

# Diffusive transport of multiwall carbon nanotubes through an HDPE geomembrane

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## ABSTRACT

Carbon nanotubes are used in a wide range of consumer products. During the last few years, the applications for, and production of, carbon nanotubes has increased substantially. Due to their potential environmental and human health risks and eventual disposal into landfills, understanding their mobility through landfill barrier system is essential. The diffusion of multiwall carbon nanotubes (MWCNTs) through a 0.5 mm high density polyethylene (HDPE) geomembrane is examined in this study. The preliminary results from two-compartment diffusion cells show no significant partitioning of MWCNTs from source to geomembrane or diffusion of MWCNT during the testing period reported. This is the first time the potential migration of nanoparticles through a geomembrane has been examined. These tests are on-going and the most recent results will be presented at the conference.

## RÉSUMÉ

Les nanotubes de carbone sont utilisés dans un large éventail de produits de consommation. Au cours des dernières années, la demande et la production de nanotubes de carbone ont augmenté considérablement. En raison des risques pour la santé humaine, pour l'environnement et des risques liés à leur élimination éventuelle dans les décharges, la compréhension de leur mobilité à travers le système barrière dans les décharges est essentielle. La diffusion des nanotubes de carbone à parois multiples (MWCNT) à travers une géomembrane en polyéthylène haute densité de 0,5 mm (HDPE) est examinée dans cette étude. Lors de la période de test, les résultats préliminaires des cellules de diffusion à deux compartiments n'ont pas montré de transfert important des MWCNT entre la source et la géomembrane ou de diffusion de MWCNT. C'est la première fois que la migration potentielle des nanoparticules à travers une géomembrane est examinée. Ces tests sont toujours en cours et les résultats les plus récents seront présentés lors de la conférence.

## 1 INTRODUCTION

Carbon nanotubes (CNTs) have a wide range of usage in preparation of biosensors for protein and enzyme detection, in anticancer therapy, in tissue engineering and as a bone growth support material facilitating healing of fractures (Ostiguy et al. 2008). They are also being used in the electronics and polymer industries and energy sector (Muller and Nowak 2008). Carbon nanotubes can be in the form of hollow cylinders with either a single layer (Single-Walled Carbon Nanotubes, SWCNT) or several layers (MultiWall Carbon Nanotubes, MWCNT) (Ostiguy et al. 2008).

Because of their tiny size, some nanoparticles can diffuse through cell membranes and enter cells (Klaine et al. 2008). Some CNTs are intentionally designed for medical purposes like interacting with proteins or nucleic acids. However, the unintentional and uncontrolled interactions could have adverse impacts on biota (Klaine et al. 2008). Some health effects of carbon nanotubes have been observed in humans and animals (Ostiguy et al. 2008).

The worldwide production of carbon nanotubes is increasing due to their increasing demand (Muller and Nowak 2008). This high volume of production and use of nanoparticles will lead to their release in the environmental receptors such as landfills.

Transport of various nanoparticles including carbon nanotubes through porous media such as the sand that may form an aquifer below a landfill barrier system have been studied in recent years (Lecoanet and Wiesner 2004, Lecoanet et al. 2004, Espinasse et al. 2007, Jaisi et al. 2008, Johnson et al. 2009, Liu et al. 2009, Mattison et al. 2011). The results show that nanoparticles can totally or partially pass through the porous media depending on the solution and nanoparticles characteristics and porous media's properties. Thus there is a need to prevent the nanoparticles from reaching the aquifer.

High density polyethylene (HDPE) geomembranes have been used on the base of landfills as a component of composite liners for 20-30 years. Diffusive properties of various aromatic and chlorinated organic compounds in landfill leachate have been studied for HDPE geomembranes (Park and Nibras 1993, Aminabhavi and Naik 1999, Sangam and Rowe 2001, Rowe et al. 2004,

Joo et al. 2005, Islam and Rowe 2009). However there is no data in the literature relating to the diffusion of carbon nanotubes through geomembranes.

