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Diffusion of Phenolic Compounds through an HDPE Geomembrane

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ABSTRACT: The experimental results obtained regarding diffusion through a high density polyethylene geomembrane of phenol, o-cresol, p-cresol, 2,4-xylenol, 3,4-xylenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, 2,3,5,6-tetrachlorophenol, pentachlorophenol and bisphenol A are presented. Partitioning coefficients range from 0.3 to 205 respectively for phenol and pentachlorophenol. Diffusion coefficients lie in the range 1.1×10^{-13} to 4.3×10^{-13} m²/s respectively for 2-methylphenol and bisphenol A. The effect of aqueous solubility, n-octanol/water partitioning coefficient, molecular diameter and molecular weight on partitioning coefficient, diffusion coefficient and permeation coefficient were studied. Different trends from the ones previously given in the literature for volatile organic compounds (VOCs) were observed. An increase in the number of chlorine atom on the phenolic nucleus results in an increase of the partitioning coefficient and permeation coefficient, probably linked to the polarity of the molecules under study.

1. INTRODUCTION

Landfills contain micropollutants which can have toxic effects (acute toxicity, genotoxicity, reproductive toxicity etc.) (Sisinno et al. 2000; Takigami et al. 2002). Indeed, the presence of organic contaminants in the leachate from municipal solid waste landfills has been clearly demonstrated in several countries (Oman and Hynning 1993; Ahel and Tepic 2000; Robinson et al. 2001; Hiroshi et al. 2002).

The most frequently encountered organic micropollutants in leachate are monoaromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene) and polyaromatic (naphthalene, phenanthrene etc.). Some chlorinated solvents (trichlorethylene, chloromethane etc.), plasticizers (phthalates, bisphenol A etc.), pesticides and phenolic derivatives are also found in leachate (Harmsen 1981; Bauer and Herrmann 1997; Staples et al. 1998; Gron et al. 1999; Christensen et al. 2001; Cousins et al. 2002; Kjeldsen et al. 2002; Niederer and Goss 2008, Van Praagh et al., 2011).

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 (Ramamoorthy and Ramamoorthy 1997; Kujawski et al. 2004; Otero et al. 2005).

Geomembranes are widely used in geoenvironmental applications where they act as barrier to water and contaminants. A number of studies regarding the use of geomembranes focused on the diffusion of sodium chloride (Rowe et al. 1995) or volatile organic compounds (VOCs) for virgin HDPE geomembranes (Park and Nibras 1993; Prasad et al. 1994; Müller et al. 1998; Sangam and Rowe 2001; Park et al. 2012) virgin PVC, LLDPE with and without a co-extruded ethylene vinyl-alcohol (EVOH) inner core geomembranes (McWaters and Rowe 2008, 2010), fluorinated HDPE geomembranes (Sangam and Rowe 2005) and aged HDPE geomembranes (Rowe et al. 2003; Islam and Rowe 2008, 2009).

Diffusion has not been up to now studied for other organic micropollutants than VOCs. It is thus the objective of this paper to present the results obtained while studying the diffusion of phenol, o-cresol, p-cresol, 2,4-xylenol, 3,4-xylenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, 2,3,5,6-tetrachlorophenol, pentachlorophenol and bisphenol A through a virgin HDPE geomembrane. Results are further compared to previous results obtained for VOCs and to trends presented in the literature as regards the evolution of the diffusion coefficient, partitioning coefficient and permeation coefficient with the solubility in water, the octanol water partitioning coefficient, the molecular diameter, and the molecular weight.

2. EXPERIMENTAL PROCEDURE

2.1 HDPE geomembrane

The study was conducted using a 2 mm thick HDPE geomembrane representative of the HDPE geomembranes encountered in landfill bottom liners in Europe. Its crystallinity measured according to ASTM E 794 is 59.1%. This geomembrane is similar to the one used by Touze-Foltz et al. (2011) while studying the diffusion of VOCs.

2.2 Phenolic compounds

2.2.1 Description of the phenolic compounds under study

The adsorption of 13 phenolic compounds was studied in this paper: 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 one, i.e. 2-chlorophenol, are in a solid state at the laboratory temperature (23°C), with their melting points between 33 and 191 °C. In general, these compounds dissolve weakly in water, but well in organic solvents. Although they are classified as acids, mainly those with a high degree of chlorination ($pK_a = 4.74$), some of them have a high pK_a . Indeed, phenol, methylphenols and bisphenol A have a pK_a around 10. In the case of chlorophenols, the dissociation constant of a compound increases (i.e. its $pK_a = -\log K_a$ decreases), with the 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 under study in this paper strongly increases with the number of chlorine atoms whereas the water solubility (hydrophilicity) decreases. The degree of dissociation of chlorophenols increases (indicated by decreasing pK_a values) with increasing number of chlorine atoms. It is thus expected that the difference in properties of the various phenolic compounds results in differences in diffusion behaviour in the geomembrane tested in this paper.

The selection of those phenolic compounds was performed taking into account 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 different elements: (1) a literature review to determine minimum, maximum and average values of concentrations of those phenolic compounds in leachate presented in Table 2 (Reinhard and Goodman 1984; Sawhney and Kozloski 1984; Oman and Hynning 1993; Schrab et al. 1993; Nininen and Kalliokoski 1994; Yasuhara et al. 1997; Lee et al. 1998; Viraraghavan and Alfaro 1998; Yamada et al. 1999; Yasuhara et al.

1999; Banat et al. 2000; Paxeus 2000; Behnisch et al. 2001; Yamamoto et al. 2001; Koumanova and Peeva-Antova 2002; Ribeiro et al. 2002; Reitzel and Lendin 2002; Schwarzbauer et al. 2002; Baun et al. 2004; Nagasaki et al. 2004; Yu et al. 2004; Ozkaya 2005; Slack et al. 2005; Richards and Bouazza 2007); and (2) on the values of limit of detection (LOD) and limit of quantification (LOQ) calculated using the method developed by Limam et al. (2010) to

analyze these compounds via the headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography-mass spectrometry (GC-MS) which was used in this paper. Concentrations chosen for the chlorophenols and methylphenols are slightly larger than average values found in leachate, since values encountered in the literature are significantly lower than the LOQ.

