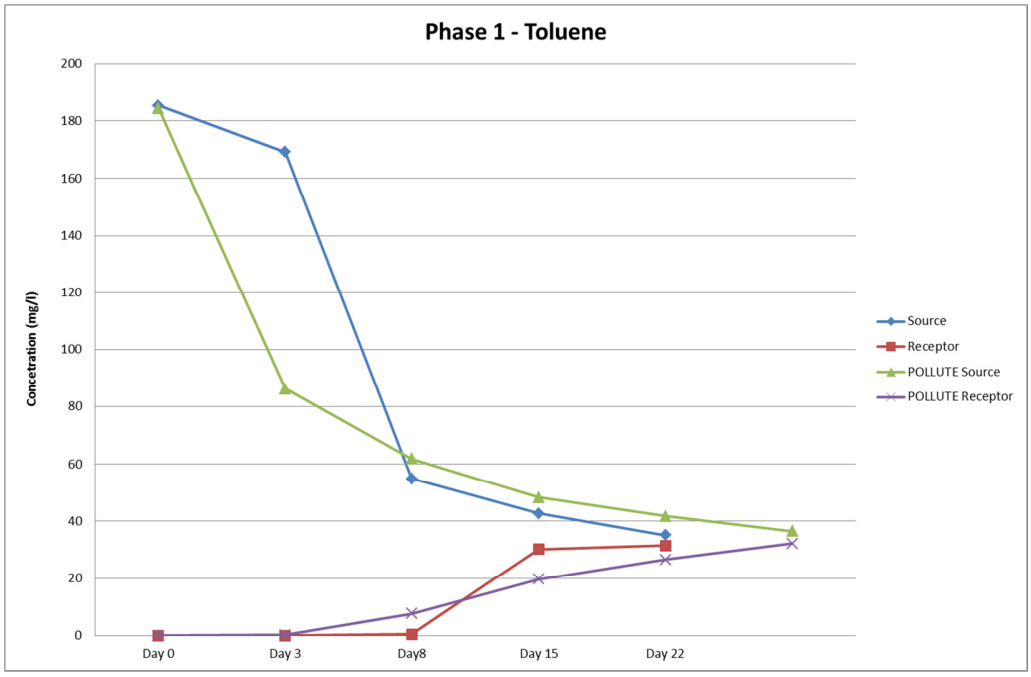


Figure 4.5: Combined Output Graph for Toluene

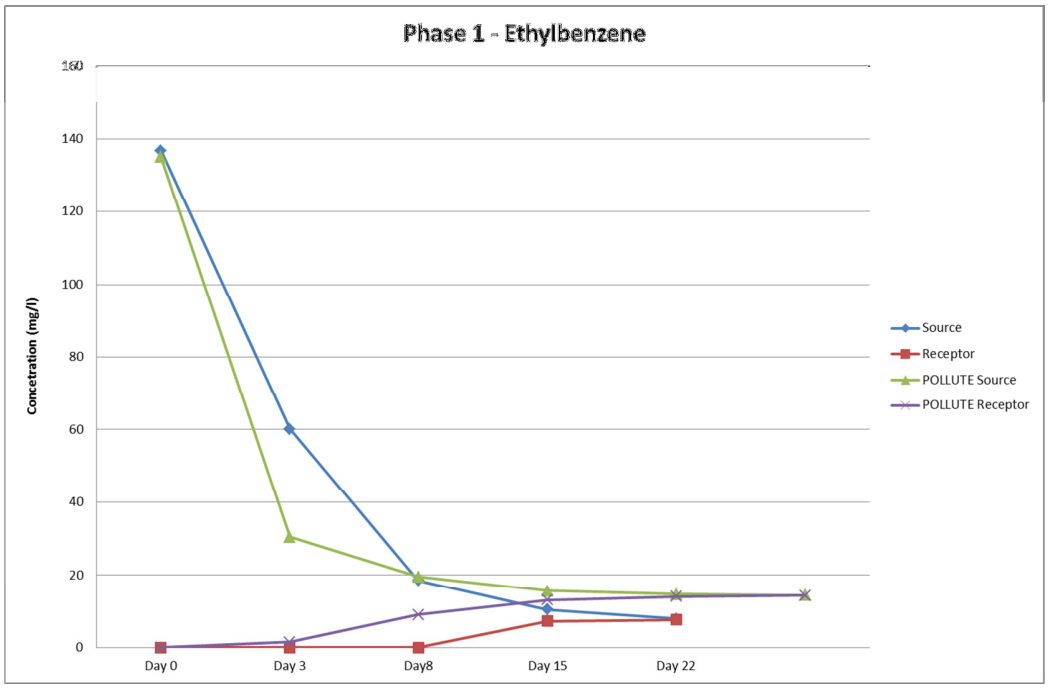


Figure 4.6: Combined Output Graph for Ethylbenzene

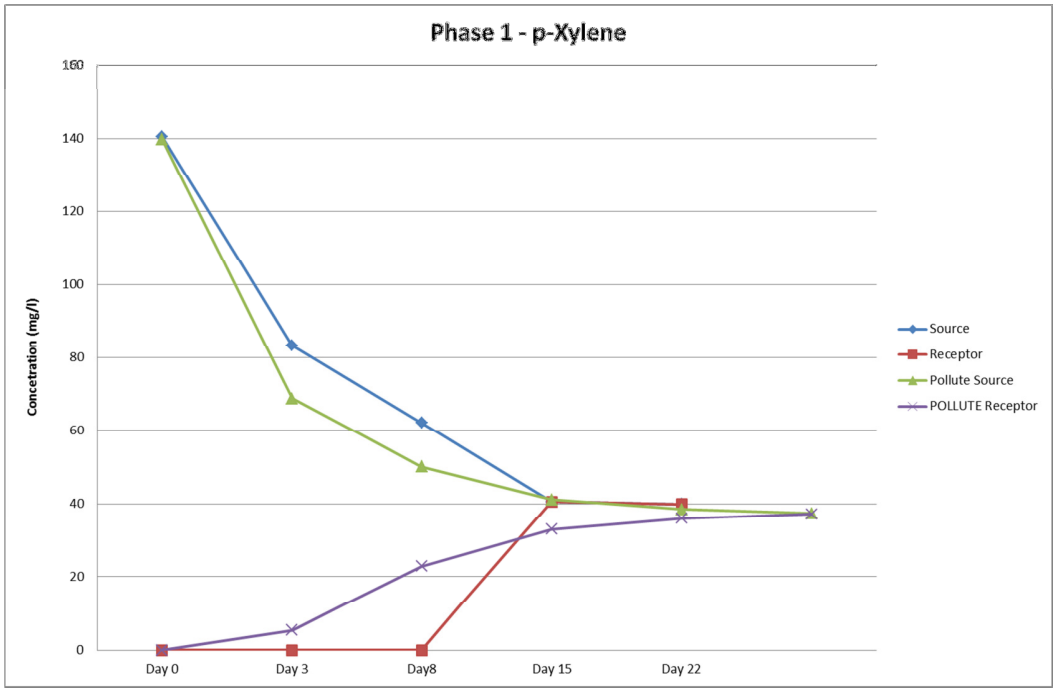


Figure 4.7: Combined Output Graph for p-Xylene

For phase 1 testing the diffusion coefficients obtained through POLLUTE in order to obtain the output graphs in **Figures 4.4** to **4.7** are given in **Table 4.9.**

Table 4.13: Calculated Diffusion Coefficients (D_g) for phase 1 testing

VOC	Diffusion Coefficient in m^2/s
Benzene	9.26×10^{-13}
Toluene	8.68×10^{-13}
Ethylbenzene	1.39×10^{-12}
p-Xylene	2.32×10^{-12}

4.5.2 Phase 2 – Diffusion tests using two GMs

Graphical Representation of results

Tests were conducted in triplicate (Cells A, B and C) with a control cell (Cell E) and a blank cell (Cell D) to measure losses and possible outside influences. Concentrations in the source and receptor cells were measured on days 0, 5, 12, 19, 28, 41, 53 and 86. Concentrations were averaged and plotted (initial concentration over measured concentration) against time for the source **Figure 4.8** and receptor **Figure 4.9** volumes. The concentrations measured in Cell E

were also plotted (initial concentration over measured concentration) against time and are given in **Figure 4.10.**

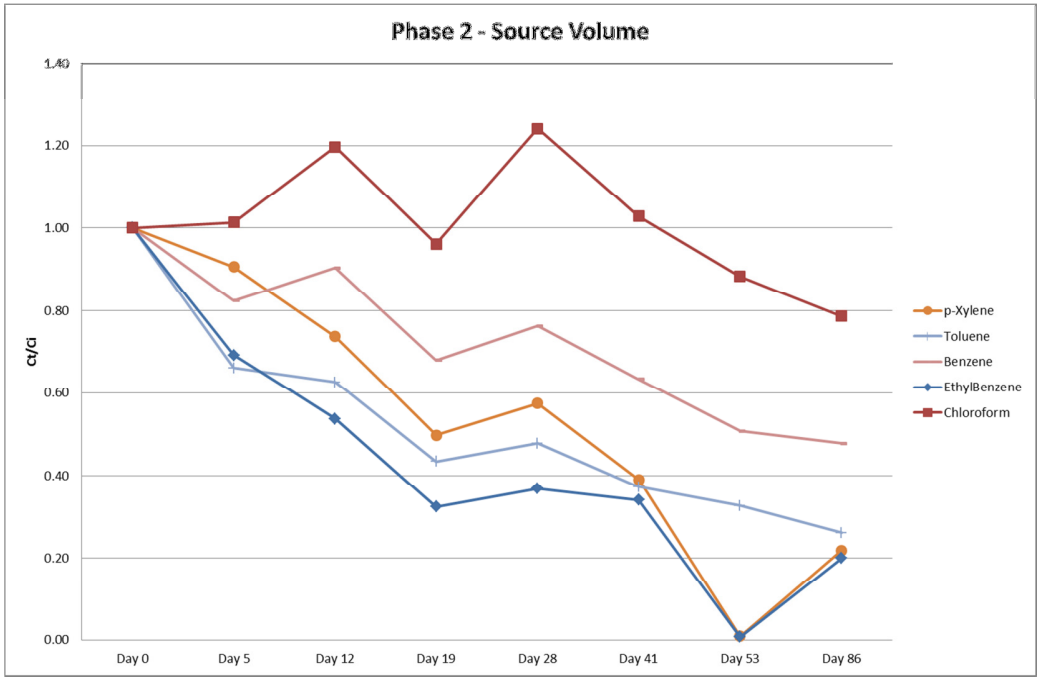


Figure 4.8: Phase 2 – Source Volume Graph

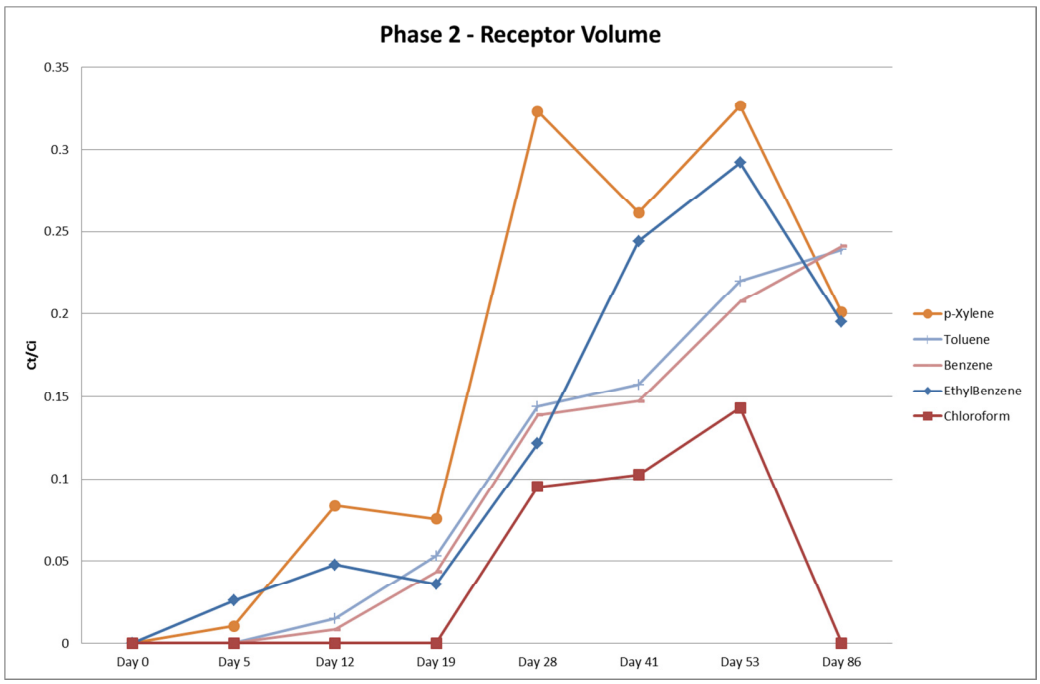


Figure 4.9: Phase 2 – Receptor Volume Graph

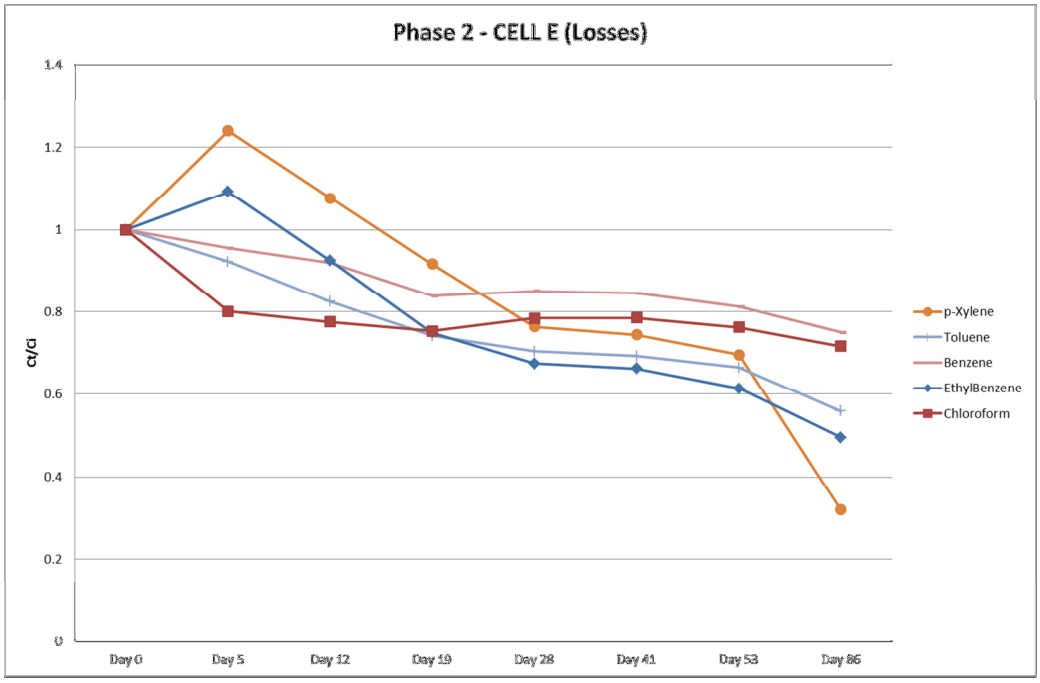


Figure 4.10: Phase 2 – Cell E - Losses

Calculation of Diffusion Coefficient

As for phase 1 testing, the Diffusion coefficient D_g was determined using POLLUTE®. The concentration versus time output graphs that POLLUTE® produced, if the methodologies in Chapter 3 were correctly followed, were combined with the actual laboratory test results and is shown on **Figures 4.11** to **4.15** for phase 2 testing. Phase 2 testing also included the VOC Chloroform and S_{gf} values used for phase 2 diffusion testing were determined with Sorption/Immersion tests.

