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ORIGINAL PAPER

Diffusive Transport of Phenolic Compounds Through Two Coextruded Geomembranes

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Abstract This paper presents experimental results of a study of the diffusion of phenolic compounds through two High density polyethylene geomembranes (1 and 1.5 mm thick) with a coextruded ethylene vinyl-alcohol (EVOH) inner core. The partition and diffusion coefficients were quantified for 2,4,6-tricholophenol (2,4,6-TCP), 2,3,5,6-tetrachlorophenol (2,3,5,6 TeCP), and pentachlorophenol, which are known to be toxic even at very low concentrations. The concentration dynamics in the source and receptor chambers of the diffusion cells was interpreted with the help of the numerical code POLLUTE. For partition coefficients greater than those obtained under the same conditions for a high-density polyethylene (HDPE) geomembrane, the diffusion coefficients are smaller than those for the same HDPE geomembrane. As a result, the permeation coefficient of the two coextruded geomembranes is the same order of magnitude as that of a 2-mm-thick HDPE geomembrane. Therefore, in contrast to the case for volatile organic compounds, the EVOH inner core brings no significant improvement. These results are compared to those previously obtained with volatile organic compounds for HDPE geomembranes and coextruded geomembranes.

Keywords Geosynthetics · Diffusion · Phenolic compounds · EVOH

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Introduction

Landfills contain micropollutants that can have toxic effects on the environment (acute toxicity, genotoxicity, reproductive toxicity, etc.) [1, 2]. In several countries, the presence of organic contaminants in the leachate from municipal solid-waste landfills has been clearly established [3–6]. The most-frequently encountered organic micropollutants in leachate are monoaromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene) and polyaromatic (naphthalene, phenanthrene, etc.). In addition, some chlorinated solvents (trichlorethylene, chloromethane, etc.), plasticizers (phthalates, bisphenol A, etc.), pesticides, and phenolic derivatives are also found in leachate [7–15]. Phenolic compounds, especially certain derivatives of halogenated phenolic compounds, are known to be toxic to humans and the environment, even at very low concentrations. These compounds are used as disinfectants, biocides, preservatives, dyes, pesticides, and organic chemicals in medicine and industry [16–18].

To minimize the dispersal of such contaminants, geomembranes are widely used in geoenvironmental applications as barriers to water and contaminants. A number of studies regarding the use of geomembranes focused on the diffusion of sodium chloride [19] or volatile organic compounds (VOCs) in virgin high-density polyethylene (HDPE) geomembranes [20–24], virgin polyvinyl chloride (PVC) [25], linear low-density polyethylene (LLDPE) [25], LLDPE with a co-extruded ethylene vinyl-alcohol (EVOH) inner core [25–27], fluorinated HDPE geomembranes [28], and aged HDPE geomembranes [29–31].

Results obtained by McWaters and Rowe [25] indicate a significant reduction in mass flux through coextruded geomembranes compared with conventional LLDPE.

Coextruded geomembranes with an EVOH inner core have the lowest permeation coefficient, about 8×10^{-15} m^2/s for diffusion from the aqueous phase. These values for coextruded geomembranes are upper bounds; the actual values may be even less. The partition coefficients for the coextruded geomembrane range from 160 to 700 with respect to aqueous-phase concentrations. The resulting permeation coefficients thus range from 2×10^{-12} to 6×10^{-12} m^2/s for the coextruded geomembrane. Thus, a coextruded geomembrane offers a five- to 12-fold decrease in the permeation coefficient compared with a 2.0-mm-thick HDPE geomembrane [25].

Diffusion of phenolic compounds in HDPE geomembranes and HDPE films has also been the subject of recent study [32, 33]. Similar measurements were recently done on other types of geomembranes, including two geomembranes with a coextruded EVOH inner core. This paper reports and discusses the results obtained for diffusion of phenolic compounds through such geomembranes in order to assess their ability to retain other micro-organic pollutants than VOCs in landfills.

Materials and Methods

Geomembranes

The diffusive transport of phenolic compounds was examined in two co-extruded geomembranes with a 0.05-mm-thick layer of EVOH. Both geomembranes had HDPE outer layers and were 1.0 and 1.5 mm thick. Their rate of cristallinity was measured to be 50 %. With its polar oxygen-hydrogen (OH) groups, EVOH has outstanding barrier properties against nonpolar gases such as oxygen, nitrogen, volatile compounds, and helium [34]. EVOH laminar typically combines a highly ordered crystalline structure interspersed with disordered amorphous regions with high resistance against diffusion of gas and solvents [25, 34]. However, to the best of our knowledge, the diffusion of phenolic compounds in EVOH has not yet been studied.

Phenolic Compounds Under Study

This work investigates the adsorption of 13 phenolic compounds: phenol, o-cresol (2-MP), p-cresol (4-MP), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-xylenol (2,4-DMP), 3,4-xylenol (3,4-DMP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,5,6-tetrachlorophenol (2,3,5,6-TeCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), pentachlorophenol (PCP), and bisphenol A (BPA). Some of the physical and chemical properties of the selected phenolic compounds are given in Table 1.

