

Protection of Groundwater Beneath Waste Containment Facilities: Possible Solution to the Diffusion of Volatile Organic Compounds through Composite Landfill Liners

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ABSTRACT

Diffusion of Volatile Organic Compounds (VOCs) in landfilled wastes can lead to contamination of groundwater underneath waste containment facilities. Diffusion takes place through the intact and installed composite liner system. Diffusion is exaggerated by a rise in temperature as is typical at the bottom of a landfill. The geomembrane (normally HDPE) in the composite liner system is believed to be the primary barrier to contaminant transport but it has been shown in many studies that VOCs diffuse through intact geomembranes at appreciable rates depending on various factors. This study aims to use the leakage detection system in a composite liner to extract air through the system which will remove VOCs from the collection system preventing them from contaminating the groundwater, and at the same time cooling the composite lining system as a whole. Field tests and laboratory tests were performed on the diffusion of BTEX and chloroform through HDPE geomembranes.

1. INTRODUCTION

Landfills and waste disposal facilities are vessels for the permanent storage of unwanted waste substances that can be harmful to the environment and to the sustainability animal and human life. Landfills are designed to protect us from these potentially harmful substances. The substances include volatile organic compounds (VOCs) which include aromatic hydrocarbons like Benzene, Toluene, Ethylbenzene and Xylenes (BTEX). VOCs can migrate into the surrounding groundwater and are considered a health risk even at low concentrations (Prosser & Janecheck, 1995). Landfills protect the environment through the design and installation of liners of which the High Density Polyethylene (HDPE) Geomembrane (GM) forms an integral part.

When used as part of a composite liner, which can include a Compacted Clay Layer (CCL) or Geosynthetic Clay Layer (GCL), the HDPE GM has been shown to be an excellent barrier to the advective-diffusive migration of inorganic and ionic contaminants (Rowe et al. 1996; Rowe, 2005). However, GMs contain small voids between the polymer segments through which small molecules can diffuse (Aminabhavi and Naik, 1998) and VOCs have been shown to diffuse through an intact HDPE GM (Sangam and Rowe, 2001).

2. AIM OF THE STUDY

The main aim of this study is to obtain reliable data on the reduction in diffusion of VOCs through HDPE Geomembranes in landfill liner systems by extracting air through an envelope in the composite liner system, to remove the VOCs from the system in order to ultimately reduce groundwater contamination. A schematic of the above premise can be seen in Figure 1 below.

