

An investigation of toluene and TCE diffusion through EVOH in aqueous solutions

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ABSTRACT: Novel geomembranes that include a thin-film of ethylene vinyl alcohol (EVOH) have the potential to minimize the migration of toxic volatile organic compounds (VOCs) from landfills or from contaminated (brownfield) sites into buildings and subsurface structures. The diffusion of toluene in dilute aqueous solution through an EVOH thin-film and a co-extruded LLDPE/EVOH/LLDPE geomembrane was investigated. The thin-film was 0.015 mm-thickness 32 mol% EVOH. The toluene permeation coefficients, P_g , through this thin film ranged from $2.5 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ at 23°C to $48 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ at 50°C. The P_g value of toluene through the co-extruded geomembrane was $5 \times 10^{-15} \text{ m}^2\text{s}^{-1}$. The diffusion of a chlorinated hydrocarbon, trichloroethylene (TCE), was also investigated for the thin-film. The TCE permeation coefficients, P_g , through this thin-film ranged from $3.5 \times 10^{-15} \text{ m}^2\text{s}^{-1}$ at 23°C to $65 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ at 50°C.

Keywords: EVOH, co-extruded geomembranes, diffusion, permeation, toluene, TCE

1 INTRODUCTION

Barrier systems are designed to control contaminant migration. Geomembranes are commonly used as part of a composite liner in landfill cover, base liner systems and sometimes vapour barriers. In landfill applications, the primary function of the geomembrane liner is to control contaminant transport from the leachate (dissolved phase) and landfill gas (vapour phase) out of the landfill thus minimizing environmental impact. In vapour barrier applications, membranes are used to mitigate intrusion of toxic volatile organic compounds (VOCs) into buildings originating from legacy contaminated sites, for example: petroleum stations, dry cleaners, industrial manufacturing sites and waste facilities (especially old dumps).

Traditional geomembranes used in well designed and constructed barrier systems have been very effective at minimizing contaminant escape but it is also known that they are not impermeable (Rowe 2005, 2009). Contaminants can migrate through geomembranes by the process of either advection or diffusion. Advection involves movement of contaminants in a fluid due to a pressure differential or hydraulic gradient (e.g. landfill gas or leachate through flaws, holes or tears in a geomembrane (Rowe 2012)). Diffusion is the transport of molecules, by random molecular motion, from areas of high to low concentrations (Crank 1968). For a well designed and constructed barrier system, diffusion becomes the dominant form of contaminant migration (Rowe et al. 2004, Rowe 1998, 2005).

The most common geomembranes used in barrier systems are made of high density or linear low density polyethylene (HDPE, LLDPE). The diffusive characteristics of HDPE liners are well established (Parks and Nibras 1993, Sangam and Rowe 2001; Joo et al. 2004, 2005) and although HDPE is substantially better than LLDPE, neither offer substantial diffusive resistance to many VOCs (McWatters 2010). Ethylene vinyl alcohol (EVOH) has the potential to be a much better diffusive barrier to VOCs than PVC, LLDPE or HDPE. To illustrate this, the diffusion of toluene and trichloroethylene (TCE) in aqueous solution through a 0.015 mm thick, 32 mol% EVOH thin-film is examined in this paper.

McWatters and Rowe (2010) presented preliminary results (obtained over a period of two years), which showed that co-extruded LLDPE/EVOH/LLDPE geomembrane provided a much improved diffusive barrier to benzene, toluene, ethylbenzene and xylenes (BTEXs) than LLDPE alone. These co-extruded LLDPE geomembranes with inner barrier materials of EVOH are designed to merge the functionality and durability of LLDPE with a very low-permeability inner barrier. This paper presents updated results for toluene after 6.5 years of testing.

Temperature plays a critical role in the diffusive process (Crank 1975). Geomembrane applications extend to barrier systems built for elevated temperature environments (Rowe 2005, 2012), however most

diffusion tests in the literature are at room temperature. This paper reports diffusive parameters for toluene and TCE through the 32 mol% EVOH thin-film over a temperature range of 23-50°C.