All phenolic compounds studied except 2-chlorophenol are in the solid state at the laboratory temperature (23 °C), with their melting points between 33 and 191 °C. In general, these compounds dissolve poorly in water but well in organic solvents. Although the phenolic compounds with a high degree of chlorination ($pKa = 4.74$) are classified as acids, some of them have a high p*K*a. For example, phenol, methylphenol, and bisphenol A have p*K*a ~ 10. For chlorophenols, the dissociation constant of the chlorine-containing compound increases (i.e., $pKa = -\log$ Ka decreases) with increasing number of chlorine atoms in a molecule, from 2.29 for 2-chlorophenol to 5.85 for pentachlorophenol.

The octanol–water partitioning coefficient K_{ow} of the pollutants concerned by this work increases strongly with the number of chlorine atoms, whereas the water solubility (hydrophilicity) decreases. The degree of dissociation of chlorophenols increases (indicated by decreasing p*K*a) with increasing number of chlorine atoms. The properties of the various phenolic compounds are therefore expected to lead to different diffusion behavior in the geomembranes investigated in this study.

The phenolic compounds were chosen based on the following criteria: (1) polarity, (2) solubility in water, (3) mobility of pollutants in soils, (4) presence in leachate, and (5) toxicity. Concentrations were chosen based on two considerations: (1) a literature review to determine the minimum, maximum, and average concentrations of the phenolic compounds in leachate (see Table 2) [35–56], and (2) the limit of detection (LOD) and limit of quantification (LOQ) calculated according to the method developed by Limam et al. [57] to analyze these compounds via headspace solid-phase microextraction (HS-SPME) coupled with gas-chromatography mass spectrometry (GC–MS). The concentrations chosen for the chlorophenols and methylphenols are slightly greater than the average values found in leachate because the values encountered in the literature are significantly less than the LOQ.

The partition and diffusion coefficients could only be determined for 2,4,6-TCP, 2,3,4,6-TeCP, and PCP. For the other compounds, either the absorption was comparable to the diffusion in the source chamber (this was the case for the methylphenols) or the results tended to be suspect because inconsistent concentrations were obtained, both in the source and receptor chambers of the diffusion cell.

Experimental Procedure

Preparation of Solutions

Prior to the experiment, a stock solution of the 13 phenolic compounds dissolved in methanol was prepared at a

Table 1 Physical and chemical properties of phenolic compounds under study

Pollutants	Formula	Molecular weight (g/mol)	Solubility at 20 °C (g/L)	p*K*a at 25 °C	Log K_{ow}
Phenol	C_6H_6O	94.04	90	9.95	1.46
Methylphenols					
2-MP	C_7H_8O	108.14	26	10.20	1.96
4-MP	C_7H_8O	108.14	24	10.26	1.94
3,4-DMP	$C_8H_{10}O$	122.17	–	10.3	2.23
2,4-DMP	$C_8H_{10}O$	122.17	5	10.6	2.30
Chlorophenols					
2-CP	C_6H_5ClO	128.56	28	8.52	2.29
4-CP	C_6H_5ClO	128.56	27	9.37	2.53
2,4-DCP	$C_6H_4Cl_2O$	163.00	4.5	7.90	3.20
2,4,6-TCP	$C_6H_3Cl_3O$	197.45	0.434	6.00	3.67
2,3,4,6-TeCP	$C_6H_2Cl_4O$	231.89	0.183	5.22	4.24
2,3,5,6-TeCP	$C_6H_2Cl_4O$	231.89	0.100	5.02	5.02
PCP	C_6Cl_5OH	266.34	0.014	4.74	5.85
BPA	$C_{15}H_{16}O_2$	228.29	0.3	9.59–11.30	3.40

Table 2 Concentrations chosen for experiments from minimum and maximum values of concentrations measured in leachate

Contaminants	Min. value (μg/L)	Max. value (μg/L)	Mean value (μg/L)	Corrected mean (μg/L)	LOD (ng/L)	*c* (μg/L)
Phenol	0.030	1200.000	127.198	46.99	345.67	100
Methylphenols						
2-MP	0.070	185.000	71.607	71.60	43.76	100
4-MP	6.000	12,000.000	4493.200	588.00	14.51	100
3,4-DMP	0.030	10.400	3.423	3.42	–	10
2,4-DMP	0.120	13.000	4.504	4.50	18.88	10
Chlorophenols						
2-CP	0.003	0.510	0.107	0.06	16.47	10
4-CP	0.070	1.300	0.611	0.61	–	10
2,4-DCP	0.010	12.820	1.026	0.30	1.04	10
2,4,6-TCP	0.002	1.870	0.162	0.06	1.11	10
2,3,4,6-TeCP	0.032	20.400	2.709	0.18	1.54	10
2,3,5,6-TeCP	0.012	0.012	0.012	0.01	1.15	10
PCP	0.015	21.610	3.798	0.83	1.07	10
BPA	0.350	25,000.000	3565.900	784.50	1.37	1000

concentration 1000 times greater than the concentration of the solution used for the diffusion experiments (see Table 2). In a volumetric flask, 0.001 g of each chlorophenol was mixed with methanol to obtain 100 mL of the stock solution, which was then stored at −20 °C. To obtain the desired concentration for the diffusion experiments the stock solution was diluted with deionized distilled water (DDW). The resulting solution was used both as the source in the diffusion cells and for preparing standards with which to calibrate the gas chromatograph. The internal standard solution was prepared with 2,4,6-tricholorophenol 13C6 and pentachlorophenol 13C6, which are compounds containing isotopes of carbon 13 (13C6).

