



A comparative assessment of volatile organic compound (VOC) sorption to various types of potential GCL bentonites

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Abstract

The potential improvement in the sorption of volatile organic compounds (VOCs) to bentonite used in Geosynthetic Clay Liners (GCLs) is examined for mixtures of bentonite and several organoclays or activated carbon. Results of batch tests performed with dichloromethane (DCM), 1,2-dichloroethane (1,2-DCA), trichloroethylene (TCE), benzene and toluene are reported. It is shown 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. The engineering relevance of this potential improvement is assessed with respect to design of municipal solid waste landfill liner systems by performing contaminant transport modeling. It is shown that only slight changes in contaminant migration will occur, despite the large potential increases in GCL sorption. This suggests that increased costs associated with modifying GCLs may outweigh the benefit of such additives to GCLs for municipal solid waste landfill applications for the conditions examined herein.

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1. Introduction

Industrialized countries use volatile organic compounds (VOCs) for a variety of applications (Montgomery and Welkom, 1990). Unfortunately, these same VOCs are periodically encountered in municipal solid waste leachate monitoring programs (Rowe, 1994; Othman et al., 1996) in combination with other inorganic and organic constituents. Properly designed municipal solid waste landfills (MSWLs) attempt to mitigate contaminant transport of VOCs (and other contaminants) from MSWLs, into the underlying groundwater by incorporating engineered and natural barrier systems. The ability of barrier systems such as compacted clay liners (CCLs) and geosynthetic clay liners (GCLs), to “sorb” or attenuate VOC migration through MSWL liner systems is an important mechanism to consider when designing such systems. Generally, there is potential for more overall VOC attenuation for thicker CCL-based liner systems compared to GCL-based liner systems when organic carbon (OC) contents are similar for both materials. For thinner GCLs to improve their VOC attenuation capacity, product enhancement would be necessary to improve their sorptive uptake with respect to VOCs. This product modification could potentially be achieved using organoclays or activated carbon.

Examples of research and utilization of organoclays (also called organophilic clays) can be found throughout the literature (Boyd et al., 1988a,b; Smith and Jaffe, 1994; Jaynes and Vance, 1996; Boldt-Leppin et al., 1996; Headley et al., 2001). Organoclays can be created by exchanging the hydrated exchangeable cations of clay (usually bentonite) with various types of quaternary ammonium cations (Xu et al., 1997) or by other techniques (Lo, 1992; Srinivasan and Fogler, 1990). Depending on the moiety associated with the organic cation (size and/or composition), the surfaces of the clay mineral become less hydrophilic and more hydrophobic, providing improved sorption properties of non-polar organics compared to the original clay (Xu et al., 1997). Within this group of bentonites modified with quaternary ammonium cations, there may be differences in the sorption mechanism depending on the type of organoclay considered. Clays with relatively large organic quaternary ammonium cations (i.e. Fig. 1) sorb non-polar organic compounds (NOCs) mainly by a partitioning process involving the hydrophobic medium formed by the long flexible chains of alkyl compounds on the clay surface (Boyd et al., 1988b). As demonstrated by Lee et al. (1990), when smaller organic cations such as tetramethylammonium (TMA) are used in exchange reactions with montmorillonite, the sorption process of BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds is one of adsorption onto the clay mineral surface that has been modified by the addition of the quaternary ammonium cations. Table 1 shows the variations of the linear distribution coefficient, K_d , reported in the literature for relatively large chain quaternary ammonium cation modified clays. Quaternary ammonium cation modified bentonites shown in Table 1 typically have K_d values several orders of magnitude higher than unmodified bentonite often used in GCLs.

A significant amount of research has been performed on the adsorption of dissolved VOCs with activated carbon, mainly for the treatment of drinking water

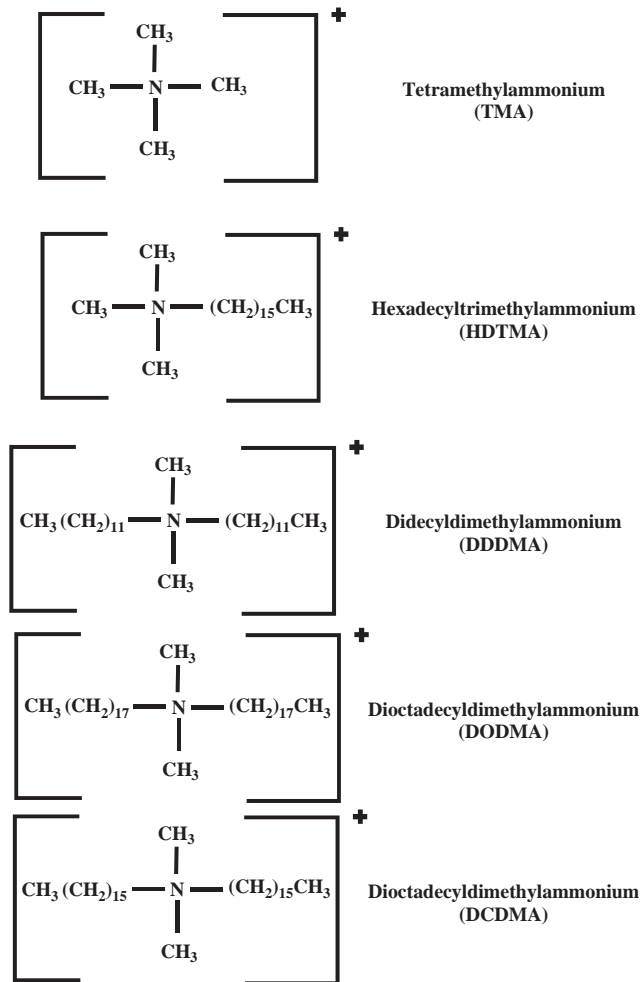


Fig. 1. Examples of quaternary ammonium cations used to develop organoclays (modified from Jaynes and Vance, 1996; Lo et al., 1997).

(Voice, 1988). Activated carbon (granular and/or powdered) refers to organic materials such as wood, coal, or coconut shells heated in the 500–700 °C range to form a charred material which is then heated in a steam or carbon dioxide environment to create a highly porous structure with a large internal surface area (Heilshorn, 1991). This large internal surface area of activated carbon is responsible for the adsorption of various contaminants and in particular, VOCs (Heilshorn, 1991). According to Voice (1988), the amount of removal of dissolved VOCs from solution will depend on the properties of the VOCs as well as the type of fluid in which they are dissolved. La Poe (1985) examined the adsorption of chlorinated

Table 1
Selected literature K_d values for batch testing with organoclays (log K_{oc} in brackets)

