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Diffusion and partitioning of different PFAS compounds through thermoplastic polyurethane and three different PVC-EIA liners.

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Abstract

Perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorobutane sulfonic acid (PFBS), 6:2 fluorotelomer sulfonic acid (6:2 FTS), and GenX are tested for diffusion and sorption through thermoplastic polyurethane (TPU) and three ethylene interpolymer alloy (PVC-EIA) liners (EIA1, EIA2, and EIA3) with decreasing ketone ethylene ester (KEE) contents. The tests were conducted at room temperature (23˚C), 35˚C, and 50˚C. The tests show significant diffusion through the TPU as manifested by a decrease in the source concentration and an increase in the receptor concentrations of PFOA and PFOS over time, especially at higher temperatures. On the other hand, the PVC-EIA liners show excellent diffusive resistance to the PFAS compounds especially at 23˚C. At higher temperatures, the diffusion resistance of the PVC-EIA liner with the lowest KEE content, EIA3, was best at 50˚C followed by EIA1 (highest KEE content) and finally EIA2. Sorption tests showed no measurable partitioning of any of the compounds to the liners examined. Based on 535 days of diffusion testing, permeation coefficients are provided for all the compounds considered for the four liners at three temperatures. In addition, the P_g values for PFOA and PFOS are provided for a linear low density polyethylene (LLDPE) and a coextruded LLDPE - ethylene vinyl alcohol (EVOH) geomembrane based on 1246 to 1331 days of testing and are compared to those estimated for EIA1, EIA2, and EIA3.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS), are a large, complex, and expanding group of anthropogenic compounds made up of a carbon chain where some or all the hydrogen atoms are replaced with fluorine atoms (Buck et al. 2011, U.S. Department of Health and Human Services 2022). Due to both the strength of the carbon-fluorine chemical bonds and their amphipathic nature, PFAS are extremely stable, highly recalcitrant, and have unique properties such as oil and water resistance (U.S. Department of Health and Human Services 2022, Milinovic et al. 2015; Bouazza 2021). Their persistence and unique chemical properties have resulted in their use in several industrial and consumer products including surfactants, lubricants, aqueous film-forming foam (AFFF), non-stick cookware, textiles, food packaging, and cosmetics (U.S. Department of Health and Human Services 2022, ATSDR 2015, CELA 2019, CONCAWE 2016, EPA 2003, EPA 2017, NTP 2016, Ahrens 2011, Cousins et al. 2016, Rowe and Barakat 2021). More than 12,000 PFAS compounds have been identified (National Academies Press 2022, Centers for Disease Control and Prevention 2021). Of the $12,000^+$ compounds, most of the research has focused on PFOA and PFOS, as these have been manufactured the longest, have associated regulations, and are the most widespread PFAS (National Academies Press 2022, Disease Control and Prevention 2022). This trend is slowly changing however, due to the previous phase-out of PFOS/PFOA, new PFAS telomers and precursors entering the market, and the development of analytical methods to detect and identify previously unknown PFAS in both consumer products and the environment. Since the production of PFOA and PFOS has been suspended, several new PFAS compounds have been developed to act as a replacement for those compounds which include perfluorobutane sulfonic acid (PFBS), 6:2 fluorotelomer sulfonate (6:2 FTS), and GenX (the ammonium salt of hexafluoropropylene oxide (HFPO) dimer acid

(HFPO-DA)) (U.S Department of Health and Human Services 2022). Despite the suspension of PFOA and PFOS production, they are still commonly found at fire training sites, landfills, industrial sites, and wastewater treatment plants (*Sources of PFAS* 2022, EPA 2017, ITRC 2020, Bouazza 2021, Baduel et al. 2017, Cousins et al. 2016, Gallen et al. 2017, Hamid et al. 2018).

Due to the current and previous extensive use of PFAS in the industry and consumer products, they will mostly end up in landfills. Landfill leachate is generated in part by the degradation of waste and in part by the percolation of water (rainfall/snow melt) through the landfill cover and then through the different layers of waste, and in the process accumulates dissolved chemicals and suspended solids which may be contaminants themselves or may be soil particles to which contaminants are attached (Rowe 1995, Rowe et al. 2008). This leachate can contain high concentrations of legacy PFAS (PFOS/PFOA) together with PFAS fluorotelomer precursors (FTS, FTCA, etc.; Busch et al. 2010; Eggen et al. 2010; Fuertes et al. 2017, Gallen et al. 2017, Yan et al. 2015, Di Battista et al. 2020, Rowe and Barakat 2021). Although the base of landfills have a composite liner comprised of a geomembrane and a clay layer to minimize the escape of contaminants, the different chemicals present in the leachate can still migrate through the liner by advection through holes and by diffusion through intact geomembrane (August and Tatzky 1984, Park and Nibras 1993, Sangam and Rowe 2001, Rowe et al. 1995, 2004, Joo et al. 2005, Rowe 2011, 2014, Di Battista et al. 2020, Crank 1979, , Jones and Rowe 2016, Giroud and Bonaparte 1989).

To limit the transport of these contaminants to the environment, the factors affecting the transport of these compounds through the different components of the landfill barrier system need study. Geomembranes are one of the most common materials used as part of the liner system for containment of contaminants in landfills. Geomembranes are practically impermeable to water if they have no holes. Assuming good construction and negligible holes, the dominant contaminant transport mechanism through an undamaged geomembrane is diffusion (Rowe et al. 2004). Polyethylene is the most used polymer in geomembranes for municipal solid waste landfills. However, for other specialized waste disposal, such as dedicated sites for PFAS contaminated soil, other geomembranes may be considered.

The properties of both the contaminant and the geomembrane influence a geomembrane's diffusive characteristics. For example, greater contaminant molecular weights correlate with a lower diffusion coefficient. However, the greater the molecular weight, M_w, and hydrophobicity (e.g., the greater the n-octanol/water coefficient, log K_{ow}) of a compound, the greater the likelihood that the compound will partition into the geomembrane (August and Tatzky 1984, Park et al. 1995, Park and Nibras 1993, Rowe et al. 2004, Sangam and Rowe 2001). Certain PFAS compounds, like those found in leachate, are complex and do not behave like other nonionic chemicals; thus, the use of K_{ow} to estimate their behaviour does not lead to accurate predictions. Ionized PFAS are both hydrophobic and oleophobic which makes them good surface protectors and surfactants, but this results in their accumulation between aqueous and non-aqueous fluids (Di Battista et al. 2020, Gluge et al. 2020, ITRC 2022). As a result, diffusion testing is required to estimate the diffusive characteristics of PFAS through such materials.

LLDPE geomembranes are common polyethylene liners used for containment in some disposal facilities as part of composite liners. Since the diffusive resistance of a geomembrane is dependent on the contaminant to be contained, geomembranes are sometimes produced with an ethylene vinyl alcohol (EVOH) core sandwiched between two polyethylene outer layers to form a polyethylene coextruded EVOH liner to provide additional resistance to certain contaminants. EVOH is known to have high diffusive resistance to organic contaminants (e.g., BTEX) and gases (McWatters and Rowe 2009a, 2010, 2015). Thus, Di Battista et al. (2020) studied the diffusion of PFOA and PFOS through linear low-density polyethylene (LLDPE) and LLDPE coextruded with ethylene vinyl alcohol (EVOH) geomembranes at room temperature, 35˚C, and 50˚C. These two liners were shown to be excellent diffusive barriers to PFOA and PFOS and based on no detectable diffusion through them throughout the 399 to 509 days of testing, upper bound permeation coefficients for PFOA and PFOS were reported. The diffusion tests used to estimate these values are still ongoing and are regularly sampled, analyzed, and their permeation coefficients are updated in this paper.

Over time, new geomembranes and liners made of different materials other than polyethylene are being developed to be used in containment applications. Two types of material that are being considered for PFAS containment geomembranes are thermoplastic polyurethane (TPU) and ethylene interpolymer alloy (PVC-EIA). TPU liners are typically reinforced by a scrim fabric and are said to be suitable for several applications such as collapsible, flexible, or portable tanks, primary or secondary containment applications, oil booms, and containment berms (Cooley Group 2022a). They are said to work well at low temperatures and to have high abrasion and tear resistance (Cooley Group 2022a). PVC-EIA geomembranes are made from polyvinyl chloride (PVC) alloyed with ketone ethylene ester (KEE), a polymeric non-liquid plasticizer, and reinforced with a polyester scrim to form a geomembrane. The addition of the KEE results in a special blend of resin said to result in a high-performance geomembrane that can resist high temperatures and aggressive chemicals including acids, oils, and methane (Scheirs 2009). Furthermore, different PVC-EIA geomembranes are being produced with a range of plasticizer content (KEE). The amount of KEE present in such liners can impact its performance in different applications. PVC-EIA geomembranes are used for water protection and preservation and primary and secondary containment of hydrocarbons, liquids, aggressive chemicals, and regulated substances (Cooley Group 2022b).