Batch-Partitioning Experiments

Experimental Procedure

Batch-partitioning experiments were performed at room temperature (23 ± 1 °C) in 200 mL glass bottles equipped

with screw-on Teflon-lined caps for sampling. The experimental procedure was based on that of Islam and Rowe [31]. The geomembranes were cut into pieces for the batch-partitioning experiments. According to Nefso and Burns [58], cutting the geomembrane into smaller pieces does not affect the ultimate sorption capacity because the equilibrium between organic-pollutant and polymer sorption is a dissolution-controlled process, not a surface-controlled process.

Four bottles were used. Bottles I1 and I2 contained 6 g of geomembrane cut into pieces and immersed in 120 mL of diffusion solution. Following Touze-Foltz et al. [32] and Mendes et al. [33], the solid/liquid ratio was 1/20. The other two bottles, C1 and C2, were used for control experiments and contained only a solution identical to that used in the diffusion tests (i.e., no geomembrane). A biocide agent (400 mg/L $HgCl_2$) was added to all four bottles to limit the effects of biodegradation, as recommended by Touze-Foltz et al. [32] and Mendes et al. [33]. To calculate the partition coefficient S_{gf}, the concentrations of the various chlorophenols were measured at the beginning (t_0) and at the end (t_f) of the diffusion experiments. To make the experiment repeatable, two samplings were taken from each of the four bottles at each specific sampling date.

Calculation of Partition Coefficient

The concentration of contaminant in the geomembranes, c_g, and in solution, c_f, are linked by Henry's Law [23]:

$$c_g = S_{gf} c_f, \tag{1}$$

where S_{gf} is the partition coefficient, which depends on temperature, fluid, geomembrane, and contaminant. The partition coefficients S_{gf} were calculated for each bottle and each phenolic compound by using the following equation adapted from Sangam and Rowe [23]:

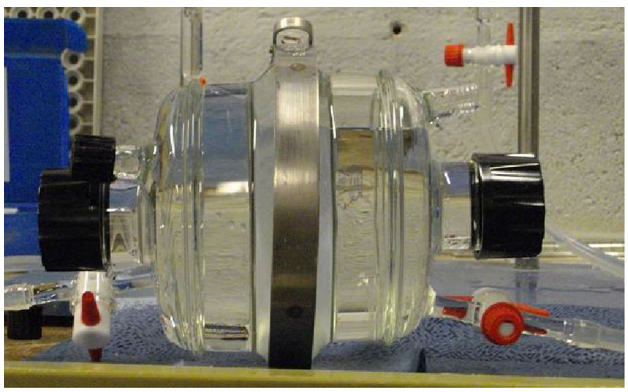

Fig. 1 Diffusion cell with two identical parts separated by the geomembrane and linked with metallic bridle. This cell is identical to the control test cell

$$S_{gf} = \frac{[(c_{f0} V_{f0})(1 - p_s) - c_{fF} V_{fF} - \Sigma c_i V_i]\rho_g}{M_g c_{fF}}, \tag{2}$$

where c_{f0} and c_{fF} are the initial and final concentrations of the solution in g/L, respectively, V_{f0} and V_{fF} are the initial and final volumes of the solution in L, respectively, p_s is the proportion of contaminant sorbed onto the glass as determined from the evolution of the concentration in bottles C_1 and C_2 and which is assumed to be independent of whether a geomembrane is present, ρ_g is the density in g/L of the geomembrane, and M_g is the initial mass in g of the geomembrane in bottles I_1 and I_2 (Fig. 1).

Diffusion Experiment

Apparatus

The apparatus, shown in Fig. 2, consists of two independent cylindrical glass chambers identical to the diffusion-experiment apparatus previously used by Touze-Foltz et al. [32, 59] to quantify the diffusion in HDPE geomembranes. Diffusion-experiment apparatus have an internal diameter of 0.12 m and the volume of each chamber is 0.73 L.

Each geomembrane specimen was placed between the two chambers of the diffusion-experiment apparatus, and the two chambers were then assembled with the help of a metal screw clamp. No sealant or O-ring was used. Each geomembrane was in direct contact with the glass cell on both sides. Each chamber contained a sampling port with a Teflon cap and a second port that could be used to fill the cell.

To assess the mass loss due to sorption onto the glass cell, the same diffusion apparatus was used as a control cell in blank experiments (i.e., with no geomembrane). Blank experiments were performed in parallel to the diffusion experiments. None of the samples were stirred.

Experimental Procedure

The experimental procedure is as follows: (i) The receptor chamber of the diffusion cell is filled with DDW, (ii) the source chamber of the diffusion cell is filled with the previously prepared diffusion solution containing chlorophenols, (iii) in both chambers, 400 mg/L of a biocide agent ($HgCl_2$) is added to minimize biodegradation of the phenolic compounds, and (iv) the cells are covered with aluminum sheets to avoid photodegradation of the phenolic compounds. The experimental configuration ensured that there was no hydraulic gradient. The experiments were performed at 23 ± 1 °C in glass cells.