Clay	Notes	OC (%)	Benzene K_d (mL/g)	Toluene K_d (mL/g)	TCE K_d (mL/g)
Jaynes and Vance (1996)					
HDTMA	BTEX mixture; maximum benzene initial conc. 11 mg/L; maximum toluene initial conc. 84 mg/L	16.7	73 (2.6)	114 (2.8)	—
DDDMA	BTEX mixture; maximum benzene initial conc. 11 mg/L; maximum toluene initial conc. 84 mg/L	20.6	170 (2.9)	339 (3.2)	—
DODMA	BTEX mixture; maximum benzene initial conc. 11 mg/L; maximum toluene initial conc. 84 mg/L	28.2	174 (2.8)	401 (3.2)	—
HDTMA	BTEX mixture; maximum benzene initial conc. 11 mg/L; maximum toluene initial conc. 84 mg/L	23.9	121 (2.7)	317 (3.1)	—
DDDMA	BTEX mixture; maximum benzene initial conc. 11 mg/L; maximum toluene initial conc. 84 mg/L	29.4	168 (2.8)	457 (3.2)	—
DODMA	BTEX mixture; maximum benzene initial conc. 11 mg/L; maximum toluene initial conc. 84 mg/L	36.0	100 (2.4)	255 (2.9)	—
DODMA	Max. toluene initial conc. 84 mg/L	28.2	—	266 (3.0)	—
HDMTA	Max. toluene initial conc. 84 mg/L	23.9	—	277 (3.1)	—
DODMA	Max. toluene initial conc. 84 mg/L	36.0	—	191 (2.7)	—
Jaynes and Boyd (1991)					
HDMTA	Maximum benzene equilibrium conc. ~800 mg/L; maximum toluene equilibrium conc. ~220 mg/L	23.0	184 (2.9)	319 (3.1)	—
HDMTA	Maximum benzene equilibrium conc. ~800 mg/L; maximum toluene equilibrium conc. ~220 mg/L	20.6	123 (2.8)	195 (3.0)	—
HDMTA	Maximum benzene equilibrium conc. ~800 mg/L; maximum toluene equilibrium conc. ~220 mg/L	18.2	59 (2.5)	71 (2.6)	—
HDMTA	Maximum benzene equilibrium conc. ~800 mg/L; maximum toluene equilibrium conc. ~220 mg/L	17.5	53 (2.5)	74 (2.6)	—
Smith and Jaffe (1994)					
HDTMA	Maximum benzene equilibrium conc. ~400 mg/L	16.6	31 (2.3)	—	—
Lo et al. (1997)					
DCDMA	Maximum benzene equilibrium conc. ~120 mg/L; maximum toluene equilibrium conc. ~100 mg/L	33	~200 (2.8)	~375 (3.1)	—
Zhao and Vance (1998)					
HDTMA	Less than ~5 mg/L equilibrium concentration	16.7	—	—	64 (2.6)

Table 1 (continued)

Clay	Notes	OC (%)	Benzene K_d (mL/g)	Toluene K_d (mL/g)	TCE K_d (mL/g)
HDTMA	Less than ~5 mg/L equilibrium concentration	23.9	—	—	149 (2.8)
DDDMA	Less than ~5 mg/L equilibrium concentration	29.4	—	—	267 (3.0)
Boyd et al. (1988b)					
HDTMA	Maximum benzene equilibrium concentration ~ 600 mg/L	17.3	61 (2.5)	—	—
HDTMA	Maximum TCE equilibrium concentration ~ 600 mg/L	17.3	—	—	44 (2.4)

Note: HDTMA: hexadecyltrimethylammonium, DDDMA: didecyltrimethylammonium, DODMA: dioctadecyltrimethylammonium, DCDMA: dioctadecyltrimethylammonium, OC: fraction of organic carbon, f_{oc} , in percent, TCE: trichloroethylene.

aliphatic compounds from solution by powdered activated carbon (PAC) and observed linear isotherms for the range of equilibrium concentrations considered (< 150 $\mu\text{g/L}$). Trichloroethylene (TCE) exhibited a K_d value of 63 700 mL/g at a soil/solution ratio of 1 g to 10 000 mL. El-Dib and Badawy (1979) performed batch tests with multi-component solutions of BTEX compounds at soil/solution ratios ranging from 1 g to 10 000 mL to 1 g to 1428 mL and equilibrium concentrations below 20 mg/L. Although they found a non-linear isotherm over the range of testing, initial linear parts of the isotherm indicate K_d values of approximately 5000 mL/g for benzene and 21 500 mL/g for toluene.

The objective of this paper is two-fold. Firstly, to evaluate the sorption of several aromatic and chlorinated VOCs to bentonites currently used in several commercially available GCLs, as well as to evaluate the improvement in sorption of these same VOCs to potential additives to the bentonite (i.e. organoclays and activated carbon). Secondly, to perform a comparative contaminant transport modeling assessment of VOCs through a MSWL geomembrane (GM)/GCL composite liner system. The purpose of this assessment is to assist in assessing the potential benefits of developing a “new and improved” modified GCL material. It is anticipated that the methods proposed in this paper can be utilized for other potential bentonite modifications with respect to GCL product development. Although other applied studies by Headley et al. (2001), and Smith and Jaffe (1994) have focused on organoclay–bentonite clay–sand mixtures with respect to VOC sorption, there is a paucity of literature related to evaluating sorption to organoclays and activated carbon mixtures in GCLs (especially at VOC concentrations typical in MSWL leachate). Lo (1992) is one of the few publications focusing on this aspect of organoclays in which dichlorobenzene was examined. There is also a lack of information on the overall implication with respect to contaminant transport of increased sorption of the GCL compared to existing GCL products in MSWL liner systems.

2. Methodology

In the present study, comparative batch tests were performed to evaluate the sorption of the five VOCs listed in Table 2 with several different sorbents (soils). These five VOCs (dichloromethane (DCM), 1,2-dichloroethane (DCA), trichloroethene (TCE), benzene and toluene) exhibit a range of physical and chemical properties as shown in Table 2. Most of the VOCs in Table 2 are relatively volatile and either non-polar or only slightly polar as is indicated by their low dielectric constants relative to a polar liquid such as water (dielectric constant of approximately 80). These VOCs were chosen for the study based on their presence in MSWL leachate (Rowe, 1994; Othman et al., 1996). As shown in Table 3, the soil materials tested consisted of 100% granular Na bentonite (GB), 100% powdered Na bentonite (PB), a 2% (by air-dried mass) PAC/powdered bentonite (PB) mixture and four modified bentonites (organoclays “A” to “D”, 100% “mixtures”). The GB was sampled directly from Bentofix NW and NS GCLs while the PB was sampled from Naue Fasertechnik’s BFG5000 GCLs. Details on chemistry and mineralogy of the GB and PB can be found in Lake (2000). The activated carbon and organoclays were obtained from various commercial sources in the USA and Germany (Lake, 2000). Due to proprietary reasons, the exact composition and nature of the organoclays and activated carbon was not obtained. However, as shown in Table 3, total OC analyses were performed on the samples. It is worthwhile to note that many variations of organoclays exist in practice and the organoclays tested herein do not necessarily represent the range of properties available from all commercially available organoclays.