The primary objectives of this paper are to: (i) assess the potential for diffusion of PFOA, PFOS, PFBS, 6:2 FTS, and GenX through TPU and three PVC-EIA geomembranes and obtain estimates of their permeation coefficients, (ii) estimate the partitioning coefficients of PFOA, PFOS, PFBS, 6:2 FTS, and GenX to TPU and PVC-EIA geomembranes by performing sorption tests, and (iii) update estimates of the diffusion and permeation coefficients of PFOA and PFOS through LLDPE and Coextruded LLDPE geomembranes based on the most recent sampling results.

2. Materials and Method

Although geomembranes typically have a thickness ≥ 0.75 mm, previous diffusion testing with LLDPE and coextruded EVOH/LLDPE has shown that the time required to reach good estimates is very long even for a 0.75 mm-thick geomembrane and that better estimates can be obtained in a reasonable time by using a much thinner film. Based on that experience, four different films were used in this study to estimate their diffusive and partitioning resistance to different types of PFAS. The films included a 0.3 mm thick TPU liner and three PVC-EIA films (denoted by EIA1, EIA2 and EIA 3) with thicknesses of 0.29, 0.33 and 0.26 mm, respectively. The PVC-EIA films varied in terms of plasticizer content with EIA1 having the highest KEE content while EIA3 had the lowest KEE content (precise details are kept confidential by the manufacturer). Diffusion tests for all four films were conducted at room temperature (23˚), 35°C, and 50°C while sorption vial tests were only conducted at room temperature and 50°C conditions.

The diffusion tests were performed using stainless steel double compartment diffusion cells (Di Battista et al. 2020). The double compartment refers to a source and receptor compartment separated by the film that is being tested. The source and receptor compartments had a 70 mm diameter cross-section and a volume of 240 ml and 106 ml, respectively. To obtain a seal between the steel compartments and film, silicon gaskets, like those used in previous studies testing PFAS diffusion (Di Battista et al. 2020), were used. Tests at 35°C and 50°C were conducted in incubators from Fisher Scientific (Model: 203FS) to maintain constant temperature conditions.

Given the EPA recently lowered its drinking water limits for PFOA and PFOS to 4 ng/L, PFBS is 3 ng/L, and GenX is 5 ng/L, the potential for diffusion becomes a critical transport mechanism for landfills built with a geomembrane liner over the last 50 years since these contaminants are significantly elevated in MSW leachate (hundreds to thousand-fold higher than drinking water limits) (EPA 2023). This paper is focused on diffusion pH~7, which is at the lower end of the common range of 7-8 for MSW landfills for most of their contaminating lifespan (Rowe et al. 2004). It is acknowledged that higher concentrations may diffuse faster if the pH is lower (e.g., pH 4), but the parameters for pH < 7 would not be realistic for most of the contaminating lifespan. The possible implications of a much higher diffusion coefficient over the first few years due to lower pH is examined later in this paper.

To get an appropriate pH and avoid analytical complications from the other components of leachate, double-deionized (DDI) water was used as the solvent for these tests. PFOS (CAS No. 1763-23-1), PFOA (CAS No. 335-67-1), PFBS (CAS No. 375-73-5), 6:2 FTS (CAS No. 27619-97-2), and GenX (CAS No. 13252-13-6) were purchased from Synquest Laboratories (Alachua, FL, 32616 USA) and used to mix separate stock solutions using double deionized (DDI) water for each compound. The stock solutions were developed to be 100 mg/L for PFOS, PFBS, 6:2 FTS, and GenX, and 1000 mg/L for PFOA. These stock solutions were used to prepare source solutions of 20 mg/L for PFOS and PFOA and 2 mg/L for the other PFAS. This was because 6:2 FTS, GenX and PFBS are often much lower than the concentrations of PFOA and PFOS in the leachate of different waste facilities. These relatively high concentrations were adopted to ensure a high concentration gradient and increase the probability of measuring diffusive transport. The concentrations of these solutions were confirmed through analysis and then used to develop the source solution used in all the diffusion tests. The receptor compartments were filled with DDI water only to develop a concentration (diffusive) gradient between the two compartments of the cell.

Once the diffusion tests were set up, sampling was performed regularly using two separate syringes for the source and receptor compartments to minimize contamination. Approximately 100 µl and 200 µl of the source and receptor were removed in each sampling and replaced with DDI water. Once the sample is taken, the syringes were rinsed three times with methanol followed by three times with DDI water before the next use.

To ensure that none of the PFAS compounds are partitioning on the liners tested in the diffusion tests, sorption tests were performed using a source solution containing about 2 mg/L of all five PFAS compounds examined. This solution was developed using the same stock solutions developed for the diffusion tests. Thirty different tests were developed, fifteen at room temperature and fifteen at 50°C. The tests were performed using 25 ml glass vials, and two duplicate tests were performed for each film. In addition, three control vials with no geomembranes were also incubated under similar conditions to those with the geomembrane at each temperature. The experiments were initiated by decanting 25 ml of the source solution into the vials containing a 2 cm by 4 cm strip of the film being tested. An initial sample of the source solution was extracted and analyzed immediately before the solution was decanted into separate vials to confirm the initial concentration. A 100 µl sample was extracted from the vials every 24 hours for a week using an adjustable volume single-channel pipette. These samples are then analyzed to check for any change in concentration that might have occurred in the solutions over time. Once the concentrations are analyzed, the partitioning coefficient, S_{gf}, onto the geomembrane tested was calculated [Eq.1], but no measurable change was observed from the output concentrations in any of the tests.

$$S_{gf} = \frac{[c_{fo}V_{fo} - c_{fF}V_{fF} - M_c]\rho_g}{M_g c_{gF}} \qquad \text{[Eq.1]}$$

where c_{fo} denotes the initial and c_{fF} the final measured concentrations in the solution, and c_{gF} denotes the final concentration in the geomembrane. V_{fo} and V_{fF} are the initial and final aqueous solution volumes in the apparatus, M_c is the mass of the PFAS considered lost to the cell (based on the control tests), M_g is the mass of the geomembrane used in the test, and ρ_g is the geomembrane density.

An Agilent 6460 LC-MS/MS on MRM mode was used to perform the PFAS analysis on all the samples. A Zorbax C18 eclipse column coupled with a guard column with the dimensions of 150 mm x 2.1 mm x 3.0 um was used to separate the samples. During the analysis process, the samples would be eluted initially at 95% water and 5% acetonitrile, and progressing to 100% acetonitrile over a period of 8 min. Once 100% acetonitrile is reached, the process will hold at this percentage for 4 minutes. Once complete, the column is returned to its original elution condition for four minutes before starting the next sample analysis.

During the analysis process, a 7-point calibration curve was used to calculate the concentrations of each sample. The concentrations along the calibration curve ranged from 0.1 µg/L to 200 µg/L (0.1, 1, 5, 10, 50, 100, 200). Since higher concentrations than those present within the calibration curve on the analysis equipment were used in the diffusion and sorption tests, the samples from the source solutions were diluted to reach a targeted concentration of around 50 μg/L. Minimum detection limits for PFAS analysis were identified by analyzing a 0.05 ug/L calibration standard 10 times (0.5 ug/L for GenX), and using the average and standard deviation of the instrument response to calculate the detection limit. As such the detection limits (conservatively) were found to be as follows; 0.5 ug/L for C3-C6 PFCAs, 0.1 ug/L for C7-C14 PFCAs, 0.1 ug/L for PFSAs and 6:2 FTS, and 0.5 ug/L for GenX.