The solutions were immediately sampled (in duplicate) to establish the initial concentrations of each phenolic compound in the source and receptor chambers. Subsequent

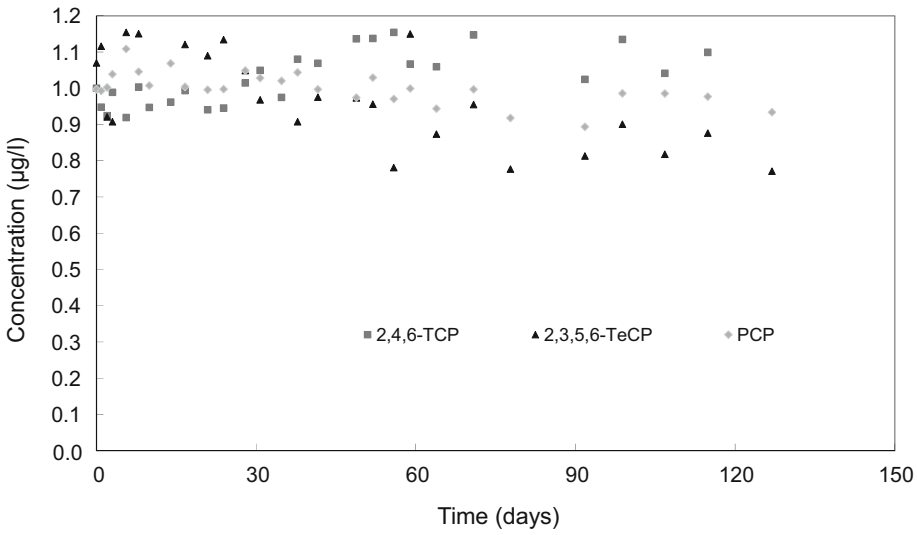

Fig. 2 Relative concentration as a function of time in blank diffusion experiment

samplings were performed at regular time intervals (in duplicate) from both the source and receptor chambers. Samples were taken by inserting a syringe through the Teflon-lined septum of the sampling ports.

Calculation of Diffusion Coefficient

The diffusion of organic compounds through geomembranes can be modeled by Fick's first law [23]:

$$f = -D_g \frac{dc_g}{dz}, \tag{3}$$

where f is the mass flux or permeation rate per unit area (g/m^2/s), D_g is the diffusion coefficient of organic compounds (m^2/s), c_g is the concentration of the compound in the geomembrane (g/L), and z is the distance parallel to the direction of diffusion (m).

According to Fick's second law, the change with time t in contaminant concentration at any point in the geomembrane is governed by the differential equation [23]:

$$\frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial z^2}. \tag{4}$$

The experimental procedure was based on concepts and theory proposed for geomembranes by Rowe et al. [29], Sangam and Rowe [23], and Islam and Rowe [31]. For these closed systems, the mass of contaminant in the source solution at any time t equals the initial mass minus the mass that diffused through the geomembrane. This can be expressed as

$$c_t(t) = c_0 - \frac{1}{H_s}\int_0^1 f_t(\tau)d\tau, \tag{5}$$

where $c_t(t)$ is the concentration in g/L of contaminants in the source solution at time t, c_0 is the initial concentration in g/L in the source solution, H_s is the height in meters of the source fluid (volume of source fluid per unit area), and $f_t(\tau)$ is the mass flux in g/m^2/s of contaminant into the geomembrane at time τ. The concentration $c_b(t)$ in the receptor compartment at any time can be expressed as

$$c_b(t) = c_{b0} - \frac{1}{H_b}\int_0^1 f_b(\tau)d\tau, \tag{6}$$

where $c_{b0}(t)$ is the initial concentration in g/L in the receptor solution, H_b is the height in meters of the receptor (volume of receptor chamber per unit area), and f_b (τ) is the mass flux in g/m/s of contaminant into the receptor chamber at time τ.

The diffusion coefficient D_g and partition coefficient S_{gf} were deduced by using the procedure described by Sangam and Rowe [23] and the finite-layer analysis program POLLUTE ver. 7© [60].

The permeation coefficient is obtained as the product of the diffusion coefficient by the partition coefficient.

Analytical Methods

The concentration of each phenolic compound in solution was measured by HS–SPME–GC–MS following the analytical method developed by Limam et al. [57]. The GC–MS (trace GC and DSQ, dual-stage quadrupole, Thermo Fischer) was equipped with a Combi PAL autosampler (CTC Analytics) to enable automatic SPME extraction. The GC split-splitless injector was operated in splitless mode. The chromatographic column was a Zebron 5 MS column

(5 % phenyl-methylpolysiloxane, Phenomenex, 60 m length, 0.25 mm inner diameter, 0.25 μm film thickness). Chromatographic separation was done by using the following eight temperature stages: (1) 40 °C for 5 min; (2) an increase to 115 °C at 15 °C/min; (3) an increase to 175 °C at 3 °C/min; (4) 175 °C for 5 min; (5) an increase to 250 °C at 30 °C/min; (6) 250 °C for 2 min; (7) an increase to 280 °C at 30 °C/min, and (8) 280 °C for 5 min. The injector temperature was held at 250 °C and the splitless time was 5 min. Helium served as carrier gas with a column flow rate of 1.1 mL/min. The Xcalibur software from Thermo Fisher was used for online data acquisition and processing. The fiber consisted of a 100 μm polydimethylsiloxane (PDMS) from Supelco. Two internal standards were used for quantification: (a) 4,6-trichlorophenol-13C for 2,4,6-TCP and (b) pentachlorophenol-13C6 for 2,3,5,6-TeCP and PCP.

