Diffusion of phenolic compounds through a flexible polypropylene geomembrane

N. Touze-Foltz i, M. Mendes ii, M. Mazeas iii and L. Rouillac iv

i) Head of the Geosynthetics research team, HBAN Unit, Irstea, 1, Rue Pierre Gilles de Gennes, 92761 Antony, France.
ii) Post Doctorate, HBAN Unit, Irstea, 1, Rue Pierre Gilles de Gennes, 92761 Antony, France.
iii) Head of the chemistry laboratory, HBAN Unit, Irstea, 1, Rue Pierre Gilles de Gennes, 92761 Antony, France.
iv) Engineer, HBAN Unit, Irstea, 1, Rue Pierre Gilles de Gennes, 92761 Antony, France.

ABSTRACT

This paper presents the experimental results of the diffusion of phenolic compounds through a flexible polypropylene geomembrane. The study considers the partition and diffusion of two chlorophenol contaminants: 2,4,6-trichlorophenol and 2,3,5,6-tetrachlorophenol that are known to be toxic even at very low concentrations. The concentration dynamics in the source and receptor chambers of the diffusion cells were interpreted using the numerical code Pollute. The values of diffusion coefficients are respectively equal to $1.2 \times 10^{-13}$ m$^2$/s and $2.5 \times 10^{-13}$ m$^2$/s for 2,4,6-TCP and 2,3,5,6 TeCP. Values of partitioning coefficients were respectively equal to 504 and 357 for 2,4,6-TCP and 2,3,5,6 TeCP. Values of diffusion coefficients obtained are similar to values previously obtained for an HDPE geomembrane. Partitioning coefficients are one order of magnitude larger than values obtained for an HDPE geomembrane, thus resulting in a larger permeation coefficient in PP than in HDPE geomembranes by one order of magnitude.

Keywords: Geosynthetics, Diffusion, Partition, Phenolic compounds, polypropylene

1. INTRODUCTION

Landfills contain micropollutants which can have toxic effects (acute toxicity, genotoxicity, reproductive toxicity etc.) (Sisinnio 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 of phenolic compounds has also been recently studied for an HDPE geomembrane and HDPE films (Touze-Foltz et al., 2012, Mendes et al., 2014). However up to the authors’ knowledge no data are available for other types of geomembranes like flexible polypropylene geomembranes (f-PP). It is thus the objective of this paper to present the results obtained while studying the diffusion of 2,4,6-trichlorophenol, and 2,3,5,6-tetrachlorophenol with a f-PP geomembrane. Results are further compared to previous results obtained for other geomembranes available in the literature.
2 EXPERIMENTAL PROCEDURE

2.1. f-PP geomembrane

The study was conducted using a 1.5 mm thick f-PP geomembrane representative of the f-PP geomembranes available on the European market, that could be used in landfills as an alternative to HDPE geomembranes. The rate of crystallinity of the f-PP geomembrane was measured to be 12.2%.

2.2. Phenolic compounds

2.2.1 Phenolic compounds under study

Results of the diffusion of 2,4,6-trichlorophenol (2,4,6-TCP) and 2,3,5,6-tetrachlorophenol (2,3,5,6-TeCP) in the f-PP geomembrane are presented in this paper. Those compounds were included in a mixture containing 13 phenolic compounds: phenol, o-cresol (2-MP), p-cresol (4-MP), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-xylene (2,4-DMP), 3,4-xylene (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).

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 previously presented by Touze-Foltz et al. (2012) and Mendes et al. (2014) which is not repeated here 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 those 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 methylphenols are slightly larger than average values found in leachate, since values encountered in the literature are significantly lower than the LOQ.

2.2.2 Preparation of the solutions

In a volumetric flask, 0.01 g of each compound were mixed with 0.1 g of phenol, o-cresol and p-cresol and 1 g of BPA in absolute methanol to obtain 100 ml 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 (400 mg/L HgCl₂) to limit the effects of biodegradation.

2.3. Analytical methods

The quantification of phenolic compounds was performed by solid phase micro-extraction 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% phenyl-methyl polysiloxane, Phenomenex, 60 m length, 0.25 mm I.D., 0.25 μm 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 100 μm polydimethylsiloxane (PDMS) from Supelco.