Using the concentrations obtained from the analysis, preliminary best estimate diffusion coefficients, D_g, were developed using a finite layer 1½ dimensional program called POLLUTE v7 (Rowe and Booker 1985, 2004, Rowe et al. 1997, Rowe 1998, Lake and Rowe 2004, Sangam and Rowe 2001). Modelling the change in the source and receptor concentrations with time was performed for the diffusion tests. This process was relatively straightforward when there was a measurable decrease in the source and an increase in the receptor concentration with time resulting in a best-fit diffusion coefficient, D_g, following procedures adopted by others (e.g., Sangam and Rowe 2005, McWatters and Rowe 2009a,b, Jones and Rowe 2016, Rowe et al, 2016a,b, McWatters et al. 2020, Di Battista et al. 2020). For the cases where there is no diffusion detected yet and the concentrations in the receptor are still below the detection limit, a conservative assumption is made by considering the concentration of that contaminant in the receptor to be equal to the detection limit. This approach has previously been adopted for other contaminants/geomembrane combinations with very low diffusion coefficients (e.g., McWatters and Rowe 2010, 2015, 2018 Saheli et al. 2016, 2017, DiBattista and Rowe 2020b, Di Battista et al. 2020) to obtain a preliminary estimate of the diffusion coefficient of that PFAS compound through the liner considered. For these cases where there is no concentration detected in the receptor yet, an equal or less than sign, ≤, is typically used to indicate that these diffusion coefficients are just preliminary inferred estimates, and they are likely to reduce further as more data becomes available over time.

3. Results

3.1. Diffusion Testing

Diffusion tests were initiated for all four geomembranes at 23˚C, 35˚C, and 50˚C and have data from samplings available for up to 535 days. The initial source concentrations were based on analyzed samples taken on day zero when starting the test and were 20,800 µg/L for PFOA, 24,400 µg/L for PFOS, 2,770 µg/L for PFBS, 2,350 µg/L for 6:2 FTS, and 2,270 µg/L for GenX.

For all the tests performed on PVC-EIA geomembranes at 23 ˚C and 35 ˚C, the source concentrations for the five compounds considered have not measurably changed over the 535 days of testing but have exhibited variability due to the large dilution required (~400x DF) to get the source's concentration into a suitable range for analysis. At the same time, the stability and lack of discernible decrease in the source concentrations over the test period indicate that there was negligible partitioning of any of the five compounds being tested to the PVC-EIA geomembranes or the test cells ($S_{gf} \leq 1$). In addition, the targeted analytical suite in this study focused on the identification of C3-C14 PFCAs alongside the five PFAS compounds employed in the experiment. Therefore, terminal PFCA breakdown products would be identified in the MS analysis. During analysis, no PFCA’s formed from the five compounds were detected. The stability of the source concentration over the 535 days of testing indicates that over the period considered, very little diffusion had occurred since there was no measurable mass flux through the geomembrane or a consistent decrease in the source concentration with time.

Receptor samples were not diluted prior to analysis if the results from the previous sampling showed concentrations that are lower than 200 µg/L. As a result, the receptor concentrations were generally used without dilution to estimate the diffusion and permeation coefficients of all the liners tested. Thus, for the purposes of interpretation of the results, a non-detect was considered to be a concentration just below the detection limit indicated earlier (i.e., erring on the safe side by tending to be too high rather than too low) estimate of the permeation coefficient.

No PFAS was detected in the receptor compartments for any of the three PVC-EIA liners at room temperature except for PFOA. PFOA was first detected in the receptor after 92 days of testing at 0.6 µg/L and had reached 1.8 µg/L after 535 days of diffusion through EIA1 (Fig. 1; Table S1 in Supporting information). For EIA2 and EIA3, PFOA was only detected in the most current sampling and is currently at 0.2 µg/L and 0.5 µg/L respectively (Fig. 1).

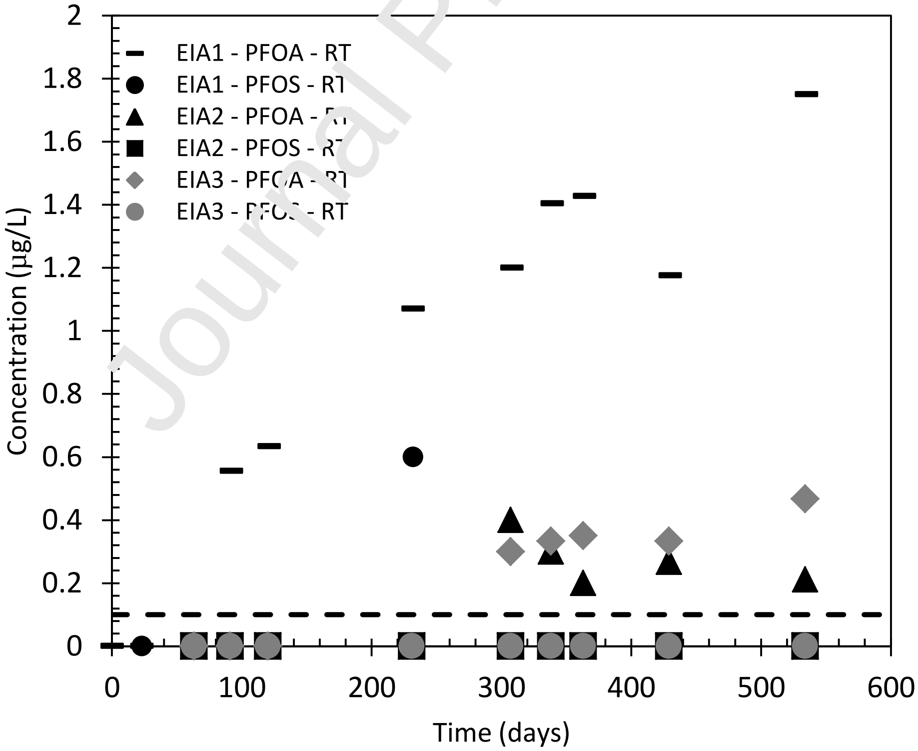

Figure 1: Receptor Concentration for PFOA and PFOS through EIA1, EIA2, and EIA3 at room temperature (23°C) conditions

For the PVC-EIA liner tests at 35˚C, PFOA was initially detected at 64 days for all three liners and had increased to 10 µg/L for EIA1, 4 µg/L for EIA2, and 2 µg/L for EIA3 after 535 days. PFOS was only first detected in the receptor compartments at 0.5 µg/L for EIA1 and at 0.6 µg/L for EIA2 after 535 days. No other PFAS compounds were detected at 35˚C after 535 days of diffusion.

PFOA was detected in the receptor compartments at 3 µg/L for EIA1, 2 µg/L for EIA2, and 1 µg/L for EIA3 after 23, 64 and 91 days diffusion at 50° C. The concentration of PFOA was 120 µg/L, 150 µg/L, and 8 µg/L in the receptor compartments of EIA1, EIA2 and EIA3, respectively at 535 days. PFOS was initially detected after 91, 64, and 232 days of testing with concentrations of 3 µg/L, 4 µg/L, and 2 µg/L for EIA1, EIA2, and EIA3 respectively. PFOS concentrations were 110 µg/L, 2,000 µg/L, and 4 µg/L in the receptor compartments of EIA1, EIA2 and EIA3 at 535 days of testing. Lastly, the concentration of PFBS was 0.3 µg/L, 1.5 µg/L, and 0.2 µg/L in the receptor compartment of EIA1, EIA2, and EIA3 at 535 days of testing.

Even with no dilution, a notable scatter could be seen in the receptor data since standard PFAS analysis acknowledges a +/ - 30% variability (EPA 2020). For the tests with the PVC-EIA geomembranes at 23 and 35˚C, no clear increasing trend in receptor concentration was observed in any of the receptors. This indicates that diffusion was very slow. The only clear trend observed was for PFOS in EIA2's diffusion test at 50˚C (Fig. 2). In this closed system, a decrease in the source indicates that these contaminants are moving into and through the geomembrane to the receptor. Quantitatively, modelling the decrease in the source (solid black line in Fig. 2) and increase in the receptor (dashed black line in Fig. 2) allows the permeation coefficient to be established. Qualitatively, the fact a decreasing trend is observed for this geomembrane and not for others implies that compared to those others, this geomembrane is a relatively poor diffusion barrier to PFOA and PFOS.