2 BACKGROUND

Diffusion through a geomembrane is characterized by a three step process: adsorption, diffusion and desorption (Parks and Nibras 1993, Sangam and Rowe 2001). First is the partitioning of contaminants between the contamination source medium and the inner surface of the geomembrane (adsorption). In the second stage, the contaminant moves through the geomembrane (diffusion). Lastly, the contaminant partitions out of the geomembrane to the receiving medium (desorption). To define the diffusive parameters associated with the thin-films or geomembranes, laboratory sorption and diffusion tests are generally conducted. In sorption tests, the first step of the diffusion process is investigated and partitioning coefficient, S_{gf} can be calculated. In diffusion tests, contaminant migration is examined, beginning at a contamination source, through the geomembrane and into a receiving medium. For adsorption: concentrations in the thin-film or geomembrane, c_g [ML⁻³] and concentrations in the source, c_f [ML⁻³] reach equilibrium over time and can be related by Henry's law:

$$c_g = S_{gf}c_f \quad (1)$$

where S_{gf} is the partitioning coefficient [-] (this is obtained by sorption and permeation tests). For diffusion: contaminants then diffuse through the thin-film or geomembrane and the diffusive mass flux, f [ML⁻²T⁻¹] through the thin-film or geomembrane is described by Fick's first law:

$$f = -D_g \frac{dc_g}{dz} \quad (2)$$

where D_g is the diffusion coefficient [L²T⁻¹], c_g , the concentration of contaminant in the geomembrane or film [ML⁻³] and z represents the distance parallel to the direction of transport. The change in contaminant concentration in the thin-film or geomembrane with time t [T], is expressed by Fick's second law:

$$\frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial z^2} \quad (3)$$

For desorption: contaminants partition out of the thin-film or geomembrane to the receiving medium. When the source and receiving mediums are the same, the partitioning coefficient out of the thin-film or geomembrane, S_{gf}^* , can be assumed to equal the partitioning coefficient, S_{gf} , into the thin-film or geomembrane (Sangam and Rowe 2001). The overall permeation coefficient, P_g [L²T⁻¹], for the geomembrane or thin-film is related by the partitioning and diffusion coefficients:

$$P_g = S_{gf}D_g \quad (4)$$

Rowe et al. (2004) showed how the experimental data can be interpreted using a finite layer analytical model (POLLUTE[®] v.7; Rowe and Booker 2004), that considers the mass transport of the contaminant from the source to the receptor, partitioning at the geomembrane surfaces (S_{gf}) and diffusion through the geomembrane (controlled by the diffusion coefficient, D_g). The method was first developed for clay soils by Rowe et al. (1988) and then for HDPE geomembranes by Sangam and Rowe (2001). Further information regarding the procedure and boundary conditions used for modeling co-extruded geomembranes are described in McWatters and Rowe (2010).

Temperature is an important driver for diffusion of contaminants through membranes and all three of the permeation parameters, partitioning, diffusion and permeation coefficients are dependent on temperature (Crank and Park 1968). All three coefficients can be related by an Arrhenius equation (Naylor 1989; Chainey 1990).

3 MATERIALS AND METHODS

3.1 Material Properties

In this experiment a 0.015 mm-thick (density = 1.19 kg/m³) ethylene vinyl alcohol (EVOH) co-polymer thin-film is studied. The film is 32 mol% EVOH with 32 mol% ethylene and 68 mol% vinyl alcohol. In

addition, a co-extruded LLDPE/EVOH/LLDPE geomembrane (0.53 mm-thickness, density = 0.92 kg/m³) with a five-layer structure comprised of approximately 42% LLDPE (with a 3.5% CaCO₃ inert filler), 6% tie resin (maleic anhydride modified LLDPE), 4% EVOH film (38 mol% EVOH content) as the inner barrier, 6% tie resin and 42% LLDPE (with 3.5% CaCO₃) is examined.

