EXPERIMENTAL DETERMINATION OF SORPTION AND DIFFUSION OF ORGANIC POLLUTANTS THROUGH GCLS

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Abstract: Compared to the United-States where mainly Wyoming natural sodium bentonite is used, Europe is facing a variety of GCLs containing either natural sodium bentonites, natural calcium bentonites or Na-activated Ca bentonites. Furthermore the manufacturing process of GCLs varies from manufacturer to manufacturer in terms of geotextiles used and mode of assembly of the GCL (needlepunched or stitch for example). The question then arises of the performance of landfill composite bottom liners depending on the nature of the GCL. An adequate modelling of contaminant advective-diffusive flow through GCLs requires the quantification of sorption parameters of the geotextile and bentonite components of those materials for a variety of contaminants contained in leachate, as well as the quantification of diffusion coefficients.

The aim of this paper will thus be to present the experimental results obtained regarding sorption on various constitutive geotextiles from GCLs of 4 volatile organic compounds (VOCs). Indeed these pollutants seem to be potentially dangerous substances for human health according to their amount found in leachate and their Toxicology Reference Value (TRV). 2 GCLs from two different manufacturers were selected for this study. They are both made of two polypropylene geotextiles, a woven and a nonwoven, which encapsulate bentonite. The nature of the geotextiles differ from one manufacturer to the other. Preliminary results regarding partitioning coefficients will be presented together with preliminary results of 1,2-dichloroethane diffusion through one of the GCLs.

Keywords: adsorption, geotextile, leachate, polymer, geosynthetic clay liner, barrier.

INTRODUCTION

VOCs are ubiquitous in landfill leachate and most VOC concentrations do not exhibit decreasing temporal trends over 20 years (Edil 2007). Investigations presented by Edil (2007) in landfills in Wisconsin indicate that the potential for VOC migration remains a problem associated with both clay and composite liner landfills. Both numerical analyses and field data imply that the current state of practice to contain VOCs is not adequate and VOCs may present a potential environmental problem as time passes. Then a careful review of landfill containment design with a focus on VOCs is needed to prevent wide-spread groundwater contamination around landfills in time. It is thus of interest to study diffusion of VOCs through GCLs.

Lake & Rowe (2004) examined diffusion of dichloromethane (DCM), 1,2 dichloroethane (DCA), trichlorethylene, (TCE), benzene and toluene through a GCL at room temperature. The GCL was composed of granular sodium bentonite encapsulated between a scrim reinforced nonwoven polypropylene carrier and a staple fiber nonwoven polypropylene cover geotextile. They concluded that the order of the rate of mass transport through the GCL was DCM≈DCA>benzene>TCE>toluene. The diffusion coefficients at room temperature and at confining pressure lower than 10 kPa ranged from approximately 2×10^{-10}m²/s to 3×10^{-10}m²/s. The difference in mass transport was attributed largely to varying degrees of sorption of the different compounds to the geotextile components of the GCL and to the bentonite. As those VOC diffusion coefficients were obtained at relatively high bulk void ratios compared with what would be encountered on the field, the results fall in the upper range of VOC diffusion coefficients expected for the case of a GCL in a base liner situation.

Rowe *et al.* (2005) extended this work by examining the effect of temperature on the diffusion of BTEX (benzene, toluene, ethylbenzene, m&p-xylene and o-xylene through a needlepunched reinforced GCL. This GCL with a mass per unit area of about 4.2kg/m² was composed of granular sodium bentonite encapsulated between a scrim reinforced nonwoven polypropylene carrier and a staple fiber nonwoven polypropylene cover geotextile. Tests were performed under a 9.5kPa load. Rowe *et al.* (2005) confirmed that the geotextile component of the GCL was the primary contributor to sorption of hydrocarbons by the GCL. The diffusion coefficients followed the order benzene>toluene>ethylbenzene>m&p-xylene≈o-xylene. Partitioning coefficients for the entire GCL followed the order m- and p-xylene>ethylbenzene>o-xylene>toluene>benzene. The reduction in both the diffusion and sorption coefficients with decreasing temperature from 22°C to 7°C had opposite effects on mass transport through the GCL. However the decrease in transport due to a reduced diffusion coefficient is more significant than the increased transport due to smaller sorption and the net effect was reduced mass transport at lower temperature (Rowe 2005). As the sodium bentonite used by Lake &Rowe (2000*a*,*b*, 2004) and Rowe *et al.* (2005) provided little sorption for volatile organic compounds Lake & Rowe (2005) examined the potential improvement in the sorption that could be achieved for several organoclays and bentonite-activated carbon mixtures. Batch tests performed showed that all organoclays could potentially increase VOC sorption to GCLs by several orders of magnitude but activated carbon generally appears to provide the most improvement for the samples tested. This result is consistent with data from Bartelt-Hunt *et al.* (2003) who studied the sorption of non-ionic organic species on organobentonites and with data from Richards