Prior to batch testing, all glass centrifuge tubes (Kimax Brand Heavy Duty—40 mL nominal capacity) and caps were thoroughly cleaned and assembled. The centrifuge tubes were subdivided into five groups of three with each group representing triplicate measurements of one concentration level for the sorption isotherm. The soil (1.5 g, unless otherwise noted) was placed in each centrifuge tube and then filled with 38 mL of deionized, distilled water until the headspace was minimized. The mass of the tube at each of these stages was recorded using an analytical balance. To achieve desired initial concentrations in each centrifuge tube, a stock solution containing a mixture of DCM, DCA, TCE, benzene and toluene was prepared (~5 g/L chlorinated compounds, ~2.5 g/L aromatic compounds) and was injected into the centrifuge tubes with a gastight syringe. Volumes added ranged from 4 to 20 μ L. Batch tests performed with the 2% PAC/PB mixture utilized a stock solution containing approximately 5 g/L of DCM and DCA and approximately 9 g/L of TCE, benzene, and toluene to account for the anticipated large amount of sorption of the 2% PAC/PB mixture for the latter three compounds. After each centrifuge tube was prepared, the tubes were manually agitated to break up any clumps of soil and placed in a shaker for 24 ± 4 h. Since the primary objective of this study was a relative comparison of the sorption ability of the soils, the shaking time described above was not varied. However, Boyd et al. (1988b) performed batch equilibrium testing with a hexadecyltrimethylammonium (HDTMA) clay and benzene and TCE and found from experimentation that equilibrium was reached

Table 2
Properties of the volatile organic compounds examined (all properties for 25 °C unless otherwise noted)

Compound	Specific density ¹ (g/mL)	Vapor pressure ² (kPa)	Dielectric constant ³	Octanol–water partition coefficient ² , log K_{ow}	Organic carbon/water partition coefficient ⁴ log K_{oc}
Dichloromethane (CH ₂ Cl ₂)	1.32 (20 °C)	~60	8.9	1.15	0.94
1,2 Dichloroethane (C ₂ H ₄ Cl ₂)	1.25	~9	10.4 (20 °C)	1.47	1.26
Trichloroethylene (C ₂ HCl ₃)	1.46 (20 °C)	~10	3.3 (28 °C)	2.42	2.21
Benzene (C ₆ H ₆)	0.87	~16	2.3 (20 °C)	2.13	1.92
Toluene (C ₇ H ₈)	0.86	~4	2.4	2.69	2.48

¹Montgomery and Welkom (1990).

²Schwarzenbach et al. (1993).

³Lide (1995).

⁴Empirical log K_{oc} values for soil organic matter estimated from K_{ow} values (Schwarzenbach et al., 1993) shown in table based on Karickhoff et al. (1979): (log K_{oc} = log K_{ow} - 0.21).

Table 3
Summary of batch test results

Sorbent (<i>Soil:Solution Ratio in Brackets</i>)	K_d (mL/g) and ($\log K_{oc}$) values obtained from batch tests. (\pm values are the 95% confidence limits)					
	OC (%)	DCM	1,2 DCA	TCE	Benzene	Toluene
Granular bentonite (GB)(1 g:11 mL)	0.3 ¹	0.3 \pm 0.1	0.3 \pm 0.1	0.9 \pm 0.3	0.4 \pm 0.1	1.2 \pm 0.4
Powdered bentonite (PB) (1 g:11 mL)	0.4 ¹	0.5 \pm 0.2	0.6 \pm 0.2	1.2 \pm 0.2	0.5 \pm 0.1	1.6 \pm 0.3
Organoclay A (1 g:80 mL)	26 ²	11 \pm 2 (1.63)	44 \pm 3 (2.23)	50 \pm 3 (2.28)	63 \pm 5 (2.38)	148 \pm 6 (2.76)
Organoclay A (1 g:25 mL)	26 ²	14 \pm 2 (1.73)	45 \pm 4 (2.24)	50 \pm 6 (2.28)	69 \pm 7 (2.42)	169 \pm 21 (2.81)
Organoclay B (1 g:25 mL)	27 ²	13 \pm 1 (1.68)	38 \pm 2 (2.15)	42 \pm 4 (2.19)	70 \pm 5 (2.41)	174 \pm 21 (2.81)
Organoclay C (1 g:25 mL)	28 ²	17 \pm 1 (1.78)	54 \pm 7 (2.29)	72 \pm 6 (2.41)	104 \pm 14 (2.57)	264 \pm 39 (2.97)
Organoclay D (1 g:25 mL)	38 ²	20 \pm 1 (1.72)	62 \pm 2 (2.21)	94 \pm 6 (2.39)	79 \pm 5 (2.32)	196 \pm 11 (2.71)
2% PAC/PB mixture (1 g:80 mL)	2.5 ²	7 \pm 2 (2.44)	41 \pm 2 (3.21)	491 \pm 56 (4.29)	369 \pm 49 (4.17)	3354 \pm 454 (5.13)
2% PAC/PB mixture (1 g:25 mL)	2.5 ²	5 \pm 1 (2.30)	37 \pm 5 (3.17)	~889 (4.55)	774 \pm 184 (4.49)	~7969 (5.50)

Note: approx. values shown are based on tests in which the lower concentration levels of the batch tests were below the detection limit of the GC methods.

¹Organic carbon (OC) values obtained at the University of Western Ontario (Walkley and Black, 1934).

²Organic carbon (OC) values obtained from Huffman Laboratories Inc., Golden, Colorado.

after 18 h. After shaking, the tubes were placed in a centrifuge to separate the soil and aqueous solution (2000 rpm for a total of 60 min). Three 0.8 mL aliquots were taken from each tube and separately placed in 2 mL gas chromatograph autosampler vials for chromatography analyses. Gas chromatography analyses were performed with a 3800 Varian gas chromatograph equipped with a Varian Saturn 2000 mass spectrometer detector. Injections were performed with a Varian 8200 autosampler equipped with a solid phase micro-extraction (SPME) polydimethylsiloxane (100 μm) fibre. Full details of batch testing procedures can be found in Lake (2000).

3. Laboratory test results

3.1. Organic carbon

As shown in Table 3, the OC content (in percent) is relatively low for the GB and PB (0.3% and 0.4%, respectively), however, the 2% PAC/PB mixture increases to 2.5% after the addition of the PAC. Since the organoclays were tested without mixing with a bentonite (GB or PB), the OC contents are relatively high, ranging from 26% to 38%.

It is usually the organic matter in soil that dominates the sorption of dissolved non-polar organic compounds (NOCs) such as those in Table 2 when the fraction of organic matter in the soil is above approximately 0.002 (Schwarzenbach et al., 1993). Organic matter present in soil is usually considered to exhibit properties that are somewhere between polar and non-polar (Schwarzenbach et al., 1993) and hence NOCs dissolved in polar water will tend to partition into the relatively more non-polar organic matter. Relationships have been developed in an attempt to predict the amount of sorption to be expected for a natural soil and NOCs based on the amount of natural organic matter in the soil. For engineering applications, OC analyses are usually performed on the soil instead of more intricate organic matter determination. Karickhoff et al. (1979) normalized the linear distribution coefficient, K_d , with the fraction of organic carbon (f_{oc}) to give the partitioning coefficient of a compound between organic carbon and water, K_{oc} :

$$K_{oc} = K_d / f_{oc}. \quad (1)$$

Karickhoff et al. (1979) also developed empirical correlations to predict K_{oc} values for a particular organic compound (for soil with natural organic matter) based on the octanol–water partition coefficient, K_{ow} (see Table 2). K_{oc} values will be discussed in the following section related to batch test results.

