

**MTBE GAS PHASE DIFFUSION IN SUBSURFACE SOIL:  
INFLUENCE OF SOIL WATER, CLAY AND ORGANIC  
CONTENT**

by

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## ABSTRACT

Volatile organic compounds (VOCs) have adverse effects on human health upon short- and long-term exposure, causing allergy and asthma in adults and respiratory problems and immune system disorders in children. The most important mechanisms responsible for VOC migration and deposition in soil include diffusion, advection, adsorption, biodegradation and chemical reaction.

MTBE (Methyl Tertiary-Butyl Ether), a very common VOC, detected in groundwater near landfills and hazardous waste dumps, can cause cancer in humans. Due to its specific physical and chemical properties such as high volatility, high water solubility, not much adsorptivity on soil particle and biodegradability, it is very mobile in the environment.

The objectives of this research were to design and build a diffusivity apparatus, determine gas-phase diffusion of MTBE in soil, and investigate major factors affecting the effective diffusivity of MTBE such as particle size distribution, soil water and organic carbon content.

Previously, sorbents and reservoir-based soil columns have been used to determine soil diffusion. A novel apparatus was designed which can overcome the limitations of conventional designs. Special features of the design include a three-segment body design stainless steel column and a very accurate humidity adjustment system, with humidity sensors at the inflow and outflow, giving the ability to determine the effective diffusivity of MTBE in soil more accurately and easily.

Soil samples in this study were at 0 to 80% saturation, with 0 to 15% clay content (Kaolinite) and 0 to 15% organic content. They were compacted in a developed stainless steel one-flow

reservoir-based column to a dry density of 1.6 to 1.7 g/cm<sup>3</sup>. Effective diffusivities were calculated based on Fick's first law. Overall MTBE effective diffusivities ranged from 0.0004 to 0.003 cm<sup>2</sup>/s.

The results demonstrate that higher water content of soil resulted in lower effective diffusivities. Increasing clay content of soil resulted in longer equilibrium time and lower effective diffusivity values. Variations of soil particle size had less effect on the effective diffusivity than changes in water content. It was also discovered that the organic content of soil has a significant capacity for adsorbing MTBE.

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## NOMENCLATURE

|                  |  |
|------------------|--|
| ASTM             | American society for testing and material  |
| B. C.            | boundary condition   |
| BET              | Brenauer-Emmett-Teller   |
| C                | VOC concentration in air [ppm]   |
| C. O. V.         | coefficient of variation   |
| CTC              | tetrachloride  |
| D                | coefficient of diffusion [ $\text{cm}^2/\text{s}$ ]                                      |
| DDT              | dichlorodiphenyltrichloroethane  |
| $D_{\text{eff}}$ | effective diffusivity [ $\text{cm}^2/\text{s}$ ]   |
| $D_g$            | effective diffusivity at temperature 25 °C [ $\text{cm}^2/\text{s}$ ]                    |
| $D_{ij}^D$       | effective molecular diffusion coefficient of component i in j [ $\text{mm}^2/\text{s}$ ] |
| $D_M$            | molecular diffusivity [ $\text{cm}^2/\text{s}$ ]   |
| $D_T$            | effective diffusivity at temperature T [ $\text{cm}^2/\text{s}$ ]                        |
| GC-MS            | gas chromatograph-mass spectrophotometer   |
| I. C.            | initial condition  |
| L                | length [mm]  |
| MTBE             | methyl tertiary-butyl ether  |
| NAPL             | non-aqueous phase liquid   |
| $N_i^D$          | total molar gas flux of component I [ $\text{mol}/\text{mm}^2\text{s}$ ]                 |
| $n_w$            | water-filled porosity  |
| PBB              | polybrominated biphenyl  |
| PCB              | polychlorinated biphenyl   |
| PCE              | tetrachloroethylene  |
| PHMSA            | pipeline and hazardous material safety administration                                    |
| s. d.            | standard deviation   |
| SM               | Stephan-Maxwell  |
| t                | time [s]   |
| T. V.            | true value   |
| TCE              | trichloroethylene  |
| TCM              | trichloromethane   |
| USEPA            | United States environmental protection agency  |
| UST              | underground storage tank   |
| $V_A$            | volume of air [ $\text{mm}^3$ ]  |
| VOC              | volatile organic compound  |
| $V_w$            | volume of water [ $\text{mm}^3$ ]  |
| WHO              | world health organization  |
| $\bar{x}$        | average  |
| x                | distance [mm]  |
| $x_i$            | mole fraction of component i   |
| $\theta_g$       | effective gas phase area for diffusion [ $\text{mm}^2$ ]                                 |
| $\tau$           | the ratio of straight pass length to the tortuous path length                            |

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## DEDICATION

I dedicate this thesis to,

My dear father, Reza, who taught me humanity.

My dear mother, Azam, who have never failed to give me moral support.

My first sister, Nastaran, who have never left me alone in hard days of my life.

My second sister, Aidin, who taught me how to love.

My third sister, Anna, who was a pattern of kindness and generosity in my life.

# CHAPTER 1

## INTRODUCTION

### 1.1 STATEMENT OF PROBLEM

Volatile organic compounds (VOCs) migration in subsurface soil raises serious concern due to its potential intrusion into buildings (Mendell, 2007; Wallace, 1987). VOCs, as classified by Health Canada and European Union, are organic compounds with low boiling points (high vapor pressures) with harmful health and environmental effects (Braida and Ong, 2000). World Health Organization (WHO) divides organic pollutants into three different categories based on their volatility. (1) very volatile organic compounds with boiling points from 0 to 50-100°C, such as propane, butane, methyl chloride, (2) volatile organic compounds with boiling points from 50-100 to 240-260°C, such as formaldehyde, toluene, acetone, and (3) semi-volatile organic compounds with boiling points from 240-260 to 380-400°C, such as pesticides (DDT, chlordane, plasticizers (phthalates), fire retardants (PCBs, PBB)) (World Health Organization, 1989).

Recent studies demonstrate that although all these compounds are not highly toxic, they have adverse effects on human health due to long and short term exposures (Table 1.1). They can cause allergy and asthma in adults (Norback *et al.*, 1995; Wieslander *et al.*, 1996) and develop respiratory problems and immune system disorders in children (Peat *et al.*, 1998; Mendell, 2007).

Table 1.1 Commonly found VOCs in groundwater near landfills and hazardous waste dumps, their physical properties, sources and health effects.

| VOC                            | Boiling point (°C) | Vapor pressure (mm Hg) | Solubility in water at 25 °C (g/L) | Henry's law constant at 25 °C (atm m <sup>3</sup> /mol) | Octanol-water partition coefficient (Log K <sub>ow</sub> ) | Soil-sorption coefficient (Log K <sub>oc</sub> ) | Maximum contaminant level (MCL) (mg/L) | Sources  | Health effects  | Reference   |
|--------------------------------|--------------------|------------------------|------------------------------------|---|--|--|--|--|---|---|
| Trichloroethylene (TCE)        | 86.7               | 74 at 25 °C            | 1.366                              | 0.011   | 2.42   | 2.03 -2.66                                       | 0.005                                  | Industrial use (dry-cleaning), water treatment facilities, landfills, municipal and hazardous incinerators                         | headaches, dizziness, damage to the facial nerves, neurological effects, Liver and kidney damage, etc | (Agency for Toxic Substances and Disease Registry, 1997)<br>(United States Environmental Protection Agency, 2009)                                     |
| Benzene                        | 80.1               | 75 at 20 °C            | 1.78                               | 0.005   | 2.13   | 1.49 -1.73                                       | 0.005                                  | Discharge from factories, leaching from gas storage tanks and landfills  | Anemia, decrease in blood platelets, cancer   | (United States Environmental Protection Agency, 2009)<br>(Lawrence, 2006)<br>(Minnesota department of health, 2005)                                   |
| Toluene                        | 110.6              | 22 at 20 °C            | 0.531                              | 0.0065  | 2.73   | 1.75-2.28  | 1                                      | Discharge from petroleum factories   | Liver, kidney, nervous system, circulatory system effects   | (United States Environmental Protection Agency, 2009)<br>(Lawrence, 2006)<br>(Minnesota department of health, 2005)                                   |
| Tetrachloroethylene (PCE)      | 121                | 18.4 at 25 °C          | 0.21                               | 0.017   | 2.88   | 2.37   | 0.005                                  | Textile industry, dry cleaning, manufacturing of pharmaceuticals, other organic compounds, and electronic components               | Liver problems, cancer  | (United States Environmental Protection Agency, 2009)<br>(Lawrence, 2006)<br>(Minnesota department of health, 2005)<br>(Sciences international, 1995) |
| Methyl tert-butyl ether (MTBE) | 55.2               | 245 at 25 °C           | 36.2                               | 0.00069   | 0.94   | 1.09   | NA                                     | leaking underground and above ground fuel storage tanks, pipe lines, refueling spills, automobile accidents damaging the fuel tank | Cancer  | (Lawrence, 2006)<br>(Minnesota department of health, 2005)<br>(Technology planning and management corporation, 1998)                                  |

Accidental release of VOCs in the form of NAPL (non-aqueous phase liquids) is a typical source of these molecules in unsaturated soil (Wang *et al.*, 2003). Subsequent horizontal and vertical migration of these compounds, through advection (Olson and Corsi, 2001; Nazaroff, 1992) and molecular diffusion (Olson and Corsi, 2001; Robinson *et al.*, 1997), result in serious environmental and health issues in residential areas. Upward migration of VOCs leads to the intrusion of soil gas into buildings (Figure 1.1) through foundation and basement cracks, accumulation of these compounds in indoor spaces and significant increase in the concentration of VOCs, up to 2 to 5 times greater than outdoors (Mendell, 2007; Wallace, 1987).