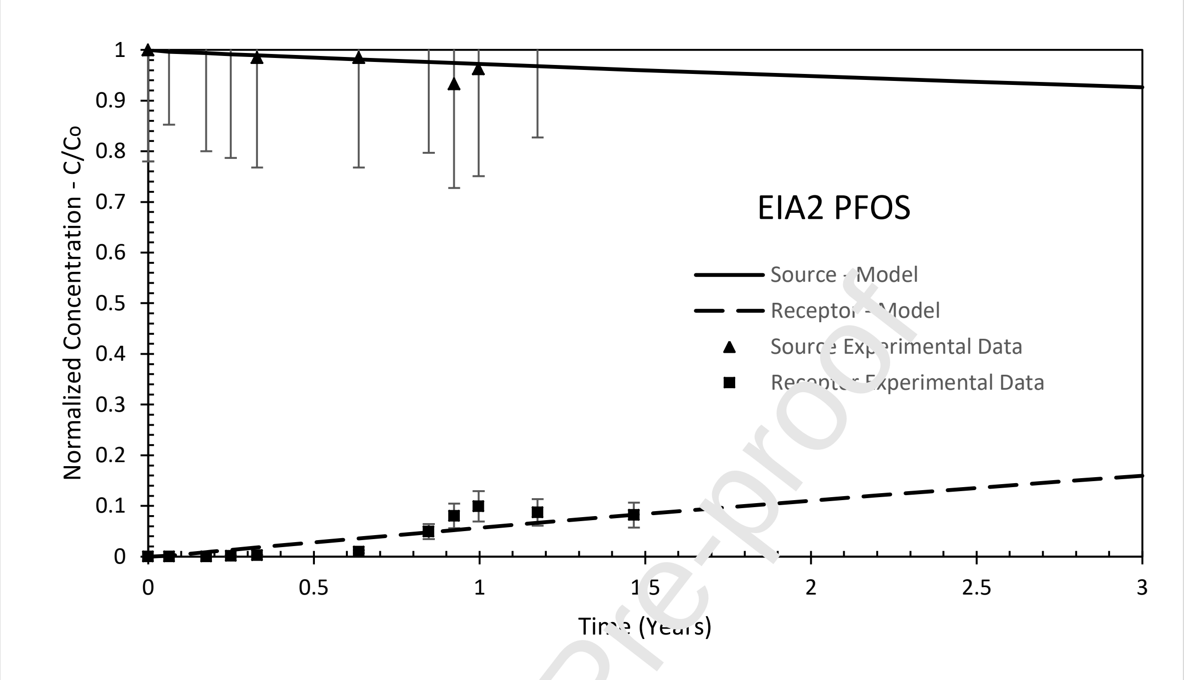

Figure 2: Normalized concentration over time of diffusion of PFOS through EIA2 at 50˚C from experimental data results and diffusion modelling of POLLUTE

In contrast to the PVC-EIA geomembranes where there was very little diffusion into the receptor compartments, for the TPU geomembranes, there were significant concentrations measured in the receptor for several PFAS at all three temperatures. Specifically, after 535 days of testing, the TPU receptor concentrations were 590 µg/L for PFOA and 7,700 µg/L for PFOS at the 23˚C cell, 1,200 µg/L for PFOA, 13,500 µg/L of PFOS, and 0.5 µg/L of PFBS at 35˚C, and 3,300 µg/L of PFOA, 14,500 µg/L of PFOS, and 50 µg/L of PFBS at 50˚C. PFBS was not detected in the receptor of the cell at 23˚C while 6:2 FTS and GenX were not detected in the receptors at any of the 3 temperatures. A decreasing trend of PFOA and PFOS could be seen in the source compartment of the cells under all three temperatures, but especially at 50˚C (e.g.,

Fig. 3). As was the case in Fig.2, in this closed system, a decrease in the source indicates that these contaminants are moving into and through the geomembrane to the receptor. The experimental data appear to hover virtually unchanged over a six-month period but when one considers the error bars, the data fits reasonably well with the theoretical prediction which shows that change is occurring, but very slowly. This means that although this geomembrane is not as good as others for which no change can be detected, it is still a good diffusion barrier to PFOA and PFOS.

3.2. Sorption Testing

Sorption tests were initiated at 23˚C and 50˚C with the initial solution containing PFOS, PFOA, PFBS, 6:2 FTS and GenX at about 2,000 µg/L. Control tests with no geomembrane were conducted at the same time to assess if there was any sorption to the apparatus itself. Three samples were taken from each test at each sampling time to eliminate outliers from the analysis results. These samples were analyzed and based on the conservation of mass, the partitioning coefficient, S_{gf}, was calculated for each compound.

At both 23˚C and 50˚C, there was no measurable change or decrease in any of the concentrations of the solutions with time for any of the four liners and five PFAS compounds examined. Thus, $S_{gf} \leq 1$ for all the compounds and liners considered. Given the value cannot be determined precisely, it is taken as 1 in the following. The implications of a lower values are explored later in the paper.

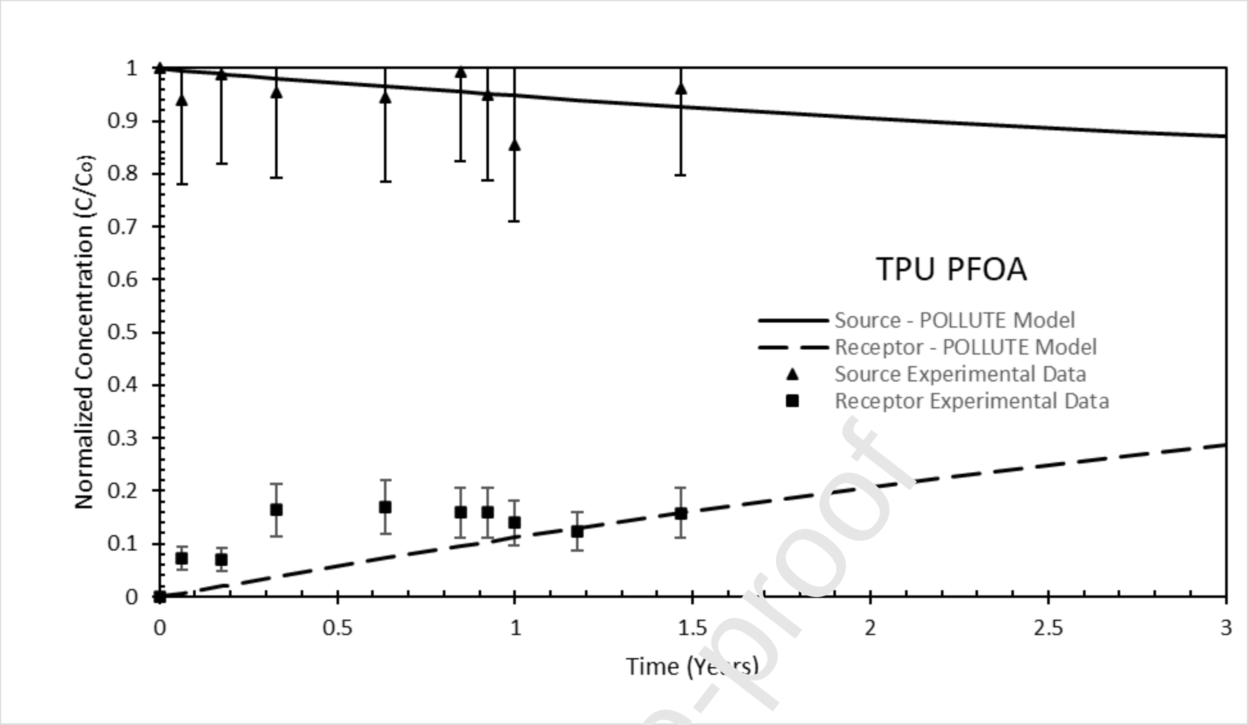

Figure 3: Normalized concentration over time of diffusion of PFOA through TPU at 50˚C using experimental and theoretical data from modelling (no discernable difference in POLLUTE model for $P_g=S_{gf}D_g$ = 3.3x10^{-14} m^2/s for $0.001 \leq S_{gf} \leq 1$.

3.3. *Diffusion Modeling*

The best estimate diffusion coefficients have been deduced and proposed for the different liners and PFAS compounds considered under the three different temperature conditions used for the tests using an S_{gf} = 1 as a conservative assumption (Table 1).