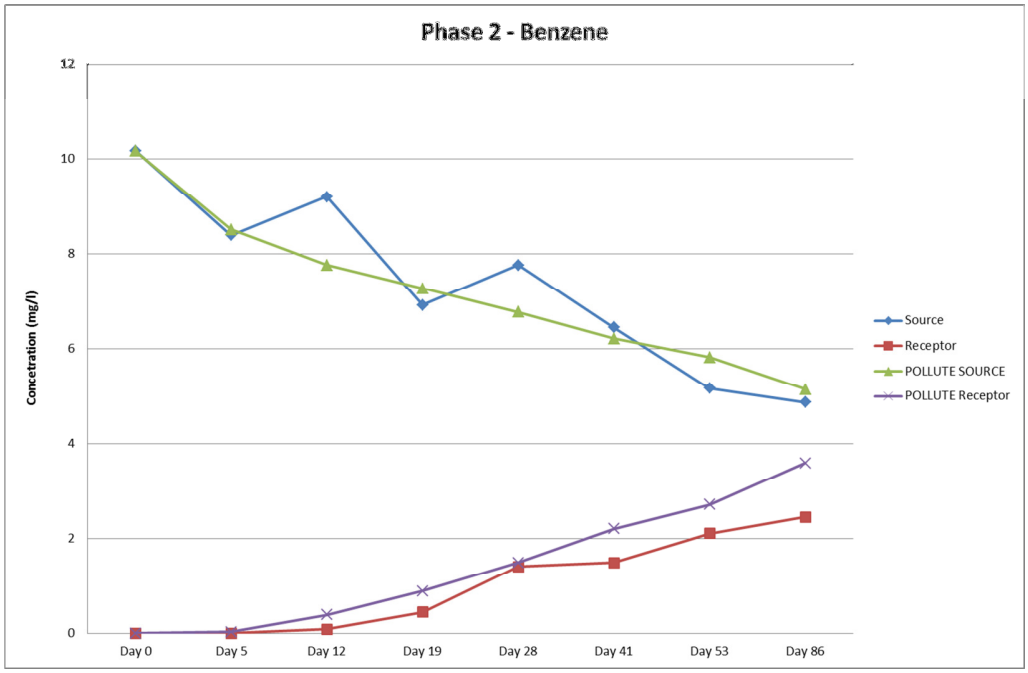


Figure 4.11: Combined Output Graph for Benzene

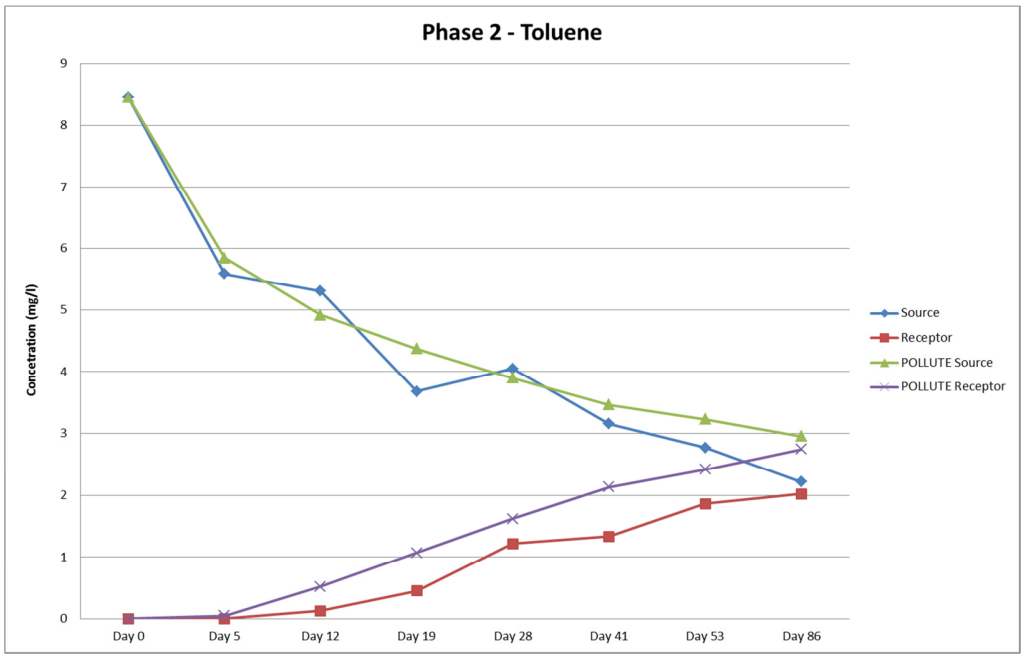


Figure 4.12: Combined Output Graph for Toluene

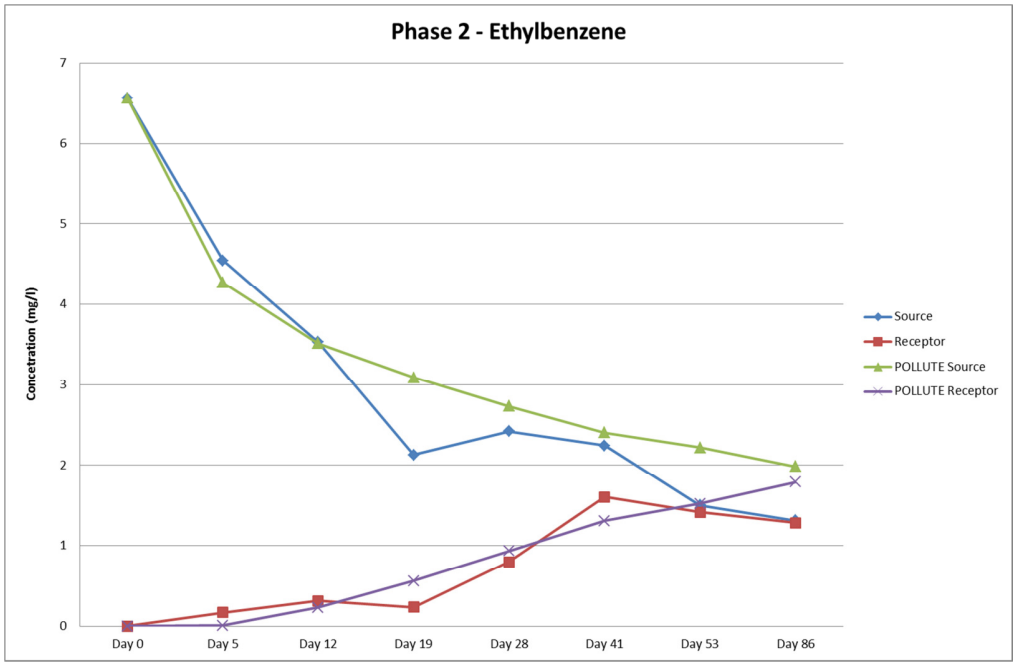


Figure 4.13: Combined Output Graph for Ethylbenzene

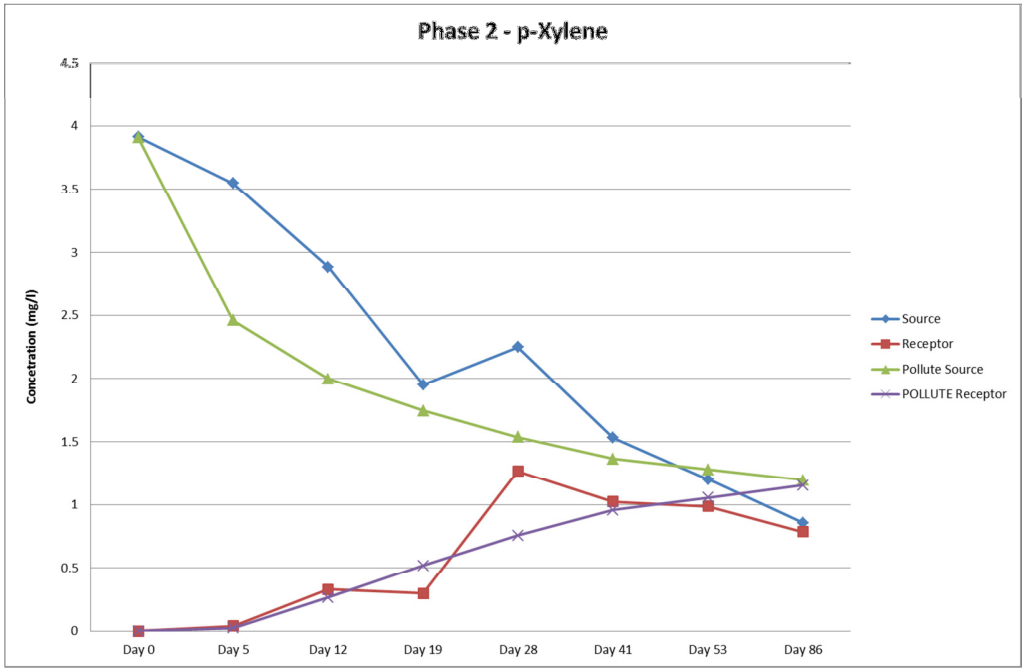


Figure 4.14: Combined Output Graph for p-Xylene

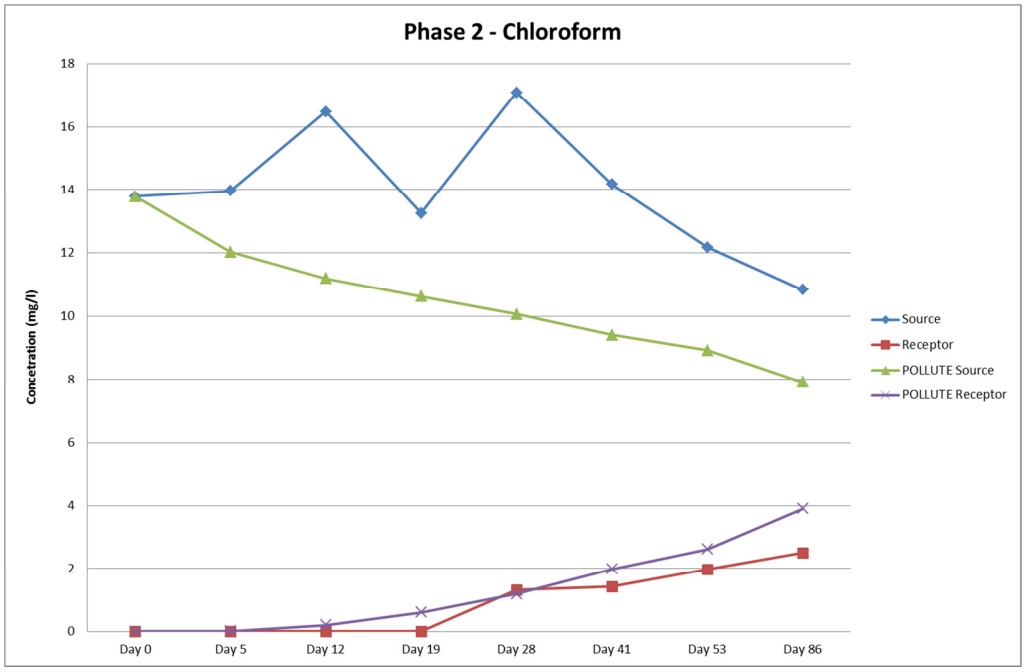


Figure 4.15:Combined Output Graph for Chloroform

For Phase 2 testing the diffusion coefficients obtained through POLLUTE in order to obtain the output graphs in **Figures 4.11** to **4.15** are given in **Table 4.14**: Calculated Diffusion Coefficients (Dg) for phase 2 testing

.

Table 4.14: Calculated Diffusion Coefficients (Dg) for phase 2 testing

VOC	Diffusion Coefficient in m^2/s
Benzene	8.10×10^{-13}
Toluene	8.10×10^{-13}
Ethylbenzene	5.79×10^{-13}
p-Xylene	8.10×10^{-13}
Chloroform	5.79×10^{-13}

4.5.3 Phase 3 – Extraction of Air

Graphical Representation of Results

Tests were conducted using test cells A, B, C and D, introducing different rates for air extraction (see Chapter 3). Cell A was left with no extraction; Cell B extraction took place every day; Cell C every third day and Cell D every week.

Concentrations in the source and receptor cells were measured on days 0, 5, 11, 18, 25, 32, 39 and 48. Concentrations were plotted (initial concentration over measured concentration) against time for the source and receptor volumes. The source and receptor concentration graphs for the four cells are shown in **Figures 4.16** to **4.23**.