3.2. Batch test results

Batch test results for each soil are also presented in Table 3 while typical batch isotherm plots are given for organoclay A (Figs. 2 and 3) and the 2% PAC/PB mixture (Figs. 4 and 5). Each solid circle on the isotherms presented in Figs. 2–5 represents the result of one centrifuge tube at a particular concentration level. Linear

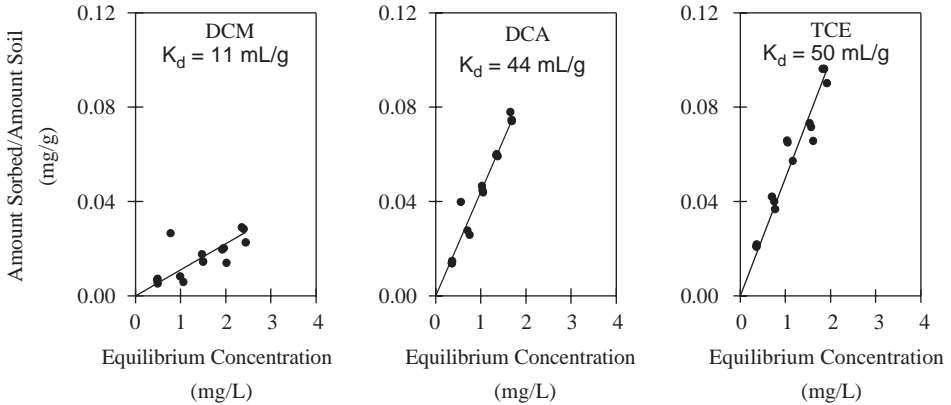


Fig. 2. Organoclay “A” batch test results for DCM, 1, 2 DCA and TCE (soil:solution ratio 1 g:80 mL).

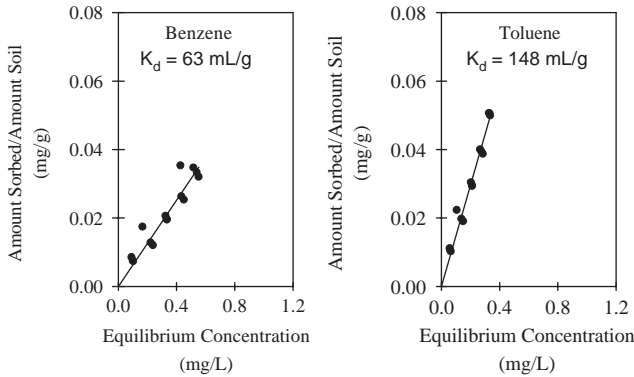


Fig. 3. Organoclay “A” batch test results for benzene and toluene (soil:solution ratio 1 g:80 mL).

regression analysis was used to establish the K_d values shown in Table 3, assuming an intercept through the origin. The 95% confidence limits (included in Table 3 as “ \pm ” values) for each K_d value obtained from the regression analysis are also presented. Adjacent to the K_d values, in brackets, in Table 3, are the $\log K_{oc}$ values. To provide a relative comparison to the data presented in Tables 2 and 3 summarizes $\log K_{oc}$ values for the VOCs examined in this study for soils composed of natural organic matter based on a relationship developed by Karickhoff et al. (1979). Comparisons between $\log K_{oc}$ values in Tables 2 and 3 are mainly of interest since the organoclays tested in this study most likely include large amounts of OC that are not composed of similar amounts of carbon as natural organic matter. As previously stated, the four “organoclays” in this study are proprietary and the nature of the organic moiety present on the bentonites is unknown. Activated carbon has a high internal surface (La Poe, 1985), unlike natural organic matter, which also makes $\log K_{oc}$ comparisons for interest sake only.

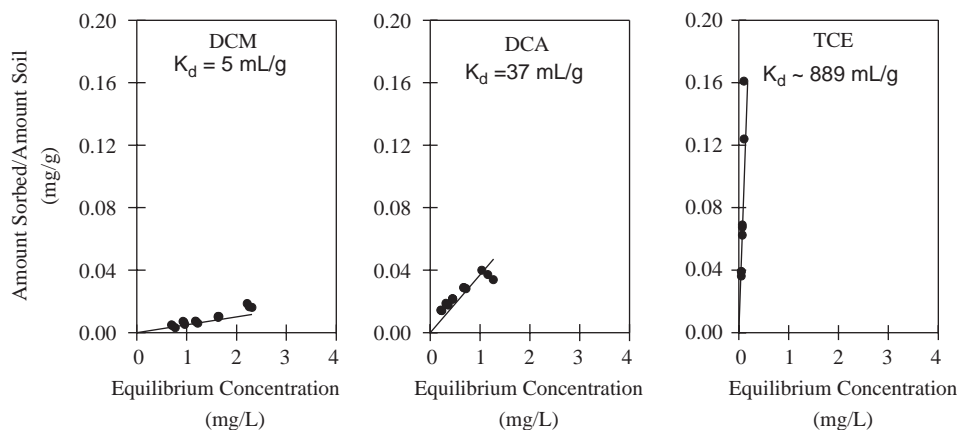


Fig. 4. 2% PAC/PB mixture batch test results for DCM, 1, 2 DCA and TCE (soil:solution ratio 1g:80mL).

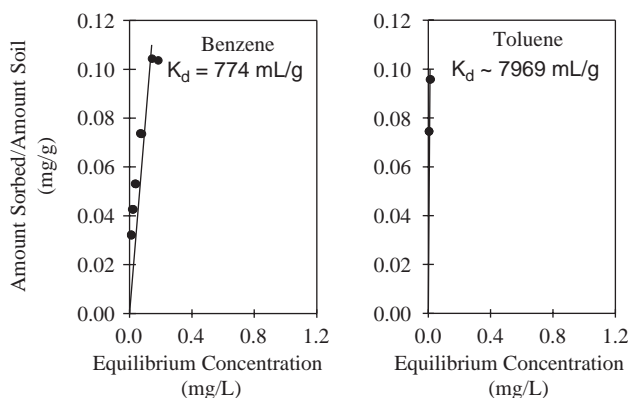


Fig. 5. 2% PAC/PB mixture batch test results for benzene and toluene(soil:solution ratio 1g:80mL).

3.2.1. GB and PB

The sorption of all VOCs was found to be low for the GB and PB relative to the other soils in the study as reflected by a comparison of K_d values. This is most likely due to the low fraction of OC in the two bentonites (PB and GB) relative to the other soils tested. It is believed that experimental scatter observed during testing, which is exhibited as large confidence limits in Table 3 for GB and PB, is due to low sorption of the VOCs to the PB and GB. Due to the hydration energy of exchangeable cations such as Na^+ and Ca^{2+} , the surface of the smectite clay minerals (bentonite) is quite hydrophilic (i.e. water loving) and is not conducive for sorption of NOCs (Schwarzenbach et al., 1993). Usually, sodium bentonite in GCLs (referred to in this study as unmodified bentonite) has a relatively low organic matter content and

hence partitioning of NOCs into organic matter will be small, for engineering purposes. For comparison, Smith and Jaffe (1994) reported a K_d value of 0.2 mL/g for benzene for a bentonite while Lo et al. (1997) reported “insignificant” sorption of BTEX compounds with bentonite. Headley et al. (2001) reported various levels of K_d for benzene and toluene, depending on soil to water ratios. As will be discussed later, from a practical standpoint, regardless of the actual low levels of sorption of the VOCs to the bentonite, the influence on overall GCL contaminant transport is minimal. It should also be noted that Lake and Rowe (2004) and Rowe et al. (2005) have observed sorption of VOCs to the polypropylene geotextile component of the GCL during VOC diffusion testing. Depending on the VOC examined and the mass of geotextile utilized for the GCL, this amount of sorption may actually be more than that to the bentonite.