3.2 Procedures for Diffusion Tests

Specially designed 500 ml double compartment (source and receptor) stainless steel cells were used, as previously described in McWatters and Rowe (2009). Thin-film EVOH samples were secured between the source and receptor with PTFE o-rings. In separate tests, toluene and TCE was injected into the water of the source for an initial aqueous concentration of 25 µg/ml. All diffusion tests were run in triplicate as this was the first time these thin-films had been studied in this type of diffusion test. Temperature was maintained for each respective test at 23±1°C for room temperature tests. Elevated temperature tests were maintained at 30, 40, and 50±1°C in three different Fisher Scientific ovens. Control cells were placed in the room/ovens at each temperature to establish mass loss to the stainless steel cells and were set up without a thin-film between the source and receptor.

Source and receptor solutions were stirred with a magnetic stirrer to ensure good mixing and hence a uniform concentration within the source and receptor before sampling. Aqueous samples (10-20 µl) were extracted and analyzed by Purge & Trap-Gas Chromatography/Mass Spectrometry. The analytical methods for analysis of toluene and TCE concentrations in water samples is described by McWatters (2010) and is based on USEPA (1996). Sampling of the source and receptor continued at regular intervals until equilibrium was reached (i.e., no change in source and receptor concentrations).

4 RESULTS

4.1 Thin-film EVOH

Table 1 shows the inferred partitioning, S_{gf} , diffusion, D_g , and overall permeation, P_g , coefficients obtained from the diffusion tests for the 32 mol% EVOH thin-films at 23, 30, 40 and 50°C. These values take into account the mass loss of contaminants to the apparatus of the cells. All three diffusive parameters increase with temperature for the 32 mol% thin-film and each of these three coefficients can be related by an Arrhenius equation over the temperature range 23-50°C. This would allow engineers to use Arrhenius relationship to calculate the appropriate S_{gf} , D_g , and P_g values for any temperature within the 23-50°C.

Table 1. Partitioning coefficients, S_{gf} , diffusion coefficients, D_g , and permeation coefficients, P_g , for 32 mol% EVOH thin-film at 23, 30, 40 and 50°C

Temperature	32 mol% EVOH Thin-film											
	23°C			30°C			40°C			50°C		
	S_{gf} (-)	$D_g \times 10^{14}$ (m ² s ⁻¹)	$P_g \times 10^{13}$ (m ² s ⁻¹)	S_{gf} (-)	$D_g \times 10^{14}$ (m ² s ⁻¹)	$P_g \times 10^{13}$ (m ² s ⁻¹)	S_{gf} (-)	$D_g \times 10^{14}$ (m ² s ⁻¹)	$P_g \times 10^{13}$ (m ² s ⁻¹)	S_{gf} (-)	$D_g \times 10^{14}$ (m ² s ⁻¹)	$P_g \times 10^{13}$ (m ² s ⁻¹)
Toluene	19	1.3	2.5	25	2.3	5.8	35	5	18	48	10	48
TCE	14	2.5	3.5	19	4	7.6	26	9	23	36	18	65

Figure 1 shows the concentration changes in the source and receptor for toluene (left) and TCE (right) during aqueous diffusion testing at 23°C. TCE permeates through the thin-film at a faster rate than toluene (also reflected by the larger diffusion and permeation coefficients in Table 1). For TCE, equilibrium between the source and receptor within the testing apparatus was achieved after about 50 days whereas equilibrium for toluene is reached at about 65 days.