The quantification procedure involved two steps: derivatization and headspace extraction. The derivatization step consists of adding 2 g of sodium chloride (NaCl; 40 % W/V), 200 mg of potassium bicarbonate ($KHCO_3$), and 30 μL of anhydride acetic acid [$(CH_3CO)_2O$] into a 20 mL PTFE-capped glass vial containing 5 mL of aqueous sample. The sodium chloride saturates the solution, which permits the phenolic compounds to pass easily into the gas phase, thereby improving the sensitivity of the measurement. The sodium bicarbonate ($KHCO_3$) avoids degradation of the phenolic compounds that would otherwise result from the addition of anhydride acetic acid [$(CH_3CO)_2O$]. The sequence in which these reagents are added is essential because introducing the anhydride acetic acid [$(CH_3CO)_2O$] first could lead to underestimating the compound concentration. The derivation reaction is completed with a 5 min 80 °C pre-incubation period.

Pre-incubation was followed by extraction of the given chlorophenol compound by using the SPME fiber covered with a 100-μm-thick PDMS film at 80 °C for 30 min under agitation (500 rpm). Injection into the GC–MS was done at 250 °C, lasted 5 min, and led to desorption of phenolic compounds from the fiber in the injector. Phenolic compounds were quantified by using the single-ion monitoring mode (SIM). The ion mass-to-charge ratio $m/Z = 196$, 232, and 266 were used for 2,4,6-TCP; 2,3,5,6-TeCP; and PCP, respectively.

Results

Control Cell

To access the mass loss due to sorption onto the glass cell, a blank diffusion experiment was done by using the diffusion apparatus with no specimen. The experiment was done in parallel with the diffusion experiments. Figure 2 presents the temporal evolution of contaminant concentrations (normalized with respect to initial concentration) in blank diffusion experiments. The decrease in concentration due to sorption is negligible for the three chlorophenols.

Partitioning Tests

Following the methodology described in "Batch-Partitioning Experiments" section, the partition coefficients S_{gf} for each phenolic compound were calculated with the assumption that the mass loss onto glass would occur even in the presence of a geomembrane. The corresponding partition coefficients are given in Table 3 where, for the sake of comparison, the values obtained by Touze-Foltz et al. [32] for a HDPE geomembrane are also reported.

The only difference is the partition coefficients obtained for 2,4,6-TCP. This result is considered very reliable because it was obtained based on the measurement of four different batch tests for each geomembrane (two for lot A and two for lot B). For all three phenolic compounds, the partition coefficients obtained for the EVOH geomembranes are larger than those measured for a HDPE geomembrane.

Diffusion Experiments

Figure 3 shows the concentration dynamics of 2,4,6 TCP in the source chamber and the adjustment made with POLLUTE with diffusion coefficients of 5×10^{-15} and 4×10^{-14} m^2/s, respectively, for the 1 and 1.5-mm-thick geomembranes. With these diffusion coefficients and partition coefficients, negligible concentrations accumulate in the receptor chamber during the measurement. The results of the model are consistent with experimental results on this score.

Figure 4a, b show the concentration dynamics of 2,3,5,6 TeCP in the source and receptor chambers, respectively. These curves were obtained for diffusion coefficients of 2×10^{-14} and 3×10^{-14} m^2/s for the 1 and 1.5-mm-thick geomembranes, respectively.

Figure 5 shows the concentration dynamics of PCP in the source chamber and the adjustment obtained made with

Table 3 Inferred partition coefficients from measurements made for present study and from HDPE geomembranes according to Touze-Foltz et al. [32]

Contaminants	$S_{gf\ 1mm}$ (−)	$S_{gf\ 1.5\ mm}$ (−)	S_{gf} for HDPE (-)
2,4,6-TCP	265	103	18
2,3,5,6-TeCP	378	377	38
PCP	480	480	205

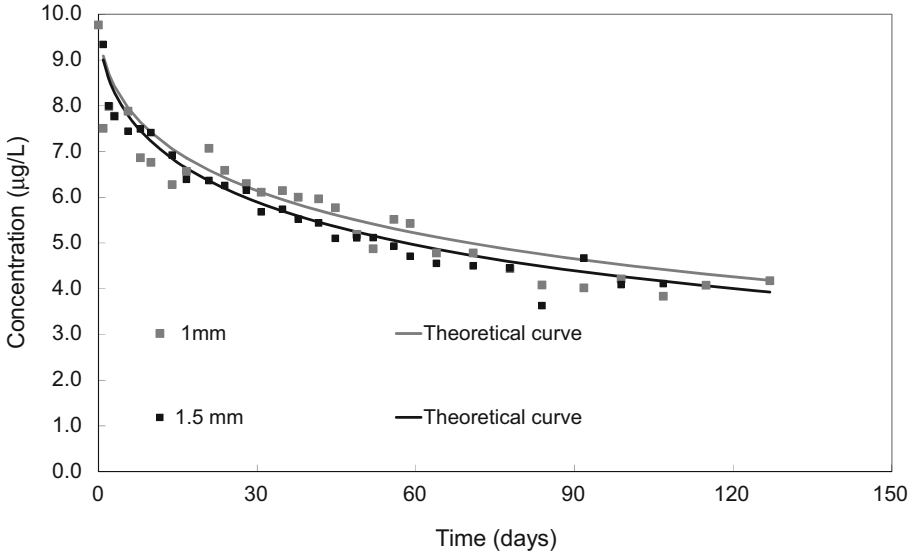

Fig. 3 Concentration as a function of time in source of diffusion cell for 2,4,6-TCP for both geomembranes and with adjustment done with POLLUTE ver. 7

POLLUTE with a diffusion coefficient of 10^{-13} m^2/s for both geomembranes.