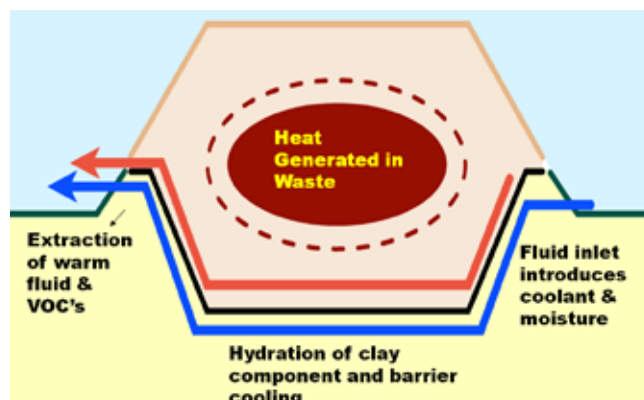


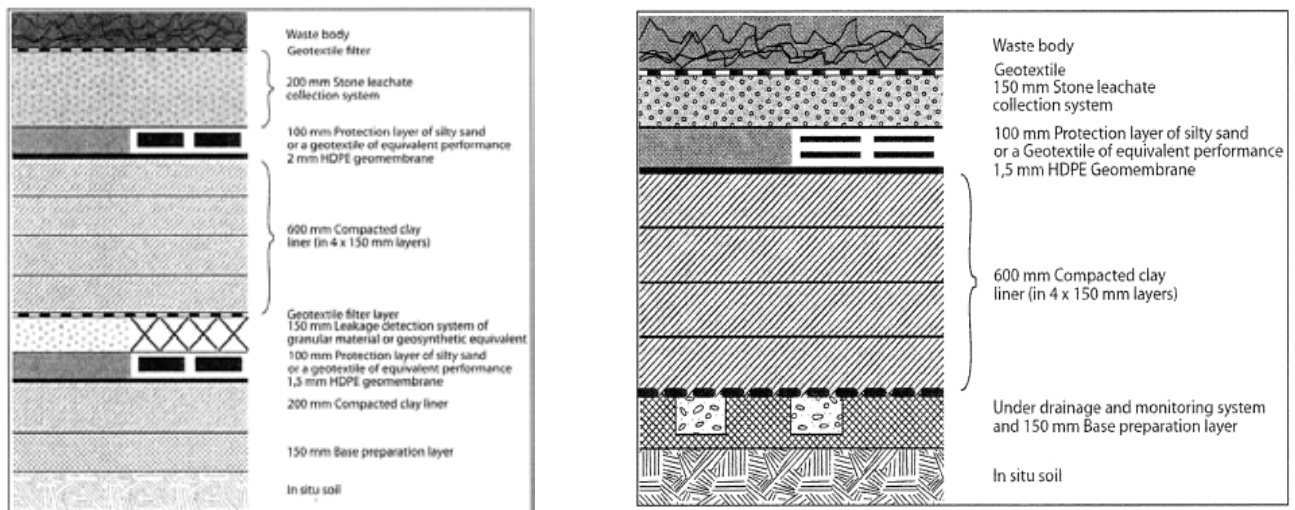
Figure 1: Extraction of Fluid through Liner System (from Legge et al,2007)

The above figure is from a presentation by K.R. Legge, P.A. Legg and P.J. Meyer given at the Sardinia conference in 2007. Aquatan (Pty) Ltd also have an illustration on the above on their official website, they call it the “Enhanced Barrier System” and it is used as the basis of this study. The medium being extracted through the liner system can be a fluid but for the purpose of this study, ambient air was used as discussed in this paper.

3. BACKGROUND

3.1 Landfill and Liner Systems

As discussed, the aim of the study is to use the leachate detection or collection systems of composite liners to act as the pathway for the extraction of a fluid or air in order to remove VOCs and increase landfill liner life. The current legislation governing the design of landfill liner systems in South Africa is the Waste Classification and Management Regulations contained in the National Environmental Management Waste Act 59 of 2008. The proposed liner systems for the Class A and Class B landfills are shown in the figures below. Class A and B landfills are landfills that will contain waste types typically associated with the production of VOCs.



Class A Landfill

Class B Landfill

Figure 2. Proposed liner system for Class A and Class B Landfills

It is proposed that the leachate collection/detection system in the proposed liners above, be replaced by a HDPE cusped drainage layer that will form the envelope for the extraction of the air. The possible dehydration of the GCL layer that may be in contact with the cusped HDPE sheet (although not expected to occur) was not investigated. It must be noted however that the GCL needs to stay hydrated to retain its design permeability characteristics and the liner designer proposing the use of the advanced barrier system will have to take cognisance of this.

3.2 Temperature and Liner Life Expectancy

Although landfill liners are generally designed to provide indefinite protection, it has been proven that the liner, and specifically the HDPE, does lose some of its properties over time and that this leads to a decay of the HDPE that will result in a significant potential for pollution of the groundwater. Rowe and Islam (2009) investigated the effect of temperature on the service life of HDPE GM in landfill liners using the graph in Figure 3 below.

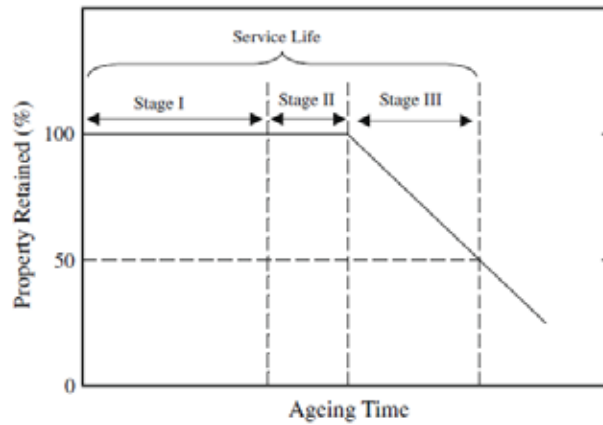


Figure 3. Stages of HDPE liner service life from Rowe and Islam (2009)