The objective of this paper is to examine diffusion of multi-walled carbon nanotubes (MWCNTs) through a thin HDPE geomembrane to allow the assessment of the potential effectiveness of modern HDPE geomembrane liners for preventing the migration of multi-walled CNTs into the subsurface environment.

## 2 MATERIALS AND METHODS

MWCNTs were purchased from Cheap Tubes Inc. According to the manufacturer, the outer diameter is less than 8 nm and the lengths are between 0.5  $\mu\text{m}$  to 2.0  $\mu\text{m}$  and the purity is more than 95% by mass.

The MWCNTs were acid treated (functionalized) with a 3 to 1 ratio of sulfuric and nitric acids to increase their stability in aqueous phase by adding hydroxyl and carboxyl functional groups (Liu et al 1998, Liu et al 2009). The mixture of MWCNTs and acids were placed in a bath sonicator (Fisher Scientific, FS110) for 2 h and then filtered through a 0.45  $\mu\text{m}$  polytetrafluoroethylene (PTFE) membrane. The filter and MWCNTs were rinsed with boiling deionized water to remove the residual acid on MWCNTs. The pH of the filtrate was measured until it was around 5 (approximately 2 L of boiling water was used). The filter, with the captured MWCNTs, then was placed in a dessicator to dry before storing the MWCNTs in a glass vial. A scanning electron microscope (SEM) image of the functionalized MWCNTs is shown in Figure 1.

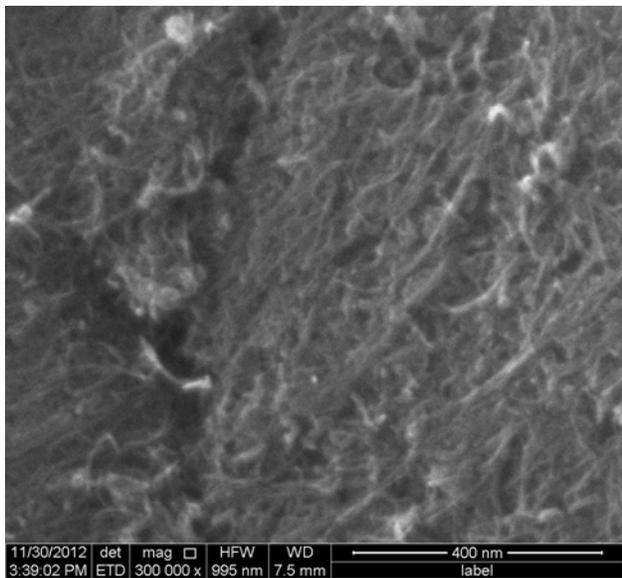


Figure 1. Scanning electron microscope (SEM) image showing the morphology of functionalized MWCNTs

MWCNTs stability and aggregation in the dispersion is dependent on the pH and ionic strength. Decreasing pH or increasing ionic strength enhances aggregation (Saleh et al 2008, Zhang et al 2011) so it is important to have a controlled and consistent “aqueous solution” for studying

the mobility of MWCNTs (referred to herein as a dispersion). The “aqueous solution” was prepared by adding 1.26 mmol/L monosodium phosphate ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ), 1.73 mmol/L disodium phosphate ( $\text{Na}_2\text{HPO}_4$ ) and 1 mmol/L sodium bromide ( $\text{NaBr}$ ) to double deionized water to reach an ionic strength of 7.5 mmol/L and pH of 7.0 which are representative of natural waters. Then 5 mg of functionalized MWCNTs was added to 200 mL aqueous solution (25 ppm) and placed in a water ice bath and dispersed in the solution using a probe sonicator (Cole-Palmer instrument, IL, US, CP 505, 500 watt, 20kHz) for one hour (Mattison et al 2011). To prevent the probe from getting hot, pulse sonicating was used with a cycle of being on for 15 min and then off for 5 min.

The MWCNT concentration of each 200 mL dispersion was measured daily for a few days using a Total Organic Carbon (TOC) analyzer (Shimadzu, TOC-5050A) until the solution was stable (i.e., there was less than a 10 % change for three days in a row). Then, the supernatants of all 200 mL dispersions were added together to make one solution for the diffusion test. The measured concentration of this homogenous solution was around 10 ppm.