Table 1 Physical and chemical properties of the phenolic compounds under study

Pollutants	Formula	Molecular weight (g/mol)	Solubility at 20°C (g/L)	pK _a 25°C	Log K _{ow}
Phenol	C ₆ H ₆ O	94.04	90	9.95	1.46
<i>Methylphenols</i>					
2-MP	C ₇ H ₈ O	108.14	26	10.20	1.96
4-MP	C ₇ H ₈ O	108.14	24	10.26	1.94
3,4-DMP	C ₈ H ₁₀ O	122.17	-	10.3	2.23
2,4-DMP	C ₈ H ₁₀ O	122.17	5	10.6	2.30
<i>Chlorophenols</i>					
2-CP	C ₆ H ₅ ClO	128.56	28	8.52	2.29
4-CP	C ₆ H ₅ ClO	128.56	27	9.37	2.53
2,4-DCP	C ₆ H ₄ Cl ₂ O	163.00	4.5	7.90	3.20
2,4,6-TCP	C ₆ H ₃ Cl ₃ O	197.45	0.434	6.00	3.67
2,3,4,6-TeCP	C ₆ H ₂ Cl ₄ O	231.89	0.183	5.22	4.24
2,3,5,6-TeCP	C ₆ H ₂ Cl ₄ O	231.89	0.100	5.02	5.02
PCP	C ₆ Cl ₅ OH	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 the 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
<i>Methylphenols</i>						
2-MP	0.070	185.000	71.607	71.60	43.76	100
4-MP	6.000	12000.000	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
<i>Chlorophenols</i>						
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	25000.000	3565.900	784.50	1.37	1000

2.2.2 Preparation of the solutions

In a volumetric flask, 0.01g of each chlorophenol, and each methylphenol were mixed with 0.1g of phenol, o-cresol and p-cresol and 1g of BPA in absolute methanol to obtain 100mL of a stock solution. The desired amount of this stock solution was introduced in the bottles in the case of partitioning tests and in the source of the diffusion cells in the case of diffusion tests. The bottles and diffusion cells were subsequently filled with deionised distilled water (DDW) to obtain the desired concentration.

A preliminary test evidenced a biodegradation of some of the phenolic compounds under study during the batch partitioning and diffusion tests. It was thus decided to add a biocide agent (400mg/L HgCl₂) to limit the effects of biodegradation.

2.3 Analytical methods

The quantification of phenolic compounds was performed by solid phase microextraction gas chromatography - mass spectrometry (SPME-GC-MS) using the analytical procedure developed by Limam et al. (2010). The GC-MS (trace GC and DSQ, Thermo Fischer) was equipped with a Combi PAL autosampler (CTC Analytics) allowing automatic SPME extraction. The GC split-

splitless injector was operating in the Splitless mode. The chromatographic column was a Zebron 5 MS column (5% phenylmethyl polysiloxane, Phenomenex, 60m length, 0.25mm I.D., 0.25µm film thickness). Chromatographic separation was performed using the following temperature program: 40°C for 5 min; ramp one to 115°C at 15°C.min⁻¹; ramp two to 175°C at 3°C.min⁻¹; 175°C for 5 min; ramp three to 250°C at 30°C.min⁻¹; 250°C for 2 min; ramp four to 280°C at 30°C.min⁻¹ and finally 280°C for 5 min. The injector temperature was held at 250°C and the splitless-time was 5 min. Helium was used as the carrier gas with a column flow rate of 1.1 ml.min⁻¹. Xcalibur Software was used for online data acquisition and processing. The fiber used was a 100µm polydimethylsiloxane (PDMS) from Supelco.

Phenol-d5 was used as internal standard for quantification of phenol, 2-MP, 4-MP, 2,4-DMP and 3,4-DMP, 2,4,6-trichlorophenol-13C for 2-CP, 4-CP, 2,4-CP and 2,4,6-TCP, pentachlorophenol-13C6 for 2,3,4,6-TeCP, 2,3,5,6-TeCP and PCP, and bisphenol A-d4 for bisphenol A.

The procedure took place in two steps: a derivatization and a headspace extraction.

In the derivatization step 5mL of aqueous sample was introduced in a 20mL PTFE-capped glass vial. Sodium chloride at

40% (W/V), 200mg of KHCO_3 and 30 μL of acetic anhydride were added. A preincubation step of 5 min at 80°C was then necessary to obtain a complete derivatization reaction prior to the extraction step.

Then the headspace extraction of target compounds was performed with a $100\mu\text{m}$ PDMS SPME fiber at 80°C for 30 min with agitation (500 rpm). Afterwards, the SPME fiber was desorbed in the injector at 250°C for 5 min. GC/MS analysis was then performed as previously described.

Phenolic compounds quantification was performed using the single ion monitoring mode. The ions m/z 94; 99; 108 ; 122; 128; 162; 196; 202; 213; 217; 232; 266; 274 were used respectively for the phenol; phenol-d5; 2-MP and 4-MP; 2,4-DMP and 3,4-DMP; 2-CP and 4-CP; 2,4-DCP; 2,4,6-TCP; 2,4,6-TCP-13C; BPA; BPA-d4; 2,3,4,6-TeCP and 2,3,5,6-TeCP; PCP; PCP-13C.

3. TEST PROCEDURES

3.1 Control cell

Control tests were performed in a cell identical to those used for the batch partitioning test and the diffusion tests to assess the losses that may occur during the test due to chemical/cell material interaction as no geomembrane is introduced in those tests.

3.2 Batch partitioning test

3.2.1 Experimental procedure

Batch partitioning tests were performed at room temperature (i.e. $23 \pm 1^\circ\text{C}$) in 120mL glass bottles equipped with screw-tight Teflon lined caps for sampling. The bottles were covered with an aluminium foil in order to avoid photooxidation. The experimental procedure followed was grounded onto the one described by Islam and Rowe (2009). In preparing the geomembranes for batch partitioning experiments, the HDPE geomembrane were cut into four pieces (30mm x 20mm) weighing 6g in total. According to Nefso (2007) cutting the geomembrane into smaller pieces does not affect the ultimate sorption capacity, because organic/polymer equilibrium sorption is a dissolution controlled process, and not a surface controlled process.