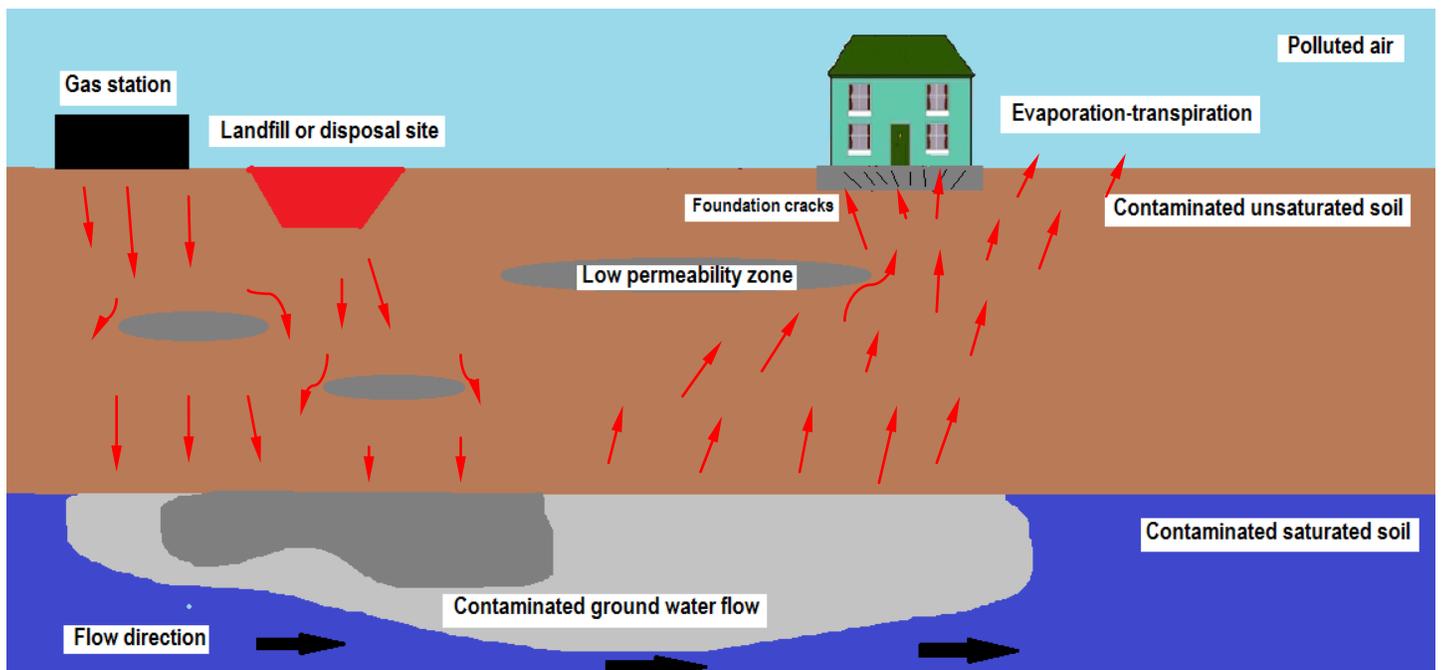


Figure 1.1 Sources and migration pathways of VOCs in soil

Landfills leachate and underground storage tanks leakage are other sources of VOCs release into the environment. Subsequent groundwater contamination caused by downward migration of VOCs poses a serious environmental hazard in countries utilizing groundwater as their main source of fresh water (such as the United States). It was estimated that the VOC concentration in 7% of American groundwater sources exceeds 0.2  $\mu\text{g/L}$  (Squillace *et al.*, 1999). This concentration is higher than the maximum contaminant level goal for many VOCs such as benzene (zero) based on United States Environmental Protection Agency's (USEPA) regulation for drinking water (United States Environmental Protection Agency, 2009). Table 1.1 provides some commonly found VOCs in groundwater near landfills and hazardous waste dumps (Lawrence, 2006), their physical properties, sources and adverse health effects.

Considering the destructive environmental and health effects of VOC distribution in the environment, different government agencies have regulated and monitored VOCs transport and disposal. For example, USEPA regulates VOCs in water, air, land, storm water, disposal and sewage treatment. VOCs that need to be transported are also regulated by the Pipeline and Hazardous Materials Safety Administration (PHMSA). As an illustration, to prevent the likelihood of leaching into the environment during transport, soil samples contaminated with gasoline or other source of VOCs should be packed internally, intermediately and externally, and cooling agent should be applied in order to keep the temperature in the range of 0 to 6°C. VOCs emission in water, soil and air also has been regulated in Canada and British Columbia. Environment Canada regulates VOCs concentration in surface coating such as road pavements and curbs. It has also developed guidelines for VOCs limit in daily life products. Environmental Management Act (2007) recommended 5  $\mu\text{g/L}$ , for raw drinking water, 40  $\mu\text{g/L}$ , for fresh water aquatic life, and 110  $\mu\text{g/L}$  for marine and estuarine aquatic life for benzene concentration.

The need for accurate prediction of VOCs migration arises in site investigation, risk assessment, contaminated site investigation and remediation. The efficacy of any remediation procedure depends on knowledge of level and extent of contamination. Therefore, knowledge of mechanisms and conditions are responsible for fate and transport of VOCs in the environment is essential (Rathbun, 1997). These demands encourage researchers to initiate experimental works (Batterman *et al.*, 1996; Ruiz *et al.*, 1998; Wang *et al.*, 2003) and modeling (Gierke *et al.*, 1990; Poulsen *et al.*, 1998; Silka, 1988) in order to predict VOCs migration and behavior in soil.

Different mechanisms are involved in determining the VOC behavior, migration pattern and fate in soil (Figure 1.2). These mechanisms include physical ones, such as diffusion, advection, and sorption, chemical ones, like chemical reaction, and biological mechanisms, such as biodegradation (Rathbun, 1997). The importance of each mechanism in transport of VOCs depends not only on the soil and VOC properties, but also on soil-VOC interaction. Diffusion, sorption and biodegradation are the most dominant mechanisms responsible for fate and transport of VOCs in subsurface soil.

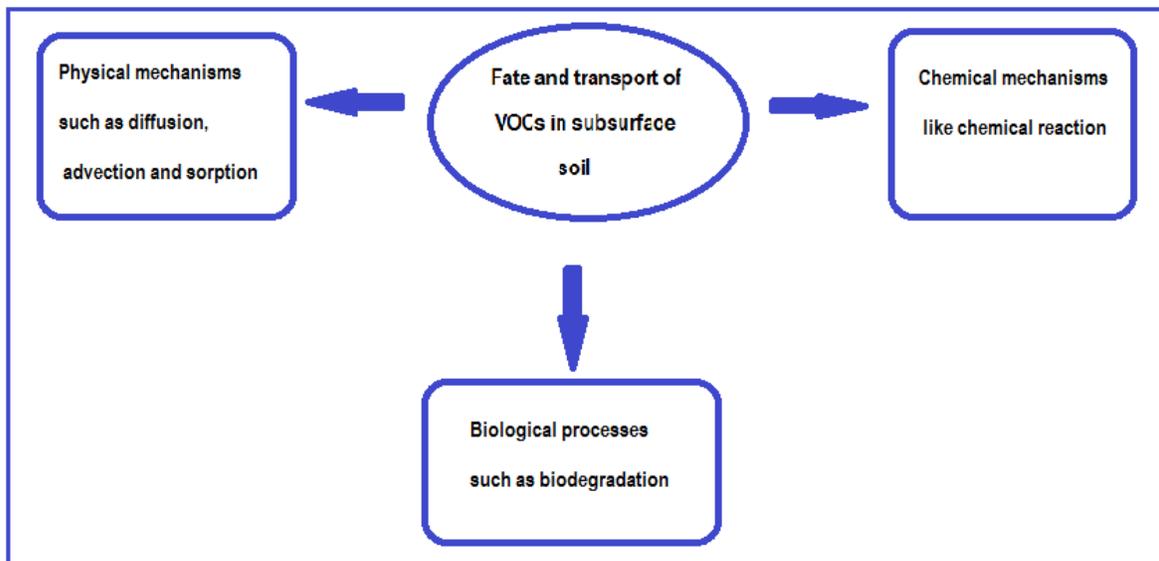


Figure 1.2 Mechanisms responsible for fate and transport of VOCs in soil.

Gas phase diffusion plays an important role in migration of VOCs especially, in vadose zone (unsaturated soil) (Batterman *et al.*, 1996). The diffusion mechanism has been investigated previously both experimentally (Batterman *et al.*, 1996; Ruiz *et al.*, 1998; Wang *et al.*, 2003) and theoretically (Gierke *et al.*, 1990; Poulsen *et al.*, 1998; Silka, 1988). Sorbent and reservoir-based, one and two-flow experimental systems were developed to measure diffusion rate in various soil-VOC systems. They all have limitations and assumptions that make them inappropriate for diffusion study in some cases, or lead to biased results such as considering one-dimensional diffusion and not having an appropriate humidity adjustment system. Furthermore, a limited number of soil conditions (particle size and organic content) and VOC types have been tested for gas-phase diffusion.

MTBE, a very common VOC, detected in groundwater near landfills and hazardous waste dumps, can cause cancer in humans. It is used as a gasoline additive in the oil industry to reduce air pollution and can be released through leakage from underground storage tanks (UST) and pipelines, surface spills in gas stations and leachate from landfills and hazardous waste dumps. It can cause problem in countries which rely on underground water as a source of drinking water or for agricultural uses such as United States (20 public wells have detectable amount of MTBE in California). Due to its specific physical and chemical properties such as high volatility, high water solubility, not much adsorptivity on soil particle and biodegradability, it is very mobile in the environment (Weaver *et al.*, 2009; Weaver, 2004; Peat *et al.*, 1998).

## 1.2 SCOPE AND OBJECTIVES

The goals of thesis are to,

- (1) Design and build an effective and improved experimental apparatus and develop a procedure that overcomes previous limitations and deficiencies regarding diffusion studies.
- (2) Investigate the effect of soil degree of saturation on gas phase diffusion rate of MTBE.
- (3) Study the influence of soil composition such as soil particle size distribution and organic carbon content on MTBE gas phase diffusion rate.

### **1.3 RESEARCH PLAN**

To accomplish the previously presented objectives of the thesis, a research plan (Figure 1.3) is created. A grading scheme is devised for determination of soil to be used in the experiments. Organic carbon content test also determines organic contents of all soil components (sand, clay and peat). Soil with different degrees of saturation, clay and peat contents then is compacted in a diffusion apparatus and tested for diffusivity investigation. MTBE profiles versus time obtained from gas phase diffusion test are analyzed to calculate MTBE gas phase diffusivities at various soil condition and composition. Finally results are discussed, compared with previous studies, and conclusions and recommendations are provided.

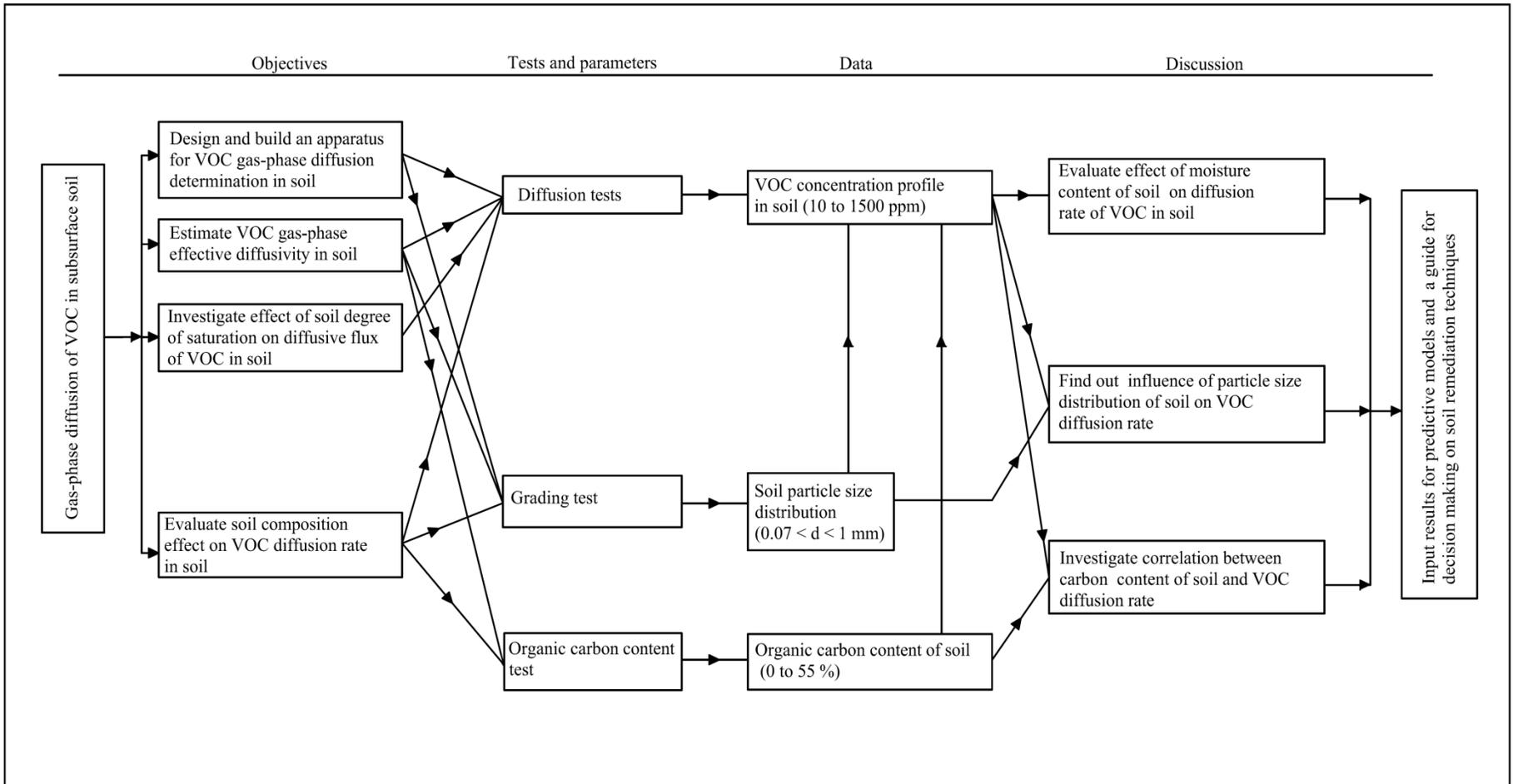


Figure 1.3 Flow chart of research plan.

