# 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 in a landfill is exposed to the chemicals and heat generated over time, producing harmful fluids in the form of leachate or landfill gas that migrate from the landfill towards the liner or capping, and include organic contaminants. The high-density polyethylene (HDPE) geomembrane (GM) component of the landfill liner is often believed to be the primary barrier to contaminant transport, but volatile organic compounds (VOCs) diffuse through geomembranes at appreciable rates. The aim of this study was to obtain reliable data on the reduction in diffusion of VOCs through the HDPE GM component in the composite liner systems of landfills by extracting air through the leakage detection layer or drainage layer of the composite liner. It was shown 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.

## INTRODUCTION AND BACKGROUND

Waste and the adverse effects of waste storage and disposal 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.

When waste materials in a landfill or any other waste body are exposed to the air and water infiltration over time, heat is generated and harmful fluids in the form of leachate and/or landfill gas are generated. Leachate and landfill gas migrate from the landfill towards the basal liner or capping, and most often 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 (GM) as part of a landfill liner 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.

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 facilities 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 liners, geomembranes, geocomposite drains and 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 subsequently that highlights diffusive transport (i.e. contaminant 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 barriers for contaminant transport, for the purpose of this study, the only application of HDPE investigated will be that of waste disposal landfill liner.

## STUDY OBJECTIVES

The aim of this study was to obtain reliable data on the reduction in diffusion of VOCs through the HDPE GM component in composite liner systems of landfills by extracting air through the leakage detection layer or drainage layer of the composite liner adjacent to the HDPE component of the liner. With the extraction of air through the liner system, some of the VOCs that could diffuse through the HDPE GM layer would be extracted with the air and thus reduce VOCs in the underlying soil and/or groundwater.

The objective was to undertake tests in the following three phases:

■ Phase 1 aimed to prove that the chosen VOCs diffuse from source to receptor through an HDPE GM layer, and to compare the results obtained with those in the literature.

■ Phase 2 aimed to prove that, even if the separation between the source and receptor consisted of two HDPE 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 HDPE GMs, the concentration of VOCs in the receptor volume (due to diffusion through the HDPE 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.

For the purposes of this study, the onsite conditions were replicated in a laboratory using diffusion test cells similar to those used by Sangam and Rowe (2001). All of the HDPE 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.

## LITERATURE REVIEW

### Waste disposal and containment barriers

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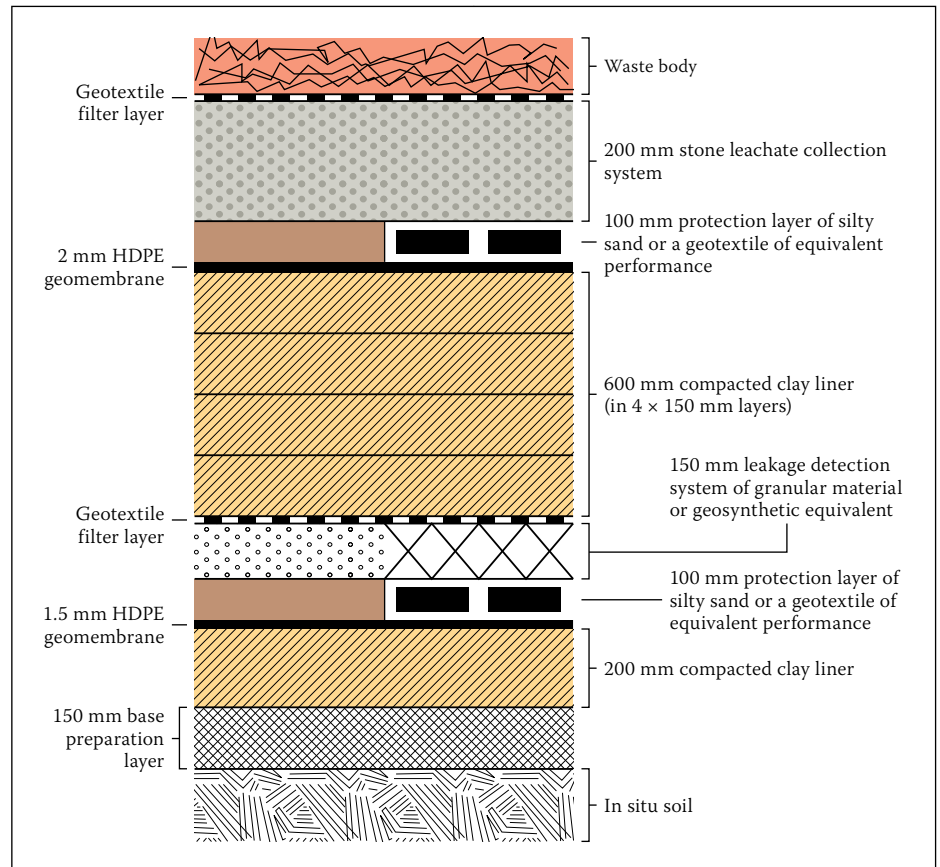


**Figure 1** Class A containment barrier design prescription (Government Gazette 36784 p 37)

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 (DWAF 1998) are presented in Figure 1.

The liner detail in Figure 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 and waste type for which it is intended. The layers can be replaced by other layers of equal or improved performance, and the compacted clay layers are often replaced with a geosynthetic clay liner (GCL). The leakage detection system normally made up of granular material can also be replaced by an approved geosynthetic equivalent alternative such as a cuspated HDPE drainage sheet or geocomposite drain. A fluid could pass through this layer in order to remove VOCs from the system and possibly cool the liner. HPDE GMs 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 was the HDPE GM, in most cases the HDPE GM is used as a primary barrier in conjunction with other engineered layers to form a composite lining system that is designed and engineered to be fit for purpose. The HDPE

GM is an integral part of a composite landfill lining system, and in South Africa the Department of Environmental Affairs has included the HDPE GM in the liner requirements for the successful application of any waste licence to own or operate a waste disposal facility.

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 HDPE GM service life (or half-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 to be a successful barrier in the landfill liner, it needs to be manufactured, installed and monitored according to the specifications given by design engineers and manufacturers.