Diffusion coefficients corresponding to the best-fit curve are given in Table 4, together with the permeation coefficient P_g, which is the product of the partition coefficient and the diffusion coefficient. In the same table, these two coefficients are compared to previous results for the same coefficients obtained by Touze-Foltz et al. [32] for a HDPE geomembrane measured under similar conditions. The permeation coefficients are comparable for both types of geomembranes. Results obtained for both coextruded geomembranes and for the HDPE geomembrane are of the same order of magnitude.

Discussion

Influence of Chlorine Atoms on Diffusion Parameters

The results indicate that the partition coefficient is closely linked to the degree of substitution of chlorine atoms on the phenolic nucleus. Larger numbers of chlorine atoms correspond to larger partition coefficients. This phenomenon is most likely due to the difference in polarity of the chlorophenols, as previously noticed by Touze-Foltz et al. [32] and Mendes et al. [33] for HDPE films and geomembranes.

Diffusion coefficients generally increase with increasing number of chlorine atoms.

Influence of *n*-Octanol–Water Partition Coefficient

Previous studies revealed that the *n*-octanol–water partition coefficient, log K_{ow}, affects the molecular diameter d_m, the solubility S, and the molecular weight and thereby affects the diffusion coefficient, partition coefficient, and permeation coefficient. As found in the present study, the diffusion coefficient is two orders of magnitude less than the diffusion coefficient for HDPE geomembranes, and the partition coefficient is two orders of magnitude greater than the partition coefficient for HDPE geomembranes. This combination results in a permeation coefficient that is the same order of magnitude because it is the product of the diffusion coefficient and the partition coefficient. The evolution of the permeation coefficient is shown in Fig. 6.

Figures 6 shows permeation coefficients for VOCs and phenolic compounds both from the literature and from this study. In Fig. 6a–d, the data displayed regarding the diffusion of VOCs in HDPE geomembranes originate from Park and Nibras [20], Prasad et al. [21], Müller et al. [22], Rowe [61], Sangam and Rowe [23], Rowe et al. [29], Joo et al. [62, 63], Nefso and Burns [58], Islam and Rowe [31], Touze-Foltz et al. [59], and Park et al. [24]. Data regarding the diffusion of VOCs in coextruded geomembranes originate from McWatters and Rowe [25] and Eun et al. [27]. The diffusion of phenolic compounds through a 2-mm-thick HDPE geomembrane was quantified by Touze-Foltz et al. [32] and by Mendes et al. [33] for 0.3-mm-thick HDPE films. These data show that the permeation coefficient increases with increasing log K_{ow}.