& Bouazza (2007) who studied the sorption of phenol on organo-modified basaltic clay and bentonite. Anyway, Lorenzetti *et al.* (2007) showed that at organobentonite amendments greater than 20% the hydraulic conductivity of GCLs could increase by as much as three orders of magnitude thus showing a detrimental effect on this parameter. Numerical simulations they performed to model benzene flow trough the sole GCL tended to show that for one of the two organobentonites tested the increased sorption was balancing the increase in hydraulic conductivity thus not conducting to increased flow of benzene. On the contrary, Lake & Rowe (2005) showed that considering the whole liner, increased sorption would only provide marginal benefits in terms of increased attenuation capacity for DCM and may even result in slightly higher benzene peak impacts for the single composite liner examined because of the relatively thin nature of the GCL the increased sorption has a limited impact on contaminant migration (Rowe 2005). Thus the increased costs associated with modifying GCLs likely outweigh the benefit of such additives when considering the use of the GCLs as part of the liner system for MSW landfills (Rowe 2005).

Through the previously mentioned studies, the nature of the bentonite studied was limited to natural sodium bentonite or organobentonites. The question of the nature of the bentonite on sorption and diffusive transfers can be raised especially as regards Europe, Asia or Australia where various types of natural sodium bentonite, sodium activated calcium bentonites and natural calcium bentonites can be encountered (Chung 2004).

The aim of this paper is thus to show some preliminary results of a study aiming at quantifying sorption onto geotextiles and diffusion through GCLs of various microorganic pollutants including VOCs. 2 different needlepunched GCLs coming from two different manufacturers, containing either natural sodium bentonite or calcium activated bentonite were studied for the preliminary study presented in this paper. Sorption onto bentonite will be studied in the following and is not presented through this paper.

MATERIALS

Presentation of GCLs studied

Two GCLs were studied. The first one (GCL1) consists of a woven carrier geotextile and a non woven needlepunched cover geotextile made of polypropylene (PP) fibers which will respectively be called GTX 2 and GTX 1 in the following. The powdered bentonite with a dry mass per unit area equal to 5.7kg/m² and the two geotextiles are attached by needlepunching. The second one (GCL2) consists of a nonwoven needlepunched carrier geotextile and a woven cover geotextile which will respectively be called GTX 4 and GTX 3 in the following. The granular bentonite with a dry mass per unit area equal to 6.1kg/m² and the two geotextiles are attached by needlepunching. A short description of the 4 geotextiles studied is given in Table 1.

Table 1. Synthesis of constitutive geotextiles from GCLs studied in this paper

Geotextiles	Products features	GTXs position in GCLs	Mass/unit area (g/m^2)
GTX 1	PP needlepunched	Cover	220
GTX 2	PP woven	Carrier	110
GTX 3	PP woven	Cover	110
GTX 4	PP needlepunched	Carrier	210

Presentation of VOCs studied

The sorption of 4 VOCs was studied in this paper: 1,2 dichloroethane, benzene, toluene and trichloroethylene.

GCL VOC SORPTION TESTING

Sampling Geotextile for sorption isotherms

In order to determine the sorption coefficient K_d for the 4 VOCs on the various geotextiles under study batch tests were performed. GCL samples 0.1m in diameter were cut from a GCL roll using a cutting shoe. Then the bentonite was removed by an air compressor before separating cover and carrier geotextiles from each other. Geotextiles were then weighed and inserted into 50mL glass bottles that were subsequently filled with deionised water. An adequate ratio solid on solution have to be found especially when the sorption is low. For the data presented in this paper, needlepunched geotextiles average ratio is 1:44 and woven geotextiles average ratio is 1: 77.