The geomembrane pieces were immersed in solutions at the concentration used in the diffusion test ($10\mu\text{g/L}$ for CPs, 2,4-DMP and 3,4-DMP, $100\mu\text{g/L}$ for phenol, 2-MP and 4-MP, and $1000\mu\text{g/L}$ for BPA). Four bottles were used in total.

All bottles were filled with osmoted water and a mixture of phenolic compounds. B3 and B4 without geomembrane were used as control tests.

Concentrations of the various phenolic compounds were measured each week in B1 and B2 in order to determine the time required to reach equilibrium. In B3 and B4 only one sampling was performed after 120 days of contact. According to the equilibrium time observed in B1 and B2, 80 days of equilibrium would have been sufficient but tests were continued as the SPME-GC-MS was not available to perform measurements immediately.

3.2.2 Calculation of partitioning coefficient

The concentration of contaminant in the geomembrane c_g and in solution c_f are linked according to Equation 1 (Henry's Law):

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

Where S_{gf} is the partitioning coefficient and is dependent on temperature, fluid, geomembrane, and contaminant of interest. The partitioning coefficients S_{gf} were calculated for each bottle and each phenolic compound according to Equation 2 adapted from Sangam and Rowe (2001):

$$S_{gf} = \frac{(c_{f0} V_{f0})(1 - p_s) - c_{fF} V_{fF} - \sum c_i V_i}{M_g c_{fF}} \rho_g \quad (2)$$

Where c_{f0} and c_{fF} were respectively the initial and final concentrations of the solution (g/L), V_{f0} and V_{fF} were respectively the initial and final volumes of the solution (L), p_s is the proportion of contaminant sorbed on glass determined based on the quantification of concentration evolution in B3 and B4 test, assumed to be independent of the presence of a geomembrane specimen or not, ρ_g is the geomembrane density (g/L) and M_g is the initial mass of geomembrane (g).

3.3 Diffusion test

3.3.1 Experimental procedure

A permeation/diffusion method in which the geomembrane divides a testing cell in two compartments was used as this kind of method simulates more closely the transport process that is expected in a landfill application than immersion/sorption tests (Sangam and Rowe 2001).

During the tests, chemical concentrations from both source and receptor were monitored with time. The test was performed in duplicate at $23^\circ\text{C} \pm 1^\circ\text{C}$ in glass cells. An example of the test cell used is shown in Figure 1.

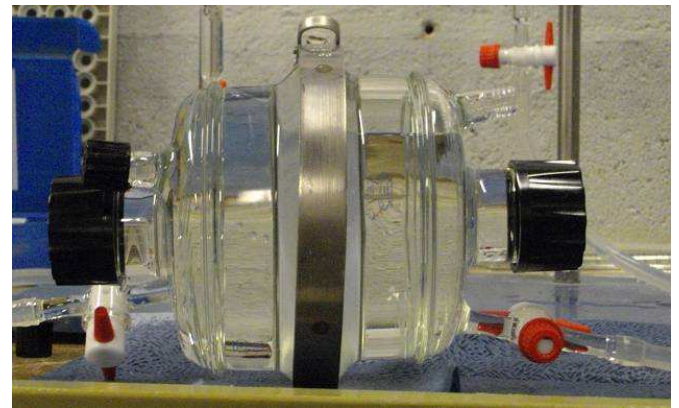


Figure 1 Diffusion cell with two identical parts separated by the geomembrane and linked with metallic bridge. This cell is identical to the control test cell

The diffusion cell consists of two 0.12m internal diameter glass cylinders terminated by rounded ends (see Figure 1). A metallic bridge is used to assemble both parts of the cell that are identical to each other. The geomembrane specimen is located between both parts of the cell. No sealant is used. This system allows a very quick test setup. Tests can be started immediately after installation of the geomembrane into the cell. Each part of the cell contains a sampling port with a Teflon cap and a second port that can be used for the filling of the cell. Cells are lying in a horizontal position while the tests are performed (see Figure 1). It is similar to the test cell previously used by Touze-Foltz et al. (2011). Those cells were especially designed to minimize the time of test set up. The volume of each chamber is equal to 0.73L. The cells were covered with an aluminium foil in order to avoid photo oxidation.

3.3.2 Calculation of diffusion coefficient

The diffusion of organic compounds through an HDPE geomembrane can be modelled by Fick's first law:

$$f = -D_g \frac{dc_g}{dz} \quad (3)$$

Where f is the mass flux or permeation rate per unit area ($\text{g/m}^2/\text{s}$), D_g is the diffusion coefficient of organic compounds through the geomembrane (m^2/s), c_g is the concentration of compound in the geomembrane (g/L), and z is the distance parallel to the direction of diffusion (m). The change in contaminant concentration at any point

in the geomembrane with time, t , is governed by the following differential equation according to Fick's second law:

$$\frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial z^2} \quad (4)$$

If the source and receptor fluids are similar, the flux associated with the diffusion process can be obtained by substituting Eq. (1) into Eq. (3):

$$f = -P_g \frac{dc_f}{dz} \quad (5)$$

Where P_g is the permeation coefficient or mass transfer coefficient (m^2/s).

The test approach was based on concepts and theory proposed by Rowe et al. (1995), Sangam and Rowe (2001) and Islam and Rowe (2009) for geomembranes. For these closed systems, the mass of contaminant in the source solution at any time t is equal to the initial mass minus the mass that diffused through the geomembrane and can be written as:

$$c_s(t) = c_0 - \frac{1}{H_s} \int_0^t f_s(\tau) d\tau \quad (6)$$

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

$$c_b(t) = c_{b0} - \frac{1}{H_b} \int_0^t f_b(\tau) d\tau \quad (7)$$

Where $c_{b0}(t)$ is the initial concentration in the receptor solution (g/L), H_b is the height of the receptor (volume of receptor chamber per unit area) (m), and $f_b(t)$ is the mass flux of contaminant into the receptor chamber at any time t ($g/m^2/s$).

The diffusion (D_g) and partitioning (S_{gf}) coefficients were deduced following the procedure described by Sangam and Rowe (2001) using the finite layer analysis program POLLUTE v6© (Rowe and Booker, 1997).