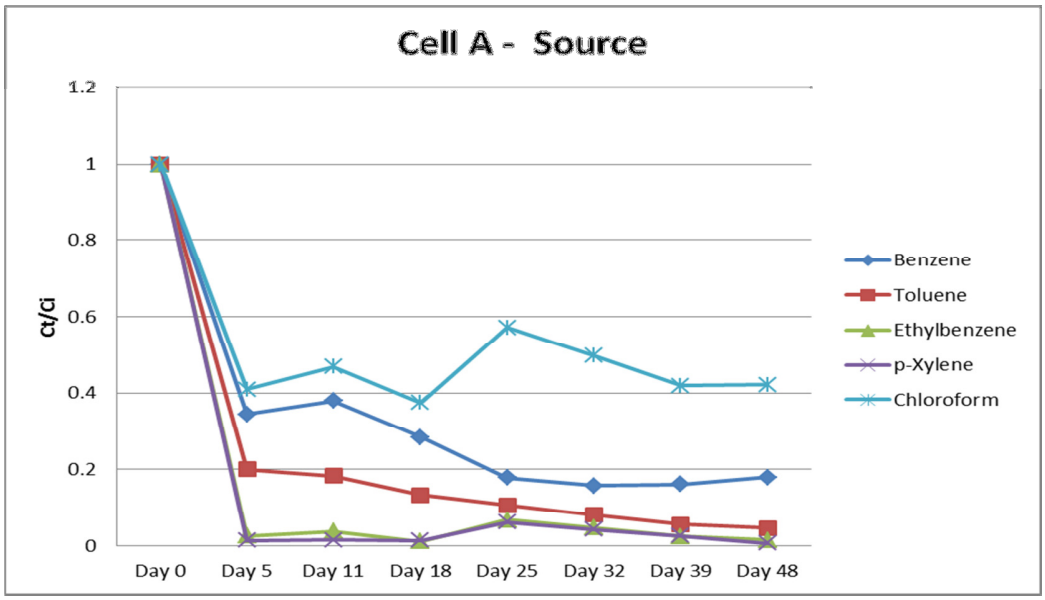


Figure 4.16: Phase 3 – Cell A Source Volume Graph

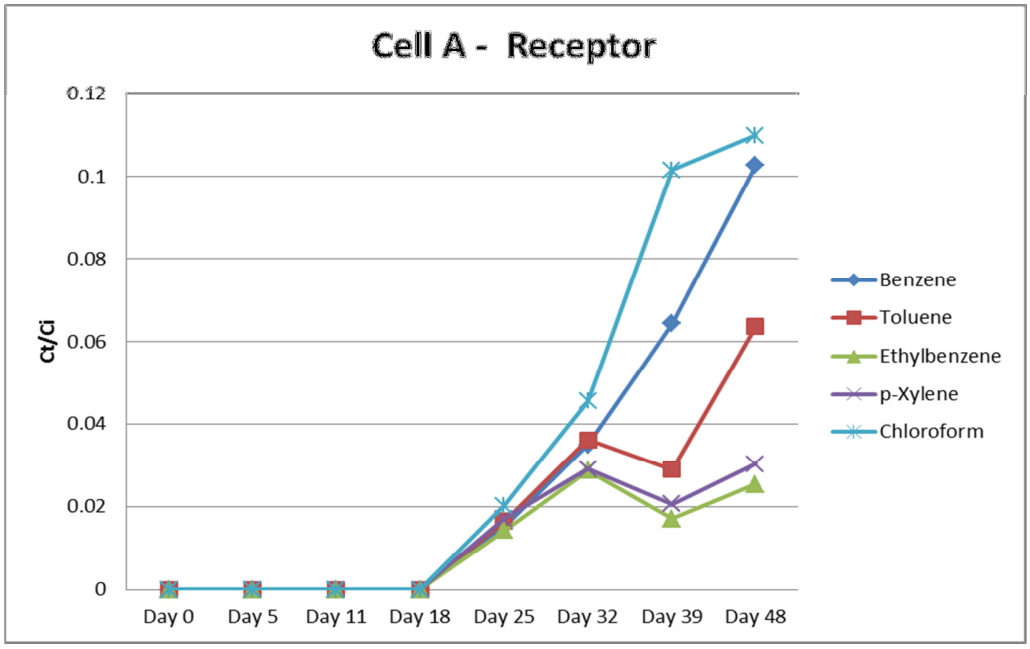


Figure 4.17: Phase 3 – Cell A Receptor Volume Graph

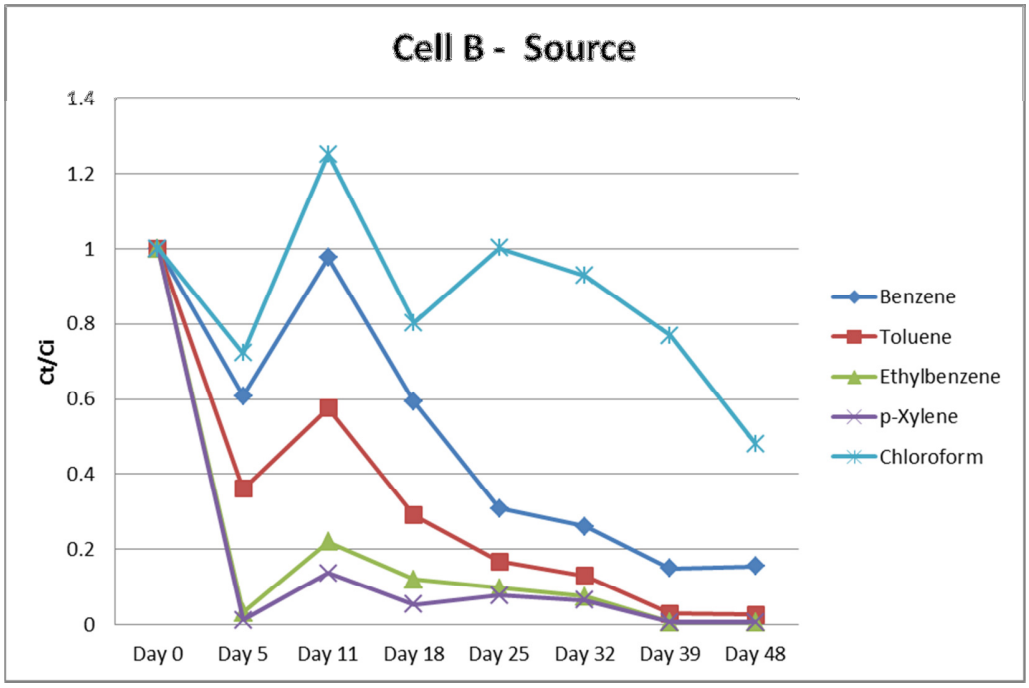


Figure 4.18: Phase 3 – Cell B Source Volume Graph

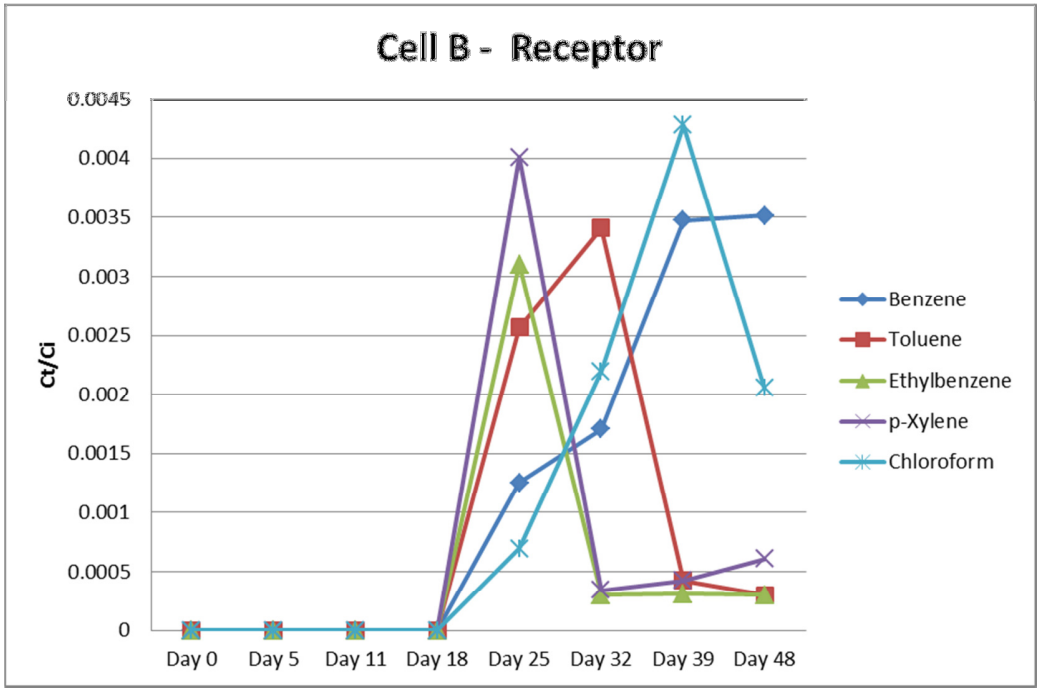


Figure 4.19: Phase 3 – Cell B Receptor Volume Graph

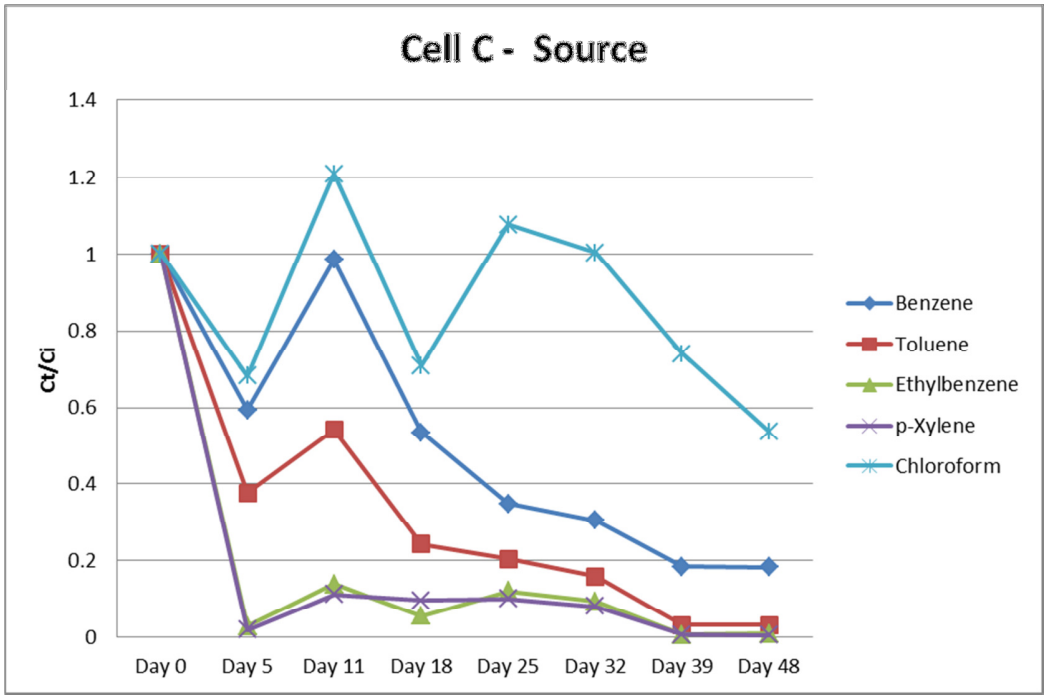


Figure 4.20: Phase 3 – Cell C Source Volume Graph

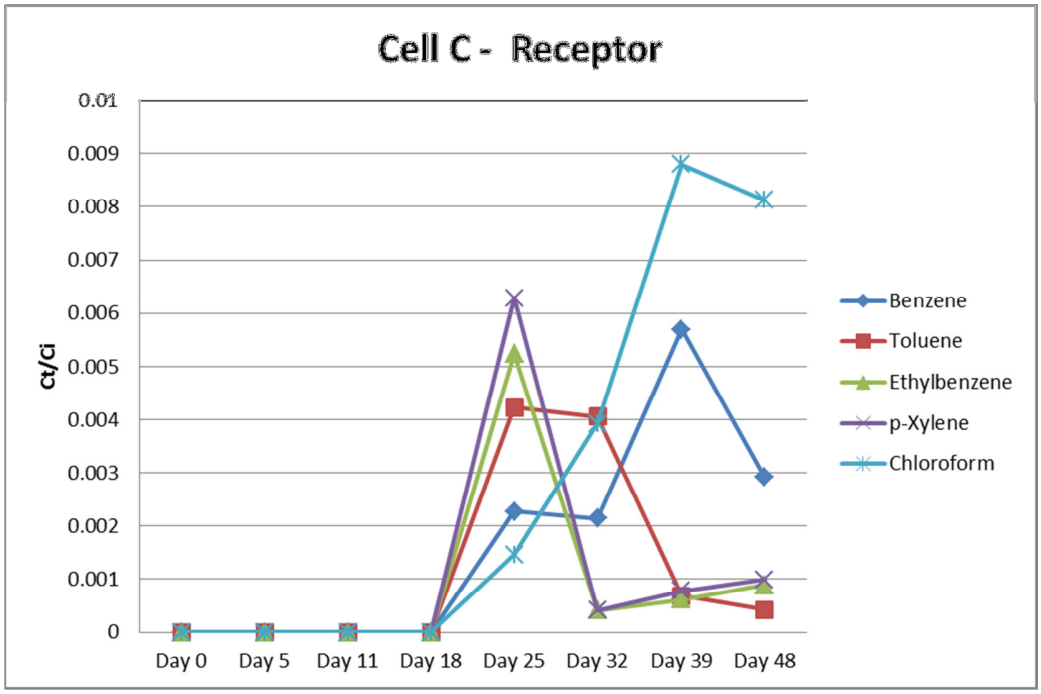


Figure 4.21: Phase 3 – Cell C Receptor Volume Graph

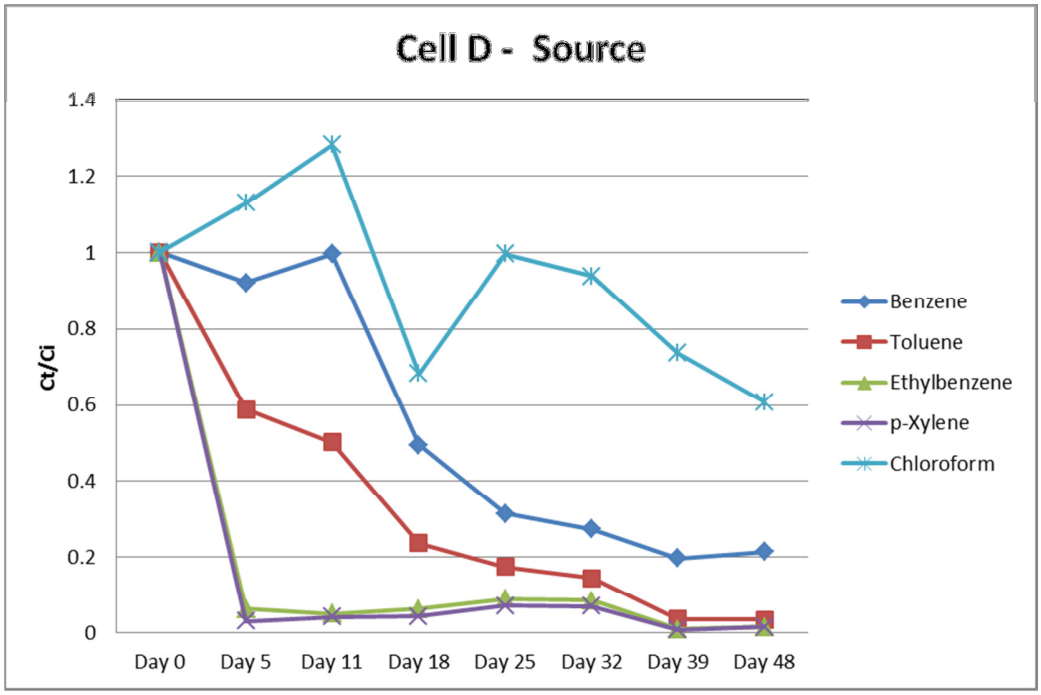


Figure 4.22: Phase 3 – Cell D Source Volume Graph

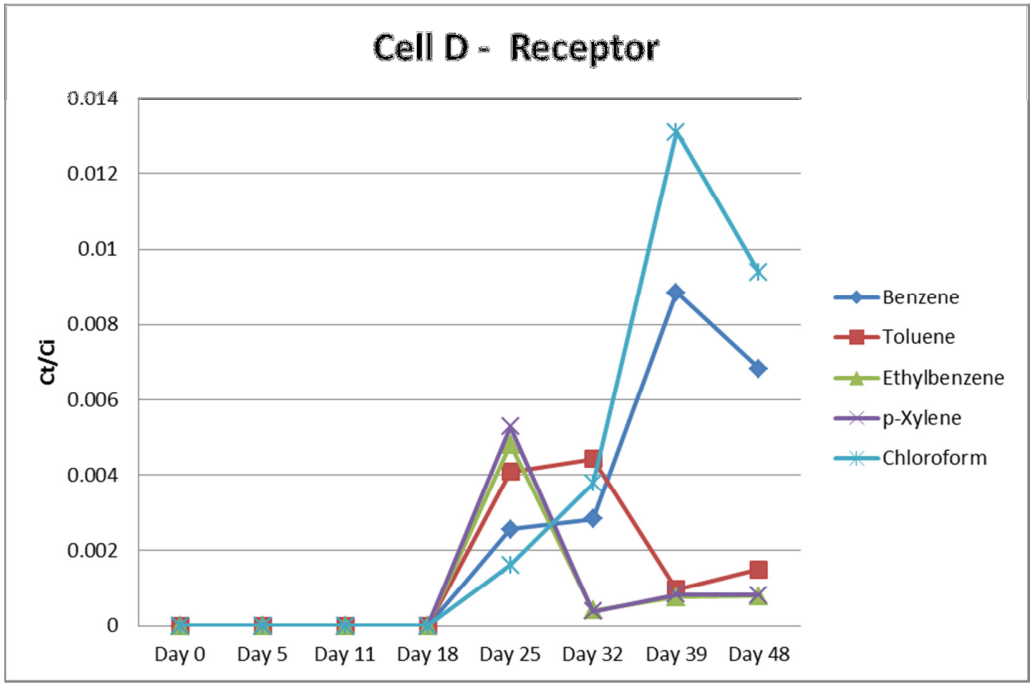


Figure 4.23: Phase 3 – Cell D Receptor Volume Graph

Figures 4.16 to **4.19** show the concentration profile over time of all VOCs per cell. An analysis of the data is provided in Chapter 5, but when looking at the graphs of concentrations (initial concentration over measured concentration) against time per individual VOC in the various cells, another trend becomes clear. **Figures 4.24** to **4.33** show each individual VOC concentration profile over time.