Pure VOCs were previously solubilised in methanol and diluted one time before injection in the bottle glass because of VOC solubility in water. Then both amount of VOC mixture was injected in glass bottles containing one geotextile. Blanks bottles were also prepared (without geotextile).

Samples were shacked during 36 hours to reach equilibrium between VOC concentration in water and VOC sorbed on geotextile. Laboratory temperature was set at 22°C. This is in agreement with test temperatures found in literature (Lake *et al.* 2004, Rowe *et al.* 2005). This is important as Rowe *et al.* (2005) have shown a great influence of temperature on VOC sorption to geotextiles.

Two internals standard toluene-d8 and 1,2 dichloroethane-d4 were used at known concentration to measure aqueous concentration of each VOC.

After reaching sorption isotherms equilibrium a certain amount of solutions was diluted and mixed with internal known solution to get 5mL of solution in 20mL special glass bottles for head space analysis.

Analytical Methodology

VOCs were analysed by head Space gas chromatography - mass detector (HS-GC-MS). 5mL of the sample were incubated at 70°C during 10 minutes. 1mL of the gas phase was injected into GC. A split/splitless injector was used in the split mode (split flow 12mL/min). The VOC mixture was then separated through a capillary columns (DB-5) 0.25mm in diameter and 60m in length). The following column oven temperature program was used with an initial temperature of 30°C, and an initial time step of 15 minutes. The temperature program rate was 30°C/min. The final temperature was 200°C and the holding time 5 minutes.

COV quantification was performed using the single ion monitoring mode. The ions m/z 62; 67; 78; 84; 91; 95; 98 were used respectively for 1,2 dichloroethane, 1,2 dichloroethane-d4, benzene, dichloromethane, toluene, trichloroethylene, toluene-d8.

A specific area per substance $A_{subs.}$ and internals standard $A_{inter.}$ were automatically integrated by GC-MS software after analysis. All data were transferred into a data bank in term of day analysis, Geotextile mass m_{GTX}, internal known concentration $C_{inter.}$ and specific response VOC on internals standard k_i. Then substances concentration C were calculated thanks to Equation 1:

$$C = k_i \frac{A_{subs.}}{A_{inter.}} C_{inter.} \quad (1)$$

Modelling sorption isotherms

Linear sorption isotherms is modelled by a proportional factor K_d between the concentration in the solid S in µg/g and the equilibrium solute concentration C_{eq} in µg/L as shown in Equation 2. K_d represents the distribution coefficient in mL/g:

$$S = 1000 K_d C_{eq} \quad (2)$$

For this paper we assume that sorption isotherm on geotextiles is a linear sorption based on the experimental results obtained.

Amounts of VOC sorbed on geotextiles expressed in µg are calculated from the difference between initial concentration C_0 given by sample without geotextile, corrected by a dilution factor, d, based on the ratio taking into account total glass bottle volume V_0 in L on total glass bottle volume minus geotextile volume V_1 in L and the equilibrium solute concentration C_{eq} given by total glass with geotextile. Then the ratio of VOC amount sorbed in µg on geotextile mass m in g is fitted depending on equilibrium solute concentration C_{eq} in µg/L.

$$S = \frac{V_1 \left(dC_0 - C_{eq} \right)}{m_{GTX}} \quad (3)$$

where d is given by Equation 4:

$$d = \frac{V_0}{V_1} \quad (4)$$

The distribution coefficient K_d in mL/g is finally inferred on a minimal of 3 points from minimal square linear experimental curve and validated if the correlation coefficient is higher than 0.75. 4 series was performed on GTX 1 and 2 and 2 series were performed on GTX 3 and 4.

SORPTION TEST RESULTS

Experimental results obtained for GTX 1, GTX 2, GTX 3 are presented respectively on Figures 1, 2, and 3. A synthesis of distribution coefficients from this study and from the literature is given in Table 2. For GTX 4 not enough point were available at the time of preparation of this paper to be fitted and to be presented in this paper. One can observe that for identical contaminants, partitioning coefficients measured through our study are in agreement with values obtained by Rowe *et al.* (2005).

