

Diffusion of organic pollutants through HDPE geomembrane and composite liners and its influence on groundwater quality

R.K. Rowe, L. Hrapovic & M.D. Armstrong

Geotechnical Research Centre, University of Western Ontario, London, Ont., Canada

ABSTRACT: The results of laboratory diffusion tests which examine the migration of chloride, volatile fatty acids and a number of chlorinated aliphatic compounds from a synthetic leachate through a geomembrane are summarized. The impact of dichloromethane and chloride beneath a hypothetical landfill is then modelled using the values of diffusion coefficients determined from the experiments. Two standard designs involving composite liner(s) are examined and it is shown that while a minimum design of a geomembrane over a 0.6 m compacted clay liner may not be adequate, a design involving a geomembrane, compacted clay and a minimum geological barrier performed very well in these analyses.

1 INTRODUCTION

Although the diffusion of various vapours through plastic has been examined in some detail (e.g. see Haxo, 1990), relatively little attention has been paid to diffusion of contaminants in dilute solutions (e.g. from landfill leachate) through high density polyethylene (HDPE) geomembranes. A review of the recent literature was presented by Rowe et al. (1995a) and will not be repeated here. In the Rowe et al. (1995a) study, attention was focused on the diffusion of chloride and dichloromethane (DCM) through a geomembrane and diffusion coefficients of $\leq 6 \times 10^{-15} \text{ m}^2/\text{s}$ and $2.2 \times 10^{-12} \text{ m}^2/\text{s}$ were deduced for these two contaminants dissolved in distilled water. However, leachate is a complex mixture of many different elements and components and the question arises as to whether the diffusion coefficients of chloride or DCM would be affected by the presence of the other constituents of leachate. To examine this question, a number of diffusion tests were performed to examine the migration of a number of constituents of leachate from a source of synthetic Keele Valley leachate (Rowe et al., 1994a). Synthetic (rather than actual) leachate was used to minimize complications that would otherwise occur due to biodegradation of organic components in actual leachate.

This paper reports on the preliminary findings from these experiments and discusses some practical implications.

2 TEST PROCEDURE

The test procedure adopted was essentially the same as that described by Rowe et al. (1995a) for DCM and involved placing a synthetic leachate source solution on one side of the geomembrane and a distilled water receptor on the other side of the geomembrane. The changes in concentration in the source and receptor (if any) were then monitored with time. The tests were performed in glass cells to minimize mass loss due to abiotic degradation as discussed by Rowe et al. (1995a).

The synthetic leachate (Rowe et al., 1994a) included ethanoic (acetic) acid (4000 mg/L), propanoic (propionic) acid (3000 mg/L), butyric acid (500 mg/L) as the principal organic constituents together with dichloromethane (DCM), 1,1 dichloroethane (1,1 DCA), 1,2 dichloroethane (1,2 DCA), cis 1,2-dichloroethene (cis 1,2-DCO), 2-butanone (methyl-ethyl ketone, MEK), toluene and xylene all in concentration in the 2-10 mg/L range. In addition, the leachate contained typical inorganic constituents, trace metals and a surfactant to simulate, as nearly as

practical, actual leachate.

The tests were performed using 2 mm thick type III copolymer HDPE with a density of 0.944 kg/m³, carbon black content of 2.5% and carbon black dispersion A-1. The testing temperature was 23°C ± 2°C. The results of the tests were analyzed as described by Rowe et al. (1995) using the finite layer analysis program POLLUTE v6 (Rowe & Booker, 1994).

3 EXPERIMENTAL RESULTS

Figure 1 shows the observed variation in the concentration of DCM in the receptor solution as a function of time over a 75 day period. Also shown is the theoretically predicted concentration variation based on a diffusion coefficient of 2.2x10⁻¹² m²/s obtained by Rowe et al. (1995) for DCM migrating alone. It can be seen that this gives a reasonable prediction of the observed behaviour (allowing for the usual scatter of experimental data) and this suggests that if there are any synergistic effects due to the presence of other organic contaminants it is not sufficient to be readily detectable and hence the diffusion coefficient obtained for a single compound solution of DCM was quite adequate for predicting migration from a more complex leachate.