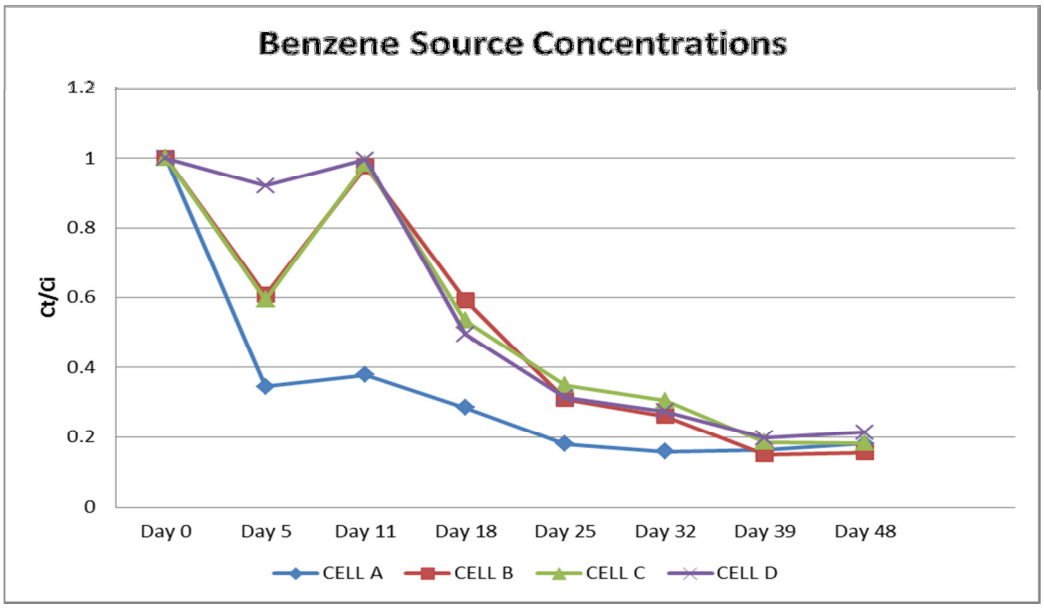


Figure 4.24: Phase 3 – Concentrations of Benzene in Source Volume

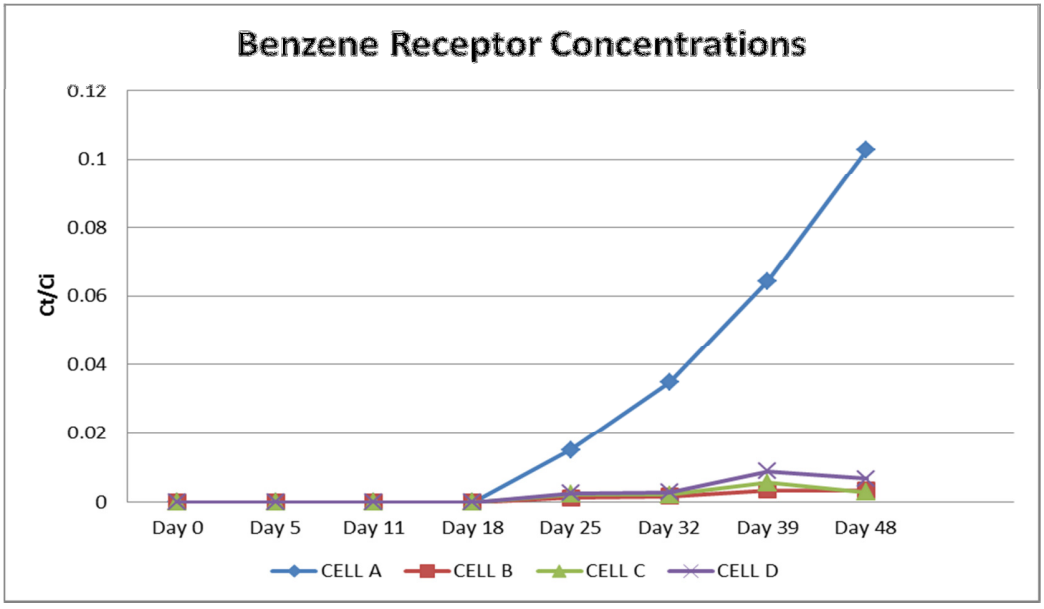


Figure 4.25: Phase 3 – Concentrations of Benzene in Receptor Volume

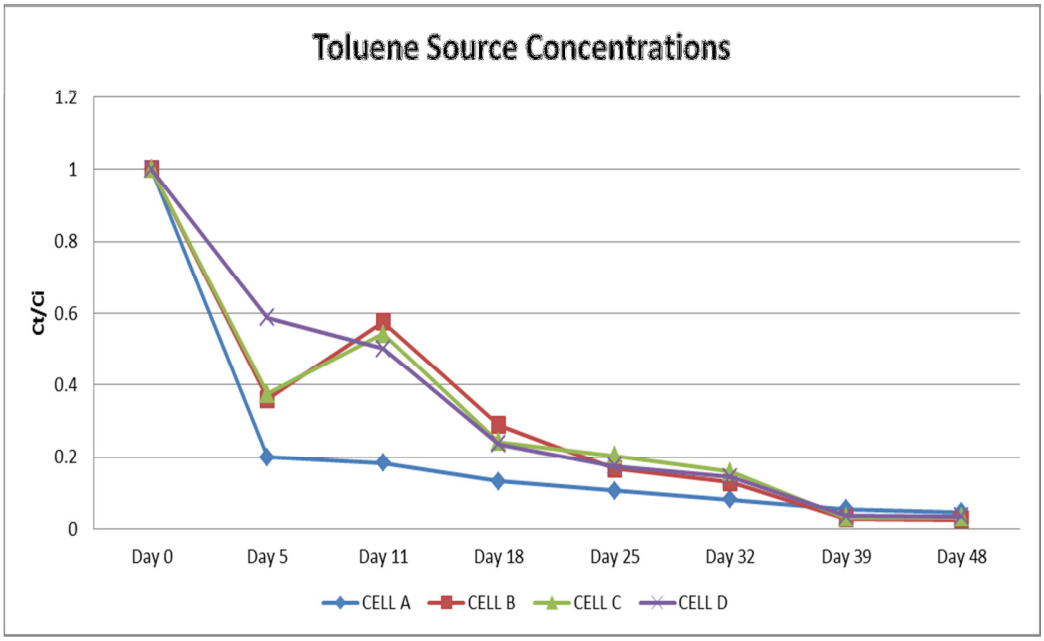


Figure 4.26: Phase 3 – Concentrations of Toluene in Source Volume

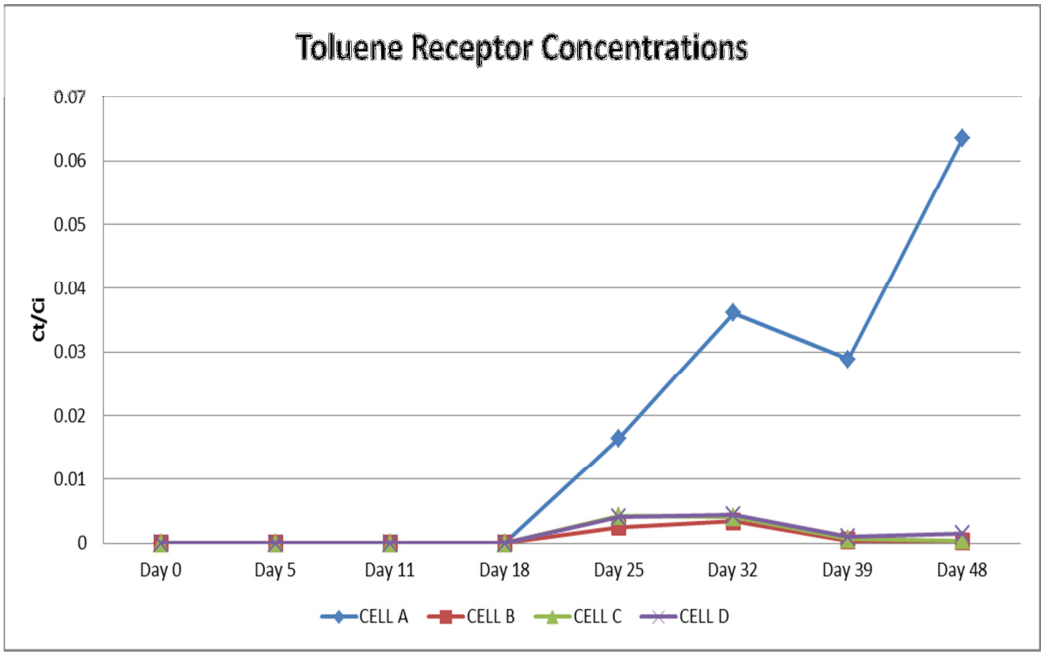


Figure 4.27: Phase 3 – Concentrations of Toluene in Receptor Volume

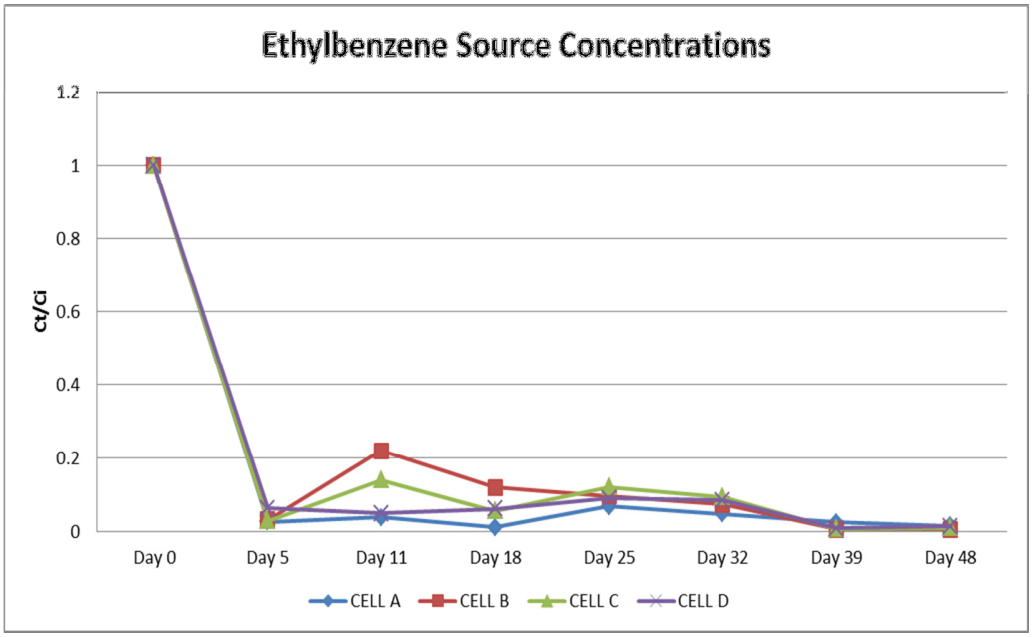


Figure 4.28: Phase 3 – Concentrations of Ethylbenzene in Source Volume

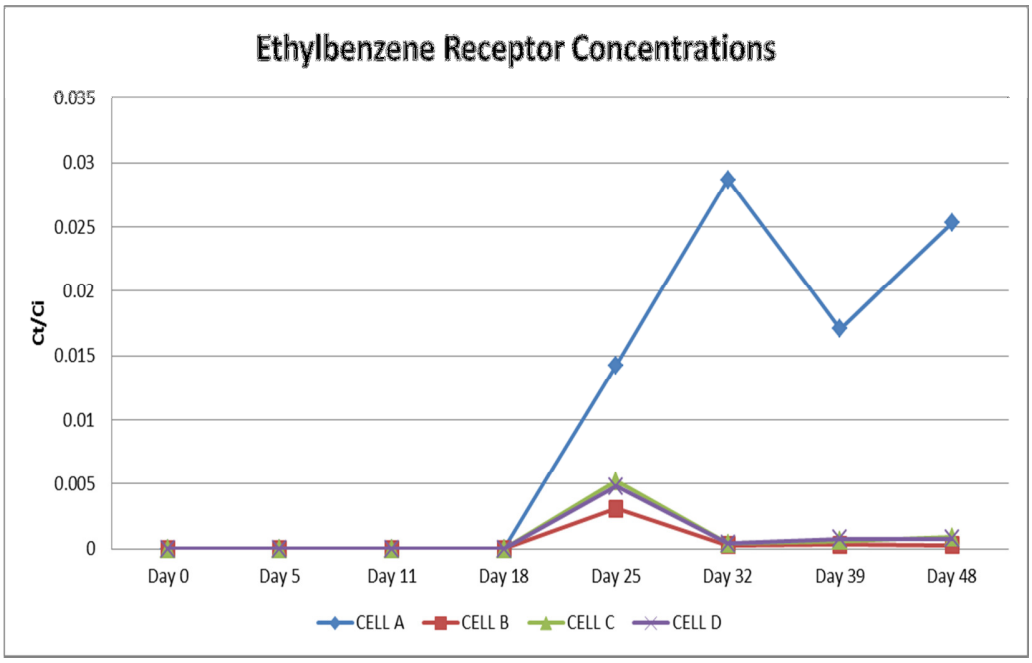


Figure 4.29: Phase 3 – Concentrations of Ethylbenzene in Receptor Volume

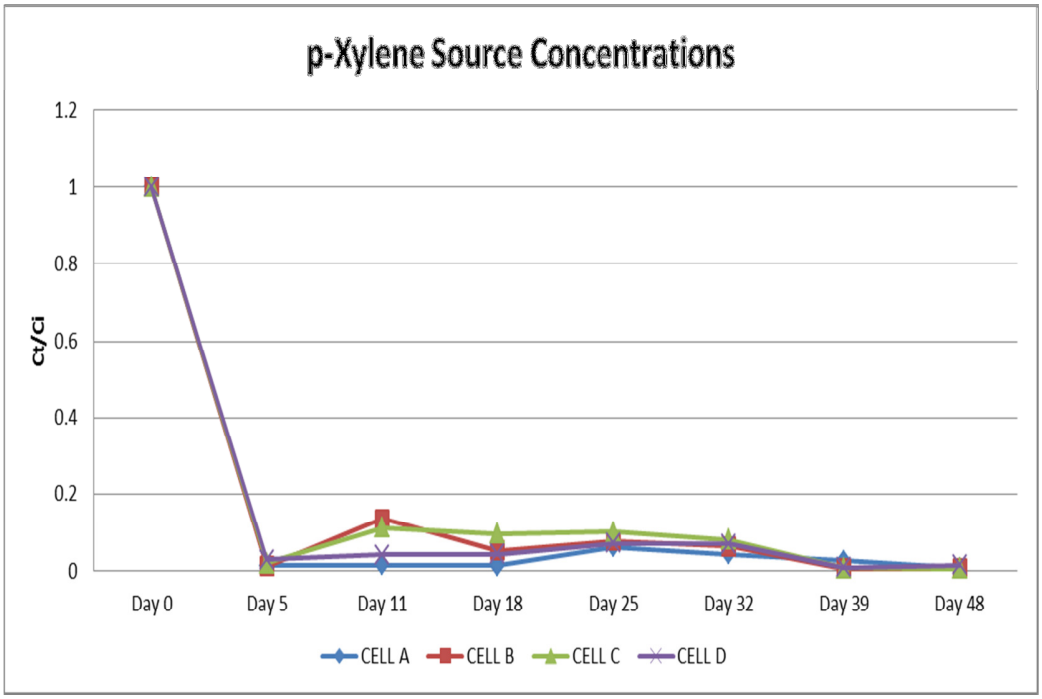


Figure 4.30: Phase 3 – Concentrations of p-Xylene in Source Volume

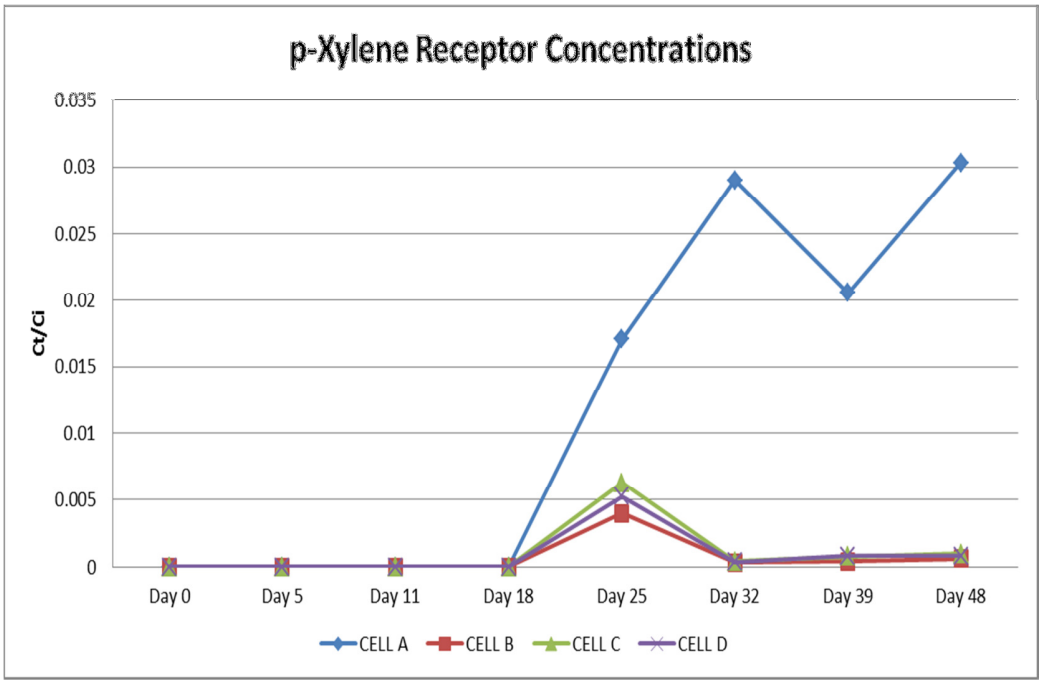


Figure 4.31: Phase 3 – Concentrations of p-Xylene in Receptor Volume

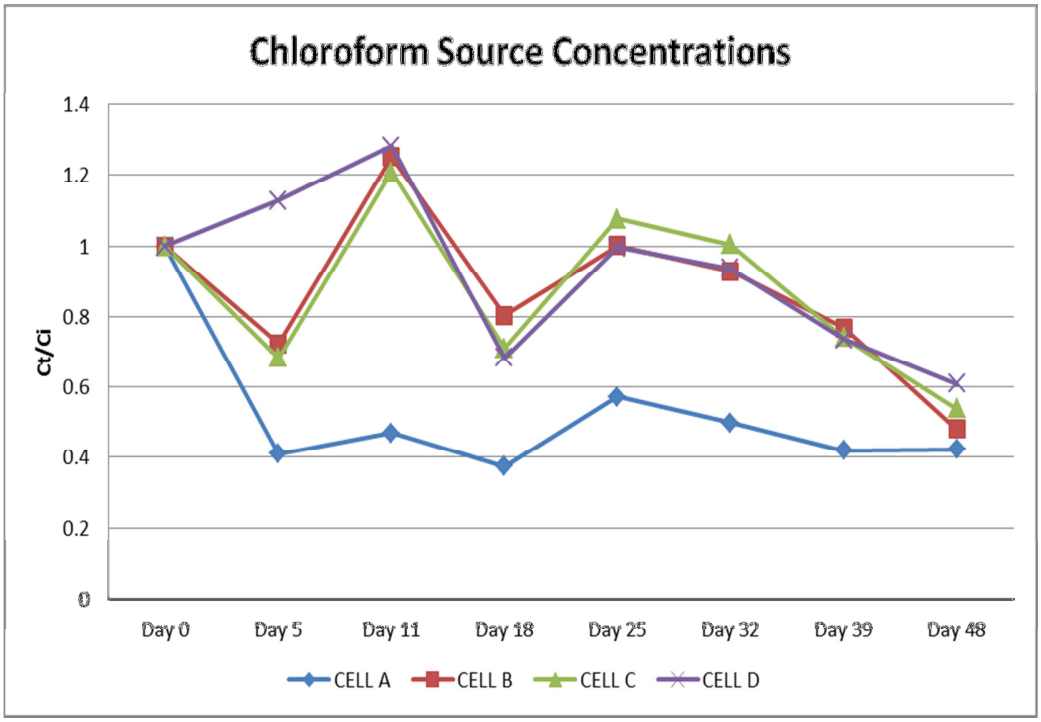


Figure 4.32: Phase 3 – Concentrations of Chloroform in Source Volume

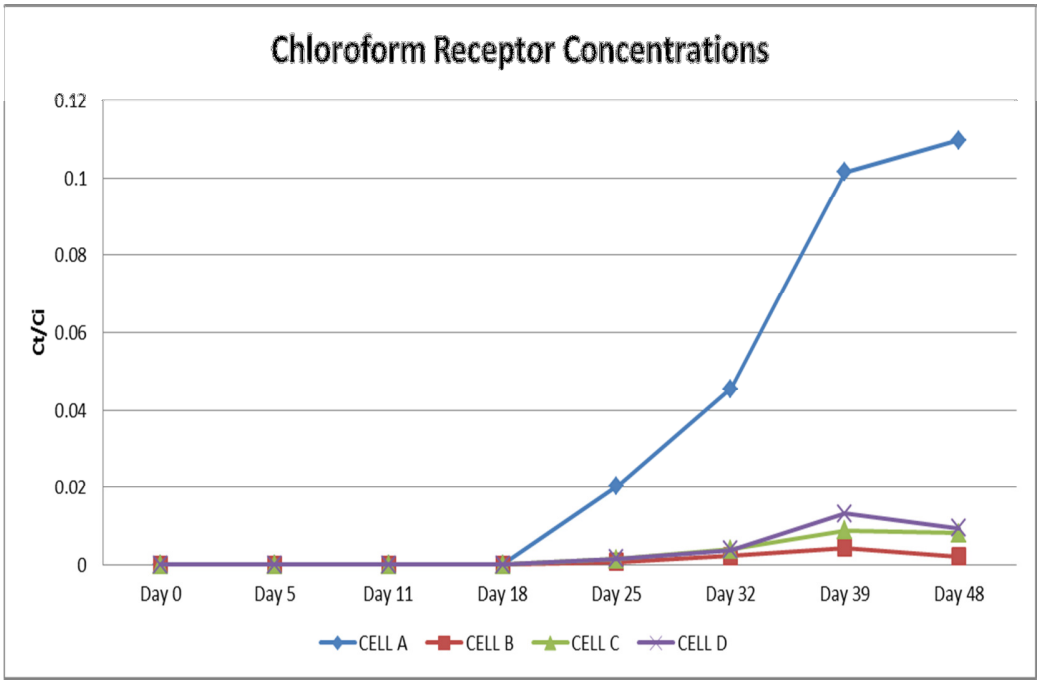


Figure 4.33: Phase 3 – Concentrations of Chloroform in Receptor Volume

Figures 4.24 to **4.33** show that concentrations of the VOCs increase more significantly in the receptor volume of Cell A where no air extraction took place, compared to the other cells' charts that represent various air extraction rates.

Calculation of Diffusion Coefficient

As for Phase 1 and 2 testing, the Diffusion coefficient D_g was determined using POLLUTE®. The concentration versus time output graphs that POLLUTE® produced, if the methodologies in Chapter 3 were correctly followed, were combined with the actual laboratory test results and are shown on **Figures 4.34** to **4.53** for Phase 3 testing.

As discussed, there was no extraction of air in Cell A in order to compare this with results obtained in Phase 2 testing. The S_{gf} values used for phase 3 diffusion testing were determined with Immersion and Weight gain sorption tests.