For 0.3 mm TPU liner at 23˚C, the best estimate of the diffusion coefficient for PFOA is D_{gPFOA} = 5.6×10^{-15} m^2/s and for PFOS is D_{gPFOS} = 7.6×10^{-14} m^2/s (Table 1). These values are based on concentrations measured in the receptor and are considered good estimates. For 0.3 mm TPU liner at 35˚C, the best estimate D_g for PFOA = 1.1×10^{-14} m^2/s is 2-fold higher than at 23°C and for PFOS = 2.0×10^{-13} m^2/s at 35˚C is 2.6-fold higher than at 23°C. For 0.3 mm TPU liner at

50˚C, the best estimate D_g for PFOA of $D_{gPFOA} = 3.3\times10^{-14}$ m^2/s is 3-fold higher than at 35°C and 5.9-fold higher than at 23°C. For PFOS, $D_{gPFOS} = 2.4\times10^{-13}$ m^2/s which is 1.2-fold higher than at 35°C and 3.1-fold higher than at 23°C. Based on diffusion coefficients at three temperatures, an Arrhenius relationship can be established between the permeation coefficients and the inverse of temperature, *1/T*, in Kelvin (Figure S1) for PFOA and PFOS (Equations 6 and 7; Table 2), where the permeation coefficient, P_g (m^2/s), is equal to the product of the diffusion, D_g, and partitioning, S_{gf}, coefficients, and it is assumed that $S_{gf} = 1$ for all the cases considered.

$$\ln(P_{gPFOA}) = -\frac{6864}{T} - 9.82 \qquad \text{[Eq.6 – TPU PFOA]}$$

$$\ln(P_{gPFOS}) = -\frac{8542}{T} - 1.54 \qquad \text{[Eq.7 – TPU PFOS]}$$

Table 1: PFOA, PFOS, PFBS, 6:2 FTS, & GenX best estimate D_g, and P_g values for TPU and PVC-EIA liners at different temperatures ($S_{gf} = 1$).

Liner	Temp.	*PFOA*	*PFOS*	*PFBS*	*6:2FTS*	*GenX*
	(˚C)	D_g & P_g (x10^{15}m^2/s)	D_g & P_g (x10^{15}m^2/s)	D_g & P_g (x10^{15}m^2/s)	D_g & P_g (x10^{15}m^2/s)	D_g & P_g (x10^{15}m^2/s)
0.3 mm TPU	23	5.6±2.4	76±31	≤0.16	≤0.17	≤0.26
0.29 mm EIA1	23	0.18±0.03	≤0.10	≤0.15	≤0.16	≤0.24
0.33 mm EIA2	23	≤0.14	≤0.12	≤0.19	≤0.20	≤0.30
0.26 mm EIA3	23	≤0.12	≤0.08	≤0.12	≤0.13	≤0.20
0.3 mm TPU	35	11±7.6	200±750	0.16±2.7	≤0.17	≤0.26
0.29 mm EIA1	35	0.34±0.10	≤0.13	≤0.15	≤0.16	≤0.24
0.33 mm EIA2	35	0.29±0.07	0.17±0.02	≤0.19	≤0.20	≤0.30
0.26 mm EIA3	35	0.15±0.03	≤0.08	≤0.12	≤0.13	≤0.20
0.3 mm TPU	50	33±25	240±890	0.24±4.5	≤0.17	≤0.26
0.29 mm EIA1	50	1.3±0.41	1.1±0.17	≤0.20	≤0.16	≤0.24
0.33 mm EIA2	50	1.9±1.2	18±5.6	0.42±0.09	≤0.20	≤0.30
0.26 mm EIA3	50	0.25±0.07	0.18±0.06	≤0.15	≤0.13	≤0.20

No apparent breakthrough into the receptor below the TPU geomembrane was observed for PFBS, 6:2 FTS, and GenX and so the detection limit was used to estimate the diffusion coefficients of $D_{gPFBS} \leq 1.6\times10^{-16}$ m^2/s for PFBS, $D_{g6:2FTS} \leq 1.7\times10^{-16}$ m^2/s for 6:2 FTS, and $D_{gGenX} \leq 2.6\times10^{-16}$ m^2/s for GenX. Since the same detection limit is used for each temperature, there is no change in the upper bound estimate of the diffusion coefficient as a function of temperature, and it can be assumed that these values are an upper value at 50°C and even more conservative at lower temperatures.

Table 2: Arrhenius relationships between permeation coefficient, P_g (m^2/s), and temperature, T (K)

Liner	PFOA	Eq.	PFOS	Eq.
0.3 mm TPU	$\ln(P_{gPFOA}) = -\frac{6864}{T} - 9.82$	6	$\ln(P_{gPFOS}) = -\frac{8542}{T} - 1.54$	7
0.29 mm EIA1	$\ln(P_{gPFOA}) = -\frac{7654}{T} - 10.6$	8	$\ln(P_{gPFOS}) = -\frac{9262}{T} - 5.80$	9
0.33 mm EIA2	$\ln(P_{gPFOA}) = -\frac{10124}{T} - 2.62$	10	$\ln(P_{gPFOS}) = -\frac{23129}{T} + 39.6$	11
0.26 mm EIA3	$\ln(P_{gPFOA}) = -\frac{2673}{T} - 27.7$	12	$\ln(P_{gPFOS}) = -\frac{4964}{T} - 20.9$	13

After 535 days of testing for EIA1 at 23˚C, the best estimate was D_{gPFOA} = 1.8×10^{-16} m^2/s for PFOA, increased 1.9-fold to D_{gPFOA} = 3.4×10^{-16} m^2/s at 35˚C, and 7.2-fold to D_{gPFOA} = 1.3×10^{-15} m^2/s at 50˚C. These three data points allow the development of an Arrhenius relationship for EIA1 (Figure S1 in Supplemental materials) as given by Eq. 8 in Table 2.

The situation is not as straightforward for PFOS since no PFOS was detected in the receptor compartment for any EIA geomembrane at 23˚C. For EIA1, assuming the PFOS concentration was just at, or below, the detection limit at 535 days gives $D_{gPFOS} \leq$ 1.0×10^{-16} m^2/s at 23˚C. Based on D_{gPFOS} at 23˚C and the measured trend giving D_{gPFOS} = 1.1×10^{-15} m^2/s at 50˚C, an approximate relationship can be developed as given by Eq. 9 (Table 2), but this relationship is likely to change with time as more information becomes available. However, to the extent that it errs, it is considered likely to overestimate the permeation coefficient for T< 50^{o}C.

After 535 days of testing of EIA1 at all three temperatures, PFBS, 6:2 FTS, and GenX were still not detected in the receptors; thus, the best estimate diffusion coefficients for these three compounds given in Table 1 can be assumed to be upper bound values at 50° C and even more conservative at lower temperatures.

The results obtained for PFOS and PFOA based on testing the EIA2 and EIA3 materials as diffusive barriers gave best estimates of D_{gPFOA}, D_{gPFOS} , D_{gPFBS}, $D_{g6:2FTS,}$ and D_{gGenX} as given in Table 1. The Arrhenius relationships using the results for EIA2 are given in Equations 10 and 11 (Table 2) while those for EIA3 are given in Equations 12 and 13 (Table 2).

Di Battista et al. (2020) reported best estimate diffusion coefficients for PFOA and PFOS (Table 3) through 0.1 mm and 0.75 mm thick LLDPE geomembranes and 0.1 mm and 0.75 mm thick Coextruded LLDPE-EVOH geomembranes at 23, 35 and 50^{o}C after 399-509 days. The tests initiated by Di Battista et al. are still running and the source and receptor chambers are periodically sampled and analyzed to obtain their concentrations. The most recent sampling for the tests at 23˚C for both thicknesses and liners was after 1331 days while those at 35 and 50 ˚C were sampled after 1246 days. These augmented data were analyzed and modelled on POLLUTEv7 and best estimate permeation coefficients were made based on the most recent data available (Table 3). With the additional data, the best estimate of P_{gPFOA} for 0.1 mm-thick LLDPE decreased 3-fold from $\leq 3.0\text{x}10^{-17}$ to $\leq 1.0\text{x}10^{-17}$ m^{2}/s at 23˚C while that for the 0.75 mm-thick LLDPE decreased 2.9-fold from $\leq 1.3\text{x}10^{-15}$ to $\leq 4.5\text{x}10^{-16}$ m^{2}/s at 23˚C. The difference in the numbers for the two thicknesses of LLDPE should not be interpreted as suggesting that the thicker geomembrane has a higher permeation coefficient. The difference is simply because the greater the thickness, the longer it takes for diffusion to occur and hence the longer the test needs to run to obtain a definitive value. In this case, there is still no definitive value for 0.1 mm-thick

LLDPE after 3.65 years of testing at room temperature or for the 0.75 mm-thick LLDPE and after 3.4 years of testing at 50° C. Thus, all these values will get lower with longer testing time.

4. Discussion

The best estimate diffusion or permeation coefficients for the four liners studied in this paper (Table 1) can be compared in terms of their resistance to the diffusion of PFOA and PFOS. This comparison indicates a significant difference in performance of the TPU and PVC-EIA geomembranes and a less significant variability between the three PVC-EIA geomembranes. Specifically, the PVC-EIA geomembranes were between 30 and 50-fold better at resisting the diffusion of PFOA than the TPU geomembrane. The difference was even more significant for PFOS with the PVC-EIA geomembrane being between 450 and 700-fold better at resisting the diffusion of PFOS than the TPU. For the other three contaminants examined (PFBS, 6:2 FTS, and GenX), no definitive conclusions can be reached other than that all 4 geomembranes appear to be offering good diffusive resistance to these three compounds with upper bound Pg/Dg values as given in Table 1.