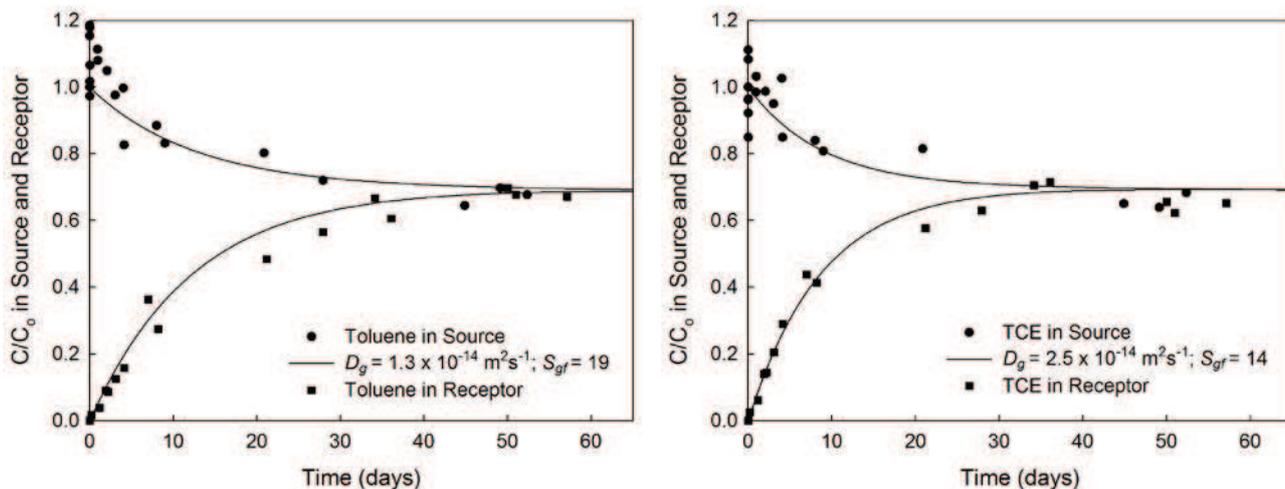


Figure 1. Toluene (left) and TCE (right) concentration changes in the source and receptor during aqueous diffusion testing at 23°C with a 32 mol% thin-film (0.015 mm-thickness).

Figure 2 shows results from aqueous diffusion tests at 30°C for contaminants toluene (left) and TCE (right) with the 32 mol% EVOH thin-film. Figures 3 and 4 show results from aqueous diffusion tests at 40 and 50°C for toluene (left) and TCE (right) with the 32 mol% EVOH thin-film. The increase in diffusion coefficient with temperature is visually evident from the shorter time for equilibrium to be reached between the source and receptor. From visual inspection of the curves for toluene in Figures 1-4, equilibrium took about 65 days at 23°C, about 30 days at 30°C, about 10 days at 40°C, and about 5 days at 50°C.