Stage 1 of the HDPE service life is the time for the antioxidant depletion to take place. Stage II is the induction time to onset of polymer degradation and Stage III is the time to reach 50% degradation of a particular GM property (Rowe and Islam, 2009). During the study by Rowe and Islam, they investigated a number of different HDPE GMs at different temperatures and found that HDPE service life was anything from 20 to 3300 years. The lower end of the range corresponded to a case where landfill temperature increased from 20°C to 60°C in 8 years and remained at 60°C for 22 years and then decreased back to 20°C in 10 years. Without reading too much into the numbers associated with the results of their study, it is quite obvious that increased temperatures on the HDPE liner reduces its ability to perform as a contaminant barrier. If there would thus be a way to cool down the liner it would greatly add to the long term effectiveness of the liner system.

The laboratory diffusion tests for this study have been carried out in ambient laboratory temperatures at the University of Pretoria which range from 15°C to 30°C and following the principles described below, the ambient laboratory temperature will make very little difference to the values of the coefficients although most of the literature indicates tests took place in controlled temperature of 25°C ± 2°C.

4. DIFFUSION OF VOC THROUGH HDPE

4.1 Theory

Diffusion is a molecular activated process that takes place in a series of steps following the path of least resistance (Sangam & Rowe, 2001). For dilute aqueous solutions this involves three steps (Park and Nibras, 1993) and is schematically represented in Figure 4 below:

- Adsorption – partitioning of contaminant between inner surface of GM and medium containing the contaminant;
- Diffusion of the permeant through the GM; and
- Desorption – partitioning of the contaminant between the outer surface of the GM and the outer medium.

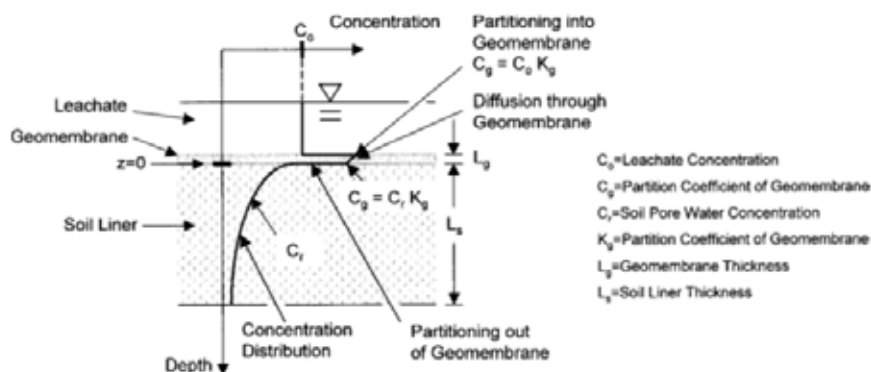


Figure 4. Schematic of Diffusion process through HDPE from Sangam and Rowwe,2001

Figure 4 shows diffusion through a HDPE GM into a soil liner like Compacted Clay but for the purposes of this study we are focussing on the diffusion directly from the GM into the groundwater.

$$f = -D_g \frac{dc_g}{dz} = -S_{gf} D_g \frac{dc_f}{dz} = -P_g \frac{dc_f}{dz}$$

For water or water based solutions, the adsorption and desorption processes can be seen to be similar and inverted (Sangam and Rowe, 2001).

The process starts with the removal of the molecule from the solution onto the surface of the GM (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 (e.g. 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 is given by (Henry's law) (Sangam and Rowe, 2001):

[1]

Where S_{gf} is called a partitioning 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. For organic compounds in aqueous solution, the value of S_{gf} is strongly related to the solubility of the compound of interest in water (Sangam and Rowe, 2001). The lower the solubility, 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 higher S_{gf} values.

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

$$\frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial z^2}$$

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

[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). Then dc/dz 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):

[3]

This then needs to be solved for the appropriate boundary and initial conditions to obtain the Diffusion coefficient of the solution/GM system at equilibrium. But 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 3 gives the flux (diffusion) within the GM so substituting Eq. 1 into Eq. 3 gives the flux on one side of the GM to a similar fluid on the other side of a GM (Rowe, 1998).

[4]

$$f = -D_g \frac{dc_g}{dz}$$

Where : $P_g = S_{gf} D_g$

[5]

P_g thus gives the relationship between the Diffusion coefficient and the Sorption coefficient and is referred to in the polymer literature as the Permeability Coefficient (Sangam and Rowe, 2001).