3.2.2. *Organoclays A, B, C, and D*

For organoclays A, B, C and D, DCM exhibited the least amount of sorption of the five VOCs examined (Table 3). When comparing individual K_d values for each organoclay, increasing amounts of sorption for DCM follows the order of Organoclay B, A, C, and D (soil/solution ratio of 1 g:25 mL) with K_d values for A and B “overlapping” when considering confidence limits. This generally follows the trend of increasing amounts of OC in each organoclay. The fact that DCM experienced the lowest amount of sorption of the five VOCs tests is consistent with what would be expected for a soil composed of natural organic matter as demonstrated when comparing relative orders of $\log K_{oc}$ values for each of the five VOCs examined in this study (Table 2). Organoclays A–D appear to sorb the chlorinated VOCs in decreasing order of TCE > DCA > DCM with differences between TCE and DCA being smaller than would be expected based on differences of $\log K_{oc}$ values deduced from the literature for natural organic matter (Table 2). When comparing $\log K_{oc}$ values of TCE for the four organoclays, it appears as if organoclays C and D are slightly more effective sorbents than organoclays A and B. For only a slight increase in OC content, organoclay C appears to be more effective at removing benzene and toluene from aqueous solution than that of both A and B. In addition, the sorption of benzene and toluene for organoclay C is more than that of organoclay D even though organoclay D has 38% OC compared to 28% of organoclay C. Jaynes and Vance (1996) also noted this general observation of decreased sorption of BTEX compounds for a high OC content (36%) DODMA clay.

Although an increase in the OC content from organoclay C to D reduced K_d values for benzene and toluene, the K_d values of the chlorinated hydrocarbons still increased. The observation of lower benzene sorption compared to TCE sorption for organoclay D is consistent with what would be expected when comparing relative natural soil organic matter K_{oc} values between benzene and TCE (Table 3). However, Boyd et al. (1988b) observed less sorption of TCE relative to benzene for an HDMTA clay in which they suggested that the HDTMA partitioning phase was similar to a bulk solvent in which TCE is probably slightly less soluble than benzene for that hydrocarbon phase. Since Organoclays A, B and C exhibited higher K_d

values for benzene sorption relative to TCE, it is possible that the hydrocarbon phase of these three organoclays are slightly more favourable for benzene sorption relative to TCE compared to that of Organoclay D.

Although the chemical compositions of the organoclays are unknown, it is interesting to compare results with other organoclays in the literature with similar OC contents. Comparing results obtained in this study with organoclays of similar OC content to those of Jaynes and Vance (1996) for benzene and toluene, it appears as if the values in this study are either similar or lower. Although organoclays A and B in this study have lower K_d values than those obtained by Jaynes and Vance (1996), organoclays C and D are similar to those of Jaynes and Vance (1996) when comparing single component toluene test results. Organoclays A and B have slightly higher benzene $\log K_{oc}$ values than that of Smith and Jaffe (1994). The K_d values reported in this study are lower than those of Zhao and Vance (1998) and Boyd et al. (1988b) as shown in Table 1. This could be due to differences in experimental techniques (e.g. concentration levels) as well as differences in soil:solution ratios used for testing (Voice et al., 1983). Regardless of the study performed, the organoclays are much better sorbents to the VOCs than the unmodified sodium bentonites currently used in the NW, NS and BFG5000 GCLs, which would suggest there could be some potential enhancement of organoclay-based GCLs.

3.2.3. Powdered activated carbon (2% PAC)/powdered bentonite(PB) mixture

The 2% PAC/PB mixture at a soil:solution ratio of 1 g:25 mL (same ratio used for each organoclay) resulted in large amounts of sorption for TCE, benzene and toluene with some of the lower concentration levels of TCE and toluene being below the detection limit of the analytical technique used. K_d values of 5 mL/g for DCM and 37 mL/g for DCA were obtained for the mixture. The DCM K_d value for the 2% PAC/PB mixture is lower than that obtained from the organoclays tested while the 1,2-DCA K_d value is similar. However, it should be remembered that the 2% PAC/PB mixture has only a 2.5% OC content compared to OC contents ranging from 26% to 38% for organoclays. This difference in OC content is demonstrated when comparing $\log K_{oc}$ values between organoclays A to D and the 2% PAC/PB mixture. Values of K_d for TCE, benzene, and toluene are much higher for than those obtained from organoclays A to D, even though there is a much higher OC content for the organoclays. As previously mentioned, La Poe (1985) suggested that the amount of organic matter in the activated carbon is not as important as the amount of internal surface area available for adsorption of the VOCs. Generally speaking, the sorption of the VOCs examined fall within the relative sequence expected based on $\log K_{oc}$ values for natural organic matter, although the actual magnitudes are larger. The K_d value for TCE is much lower than that obtained by La Poe (1985) for TCE (63 700 mL/g). This is most likely due to portions of the surfaces of the PAC being “covered” with the bentonite present in the mix and hence not being accessible to the VOC compounds in solution. It may also have to do with the multi-component solution being used for testing in this study as well as slightly higher concentrations used relative to La Poe (1985).

3.2.4. Discussion of laboratory results

The main objective of this study was to perform a relative sorption comparison between different “modified” bentonites for non-polar VOCs in an attempt to identify the potential benefit of improving the sorption of bentonites currently used in the GCLs. Generally, for this reason, the soil:solution ratio was kept constant for batch testing. In the literature there are various soil:solution ratios used for batch testing with modified bentonites. For example, Boyd et al. (1988b) used a soil:solution ratio of 1 g:25 mL, Lo et al. (1997) used varying soil:solution ratios ranging from 1 g:160 mL to 1 g:27 mL and Jaynes and Vance (1996) used soil solution ratios from 1 g:250 mL to 1 g:63 mL. As discussed by Voice et al. (1983) and Barone et al. (1992), the soil:solution ratio can have an effect on the results obtained from batch testing. To examine the effect of the soil:solution ratio for organoclay A and the 2% PAC/PB mixture, two additional batch tests were performed at a soil:solution ratio of 1 g:80 mL. As shown in Table 3, there was very little difference in results for organoclay A at the lower solids content. However, for the 2% PAC/PB mixture, there was a substantial drop in K_d values for TCE, benzene, and toluene. Others (Voice et al., 1983; Barone et al., 1992) have observed this variation in K_d values for batch tests for different soil:solution ratios. However, they observed decreases in K_d values when the solid concentration increased in the batch test solutions. This was attributed to organic matter being washed off the soil during testing which then could not be separated from the solution. These non-settling organic particles were thought to increase the capacity of the solution to retain the solute and hence produce lower K_d values as the solids content increased in the test solution. The analytical technique used in this study varies from that of Barone et al. (1992) and Voice et al. (1983) in that a SPME fibre was used to absorb the VOCs from the solution in the headspace of the gas chromatograph autosampler vial. Based on the hypothesis presented by Voice et al. (1983), at the higher solids concentration for the 1 g:25 mL test, it would be expected that this would tend to keep the VOCs sorbed to these non-settling particles in solution, competing with the non-polar SPME fibre used to absorb the VOCs in the autosampler vial used for GC analyses. This would result in less VOCs being absorbed on the SPME fibre and hence lower analytical concentrations obtained from gas chromatography compared to solvent extraction methods. This would tend to suggest that as the solids to water content rose from 1 g:80 mL to 1 g:25 mL, K_d values would also increase, as was the case for the 2% PAC/PB mixture observed from Table 3. It would also be expected that the VOCs with higher K_{oc} values (benzene, TCE, and toluene) would exhibit larger differences than the slightly polar VOCs, DCM and DCA; as was observed. The fact that there was almost no difference for organoclay A may be due to the highly non-polar nature of the organoclay that does not tend to be suspended or dissolved in the relatively highly polar water during the separation process, relative to the activated carbon material.