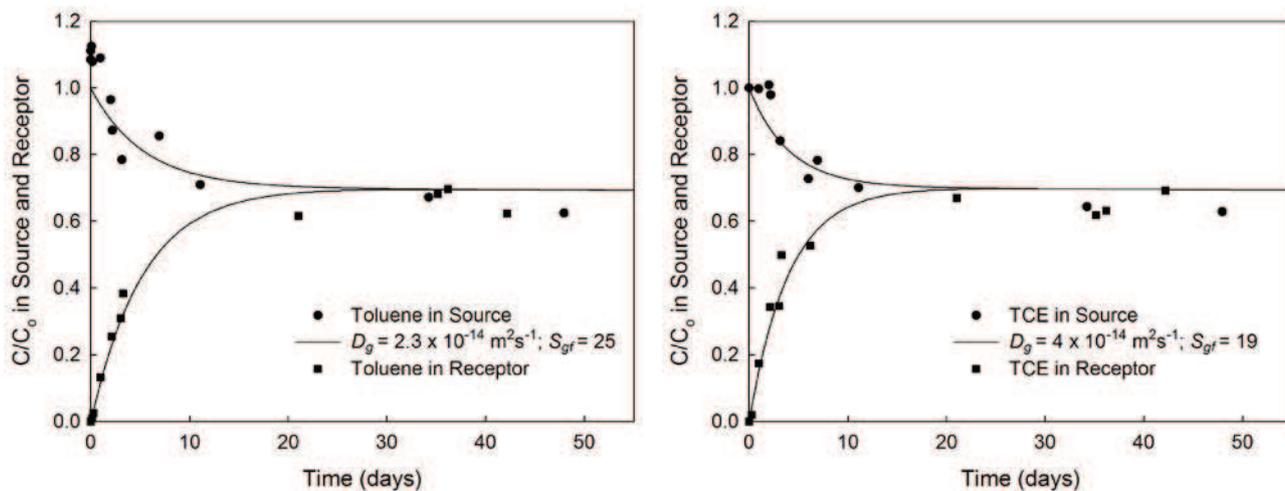


Figure 2. Toluene (left) and TCE (right) concentration changes in the source and receptor during aqueous diffusion testing at 30°C with a 32 mol% thin-film.

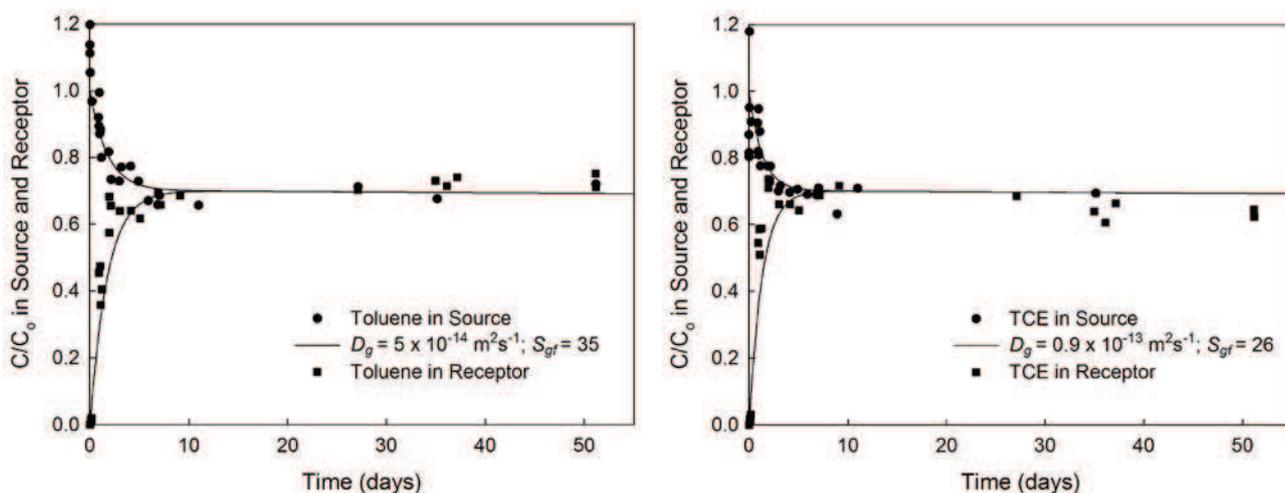


Figure 3. Toluene (left) and TCE (right) concentration changes in the source and receptor during aqueous diffusion testing at 40°C with a 32 mol% thin-film.