### Volatile organic compounds

Volatile organic compounds (VOCs) are organic chemical compounds that have high enough vapour pressures under normal

conditions to significantly evaporate 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 contaminate soil and groundwater, for example the deposition of waste and waste-related products into 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 a significant contributor to environmental pollution. Methane generally migrates to the surface of landfills, while other VOCs, such as the aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene (BTEX)) commonly found in petroleum products, migrate to the base of the landfill and contribute 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 in close proximity to 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) and are also significant contributors to groundwater contamination. Exposure to VOCs in the short and long term can be detrimental to human health in various ways.

## Diffusion of VOCs

Diffusion is often referred to as molecular diffusion and is the 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 GMs prevent advective flow of contaminants through their structure, hence their widespread use in the containment of water and other liquids. HDPE GMs do, however, allow movement of certain contaminants through their structure 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 GM, the process requires the
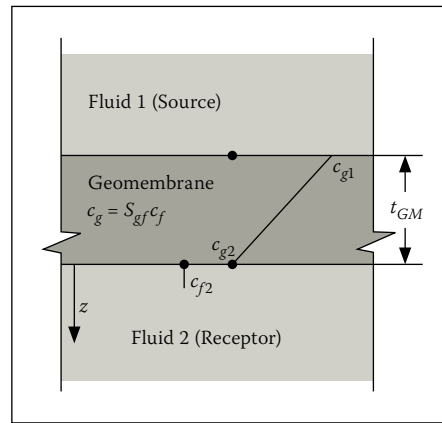


**Figure 2** Schematic diagram of diffusion through HDPE GM (adapted from Rowe 1998)

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 contaminant or leachate and polymer chains in the HDPE. In turn, this will depend on temperature, concentration, the size and shape of the penetrant and the nature of the polymer itself (Rowe 1998).

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

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

For water or water-based solutions like those used in this experiment, the adsorption and desorption processes can be seen as similar and inverted (Sangam & Rowe 2001). In the Keynote Lecture for the 6th International Conference on Geosynthetics held in Atlanta in 1998, Professor Kerry Rowe presented a schematic drawing similar to the one shown in Figure 2 to illustrate the diffusive transport of contaminants through an HDPE GM. The figure shows partitioning between the concentration in solution and the concentration dissolved in the GM.

Figure 2 illustrates that the process starts with the removal of the molecule from the solution fluid onto the surface of the HDPE 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 depends upon the activity of the permeant within the polymer at equilibrium (Mueller *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 HDPE GM (solid) is given by the Nernst distribution function which takes the linear form shown in Equation 1 (Henry's Law) (Sangam & Rowe 2001):

$$C_g = S_{gf} C_f \tag{1}$$

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

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 HDPE 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 Equation 1 also holds true, meaning the partitioning coefficient for adsorption and desorption of BTEX and chloroform in aqueous solutions are equal (Sangam & Rowe 2001).

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

$$f = -D_g \frac{\partial c_g}{\partial_z} \tag{2}$$

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 HDPE GM [L$^2$T$^{-1}$] (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 HDPE GM).

$\partial_c / \partial_z$ 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):

$$\frac{\partial c_g}{\partial_t} = D_g \frac{\partial^2 c_g}{\partial z^2} \tag{3}$$

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

To measure the concentration change in the HDPE 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 & Rowe 2001). Equation 1 gives the relationship between the concentrations in the GM and the adjacent fluid. Equation 3 gives the flux (diffusion) within the HDPE GM, so substituting Equation 1 into Equation 2 gives the flux on one side of the HDPE GM to a similar fluid on the other side of a HDPE GM (Rowe 1998), i.e. Equation 4.

$$f = -D_g \frac{\partial c_g}{\partial z} = -S_{gf} D_g \frac{\partial c_f}{\partial z} = -P_g \frac{\partial c_f}{\partial z} \quad (4)$$

Where: $P_g = S_{gf} D_g$ \hfill (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 & Rowe 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 an HDPE GM of thickness $t_{GM}$ is thus given by:

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

Where: $S_{gf} D_g$ can be replaced by $P_g$ (Equation 5) and where $\Delta c_f$ is the difference in concentration in the fluid on either side of the GM ($c_{f1}$ and $c_{f2}$ in Figure 2).

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.

For the purpose of this study, it was 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. The two GMs would 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 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 above.

## Calculating coefficients in diffusion process

When undertaking diffusion tests the sorption ($S_{gf}$) and diffusion ($D_g$) coefficients need to be calculated in order to understand and comment on the diffusion process.

$S_{gf}$ 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 HDPE GM at equilibrium to the concentration of the chemical in the solution in contact with the HDPE GM (Park & Nibras 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 the computer software program POLLUTE® which was first developed by R K Rowe and J R Booker in 2004 (POLLUTE 2004). This program implements a one-and-a-half dimensional solution to the advection-dispersion equation (Equation 3).

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 proportional 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.

When the flux across one HDPE GM is investigated, the $S_{gf}$ value can be determined in various ways, as described by Rowe (1998),

and Sangam and Rowe (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 Equation 7 (Rowe 1998).

$$S_{gf} = \frac{C_{fo} V_s - C_{fF}(V_s + V_r) - \Sigma V_i C_i}{A t_{GM} C_{fF}} \quad (7)$$

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].

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 POLLUTE v7®, which solves the one-dimensional contaminant migration equation subject to boundary conditions at the top and bottom of the GM being modelled (Sangam & Rowe 2005).

## EXPERIMENTAL METHODOLOGY
Laboratory tests were carried out at the University of Pretoria in South Africa. The tests undertaken were based on the methods used by Sangam and Rowe (2001).