Table 3: Best Estimate Permeation Coefficients for LLDPE and Coextruded EVOH/LLDPE at different time intervals.

Material	Temp.	Test* Duration	PFOA*	PFOS*	Test Duration	PFOA	PFOS
	(˚C)	(Days)	P_{gPFOA}* (m^2/s)	P_{gPFOS}* (m^2/s)	(Days)	P_{gPFOA} (m^2/s)	P_{gPFOS} (m^2/s)
0.1 mm LLDPE	23	483	$\leq 0.3\text{x}10^{-16}$	$\leq 1.6\text{x}10^{-16}$	1331	$\leq 0.1\text{x}10^{-16}$	$\leq 0.33\text{x}10^{-16}$
0.75 mm LLDPE	23	509	$\leq 13\text{x}10^{-16}$	$\leq 34\text{x}10^{-16}$	1331	$\leq 4.5\text{x}10^{-16}$	$\leq 13\text{x}10^{-16}$
0.75 mm LLDPE	35	399	$\leq 13\text{x}10^{-16}$	$\leq 40\text{x}10^{-16}$	1246	$\leq 4.9\text{x}10^{-16}$	$\leq 17\text{x}10^{-16}$
0.75 mm LLDPE	50	399	$\leq 19\text{x}10^{-16}$	$\leq 52\text{x}10^{-16}$	1246	$\leq 3.8\text{x}10^{-16}$	$\leq 14\text{x}10^{-16}$

0.1 mm CoEx	23	483	≤0.26x10^{-16}	≤0.55x10^{-16}	1331	≤0.11x10^{-16}	≤0.13x10^{-16}
0.75 mm CoEx	23	509	≤8.6x10^{-16}	≤6.8x10^{-16}	1331	≤3.3x10^{-16}	≤3.3x10^{-16}
0.75 mm CoEx	35	399	≤11x10^{-16}	≤8.3x10^{-16}	1246	≤3.5x10^{-16}	≤3.5x10^{-16}
0.75 mm CoEx	50	399	≤10x10^{-16}	≤8.2x10^{-16}	1246	≤3.71x10^{-16}	≤3.5x10^{-16}

* Di Battista et al. 2020

With respect to the three PVC-EIA geomembranes, EIA3 generally appears to be have the best resistance to both PFOA and PFOS. It is more difficult to generalize relative performance between EIA1 and EIA2 with the permeation coefficients being very similar at 23 and 35° C but with EIA2 being more sensitive and giving a notably higher permeation coefficient than EIA1 at 50° C (especially for PFOS).

When the PVC-EIA geomembranes (Table 1) are compared with LLDPE (Table 3) for PFOA, EIA3 has $P_{gPFOA} \leq 1.2\text{x}10^{-16}$ m^2/s whereas P_{gPFOA} for the 0.1 mm-thick LLDPE had ≤0.3x10^{-16} m^2/s with a similar time of testing and has now decreased to ≤ 0.1x10^{-16} m^2/s at 23˚C. While it could be argued that the diffusion coefficient of EIA3 is somewhat higher, given the difference in thickness, such conclusion should be viewed with caution. What is known with confidence is that in both cases, the permeation coefficient is very low. At 50°C, EIA3 has P_{gPFOA} ~ 2.5x10^{-16} m^2/s whereas P_{gPFOA} for the 0.75 mm-thick LLDPE had ≤19x10^{-16} m^2/s based on a similar period of testing and had reduced to $P_{gPFOA} \leq 3.8\text{x}10^{-16}$ m^2/s with 1246 days of testing. Again, it is difficult to draw firm conclusion as to which material is better, but it is certain that both are very good diffusive barriers.

When the PVC-EIA geomembranes (Table 1) are compared with LLDPE (Table 3) for PFOS, EIA3 has $P_{gPFOS} \leq 0.8\text{x}10^{-16}$ m^2/s whereas the 0.1 mm-thick LLDPE had $P_{gPFOS} \leq 1.6\text{x}10^{-16}$ m^2/s with a similar time of testing and has now decreased to ≤ 0.33x10^{-16} m^2/s at 23˚C. At 50° C, EIA3 has P_{gPFOS} ~ 1.8x10^{-16} m^2/s whereas the 0.75 mm-thick LLDPE had $P_{gPFOS} \leq 52\text{x}10^{-16}$ m^2/s based on a similar period of testing and had reduced to $P_{gPFOS} \leq 14\text{x}10^{-16}$ m^2/s with 1246 days of testing. Again, it is difficult to draw a firm conclusion as to which material is better, but both are very low.

When the TPU geomembrane (Table 1) is compared with LLDPE (Table 3) for PFOA, TPU has $P_{gPFOA} \leq 56\text{x}10^{-16}$ m^2/s whereas the 0.1 mm-thick LLDPE had $P_{gPFOA} \leq 0.3\text{x}10^{-16}$ m^2/s with a similar time of testing and has now decreased to $\leq 0.1\text{x}10^{-16}$ m^2/s at 23˚C. Thus, the diffusion coefficient for TPU is demonstrably much higher than for LLDPE. At 50°C, TPU has $P_{gPFOA} \sim 330\text{x}10^{-16}$ m^2/s whereas the 0.75 mm-thick LLDPE had $P_{gPFOA} \leq 19\text{x}10^{-16}$ m^2/s based on a similar period of testing and had reduced to $P_{gPFOA} \leq 3.8\text{x}10^{-16}$ m^2/s with 1246 days of testing. Again, the diffusion coefficient for TPU is demonstrably much higher than for LLDPE. A generally similar conclusion is reached for P_{gPFOS}.

A comparison of the coextruded in the EVOH/LLDPE with those for the PVC-EIA and TPU geomembranes leads to similar conclusions and comments to those reached for LLDPE except that the coextruded geomembrane appears to be even better than the LLDPE alone.

To put the numbers in Table 1 in context, it is useful to compare the permeation coefficients for PFOS and PFOA with those for other contaminants that exist in landfill leachate (Table 4) to estimate the relative diffusive resistance offered by these liners. Because the LLDPE and coextruded EVOH/LLDPE have an advantage of having been running much longer with a thin film which will tend to minimize the permeation coefficient when there is no breakthrough since the same detection limit is used, it is not surprising that they have the lowest values for P_{gPFOA} and P_{gPFOS}. However, EIA1 and EIA3 appear very low on the list and more than an order of magnitude below the permeation coefficient of BPA through HDPE; even TPU offers resistance to PFOA better than HDPE offers to phenol and is many orders of magnitude lower than that offered by LLDPE to benzene, toluene, ethylbenzene or the xylenes (Table 4). Thus, PVC-EIA liners can be considered as relatively good diffusive barriers to PFOA and PFOS when looking at other contaminants' diffusive characteristics, but LLDPE and Coextruded LLDPE liners would still be considered as better diffusive barriers to PFOA and PFOS (Table 4).

The best estimate diffusion coefficients of PFOA and PFOS for TPU are relatively high compared to what was estimated for the PVC-EIA, LLDPE, and Coextruded LLDPE liners, but they are still approximately three to four orders of magnitudes lower than what was estimated for benzene, toluene, ethylbenzene, *m&p*-xylene, and *o*-xylene with LLDPE geomembranes; thus, they are not the best diffusive barriers to PFAS (Table 4).

Table 4: PFOA and PFOS best estimate S_{gf} and P_g values compared to literature values for other chemicals at room temperature.