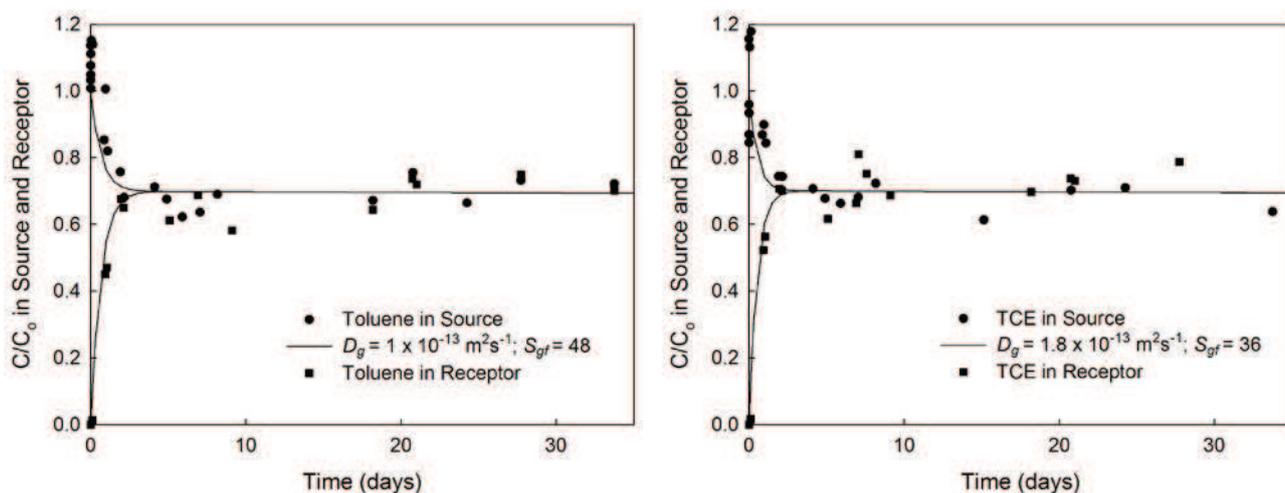


Figure 4. Toluene (left) and TCE (right) concentration changes in the source and receptor during aqueous diffusion testing at 50°C with a 32 mol% thin-film.

4.2 Co-extruded LLDPE/EVOH/LLDPE geomembrane

For the co-extruded geomembrane, diffusion tests were carried out with toluene in aqueous solution. This paper shows updated results of the diffusion tests at 23°C for the co-extruded LLDPE/EVOH/LLDPE geomembrane after 6.5 years of testing. Figure 5 shows the changes in toluene concentration in the source and receptor during aqueous diffusion testing.

The co-extruded geomembrane had to be modeled as a three-stage layer system with distinct partitioning and diffusion coefficients for the LLDPE and EVOH layers. Because of the length of the tests and the low concentrations in the receptor (less than 10% of the initial source concentration; Figure 6) there is some scatter of the data. The best estimate of the diffusion parameters was based on the data collected over 2500 days.

The LLDPE diffusion parameters ($S_{gf} = 375$, $D_g = 8.5 \times 10^{-14} \text{ m}^2\text{s}^{-1}$) were inferred from the early time in the source since, given the very large difference in the diffusion coefficients of the EVOH and LLDPE, is dominated by the LLDPE on the source side of the EVOH layer. The EVOH partitioning coefficient ($S_{gf} = 20$) was inferred from the results of the diffusion tests of the 32 mol% thin-film EVOH for the 38 mol% EVOH layer. The EVOH layer diffusion coefficient ($D_g = 2.5 \times 10^{-16} \text{ m}^2\text{s}^{-1}$) was then obtained from the best model fit to the data from the co-extruded geomembrane.

There is a substantial difference between the diffusion coefficients of the thin-film ($D_g = 1.3 \times 10^{-14} \text{ m}^2\text{s}^{-1}$) and the EVOH layer of the co-extruded geomembrane ($D_g = 2.5 \times 10^{-16} \text{ m}^2\text{s}^{-1}$). This is likely because the EVOH layer in the thin-film test was in the direct contact between the water in the aqueous solution which is known to cause swelling of EVOH thereby increasing its permeability. In contrast, the EVOH layer in the co-extruded LLDPE/EVOH/LLDPE geomembrane was isolated from contact with water by the hydrophobic LLDPE layers.

When modeling the co-extruded geomembrane for design applications (e.g., in a landfill barrier system), there is no single equivalent S_{gf} and D_g (or P_g) value that allows correct modelling of diffusion through the co-extruded geomembrane with time. The geomembrane must be modeled as a three-layer system to obtain permeation parameters for the layers that correlate with the laboratory test because of the very different S_{gf} and D_g values for the LLDPE and EVOH layers (as shown in Figures 5 and 6). In the co-extruded geomembrane the first stage of contaminant partitioning into the upper LLDPE layer is relatively quick and similar to a standard LLDPE geomembrane. However, the second stage of transport to the lower LLDPE layer is substantially inhibited by the very low diffusion coefficient in the EVOH layer.