Although 1.5 mm thick geomembranes are typically used in landfill applications (Rowe et al. 2004), to allow faster diffusion in these experiments, a thinner, 0.5 mm, high density polyethylene (HDPE) geomembrane (manufactured by Solmax International Inc., Quebec) was examined in this study.

## 3 DIFFUSION TEST

### 3.1 Cell Setup

For the diffusion test, two-compartment (source and receptor) stainless steel cells were used (Figure 2). Five cells were set up. Two diffusion cells contained the MWCNT dispersion in the source chamber and an identical aqueous solution but without MWCNTs in the receptor chamber; the chambers were separated by a 0.5 mm HDPE geomembrane. Two control cells where the entire cell was filled with the MWCNT dispersion (no geomembrane) were used to quantify the MWCNT stability. In addition, there was one blank diffusion cell with the aqueous solution but no MWCNTs in both the source and receptor chambers, which were separated by a 0.5 mm HDPE geomembrane. Samples were taken immediately after cell set-up to confirm the initial MWCNT concentration. The cells were sampled at regular time intervals to monitor the change in the concentration of MWCNTs in both the source and receptor chambers of the diffusion cells, control cells, and blank diffusion cell.

### 3.2 Analyzing Samples

A TOC analyzer was used to quantify MWCNT concentrations. The minimum sample volume for TOC analyser is 2 mL. To minimize the sampling volume withdrawn from the cells, 0.5 mL from the relevant chamber was removed each time and diluted with 2 mL

aqueous solution (1:5 dilution). Before setting up diffusion cells, 2 L of extra aqueous solution was prepared for diluting samples. The detection limit of TOC analyzer for total carbon is 0.5 ppm. The dilution factor was reduced if the measured concentration was close to the analyzer detection limit.

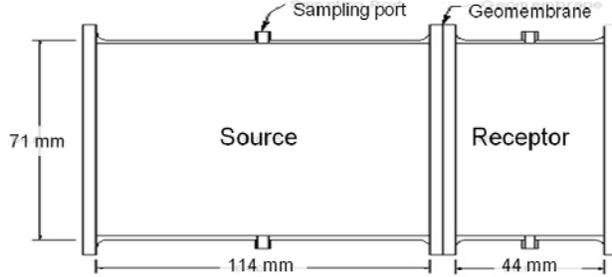


Figure 2. Schematic of the diffusion cell

### 3.3 Diffusion through Geomembrane

Diffusive transport through a geomembrane occurs in three steps (Sangam and Rowe 2001): adsorption, diffusion and desorption. First, the contaminant partitions between the source and the surface of the geomembrane. Then it diffuses through the geomembrane due to the contaminant concentration gradient in the geomembrane. At the end, the contaminant partitions between the outer surface of the geomembrane and the receptor.

Eventually, concentrations in the geomembrane and the source and the receptor are in equilibrium. The equilibrium between the concentration in the geomembrane and the concentration in the source can be described by Henry's law:

$$c_{gF} = S_{gf} C_{fF} \quad [1]$$

where  $c_{gF}$  is the concentration of the contaminant in the geomembrane [ $\text{ML}^{-3}$ ],  $S_{gf}$  is the partitioning coefficient and  $C_{fF}$  is the final contaminant concentration in the source fluid [ $\text{ML}^{-3}$ ].

The next step, diffusion of the contaminant through the geomembrane, is expressed by Fick's first law:

$$f = -D_g \frac{dc_g}{dz} \quad [2]$$

where  $f$  is the mass flux [ $\text{ML}^{-2}\text{T}^{-1}$ ],  $D_g$  [ $\text{L}^2\text{T}^{-1}$ ] is the diffusion coefficient specific to the geomembrane and contaminant of interest,  $c_g$  is the concentration of the contaminant in the geomembrane [ $\text{ML}^{-3}$ ] and  $z$  is the distance parallel to the direction of transport. When the diffusion coefficient is constant, the change in contaminant concentration in the geomembrane with time  $t$ , is described by Fick's second law:

$$\frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial z^2} \quad [3]$$

The final step is described by Henry's law:

$$c'_{gF} = S'_{gf} C_{fF} \quad [4]$$

When the source and receptor media are the same, the partitioning coefficient into the geomembrane and out of geomembrane can be assumed to be the same ( $S_{gf} = S'_{gf}$ ) (Sangam 2001).