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 P_g 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 the VOCs can successfully be extracted through an envelope in the liner system.

4.2 Calculation of the Sorption and Diffusion Coefficients

The Sorption coefficient S_{gf} is a unitless coefficient linked to the solution/GM system. Each fluid, permeant and polymer combination will thus have its own sorption coefficient value. As described earlier the S_{gf} is a relationship between the concentration in the GM and the concentration in the Fluid at equilibrium and may often be described by the Nernst distribution function (Rogers, 1985) which may take the linear form of Henry's Law as shown above. The S_{gf} value can be determined in a variety of ways as described by Rowe (1998) and Sangam and Rowe (2001), but for VOCs 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 ; Sangam and Rowe, 2001):

[6]

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 through the computer program POLLUTE[®] which solves the one-dimensional contaminant migration equation subject to

$$S_{gf} = \frac{C_{fo}V_s - C_{fF}(V_s + V_r) - \Sigma V_i C_i}{At_{GM}C_{fF}} \quad \text{boundary conditions at the top and bottom of the GM being modelled (Sangam and Rowe, 2005).}$$

5. TESTING

5.1 Field Tests

In 2006 and 2007, a Hazardous Waste Disposal Site near the town of Springs in South Africa agreed to the use of one of their hazardous waste leachate dams for this study. Because of the fact that the dam was already in use, meaning that the liner had already been installed without the cusped drainage layer or fluid extraction equipment, it was not possible to recreate the complete composite liner at the leachate dam as planned.

It was thus decided to insert hollow 1,5mm thick 100mm diam. Poly-Ethylene pipes 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. The three pipes (one Low Density Poly-Ethylene and two High Density Poly-Ethylene) pipes were inserted above the HDPE liner of the leachate dam and can be seen in Figure 5 below.



Figure 5: Pipe layout at leachate dam during field tests

The measured parameter included the air quality inside the pipes at certain time frames and was compared to proven diffusion rates of certain VOCs through HDPE GMs.

The samples were analysed by Infotox (Pty) Ltd in Pretoria and only the low-volume samples collected in each of the three pipes were analysed, as these samples were found to be sufficiently concentrated to achieve quantification of the VOCs. The compounds detected in each of the four samples are listed in Table 1 below. The results are reported as air concentrations in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$).

Table 1. Air concentrations of compounds detected in the samples (measured in $\mu\text{g}/\text{m}^3$)

Compound	HDPE	LDPE	Background	Control
Toluene	149.03	194.37	82.48	136.57
Perchloroethylene	<0.1	<0.08	2.94	< 0.08
n-Butylacetate	9.96	14.84	6.94	11.26
Ethylbenzene	31.85	15.32	24.41	22.98
Xylene	109.32	134.28	87.32	75.83
Propyl benzene	4.55	5.85	5.58	3.66
1,2,3-Trimethylbenzene	6.75	8.33	6.6	4.82

Most of the volatile organic substances that were detected may be found in ambient air and are commonly present in the vicinity of industrial areas, refuelling stations and busy highways. It is therefore difficult to determine whether the presence of these compounds can be attributed to diffusion through the leachate dam liner, given the uncertainties regarding compounds expected to diffuse through the liner and the complex chemical nature of the leachate contained in the dam.

The reported concentrations indicate that many of the compounds detected are present at similar or even higher concentrations in the ambient air (represented by the “background” sample) than in either the control or open pipe samples. The uncertainties related to the source of some of the observed compounds therefore remained and it was recommended that controlled laboratory tests be undertaken using BTEX and Chloroform as the target VOCs.

5.2 Laboratory Tests

5.2.1 Diffusion Test Cells

The diffusion tests cells were based on the cells used by Kerry Rowe and his students at the Queens University in Kingston, Canada. They were made out of stainless steel by Interlock Systems (Pty) Ltd in Pretoria and are made up of two main parts (Source and Receptor) as indicated on Figure 6 below.



Figure 6. Diffusion Test Cells used in this study

Five test cells were made and numbered (a) to (e) (see Figure 7a). Cells a, b and c were used for diffusion testing by having the source volume filled with an artificial leachate solution and the receptor volume filled with ultrapure deionized water. Cell d was filled with water in the source and receptor to measure possible outside influences on the concentrations in the system and Cell e was filled with the artificial leachate solution but contained no GM so that possible losses could be measured.