## **1.4 POTENTIAL RESEARCH CONTRIBUTIONS**

The results of this research are intended to provide better understanding of VOCs migration in soil. The need for accurate prediction of VOCs migration arises in risk assessment and contaminated site investigation. More accurate effective diffusivity values will lead to better understanding of the contamination level and help environmental engineers and risk assessors in site investigation and risk assessment.

The efficacy of any remediation procedure depends on knowledge about background contaminant level. Both gas phase and liquid phase diffusion are two important mechanisms associated with many soil remediation techniques. For this purpose, accurate prediction of contaminant level compared to safe level improves efficiency of any remedial activity. In addition, to obtain a reliable computational simulation of remediation techniques, accurate estimation of effective diffusivity will become necessary. The output of this project also provides modelers high quality and reliable data as input for validation of computational simulations. This could lead to better prediction of contamination level.

## **1.5 ORGANIZATION OF THESIS**

The thesis includes five chapters:

Chapter 1: Presents statement of problem, scope and objectives of research and its contributions.

Chapter 2: Includes literature review on physical mechanisms of VOCs fate and transport in soil, previous experimental systems, and factors affecting VOCs diffusion in soil.

Chapter 3: Explains experimental design details, methods and materials used in the study.

Chapter 4: Presents results of research program. In addition, discusses effects of soil degree of saturation, soil particle size distribution and soil organic carbon content on MTBE gas phase effective diffusion and compares results with those of previous studies.

Chapter 5: Presents conclusions and recommendations for future research.

## CHAPTER 2

### PHYSICAL MECHANISMS OF VOC TRANSPORT IN SOIL

In this chapter a comprehensive literature review on VOCs physical migration transport in soil is provided. It includes previous experimental systems for diffusion and adsorption studies, factors affecting this migration and results of different studies.

#### 2.1 DIFFUSION

The term “diffusion” in soil can be interpreted as both gas phase diffusion, and sorptive diffusion (Figure 2.1). Gas phase diffusion plays an important role in transportation of VOCs in subsurface soil (Batterman *et al.*, 1996; Bartelt-Hunt and Smith, 2002; Wang *et al.*, 2003; Hers *et al.*, 2000). Gas phase diffusion flux can be defined as random-walk transfer of mass, down the concentration gradient, due to thermal movement of molecules and atoms. It is represented by Stephan-Maxwell (SM) (Baehr and Bruell, 1990) and Fick’s first (for steady state condition) and second law (for transient condition) of diffusion. SM relationship presented in equation 2.1 can be used to predict flux of one gas in mixture of gases (Scanlon *et al.*, 2001).

$$\sum_{\substack{j=1 \\ j \neq i}}^V \frac{x_i N_j^D - x_j N_i^D}{D_{ij}^e} = \frac{\nabla P_i}{RT} \quad (2.1)$$

where,

$x_i, x_j$  are mole fraction of components i and j.

$N_i^D, N_j^D$  are total molar gas flux of component i and j (mol/L<sup>2</sup>t).

$D_{ij}^e$  is the effective molecular diffusion coefficient of component i in j (L<sup>2</sup>/ t).

$T$  is absolute temperature.

$P$  is pressure (M/ Lt<sup>2</sup>).

$R$  is the ideal gas constant.

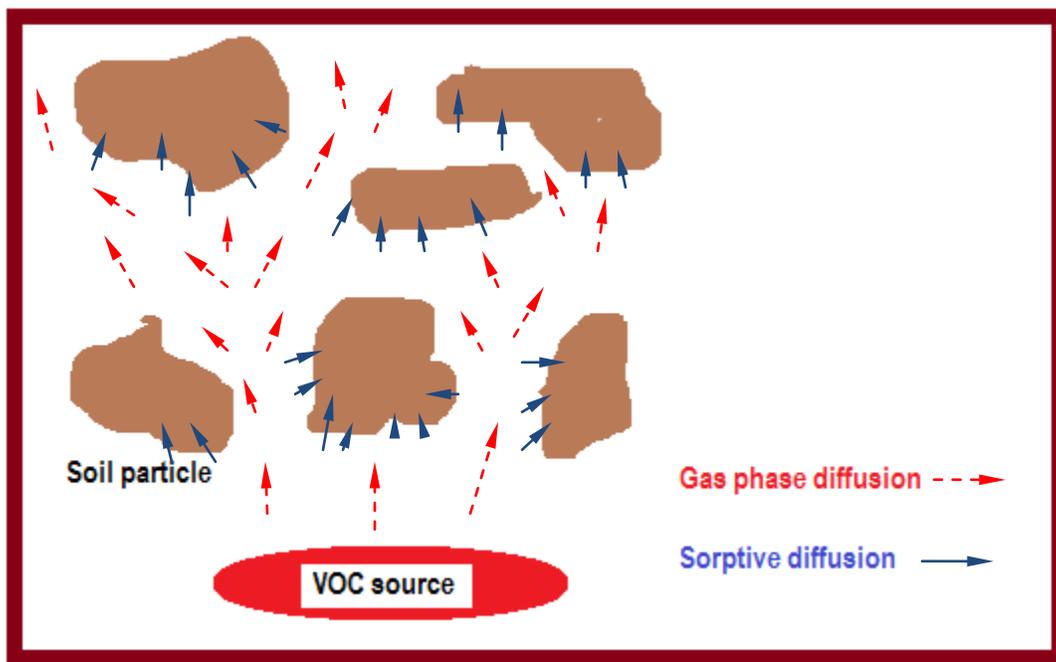


Figure 2.1 Schematic of gas phase diffusion and sorptive diffusion.

Since the VOC vapor pressures are low in comparison with other gases in the atmosphere such as N<sub>2</sub> and O<sub>2</sub>, Fick's second law provides a reliable estimation of VOCs diffusion in soil (Mendoza *et al.*, 1996; Rehfeldt and Stichlmair, 2007).

Fick's second law of diffusion is presented as below for a non-porous medium,

$$\frac{\partial C}{\partial t} = \frac{D \partial^2 C}{\partial x^2} \quad (2.2)$$

where,

$C$  is the VOCs concentration in air.

$t$  is time.

$D$  is coefficient of diffusion.

$x$  is distance traveled.

Gas phase diffusivity in soil is less than molecular diffusivity due to porosity and pore tortuosity of soil. Therefore, effective gas phase diffusivity is used in order to simulate VOCs movement in soil. Molecular diffusivity of different vapors in air is available in literature at 25°C (Lugg, 1968). This parameter can also be adjusted for change in temperature  $T(K)$  (Bird 2002) by,

$$D_T = D_g \frac{T^{1.5}}{298} \quad (2.3)$$

where,

$D_T$  is diffusivity at temperature  $T(K)$ .

$D_g$  is diffusivity at 25°C.

Effective diffusivity can be calculated by equation 2.4 based on Batterman *et al.* (1996) study,

$$D_{eff} = \theta_g \tau D_g \quad (2.4)$$

Where,

$D_{eff}$  is soil effective diffusivity.

$\theta_g$  is effective gas-phase area for diffusion.

$\tau$  is the ratio of straight pass length to the tortuous path length.

Since effective diffusivity is a major parameter affecting reliability of VOCs migration prediction and there are substantial uncertainties associated with its estimation, several previous experimental works have been done and empirical equations have been developed to relate effective diffusivity to the soil properties such as air-filled and total porosity (Penman, 1940; Millington 1959; Millington and Quirk, 1960; Millington and Quirk, 1961; Marshall, 1959; Moldrup *et al.*, 1997).

## 2.2 ADSORPTION

Sorptive diffusion or adsorption of VOCs onto soil minerals and organic material of soil is another factor affecting VOCs' mobility in subsurface soil (Gierke *et al.*, 1992; Voudrias and Li, 1993; Conklin *et al.*, 1995; Ong *et al.*, 1992; Shonnard *et al.*, 1993; Cabbar, 1999). VOC adsorption in soil is a two-stage process including (1) equilibrium sorption and (2) non-equilibrium sorption (Morrissey and Grismer, 1999; Karickhoff, 1980). Mechanisms involved in VOC adsorption onto soil material have been interpreted differently. Leenheer and Ahlrichs (1971) explained the first stage of sorption as surface related, and the second stage as diffusive flux of substance into soil minerals and organic matter. Arocha *et al.* (1996) came up with a model, called a two-site model, to explain adsorption of toluene onto soil minerals. According to this model, the first stage of toluene adsorption is mediated by its fast diffusion onto macropores; while, the second phase is mediated by slow diffusion onto micro-pores. BET (Brunauer, Emmett and Teller) (1938) multi-layer theory suggests that the fast adsorption takes place due to sorption onto external layer of particles, and the non-equilibrium stage is accumulation of more sorbate. Morrissey and Grismer's experiments (1999) on clay minerals proved that adsorption/desorption can be modeled by the bi-phasic Fickian diffusion model. Their results also showed the high capacity of clayey soil to adsorb VOCs from the gas phase.

## **2.3 EXPERIMENTAL METHODS FOR GAS PHASE DIFFUSION AND ADSORPTION STUDIES**

Macro and micro scale experiments have been developed to estimate effective diffusivity (both gas phase and sorptive) in different soil-VOC systems (Table 2.1). Figure 2.2 shows schematics of some of these experimental facilities. Macro-scale setups typically use larger columns with more soil than micro-scale tests.