## Sorption tests
Sorption tests were done to determine the sorption coefficient ($S_{gf}$) for the HDPE GM and permeant in question. The coefficient is defined as the ratio of the concentration of the chemical in the HDPE GM at equilibrium to the concentration of the chemical in the solution in contact with the HDPE GM (Park & Nibras 1993). Sorption tests were done using glass vials with sampling caps, about 80 mm high and 50 mm diameter, as shown in Figure 3. The glass sorption cells are similar in shape and size to the glass sorption cells used by Sangam and Rowe (2001).
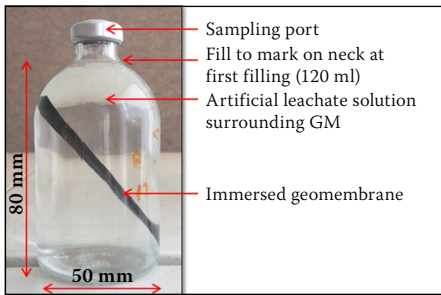
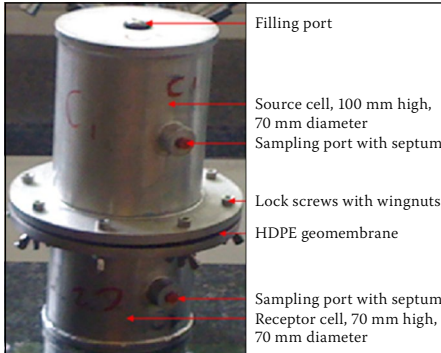**Figure 3** Sorption test vials used



**Figure 4** Diffusion test cell

Tests were done on both the 1 mm and 2 mm GM using an aqueous solution containing BTEX and chloroform. The tests were done in duplicate for both the 1 mm and the 2 mm GMs, and two control cells were included to measure and assess losses. The control vials were identical to the test vials, except that they contained no GM. Experiments were performed at room temperature in the laboratory (24 ± 2°C) and 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. The sorption coefficient of each contaminant was then calculated using Equation 7. The synthetic leachates used in the sorption vials were made up in the laboratory using laboratory-grade BTEX and chloroform made by SAAR Chem-Trade (Pty) Ltd.

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

■ **Phase 1 – Diffusion tests using one HDPE 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) of a diffusion test cell.

■ **Phase 2 – Diffusion tests using two HDPE GMs:** The second phase of testing replicated the first, with the 2 mm HDPE GM being replaced by 2 x 1 mm HDPE GMs separated by an 8 mm 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 HDPE GMs (separated by air in the pervious zone) and still reach groundwater beneath the liner system. The two HDPE GMs were assumed identical since they were cut from the same roll and when there is no flow through the system the VOC concentration in the water above and below the HDPE 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 HDPE GMs.

■ **Phase 3 – Extraction of air:** The third phase replicated Phase 2, with air being extracted through the gap between the two HDPE 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 HDPE GMs at regular intervals, the VOCs would be removed from the system and would not reach the groundwater. The two HDPE 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 HDPE GMs.

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 4.

Five cells were made so that tests could be done in triplicate (for each phase of testing), with one control cell and one blank cell to measure losses and outside influences. The receptor reservoir represented the groundwater beneath lined landfill facilities and was filled with deionised water at the start of testing. The source reservoir represented the

leachate in a lined landfill and was filled with a prepared synthetic leachate solution using the filling port.

For the Phase 1 diffusion tests, the source and receptor cells were separated only by the HDPE GM, and during Phases 2 and 3 a centre-piece was added to introduce the pervious zone into the liner system. The centre-piece was separated from the source and receptor reservoirs by HDPE GMs so that the configuration was Source-GM-Pervious Zone-GM-Receptor. During Phase 3 testing the holes in the centre-piece were used to introduce air flow to the system. Using four test cells (A to D), different air flow rates were introduced in three of the cells, leaving one cell permanently closed as for Phase 2 testing in order to provide a control. The air flows were achieved by replacing the air in the pervious zone between the GMs with clean ambient air once every 24 hours, 72 hours and 7 days. In addition to the sorption test described earlier, the $S_{gf}$ value was also obtained from the diffusion test using Equation 7 after the completion of diffusion tests at equilibrium. The diffusion coefficient ($D_g$) was then inferred using Equation 3, and the variation in source and receptor concentrations with time (Fick's Second Law) at the given boundary conditions using the software POLLUTE®, which solves the one-dimensional contaminant migration equation subject to boundary conditions at the top and bottom of the GM being modelled (Sangam & Rowe 2005).

## RESULTS

### Sorption
Table 1 summarises the averaged and corrected $S_{gf}$ values obtained.

**Table 1** Summary of $S_{gf}$ values obtained using different test methods

| VOC | Aqua sorption | | Diffusion test | |
|---|---|---|---|---|
| | 1 mm | 2 mm | 1 mm | 2 mm |
| Benzene | 27.8 | 14.1 | – | 116 |
| Toluene | 61.9 | 198 | – | 183 |
| Ethylbenzene | 87.2 | 326 | – | 391 |
| p-Xylene | 80.2 | 102 | – | 188 |
| Chloroform | 25.1 | 14.2 | – | – |

## Diffusion

*Phase 1 – Diffusion tests using one HDPE GM*
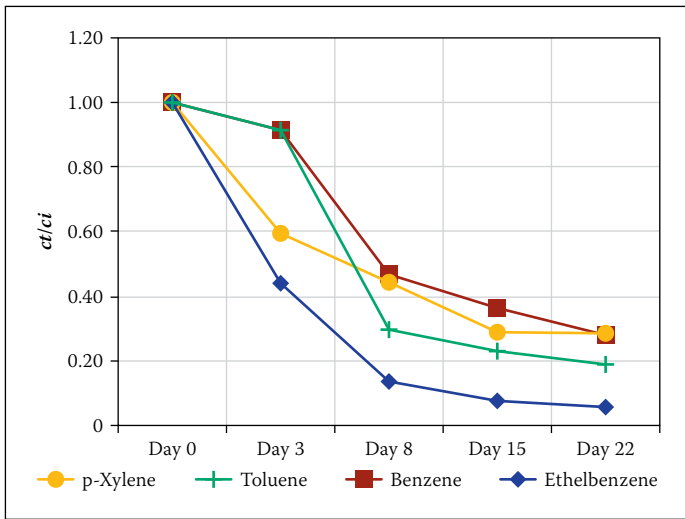Concentrations in the source and receptor cells were measured, averaged and plotted