Similar analyses were performed for 1,1 DCA. Here there is a little more scatter of the experimental data, however the data was reasonably well approximated by a diffusion coefficient in the range 1x10⁻¹² m²/s to 2.5x10⁻¹² m²/s with a preliminary best estimate of 1.5x10⁻¹² m²/s (see Table 1).

The diffusion coefficient for 1,2 DCA was between 3x10⁻¹² m²/s and 6x10⁻¹² m²/s (best estimate ≈ 4.5x10⁻¹² m²/s) and was a little larger than for DCM or 1,1 DCA. This diffusion coefficient is also a little larger than the value of 2.3x10⁻¹² m²/s obtained by Britton et al. (1988, 1989) by measuring weight gain of a geomembrane immersed in pure solvent but is of a similar order of magnitude.

In contrast to the relatively rapid diffusion of DCM, 1,1 DCA and 1,2 DCA through the geomembrane, methyl-ethyl ketone (MEK) diffuses much slower with a diffusion coefficient (see Figure 2) that appears to be in the range 3x10⁻¹³ m²/s to 8x10⁻¹³ m²/s with a best estimate of about 5x10⁻¹³ m²/s (Table 1).

Volatile fatty acids (VFAs) represent a major constituent of landfill leachate and of these VFAs, acetic acid is the smallest and generally

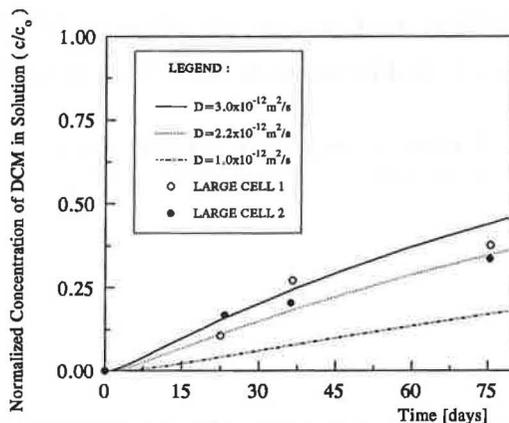


Figure 1. Diffusion of dichloromethane (DCM) from synthetic KVL leachate through HDPE geomembrane into receptor solution.

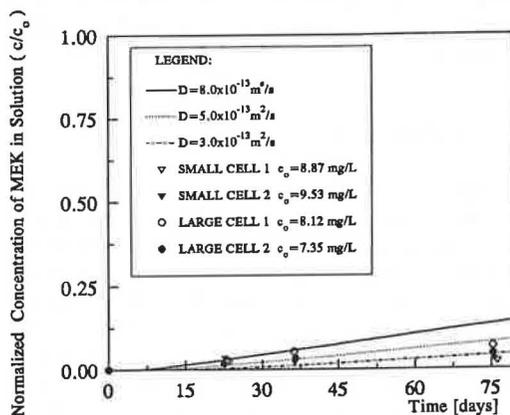


Figure 2. Diffusion of methyl-ethyl ketone (MEK) from synthetic KVL leachate through HDPE geomembrane into receptor solution.

most predominant. Figure 3 shows data for diffusion of acetic acid through a geomembrane over a period of 360 days. Whereas for DCM, 1,1 DCA, 1,2 DCA and even MEK there was a clearly measurable increase in receptor concentration over a 75 day period (and a corresponding decrease in source concentration since the experiment is a closed system), for acetic acid there was very little increase in receptor concentration over a 360 day test period reported in Figure 3. The very low concentrations being measured are close to the method detection limit (MDL) and due to the experimental "noise" in the data at these low concentrations which are