2,4,6-trichlorophenol-13C was used as internal standard for the quantification of 2,4,6-TCP, and pentachlorophenol-13C6 was used as internal standard for the quantification of 2,3,5,6-TeCP.

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

In the derivatization step 5 ml of aqueous sample was introduced in a 20 ml PTFE-capped glass vial. Sodium chloride at 40% (W/V), 200 mg of KHCO₃ 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 μm 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 196 and 232 were used respectively for the 2,3,4,6-TeCP and 2,3,5,6-TeCP.

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

Batch partitioning tests were performed at room temperature (i.e. 23 ± 1°C) in 120 ml glass bottles equipped with screw-tight Teflon lined caps for sampling. The bottles were covered with an aluminium foil in order to avoid photoxidation. 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 pieces (30mm x 20mm) weighing 6g in total. According to Neffso and Burns (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. Initial concentrations of 2,4,6-TCM and 2,3,5,6-TeCP were equal to 10 μg/L. Two bottles were filled with osmosed water and a mixture of phenolic compounds. One of the two bottles without geomembrane was used as control test.

Concentrations of the various phenolic compounds were measured initially and after a period of 157 days which is, based on previous experiments, long enough to reach equilibrium in the bottles.

### 3.3 Calculation of partition coefficient

The concentration of contaminant in the geomembrane is described in Equation 1 (Henry's Law):

\[
c_g = S_{gf} c_f
\]

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 phenolic compound according to Equation 2 adapted from Sangam and Rowe (2001):

\[
S_{gf} = \left( \frac{c_f v_f}{f_0} \right) \left( 1 - \frac{c_f V_f}{p_f} \right) - \sum c_i V_i \rho_g
\]

Where \( c_f \) and \( V_f \) were respectively the initial and final concentrations of the solution (g/L), \( V_f \) is respectively the initial and final volumes of the solution (L), \( p_f \) 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, \( \rho_g \) is the geomembrane density (g/L) and \( M_g \) is the initial mass of geomembrane (g).

### 3.4 Diffusion test

#### 3.4.1 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. A single test was performed at 23°C±1°C in a glass cell.

The diffusion cell consists of two 0.12m internal diameter glass cylinders terminated by rounded ends. A metallic bridle 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, 2012). 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 aluminum foil in order to avoid photo oxidation.

#### 3.4.2 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 (g/m²/s), \( D_g \) is the diffusion coefficient of organic compounds through the geomembrane (m²/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 (m²/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:

$$c_t(t) = c_0 - \frac{1}{H_s} \int_0^t f_s(t')dt'$$

(6)

where $c(t)$ 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/m²/s). The concentration in the receptor compartment at any time $c_b(t)$, can be expressed similarly as:

$$c_b(t) = c_{b0} - \frac{1}{H_b} \int_0^t f_b(t')dt'$$

(7)

where $c_{b0}$ 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/m²/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 v7© (Rowe and Booker, 1997).

4 RESULTS AND DISCUSSION

4.1 Control cells

4.1.1 Blank sorption tests

No significant sorption was not noticed on glass for the two phenolic compounds under study in the bottle which did not contain geomembrane pieces.

4.1.2 Blank diffusion tests

Figure 1 shows the variation in phenolic compounds concentration as measured during the test period in the control cell. Concentrations did not exhibit a significant decrease along time for the two phenolic compounds under study.

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 $S_{gf}$ value of 2,4,6-TCP and 2,3,5,6-TCP are respectively equal to 504 and 357.

4.3 Diffusion test

Figure 2 shows the variation in concentration with time of 2,4,6-TCP in the source chamber and Figure 3 the variation in concentration with time of 2,3,5,6-TeCP in the source chamber. No concentration of 2,4,6-TCP or 2,3,5,6-TeCP was detected in the receptor chamber along the 126 days of testing, probably in relation with the large values of partitioning coefficients. The adjustment was thus only performed on the concentration measured in the source chamber.
Values of diffusion coefficients obtained are respectively equal to 1.2×10^{-13} m²/s and 2.5×10^{-13} m²/s for 2,4,6-TCP and 2,3,5,6 TeCP respectively. Table 1 gives a synthesis of the results obtained for the PP geomembrane tested in this study and for the HDPE geomembrane previously tested by Touze-Foltz et al. (2012), tested in the same conditions and similar test cells. One can notice that the diffusion coefficients are in the same order of magnitude for both geomembranes. However, the partitioning coefficients are one order of magnitude larger for the PP geomembrane than for the HDPE geomembrane, probably in relation with a larger affinity of the two phenolic compounds tested with the f-PP geomembrane than with the HDPE geomembrane.