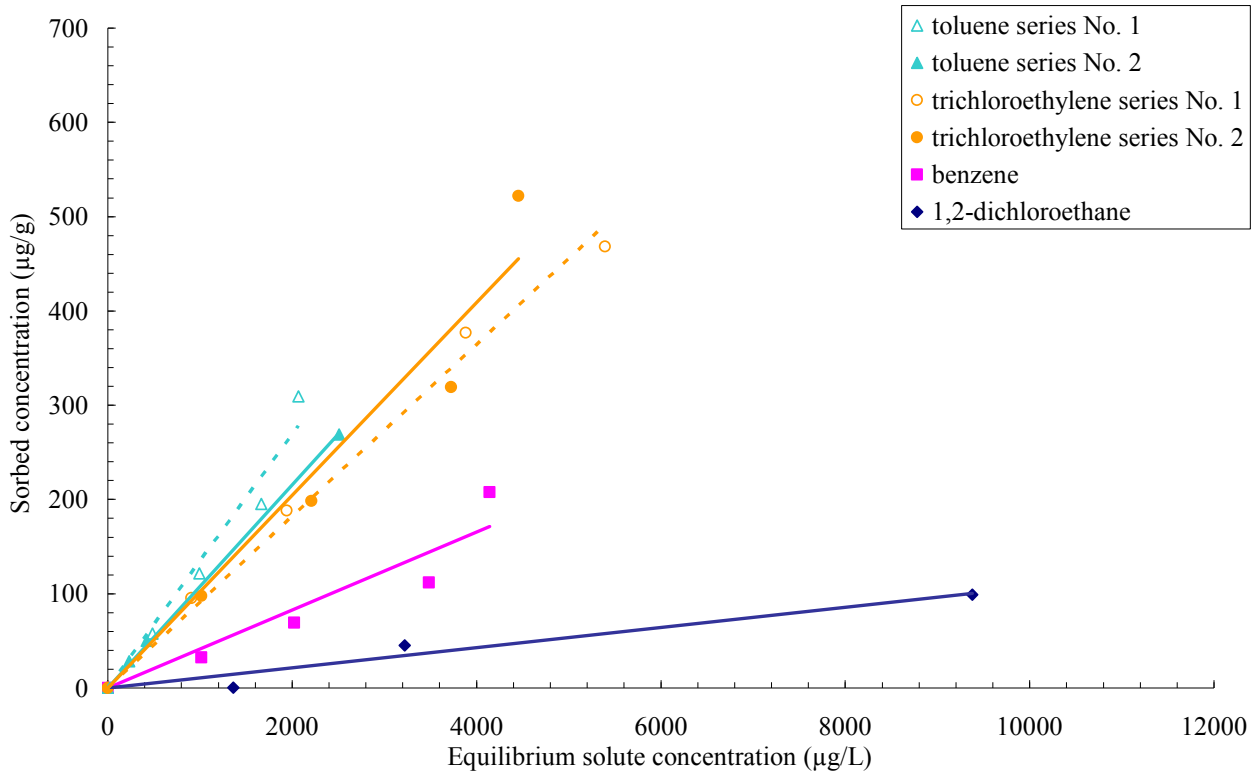

Figure 1. Results of batch tests for GTX 1

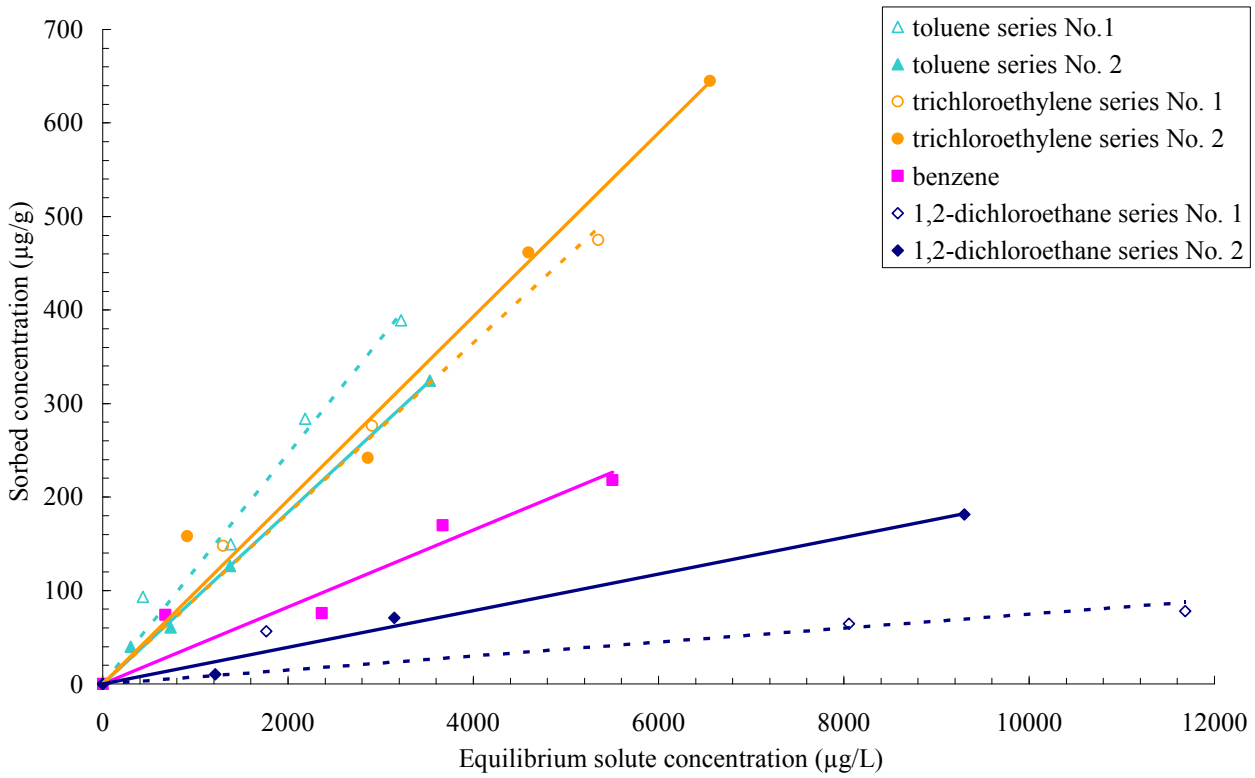

Figure 2. Results of batch tests for GTX 2

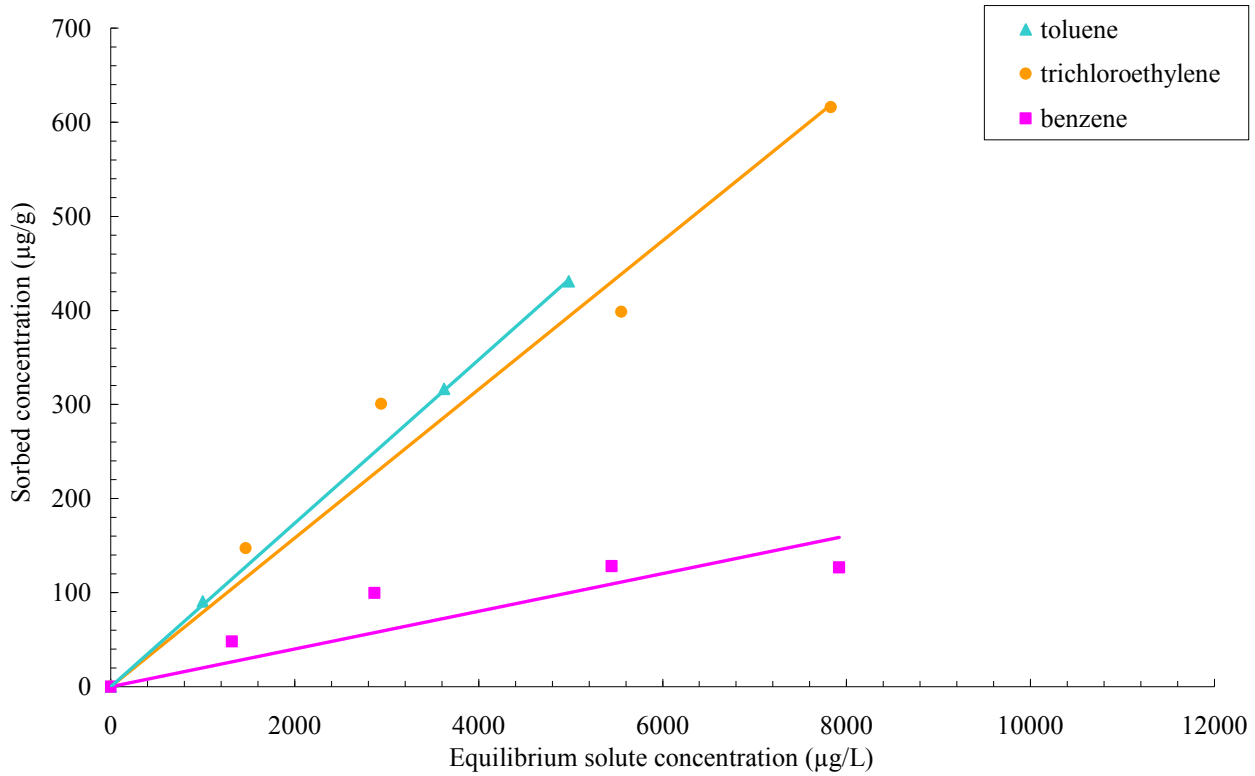

Figure 3. Results of batch tests for GTX 3

Table 2. Synthesis of partitioning coefficients K_d in mL/g for the geotextiles of various VOCs at 22°C from Rowe *et al.* (2005) and from this study

Nature of geotextile	**Needlepunched non woven**			**Woven**	
Contaminants	GTX 1	GTX Carrier*	GTX Cover*	GTX 2	GTX 3
1.2-dichloroethane	11			7 - 20	
trichloroethylene	91 - 102			91 - 98	79
benzene	41	32.2	25.8	41	20
toluene	108 - 135	97.4	86.7	92 - 123	87

*from Rowe *et al.* (2005)

PRELIMINARY DIFFUSION TEST RESULTS

Diffusion test took place in a glass cell shown in Figure 4. A GCL sample from GCL1 was put in the middle of the cell between two stainless steel sintered plates maintained at each side by glass funnels. GCL split the diffusion cell into two 1.6L waterproof tanks called respectively source and receptor reservoirs.