### **2.3.1 Macro-scale tests**

Voudrias and Li (1993) designed a one-meter long horizontal soil column faced to benzene saturated air in one cap and to the free air at the other end. They found out that the diffusion coefficient based on water phase partitioning and linear sorption isotherm has a good compatibility with the benzene concentration profile in soil column. Batterman *et al.* (1995) performed a column test on four different soils with different carbon contents and porosities to measure the diffusive flux of different VOCs. Batterman *et al.* (1996) developed a one-flow soil sorbent-based column (Figure 2.2a), in which the sieved sand was exposed to the TCE concentrated nitrogen flow. In this study, Fick's first law and mass conservation equation were used to correlate the experimental results to theoretical concepts. Ruiz *et al.* (1998) determined the diffusional adsorptive flux into soil particles by exposing soil columns to VOCs under isothermal conditions. In their experiments, natural air after passing a silica filter and activated charcoal, was concentrated with different VOCs and passed through columns of different soil materials (sand, clay and limestone). Results were used to estimate BET model constants. Bartelt-Hunt and Smith (2002) used a one-flow sorbent based column (Figure 2.2d) and intact soil cores with different moisture contents and air filled porosities to determine the effective

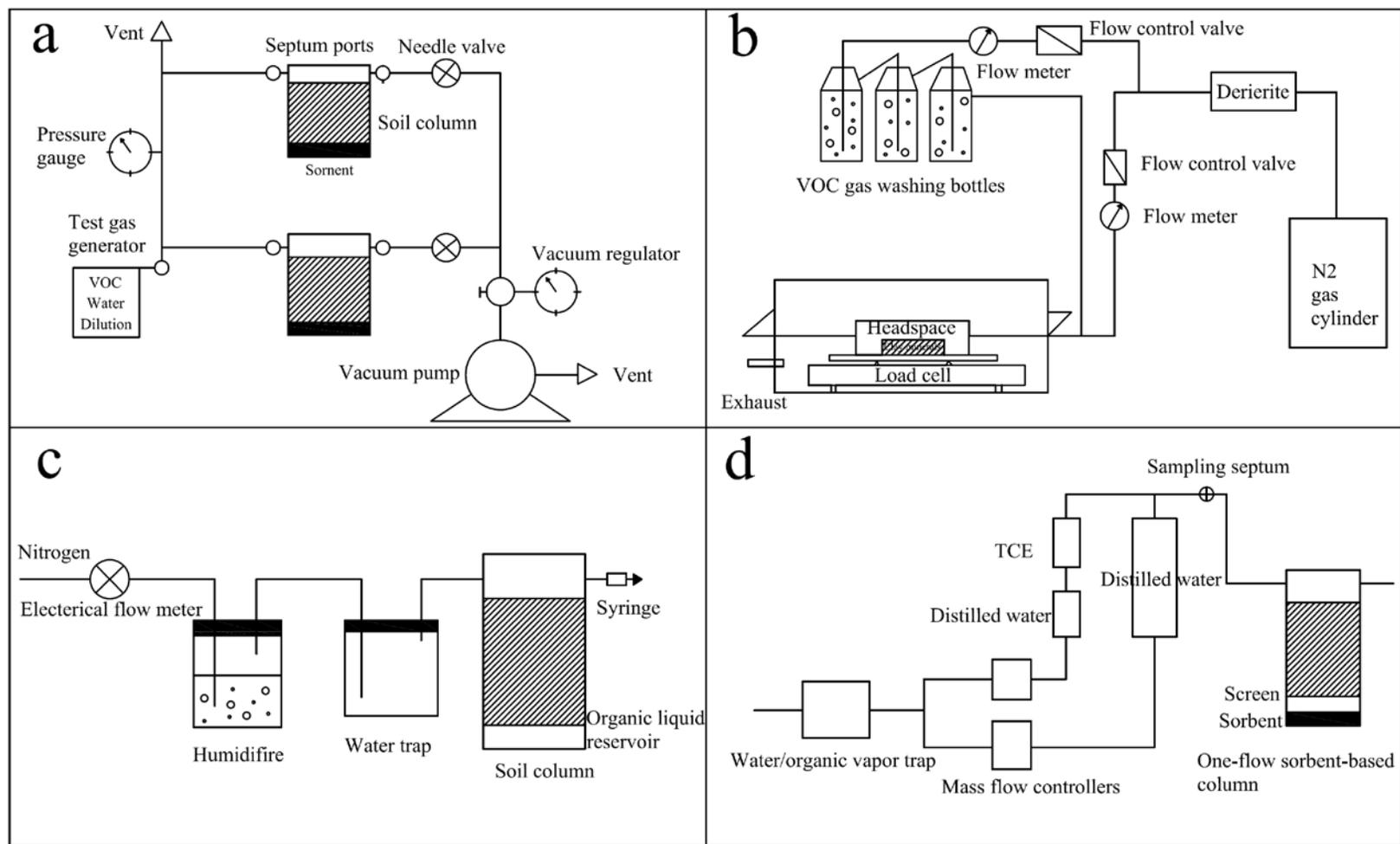


Figure 2.2 Schematics of some experimental setups, (a) One-flow sorbent-based experimental system, for determination of effective diffusivity, Batterman *et al.*, (1996), (b) Sorption/desorption study on clay minerals, Morrissey and Grismer, (1999), (c) Diffusion study of mixture of VOCs, Wang *et al.*, (2003), (d) Diffusion study of TCE in intact soil samples, Bartelt-Hunt and Smith, (2002).

Table 2.1 Summary of previous experiments and ranges of results.

| Study topic          | Exp. system             | Theory                                     | Soil type                                    | VOC type  | Degree of saturation (%) | Carbon content (%)   | Measured parameters                | Range of results  | Reference                        |
|----------------------|-------------------------|--|--|---|--------------------------|--|------------------------------------|---|----------------------------------|
| Diffusion/adsorption | Soil column (macro)     | Fick's first law                           | Sand, fill, loam and glass beads             | Toluene, TCE and methane  | 0 to 100                 | 0, 0.014, 0.045, 0.551 for glass beads, sand, fill and loam        | Retardation factor, diffusive flux | Flux from 2.73 to 4.22 ( $\mu\text{g/s}$ ), retardation factor from 0.92 to 80  | (Batterman <i>et al.</i> , 1995) |
| Gas phase diffusion  | Soil column (macro)     | Fick's first law                           | Sand   | TCE   | 0, 20, 40, 60, 80        | 0.01   | Gas phase effective diffusivity    | $2.5 \times 10^{-3}$ to $3.34 \times 10^{-2}$ ( $\text{cm}^2/\text{s}$ )  | (Batterman <i>et al.</i> , 1996) |
| Gas phase diffusion  | Soil column (macro)     | Fick's first law                           | Real soil cores (mixture of sand, clay, etc) | TCE   | 3 to 39                  | N/A  | Gas phase effective diffusivity    | $5.3 \times 10^{-3}$ to $6.09 \times 10^{-2}$ ( $\text{cm}^2/\text{s}$ )  | (Bartelt-Hunt and Smith, 2002)   |
| Gas phase diffusion  | Soil column (macro)     | Fick's second law                          | Sand   | Toluene and MTBE  | <20                      | 0.0001 and 0.00016   | Gas phase effective diffusivity    | $1.34 \times 10^{-2}$ to $2.19 \times 10^{-2}$ ( $\text{cm}^2/\text{s}$ )   | (Wang <i>et al.</i> , 2003)      |
| Adsorption           | Soil pellet (micro)     | Porous sphere model                        | SSM, McAFB and sand                          | Benzene and TCE   | 15, 30, 50, 70 and 90    | 0.25, 0.43 and 0.014 for SSM, McAFB and sand                       | Sorption effective diffusivity     | $1.6 \times 10^{-7}$ to $2 \times 10^{-6}$ ( $\text{cm}^2/\text{s}$ )   | (Lin <i>et al.</i> , 1994)       |
| Adsorption           | Humic acid disk (micro) | One-directional mass conservation equation | Humic acid (SOM)                             | Toluene, n-hexane, and acetone  | 0                        | Very high  | Sorption effective diffusivity     | For sorption $4.4 \times 10^{-9}$ to $20.9 \times 10^{-9}$ , for desorption $1.1 \times 10^{-9}$ to $6.9 \times 10^{-9}$ ( $\text{cm}^2/\text{s}$ ) | (Chang <i>et al.</i> , 1997)     |
| Adsorption           | Soil column (macro)     | Non-linear BET model                       | Sand, clay and limestone                     | n-hexane, n-heptane, n-octane, toluene, xylene, ethylbenzene, and methyl ethyl ketone | 0, 20, 50                | <0.1   | BET model parameters, B and $C_m$  | B, 7.09 to 1094, $C_m$ , $1.38 \times 10^{-5}$ to $5.89 \times 10^{-3}$   | (Ruiz <i>et al.</i> , 1998)      |
| Adsorption           | Soil disk (micro)       | Fick's second law                          | Kaolanite, illite and montmorillonite        | Acetone, benzene and toluene  | 0                        | 0.08, 1.30, and 0.07 for the kaolinite, illite and montmorillonite | Sorption effective diffusivity     | $2.3 \times 10^{-5}$ to $3.5 \times 10^{-3}$ ( $\text{cm}^2/\text{s}$ )   | (Morrissey and Grismer, 1999)    |
| Adsorption           | Soil pellet (micro)     | Mass balance equation                      | Montmorillonite                              | TCM and CTC   | 0, 5, 20, 40, 60, 80, 90 | 2 and 5  | Sorption effective diffusivity     | $8 \times 10^{-3}$ to $1.9 \times 10^{-2}$ ( $\text{cm}^2/\text{s}$ )   | (Cabbar, 1999)                   |
| Adsorption           | Soil pellet (micro)     | Conservation of mass equation              | Clay   | Methanol, acetone, benzene and toluene  | 0, 20, 40                | N/A  | Sorption effective diffusivity     | $1.6 \times 10^{-2}$ to $1.15 \times 10^{-1}$ ( $\text{cm}^2/\text{s}$ )  | (Kalender and Akosman, 2004)     |

diffusivity by fitting the data to Fick's first law of diffusion. They found that Millington's equation have a good agreement with experimental results. Wang *et al.* (2003) constructed a reservoir-based one-flow column (Figure 2.2c) to estimate diffusivity in sandy soil. Diffused VOC adsorbed by nitrogen as an inert carrier gas was measured by a Gas Chromatograph-Mass Spectrometer (GC-MS) and fitted to Fick's second law.

Greater cross-section of soil in macro-scale column tests provides more pathways for VOCs to diffuse making these methods more accurate for estimation of gas phase diffusion. The sample size in macro-scale setups also provides the ability to run column tests on real soil samples (Bartelt-Hunt and Smith, 2002). Due to larger scale of these columns, they are also less sensitive to lab environment background contamination.

There are also some issues associated with the macro-scale setups, both one-flow (reservoir-based and sorbent-based) and two-flow methods (experimental systems with two carrier gas flows at the top and bottom of soil column), which decrease the accuracy of the results. The problem is that the soil column may not be fully representative of real site conditions. Boundary effects, concentration gradients at the both ends of soil column, and lack of sufficient dilution may lead to biased results. Furthermore, other phenomena such as biodegradation and advection with significant effects on VOCs' fate are neglected in these setups, reducing their reliability.

### **2.3.2 Micro-scale tests**

Micro-scale experiments were conducted to determine sorptive diffusivities and adsorption isotherms for different soil-VOC systems. In these experiments small soil pellets (samples) were monitored in mass to determine diffusional flux in one or two sides of a thin soil pellet.

Lin *et al.* (1994) determined the effective diffusivity of two different VOCs and water in natural and synthetic soil samples. Small samples of soil were placed in an electro-balance under isothermal conditions. The diffusivities of soil-VOC systems were determined based on the Freundlich equation (Ruthven, 1984). Chang *et al.* (1997) used humic acid as a main constituent of soil organic matter to determine the adsorption and desorption rate of toluene, n-hexane and acetone under different humidity conditions. They found that only a minor fraction of sorbed VOCs can be recovered, and desorption takes more time to complete. They also proved that adsorption and desorption processes in soil organic matter are physical processes due to enthalpy changes of less than 20 kcal/mole. Morrissey and Grismer (1999) designed one-sided soil pellet experiments (Figure 2.2b) and studied the kinetics of sorption and desorption of three different VOCs on soil minerals. They used nitrogen as a carrier gas and measured the adsorbed VOCs on three different clay minerals and three thicknesses of soil pellet by monitoring mass change of soil in an isolated chamber. They found a direct relationship between the migration of VOCs and the path length. They also fitted the results to theoretical approaches (Fick's second law) to determine the diffusivity and partitioning coefficients. Cabbar (1999) studied the sorption of chlorinated VOCs in synthetic humic-clay complexes over a wide range of humidity with two different carbon contents. He used helium as a carrier gas passes through a double-sided soil pellet and determined the sorption coefficient of TCM (trichloromethane) and CTC (tetrachloride). Kalender and Akosman (2004) investigated the mobility and adsorption of both water-miscible and water-immiscible VOCs on clay minerals with three different moisture contents in a one-sided single pellet adsorption cell (see (Dogu and Smith, 1976; Cabbar *et al.*, 1994)) to determine the effective diffusivity and adsorption equilibrium constant. They observed

a decrease in adsorbed VOCs with an increase in soil moisture content. They also found that the humidity has no significant effect on the effective diffusivity of benzene.