4. RESULTS AND DISCUSSION

4.1 Control cells

4.1.1 Blank sorption tests

Sorption was noticed on glass for all phenolic compounds in bottles B3 and B4. Based on the average remaining concentration in those bottles a percentage of each phenolic compound was calculated and assumed to be identical to the one in bottles B1 and B2 containing geomembranes. The percentages sorbed on glass at equilibrium were respectively 54% for phenol, 62 % for 2-MP, 59 % for 4-MP, 60% for 2-CP, 51% for 4-CP, 71% for 2,4-DMP, 86 % for 3,4-DMP, 46% for 2,4-DCP, 48% for 2,4,6-TC), 56% for 2,3,5,6-TeCP, 50 % for 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), 31% for PCP and 17% for bisphenol A (BPA).

4.1.2 Blank diffusion tests

Figure 2 shows the variation in phenolic compounds concentration as measured during the test period in the control cell for diffusion for the various phenolic compounds, except phenol and 3,4-DMP for which diffusion could not be modelled as no contaminant was detected along the test in the receptor. Concentrations decreased for all phenolic compounds with time before reaching a stabilization. The decrease in concentration for phenol was around 30% of the initial concentration while for methylphenols a 45% decrease was observed. In contrast, the concentration of chlorophenols experienced a decrease of 20% except for 4CP which experienced a significant decrease by 38%. The decrease in concentration for bisphenol A is about 20%.

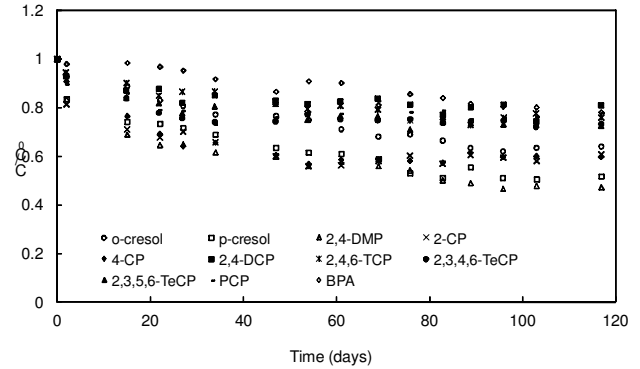


Figure 2 Observed normalized concentrations of the various phenolic compounds in control cells for diffusion tests.

This decrease in concentration was attributed to the sorption of the various phenolic compounds onto the glass cell. To account for these losses in diffusion tests a 5mm thick layer with a sorption coefficient able to represent the sorption observed was added in the numerical analysis following the rationale developed by Krol (2000), assuming once again that sorption onto glass is independent of the presence or not of a geomembrane in the testing cell.

4.2 Partitioning test

S_{gf} values for each phenolic compound were calculated assuming that the mass loss onto glass would occur even in the presence of a geomembrane specimen, following the methodology described in Section 3.2. The corresponding values of S_{gf} are given in Table 3. The S_{gf} value of phenol and bisphenolA are equal to 0.3 and 4.03 respectively. As regards methylphenols, 2-MP has the highest S_{gf} equal to 4.59 followed by 4-MP, 3,4-DMP and 2,4-DMP with S_{gf} values respectively equal to 3.73, 1.70 and 1.36 . For chlorophenols, the largest value of S_{gf} equal to 205.51 was observed for PCP, followed by 2,3,5,6-TeCP ($S_{gf} = 38.49$), 2,4,6-TCP ($S_{gf} = 18.01$), 2,3,4,6-TeCP ($S_{gf} = 11.33$), 2,4-DCP ($S_{gf} = 8.56$) and 2-CP ($S_{gf} = 6.21$). 4-CP has the lowest S_{gf} value of all equal to 2.65.

Results obtained are plotted on Figure 3 as a function of the aqueous solubility, the n-octanol/water partitioning coefficient and the molecular diameter. As the influence of those parameters on the partitioning coefficient were previously studied by other authors in the case of VOCs, values from the literature together with empirical equations determined based on experimental data for VOCs were plotted on the same graphs for the sake of comparison. Data used to elaborate those figures regarding VOCs originate from Park and Nibras (1993), Prasad et al. (1994), Müller et al. (1998), Rowe (1998), Sangam and Rowe (2001), Rowe et al. (2003), Joo et al. (2004, 2005), Nefso and Burns (2007), Islam and Rowe (2009), Touze-Foltz et al. (2011), Park et al. (2012).

Table 3 Inferred partitioning, diffusion and calculated permeation coefficients from diffusion tests

Contaminants	S_{gf} (-)	D_g ($\times 10^{-12}$ m ² /s)	P_g ($\times 10^{-12}$ m ² /s)
Phenol	0.3	-	-
<i>Methylphenols</i>			
2-MP	4.59	0.11	0.51
4-MP	3.73	0.12	0.45
3,4-DMP	1.70	-	-
2,4-DMP	1.36	0.28	0.38
<i>Chlorophenols</i>			
2-CP	6.21	0.23	1.43
4-CP	2.65	0.59	1.56
2,4-DCP	8.56	0.24	2.06
2,4,6-TCP	18.01	0.15	2.70
2,3,4,6-TeCP	11.33	0.39	4.42
2,3,5,6-TeCP	38.49	0.23	8.85
PCP	205.51	0.18	36.99
BPA	4.03	0.43	1.73