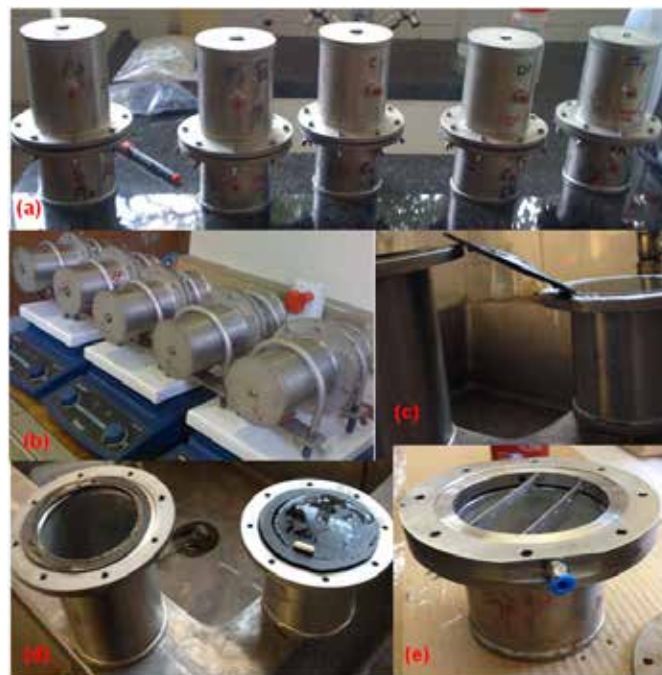


Figure 7. (a) Diffusion test cells, 3 x plus one control and one blank cell. (b) Test cells clamped and placed on magnetic tables. (c,d) After sampling showing GM and (e) The centerpiece to be used for follow up tests.

5.2.2 Test Cell setup and Laboratory Plan

The artificial leachate solution used in the source cell contained Benzene, Toluene, Ethylbenzene, Xylene (BTEX) and chloroform which are all aromatic hydrocarbons commonly found in landfill leachates.

- Make sure test cells are clean and dry;
- Insert septa into sample ports making sure that they are as gas tight as possible;
- For Test Cells a,b,c and d - Place receptor volume on table, insert gaskets and fill with water until meniscus forms;
- Insert magnetic stirrer bar into cells;
- Place HDPE disk onto gasket and place another stirrer bar onto HDPE disk so that each half of the test cell has a stirrer bar;
- Place another gasket onto the HDPE;
- Place top (receptor) half of test cell on top and fasten tightly using screws and wing nuts;
- Assemble Test Cell e by placing gasket but with no HDPE;
- Fill all cells with water through opening ensuring that they are completely full;
- Extract 1 000ul (1ml) from source cells of cell a,b,c and e;
- Extract 100ul each of Benzene, Toluene, Ethylbenzene, P Xylene and Chloroform, using a clean nozzle each time, mix with 500ul of methanol and inject into source volumes of cells a,b,c and e;
- Secure with clamps over nozzles to minimize potential losses through septums;
- Place on magnetic tables until sampling making sure the stirrer bars are working.

Figure 7a shows the assembled test cells (without clamps) and Figure 7b shows test cells on magnetic tables ready for sampling.

The laboratory testing was planned in three phases. Phase one was be diffusion testing as done mainly by Prof Rowe at Queens University by separating the source and receptor volumes with a 2mm HDPE GM and measuring the concentrations in the source and receptor over time until equilibrium is reached in order to confirm the diffusion of the VOCs through the HDPE and calculate the S_{gr} and D_g values to compare to the literature.

Phase two introduced the centrepiece (Figure 7e) between the source and receptor volumes. The centrepiece has a 1mm HDPE GM above it and another 1mm HDPE below, creating a 10mm void between the two GMs. Diffusion tests was then carried out as for phase one in order to determine if the VOCs will diffuse through the two 1mm GMs separated by a 10mm void.

Phase three replicates phase two and introduced extraction of air through the system using the nozzles shown in Figure 7e. Concentrations in the source and receptor was then be measured over time and compared to the results of phase two at the same intervals in order to ascertain the possible removal of VOCs from the system. Figure 7d shows a test cell after phase one testing. At the time of submission for this paper, testing was in the middle of phase two.