The diffusion coefficients of the co-extruded geomembrane ($D_g = 2.5 \times 10^{-16} \text{ m}^2\text{s}^{-1}$) is much lower than a standard LLDPE geomembrane ($D_g = 30 \times 10^{-14} \text{ m}^2\text{s}^{-1}$) or HDPE geomembrane ($D_g = 18 \times 10^{-14} \text{ m}^2\text{s}^{-1}$). This suggests that thin-films and geomembranes with EVOH content are superior to traditional LLDPE and HDPE alone in terms of providing a diffusive barrier to toluene. This also suggests that these new membranes could provide a better barrier to other aromatic and chlorinated VOC contaminants. Finally, this study suggests that a geomembrane co-extruded with an EVOH layer could be used to substantially reduced VOC migration through engineered liners.

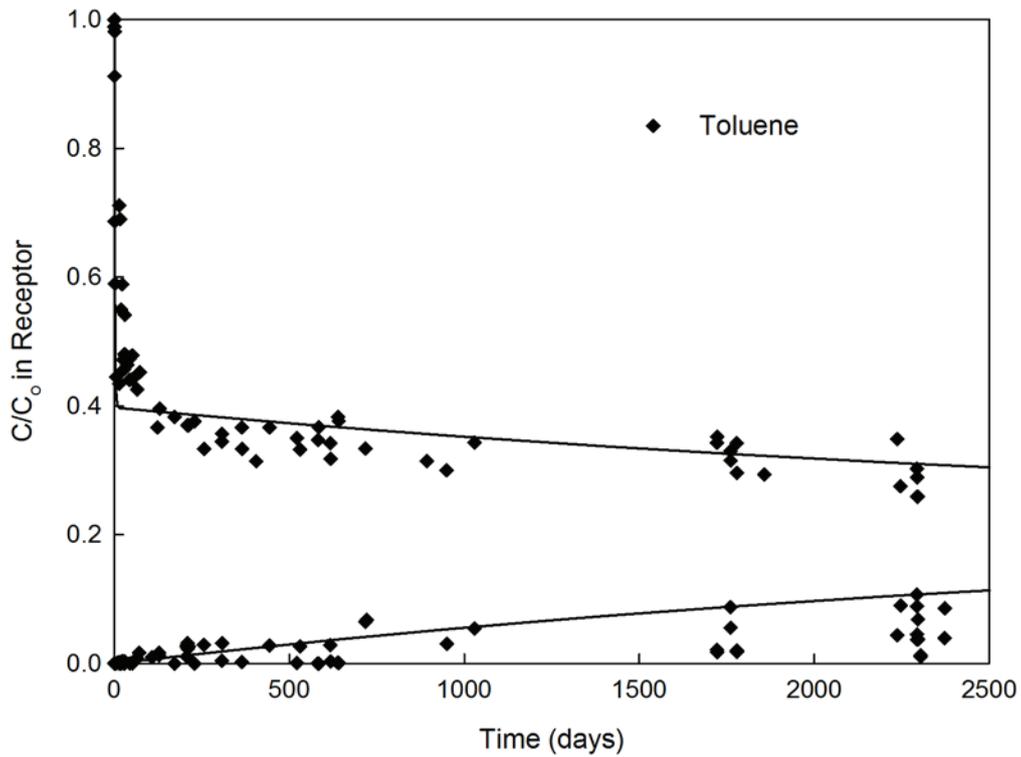


Figure 5. Toluene concentrations changes in the source and receptor during aqueous diffusion testing at 23°C with a 0.53 mm-thick co-extruded LLDPE/EVOH/LLDPE geomembrane.