Regardless of the actual K_d values of the organoclays and 2% PAC/PB mixture, their sorptive capacity to the VOCs in this study are much more than the sodium PB and GB used in the Bentofix GCLs previously described in this paper. It should also

be noted that the organoclays examined in this study were tested without mixing with the sodium bentonite as was done for the 2% PAC/PB mixture. To retain adequate hydraulic properties of the GCL that make it so attractive as an advective barrier as well as to maintain competitive cost pricing, it is probable that organoclays tested in this study would be added as a amendment material at a percentage of 10% or less. This would result in much less sorption of the “organoclay bentonite” in a GCL compared to a GCL, which has 10% PAC in the bentonite mixture. Therefore, it appears that both PAC and the organoclays will assist in increasing the amount of sorption of VOCs to GCLs, however the increase may be much greater for an activated carbon modified GCL (when considering similar percentages of additives to the bentonite). Other short-chain quaternary ammonium organoclays (Lee et al., 1990) may have stronger solute uptake than the organoclays tested in this study. However, their adsorption may be selective with regards to the VOCs adsorbed compared to activated carbon which is a much more general adsorbent. It is useful to examine the implications of these test results with respect to performance of an enhanced GCL containing activated carbon in contaminant transport through a MSWL liner.

4. Implications of test results

Modern landfills often employ single or double composite GM/CCL to assist in mitigating contaminant transport through MSWL barrier systems. As discussed by Rowe (1998) and Rowe et al. (2004), there is often a desire from an economic standpoint to replace or reduce the thickness of the compacted clay liner in MSWL barrier systems by utilizing GCLs. In many regulatory jurisdictions, GCLs can take the place of the CCL provided the GCL is “equivalent” to the CCL it is replacing. As discussed by Rowe (1998) and Rowe et al. (2004), equivalency comparisons should involve a contaminant transport assessment that includes factors such as diffusion, advection (including leakage between the GM and liner contact), sorption, biodegradation and finite service lives of engineered components. When these factors are considered in conjunction with the landfill characteristics (i.e. size and leachate characteristics) and the hydrogeological setting, a proper comparison of equivalency between a CCL and GCL can be made. If a GCL-based liner system can be shown to be equivalent to or better than the CCL liner system it is replacing, there could be significant cost savings associated with utilizing GCL-based systems.

When assessing potential GCL improvements in VOC sorption (or any other engineering property) by adding organoclays or activated carbon, similar contaminant transport equivalency assessments can be very helpful at establishing the “true” benefit of increased GCL VOC sorption parameters. Hence, a detailed comparison of the entire engineered barrier system and landfill hydrogeological regime is most realistic at assessing any “enhancement” of a GCL (i.e. increased VOC sorption). Comparisons to CCL-based liner systems will also assist in assessing potential value-added capabilities of any enhanced GCL product.

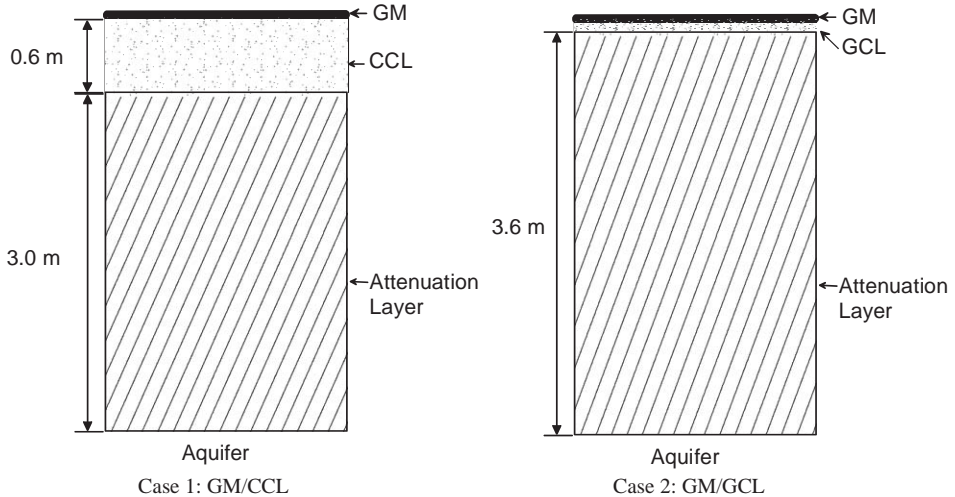


Fig. 6. Schematic of single composite liners examined for contaminant transport assessment.

In this regard, Fig. 6 shows two single composite liners: (a) Case 1, a GM/CCL composite liner overlying an 3.0 m attenuation layer (subgrade soil present on the site), and (b) Case 2, a GM/GCL (no enhancement) composite liner overlying a 3.6 m attenuation layer with similar contaminant transport properties. To examine “enhancement” of the GCL with respect to GCL sorption, the K_d values of the GCL in Case 2 were increased as shown in Table 4 for DCM and benzene (VOC contaminants used for the modeling exercise). The “enhancement” essentially assumes that the existing bentonite contains 2% PAC and K_d values increase to the values as shown in Table 3. It has also been assumed that this “enhancement” would result in increase in hydraulic conductivity as shown in Table 4. To assess a feasible upper range of PAC enhancement (i.e. existing bentonite containing 10% PAC), K_d values were proportionally increased by a factor of 5. Hydraulic conductivity values were also increased. DCM and benzene were chosen to represent the chlorinated and aromatic VOCs contaminants found in similar concentrations in MSWL leachate (Rowe, 1994). These concentrations are essentially within an order of magnitude of the initial concentrations utilized for batch testing with the exception of benzene. These parameters do not necessarily represent the exact sorption parameters of an enhanced GCL but typical of the range in parameters to be expected. The parameters used for modeling the various barrier components are also provided in Table 4 and those used for the hypothetical landfill are shown in Table 5. To perform this VOC contaminant transport assessment, the one-dimensional contaminant transport program POLLUTE (Rowe and Booker, 2004) was utilized. POLLUTE was specifically developed for modeling contaminant transport through the base of engineered MSWLs. Details of this model can be found in Rowe et al. (2004) and Rowe and Booker (2004). For modeling purposes, as shown in Table 6, it was

Table 4
Barrier parameters used in contaminant migration assessment

	GM	CCL	GCL (no activated carbon)	GCL (2% activated carbon)	GCL (10% activated carbon)	Attenuation layer (AL)
Thickness (m)	0.0015	1.0	0.01	0.01	0.01	3.6 m and variable (see text)
Diffusion coefficient DCM (m ² /s)	6.5×10^{-13}	6×10^{-10}	3×10^{-10}	3×10^{-10}	4×10^{-10}	8×10^{-10}
Diffusion coefficient Benzene (m ² /s)	4×10^{-13}	6×10^{-10}	3×10^{-10}	3×10^{-10}	4×10^{-10}	8×10^{-10}
Diffusion coefficient Toluene (m ² /s)	3×10^{-13}	6×10^{-10}	3×10^{-10}	3×10^{-10}	4×10^{-10}	8×10^{-10}
Henry's coefficient DCM S_{gr} (-)	6	—	—	—	—	—
Henry's coefficient Benzene S_{gr} (-)	30	—	—	—	—	—
Henry's coefficient Toluene S_{gr} (-)	100	—	—	—	—	—
No of holes/ha	2.5	—	—	—	—	—
Hole radius (mm)	0.005	—	—	—	—	—
Service life (a)	See Table 6	∞	∞	∞	∞	∞
Primary GM	150	—	—	—	—	—
Hydraulic conductivity (m/s)	—	1×10^{-9}	5×10^{-11}	1×10^{-10}	5×10^{-10}	1×10^{-7}
Geomembrane-clay Transmissivity (m ² /s)	—	1.6×10^{-8}	2×10^{-10}	2×10^{-10}	2×10^{-10}	—
Sorption, K_d (-)	—	—	—	—	—	—
DCM	—	0	0	5	25	0
Benzene	—	0.4	3	320	1600	0
Porosity	—	0.35	0.35	0.70	0.70	0.3

Notes: References: Rowe (1998), Lake and Rowe (2000), Lake and Rowe (2004), Sangam and Rowe (2001), Rowe et al. (2004), Ministry of the Environment, Ontario (1998).