Table 1 Preliminary Diffusion Coefficients Through 2 mm Thick HDPE Geomembrane

Parameter	Diffusion Coefficient		
	Range (m ² /s)	Best Estimate (m ² /s)	Best Estimate (m ² /a)
Dichloromethane (DCM)	1-3 x 10 ⁻¹²	2.2 x 10 ⁻¹²	7 x 10 ⁻⁵
1,1 Dichloroethane (1,1 DCA)	1-2.5 x 10 ⁻¹²	1.5 x 10 ⁻¹²	5 x 10 ⁻⁵
1,2 Dichloroethane (1,2 DCA)	3-6 x 10 ⁻¹²	4.5 x 10 ⁻¹²	1 x 10 ⁻⁴
2-Butanone (MEK)	3-8 x 10 ⁻¹³	≤5 x 10 ⁻¹³	2 x 10 ⁻⁵
Ethanoic (Acetic) Acid	≤5 x 10 ⁻¹⁴	≤3 x 10 ⁻¹⁴	9 x 10 ⁻⁷
Chloride	≤6 x 10 ⁻¹⁵	≤4 x 10 ⁻¹⁵	1 x 10 ⁻⁷

typically less than 1% of the source concentration, it is difficult to obtain a good theoretical fit to the data. However, despite some uncertainty, it appears that the diffusion coefficient for acetic acid is less than 5x10⁻¹⁴ m/s and may well be less than 3x10⁻¹⁴ m/s (i.e. two orders of magnitude lower than DCM or 1,1 DCA).

The difficulties of detection are even greater for chloride. Rowe et al. (1995) provided data for diffusion tests which examined chloride migration through a geomembrane over a period of 2.4 years and obtained a conservative (upper bound) estimate of diffusion coefficient of 6x10⁻¹⁵ m²/s. These tests were continued and when one of the cells was terminated after three years the concentration of chloride in the receptor cell was only 0.151 mg/L (c/c₀ ≈ 7.74x10⁻⁵). Based on this, the diffusion coefficient appears to be less than 4x10⁻¹⁵ m²/s (Table 3) and may be of the order of 3x10⁻¹⁵ m²/s. Tests are continuing in two other cells and the diffusion coefficient will be refined as more long term diffusion data becomes available.

4 IMPLICATIONS

Results from diffusion experiments such as those described above and as summarized in Table 1 can be used as input in contaminant transport models to assess the level of potential contaminant migration that could occur for different

barrier systems involving geomembranes. To illustrate the potential implications, consideration will be given to modelling two barrier systems: (A) a US EPA "Subtitle D" standard design which involves a 1.5 mm thick HDPE geomembrane over a 0.6 m compacted clay liner with a hydraulic conductivity of 1x10⁻⁹ m/s or less and no other required attenuation layer, and (B) a basic design which involves a minimum 2.5 mm thick geomembrane over a 0.75 m compacted clay liner with a hydraulic conductivity of 5x10⁻¹⁰ m/s or less, over a 3 m "geological barrier" with a

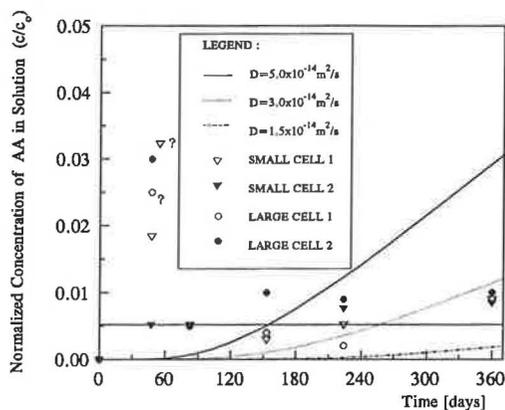


Figure 3. Diffusion of acetic acid (AA) from synthetic KVL leachate through HDPE geomembrane into receptor solution.

hydraulic conductivity of 10^{-7} m/s or less (i.e. similar to that proposed by German authorities).

The leakage through the geomembrane was calculated based on Bonaparte and Giroud (1992) for a well constructed geomembrane with small 2.5 holes/ha and was negligible in both cases provided that the geomembrane and leachate collection system maintain their design functionality. The service life of the geomembrane and leachate collection system are important issues (e.g. see Rowe et al., 1995b, Rowe et al., 1994) but this is beyond the scope of the present paper. For the following it will be assumed that both function as designed for the period of time modelled. The validity of this assumption needs to be carefully evaluated on a case by case basis in actual design calculations.