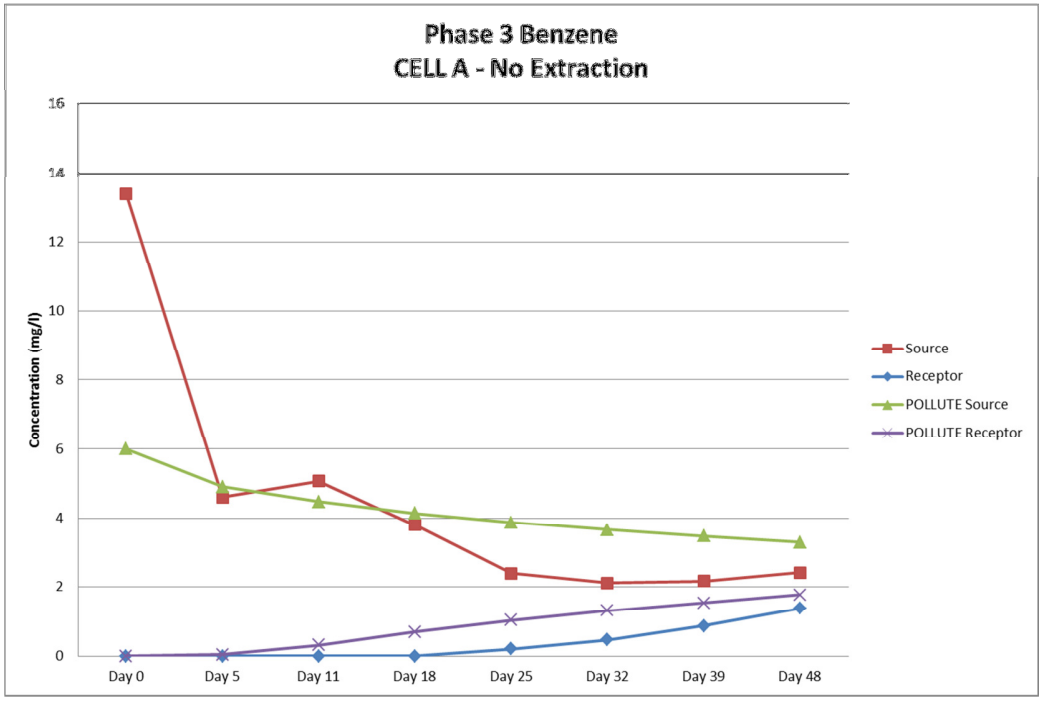


Figure 4.34: Phase 3 - Combined Output Graph – Cell A Benzene

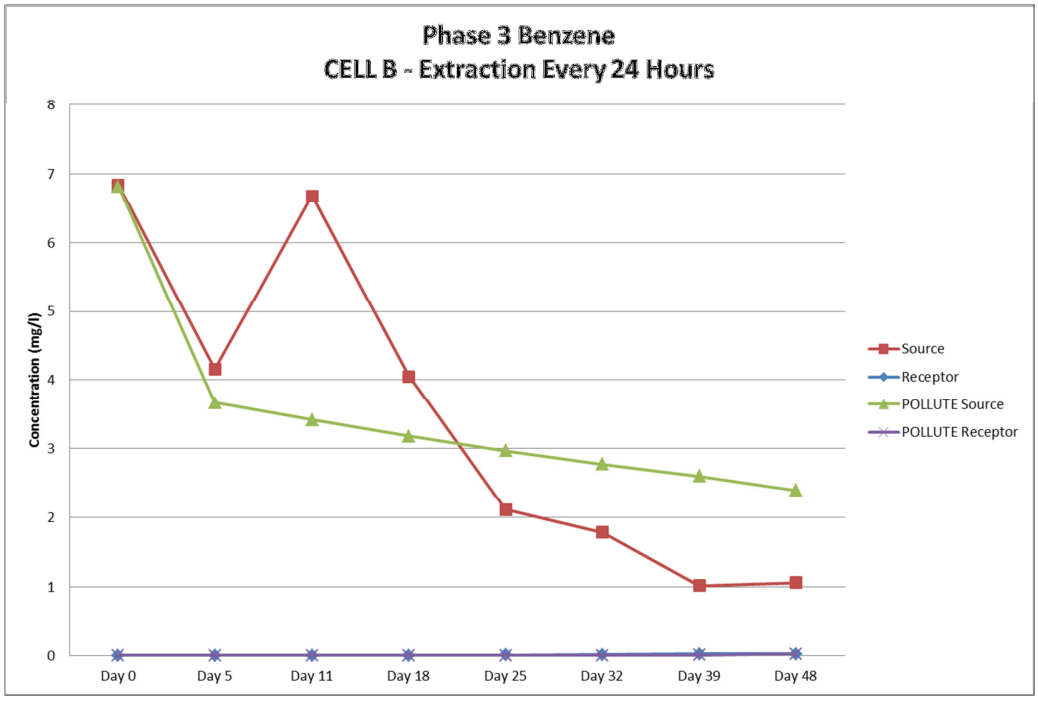


Figure 4.35: Phase 3 - Combined Output Graph – Cell B Benzene

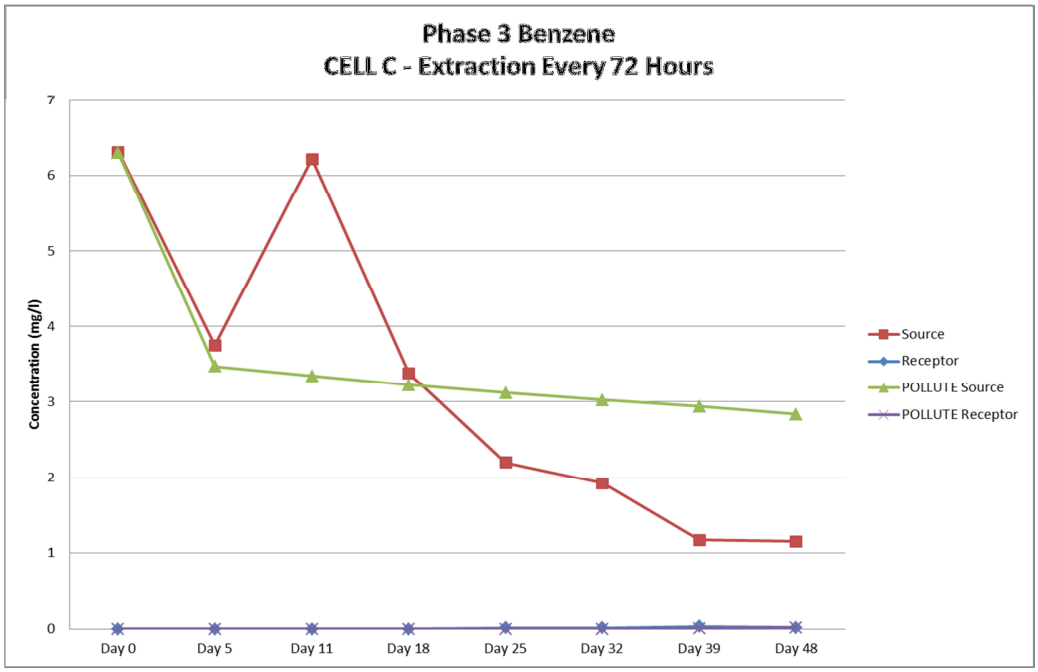


Figure 4.36: Phase 3 - Combined Output Graph – Cell C Benzene

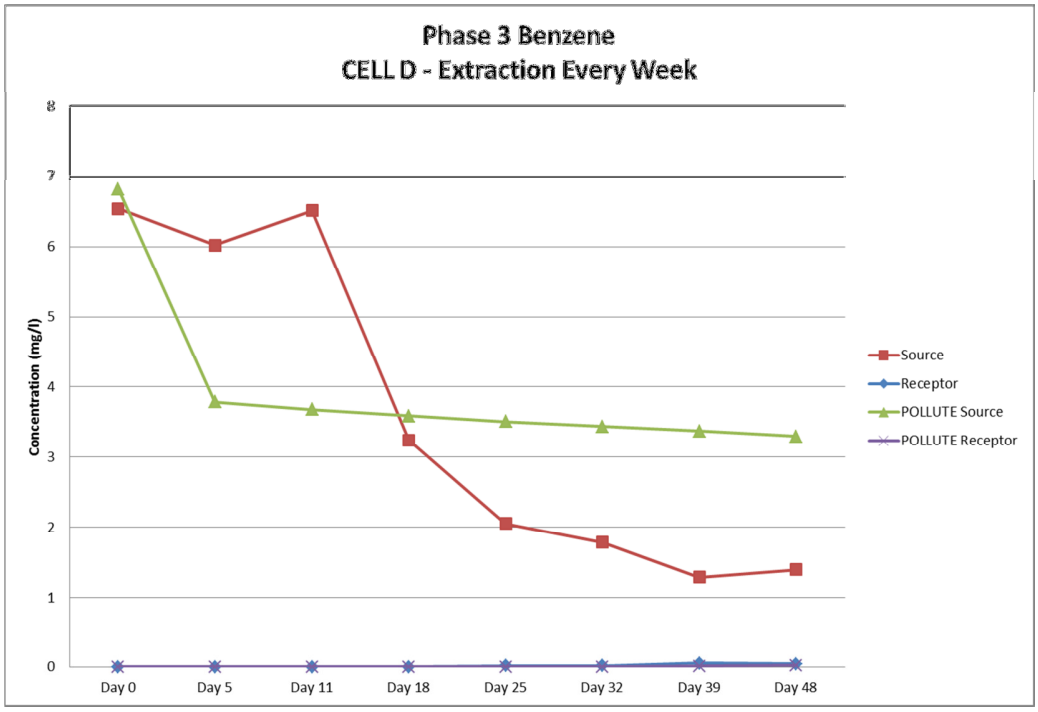


Figure 4.37: Phase 3 - Combined Output Graph – Cell D Benzene

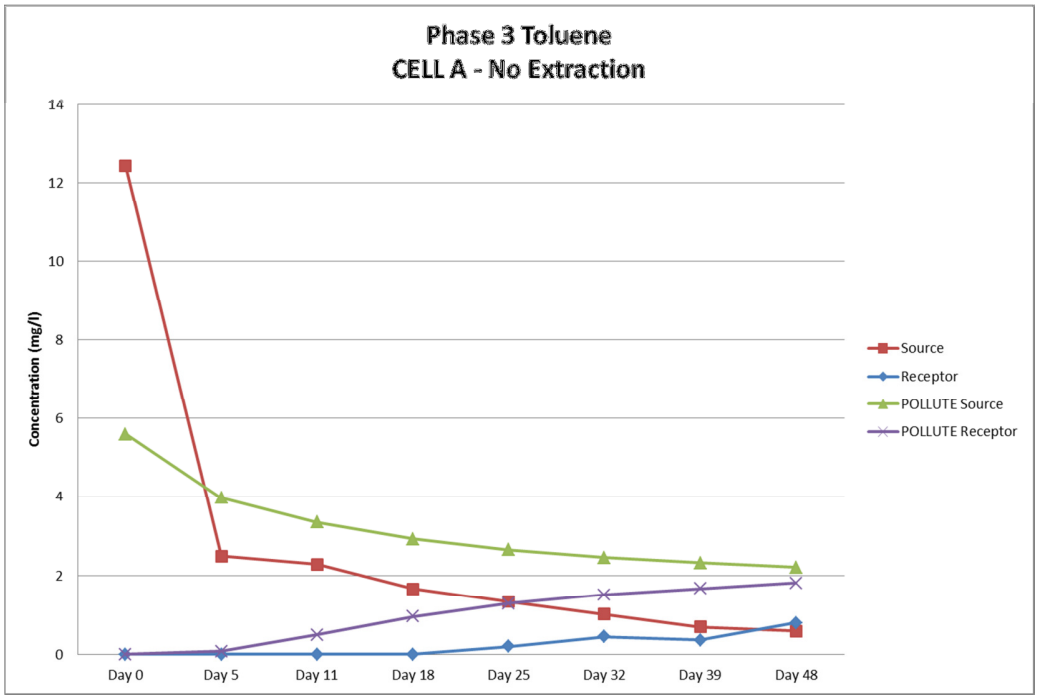


Figure 4.38: Phase 3 - Combined Output Graph – Cell A Toluene

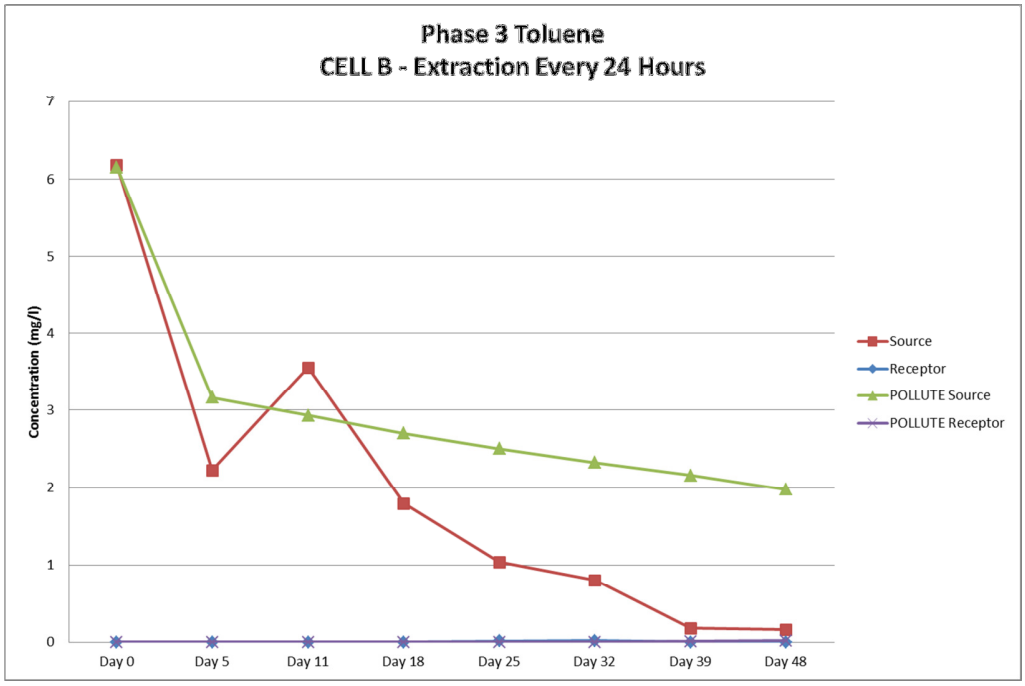


Figure 4.39: Phase 3 - Combined Output Graph – Cell B Toluene

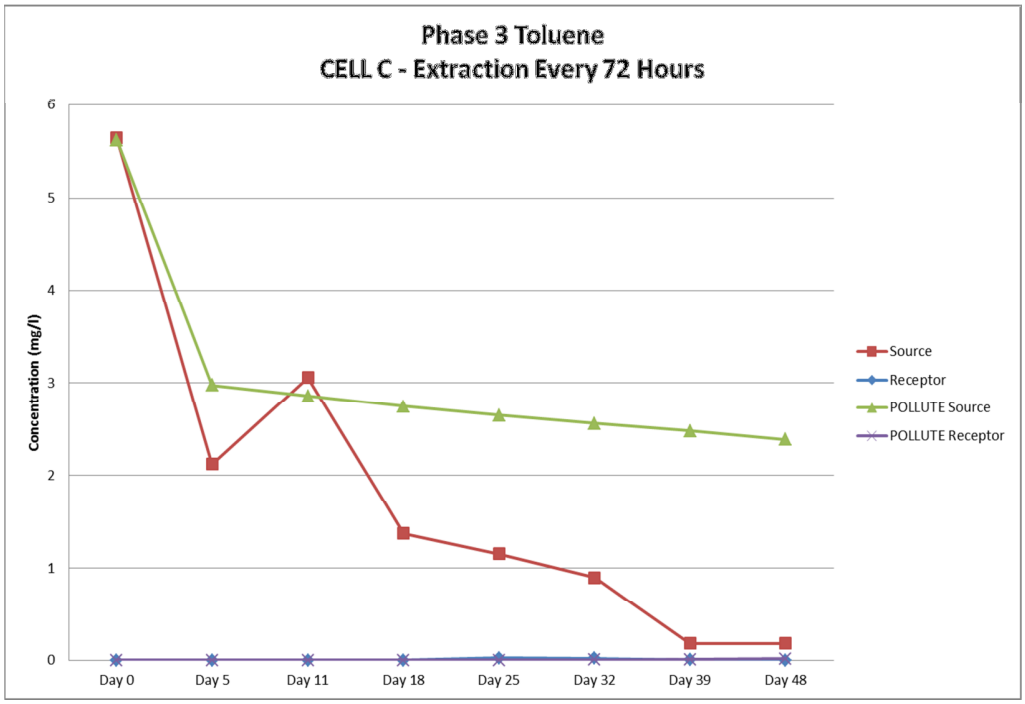


Figure 4.40: Phase 3 - Combined Output Graph – Cell C Toluene

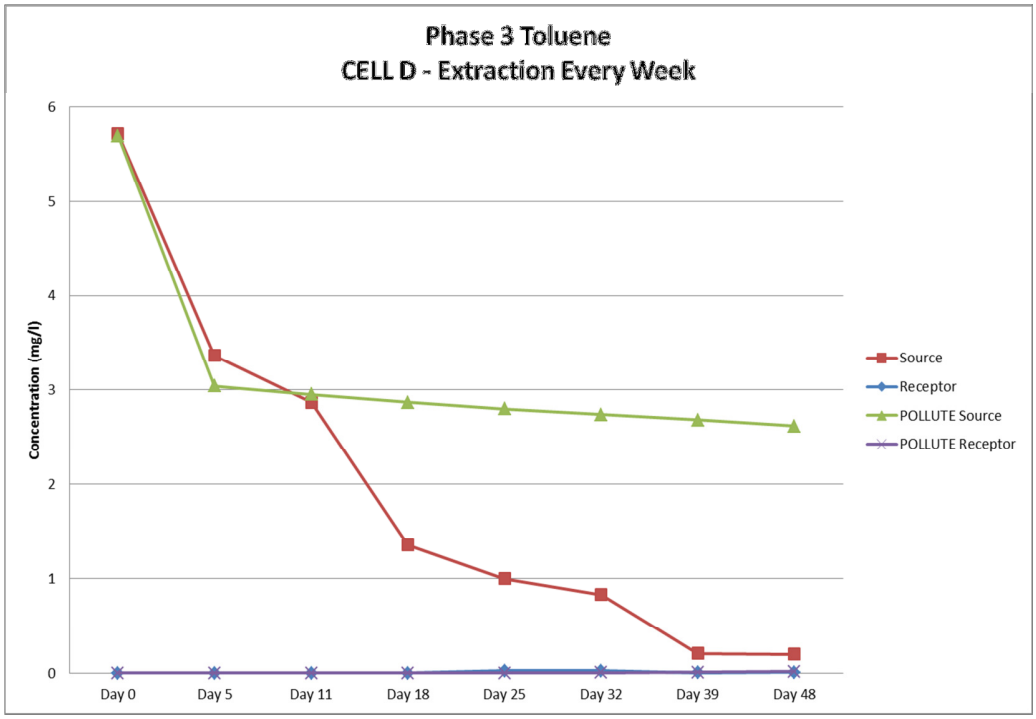


Figure 4.41: Phase 3 - Combined Output Graph – Cell D Toluene

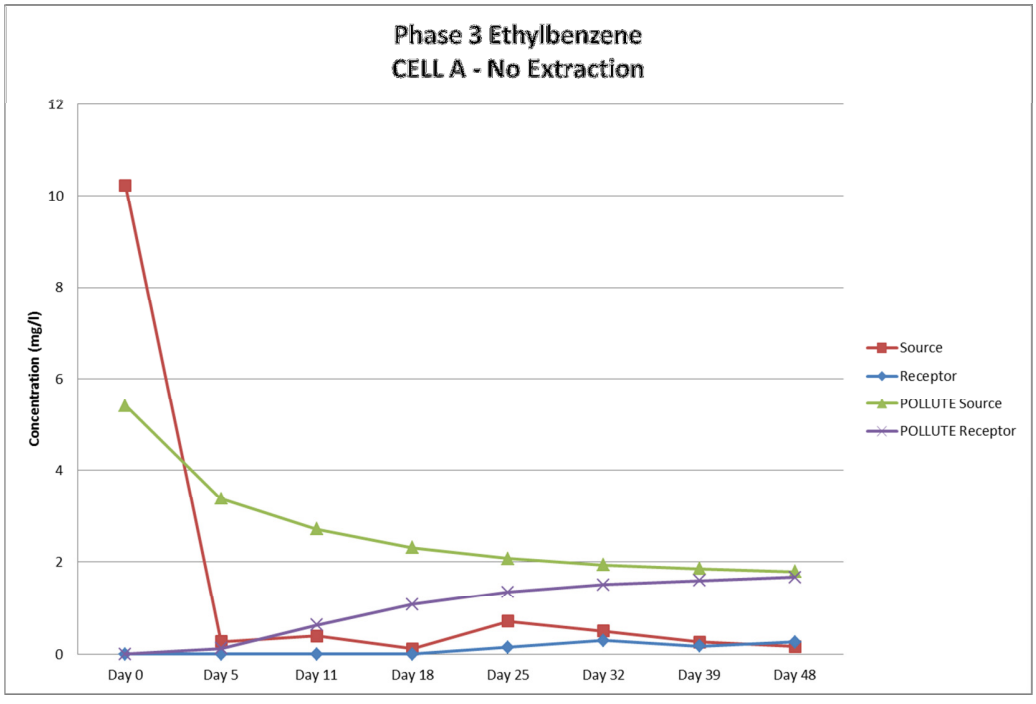


Figure 4.42: Phase 3 - Combined Output Graph – Cell A Ethylbenzene

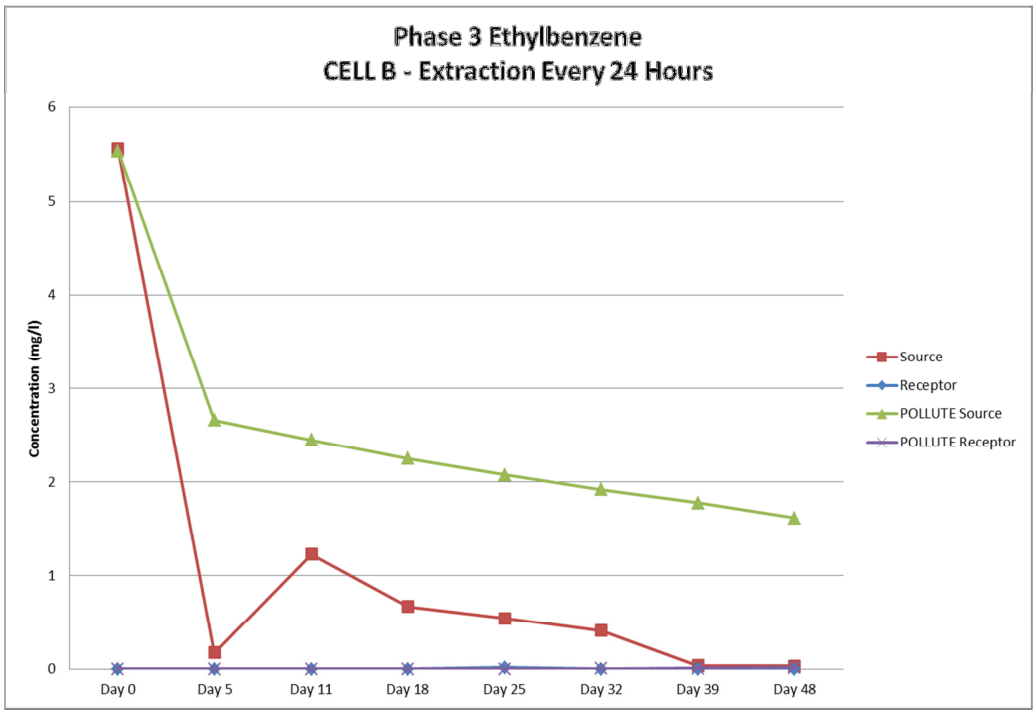


Figure 4.43: Phase 3 - Combined Output Graph – Cell B Ethylbenzene

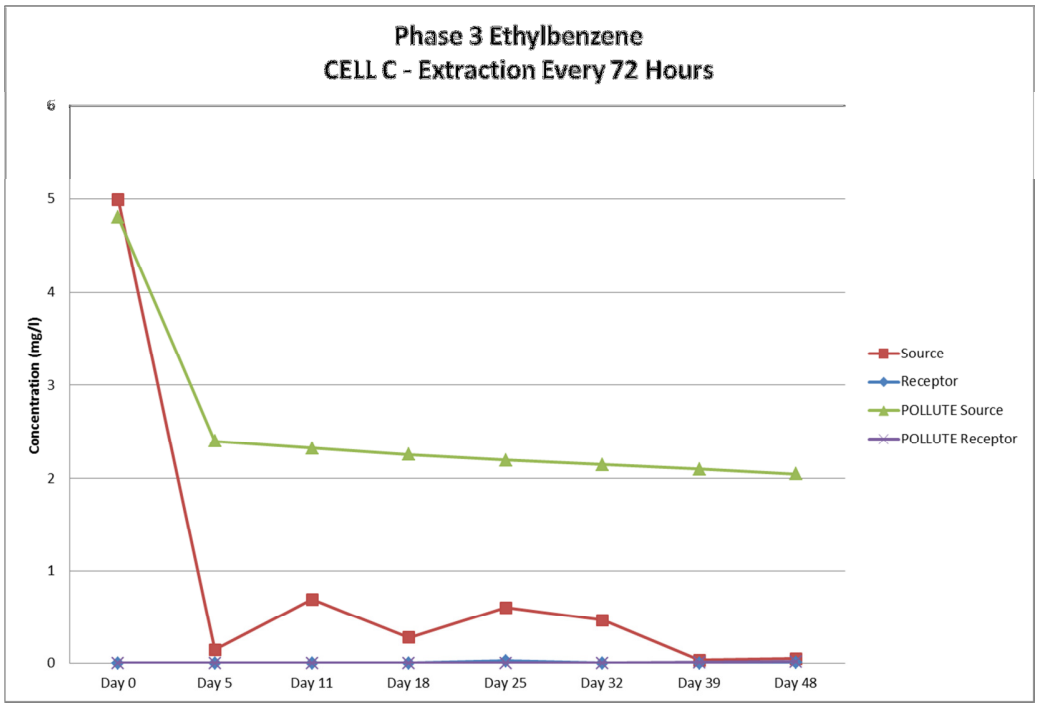


Figure 4.44: Phase 3 - Combined Output Graph – Cell C Ethylbenzene

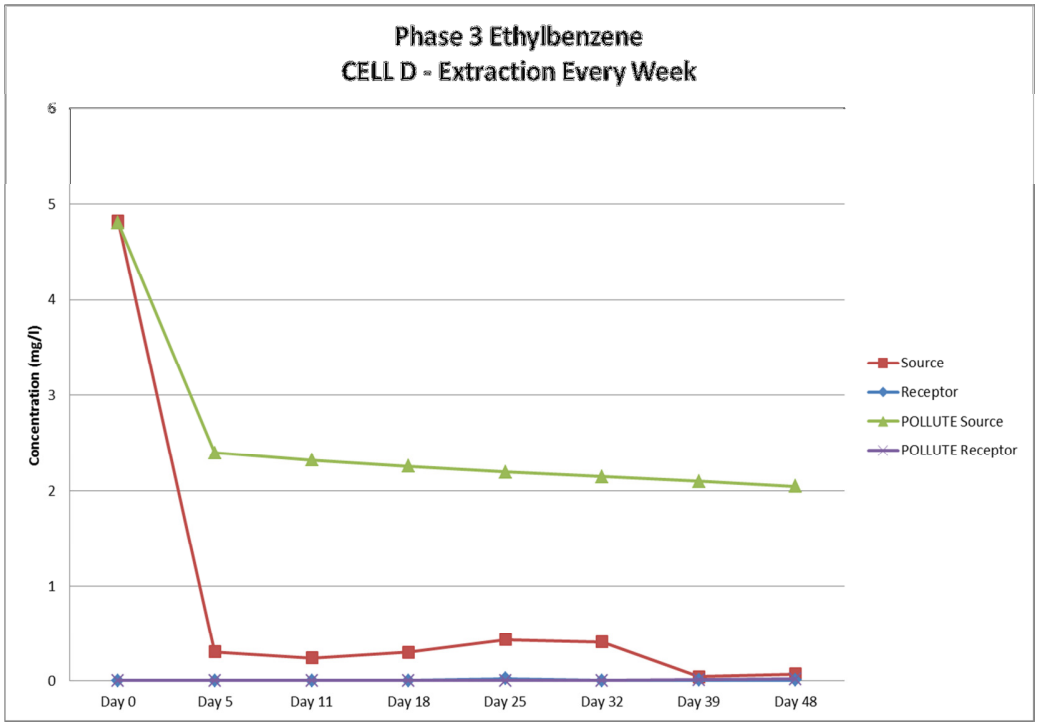


Figure 4.45: Phase 3 - Combined Output Graph – Cell D Ethylbenzene

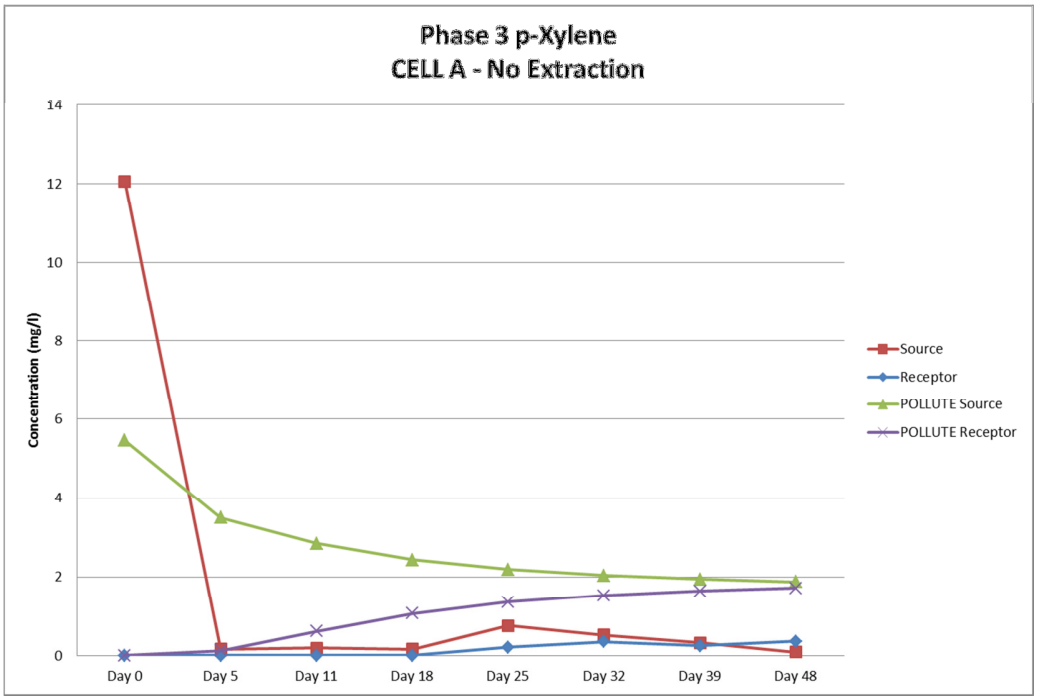


Figure 4.46: Phase 3 - Combined Output Graph – Cell A p-Xylene

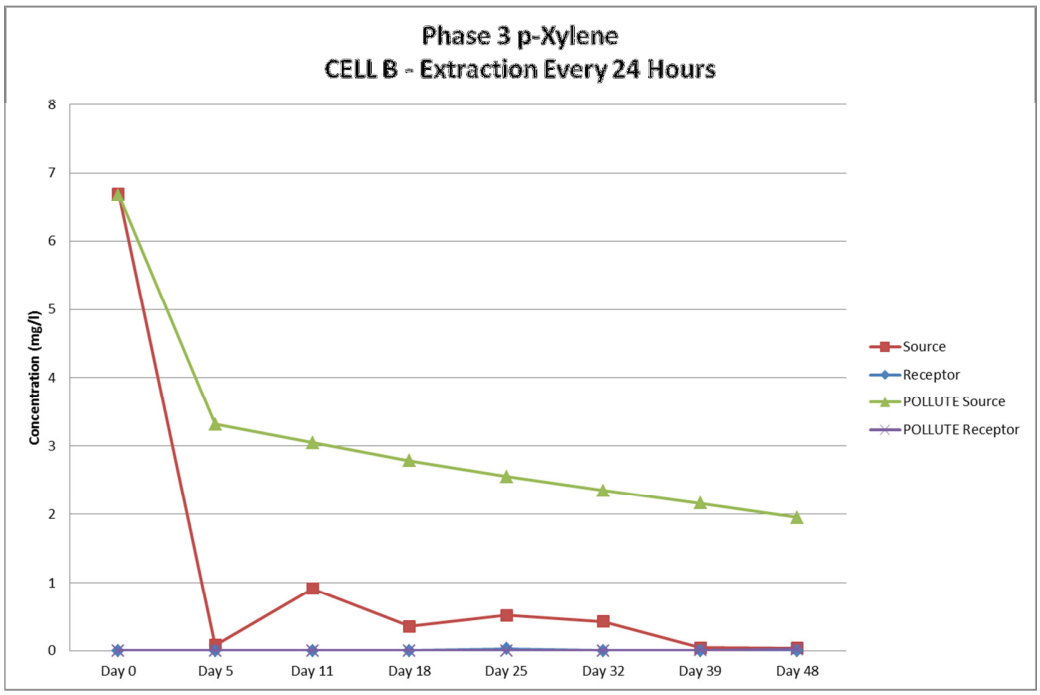


Figure 4.47: Phase 3 - Combined Output Graph – Cell B p-Xylene

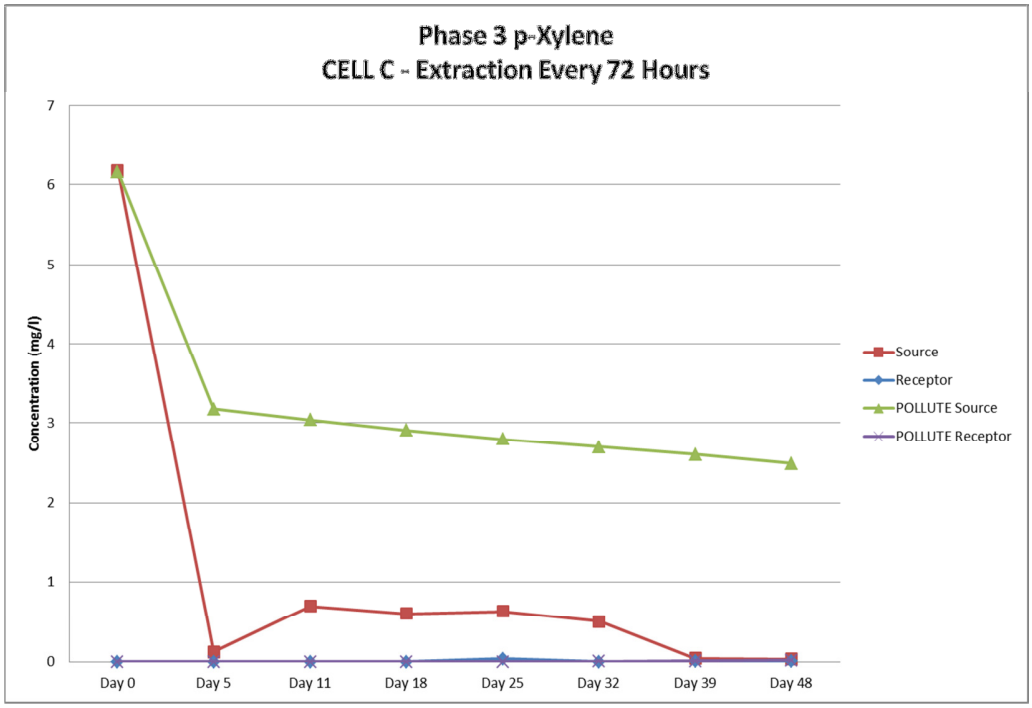


Figure 4.48: Phase 3 - Combined Output Graph – Cell C p-Xylene

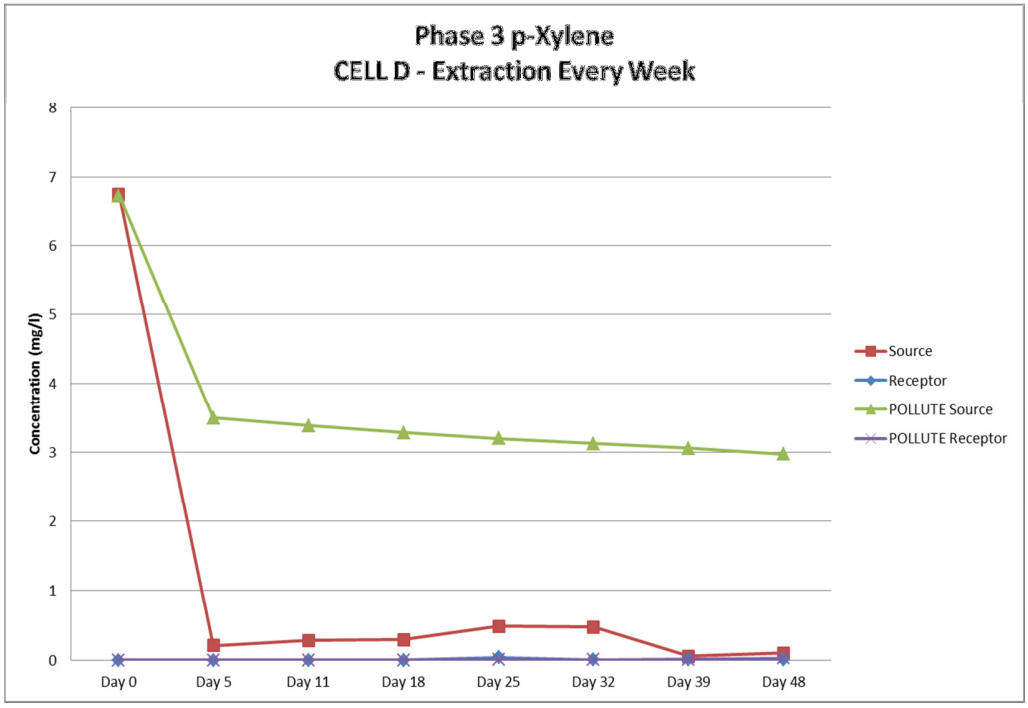


Figure 4.49: Phase 3 - Combined Output Graph – Cell D p-Xylene

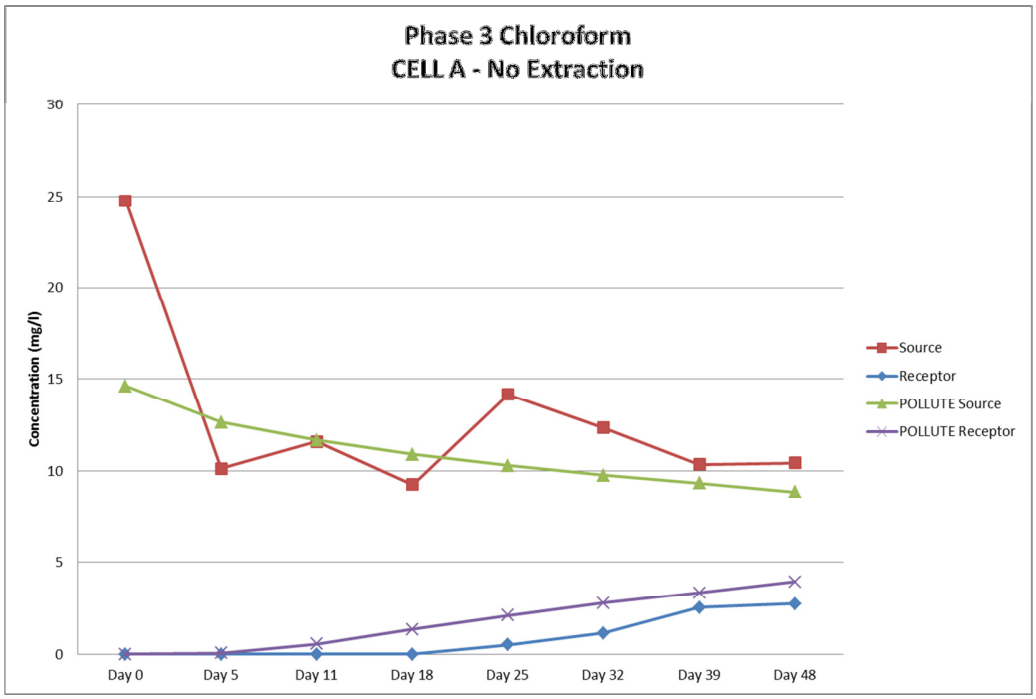


Figure 4.50: Phase 3 - Combined Output Graph – Cell A Chloroform

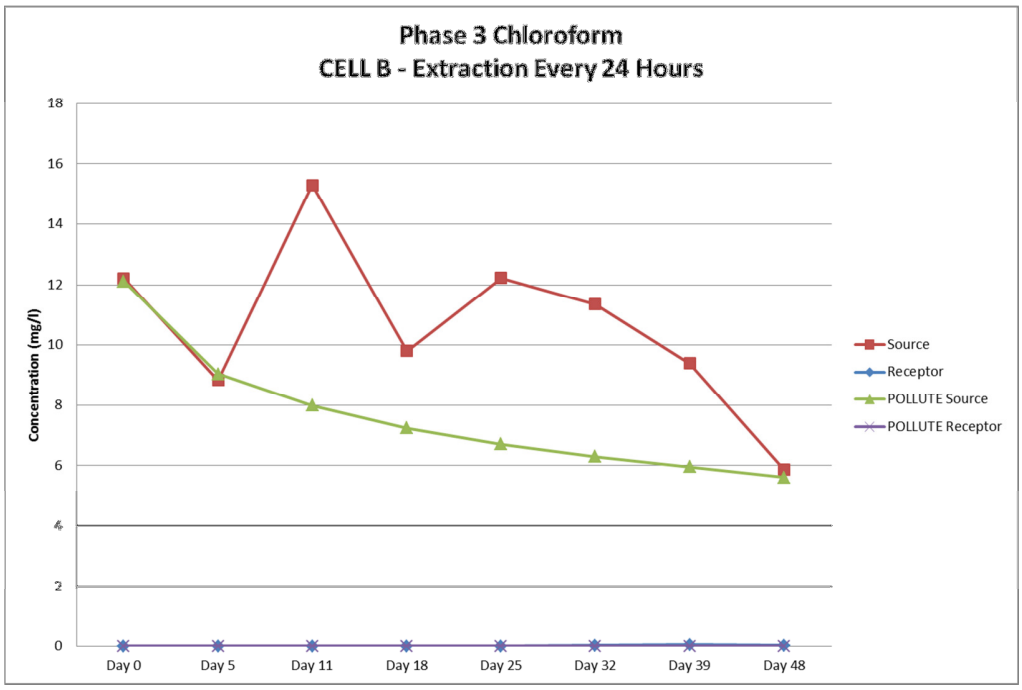


Figure 4.51: Phase 3 - Combined Output Graph – Cell B Chloroform

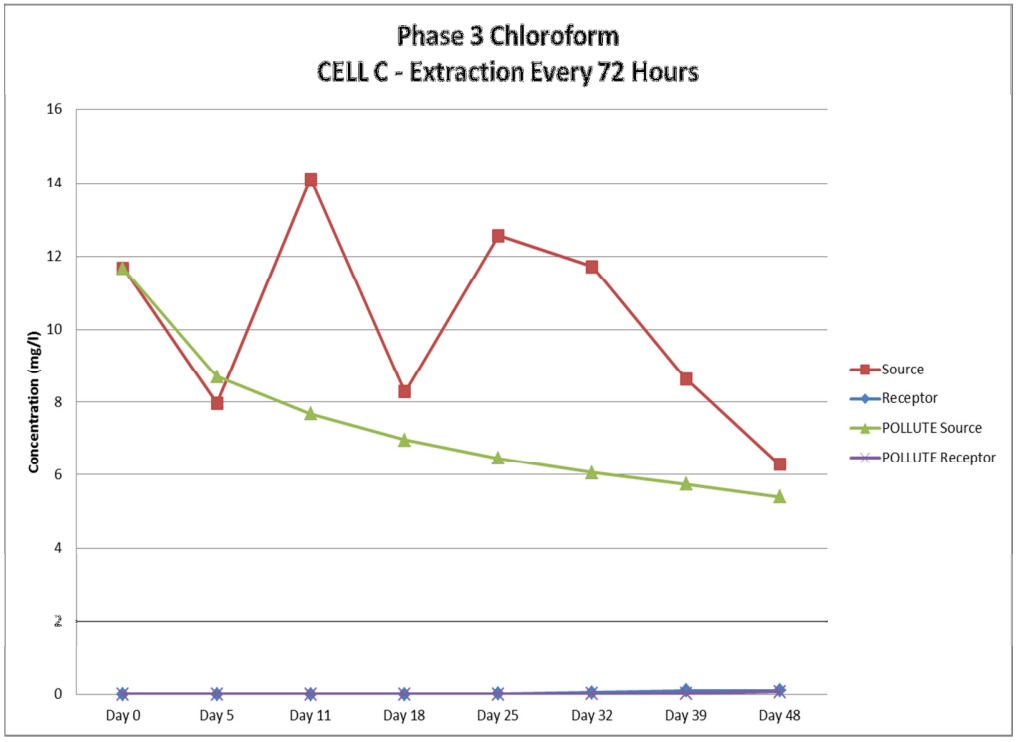


Figure 4.52: Phase 3 - Combined Output Graph – Cell C Chloroform

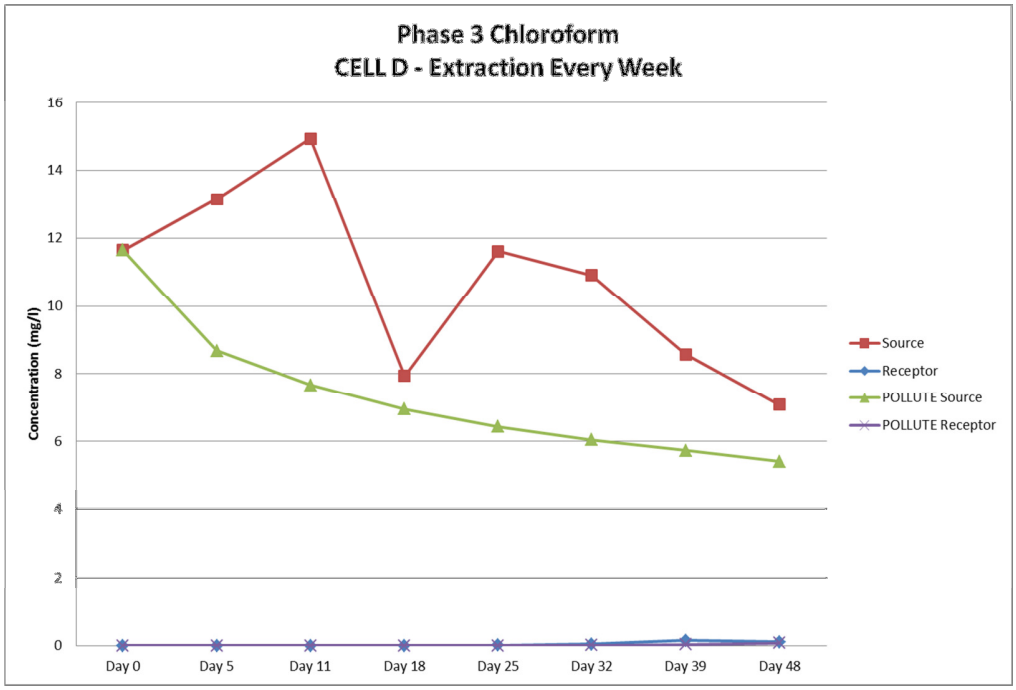


Figure 4.53: Phase 3 - Combined Output Graph – Cell D Chloroform

For Phase 3 testing the diffusion coefficients obtained through POLLUTE in order to obtain the output graphs in **Figures 4.34** to **4.53** is given in **Table 4.15**. As discussed the D_g values for the top GM (GM1) and the bottom GM (GM2) will differ (except for Cell A).

Table 4.15: Calculated Diffusion Coefficients (D_g) for Phase 3 testing

VOC	Diffusion Coefficient in m^2/s						
	Cell A	Cell B		Cell C		Cell D	
	$D_{g(GM1=GM2)}$	D_{gGM1}	D_{gGM2}	D_{gGM1}	D_{gGM2}	D_{gGM1}	D_{gGM2}
Benzene	$1.04x10^{-12}$	$1.16x10^{-10}$	$2.31x10^{-14}$	$1.04x10^{-10}$	$2.31x10^{-14}$	$9.84x10^{-11}$	$2.31x10^{-14}$
Toluene	$1.04x10^{-12}$	$1.16x10^{-10}$	$2.31x10^{-14}$	$1.04x10^{-10}$	$2.31x10^{-14}$	$9.84x10^{-11}$	$2.31x10^{-14}$
Ethylbenzene	$1.15x10^{-12}$	$1.16x10^{-10}$	$2.31x10^{-14}$	$1.04x10^{-10}$	$2.31x10^{-14}$	$9.84x10^{-11}$	$2.31x10^{-14}$
p-Xylene	$1.15x10^{-12}$	$1.16x10^{-10}$	$2.31x10^{-14}$	$1.04x10^{-10}$	$2.31x10^{-14}$	$9.84x10^{-11}$	$2.31x10^{-14}$
Chloroform	$9.26x10^{-13}$	$1.16x10^{-13}$	$5.79x10^{-14}$	$1.16x10^{-13}$	$5.79x10^{-14}$	$1.16x10^{-13}$	$5.79x10^{-14}$

4.5.4 Summary of determined Sorption, Diffusion and Permeation Coefficients

The diffusion and sorption tests in phases 1 and 2 resulted in the coefficients shown in **Table 4.16** and **4.17** after using POLLUTE® to model the laboratory results. The Permeation coefficient P_g is calculated by multiplying S_{gf} and D_g and accounts for the effects of both diffusion and partitioning (see Chapter 2).

Table 4.156: Summary of Calculated Phase 1 Coefficients