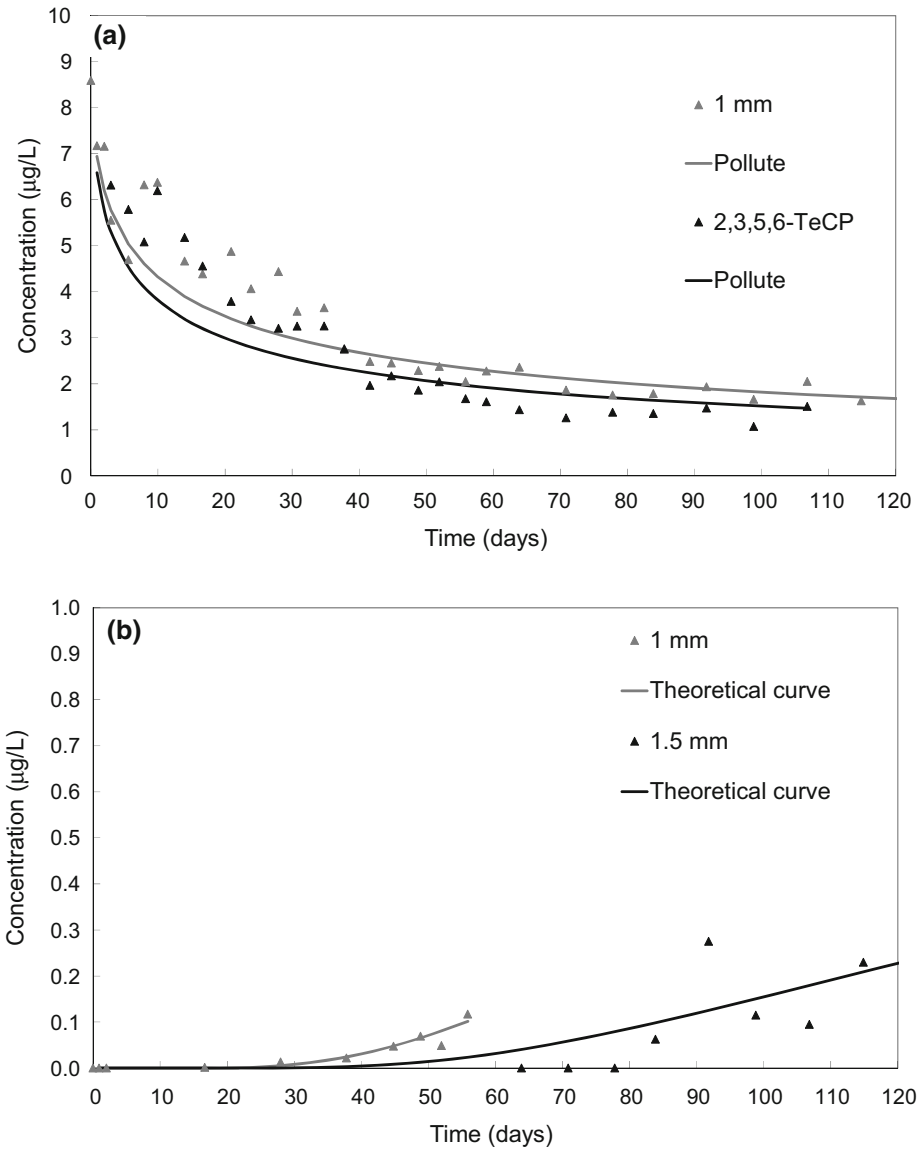

Fig. 4 Concentration as a function of time **a** in source of diffusion cell and **b** in receptor of diffusion cell for 2,3,5,6-TeCP and adjustment with POLLUTE ver. 7 for both geomembranes

Two different trends appear in Fig. 6a: a first cloud of data points that corresponds to the diffusion of VOCs (squares) and a second cloud of data points that corresponds to data for the diffusion of phenolic compounds (triangles). These data show that the permeation coefficient is larger for VOCs than for phenolic compounds.

Note that, although the permeation coefficient for VOCs in coextruded geomembranes is less than that obtained in HDPE geomembranes, this is not the case for the diffusion of phenolic compounds. In fact, as previously noticed in Table 3, for a given contaminant (which also means a given log K_{ow}), the permeation coefficient obtained for co-extruded geomembranes are similar to that obtained for HDPE geomembranes. The smallest permeation coefficients are obtained from the HDPE films measured by Mendes et al. [33].

Influence of Solubility

Figure 6b shows the permeation coefficient as a function of solubility. The permeation coefficient decreases with increasing solubility. Again, two very distinct trends appear, with the cloud of data for the diffusion of VOCs being separate from the cloud of data for the diffusion of phenolic compounds, which is attributed to both families having different ranges of solubility. The decrease of the permeation coefficient with solubility is almost linear for phenolic compounds, whereas no clear trend appears for the permeation coefficient with VOCs. This result may be connected with the number of data, which is greater for phenolic compounds because they have been more studied up to now.

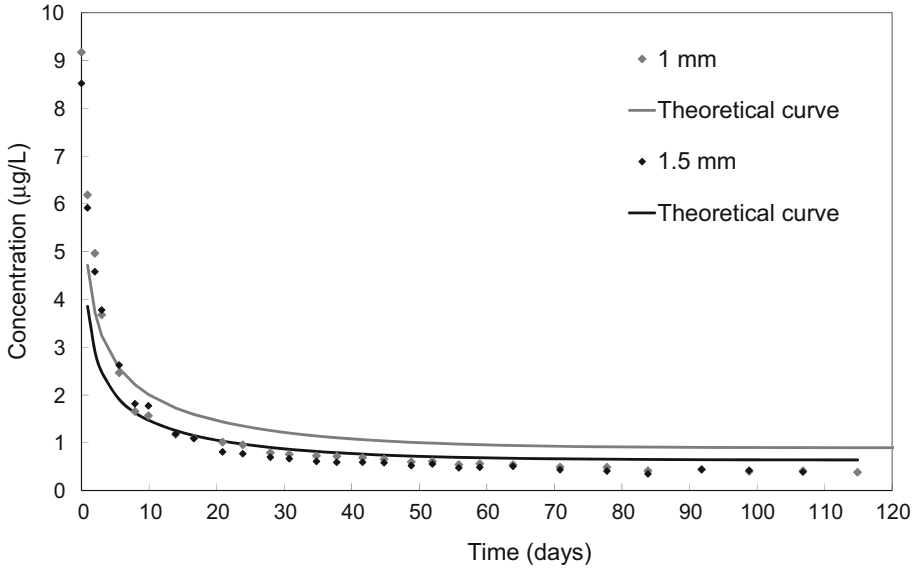

Fig. 5 C oncentration as a function of time in source of diffusion cell for PCP and adjustment with POLLUTE ver. 7 for both geomembranes

Table 4 Inferred diffusion and permeation coefficients from measurements made for present study and from a HDPE geomembrane according to Touze-Foltz et al. [32]

Contaminants	1 mm GMB		1.5 mm GMB		HDPE GM	
	Dg ($\times 10^{-14}$m^2/s)	Pg ($\times 10^{-14}$m^2/s)	Dg ($\times 10^{-14}$ m^2/s)	Pg ($\times 10^{-14}$m^2/s)	Dg ($\times 10^{-14}$m^2/s)	Pg ($\times 10^{-14}$m^2/s)
2,4,6-TCP	0.5	132	4	412	15	270
2,3,5,6-TeCP	2	756	3	1131	23	885
PCP	10	4800	10	4800	18	3699

Influence of Molecular Diameter

Figure 6c shows the partition coefficients as a function of molecular diameter. Again, the data for the diffusion of VOCs are distinct from those for phenolic compounds. No clear trend appears regarding the evolution of the permeation coefficient with molecular diameter. This parameter seems to be the less explicative of all.

Influence of Molecular Weight

Figure 6d shows the permeation coefficients as a function of molecular weight. The results show that the permeation coefficient increases with molecular weight. The range of molecular weights for phenolic compounds is larger than for VOCs, which results in a wider distribution of partition coefficients for the former.