Consideration was given to the migration of two parameters: chloride and dichloromethane for a landfill assumed to have 250 000 tonnes/ha of waste (on average) and assuming an infiltration through the landfill cover of 0.15 m/a (soil cover). It should be noted that a lower permeable geomembrane/clay cover could result in greater impacts due to reduced dilution and, possibly, a longer half-life for DCM. Based on existing landfill leachate data (Rowe, 1995), the source concentration of chloride and DCM were taken to be 2500 mg/L and 3300 μ g/L respectively and the leachable mass was taken to be 1.8 g/kg and 2.3 mg/kg respectively. As discussed by Rowe (1995), the dichloromethane can be expected to experience a decrease in concentration with time in landfill leachate due to biodegradation. The half-life of DCM in leachate was taken to be 10 years (Rowe et al., 1994b) although there is some evidence that the half-life could be as low as 2 years.

The compacted clay was assumed to have a compacted dry density of 1.9 t/m³, porosity of 0.38 and an organic carbon content, f_{oc} , of 0.2%, K_{oc} for DCM was taken to be 350 mL/g (see Rowe et al., 1995b) and a diffusion coefficient of 0.018 m²/a which no sorption being considered. All modelling was performed using the program POLLUTE v6 (Rowe & Booker, 1994).

4.1 Dichloromethane

Figures 4 and 5 respectively show the calculated variation in DCM concentration with time at the bottom of the two barrier systems examined. Results are presented for four cases. Case 1 assumes that the half-life of 10 years is applicable

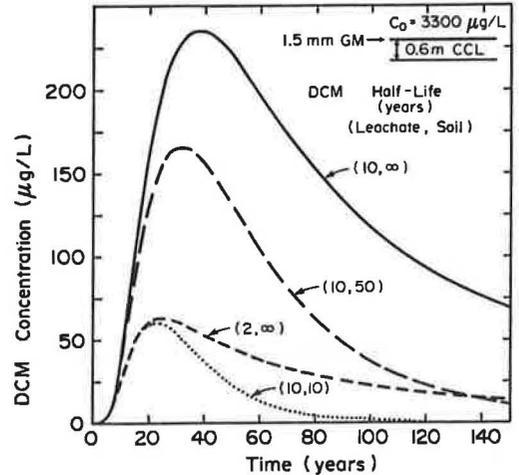


Figure 4. Calculated variation in dichloromethane (DCM) concentration with time at bottom of barrier system: Design A (curves shown are for different assumed half-lives for DCM in leachate and soil).

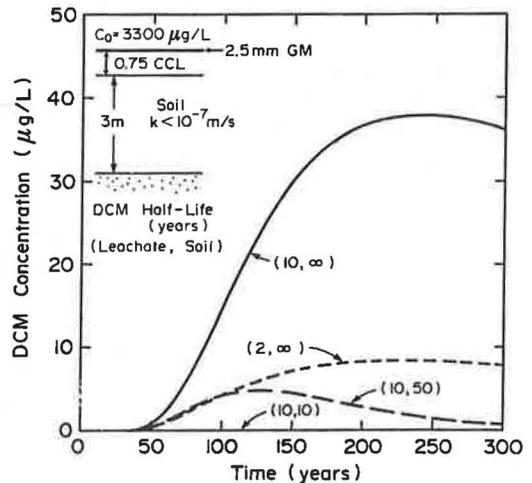


Figure 5. Calculated variation in dichloromethane (DCM) concentration with time at bottom of barrier system: Design B (curves shown are for different assumed half-lives for DCM in leachate and soil).

both in the landfill and in the soil below the geomembrane. For this most optimistic case the peak concentration at the bottom of the barrier system is 60 μ g/L for design A and <1 μ g/L for design B. These may be compared to the maxi-

imum acceptable concentration for DCM (a suspected carcinogen) of 50 µg/L and an allowable increase in concentration in Ontario, Canada (MOEE, 1994) of 12.5 µg/L. Putting aside for the moment the optimistic nature of the analysis, Design A would not be acceptable whereas Design B gives a peak concentration below normal analytical detection limits and hence would be acceptable.