Measuring the concentration of contaminant inside the geomembrane is very difficult. It is easier to measure the concentration in the source and receptor and then calculate the diffusive parameters based on the mass transport from the source to the receptor.

The steady state contaminant mass flux from the source to the receptor through the geomembrane can be described by rearranging Equations 1 and 2:

$$f = -D_g \frac{\Delta c_g}{\Delta z} = -S_{gf} D_g \frac{\Delta c_f}{\Delta z} = -P_g \frac{\Delta c_f}{\Delta z} \quad [5]$$

where the permeation coefficient,  $P_g$  [ $\text{L}^2\text{T}^{-1}$ ] is the mass transfer across the geomembrane (Sangam and Rowe 2001) and is given by:

$$P_g = S_{gf} D_g \quad [6]$$

## 4 MODELING DIFFUSION PARAMETERS

In the diffusion test, the source can be modelled as a finite mass boundary condition. At a given time, the contaminant mass in the source is equal to the initial mass minus the mass that has partitioned/diffused into the geomembrane. The concentration in the source at time  $t$  can be described by equation 7:

$$c_{ss}(t) = c_{s0} - \frac{1}{H_{ss}} \int_0^t f_{ss}(\tau) d\tau \quad [7]$$

where  $c_{ss}(t)$  is the contaminant concentration in the source at time  $t$  [ $\text{ML}^{-3}$ ],  $c_{s0}$  is the initial contaminant concentration in the source [ $\text{ML}^{-3}$ ],  $H_{ss}$  is the reference height of the source reservoir (i.e., volume of fluid divided by the area of the geomembrane sample) [L]. The integral gives the total contaminant mass diffused from the source fluid into the geomembrane per unit area up to some time  $t$  and  $f_{ss}(\tau)$  is the contaminant mass flux into the geomembrane at time  $\tau$  [ $\text{ML}^{-2}\text{T}^{-1}$ ]. Equation 7 can be used to model the decrease in concentration of the contaminant in the source (Rowe et al. 2004). A similar equation can be used to model the increase in the contaminant concentration in the receptor as the contaminant partitions out of the geomembrane into the receptor:

$$c_{rs}(t) = c_{r0} + \frac{1}{H_{rs}} \int_0^t f_{rs}(\tau) d\tau \quad [8]$$

where  $c_{rs}(t)$  is the contaminant concentration in the receptor at time  $t$  [ $\text{ML}^{-3}$ ],  $c_{r0}$  is the initial contaminant concentration in the receptor [ $\text{ML}^{-3}$ ],  $H_{rs}$  is the reference height of the receptor solution [L]. The integral gives the total contaminant mass diffused out of the geomembrane into the receptor per unit area up to some time  $t$  and  $f_{rs}(\tau)$  is the contaminant mass flux out of the geomembrane at time  $\tau$  [ $\text{ML}^{-2}\text{T}^{-1}$ ] (Rowe et al. 2004).

The governing differential equation (Eq. [3]) was solved taking account of the phase change (Eqs. [1] and [4]) subject to the boundary conditions describing the source concentration (Eq. [7]) and the receptor concentration (Eq. [8]) using the finite layer analysis program POLLUTE<sup>®</sup> v.7 (Rowe and Booker 2004). By fitting the observed and calculated decrease in source and increase in receptor concentrations with time, the diffusion ( $D_g$ ), partition ( $S_{gf}$ ) and permeation ( $P_g$ ) coefficients can be deduced for an HDPE geomembrane (Sangam and Rowe 2001, Rowe et al. 2004). If, as in this case, there is no detectable increase in receptor concentration, a conservative upper bound to the permeation coefficient can be inferred assuming that the value in the receptor concentration at the last sampling time was equal to the detection limit. For the same detection limit, the estimate of the permeation coefficient will be reduced as the testing time increases. For example, the estimate of the permeation coefficient of chloride through a geomembrane has been reduced to  $\leq 4 \times 10^{-18} \text{ m}^2/\text{s}$  over the past 20 years with continued monitoring (Rowe 2012).