Contaminant	S_{gf} (-)	P_g (m^2/s)
PCE (0.75 mm LLDPE) [1]	1250	$2.5x10^{-10}$
PCE (1.5 mm Polyurethane)[1]	900	$1.6x10^{-10}$
TCE (0.75 mm LLDPE)[1]	300	$1.2x10^{-10}$
TCE (1.5 mm Polyurethane)[1]	275	$1.1x10^{-10}$
PCE (1.5 mm HDPE)[1]	850	$1.0x10^{-10}$
Ethylbenzene (LLDPE) [2]	925	$9.2x10^{-11}$
Toluene (LLDPE) [2]	350	$7.7x10^{-11}$
m&p-Xylene (LLDPE) [2]	900	$7.2x10^{-11}$
o-xylene (LLDPE) [2]	900	$7.2x10^{-11}$
Benzene (LLDPE) [2]	200	$4.4x10^{-11}$
TCE (1.5 mm HDPE)[1]	160	$1.0x10^{-11}$
PFOS (0.3 mm TPU)	1	$7.6x10^{-14}$
Phenol (HDPE) [3]	3.5	$5.9x10^{-14}$
PFOA (0.3 mm TPU)	1	$5.6x10^{-15}$
BPA (HDPE) [3]	-	$2.9x10^{-15}$
PFOA (0.29 mm EIA1)	1	$1.8x10^{-16}$
PFOA (0.33 mm EIA2)	1	$\leq1.4x10^{-16}$
PFOS (0.33 mm EIA2)	1	$\leq1.2x10^{-16}$
PFOA (0.26 mm EIA3)	1	$\leq1.2x10^{-16}$
PFOS (0.29 mm EIA1)	1	$\leq1.0x10^{-16}$

PFOS (0.26 mm EIA3)	1	$\leq 8.0 \times 10^{-17}$
PFOS (0.1 mm LLDPE)	4	$\leq 3.3 \times 10^{-17}$
PFOA (0.1 mm EVOH/LLDPE)	1	$\leq 1.3 \times 10^{-17}$
PFOS (0.1 mm EVOH/LLDPE)	1	$\leq 1.1 \times 10^{-17}$
PFOA (0.1 mm LLDPE)	1.2	$\leq 1.0 \times 10^{-17}$

[1]Di Battista and Rowe 2020a, [2]Di Battista and Rowe 2020b, [3] Saheli et al. 2016.

5. Practical implications

Consider a 400 m x 400 m (16 ha) closed MSW landfill with an infiltration rate of 0.15 m/a (minimum permitted by MoE 1998) through the cover and 25,000 kg/m^2 (~ 25 t/m^2) as considered by Rowe and Barakat (2021). The base of the landfill has an operating leachate collection system and is lined with a single composite liner comprised of a 1.5 mm-thick geomembrane, a 7 mm-thick geosynthetic clay liner, over a 3.743 m thick attenuation layer (to meet the requirements of O.Reg. 232; MoE 1998) underlain by a 3 m thick aquifer with a horizontal Darcy flux of 1 m/a. Rowe and Barakat (2021) examined the effect of leakage through holes in wrinkles in the geomembrane. For the purposes of this paper, it is assumed that there are no holes and that the only transport mechanism is diffusion. Considering PFOA with an initial concentration of 750 ng/L based on an average of data from landfills in Australia, Canada, Germany, and USA (Li 2011, Lang 2016, Gallen et al. 2018, Benskin et al. 2012, Clarke et al. 2015, Huset et al. 2011, Eggen et al. 2010), analyses were performed with the computer program POLLUTE (Rowe et al. 1997) using diffusion coefficients for the geomembranes (GMBs) based on the current study. A preliminary diffusion coefficient for PFOA through GCL's is used based on unpublished data from current tests being performed by the authors. For the attenuation layer, the diffusion coefficient of chloride was used as an approximate based on Badv and Rowe (1996) and Rowe and Badv (1996a,b).

Based on the detection limit and upper bond estimate of S_{gf} can be calculated or the diffusion tests with no observable change in source concentration and all sorption tests. This calculation gives a maximum S_{gf} < 0.4 for GenX and PFBS based of diffusion test and 0.25 based on sorption tests. For PFOA, PFOS and 6:2FTS, S_{gf} < 0.05. However, S_{gf}=1 has been assumed. This raises the practical question: "What is the effect of the uncertainty regarding S_{gf}". This questions was examined by analyzing the data shown in Figure 3 for four combination of S_{gf} and D_g giving a value of P_g = 3.3x10^{-14} m^2/s for $0.001 \leq S_{gf} \leq 1$. The theoretical fit to the data shown in Figure 3 did not change perceptibly for any combination. Likewise, in modelling the landfill cases 1-4 (Table 5) there was negligible difference in the peak impact in the aquifer in all cases with a TPU geomembrane having a peak impact of 3.1-3.2 ng/L at about 280 years (Table 5).

Table 5: PFOA concentration in aquifer due to pure diffusion through liner and attenuation layer

Case	GMB	T (^oC)	P_g (m^2/s) 1-5 yr	P_g (m^2/s) > 5 yr	D_g (m^2/s) 1-5 yr	D_g (m^2/s) > 5 yr	S_{gf} (-)	c_p (ng/l)	t_p (yr)
1	TPU	50	3.3×10^{-14}	3.3×10^{-14}	3.3×10^{-11}	3.3×10^{-11}	0.001	3.1	280
2	TPU	50	3.3×10^{-14}	3.3×10^{-14}	3.3×10^{-12}	3.3×10^{-12}	0.01	3.1	280
3	TPU	50	3.3×10^{-14}	3.3×10^{-14}	3.3×10^{-13}	3.3×10^{-13}	0.1	3.1	280
4	TPU	50	3.3×10^{-14}	3.3×10^{-14}	3.3×10^{-14}	3.3×10^{-14}	1	3.2	280
5	TPU	40	1.6×10^{-14}	1.6×10^{-14}	1.6×10^{-14}	1.6×10^{-14}	1	1.7	300
6	EIA2	40	6.6×10^{-16}	6.6×10^{-16}	6.6×10^{-16}	6.6×10^{-16}	1	0.079	330
7	EIA1	40	6.1×10^{-16}	6.1×10^{-16}	6.1×10^{-16}	6.1×10^{-16}	1	0.073	330
8	EIA3	40	1.8×10^{-16}	1.8×10^{-16}	1.8×10^{-16}	1.8×10^{-16}	1	0.021	390
9	EIA3	40	1.8×10^{-15}	1.8×10^{-16}	1.8×10^{-15}	1.8×10^{-16}	1	0.036	370
10	EIA3	40	1.8×10^{-13}	1.8×10^{-16}	1.8×10^{-13}	1.8×10^{-16}	1	2.0	270

The second practical question is: "What is the effect of using the different polymers on the peak impact within the aquifer?". To answer this question, diffusive transport was modelled for 1.5 mm-thick geomembranes comprised of TPU, EIA2, EIA1, and EIA3 at 40^{o}C using P_g deduced from Eqs. in Table 2 for the four polymers and S_{gf}=1.

For PFOA and TPU with the highest P_g = 1.6x10^{-14} m^2/s, the purely diffusive impact was 1.7 ng/L at 300 years (Case 5; Table 5). This was still less than half US EPA's allowable value of 4 ng/L but nowhere as good as is achieved with the other three EIA GMBs. Of the three EIA polymers, EIA2 gave the highest impact of 0.079 ng/L at 330 years and EIA3 the lowest at 0.021 ng/L at 390 years. For TPU, at peak impact (300 years), 1.44% of the mass of PFOA in the landfill was lost due to diffusive contaminant transport through TPU; on the other hand, only 0.027% of the mass of PFOA in the landfill was lost due to diffusive transport at peak aquifer impact (390 years) using an EIA3 geomembrane.

If PFOS is the contaminant being modelled, and using a source concentration of 4800 ng/L in landfill leachate (Rowe and Barakat 2021) then for the parameters and model described above and a 1.5 mm-thick TPU geomembrane with P_g = 3.1x10^{-14} m^2/s, the purely diffusive aquifer impact was 73.1 ng/L at 230 years, where 7.5% of the mass of PFOS in the landfill being lost due to diffusive transport. If EIA3 was used as the geomembrane with P_g = 1.1x10^{-16} m^2/s, the peak impact was 0.08 ng/L at 440 years where 0.02% of the mass of PFOS in the landfill was lost due to diffusive transport only.