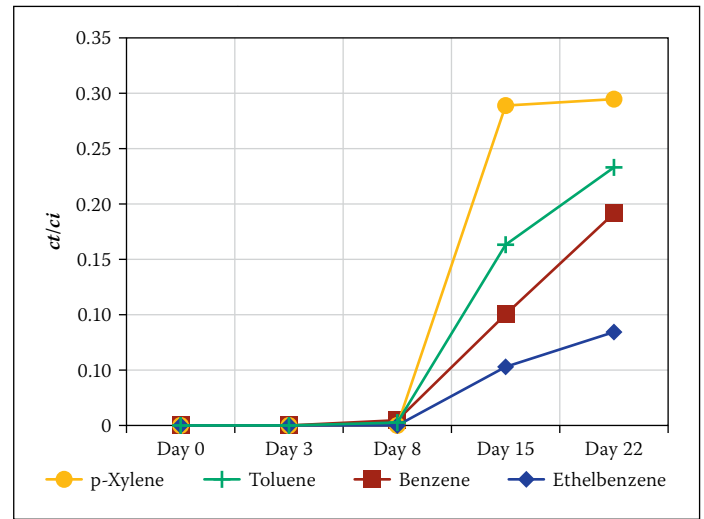**Figure 5** Phase 1 – VOC concentration in source volume



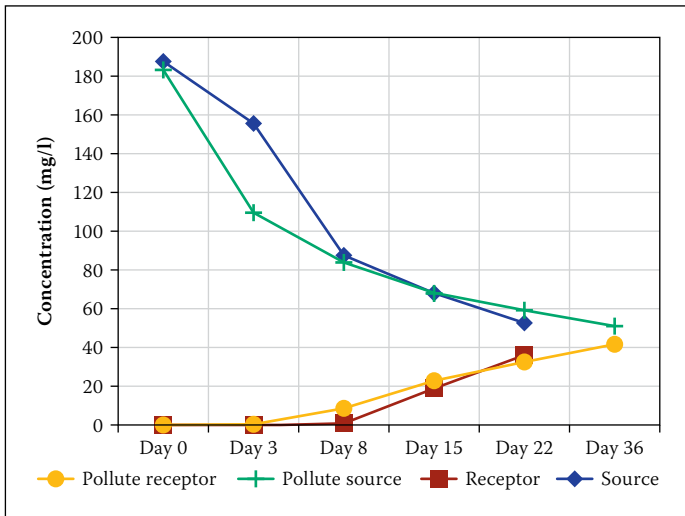**Figure 6** Phase 1 – VOC concentration in receptor volume



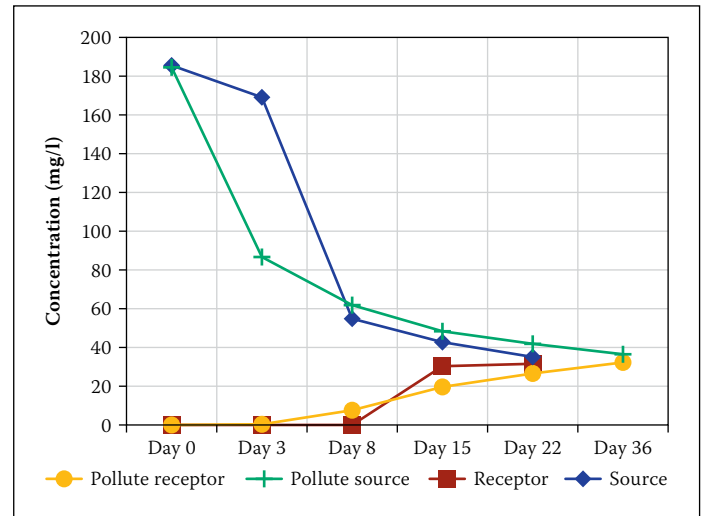**Figure 7** Phase 1 – Combined output graph for benzene



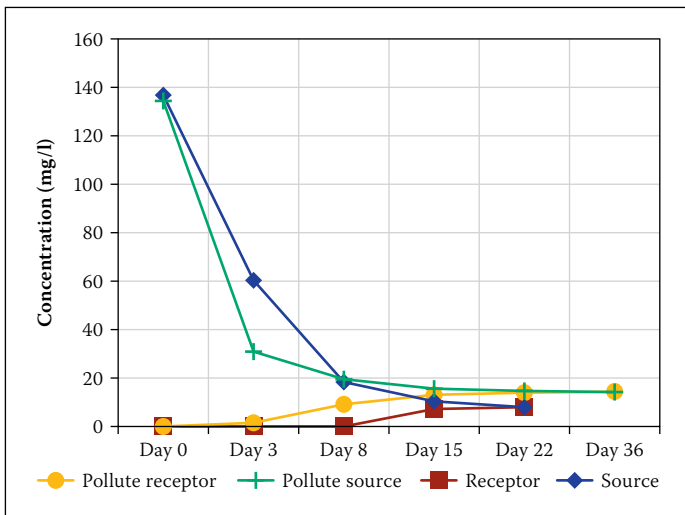**Figure 8** Phase 1 – Combined output graph for toluene



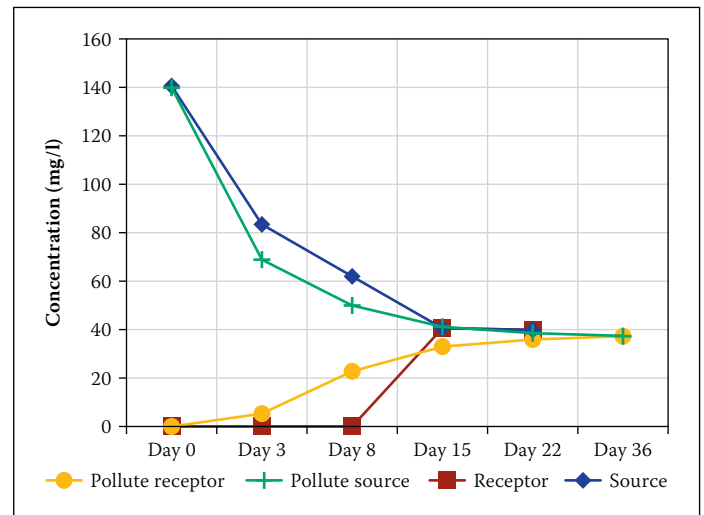**Figure 9** Phase 1 – Combined output graph for ethylbenzene



**Figure 10** Phase 1 – Combined output graph for p-xylene

(initial concentration over measured concentration) against time for the source Figure 5 and receptor Figure 6 volumes.