VOC	S_{gf}	D_g (m^2/sec)	P_g (m^2/s)
Benzene	116.4	9.26×10^{-13}	1.07×10^{-10}
Toluene	183.7	8.68×10^{-13}	1.59×10^{-10}
Ethylbenzene	391.9	1.39×10^{-12}	5.45×10^{-11}
p-Xylene	188.0	2.32×10^{-12}	4.36×10^{-11}

Table 4.167: Summary of Calculated Phase 2 Coefficients

VOC	S_{gf}	D_g (m^2/sec)	P_g (m^2/s)
Benzene	27.8	8.10×10^{-13}	2.25×10^{-11}
Toluene	61.9	8.10×10^{-13}	5.01×10^{-11}
Ethylbenzene	87.2	5.79×10^{-13}	5.05×10^{-11}
p-Xylene	80.2	8.10×10^{-13}	6.49×10^{-11}
Chloroform	25.1	8.10×10^{-13}	1.45×10^{-11}

The diffusion and sorption tests undertaken for phase 3 resulted in the permeability coefficients shown in **Table 4.178** after using the POLLUTE software program to model the laboratory results. The D_g values from **Table 4.15** (S_{gf} from Immersion or Weight Gain tests) were used to obtain the P_g values in **Table 4.18.**

Table 4.178: Summary of Calculated Phase 3 Permeability Coefficients

VOC	Permeability Coefficient in m^2/s						
	Cell A	Cell B		Cell C		Cell D	
	$P_{g(GM1=GM2)}$	P_{gGM1}	P_{gGM2}	P_{gGM1}	P_{gGM2}	P_{gGM1}	P_{gGM2}
Benzene	$2.89x10^{-11}$	$8.02x10^{-9}$	$1.60x10^{-12}$	$7.19 x10^{-9}$	$1.60x10^{-12}$	$6.81x10^{-9}$	$1.60x10^{-12}$
Toluene	$6.44x10^{-11}$	$8.80x10^{-9}$	$1.75x10^{-12}$	$7.89 x10^{-9}$	$1.75x10^{-12}$	$7.46x10^{-9}$	$1.75x10^{-12}$
Ethylbenzene	$9.99x10^{-11}$	$1.01x10^{-8}$	$2.01x10^{-12}$	$9.07 x10^{-9}$	$2.01x10^{-12}$	$8.58x10^{-9}$	$2.01x10^{-12}$
p-Xylene	$9.18x10^{-11}$	$9.30x10^{-9}$	$1.85x10^{-12}$	$8.34 x10^{-9}$	$1.85x10^{-12}$	$7.89x10^{-9}$	$1.85x10^{-12}$
Chloroform	$2.32x10^{-11}$	$1.47x10^{-11}$	$2.93x10^{-12}$	$1.47x10^{-11}$	$2.93x10^{-12}$	$1.47x10^{-11}$	$2.93x10^{-12}$

The coefficients calculated using the methodology in Chapter 3, as well as all the other results presented in this Chapter are analysed in Chapter 5 to determine if the objectives of the study were met.

CHAPTER 5. DATA ANALYSIS

5.1 INTRODUCTION

This chapter analyses and discusses the data presented in Chapter 4. As indicated in Chapter 3, the results from the field tests undertaken will not be further analysed and this chapter will thus only analyse data from laboratory tests.

5.2 SORPTION/IMMERSION TESTS

5.2.1 Methanol Sorption

Table 4.1 shows the results of methanol sorption tests. The measured concentrations in the control cells used indicated that loss occurred over time was negligible. This indicates that the BTEX (Chloroform was not used in the methanol sorption tests) did not escape the methanol solution easily to sorb onto the glass vial or sampling caps. The VOCs were mostly kept in solution as can be expected since BTEX and Chloroform are soluble in methanol and would require more energy to leave the solution than is supplied by the conditions during this test. Thus, if the resultant sorption coefficients obtained from methanol sorption tests are compared to those obtained doing aqueous sorption tests, the methanol S_{gf} values are lower by at least an order of magnitude. This indicates that VOCs are reluctant to sorb onto the GM when in methanol solution and that it would take much longer to reach equilibrium when doing sorption or diffusion tests using methanol as the only medium to store the VOCs. Therefore, diffusion testing using methanol as a medium was not continued and aqueous (deionised water) solutions that would more accurately replicate actual landfill conditions were used instead.

5.2.2 Aqueous Sorption

The VOC concentrations in the sorption test cells were measured over time and the resultant concentrations in the control cells from aqueous sorption tests, given in **Table 4.3**, shows that significant losses occurred in the control cells over the time of testing (21 days). The BTEX and Chloroform concentrations in the