Table 1. Synthesis of diffusion results

| Geomembrane | f-PP | HDPE |
|-------------|------|------|
| 2,4,6-TCP   | 1.2×10^{-13} | 1.5×10^{-13} |
| D (m²/s)    | 504  | 18.01 |
| P (m³/m²)   | 6.05×10^{-11} | 2.7×10^{-11} |
| 2,3,5,6 TeCP| 2.5×10^{-13} | 2.3×10^{-13} |
| D (m²/s)    | 357  | 38.49 |
| P (m³/m²)   | 8.93×10^{-11} | 8.85×10^{-12} |

5 CONCLUSIONS

The objective of this paper was to show the results of an experimental study performed in order to determine the values of diffusion coefficients of phenolic compounds in a f-PP geomembrane. Mesurable concentrations were only obtained in the source chamber for 2,4,6-TCP or 2,3,5,6 TeCP. The values of diffusion coefficients are respectively equal to 1.2×10^{-13} m²/s and 2.5×10^{-13} m²/s for 2,4,6-TCP and 2,3,5,6 TeCP. Values of partitioning coefficients were respectively equal to 504 and 357 for 2,4,6-TCP and 2,3,5,6 TeCP. Values of diffusion coefficients obtained are similar to values previously obtained for an HDPE geomembrane. Partitioning coefficients are one order of magnitude larger than values obtained for an HDPE geomembrane. The potential for diffusive transfers is thus higher in the PP geomembrane than in the HDPE geomembrane in relation with a larger permeation coefficient, probably in relation with a larger affinity of the two phenolic compounds tested with the f-PP geomembrane than with the HDPE geomembrane.

ACKNOWLEDGEMENTS

The study presented in this paper was funded RGC&U (C2D2) for the Duragéos research program labelled by Axelera and Advancy which partners were IFSTTAR, IRSTEA, LTHE, ENTP, PIMM Arts et Métiers ParisTech, Suez-Environnement and Veolia Proprété.

REFERENCES

1) Abel M. and Tepic, N. (2000). Distribution of polycyclic aromatic hydrocarbons in a Municipal solid waste landfill and underlying soil. Bulletin of environmental contamination and toxicology, 65(2): 236-243.
2) Bauer, M. J. and Herrmann, R. (1997). Estimation of the environmental contamination by phthalic acid esters leaching from household wastes. The Science of the Total Environment, 208(1-2): 49-57.
3) Christensen, T. H., Kjeldsen, P., Bjerg, P. L., Jensen, D. L., Christensen, J. B., Baun, A., Albrechtsen, H. and Heron, G. (2001). Biogeochemistry of Landfill leachate plumes. Applied Geochemistry, 16(7-8): 659-718.
4) Cousins, I. T., Staples, C. A., Klecka, G. M. and Mackay, D. (2002). A Multimedia Assessment of the Environmental Fate of Bisphenol A. Human and Ecological Risk Assessment, 8(5): 1107-1135.
5) Gron, C., Christensen, J. B., Jensen, D., Kjeldsen, P. and Ostfeldt, P. (1999). Organic halogens in landfill leachates. Water, Air, and Soil Pollution, 120(3-4): 331–345.
6) Harmsen, J. (1981). Identification of organic compounds in leachate from a waste tip. Water Research, 17(6): 699-705.
7) Hiroshi, A., Toshihiko, M. and Nobutoshi, T. (2002). Endocrine disrupters in leachate from two MSW landfills of different waste compositions in Japan. Proceedings of the 2nd Asian Pacific Landfill Symposium, Seoul 2002: 728-736.
8) Islam, M.Z. and Rowe, R.K. (2008). Effect of geomembrane ageing on the diffusion of VOCs through HDPE geomembranes. Proceedings of The First Pan American Geosynthetics Conference & Exhibition, Cancun, Mexico (CD-ROM): 459-467.
9) Islam, M.Z. and Rowe, R.K. (2009). Permeation of BTEX through unaged and aged HDPE geomembranes. Journal of Geotech. and Geoenv. Eng., 135 (8): 1130-1140.
10) Kjeldsen, P., Balaz, M. A., Rooker, A. P., Baun, A., Ledin, A. and Christensen, T.H. (2002). Present and long-term composition of MSW landfill leachate: A review. Critical Reviews in Environmental Science and Technology, 32(4): 297–336.
11) Kujawski W., Waszawski A., Ratajczak W., Porebski T., Capala W. and Ostrowska I. (2004). Removal of phenol from
wastewater by different separation techniques. Desalination, 163(1-3): 287-296.