The concentration versus time output graphs that POLLUTE® produces if the methodologies described earlier were correctly followed, were combined with the actual laboratory test results and are shown in Figures 7 to 10 for Phase 1 testing.

The Phase 1 diffusion coefficients obtained are then given in Table 2 (chloroform was not tested during Phase 1).

### Phase 2 – Diffusion tests using two HDPE GMs

Concentrations in the source and receptor cells were measured, averaged and plotted (initial concentration over measured

**Table 2** Calculated diffusion coefficients ($D_g$) for Phase 1 testing

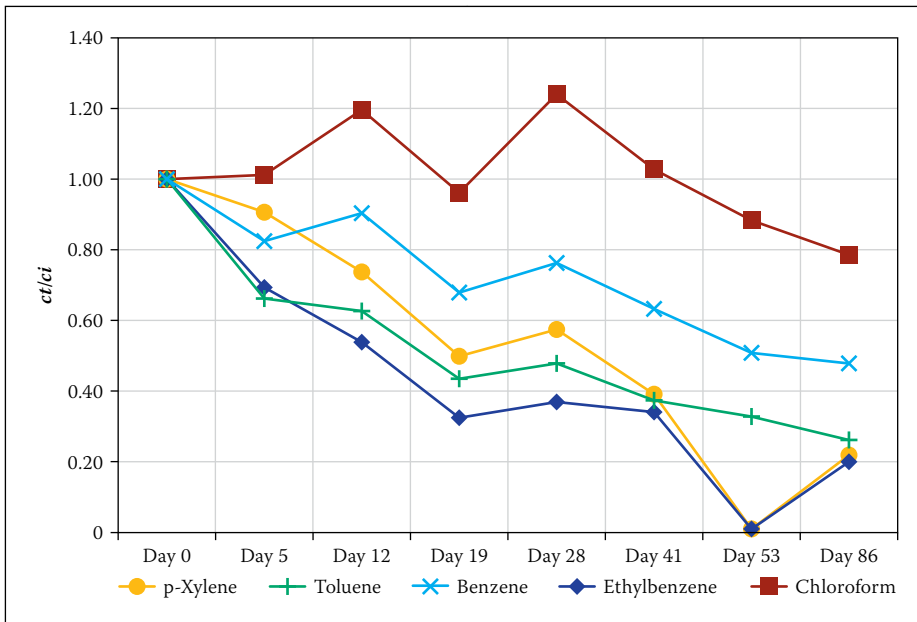| VOC | Diffusion coefficient in m²/s |
|---|---|
| Benzene | $9.26 \times 10^{-13}$ |
| Toluene | $8.68 \times 10^{-13}$ |
| Ethylbenzene | $1.39 \times 10^{-12}$ |
| p-Xylene | $2.32 \times 10^{-12}$ |

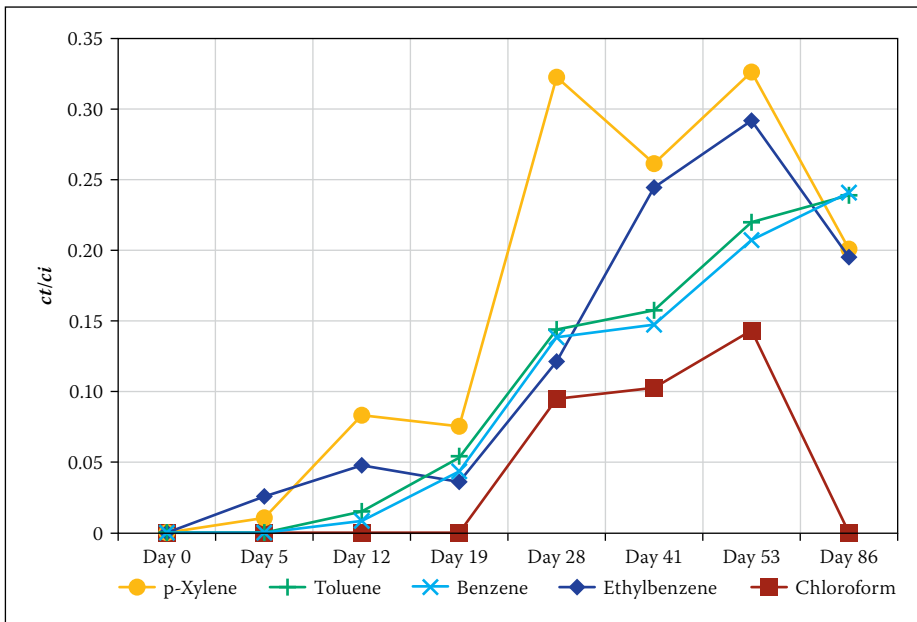**Figure 11** Phase 2 – VOC concentration in source volume



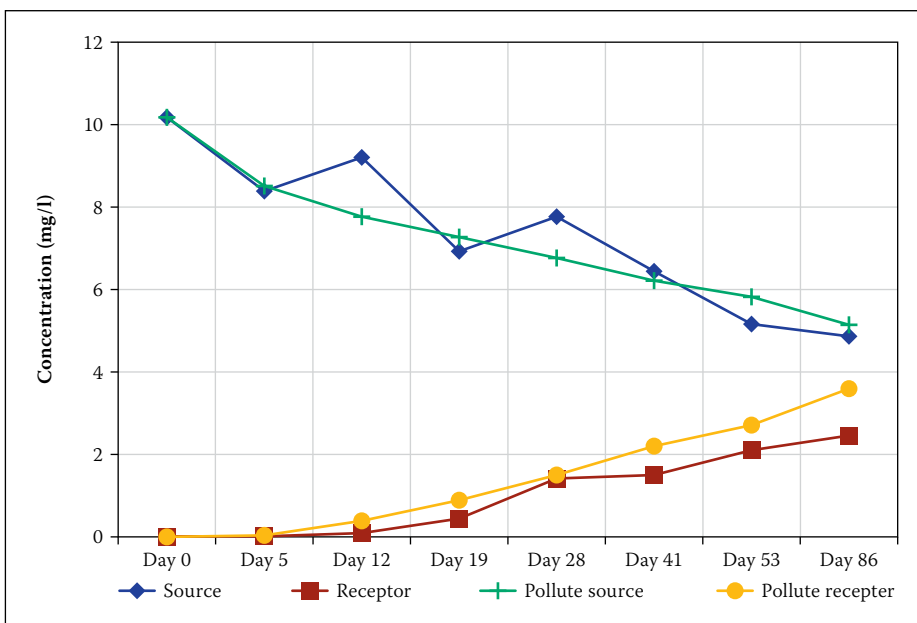**Figure 12** Phase 2 – VOC concentration in receptor volume