The good correlation observed for phenolic compounds may be explained by the fact that differences in molecular weight are due to the number of chlorine atoms in a molecule: The more chlorine atoms in a molecule, more apolar it is. Thus, for chlorophenols, the good correlation between molecular weight and partition coefficient may be related to polarity.

Conclusion

The diffusion of three phenolic compounds, 2,4,6-TCP, 2,3,5,6-TeCP, and PCP was quantified for 1 and 1.5-mm-thick coextruded geomembranes. The results for the partition coefficient and diffusion coefficient are very consistent for both geomembranes for 2,3,5,6-TeCP and PCP. For 2,4,6-TCP, the coefficients are slightly different for geomembranes of different thickness.

The partition coefficients are larger for the coextruded geomembranes than for HDPE geomembranes. This result is balanced by smaller diffusion coefficients for both coextruded geomembranes. This leads to permeation coefficients that are of the same order of magnitude for coextruded geomembranes and HDPE geomembranes.

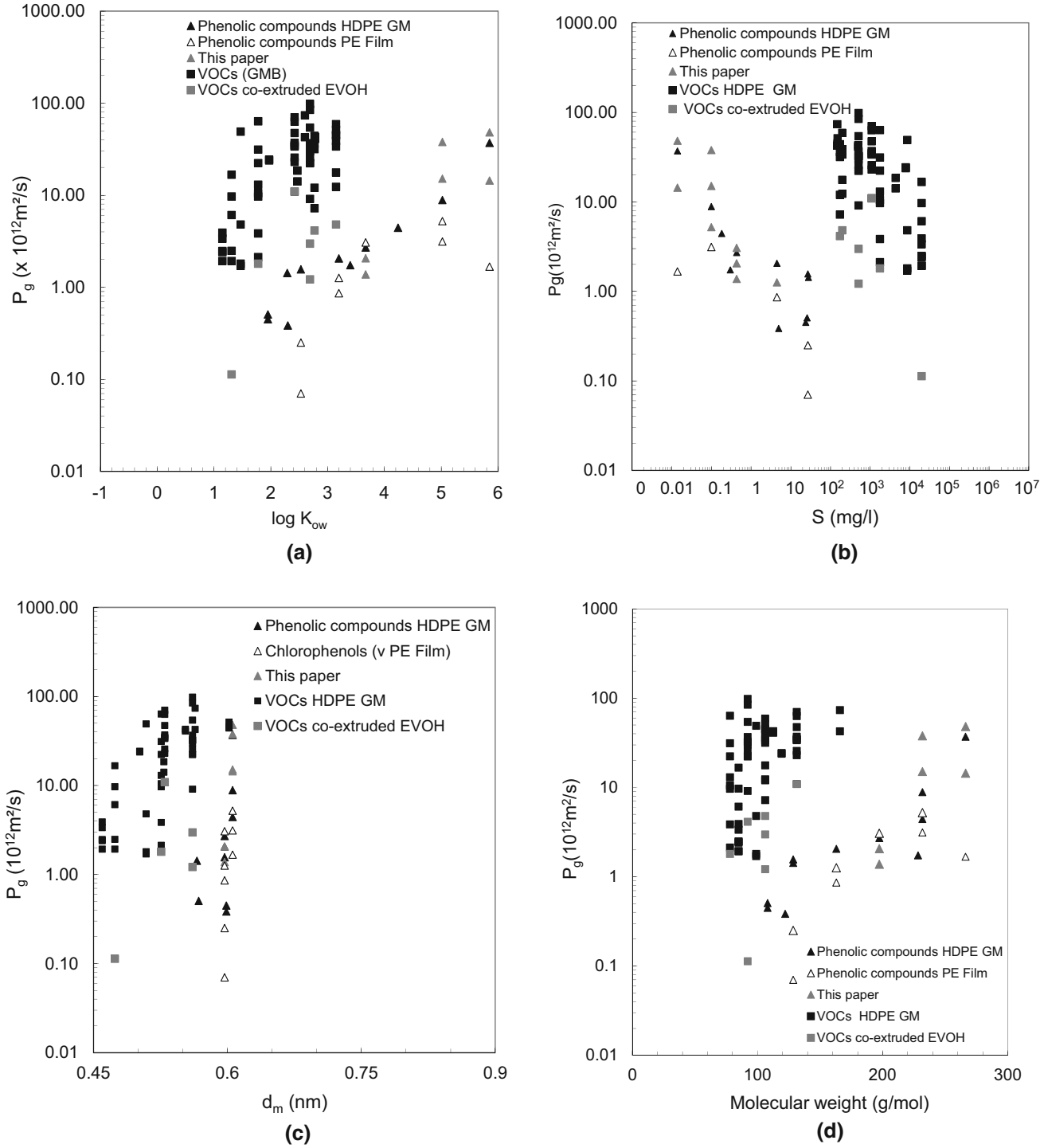

Fig. 6 Overview of permeation coefficients for the diffusion of VOCs and phenolic compounds in HDPE and coextruded geomembranes

These results thus differ from those previously obtained for the diffusion of VOCs in coextruded geomembranes and HDPE geomembranes. In fact, smaller permeation coefficients were obtained with coextruded geomembranes than with HDPE geomembranes. Nevertheless, the results of this study of the diffusion of phenolic compounds in a coextruded HDPE geomembrane tested indicate that the two coextruded HDPE geomembranes perform similarly to a HDPE geomembrane with respect to the diffusion of 2,4,6 TCP, 2,3,5,6 TECP, and PCP.

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