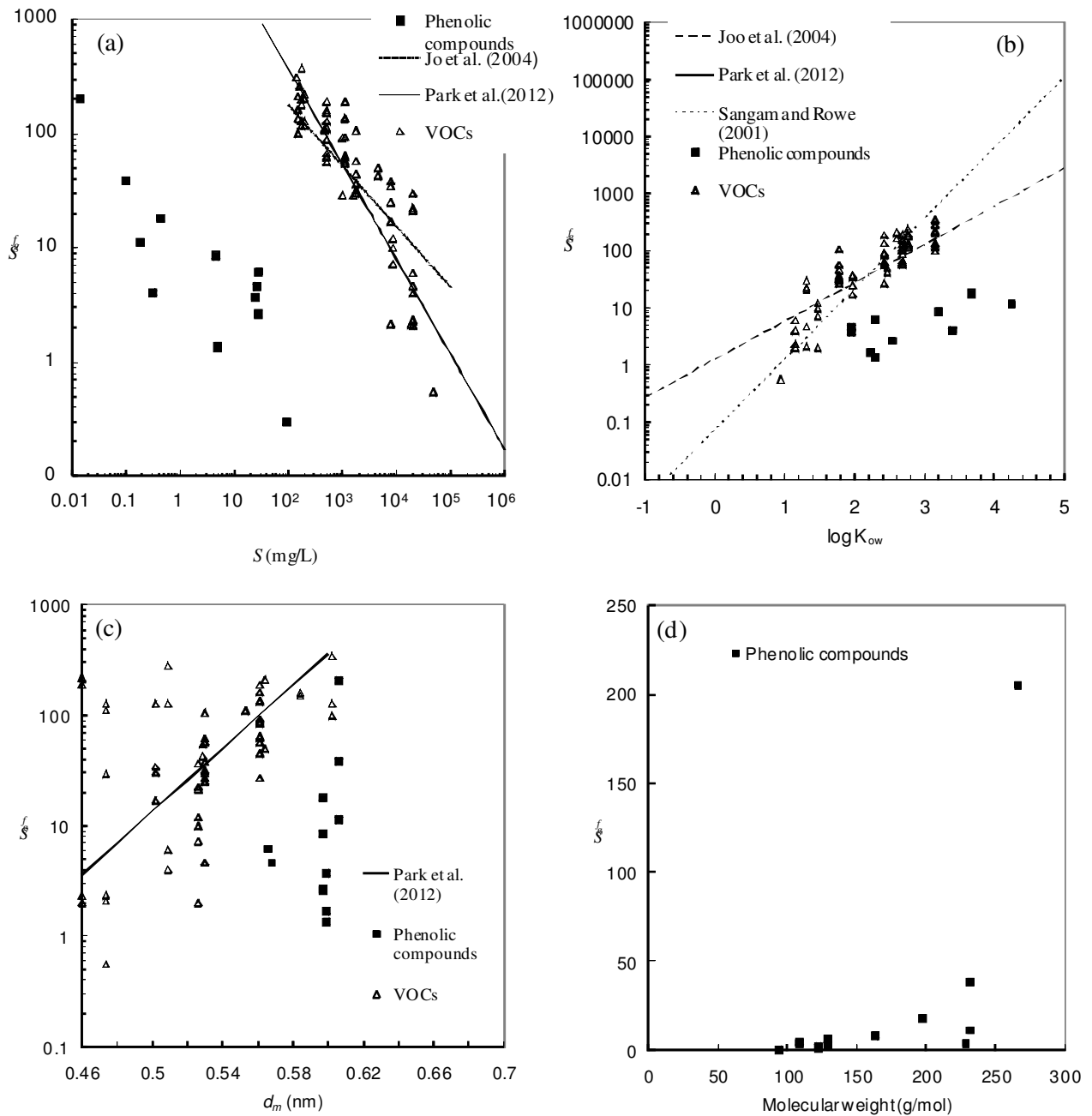


Figure 3 Relationship between partitioning coefficient, S_{gf} , and: (a) aqueous solubility, (b) octanol-water partitioning coefficient, K_{ow} , (c) molecular diameter, d_m , and (d) molecular weight for phenolic compounds and VOCs.

Based on the results of this study, it appears that the partitioning coefficient decreases with an increase in the aqueous solubility and increases with an increase in the molecular diameter.

The partitioning coefficient also increases with an increase in $\log K_{ow}$. This result is logical as the less polar the contaminant is, the less it is soluble in water. This results in a potential for a larger adsorption on the geomembrane.

No general trend can be detected as regards the effect of the molecular weight on the partitioning coefficient. Indeed, significantly different values of S_{gf} were obtained for 2,3,5,6-TeCP and BPA despite the fact that they exhibit very close molecular weights. The good correlation observed for the other compounds may be explained by the fact that differences in molecular weight are explained by the number of chlorine atoms in the molecule: The more chlorine atoms in the molecule, the more apolar it is. The good correlation for chlorophenols between molecular weight and partitioning coefficient may thus be related to polarity.

An analysis of the sole chlorophenols (2-CP, 4-CP, 2,4-DCP, 2,3,6-TCP, 2,3,4,6-TeCP, 2,3,5,6-TeCP et PCP) tends to show that the partitioning coefficient is closely linked with the degree of substitution of chlorine atoms on the phenolic nucleus. Indeed the larger the number of chlorine atoms, the larger the S_{gf} value, except for 2,3,4,6-TeCP. This phenomenon is certainly due to the difference in polarity of the chlorophenols as previously mentioned.

Those results are consistent with previous results obtained for VOCs. However, the range of parameters obtained is significantly different so that the empirical equations derived for VOCs are no longer valid to predict the evolution of the partitioning coefficient of phenolic compounds. For the phenolic compounds under study, the chlorophenols exhibit larger partitioning coefficients because of the relatively high $\log K_{ow}$ varying from 2.29 to 5.85 compared to methylphenols with $\log K_{ow}$ varying from 1.95 to 2.30.

The S_{gf} values of phenolic compounds obtained in this study are low compared to those of VOCs whose chemical structure is similar, obtained by different authors, as evidenced by Table 4, where the structure of benzene can be compared to the structure of phenol and the structure of toluene to the one of p-cresol and o-cresol. It does thus seem that the partitioning coefficient decreases as the hydroxyl group, hydrophilic (due to its hydrogen bonds) tends to make the molecule soluble. Indeed, while the solubility of benzene is only 1.78g/L at 20°C the one of phenol is 90g/L.

4.3 Diffusion test

Figures 4, 5 and 6 show the variation in concentration with time of some chlorophenols, methylphenols and bisphenol A respectively in the source and the receptor over the testing period. The concentration of contaminants in the source decreased with time, whereas the concentrations in the receptor increased as the contaminants diffused through the geomembrane, as usually noticed in diffusion tests. The figures also exhibit the theoretical curves obtained using a best fit analysis on the experimental data, using the partitioning coefficient previously determined. Values of diffusion parameters thus obtained are given in Table 3. No adjustment could be performed for phenol and 3,4-DMP as no significant concentration in the receptor could be detected along the test.

Values obtained were also plotted against the aqueous solubility, the n-octanol/water partitioning coefficient and the molecular diameter.