It must be recognized that the half-life of 10 years adopted above assumes that the DCM is in a solution that includes other substrates (most notably the volatile fatty acids). Since the diffusion of the VFAs through the geomembrane is much slower than for DCM it could be argued that this will serve to decrease the rate of degradation in the soil below the geomembrane and hence Cases 2 and 3 assume a half-life of 10 years in the landfill leachate but a half-life of 50 years and infinity (i.e. negligible degradation), respectively, in the underlying soil.

Inspection of the results for Cases 2 and 3 in Figure 4 shows that for Design A the peak impacts of 166 and 235 µg/L (which occur at 30 and 40 years respectively) are well above the maximum acceptable concentration. In contrast, Design B is calculated to give peak impacts of 5 µg/L and 38 µg/L (at 120 and 240 years) for Cases 2 and 3 respectively and these are both well below the maximum acceptable concentration of 50 µg/L. Thus it can be seen that reasonable uncertainty regarding the half-life of DCM below a geomembrane does not affect the initial conclusion that at the base of the barrier system the concentrations of DCM are not acceptable for Design A but are acceptable for Design B.

As a final examination, an analysis was performed for Case 4 where the half-life in the leachate was taken to be 2 years but no degradation was assumed below the geomembrane. This analysis gave a peak impact of more than 60 µg/L for Design A and less than 10 µg/L for the basic Design B confirming the earlier observation regarding the suitability of the two minimum designs.

The results of the analyses for chloride indicated that over the 150 year period modelled, the concentration of chloride reached the bottom of the barrier system and was still increasing with the value at 150 years being 35 mg/L and 3 mg/L for Designs A and B respectively. This shows that the geomembrane provides an excellent barrier to both advective and diffusive migration

of chloride for so long as the leachate mound can be controlled and the geomembrane maintains its design function. It should, however, be noted that at 100 and 150 years, the concentration of chloride in the landfill is calculated to be 1090 mg/L and 720 mg/L respectively and hence for a landfill of this size a failure of the geomembrane at even 150 years would result in significant potential impact. In contrast, if the landfill contained 125 000 tonnes/ha then the concentration of chloride at 100 and 150 years would be 470 mg/L and 205 mg/L and hence a failure of the geomembrane at 150 years would cause an impact at the bottom of the barrier system of 200 mg/L (or less) which is below the drinking water objective for chloride (250 mg/L) and hence, at least in some jurisdictions, might be judged acceptable.

5 CONCLUSION

Experimental studies reported in this paper have shown that organic compounds such as dichloromethane, 1,2 dichloroethane and 1,2 dichloroethane can quite readily diffuse through an HDPE geomembrane. However, it was also demonstrated that when consideration is given to the half-life of DCM in leachate, an appropriate combination of geomembrane, compacted clay and geological barrier can be used to result in negligible impact at the bottom of the barrier system. It was shown for the conditions examined that a minimum US EPA Subtitle D design gave calculated impacts for DCM that were unacceptable that but a barrier system such as that proposed by German authorities did provide adequate attenuation and the impact of DCM below the geological barrier was negligible.

The experimental studies have also shown that some organic compounds migrate much slower than the three chlorinated solvents examined, with the diffusion coefficient for 2 butanone (methyl-ethyl ketone) being about an order of magnitude lower and the diffusion coefficient for acetic acid being about two orders of magnitude lower than for the chlorinated solvents. Thus the geomembrane provides an excellent barrier to the diffusion of acetic acid and chloride. This is an advantage since it minimizes the potential for these major constituents of leachate from impacting on groundwater. However, the fact that the geomembrane does appear to be such a good

barrier to acetic acid needs to be considered in assessing half-lives of chlorinated solvents in the soil below the barrier system.

In summary, the paper presents diffusion coefficients and illustrated their application for use in analyzing the potential impact of a landfill for two different barrier systems. It also demonstrates that with the appropriate choice of barrier system (e.g. geomembrane, compacted clay and geological barrier) the geomembrane can play a very important role in minimizing contaminant impact due to both diffusion and advection.

6 ACKNOWLEDGEMENT

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