The GCL initial water content and mass was determined in order to adjust the GCL height to reach an expected GCL bulk void ratio e_b. Bulk GCL void ratio is defined as the ratio of volume of voids within the geotextile and bentonite components of the GCL to the volume of voids within the GCLs. Further details on the computations can be found in Petrov & Rowe (1997). The GCL height was finely adjusted thanks to an appropriate height known reference and a set of 0.0015m teflon shims. In the diffusion test presented in this paper e_b was equal to 3.51.

GCL was then hydrated by deionised water during 2 weeks until it reached water saturation. A minimum hydraulic head was applied on the GCL during the hydratation process. Diffusion test could then begin after a one month and a half to let ionic equilibrium reaching between GCL and both reservoirs. Both reservoirs were filled with deionized water without applying a hydraulic head.

At the beginning of a diffusion test a know initial concentration of VOCs is introduced into the source reservoir. Then 1-2mL water in each tanks were collected three times per week from the analysis collector shown in Figure 4. Samples were analysed by head space - gas chromatography - mass detector (HS-GC-MS). Then specific area per pollutants was determined by GC-MS software and stored in a data bank before deduced concentration thanks to Equation (1). The evolution with time of the 1,2-dichloroethane normalised concentration C/C_0 in the receptor is shown in Figure 5. This data represents preliminary results. Pollute v6 (Rowe & Booker 2005) was used to determine the 1,2-dichloroethane GCL diffusion coefficient. We checked through the calculations that the range of values obtained for the partitioning coefficient for GTX 2 did not significantly impact the value of diffusion coefficient

measured. The diffusion coefficient measured for the bentonite was found to be 1.5×10^{-10}m²/s among the assumptions of parameters presented on Figure 5 regarding the other parameters and a bulk void ratio equal to 3.51.