control cells were, on average, between 50% and 90% lower on day 21 than the original day-zero concentrations as shown in **Table 5.1**. These losses are excessive and are most probably attributable to the amount of VOCs that evaporated from the aqueous solution into gaseous zone between the solution and the vial caps (refer to **Figure 3.2** for Sorption test cell). This was further aggravated by the fact that, with each sampling event, the gaseous zone increased with 1ml providing more volume for the evaporation of the VOCs. This was unavoidable since filling the sampling vials to capacity would have meant intimate contact between the solution and the vial caps which would have caused the vial caps to be a sink for sorption of the VOCs, and the aim was to focus sorption onto the GMs in the solution.

Table 5.1: Losses Incurred during Aqueous Sorption Tests

VOC	Day 0 Concentration (mg/l)	Day 21 Concentration (mg/l)	Losses (%)
Benzene	0.7571	0.3198	58
Toluene	0.7855	0.0827	89
Ethylbenzene	0.8432	0.0333	96
p-Xylene	0.8282	0.0196	98
Chloroform	1.5904	0.4786	70

Other possible causes for the losses would however be the sorption onto the vial cap from the gaseous phase and escape from the system during sampling events, where the vial cap septum was punctured with the sampling needle, or during use of the GC.

The S_{gf} values obtained from the results were corrected to account for the losses incurred and the values of S_{gf} taken forward for use in the calculation of Diffusion and Permeability coefficients are the average corrected values shown in **Table 5.2**. This table also compares the S_{gf} values obtained from a range literature articles to the S_{gf} values obtained from this study. In comparing theses values it must be noted that the concentrations, temperatures, test length, laboratory setup etc. for the test done to obtain the various S_{gf} values were not always given in the literature. Still, it is evident from the results that the S_{gf} values obtained from this study are mostly comparable to the values obtained from literature.

Table 5.2: S_{gf} Values Compared to Results from Literature

1mm GM	S_{gf}	Literature Sgf value range	1.5mm GM Sgf values from Literature
Benzene	27.8	9 to 57	35 to 60
Toluene	61.9	11 to 192	130 to 140
Ethylbenzene	87.2	10 to 100	260 to 340
p-Xylene	80.2	498 to 556	300 to 440
Chloroform	25.1	0.1 to 9	-
2mm GM	**S_{gf}**		
Benzene	14.1	30 to 51	35 to 60
Toluene	198	100 to 193	130 to 140
Ethylbenzene	326	285	260 to 340
p-Xylene	103	347	300 to 440
Chloroform	14.2	-	-

5.2.3 Weight Gain

As discussed, the weight gain method is not generally preferred as a method of calculating the S_{gf} values for BTEX sorption onto HDPE, mostly because of the volatility of the VOCs. **Table 4.8,** however, shows that the values obtained correlates to the values obtained using the immersion method and values from literature although there are some exceptions. The S_{gf} values from weight gain tests were used in the POLLUTE® modeling for the calculation of the diffusion coefficients of phase 3 work for Benzene, Toluene and Chloroform. This shows that these values are comparable and, if carefully done, the weight gain method can be used for the calculation of S_{gf} values if budgetary or other constraints rule out the use of a GC.

5.2.4 Summary of Sorption tests

The S_{gf} values in **Table 4.126, 4.17** and **4.18** were used to model results in POLLUTE to obtain the diffusion coefficients D_g. For phase 1 modelling, they were obtained doing diffusion tests and for phase 2 and 3 modelling, they were obtained doing sorption and weight gain tests.