The diffusion coefficient increases with an increase in the aqueous solubility and a decrease in the $\log K_{ow}$ as can be noticed on Figure 7. No general trend can be given as regards the molecular diameter. Indeed, the molecular diameter of BPA is significantly different from the molecular diameter of the other phenolic compounds, and the diffusion coefficient of BPA falls in the range of all the other diffusion coefficients obtained. If one excludes BPA, previously given empirical equations linking diffusion coefficient and molecular diameter for VOCs could be acceptable for phenolic compounds. This is not true as regards the evolution of the diffusion coefficient with the aqueous solubility and $\log K_{ow}$. One can observe

that diffusion coefficients for VOCs and phenolic compounds fall in the same range, except for o-cresol, p-cresol and 3,4-DMP for which the lowest values of diffusion coefficients were obtained.

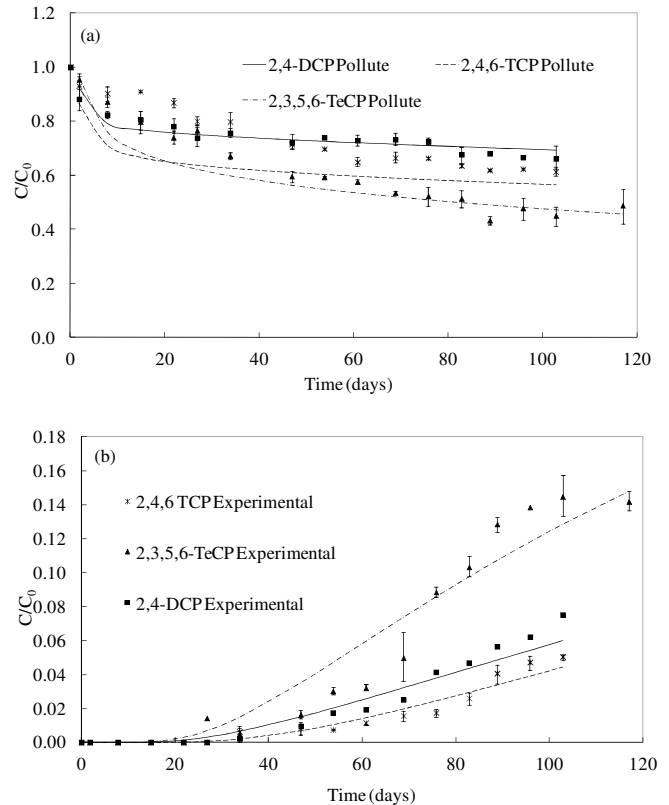


Figure 4 Evolution of the concentrations in (a) source and (b) receptor with time for chlorophenols

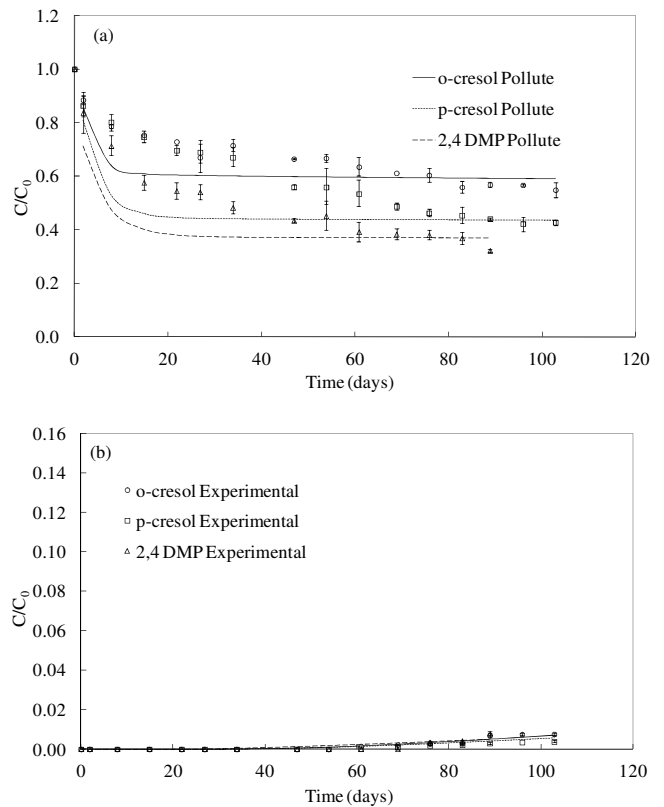
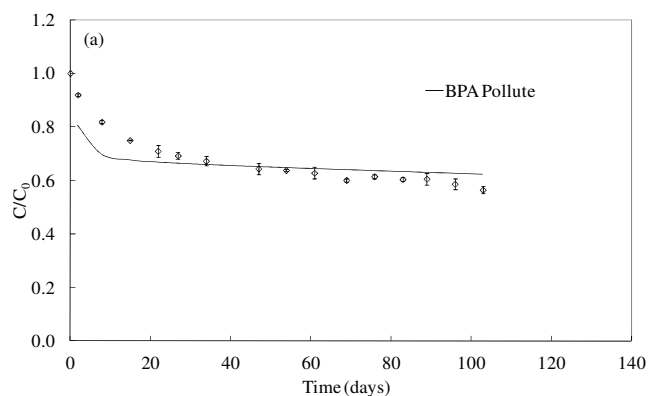
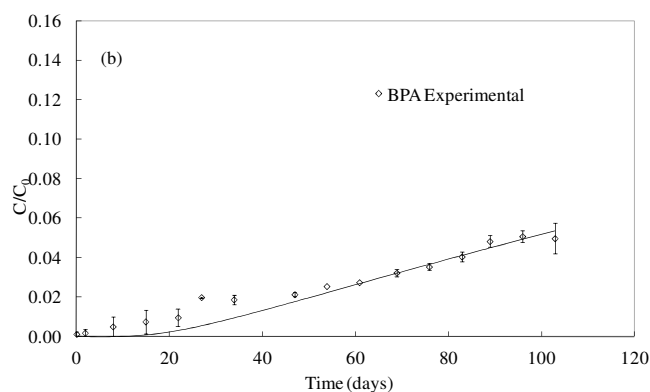


Figure 5 Evolution of the concentrations in (a) source and (b) receptor with time for methylphenols



(a)



(b)


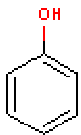
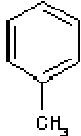
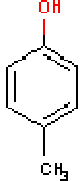
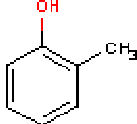
Figure 6 Evolution of the concentrations in (a) source and (b) receptor with time for bisphenol A

Results in terms of permeation coefficient as a function of the aqueous solubility, the n-octanol/water partitioning coefficient and the molecular diameter are plotted on Figure 8. One can observe that as for diffusion coefficients, values of permeation coefficients for VOCs and phenolic compounds fall in the same range, except for o-cresol, p-cresol and 3,4-DMP for which the lowest values of diffusion coefficients were obtained.