Even though micro-scale experiments are very sensitive and the adsorbed mass of chemicals can be detected easily, they are also sensitive to the environmental conditions. For example if the lab atmosphere is contaminated with the relevant VOC, it can lead to biased results. (This problem can be solved by taking blank samples during the test). The need for sieving soil due to the very small sizes of the samples, make these methods unable for testing real soil cores.

## 2.4 FACTORS AFFECTING DIFFUSION AND ADSORPTION IN SOIL

### 2.4.1 Relative humidity

Previous studies both theoretical (Troeh *et al.*, 1982; Patwardhan *et al.*, 1988) and experimental (De Vries, 1952; Ostendorf *et al.*, 1993) have proved that effective diffusivity in porous media such as soil is a function of macro properties of the media such as porosity (total, air-filled and water-filled), pore connectivity, pore geometry, and tortuosity. Soil water content as a liquid phase plays an important role in migration and retardation of VOCs in subsurface soil. First, water reduces the adsorption of VOCs on the mineral surface (Ruiz *et al.*, 1998; Kalender and Akosman, 2004); second, it reduces the air-filled porosity leading to decreased gas phase diffusion.

Batterman *et al.* (1996) conducted one-flow and two-flow experiments to measure the diffusive flux of TCE in sandy soil with different degrees of saturation. They demonstrated a direct relationship between air-filled porosity and diffusion coefficient. They also proved that the diffusive flux of TCE decreases as the soil degree of saturation increases. Other previous empirical equations developed by different researchers are given in Table 2.2. Those empirical equations relate effective diffusivity to the total and air-filled porosity of soil. Figure 2.3 was produced based on the empirical equations given in Table 2.2 and soil properties Batterman *et al.* (1996) used in their studies. These properties include  $2.6 \text{ g/cm}^3$  particle density, 0.014% organic content and 0.383 total porosity. In all previous works deterioration of effective diffusivity when water content of soil increases was observed. The effective diffusivities and their reduction from the Batterman *et al.* (1996) experiments are greater than previous equations in the range of 0 to 20% degrees of saturation. This difference can be related to other characteristics of soil such as

carbon content, soil geometry, etc, which can affect the diffusion process. Diffusion rate will tend to zero, while water content of the soil increases and pore spaces available for diffusion are filled with water.

Ruiz *et al.* (1998) studied the adsorption of different VOCs such as n-hexane, n-heptane, etc in clay, sand and limestone having different moisture contents (0, 20 and 50%). They found that the VOC adsorption decreases significantly for aromatic and aliphatic compounds as the moisture content increases in unsaturated soil. They found a linear inverse correlation between relative humidity and the ratio of VOCs' adsorbed concentration over its concentration in the gas phase. They also revealed that the adsorption reduction on minerals in the presence of water depends on the mineralogical composition of soil. Bartelt-Hunt and Smith (2002) also observed a reduction in effective diffusivity during testing of undisturbed soil cores for diffusional flux when the water content of soil increased. Kalender and Akosman (2004) conducted a dynamic analysis using the single pellet moment technique. They observed a reduction in adsorption equilibrium constant and diffusional flux in clayey soil containing no organic matter in the presence of water for both water-miscible and water-immiscible VOCs. Their results also suggested that the reduction of adsorption constant for water-miscible VOCs was higher than for water-immiscible VOCs. Cabbar (1999) also used single pellet moment technique to investigate the effect of humidity on sorption of CTC and TCM on clayey soil. The results showed that sorption mainly occurs on dry mineral surfaces.

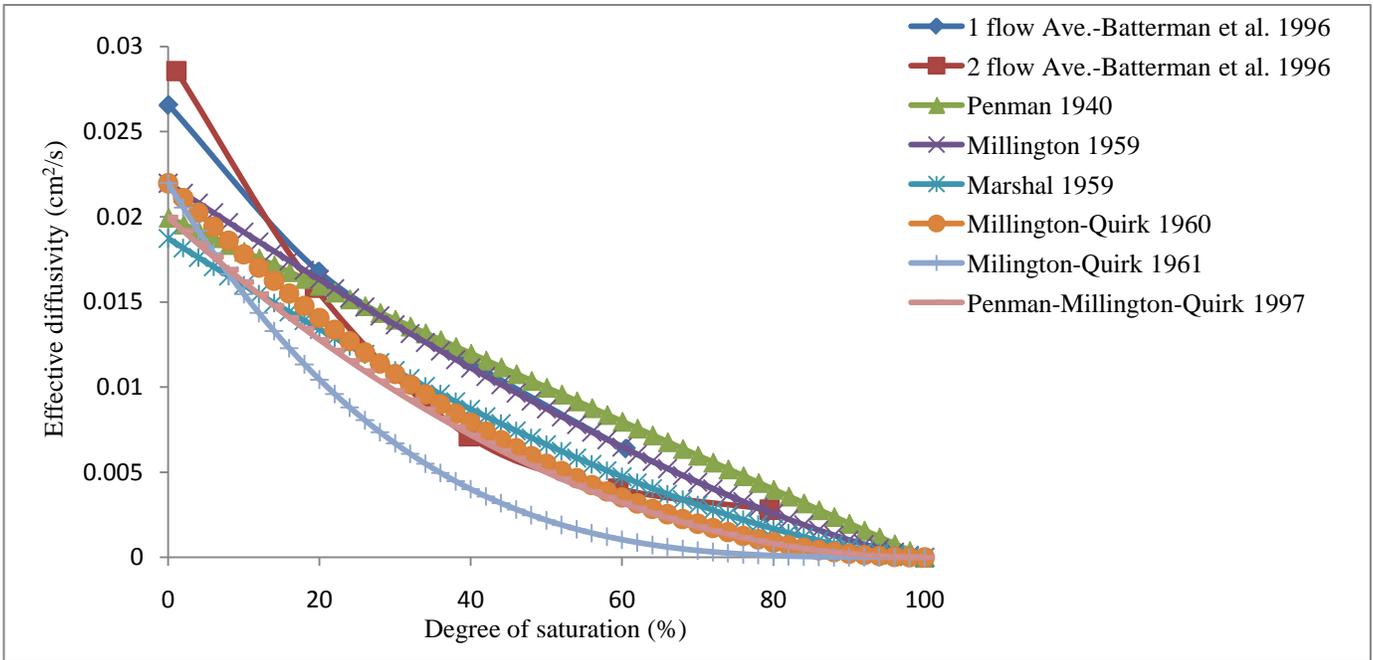


Figure 2.3 Effect of degree of saturation on TCE diffusion coefficient based on Batterman *et al.* experiments (1996) and previous empirical relationships.

Table 2.2 Empirical equations for effective diffusivity determination in soil.

| Equation   | Reference  |
|--|--|
| $\frac{D_{eff}}{D_M} = 0.66n_G$                  | (Penman, 1940)                                     |
| $\frac{D_{eff}}{D_M} = n_G^{1.33}$               | (Millington, 1959)                                 |
| $\frac{D_{eff}}{D_M} = n_G^{1.5}$                | (Marshall, 1959)                                   |
| $\frac{D_{eff}}{D_M} = \frac{n_G^2}{n_T^{0.66}}$ | (Millington and Quirk, 1960)                       |
| $\frac{D_{eff}}{D_M} = \frac{n_G^{3.33}}{n_T^2}$ | (Millington and Quirk, 1961)                       |
| $\frac{D_{eff}}{D_M} = 0.66 \frac{n_G^2}{n_T}$   | (Moldrup <i>et al.</i> , 1997) (PMQ <sup>a</sup> ) |

<sup>a</sup> Penman-Millington-Quirk

$D_{eff}$  is the effective diffusivity,  $D_M$  is the molecular diffusivity,  $n_G$  is the gas-filled porosity and  $n_T$  is the total porosity.

### 2.4.2 VOCs types

VOCs' mobilities in soil are highly affected by their physical and chemical characteristics, including molecular weight, solubility, polarity, Henry's law constant, and partition coefficient (Batterman *et al.*, 1996). Soil-VOCs interactions also have a significant effect on VOC mobility in soil. Ruiz *et al.* (1998) indicated a direct correlation between VOC polarity and its adsorbed concentration. For instance, they revealed that organic molecules with high levels of polarity, such as methyle ethyl ketone, have greater adsorption onto sand, clay and limestone than aromatics and aliphatics, such as toluene and n-hexane with lower levels of polarity. Among aliphatic compounds, the longer the molecule length, the higher adsorption was observed. The fact that polarity improves adsorption makes water a strong competitor for VOCs (Chiou and Shoup, 1985). In addition, a direct correlation was observed between Henry's law constant and VOCs' gas phase diffusion. The Kalender and Akosman (2004) adsorption experiments on different VOCs proved this relationship with Henry's law constants varying between 0.026 for MTBE to 14.90 for Methylcyclohexane.

### 2.4.3 Soil type

Migration of VOCs through soil media depends not only on the VOCs characteristics, but also on the physical and chemical properties of soil, such as air-filled, water-filled and total porosity, geometry of pores, tortuosity, size of grains, and organic content (Batterman *et al.*, 1996; Lyman *et al.*, 1982; Batterman *et al.*, 1995; Chiou and Shoup, 1985). Previous diffusion studies have mainly been performed on sandy soil (Batterman *et al.*, 1996; Ruiz *et al.*, 1998; Wang *et al.*, 2003; Batterman *et al.*, 1995). Sandy soils' higher air-filled porosities (larger grain size) (Figure 2.4) result in faster establishment of equilibrium conditions in comparison with

clayey soils. On the other hand, since the adsorption process is much more extensive in clayey soil due to its larger surface area, adsorption tests have mainly been done on clay minerals (Morrissey and Grismer, 1999; Kalender and Akosman, 2004; Cabbar, 1999). Surface area has significant effect on adsorption. This can be interpreted from Ruiz *et al.* (1998) adsorption experiments on three different soils. In their experiments, the adsorption capacity of clay minerals was one order of magnitude higher than for sand and two orders greater than for limestone. This effect was also observed by Campagnolo and Akgerman (1994) for several clay minerals. Surface area varies widely in different clay minerals. For example montmorillonite, with a surface area of 800 m<sup>2</sup>/g, is two orders of magnitude more adsorptive of acetone, benzene and toluene than illite which has a surface area of 15 m<sup>2</sup>/g (Morrissey and Grismer, 1999).