Table 5
Hypothetical landfill characteristics

Landfill properties	
Length (m)	1000
Width (m)	1000
Mass of waste/unit area (t/m^2)	24
Proportion of DCM in waste (mg/kg)	2.3
Proportion of benzene in waste (mg/kg)	0.014
Proportion of toluene in waste (mg/kg)	0.7
Initial concentration in leachate	
DCM, c_o (mg/L)	3.3
Benzene, c_o (mg/L)	0.02
Toluene, c_o (mg/L)	1.0
Percolation through waste (m/a)	0.15
DCM in landfill, $t_{1/2}$ (a)	10
DCM below GM, $t_{1/2}$ (a)	50
Benzene in landfill, $t_{1/2}$ (a)	25
Benzene below GM, $t_{1/2}$ (a)	125
Toluene in landfill, $t_{1/2}$ (a)	15
Toluene below GM, $t_{1/2}$ (a)	75
Aquifer properties	
Thickness modelled (m)	3
Porosity (-)	0.3
Base darcy flux (horizontal), v_b (m/a)	1

Note: a: annum or year, $t_{1/2}$: half-life.

assumed that the primary leachate collection system was functioning as designed (design leachate level of 0.3 m) and removing leachate for a period of 50 years. At this time, the primary leachate collection system underwent a gradual “failure”; a leachate mound instantaneously developing above the primary liner system to 50% of its maximum height (5 m). At 70 years, it reached its maximum height of 10 m. At 150 years, the primary GM was assumed to instantaneously fail, causing the leachate mound height to decrease to the point where all infiltration coming into the landfill (0.15 m/a) was being transferred into the underlying hydrogeological system. A summary of the leakage rates (calculated using the methods outlined by Rowe, 1998) for the three cases considered is shown in Table 6.

Results of the DCM modeling are shown in Fig. 7. The solid line represents Case 1 (GM overlying a CCL overlying an attenuation layer (AL)), the medium dash line represents Case 2 (GM overlying a GCL overlying an AL), and the dotted line represents a variation of Case 2 in which the GCL has been “enhanced” by increasing the K_d sorption of DCM to 5 mL/g. The dash-dotted line represents another variation of Case 3 in which the GCL has been further enhanced to by increasing the sorption to 25 mL/g. These latter two increases in DCM sorption levels are based on previous results presented in this paper for the activated carbon and bentonite mixture assuming a 2% PAC/PB mixture and a 10% PAC/PB mixture. The K_d value for the 10% PAC/PB mixture assumes a proportional

Table 6
Leakage rates for systems considered

Time period	Description	Leakage (m/a)				
		AL: 3.0 m <i>GM/CCL</i>	AL: 3.6 m <i>GM/GCL (no PAC)</i>	AL: 3.6 m <i>GM/GCL (2% PAC mixture)</i>	AL: 3.6 m <i>GM/GCL (10% PAC mixture)</i>	AL: 3.0 m <i>GM/GCL (10% PAC mixture)</i>
0–60 years	Operating PLCS	4.7×10^{-5}	1.1×10^{-6}	1.2×10^{-6}	1.4×10^{-6}	9.5×10^{-7}
60–70 years	Failure of PLCS, mound height: 5 m	6.4×10^{-4}	1.4×10^{-5}	1.5×10^{-5}	1.7×10^{-5}	1.6×10^{-5}
70–150 years	Mound height: 10 m	1.3×10^{-3}	2.7×10^{-5}	2.9×10^{-5}	3.3×10^{-5}	3.1×10^{-5}
> 150	Failure of primary GM	0.15	0.15	0.15	0.15	0.15

Notes: PLCS: primary leachate collection system, Design leachate level 0–50 years for PLCS = 0.3 m; AL: attenuation layer, PAC: powdered activated carbon mixture.

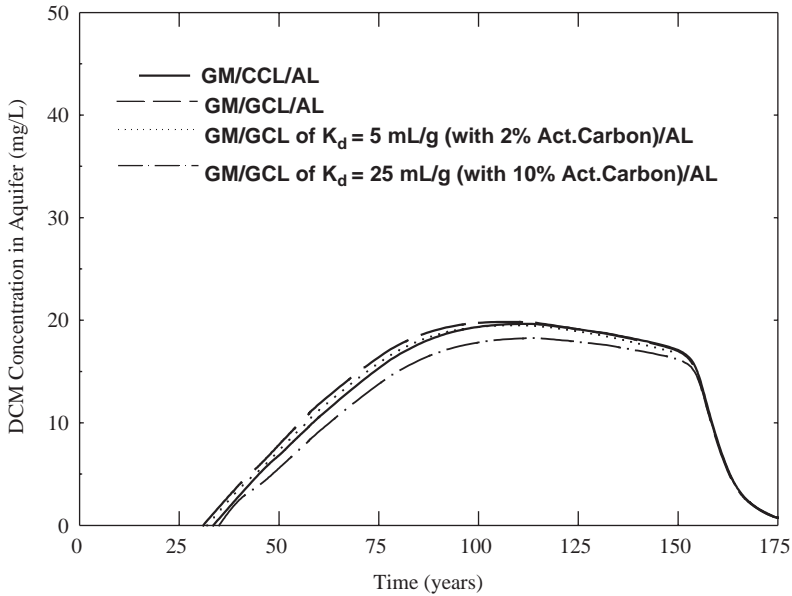


Fig. 7. Results of DCM contaminant transport modeling.

increase in sorption for 5 times the amount of PAC added. As can be seen from Fig. 7, there is essentially very little difference between Cases 1 and 2 (solid and medium dash line) which is similar to results presented by Rowe (1998) that showed GCL-based liner systems can be equivalent to CCL-based liner systems provided the total thickness of the GM/CCL/AL or GM/GCL/AL is the same (3.6 m in these cases). Also observed from Fig. 7 is that there is very little reduction in DCM impact in the aquifer when a K_d of 5 mL/g is assumed (dotted line). Although there is a somewhat lower contaminant impact obtained for a K_d value of 25 mL/g (dash-dotted line), the reduction from Case 2 is less than 10%. The main reason for this small reduction in DCM impact, even though sorption of the GCL has increased considerably is that the GCL is relatively thin and presents a small mass available for VOC sorption and hence a relatively large K_d value of 25 mL/g does not substantially reduce the DCM impact in the aquifer. This suggests that although this level of sorption could be over 25 times that of the original GCL without any activated carbon, it is still not sufficient to “overshadow” diffusion and degradation processes occurring during contaminant transport. Similar types of analysis as those used to obtain results in Fig. 7 were performed for a GCL with a K_d of 25 mL/g with reduced attenuation layer thickness and it was found that higher peak impacts resulted, mainly due to the higher diffusive flux (i.e. higher concentration gradient) induced by the thinner attenuation layer. Based on these results for DCM, it is questionable as to whether there is value-added to increasing the amount of activated carbon to 10% if there is only marginal improvement in GCL performance with respect to DCM contaminant transport through the entire liner system. It could be