Very different trends are observed as compared to the trends obtained for VOCs, except again for the molecular diameter when one disregards the value obtained for BPA. Variations obtained with aqueous solubility and $\log K_{ow}$ would require a new adjustment which is beyond the scope of this paper. Indeed it seems more justified to try and find general relationships of evolutions of diffusion coefficients, partitioning coefficients and permeation coefficients for all families of pollutants than to derive empirical equations for each family. This work requires the knowledge of transport parameters for other families of pollutants with different properties to be conducted first.

A final comment as regards permeation is again the clear trend for an increase with the increasing number of chlorine atoms substituted on the phenolic core on the permeation coefficient. Indeed it increases from $1.43 \times 10^{-12} \text{ m}^2/\text{s}$ for 2-CP to $36.99 \times 10^{-12} \text{ m}^2/\text{s}$ for PCP. On the contrary, no significant evolution is observed on the permeation coefficient for methylphenols which all are close to $0.45 \times 10^{-12} \text{ m}^2/\text{s}$.

Table 4 Synthesis of partitioning coefficients of aromatic compounds

Pollutants	S_{gr} (-)	Reference
 Benzene	51	Touze-Foltz et al. (2011)
	45	Islam and Rowe (2009)
	32	Rowe et al. (2003)
	57.2	Prasad et al. (1994)
Phenol		
 	0.3	This paper
Toluene		
 	101	Touze-Foltz et al. (2011)
	100-125	Islam and Rowe (2009)
	65-70	Rowe et al. (2003)
	193	Prasad et al. (1994)
p-cresol		
 	3.73	This paper
o-cresol		
 	4.59	This paper

5. CONCLUSION

The aim of this paper was to present the experimental results obtained regarding diffusion through a high density polyethylene geomembrane of phenol, four methylphenols (o-cresol, p-cresol, 2,4-xyleneol, 3,4-xyleneol), seven chlorophenols (2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, 2,3,5,6-tetrachlorophenol, pentachlorophenol) and bisphenol A. Those contaminants, including certain derivatives of halogenated phenols, are known to be toxic even at very low concentrations.

The results show that the partitioning coefficient is linked to the aqueous solubility and the n-octanol/water partitioning coefficient of the contaminant. This latest result is logical as the less polar the contaminant is, the less it is soluble in water. This results in a potential for a larger adsorption on the geomembrane. No clear link could be evidenced with the molecular weight and the molecular diameter when all phenolic compounds are taken into account (especially BPA). However a good correlation was observed for chlorophenols between molecular weight and partitioning coefficient which may be related to polarity.

An analysis of the sole chlorophenols (2-CP, 4-CP, 2,4-DCP, 2,3,6-TCP, 2,3,4,6-TeCP, 2,3,5,6-TeCP et PCP) tends to show also that the partitioning coefficient is closely linked with the degree of substitution of chlorine atoms on the phenolic nucleus, phenomenon

which may also be attributed to a difference in polarity of the various chlorophenols studied.

The S_{gf} values of phenolic compounds obtained in this study are low compared to those of VOCs whose chemical structure is similar, tending to show that the partitioning coefficient decreases as the hydroxyl group tends to make the molecule more soluble.

As regards the diffusion coefficient and the permeation coefficient, a good correlation with the aqueous solubility and the n-octanol/water partitioning coefficient of the phenolic compounds is

observed. A good correlation with the molecular diameter is also obtained when one disregards the values obtained for BPA.

Those trends are consistent with previous trends obtained for VOCs. However, the range of parameters obtained is significantly different so that the empirical equations derived for VOCs and available in the literature are not valid to predict the evolution of the partitioning coefficient of phenolic compounds except as regards the evolution with the molecular diameter when disregarding the parameters obtained for BPA.