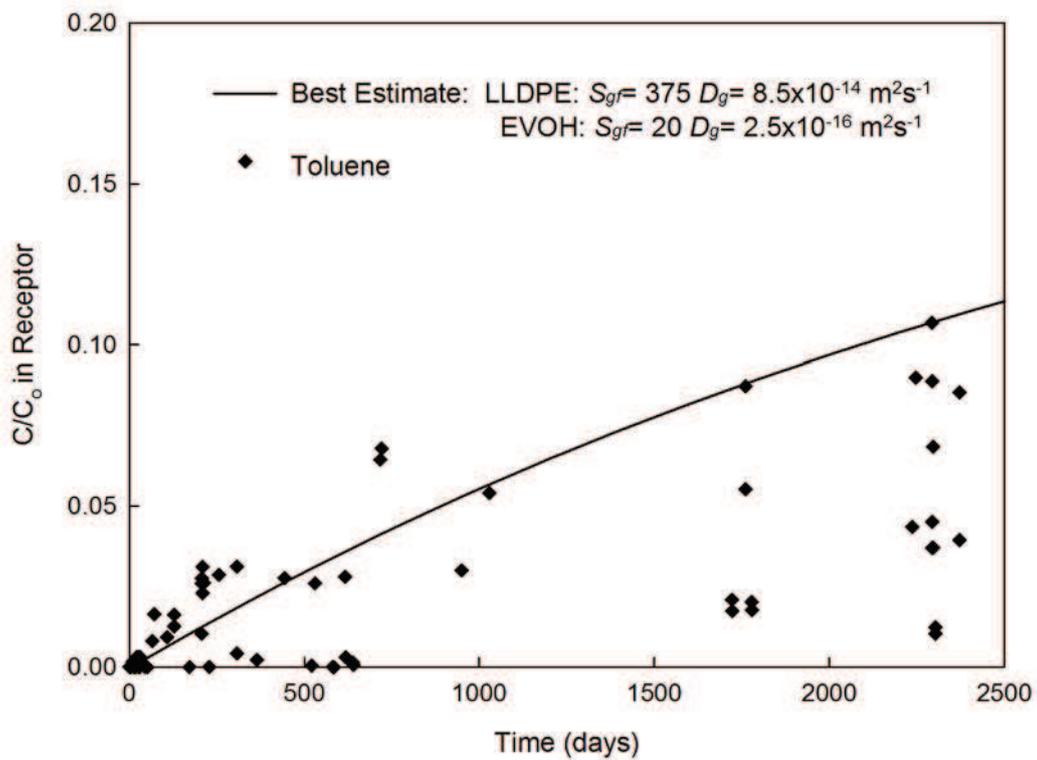


Figure 6. Toluene concentrations changes in the receptor during aqueous diffusion testing at 23°C with a 0.53 mm-thick co-extruded LLDPE/EVOH/LLDPE geomembrane. Note scale of normalized concentration changes on y-axis.

5 CONCLUSIONS

The diffusive properties of a 32 mol% 0.015mm-thick EVOH thin-film was investigated for toluene in aqueous solution at temperatures of 23, 30, 40 and 50°C. The diffusive properties of the 32 mol% EVOH thin-film were also established for TCE in aqueous solution 23°C. At room temperature, the permeation coefficient, P_g , was $2.5 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ for toluene and $3.5 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ for TCE. To put this in context, the published values of P_g for toluene through LLDPE is $1.1 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ (McWatters and Rowe 2010) or about 400 times higher.

Data was presented for diffusion of toluene in aqueous solution through a co-extruded LLDPE/EVOH/LLPE geomembrane at 23°C based on a test that has been running for 6.5 years and is still not close to reaching equilibrium. This data shows how extremely effective this co-extruded geomembrane is as a diffusion barrier to toluene and highlights the potential applications for coextruded geomembranes with EVOH as barriers for VOCs in landfills or in situations where a vapour barrier is needed for construction over brownfield sites. As one example of the many potential applications for these geomembranes, McWatters et al. (2014) highlight the use of a co-extruded HDPE/EVOH/HDPE geomembrane in a biopile containing hydrocarbon contaminated soil in Antarctica.

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