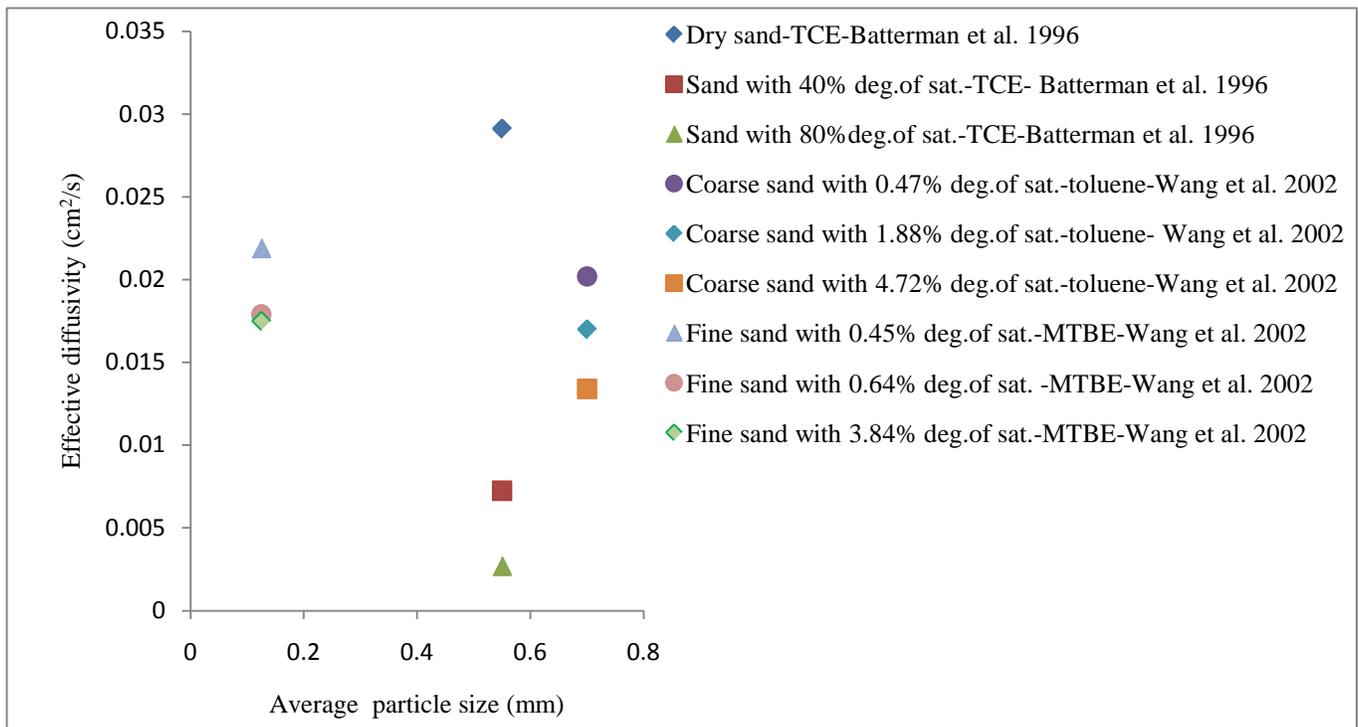


Figure 2.4 Effective diffusivities of TCE, toluene and MTBE in sands with different grain sizes and water contents.

Soil organic material (SOM) acts as a very strong adsorbent for VOCs. This can be interpreted as diffusional flux (Michaels and Bixler, 1961; Del Nobile *et al.*, 1995; Park and Crank, 1968; Schneider *et al.*, 1994) of VOC molecules inside the homogeneous polymeric texture of SOM. This is not as a reason of SOM large surface area, since they do not have a large surface area (Chiou *et al.*, 1990). Therefore, SOM is the dominant medium for VOC partitioning rather than soil minerals, especially in soils with high water content such as natural soils and sediments, even those with low organic carbon fraction ( $f_{oc}$ ) (Kleineidam *et al.*, 1999; Ong and Lion 1989). On the other hand, the importance of soil minerals becomes more significant when the water content of soil decreases (Chiou and Shoup, 1985).

Cabbar (1999) cast doubts on the effect of carbon content on the effective diffusion coefficient. His study indicated that the carbon content of soil does not have a significant effect on the diffusivities of TCM and CTC. He interpreted these results based on the assumptions that the effective diffusion coefficient is a function of macro-pore structure and changes in carbon content of soil do not affect the pore structure. Lin *et al.* (1994) also showed that the organic content of soil did not play a significant role in VOCs' gas-phase adsorption. Table 2.1 summarizes some previous specifications and results obtained for diffusivities and adsorption constants.

## **CHAPTER 3**

### **MATERIALS AND METHODS**

#### **3.1 DIFFUSION APPARATUS**

A one-flow reservoir-based system was designed and built for VOCs gas phase diffusion determination. It consists of two main sections: (1) soil cylindrical column (Figures 3.1 and 3.2) and (2) nitrogen flow provider (Figures 3.1 and 3.3).

Design criteria for the soil column include column diameter, height, and material. However there was no limitation for maximum diameter of the column, it could not be too long. Longer soil column leads to longer equilibrium time and each test takes more time. 207 mm was chosen as the total height of the column (127 mm height of the middle section, 50 mm height of the bottom section and 30 mm height of the top section). 105 mm was selected for the column as an appropriate inner diameter for compaction of the soil components (sand, clay and peat) that were used in the tests. Stainless steel was used as material of the soil column to prevent any chemical reaction between VOC, soil and inner walls of the column.

##### **3.1.1 Soil cylindrical column**

The soil column was made of three flanged stainless steel pipes (inner diameter of 105 mm) (Figure 3.4a), each containing a gas sampling port. The top and bottom ones were capped. Soil

was compacted inside the cylindrical column (Appendix B) and supported by a frame and fine mesh (0.05 mm) (Figure. 3.4b).

#### 3.1.1.1 Pressure transducer

The pressure at the top and bottom of the column were monitored continuously by pressure transducers (PX209, 015G5V, Omega) to study the effect of advection. They were calibrated by the supplier company (Omega) and five calibration points were provided.

#### 3.1.1.2 Load cell

A full-bridge thin-beam load cell (LCL, 113G, Omega) with maximum capacity of 113 g and accuracy of 0.001 g was used to monitor the mass loss of MTBE during tests. Load cell signals were transferred out by a cable through a gas tight tap at the bottom section. Load cell was calibrated with known loads. After installing the load cell inside the bottom section of the soil column, known loads (1, 2, 5, 10, 20, 40 and 80 g) were placed on top of the mounting bar and output signals were measured.

#### 3.1.1.3 Tubing

¼ inch (6.3 mm) stainless steel, high pressure plastic and flexible tubing were used to carry the nitrogen flow to the column and the off-gases to the fume hood.

#### 3.1.1.4 Column body

Column body was made of three flanged stainless steel pipes (inner diameter of 105 mm, height 207 mm), assembled by bolts and nuts (Figures 3.2 and 3.4), with sections sealed by rubber O-rings.

### 3.1.1.5 Stainless steel frame and mesh

Soil weight was supported by applying a frame and 0.05 mm stainless steel mesh (Figure 3.4b). Since mesh is flexible and cannot bear vertical load, four circular stiffeners were placed inside the main circular frame to increase the rigidity. The stiffeners are circular steel rings with 42 mm inner diameter and 1 mm thickness. Rings were fixed to the frame with small bolts and nuts.

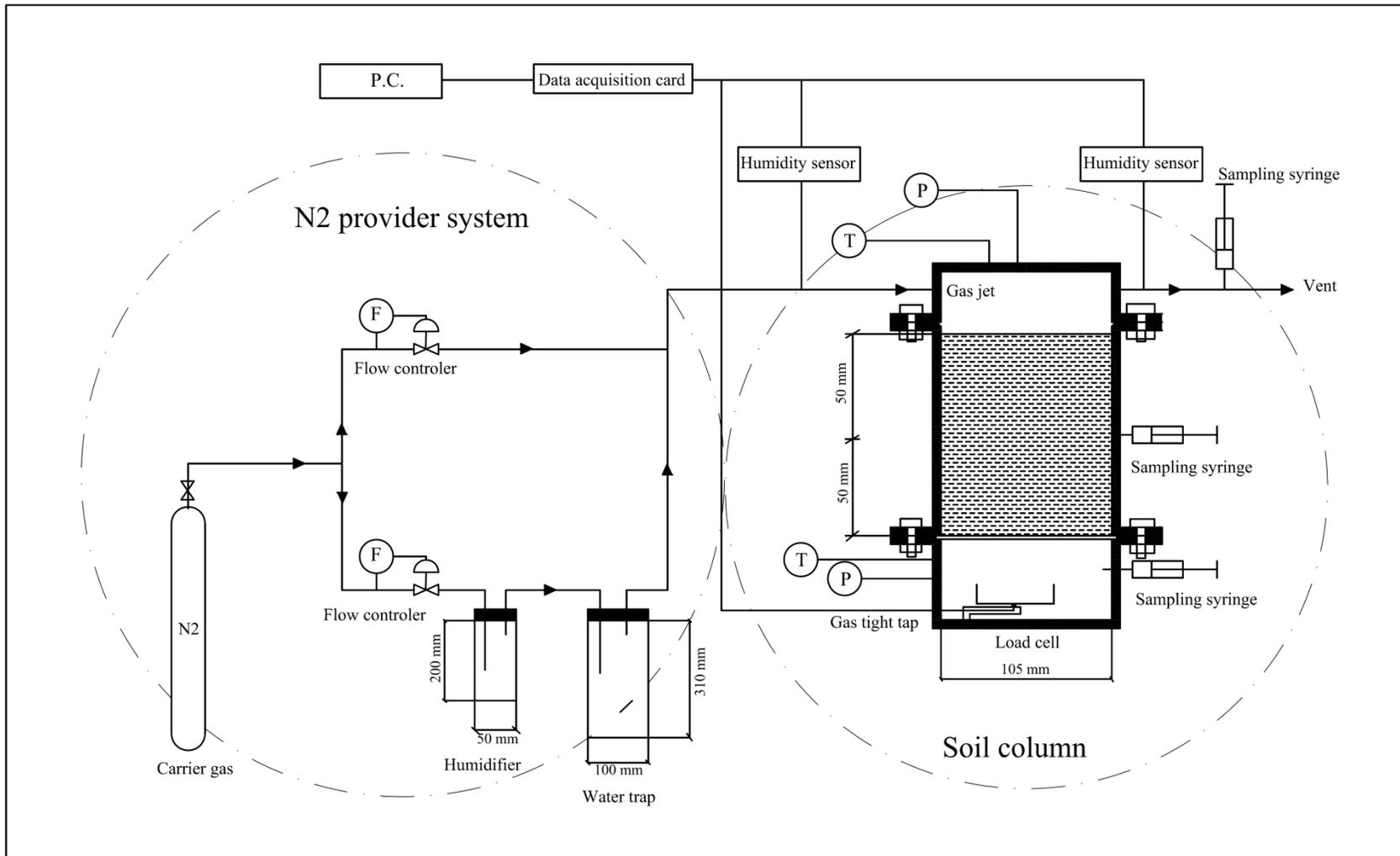


Figure 3.1 Schematic of soil diffusivity apparatus.

P: Pressure transducer  
 T: Temperature sensor  
 F: Flow meter



Figure 3.2 Effective diffusivity test apparatus (soil column).



Figure 3.3 Effective diffusivity test apparatus (nitrogen flow provider).