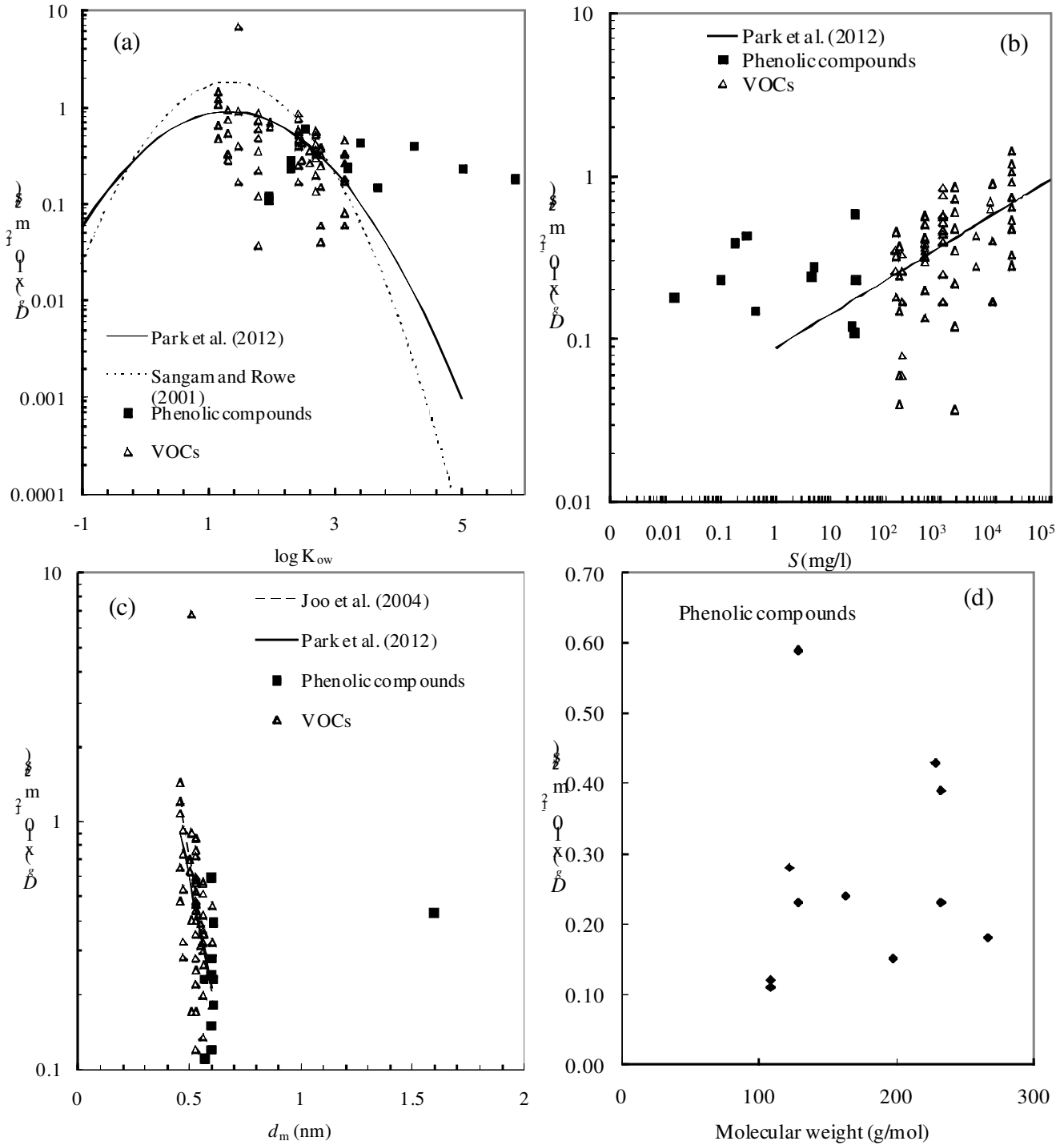


Figure 7 Relationship between diffusion coefficient, D_g , and: (a) aqueous solubility, (b) octanol-water partitioning coefficient, K_{ow} , (c) molecular diameter, d_m , and (d) molecular weight for phenolic compounds and VOCs.

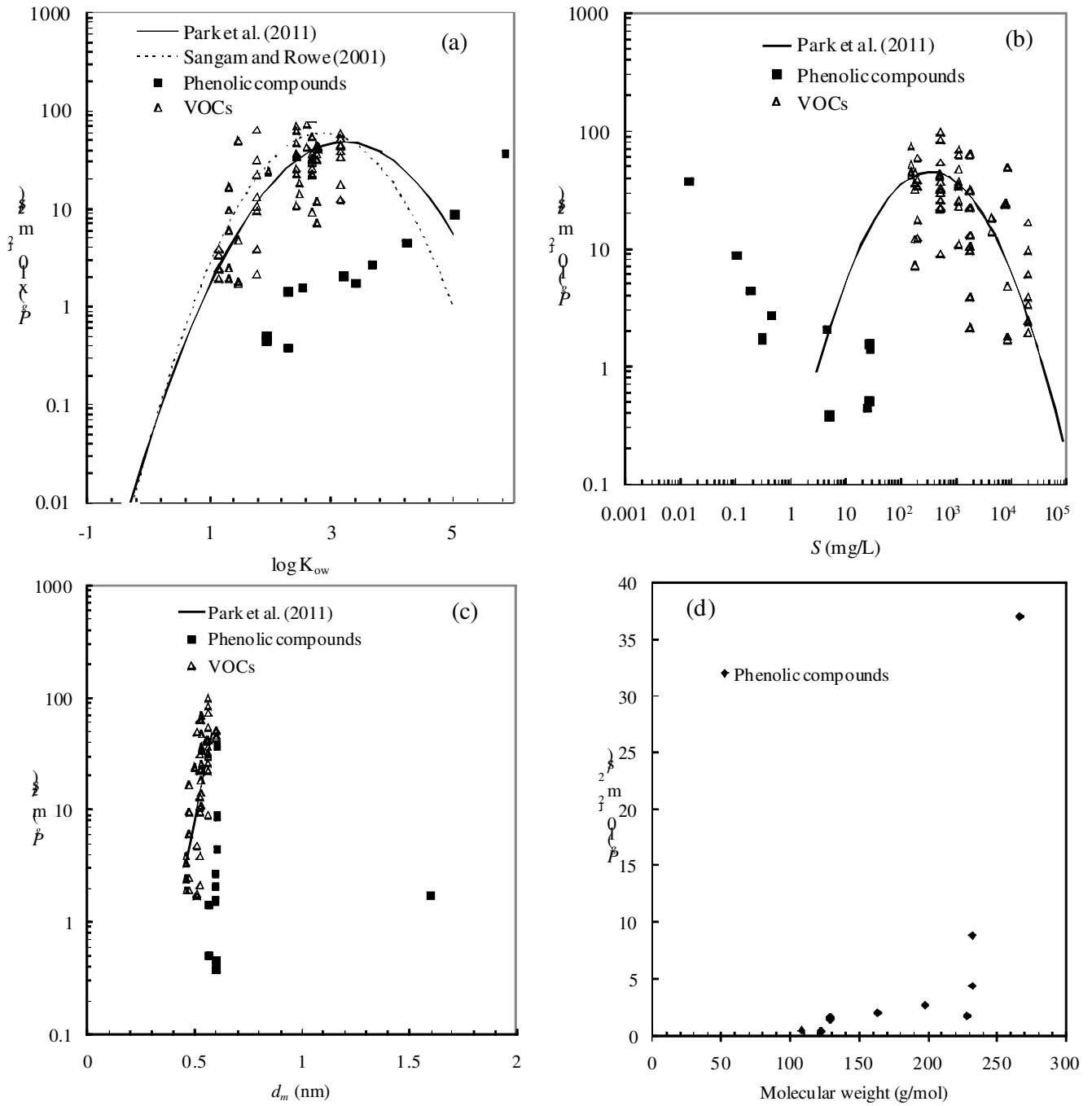


Figure 8 Relationship between permeation coefficient, P_g , and: (a) aqueous solubility, (b) octanol-water partitioning coefficient, K_{ow} , and (c) molecular diameter, d_m , and (d) molecular weight for phenolic compounds and VOCs

6. ACKNOWLEDGEMENTS

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