**Figure 13** Phase 2 – Combined output graph for benzene

concentration) against time for the source Figure 11 and receptor Figure 12 volumes.

As for Phase 1 testing, the diffusion coefficient $D_g$ was determined using POLLUTE®. The concentration versus time output graphs that POLLUTE® produced were combined with the actual laboratory test results and then plotted as shown in the example for benzene in Figure 13.

The Phase 2 diffusion coefficients obtained are then given in Table 3.

**Table 3** Calculated diffusion coefficients ($D_g$) for Phase 2 testing

| VOC | Diffusion coefficient in m²/s |
|---|---|
| Benzene | $8.10 \times 10^{-13}$ |
| Toluene | $8.10 \times 10^{-13}$ |
| Ethylbenzene | $5.79 \times 10^{-13}$ |
| p-Xylene | $8.10 \times 10^{-13}$ |
| Chloroform | $5.79 \times 10^{-13}$ |

*Phase 3 – Extraction of air*

Concentrations in the source and receptor cells were measured and plotted (initial concentration over measured concentration) against time for the source and receptor volumes of each cell. The results showed that the VOC concentrations in the source gradually decreased while concentrations in the receptor gradually increased over the 48-day testing period. 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 14 and 15 show this trend for benzene, but the trend was also the same for the other VOCs (not shown due to article space constraints).

These figures 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. The concentration versus time output graphs that POLLUTE® produced were combined with the actual laboratory test results and are shown in Figures 16 to 19 for Phase 3 testing, again using only benzene as an example.

For Phase 3 testing the diffusion coefficients obtained through POLLUTE® are given in Table 4 on p 44.

## DISCUSSION

Phase 1 results 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 HDPE GM, and gradually decreased over the 22-day testing period to between 5% and 30% of the original source concentration. Measured losses can be attributable to sorption of the VOCs onto items such as the stainless steel cell, 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 the sampling process. Phase 1 testing met its objective of proving that the VOCs in question diffuse from the source, through the 2 mm HDPE GM, into the receptor that represents the groundwater, and the diffusion coefficients obtained compare well with those from literature.

Phase 2 results 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. 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 HDPE 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 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. 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 HDPE GMs and the 8 mm air-filled pervious zone. For diffusion to occur through HDPE 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. Phase 2 testing proved that the diffusion of BTEX and chloroform takes place from source to receptor across a divide consisting of two 1 mm HDPE GMs separated by an air-filled pervious zone.

Phase 3 results show that concentrations in the source volumes decreased over the testing time to about 20% of the original source concentration. Chloroform is the
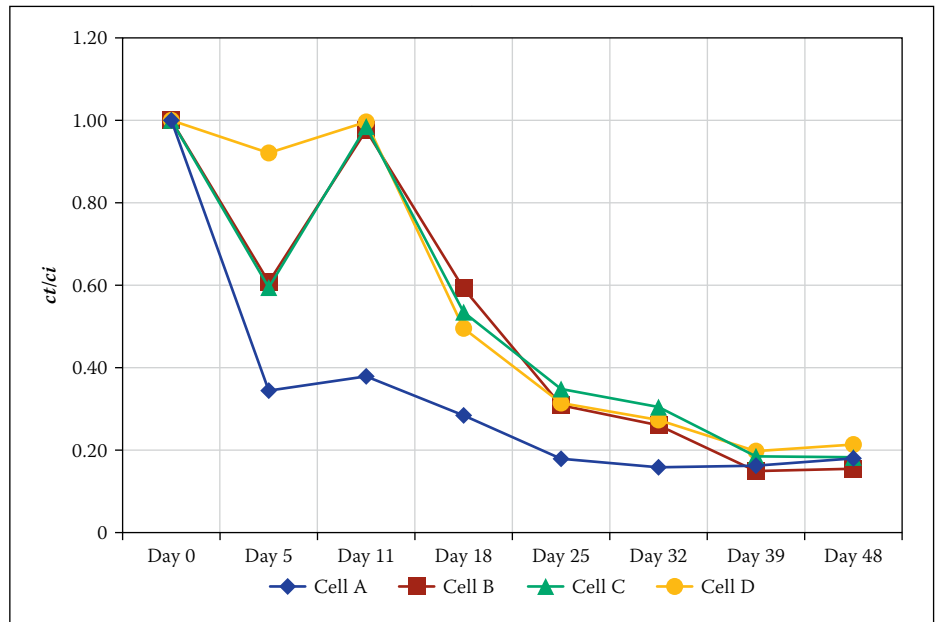