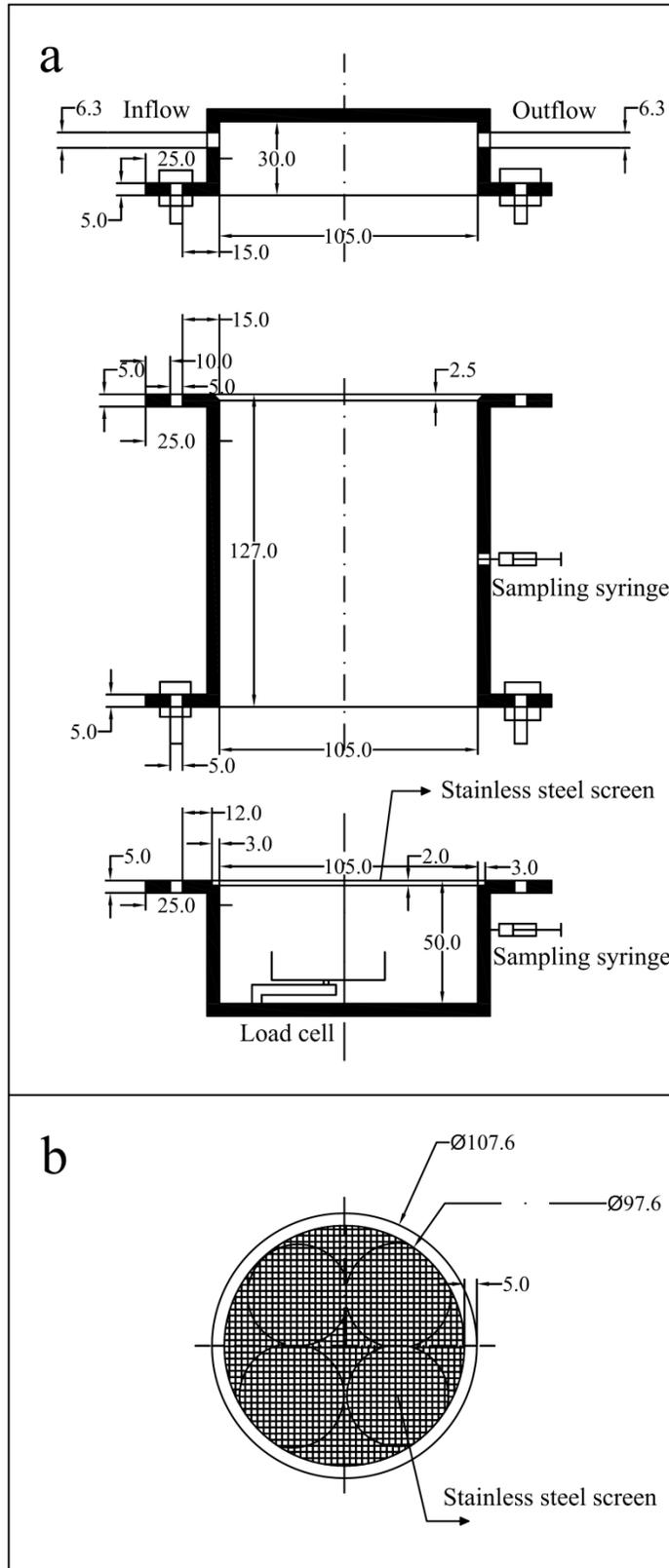


Figure 3.4 Effective diffusivity test apparatus (a) soil column side view (b) plan view of support frame and mesh (dimensions in mm).

### 3.1.2 Nitrogen flow provider

This part of apparatus had provided nitrogen of the appropriate flow rate and relative humidity (Figure 3.1).

#### 3.1.2.1 Flow controller

Two manually controlled flow meters (rotameter) (Q-flow, Vogtlin, Switzerland) with maximum capacity 120 mL/min were installed at nitrogen inflow to control and mix the right proportions of dry and saturated nitrogen. The flow meter consists of an aluminum body, a glass measuring tube and a turning control valve for flow adjustment. The flow meters were calibrated by a digital flow meter (ADM 1000, Agilent Technologies) before the tests. Calibration curves are provided in Appendix A.

#### 3.1.2.2 Humidifier and Water trap

The humidifiers were simply three glassy cylindrical flasks with 50mm diameter and 200 mm height filled with distilled water. Nitrogen was about 90% saturated with water after bubbling through the water. Water trap was also a cylindrical glassy flask with 100 mm diameter and 310 mm height. Small water drops were separated from the nitrogen flow while passing through it. Installing humidifier and water trap, made it possible to provide an even flow of partially moisture- saturated nitrogen without water drops.

#### 3.1.2.3 Humidity/Temperature sensor

Three humidity/temperature sensors and transmitters (HX93AC, Omega) with accuracy of  $\pm 2.5\%$  (of actual readings) for relative humidity and  $\pm 0.6^\circ\text{C}$  (of actual readings) for temperature were installed at the inflow, outflow and column bottom to monitor the relative humidity and

temperature continuously during the tests. These data were used to choose the appropriate mixing ratio of saturated and dry nitrogen so that there was no evaporation from, or water condensation onto, the upper surface of the soil. The aim was to have the same reading of the two sensors. It was achieved by changing saturated and dry flow rates.

#### 3.1.2.4 Data Acquisition

A data acquisition (NI USB-6211, National Instruments) (with frequency of 250000 Hz) converted the sensors and load cell signals to numeric values. Lab view software was used to visualize the data acquisition signals in computer.

### **3.1.3 Summary of new features of diffusion apparatus**

Novel features of the apparatus allowed us to overcome previous limitations and issues associated with diffusion tests. These new features include:

- Humidity/temperature sensors along the flow direction assigned to determine the relative humidity and temperature and give us the ability to determine the exact ratio of saturated and dry nitrogen. Based on humidity sensors readings, the ratio of saturated and dry flow can be adjusted to keep water content of the soil constant.
- Pressure transducers also measure the pressure at the top and bottom to take into account the effect of advection on VOC migration.
- The mass loss of VOCs by time also can be determined by the load cell at the bottom. This feature makes it possible to monitor VOCs mass transfer through the soil column and confirm the flux from concentration and flow analysis.

## **3.2 MATERIALS**

Fraser river sand (silica sand) (Fraser River Pile and Dredge Inc., New Westminster, Canada) was used as one component of the soil samples. Kaolinite (Unimin Corporation, Hephzibah, United States) and Canadian peat moss (Schultz, Canada) were added as filler (fine aggregate) and organic material respectively. Due to budget and time limitation for the master project, running diffusion tests on real soil samples (soil cores) was not feasible.

### **3.2.1 Particle size distribution**

The grain size distribution for sand was determined using the dry sieve method based on ASTM D 421-85 (American Society for Testing and Materials). Test results are provided in Appendix C.

### **3.2.2 Organic carbon content**

The organic content of sand, clay and peat were determined based on ASTM D 2974-87. Soil samples were burned in muffle furnace at 440°C until no mass change was observed. The test procedure and results are provided in Appendix D.

MTBE with purity of higher than 99.8% (0.2% water) (Sigma, Aldrich Inc., USA) was used as the representative VOC for all tests. The properties of MTBE are provided in Table 1.1.

### **3.3 TEST PROCEDURE**

#### **3.3.1 Preparation of soil samples**

Sand, clay and peat were dried in oven at 104°C (until no mass change was observed, between one to five days depending on the soil type). Peat was grinded and passed through Sieve number 18 (1 mm) to increase its surface area. Sand also passed through sieve number 10 (2 mm) to remove coarse aggregates. After being completely dried, the appropriate weight ratio of the sand, clay and peat (Table B1) was mixed and placed into a gas tight plastic bag. Water was added to the soil bag and samples were mixed and kept at room temperature for 24 hours (for provision of an even distribution of water content). Afterward, soil was statically compacted (Appendix B) in the steel column before conducting the diffusion test.

#### **3.3.2 Soil diffusivity testing procedure**

Before running the test, all parts including column body, liquid pan and steel mesh were cleaned by methanol and left to dry to avoid any background contamination in the system. The middle part of the column containing the compacted soil was placed between the upper and lower parts. The whole system was then checked to be gas tight by applying 2 psi (13.8 kPa) gas pressure inside the system and using soap foam. The nitrogen flow was adjusted to 90 to 100 mL/min in total (dry and wet flow) to purge the top surface of the soil. The ratio of saturated and dry nitrogen flow was depended on the soil humidity. 20 mL of liquid MTBE was injected into a pan by a glass 30 mL syringe through the bottom sampling port at time zero. The entire system was at room temperature (21 to 23°C). The total nitrogen flow was checked at every sampling time to be constant by a digital volumetric flow meter (ADM 1000, Agilent Technologies). The pan was filled at the beginning with MTBE and also refilled during the test if needed (The pan

should contain liquid MTBE during the entire test period). The outflow gas containing MTBE was directed to the fume hood. The test conditions (temperature, flow rate and dry/saturated flow ratio) were kept constant during each entire experiment.

### 3.3.3 Soil diffusivity testing conditions

Soil samples with 0 to 80% degrees of saturation, 0 to 15% clay contents and 0 to 15% peat contents were tested for MTBE diffusion. Table 3.1 shows the soil composition, degree of saturation and total porosity for each set of experiments.

Table 3.1 Soil composition, degree of saturation and total porosity for each set of MTBE diffusion experiments.

| Run no. | Degree Of Saturation | Soil type                           | Soil total porosity |
|---------|----------------------|-------------------------------------|---------------------|
| 1       | 0                    | Sand                                | 0.38                |
| 2       | 20                   | Sand                                | 0.38                |
| 3       | 50                   | Sand                                | 0.38                |
| 4       | 50                   | Sand <sup>a</sup>                   | 0.38                |
| 5       | 80                   | Sand                                | 0.38                |
|         |                      |                                     |                     |
| 6       | 0                    | Sand+ 5% clay                       | 0.34                |
| 7       | 0                    | Sand+ 10% clay                      | 0.34                |
| 8       | 0                    | Sand+ 10% clay <sup>a</sup>         | 0.34                |
| 9       | 0                    | Sand+ 15% clay                      | 0.34                |
|         |                      |                                     |                     |
| 10      | 20                   | Sand+ 5% clay+ 5% Peat              | 0.36                |
| 11      | 20                   | Sand+ 5% clay+ 5% Peat <sup>a</sup> | 0.36                |
| 12      | 20                   | Sand+ 5% clay+ 10% Peat             | 0.36                |
| 13      | 20                   | Sand+ 5% clay+ 15% Peat             | 0.36                |

<sup>a</sup> Repeated run

### 3.4 SAMPLING AND ANALYSIS

Three gas sampling ports were provided at the top, middle and bottom of the column for gas sampling (Figure 3.1). 50  $\mu\text{L}$  gas samples were taken from each by gas tight syringes (Hamilton Company) during entire test period. Sampling intervals varied from 1 to 10 hours. More samples were taken in the first hours since the concentration variation was much greater during the early hours of the tests. Samples were immediately injected into a HP HEWLETT 5890 GC (gas chromatograph) equipped with FID (flame ionized detector) for quantification of MTBE. A 30 m long 0.53 Inner diameter capillary column (CAT number 125-1334, phase: DB624) was used in the GC. The GC settings include 30 mL/min hydrogen flow, 100 mL/min air flow, 35°C oven temperature, 180°C injector temperature and 200°C detector temperature. Sampling continued until equilibrium condition had been virtually achieved. Flux of MTBE through sampling was negligible (less than 0.001%) in comparison with its upward flux. So sampling from the middle port cannot lead to biased results.

In order to minimize sample contamination and interference, the following steps were taken,

- Field blanks (samples from lab air) were taken at each sampling time to consider the effect of laboratory background contamination (no MTBE detected in all blanks)
- Sampling syringes were plugged with a small piece of rubber after taking samples and before injecting into the GC.
- After each sampling time, syringes were purged with pressurized air for 30 s to be clean for the next sampling time.
- Needles were checked periodically not to be plugged.
- Sampling septa were replaced after each test.

### 3.5 QUALITY CONTROL/QUALITY ASSURANCE

A set of steps were taken to assure the accuracy, precision and overall reliability of results. Precision can be described by standard deviation of measurements under identical conditions. Since standard deviation is more meaningful with knowledge of the mean value, the coefficient of variation (C.O.V.) was used to measure the precision of analytical method. It is defined as,

$$C.O.V = \frac{s.d.}{\bar{x}} .100 \quad (3.1)$$

where,  
*s.d.* is standard deviation  
 $\bar{x}$  is average

Systematic error or bias, known as the difference between average of a series of replicate samples and true value, can be calculated as below,

$$Bias (\%) = \left| \frac{\bar{x} - T.V.}{T.V.} \right| .100 \quad (3.2)$$

where,  
 $\bar{x}$  is average concentration of replicates  
*T.V.* is true value

In each run four replicate standards (samples with known concentrations) were analyzed by the GC. (These standard samples obtained by adding known volume of MTBE to a container with known volume, so they can be subjected to human errors). The results of biases and coefficients of variation are presented in appendix E. To estimate the repeatability of the diffusion tests, one test in each set of experiments were repeated. MTBE mass flux through the column was determined both by load cell results and MTBE concentration of nitrogen flow. The results are provided and compared in Appendix F.