5.2.3 Testing and Sampling Procedures

Samples were taken from the source and receptor volumes of the cells (only one sample from Cell e) through the septum by using a 500ul syringe. Sample sizes of 1ml were injected into clamped and sealed sampling jars for analysis by the Gas Chromatograph. The 1ml sample was replaced by 1ml of ultra-pure water and the clamps replaced as soon as possible.

5.2.4 Results

Phase one samples were taken on Days 3, 8, 15, 22 and 36. Concentrations in the source and receptor were (initial concentration over measured concentration) plotted against time for the source (Figure 8) and receptor (Figure 9) volumes.

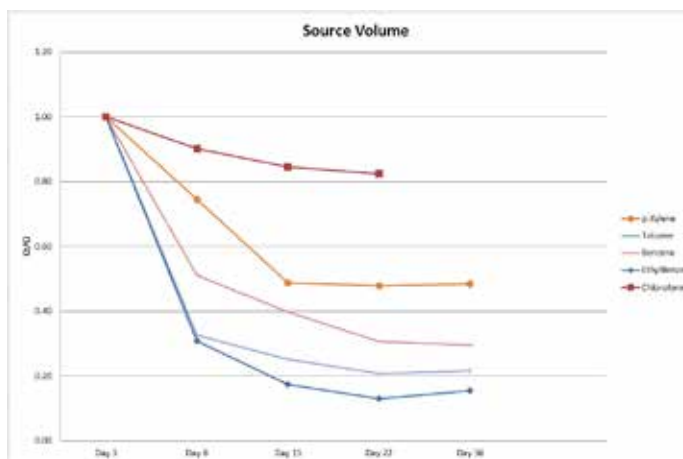


Figure 8. Concentration over time for Source Volume

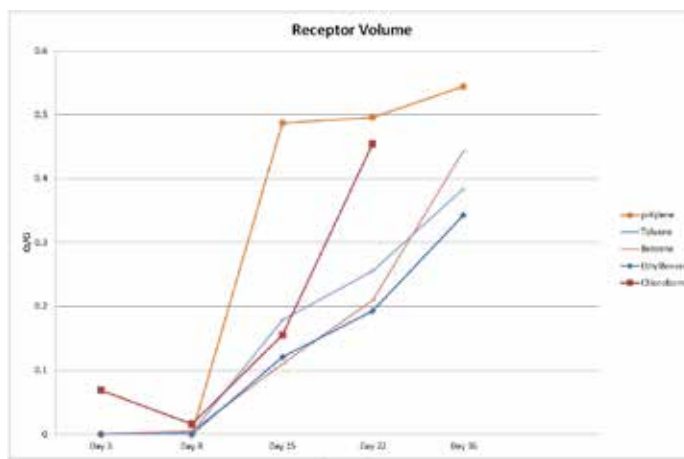


Figure 9. Concentration over time for Receptor Volume

In order to ascertain if any losses occurred from VOC sorbing onto the septums, gaskets, cell walls etc. or if any losses occurred during sampling or testing, Cell e samples were also plotted over time as shown on the graph in Figure 10.



Figure 10. Concentration over time for Cell E (losses)

5.2.5 Way Forward

Phase two testing is due to start in June 2014 followed by phase 3 testing and results will be discussed at the presentation of this paper.

6. ANALYSIS AND CONCLUSION

The initial concentrations of VOCs used in the study ranged from 60mg/l to 170mg/l which is much higher than the concentrations typically found in landfill leachates and used in most of the literature. This resulted in discrepancies in the calculations of the initial concentrations and in the time required to reach equilibrium. Also, chloroform was not available at the day of test cell setup and it was only added 8 days after the initial setup. This resulted in changes to the concentration profiles in the system.

Results for the sorption and diffusion coefficients could thus not accurately be compared to literature but it was confirmed that diffusion of the VOCs does take place through the HDPE GM. From Figure 10 it can be seen that significant losses occurred initially and then normalised for the remainder of the study. This is most probably due to VOC sorption onto the septums and gaskets etc.

Phase two and three testing will be done with an initial concentration closer to 5mg/l and will include all target VOCs from the start. Tests will also be done at a controlled temperature in order to accurately compare to literature.

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