## 5 RESULTS

The MWCNT concentrations in the receptor and source compartments of the diffusion cells were measured with a TOC analyzer. The MWCNT dispersion showed settling during the 30 d test period. Thus, the source and receptor concentrations in the test diffusion cells were corrected by the concentration that had settled in the two control cells. In addition, the TOC concentrations from the blank diffusion cell were subtracted from all numbers. The modified concentrations from the receptor chambers and source chambers are shown in Figure 3. The reported results are the concentration of 1:5 diluted samples.

## 6 DISCUSSIONS AND CONCLUSIONS

The concentration in the receptor chambers (Figure 3) varied slightly with increasing time. This variation was likely due to  $\text{CO}_2$  dissolution from air into the receptor solution. This was confirmed by additional analysis of the aqueous solution which was used for diluting cell samples. When the aqueous solution was purged with nitrogen gas to remove dissolved  $\text{CO}_2$ , the measured TOC concentration decreased as the purging duration increased (data not shown). Due to sampling from the cells without replacing fluid, the ratio of the air space to the liquid volume in the receptor was greater than in the blank cell. Therefore  $\text{CO}_2$  dissolution in the receptor is

higher than in the blank cell and this is not corrected by subtracting the concentration of the blank cell.

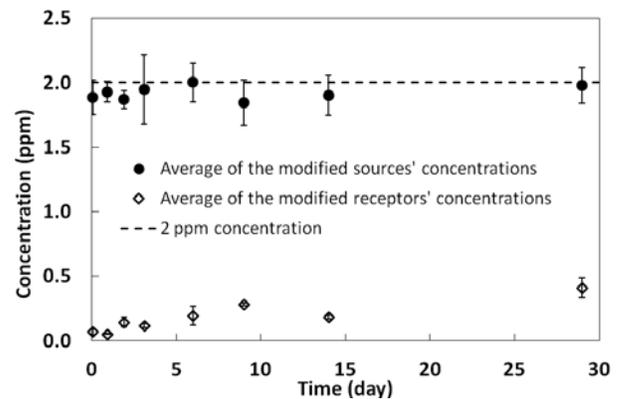


Figure 3. Diffusion of MWCNTs through HDPE GMB. Values are the mean MWCNT concentration of duplicate samples for the source and receptor cells, and error bars represent standard deviation values. The dotted line at the 2 ppm concentration indicates the initial MWCNT concentration in the source cells.

The data points in Figures 3 show that there was no detectable decrease in the concentration of MWCNTs in the source chambers of the two diffusion cells. This result suggests that sorption of MWCNTs to HDPE geomembrane or transport through the membrane was not detectable after about 1 month.

POLLUTE<sup>®</sup> v.7 (Rowe and Booker 2004) was used to estimate the permeation coefficient for MWCNTs and HDPE geomembrane. The detection limit of TOC analyzer was used as MWCNTs concentration in the receptor (0.5 ppm) and the model was run for 29 days. The permeation coefficient is estimated to be  $< 1.3 \times 10^{-14} \text{ m}^2/\text{s}$ . This number can be compared to the permeation coefficient for benzene ( $1 \times 10^{-11} \text{ m}^2/\text{s}$ ) and for Dichloromethane (DCM) ( $4 \times 10^{-12} \text{ m}^2/\text{s}$ ) for an HDPE geomembrane as reported by Sangam and Rowe (2001). The estimate of the permeation coefficient is expected to decrease as more data is collected over a longer time period.

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Certain commercial equipment or materials are identified in this paper in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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