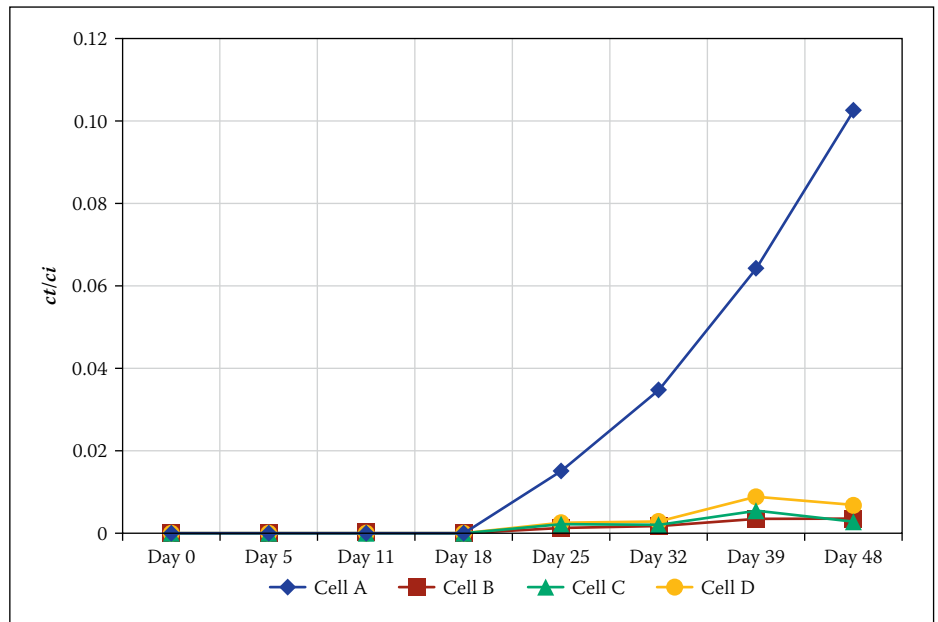**Figure 14** Phase 3 – Concentrations of benzene in source volume



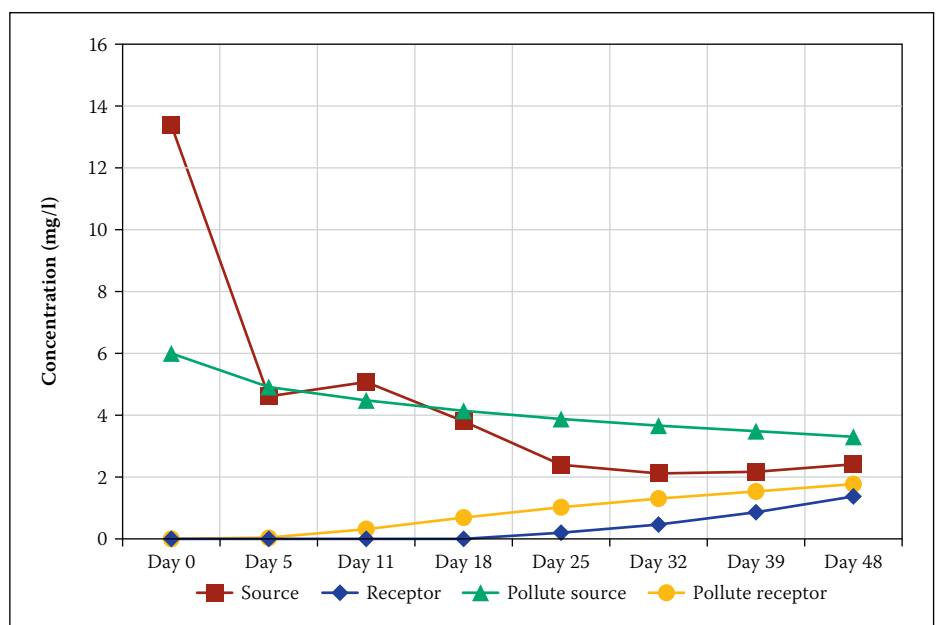**Figure 15** Phase 3 – Concentrations of benzene in receptor volume



**Figure 16** Phase 3 – Combined output graph: Cell A benzene (no extraction)
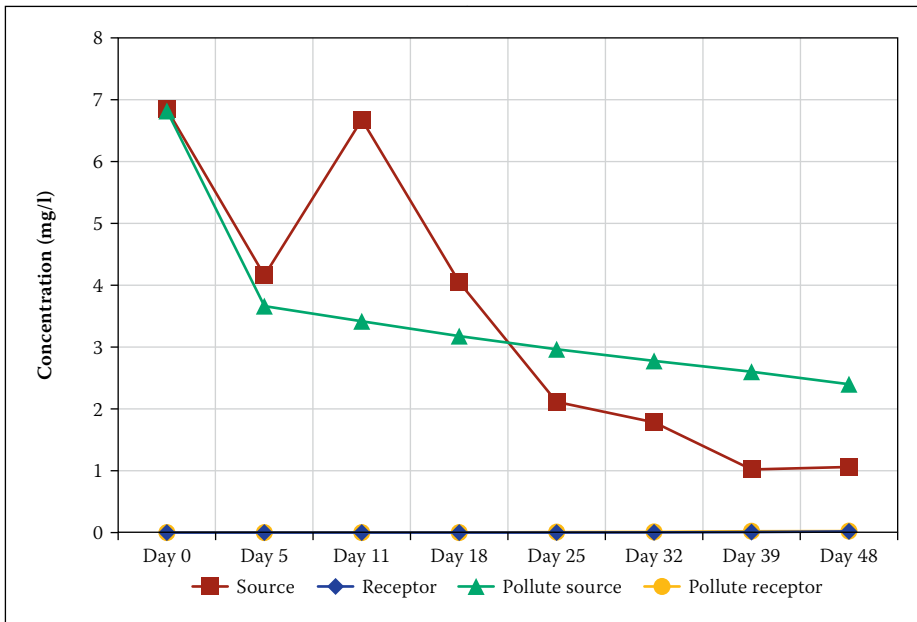
**Figure 17** Phase 3 – Combined output graph: Cell B benzene (extraction every 24 hours)
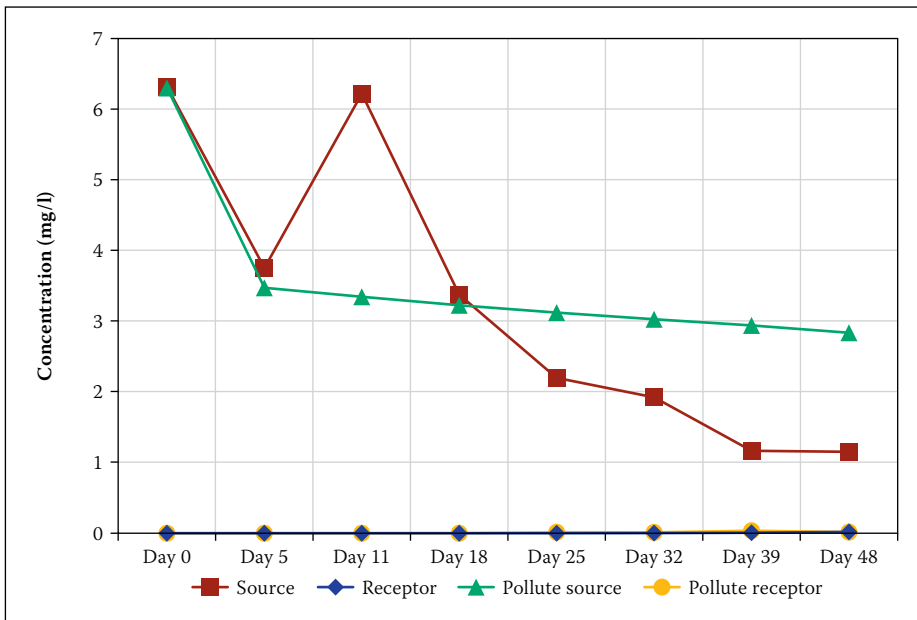