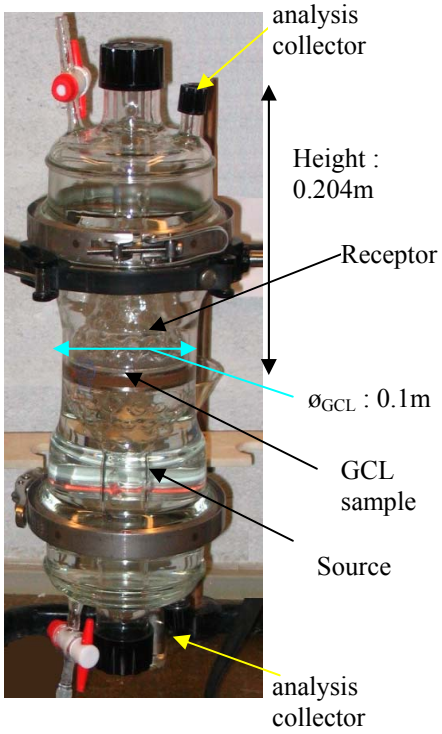

Figure 4. Diffusion cell

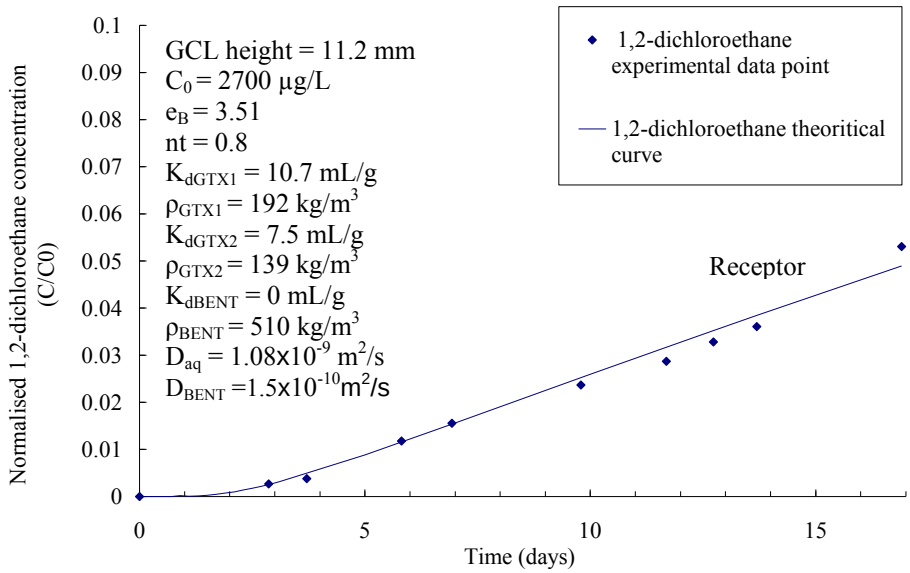

Figure 5. Preliminary results of 1,2-dichloroethane diffusion test on GCL 1

DISCUSSION ON SORPTION AND DIFFUSION RESULTS

As regards the value of partition coefficients obtained, the same trend as the one noticed by Rowe *et al.* (2005) could also be observed on our data. Indeed toluene and trichloroethylene have a trend for a larger sorption followed by benzene and 1,2-dichloromethane.

Two different series of tests lead to a range of partitioning coefficients especially with 1,2-dichloroethane on GTX 2. We thus cannot guarantee at the moment a unique sorption value without checking error source and confirming the present data. Nonetheless regarding diffusion test interpretation we have noticed that there was no influence of the sorption coefficient adopted for GTX 2 in the range of values measured.

The origin of the discrepancy might lead on the one hand in the substances volatility and on the second hand in the methanol used as an initial solvent. Indeed methanol has a huge vapour tension and substances could be lost during dilution in water. This value of diffusion coefficient is lower than values measured by Lake & Rowe (2004) which ranged from approximately 2×10^{-10}m²/s to 3×10^{-10}m²/s at confining pressures lower than 10kPa, for dichloromethane

(DCM), 1,2 dichloroethane (DCA), trichlorethylene, (TCE), benzene and toluene at room temperature. Additional tests have to be performed for other VOCs.

CONCLUSION

Results of sorption tests of VOCs on constitutive geotextiles of two GCLs were presented in this paper. VOCs tested were 1,2 dichloroethane, benzene, toluene and trichloroethylene. Range of values obtained are in agreement with previous studies performed by other authors.

A diffusion tests was also performed on one of the GCL studied, with 1,2 dichloroethane at room temperature. The diffusion coefficient obtained was found to be 1.5×10^{-10}m²/s and corresponded to a bulk void ratio equal to 3.51.

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