The third practical question is: "What is the possible effect of changes in pH in the landfill?". The diffusion coefficients presented in this paper are for pH ~7. In the very early (acetogenic phase during the first few years) of the landfill, the pH can range from 3.7 to 6.5 until the methanogenic phase shifts the pH to 7.0-8.5 for most of its contaminating lifespan (Armstrong and Rowe 1999; Wdowczyk & Szymańska-Pulikowska, 2021). The very low pH cited above is typical of landfills filled very quickly. More commonly, the pH is in the 5.8 to 7 range when new waste is placed over older waste for about the first decade of the landfill life and then in the 7 < pH < 8 range subsequently (Armstrong and Rowe 1999). It is possible that an acidic leachate solution could increase the mass unionised PFOA available for transfer by diffusion by about an order of magnitude per unit increase in pH. If this is assumed, then P_g with a pH = 6 is one order of magnitude higher than in Table 1 or calculated form Table 2 . Similarly, a pH ~4 would by the same argument increase P_g a 1000-fold, at the same total PFOA concentration, as examined in this study. This hypothesis is deserving of testing since it could be important for a small number of landfills. To evaluate the possible significance of a shift in pH between the first 5 years and subsequently, two analyses were performed for EIA3. In the first, the diffusion coefficient was increased by one order of magnitude for the first 5 years and then decreased to the value inferred for the Arrhenius plot for 40^{o}C (Table 2). The high initial P_g = 1.8x10^{-15} m^2/s for pH ~6 between 0 < t ≤ 5 years and subsequent 1.8x10^{-16} m^2/s, gave a diffusive impact of 0.036 ng/L at 370 years instead of 0.02 ng/L at 390 years if there is no change in the P_g value for the first 5 years (Table 5). The higher initial P_g = 1.8x10^{-13} m^2/s for pH ~4 between 0 < t ≤ 5 years and subsequent 1.8x10^{-16} m^2/s, gave a diffusive impact of 2 ng/L (half the allowable value) at 270 years instead of 0.02 ng/L at 390 years if there is no change in the P_g value for the first 5 years.(Table 5). Thus, there would be value in future studies examining the effect of pH.

6. Conclusion

Diffusion and sorption tests of PFOA, PFOS, PFBS, 6:2 FTS and GenX were conducted using three different PVC-EIA liners and TPU to investigate the diffusive and partitioning characteristics of these compounds through these new geomembranes. Tests were conducted at 23˚C, 35˚C and 50˚C. In addition, the permeation coefficients for PFOA and PFOS through LLDPE and Coextruded EVOH/ LLDPE liners are updated based on more than 3 years of test data. Based on the currently available data for the contaminants and materials examined, the following conclusions have been reached:

1. The diffusion rates for PFOA and PFOS through thermoplastic polyurethane (TPU) were substantially higher than through the PVC-EIA or LLDPE geomembranes.

2. The permeation coefficient for PFOA and PFOS diffusing through TPU and PVC-EIA, P_g, can be estimated over a range of temperatures from about 10° C (283 K) to 50° C (323 K) from equations given in the paper.
3. PFBS, 6:2 FTS, and GenX demonstrated very limited diffusion (concentration in the receptor <0.025%, <0.005% and <0.025% of that in the source, respectively) through the TPU or PVC-EIA geomembranes over the 535 days of testing reported herein.
4. The test data demonstrates that all three PVC-EIA geomembranes examined are excellent barriers to PFAS at temperatures at and below 35° C. For temperatures between 35 and 50° C, EIA3 may be regarded as an excellent diffusion barrier, EIA1 as a good diffusion barrier, and EIA2 as an acceptable diffusion barrier for the PFAS examined (i.e., it is very effective but not as effective as the other two PVC-EIA products tested).
5. Analysis of samples from the sorption test vials indicated negligible or no partitioning of contaminants to TPU and PVC-EIA which was consistent with the absence of any detectable decrease in source concentrations in many PVC-EIA experiments over the 535 days of testing.
6. Continued testing and analysis of the diffusion tests initiated by Di Battista et al. (2020) for PFOA and PFOS through LLDPE and Coextruded LLDPE EVOH geomembranes resulted in new estimates for their diffusion coefficients based on more than 3.4 years of accumulated data. The results prove that LLDPE and Coextruded LLDPE geomembranes are outstanding diffusive barriers to PFOA and PFOS.
7. No PFAS has been detected in the receptors of the LLDPE and coextruded LLDPE geomembranes even at 50℃ making them better diffusive barriers to PFAS when compared to the performance of the EIA3 geomembrane under the same conditions.

This paper has only considered diffusive contaminant transport. The other key factor that may impact contaminant transport through these geomembranes, the advective transport through holed wrinkles in the geomembrane, has not been considered. In addition, the possible effects of PFAS on geomembrane service life has not been considered in this paper and requires study for geomembranes used for long-term containment.

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Declaration of interests

☐The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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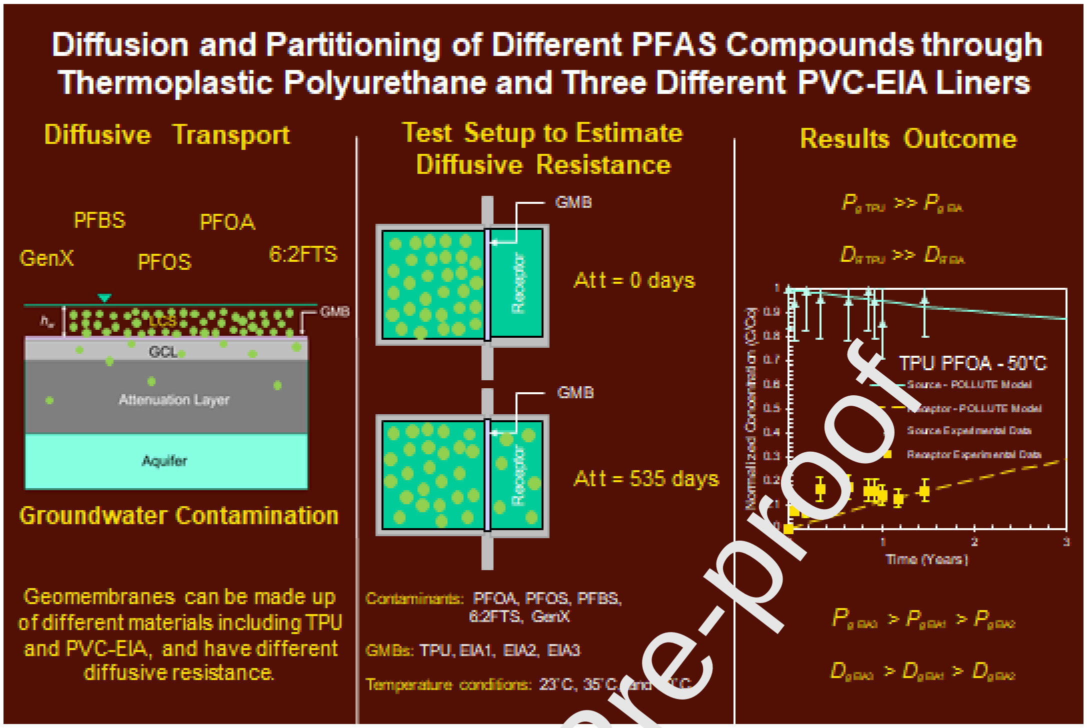
Graphical abstract



Diffusion and Partitioning of Different PFAS Compounds through Thermoplastic Polyurethane and Three Different PVC-EIA Liners

Diffusive Transport

Groundwater Contamination

Geomembranes can be made up of different materials including TPU and PVC-EIA, and have different diffusive resistance.

Test Setup to Estimate Diffusive Resistance

Contaminants: PFOA, PFOS, PFBS, 6:2FTS, GenX

GMBs: TPU, EIA1, EIA2, EIA3

Temperature conditions: 23°C, 35°C, and [illegible]°C

Results Outcome

$P_{g\,TPU} >> P_{g\,EIA}$

$D_{g\,TPU} >> D_{g\,EIA}$

$P_{g\,EIA3} > P_{g\,EIA1} > P_{g\,EIA2}$

$D_{g\,EIA3} > D_{g\,EIA1} > D_{g\,EIA2}$

Highlights of the Paper:

1. Provides the first estimates for the permeation and diffusion coefficients of PFOS, PFOA, PFBS, 6:2FTS and GenX through thermoplastic urethane and ethylene interpolymer alloy geomembrane liners based on diffusion tests from source through the geomembrane to the receptor at temperatures of 23 °C, 35 °C and 50 °C.
2. Compares the relative diffusive resistance of thermoplastic urethane and ethylene interpolymer alloy geomembrane liners to PFOS, PFOA, PFBS, 6:2FTS and GenX with linear low density polyethylene liners.
3. Significant diffusion of PFAS through the TPU geomembranes is observed relative to the PVC-EIA and LLDPE geomembranes tested. PVC-EIA and LLDPE geomembranes show very little PFAS diffusion through them making them excellent diffusion barriers PVC-EIA3 while the two LLDPE geomembranes allowed no measurable PFAS diffusing through them in 500 days under all temperature conditions making them better than PVC-EIA 1 and PVC-EIA 2 at PFAS resistance.

Keywords (6): diffusion, PFAS, geomembranes, sorption, PFOA, PFOS