Many factors play a role in the calculation of sorption coefficients; thus, using S_{gf} values from literature should be done with caution unless the contributing factors are carefully described in the literature source and can be accurately compared to the desired use. The S_{gf} values used in this dissertation are experimentally

determined values that accurately reflect the conditions under which the work was done.

5.3 DIFFUSION TESTS

Diffusion tests were carried out in three phases (see Chapter 3). The aim of phase 1 was to prove that the chosen VOCs diffuse from the source volume, through the 2 mm GM, into the receptor volume and to compare these to the results obtained in the literature. The aim of phase 2 was to prove that, even if the separation between the source and receptor consisted of two 1 mm GMs separated by an air-filled pervious zone, diffusion of the VOCs would still occur from the source to the receptor volumes. The aim of phase 3 was to prove that by introducing airflow into the pervious zone between the two 1 mm GMs, the concentration of VOCs in the receptor volume (due to diffusion through the GM) could be reduced significantly. Phase 3 testing also aimed to determine if the rate of air removal would play a role in the diffusive process and the resultant VOC concentrations in the receptor.

5.3.1 Phase 1 – Diffusion tests using one GM

Concentrations

The graphs on **Figure 4.1** and **Figure 4.2** show that over the 22-day diffusion test period, the VOC concentrations in the source decreased and the VOC concentrations in the receptor increased.

The detection of VOC concentrations in the receptor started on day 8 and increased to between 10% and 30% of the original source concentration at day 22. The VOC concentrations in the source immediately decreased as the VOC sorbed onto the GM, and gradually decreased over the 22-day testing period to between 5% and 30% of the original source concentration. **Figure 4.3** shows that losses occurred over the 22-day testing period, with the day 22 concentration in the test cell being about 40% of the original concentration. This can be attributable to sorption of the VOCs onto items such as the stainless steel cell (although VOC sorption onto stainless steel is minimal) , the septa, the gaskets or the screw in the filling port, but since great care was taken to limit losses due to sorption to these areas, the most plausible reason for the losses would be due

to sampling. As described, the septa were punctured four times for every sample taken and the sample volume was replaced by deionised water. Also, the initial concentrations of phase 1 testing were very high and due to the volatility of the compounds in question, large losses could be expected.

The time to reach equilibrium in the system differs from among literature sources and depends on the magnitude of the initial concentration, the size and materials of the test cell, the thickness of the GM and the temperature of the experiment. The initial aim was to run the phase 1 tests until about day 35 or 40 as this was the indicative time to equilibrium for similar setups, but due to challenges with the availability of the GC, the phase 1 tests had to stop on day 22.

Phase 1 testing had challenges and limitations but it met its objective of proving that the VOCs in question diffuse from the source, through the 2 mm GM, into the receptor that represents the groundwater.

Diffusion Coefficients

Figures 4.4 to **4.7** show the measured concentrations over time for the laboratory tests, versus the concentration/time graph obtained from POLLUTE® when entering the data into the software (see Chapter 3). The data was entered into POLLUTE® to fit the graph as accurately as possible to the results from laboratory tests. **Table 5.3** shows the diffusion coefficient (D_g) values calculated for the phase 1 work on this study compared to similar study done by **Rowe *et. al*. (2001)** using BTEX and a 2 mm GM.

Table 5.3: Phase 1 Diffusion Coefficients Compared to Literature

VOC	Diffusion Coefficient from this study (m^2/s)	Diffusion Coefficient from Rowe et al (2001) (m^2/s)
Benzene	9.26×10^{-13}	3.5×10^{-13}
Toluene	8.68×10^{-13}	3.0×10^{-13}
Ethylbenzene	1.39×10^{-12}	1.8×10^{-13}
p-Xylene	2.32×10^{-12}	1.7×10^{-13}

Table 5.3 shows that even with the described limitations during phase 1 testing, the resultant diffusion coefficients compare well with values from literature.

5.3.2 Phase 2 – Diffusion tests using two GMs

5.3.2.1 Concentrations

The graphs on **Figures 4.8** and **4.9** show that over the 86-day diffusion test period, the VOC concentrations in the source decreased and the VOC concentrations in the receptor increased.

The detection of VOC concentrations in the receptor were evident from the samples taken on day 5 already, and increased to between 15% and 32% of the original source concentration at day 86. Although the graph of results in the receptor indicates that some VOC concentrations reduced significantly from day 53 to day 86, the reduction could be attributable to errors in the testing process. Importantly, however, the trend in the data shows an increase in the receptor and a decrease in the source concentrations over time, indicating that diffusion took place across the divide between the source and receptor.

The VOC concentrations in the source immediately decreased as the VOC sorbed onto the GM, and continued to decrease gradually over the 86-day testing period to between 80% and 20% of the original source concentration.

It is also evident from the graphs in **Figures 4.8** and **4.9** that the concentrations of Chloroform in the Source reduced at a slower rate than the other VOCs, indicating that it would take longer for the Chloroform in the system to reach equilibrium.

Figure 4.10 shows that losses occurred over the 86-day testing period, with the day 86 concentration in the test cell being between 55% and 80% of the original concentration, which is considerably less than the losses experienced during phase 1 testing. This could be because the initial concentrations of the phase 2 tests were much lower than the original concentrations in phase 1. It also means that the sealing mechanism of the centerpiece was sound and that losses attributable to the centerpiece are minimal.

It took longer to reach equilibrium in the system than for phase 1 testing since the sorption and diffusion process had to take place over two GMs and the 0.8 cm air-filled pervious zone. For diffusion to occur through GM separating the receptor from the pervious zone, the concentration of the VOCs in the pervious zone had to be higher than in the receptor to drive the diffusive process. As seen

during the field tests, and mentioned in literature, there are concentrations of BTEX and Chloroform in the ambient air surrounding landfills, leachate lagoons and fuel stations. It thus makes sense that the ambient laboratory air, used to fill the pervious zone between the GMs for phase 2 and 3 testing, already contained certain levels of BTEX and Chloroform, which assisted the concentration gradient required for diffusion.

The temperature under which phase 2 tests were undertaken was higher than that of phase 1 and, as indicated by literature, diffusion occurs faster at elevated temperatures. Data on the diffusion across two GMs separated by air was not readily available to compare the difference that the increased temperature had on the system.

Phase 2 testing had its challenges and limitations, but the aim of proving that the diffusion of BTEX and Chloroform takes place from source to receptor across a divide consisting of two 1 mm GMs separated by an air filled pervious zone, was successfully met.

5.3.2.2 Diffusion Coefficients

Figures 4.11 to **4.15** show the measured concentrations over time for the laboratory tests, versus the concentration/time graph obtained from POLLUTE® when entering the data (see Chapter 3). The data was entered into POLLUTE® to fit the graph as accurately as possible to the results from laboratory tests. **Table 5.4** shows the diffusion coefficient (D_g) values calculated for the phase 2 work on this study compared to a study done by **Chao et al (2007)** using BTEX, Chloroform and a 1mm GM.

Table 5.4: Phase 2 Diffusion Coefficients Compared to Literature

VOC	Diffusion Coefficient from this study (m^2/s)	Diffusion Coefficient from Chao et al (2007) (m^2/s)
Benzene	8.10×10^{-13}	5.3×10^{-12}
Toluene	8.10×10^{-13}	6.1×10^{-12}
Ethylbenzene	5.79×10^{-13}	4.5×10^{-12}
p-Xylene	8.10×10^{-13}	-
Chloroform	5.79×10^{-13}	5.1×10^{-12}

This shows that the calculated diffusion coefficients for the phase 2 work on this study are smaller than those observed by **Chao *et. al.* (2007)**. Even though these

coefficients are difficult to compare due to the uncertainties in the conditions during tests from literature, it appears that the diffusion rate across the GM system for the phase 2 work in this study is slightly slower than results from literature. This could be due to the GM being adjacent to an air-filled pervious zone, which was not the case for the literature reference or it could be the type of GM used for the two studies or the modeling methodology.

5.3.3 Phase 3 – Extraction of Air

Concentrations:

Cell A (no Air Extraction)

The graphs on **Figure 4.16** show that, over the 48-day diffusion test period, the VOC concentrations in the source of Cell A decreased and the VOC concentrations in the receptor increased. The centerpiece of Cell A was kept sealed as for phase 2 tests and the results indicate the same trend identified during phase 2, proving that diffusion takes place across the two GMs separated by the air-filled pervious zone. It is worth noting the differences in rate of diffusion between the phase 2 work and Cell A in the phase 3 work, as can be seen when looking at the graphs representing Cell A in phase 3 and the results from phase 2 testing. Concentrations in the receptor of Cell A of phase 3 were only measured after day 18, while during phase 2 they were identified at day 5 already. This could be due to differences in temperature, mixing of the source/receptor volumes or due to sampling methods and instruments. This is also the main reason for the difference in calculated D_g values for phase 2 work and Cell A of phase 3.

The detection of VOC concentrations in the receptor of Cell A increased to between 3% and 11% of the original source concentration at day 48. The VOC concentrations in the source immediately decreased as the VOC sorbed onto the GM, and continued to decrease gradually over the 48-day testing period to between 40% and 5% of the original source concentration. Cell A concentrations of Chloroform in the Source reduced at a slower rate than the other VOCs.

Cell B, C and D (Extraction of Air)

Figures 4.18 to 4.23 show the concentration profiles of the source and receptor of the cells that underwent air extraction through the pervious zone. They indicate that concentrations in the source volumes decreased over the testing time to about 20% of the original source concentration. Chloroform is the exception and its concentration reduced to about 50% of the initial concentration. This is very similar to the data shown on the source graph of Cell A (no air flow) in **Figure 4.16**, indicating that the reduction in source concentrations are comparable regardless of air flow through the pervious zone and that the assumption to use the same sorption coefficient in the modelling of phase 2 and three work was sound.

These figures also show that VOC concentrations in the receptor volumes of Cells B, C and D increased over the testing period, indicating that even with airflow through the system, concentrations of BTEX and Chloroform were observed in the receptor. However, the concentrations of the VOCs in the receptor volumes were at most 0.9% (average 0.4%) of the original source concentrations compared to 20% found during phase two tests. This indicates that airflow resulted in diffusion taking place significantly slower.

The maximum contaminant level shown in **Table 2.2** is the allowable concentration that the United States Environmental Protection Agency (USEPA) allows in drinking water, and BTEX ranges between 0.05 mg/l for benzene, to 10 mg/l for Xylene (total). The BTEX concentrations measured in the receptor volumes of Cells B, C and D ranged from 0.002 mg/l to 0.02 mg/l (0.1 mg/l for Chloroform) which, with the exception of benzene, is significantly lower than the USEPA regulations. As a control, samples of the clean deionised water used in the experiments were tested in the GC-MS and showed concentrations of BTEX ranging from 0.0002 mg/l to 0.0007 mg/l (0.005 mg/l for Chloroform).

Due to the very low VOC concentrations measured in the receptor volumes of Cells B, C and D, the graphs on **Figures 4.19, 4.21** and **4.23** look slightly distorted and trend identification is difficult. The receptor graphs on **Figures 4.25, 4.27, 4.29, 4.31** and **4.33** shows the concentration profile per Cell for each individual VOC against time. These graphs show that the concentrations measured in the receptor volumes of Cell A, where airflow was not introduced, is

much higher than the concentrations measured in the receptor volumes of Cells B, C and D, again indicating that diffusion took place significantly slower in the cells where airflow was introduced.

The aim of phase 3 was to prove that by introducing airflow into the pervious zone between the two 1 mm GMs, the concentration of VOCs in the receptor volume (due to diffusion through the GM) could be reduced significantly and the results indicate that this aim was comfortably achieved.

Diffusion Coefficients

Figures 4.34 to **4.53** show the measured concentrations over time for the laboratory tests, versus the concentration/time graph obtained from POLLUTE® when entering the data into the software (Chapter 3). The data was entered into POLLUTE® to fit the graph as accurately as possible to the results from laboratory tests. The calculated diffusion coefficients are shown in **Table 4.11**. The graphs indicate a drastic drop in concentration in Cell A between day 0 and day 5. The day 0 concentrations of Cell A were much higher than that of Cells B to D. Taking into account the concentration profile over time for all the cells, the day 0 concentration in Cell A could be a GC error and the initial concentration in the comparative POLLUTE® graph was thus adjusted accordingly to most accurately fit the required results. The graphs also show that the POLLUTE® outputs do not exactly match the results from laboratory tests.

The D_g values used to obtain the graphs (**Table 4.15**) are high for the GM closest to the source and lower for the GM closest to the receptor. This means that the required concentration profile across the GM between the pervious zone and the receptor was much lower than that across the GM between the source and the pervious zone. This indicates that BTEX concentrations in the pervious zone were reduced by introducing airflow into the system, which indicates that VOCs were removed by extracting air through the system. Certain parameters in the POLLUTE® program can be altered to more accurately represent the graph from laboratory tests, and this will have an impact on the D_g values assumed for the two GMs. The principle will, however, hold true that D_g values for the GM closest to the source volume in phase 3 testing (under airflow conditions) will be higher

than those obtained for phase 2 testing (**Table 4.16**). This shows that the introduction of airflow into the system increased the rate of diffusion through the GM closest to the source volume.

The results for Chloroform look slightly different due to Chloroform's tendency to stay in aqueous solution; and the concentration change in the source was thus much less than for BTEX and would take much longer to reach equilibrium. This resulted in the D_g values for both GMs being much lower than that for BTEX.

The results from **Table 4.115** shows that the diffusion coefficient for the GM closest to the source did not increase or decrease from Cell B to Cell D which seems to indicate that the rate of air extraction had no significant impact on the rate of diffusion. This is not completely true and is distorted because POLLUTE® graphs could not be accurately fit onto graphs from laboratory results. It is important to note that when looking at the concentrations observed in the receptor volumes of Cells B, C and D, they followed the trend Cell D > Cell C > Cell B. The rate of air extraction decreased from once every 24 hours in Cell B, to once every week for Cell D, and this indicates that the more regularly air in the pervious zone was replaced by ambient air, the more VOCs were removed from the system, with less concentrations measured in the receptor. This would indicate that introducing a flow of air through a pervious zone adjacent to the GM layer in a landfill liner, would significantly reduce the concentrations of VOCs in the groundwater beneath landfills and waste containment facilities.
The rate of airflow and the possible introduction of liquid flow needs further investigation.

CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

6.1 STUDY OBJECTIVES

The aim of this study was to obtain reliable data on the reduction in diffusion of VOCs through the HDPE geomembranes (GM) component in composite liner systems of landfills by extracting air through the leakage detection layer or drainage layer of the composite liner.

With the extraction of air an added benefit should be that some of the VOCs that diffuse through the composite liner system will be extracted with the air and lead to a reduction of VOCs in the underlying soil and/or groundwater. The objective was to undertake tests in three phases.

The aim of phase 1 was to prove that the chosen VOCs diffuse from source to receptor through a GM layer, and to compare the results obtained to those in the literature. The aim of phase 2 was to prove that, even if the separation between the source and receptor consisted of two GMs separated by an air-filled pervious zone, diffusion of the VOCs would still occur from the source to the receptor volumes. Finally, the aim of phase 3 was to prove that by introducing airflow into the pervious zone between the two GMs, the concentration of VOCs in the receptor volume (due to diffusion through the GM) could be reduced significantly. A further aim of the phase 3 testing was to determine if the rate of air removal would play a role in the diffusive process and the resultant VOC concentrations in the receptor.

6.2 CONCLUSIONS

Recent years have seen great strides in the efforts of developed and developing countries to reduce the volume of waste that gets disposed of on landfills but there will always be a need to contain waste in lined waste-disposal facilities.

When waste is disposed of in landfills or waste containment facilities, it generates leachate and landfill gas as it is exposed to heat and chemicals over time. The leachate and landfill gas contains harmful contaminants such as Volatile Organic

Compounds (VOCs) like Benzene, Toluene, Ethylbenzene, Xylene (BTEX) and Chloroform.

Materials used in the design of landfill liners have also undergone great improvements since they were first used to contain waste and protect groundwater, but there is still much to learn and understand about the ways in which technology can assist to protect groundwater beneath waste facilities. Clean water critical for the survival of all living things and the protection of groundwater resources should be a global priority.

Various studies have shown that VOCs can penetrate even the most well-designed liners of waste containment facilities to pollute the groundwater. The method of penetration is advection and/or diffusion with the main contributor to pollution of groundwater beneath landfills being diffusion.

Diffusion is a molecular activated process that occurs in a series of steps following the path of least resistance. The process begins with removal of the contaminant from the solution and adsorption onto the liner, then diffusion across the GM and finally desorption from the GM and entry into underlying water resources. Phase one of the tests undertaken for this study showed that BTEX diffuses through a 2 mm HDPE GM over time with significant concentrations found in the receptor volumes of diffusion test cells specially made for this project. This confirmed studies undertaken by many researchers in the past.

Phase two of the tests undertaken for this dissertation project proved that diffusion of BTEX and Chloroform take places from a source to a receptor reservoir separated by two 1 mm GMs with an air-filled pervious zone between them. This confirms the findings of **McWatters & Rowe (2009)** that the "*diffusive transport of VOC contaminants through geomembranes is identical despite the phase they originated from".*

Phase three of the tests undertaken for this dissertation project proved that by extracting air through a pervious zone beneath the GM component of a landfill liner, the concentration of VOCs present in the underlying groundwater can be reduced, since the air removed from the system also removes the majority of VOCs. This phase of testing also confirmed that more frequent removal of air further reduces the VOC concentrations in the receptor thus implying that a

constant airflow though a pervious zone in a landfill liner can significantly reduce concentrations of VOCs in the groundwater beneath landfills and waste containment facilities.

6.3 RECOMMENDATIONS

The work undertaken for this dissertation study had a determined scope and as the work progressed, opportunities for further studies became clear. It is thus recommended that the following areas receive more attention through additional studies:

Extraction Fluid

This study used ambient laboratory air but it is conceivable that by using water or some other fluid, results can be optimised. This could include the use of a GCL in testing to understand whether continuous hydration of the bentonite in the GCL will benefit the reduction in contaminant transport.

Rate of Extraction

The scope of this study was limited to a number of ranges of different air extractions through the pervious zone, which was not a constant flow. It needs to be further investigated how the constant flow of air will affect the results if contaminant transport and what the optimal extraction rate needs to be for certain applications.

Mass Balance and Treatment of VOCs

The VOCs that were extracted from the system in the tests undertaken for this study were not captured or measured. If the VOCs are removed from beneath the liner, they need to be routed somewhere and releasing it into the atmosphere does not protect the environment. It needs to be further investigated how to trap the VOCs and treat them after removal.

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