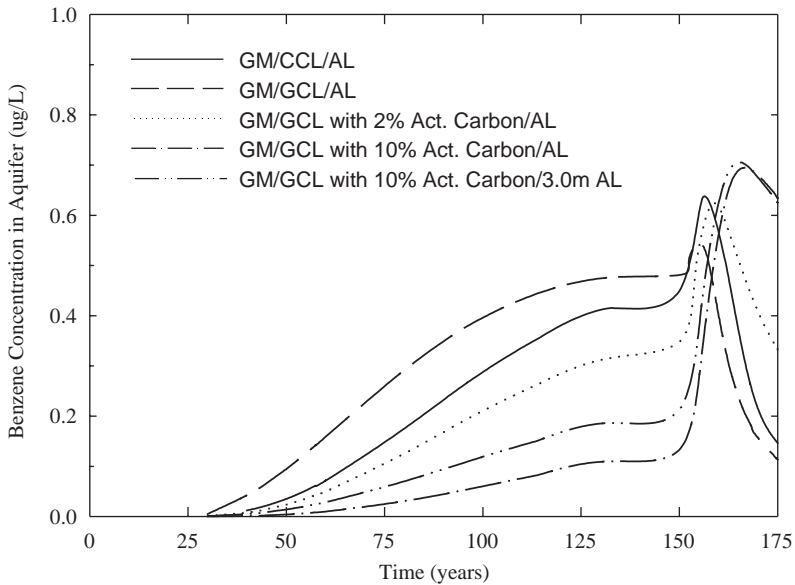


Fig. 8. Results of benzene contaminant transport modeling.

argued that further addition of activated carbon may be more effective to increase DCM sorption, however, this would most likely negatively impact the hydraulic performance of the GCL (its most appealing quality). Single layers of activated carbon may be more effective but this would also provide an added cost in addition to using a GCL.

Results from benzene modeling are shown in Fig. 8. As with the DCM modeling, the solid line represents Case 1 (GM overlying a CCL overlying an attenuation layer), the dashed line represents Case 2 (GM overlying a GCL overlying an attenuation layer), the dotted line represents a variation of Case 2 in which the GCL has been “enhanced” by increasing the sorption of benzene to 320 mL/g (2% PAC/PB mixture). The dash-dotted line represents another variation of Case 2 in which the GCL has been further enhanced by increasing the sorption to 1600 mL/g (assuming a 10% PAC/PB mixture). Modeling results for Cases 1 and 2 show that the GCL-based liner system (dash line) has a slightly lower peak impact than that of the CCL-based liner system (solid line), without any enhancement. It is also noted that benzene levels are higher for the GCL-based system prior to primary GM failure at 150 years. This is most likely due to the thicker CCL providing more sorption than the GCL for the conditions modeled and hence resulting in lower benzene levels prior to geomembrane failure at 150 years. This also implies more available mass left in the CCL system at 150 years, resulting in the slightly higher benzene impacts observed for the CCL system.

Also seen from Fig. 8, as the benzene sorption level of the GCL increases, the benzene levels prior to GM failure at 150 years are lower relative to the original

GCL. However, the peak benzene aquifer impacts actually increase with increased GCL sorption. This may seem counter-intuitive but the increased sorption actually delays migration into the aquifer for the low leakage rates calculated until the failure of the GM at 150 years, which results in flushing of the benzene into the aquifer. This can also be seen as delayed peak concentrations for higher values of sorption in the GCL. This is similar to the process described when comparing Case 1 and 2 for benzene. To see if there is potential for reducing attenuation layer thickness for benzene, additional modeling was performed for a GCL K_d value 1600 mL/g and an attenuation layer thickness of 3.0 m. As shown in Fig. 8, although benzene levels prior to 150 years are slightly higher compared to case of a GCL of K_d of 1600 mL/g and an attenuation layer thickness of 3.6 m, the peak value is essentially the same. This suggests that at least for benzene there may be potential to decrease attenuation layer thickness (increased landfill volume) with an enhanced GCL. Of course, if the municipal solid waste leachate has both DCM and benzene, this may not be possible. It should be noted that different assumptions regarding VOC half-lives could affect the modeling results presented herein (Lake, 2000) although the same general observations discussed above can be made.

Based on observations of the modeling performed above, it would appear that if both DCM and benzene are present in municipal solid waste leachate, there may be little technical benefit to enhancing the GCL to improve GCL sorption. There may be a slight advantage to using an enhanced GCL if non-polar compounds such as benzene are present in solution with slightly non-polar chlorinated compounds such as DCM. However, the implications of utilizing such a product could be assessed using the methods outlined in this paper. The marginal increase in contaminant migration performance may be outweighed by the increased cost of such an enhancement.

5. Summary and conclusions

This paper has: (1) examined the potential increased VOC sorption of the bentonite currently used in two GCLs by using a relative batch test comparison between different potential bentonite additives, and (2) assessed the effect of this increased sorption in terms of potential benefits with respect to contaminant migration through single composite liner systems utilizing these “enhanced sorption” GCLs.

The sorption of the bentonites currently used in the two GCLs examined in this paper is low relative to the organoclays and powdered activated carbon (PAC) tested. Four different organoclays tested exhibited two to three orders of magnitude higher sorption to DCM, DCA, TCE, benzene, and toluene relative to the existing bentonite material. However, these organoclay results were obtained without mixing with a specified percentage of bentonite as would most likely be done in practice for a modified GCL. When only 2% of PAC was mixed by air-dried weight with powdered bentonite (PB), the sorption of the mixture was much higher than organoclays A, B, C, and D for TCE, benzene, and toluene. DCM sorption to the

2% PAC/PB mixture was lower than that of organoclays A, B, C, and D while DCA sorption was similar between the 2% PAC/PB mixture and organoclays A to D. However, mixing 2% of any of the organoclay examined (Table 3) with PB would, based on the data, be expected to be less than that obtained by mixing 2% PAC with the bentonite for the VOCs examined.

Conclusions reached for this study are based on the organoclays that were tested and do not represent all commercially available organoclays. However, comparative studies such as those performed herein could be used to assess any material that may be included in a GCL modified to increase the sorption to VOCs. It is also acknowledged that other factors such as long-term stability and the influence of additional inorganic constituents in the aqueous solution may influence the choice of material used as an additive or modifier to a GCL to improve VOC sorption. If a potential modifier was chosen for a GCL, the modified GCL should be subjected to diffusion testing, such as that described by Lake and Rowe (2004), to properly assess diffusion and sorption parameters to be used for contaminant migration assessments. However, results of a parametric study performed using a hypothetical landfill showed that increased sorption of a 2% PAC/PB GCL or 10% PAC/PB mixture would provide only marginal benefits in terms of increased attenuation capacity for DCM migration and may even result in slightly higher benzene peak impacts for the single composite liner examined. The practical implications of utilizing any type of enhanced GCL product could be assessed using the methods outlined in this paper.

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