12) Limam, I., Guenne, A., Driss, M. and Mza'ez, L. (2010). Simultaneous determination of phenol, methylphenols, chlorophenols and bisphenol-A by headspace solid-phase microextraction-gas chromatography-mass spectrometry in water samples and industrial effluents. International Journal of Environmental Analytical chemistry, 90(3-6): 230-244.

13) McWaters, R.S. and Rowe, R.K. (2010). Diffusive Transport of VOCs through LLDPE and Two Coextruded Geomembranes. Journal of Geotechnical and Geoenvironmental Engineering, 136(9), 1167-1177.

14) McWaters, R.S. and Rowe, R.K. (2008). Transport of volatile organic compounds through PVC and LLDPE-geomembranes from both aqueous and vapour phases. Geosynthetics International, 16(6), 468–481.

15) Mendes, M., Touze-Foltz, N., Gardoni, M., Mazèas, L., 2014. Diffusion of phenolic compounds through polyethylene films. Geosynthetics International, 21(2), 137-150.

16) Müller, W., Jakob, R., Tatsky-Gerth and August, H. (1998). Solubilities, diffusion and partitioning coefficients of organic pollutants in HDPE geomembranes: experimental results and calculations. Proc. 6th ICG, Atlanta, IFAI, 1: 239-248.

17) Nefto, E.K. and Burns, S.E. (2007) Comparison of the equilibrium sorption of five organic compounds to HDPE, PP, and PVC geomembranes. Geotextiles and Geomembranes, 25:360-365.

18) Niederee, C. and Goss, K. (2008). Effect of ortho-chlorine substitution on the partition behavior of chlorophenols. Chemosphere, 71(4): 697-702.

19) Oman, C. and Hynning, P. A. (1993). Identification of organic compounds in municipal landfill leachates. Environmental Pollution, 80(3): 265-271.

20) Otero M., Zabkova M. and Rodriguez A. L. (2005) Adsorptive purification of phenol wastewaters: Experimental basis and operation of a parametric pumping unit. Chemical Engineering Journal, 110(1-3): 101-111.

21) Park, J.K. and Nibras, M. (1993). Mass flux of organic chemicals through polyethylene geomembranes. Water Environ. Res., 65: 227-237.

22) Park, M., Benson, C. H. and Edil, T. B. (2012). Comparison of batch and double compartment test for measuring volatile organic compound transport parameters in geomembranes. Geotextiles and Geomembranes, 31, 15-30.

23) Prasad, T.V., Brown, K.W. and Thomas, J.C. (1994). Diffusion coefficients of organics in high density polyethylene (HDPE). Waste Management and Research, 12: 61-71.

24) Ramamoorthy S. and Ramamoorthy S. (1997). Chlorinated Organic Compounds in the Environment. CRC Press, Boca Raton, FL, 384 p.

25) Robinson H. D., Knox K., Van Santen A. and Tempany P. R (2001). Compliance of UK landfills with EU pollution emissions legislation: Development of a reporting protocol. Proceedings Sardinia 2001, Eighth International Waste Management and Landfill Symposium Cagliari, Italy, 1-5 october 2001: 21-30.

26) Rowe, R.K., Sangam, H.P. and Lake, C.B. (2003). Evaluation of an HDPE geomembrane after 14 years as a leachate lagoon liner. Canadian Geotechnical Journal, 40(3): 536-550.

27) Rowe, R.K., Hrjavovic, L., Kosaric, N. (1995). Diffusion of chloride through an HDPE geomembrane. Geosynthetics International, 2(3), 507-536.

28) Rowe, R. K., and Booker, J. R. (1997) POLLUTE v. 6.3: 1D Pollutant Migration Through a Non-Homogeneous Soil. Distributed by GAEA Environmental Engineering Ltd, Whithby, Ontario.