**Figure 18** Phase 3 – Combined output graph: Cell C benzene (extraction every 72 hours)
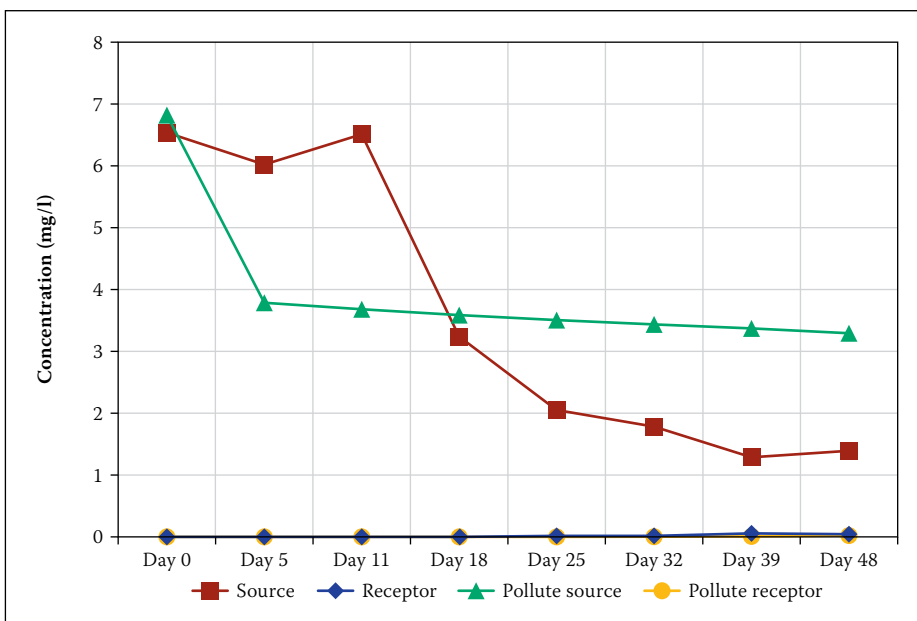


**Figure 19** Phase 3 – Combined output graph: Cell D benzene (extraction every week)

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), 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 Phase 3 work was sound. Results 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 2 tests. This indicates that airflow resulted in diffusion taking place significantly slower. Due to the very low VOC concentrations measured in the receptor volumes of Cells B, C and D, the graphs look slightly distorted and trend identification is difficult. The receptor graphs showing the concentration profile per cell for each individual VOC against time indicate 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 HDPE GMs, the concentration of VOCs in the receptor volume (due to diffusion through the HDPE GM) could be reduced significantly, and the results indicate that this aim was comfortably achieved.

## CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

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.

Phase 1 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 2 testing proved that diffusion of BTEX and

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**Table 4** Calculated diffusion coefficients ($D_g$) for Phase 3 testing

| VOC | Diffusion coefficient in m²/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 | $1.04 \times 10^{-12}$ | $1.16 \times 10^{-10}$ | $2.31 \times 10^{-14}$ | $1.04 \times 10^{-10}$ | $2.31 \times 10^{-14}$ | $9.84 \times 10^{-11}$ | $2.31 \times 10^{-14}$ |
| Toluene | $1.04 \times 10^{-12}$ | $1.16 \times 10^{-10}$ | $2.31 \times 10^{-14}$ | $1.04 \times 10^{-10}$ | $2.31 \times 10^{-14}$ | $9.84 \times 10^{-11}$ | $2.31 \times 10^{-14}$ |
| Ethylbenzene | $1.15 \times 10^{-12}$ | $1.16 \times 10^{-10}$ | $2.31 \times 10^{-14}$ | $1.04 \times 10^{-10}$ | $2.31 \times 10^{-14}$ | $9.84 \times 10^{-11}$ | $2.31 \times 10^{-14}$ |
| p-Xylene | $1.15 \times 10^{-12}$ | $1.16 \times 10^{-10}$ | $2.31 \times 10^{-14}$ | $1.04 \times 10^{-10}$ | $2.31 \times 10^{-14}$ | $9.84 \times 10^{-11}$ | $2.31 \times 10^{-14}$ |
| Chloroform | $9.26 \times 10^{-13}$ | $1.16 \times 10^{-13}$ | $5.79 \times 10^{-14}$ | $1.16 \times 10^{-13}$ | $5.79 \times 10^{-14}$ | $1.16 \times 10^{-13}$ | $5.79 \times 10^{-14}$ |

chloroform takes place from a source to a receptor reservoir separated by two 1 mm GMs with an air-filled pervious zone between them. Phase 3 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 through a pervious zone in a landfill liner can significantly reduce concentrations of VOCs in the groundwater beneath landfills and waste containment facilities.

## Recommendations

To add to the work done for this study it is recommended that extraction fluids other than air be used at more frequent rates. 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. Also, 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 (releasing them 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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