### 3.6 THEORY

Gas phase diffusion in soil under steady state conditions can be presented by Fick's first law of diffusion,

$$F = D_{eff} \frac{\Delta C}{l} \quad (3.3)$$

where,

$F$  is VOC mass flux per unit area of soil section ( $\frac{\mu g}{s \cdot mm^2}$ ).

$D_{eff}$  is the effective diffusivity ( $\frac{mm^2}{s}$ )

$C$  is VOC concentration in the gas sample ( $\frac{\mu g}{mm^3}$ )

$l$  is length (mm)

Fick's first law assumes pressure, effective diffusivity, degree of saturation and temperature are constant and uniform throughout the soil column and diffusion is a one-dimensional process.

First Fick's law of diffusion (that I have used in my study) with consideration of mass conservation leads to second Fick's law of diffusion (equation 2.2), that can be used for transient analysis. This equation can be solved analytically. Boundary and initial conditions of the experimental system provided below,

|        |          |                                       |
|--------|----------|---------------------------------------|
| B.C. 1 | $C=C_0$  | $0 < t < \infty$ (s) and $x=0$ (mm)   |
| B.C. 2 | $C=f(t)$ | $0 < t < \infty$ (s) and $x=100$ (mm) |
| I.C.   | $C=0$    | $t=0$ (s) and $0 < x < 100$ (mm)      |

Analytical solution provided by Carslaw and Jaeger (1948),

$$C(x, t) = \sum_{n=1}^{\infty} e^{-D \cdot n^2 \cdot \frac{\pi^2 t}{l^2}} \cdot \text{Sin}\left(\frac{n \cdot \pi \cdot x}{l}\right) \left[ \frac{n \cdot \pi \cdot x}{l} \int_0^t e^{D \cdot n^2 \cdot \frac{\pi^2 \lambda}{l^2}} \cdot \{C_0 - (-1)^n \cdot f(\lambda)\} d\lambda \right] \quad (3.4)$$

## CHAPTER 4

### RESULTS AND DISCUSSION

In this chapter, first the MTBE diffusivity results are presented. These include the effect of degree of saturation, particle size distribution and organic content of soil on MTBE gas phase diffusion. Secondly, results are discussed and explained. Finally previous results are considered and compared with those of this study.

#### 4.1 INFLUENCE OF DEGREE OF SATURATION ON MTBE GAS PHASE EFFECTIVE DIFFUSIVITY

Figures 4.1 and 4.2 show MTBE concentrations versus time at 50 and 100 mm above the screen. The concentrations in soil gas rose sharply during the first hours of the test and then approached to a steady state condition after 5 to 15 hours, depending on the degree of saturation of the soil samples. The concentrations remained nearly constant after this time. Increasing the soil degree of saturation significantly affected the MTBE concentration profile along the soil column as shown previously by Batterman *et al.* (1996) for TCE. Concentrations dropped drastically for samples with higher degrees of saturation. MTBE concentrations varied from 406 to 830 ppm at 50 mm and from 6 to 106 ppm at 100 mm above the screen.

Concentrations after establishment of steady state condition were used to calculate effective diffusivities based on first Fick's first law of diffusion (equation 3.3). The MTBE mass flux through the soil column was obtained by multiplying nitrogen flow rate by the MTBE mass concentration at the column top. Effective diffusivities were calculated using the concentrations

at the bottom 50 mm, above 50 mm and over the height of 100 mm of the soil. The tests condition, diffusivity values and their variations are provided in Table 4.1. Figure 4.3 shows the effective diffusivities and their variations at different soil degrees of saturation. Diffusivities varied from 0.001 to 0.017 cm<sup>2</sup>/s. Variations are  $\pm\sigma$  of different calculations (top 50 mm, bottom 50 mm and total 100 mm).

The change in MTBE concentration profiles due to the variation in degree of soil saturation can be explained by different reasons. Greater water content of soil leads to less air-filled porosity, the available space through which MTBE diffuses. Furthermore, water in the soil matrix makes the pathways more tortuous since water drops clog the air pathways in soil and cut the connectivity between pores. Finally MTBE can dissolve in water content of soil rather than being diffused. The greater the water content of soil, the higher the dissolution.

In addition, greater water content of the soil, leads to longer time to reach equilibrium. Water in the soil lessens MTBE diffusion speed by clogging the pores and their connectivity and dissolving MTBE inside the matrix. The effect of dissolution disappeared after some hours since, water content of soil become saturated with MTBE and cannot dissolve more.

MTBE migrates faster in soils with higher degrees of saturation. In the winter and spring time when the precipitation is at its maximum level, the soil is completely or partially saturated with water. In contrast, in the summer and fall, due to evaporation of soil water, downward infiltration of water and less precipitation, soil tends to be partially dry. This means that migration of MTBE due to any source of release is faster in summer and fall than in the winter and spring. As a result, people who live in residential areas near sites contaminated with MTBE are at more risk of exposure in the summer and fall than in the winter and spring.

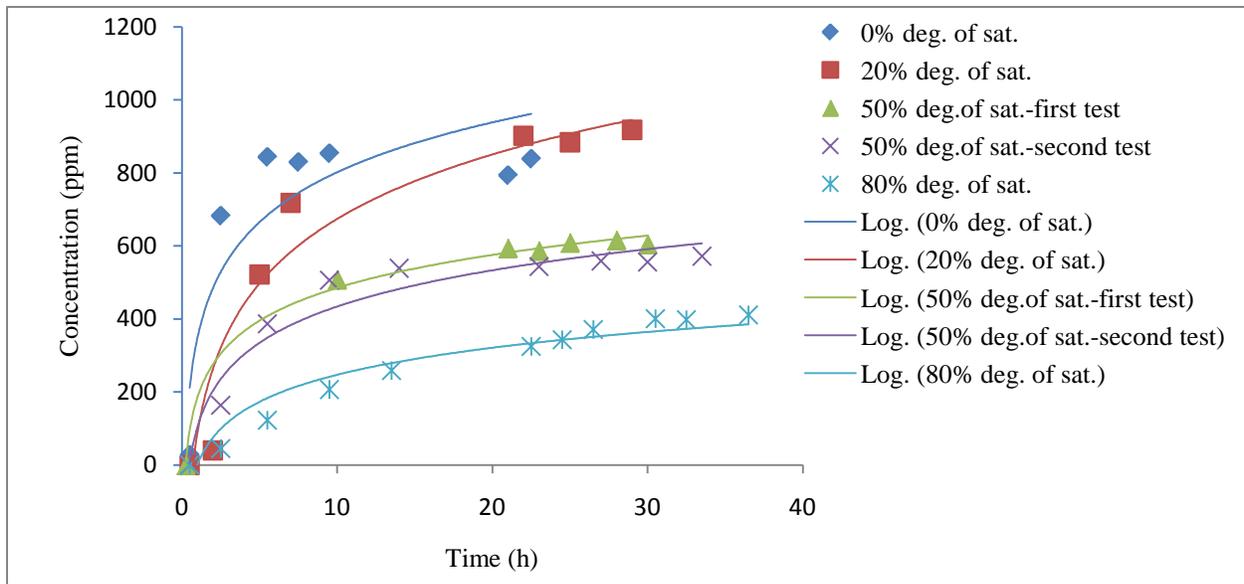


Figure 4.1 MTBE concentration in gas phase versus time at various soil degrees of saturation at 50mm above the screen (more details in Tables 3.1 and B1).

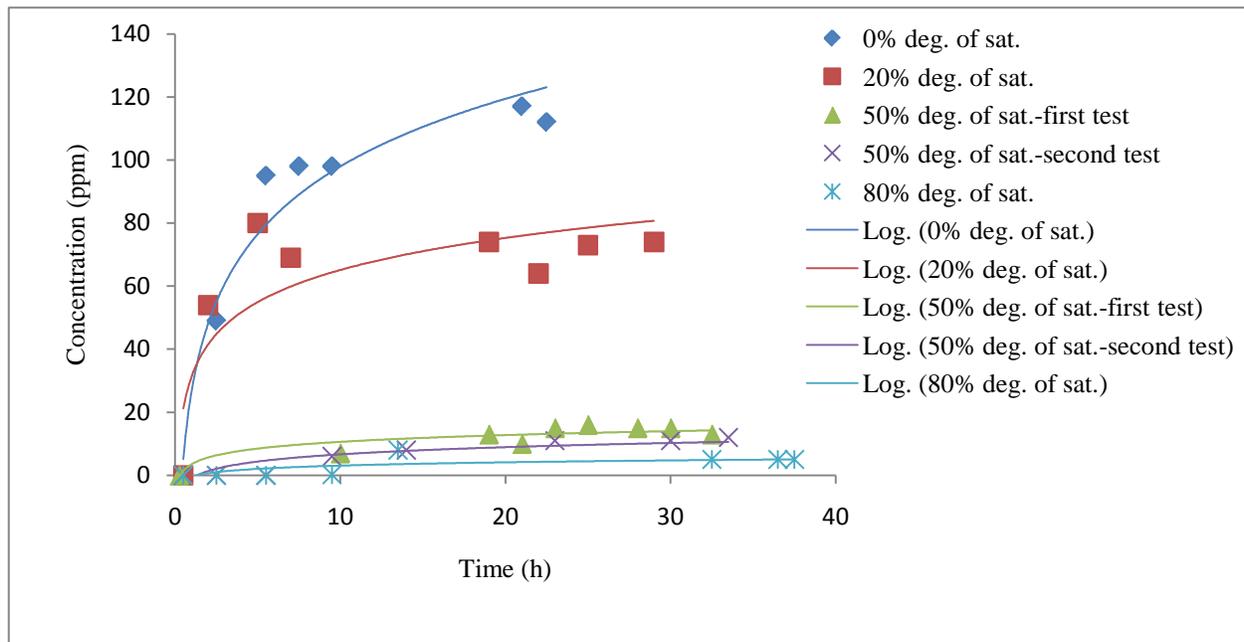


Figure 4.2 MTBE concentration in gas phase versus time at various soil degrees of saturation at 100 mm above the screen (more details in Tables 3.1 and B1).

Table 4.1 Conditions and results of diffusion experiments showing influence of degree of saturation.

| Deg. Of Sat. (%) | run no. | Soil height (mm) | Flow (mL/min) | Concentration ( $\mu\text{g/mL}$ ) |    | Effective diffusivity ( $\text{cm}^2/\text{s}$ ) |       |
|------------------|---------|------------------|---------------|------------------------------------|----|--|-------|
|                  |         |                  |               | avg                                | SD | avg  | SD    |
| 0                | 1       | 50               | 92            | 832                                | 23 | 0.020  | 0.003 |
|                  | 1       | 50               | 92            | 832                                | 23 | 0.014  |       |
|                  | 1       | 100              | 92            | 106                                | 9  | 0.017  |       |
|                  | Average |                  |               |                                    |    |  |       |
| 20               | 2       | 50               | 100           | 789                                | 17 | 0.016  | 0.003 |
|                  | 2       | 50               | 100           | 789                                | 17 | 0.011  |       |
|                  | 2       | 100              | 100           | 72                                 | 5  | 0.013  |       |
|                  | Average |                  |               |                                    |    |  |       |
| 50               | 3       | 50               | 100           | 602                                | 12 | 0.003  | 0.000 |
|                  | 3       | 50               | 100           | 602                                | 12 | 0.003  |       |
|                  | 3       | 100              | 100           | 14                                 | 2  | 0.003  |       |
|                  | 4       | 50               | 100           | 554                                | 13 | 0.002  |       |
|                  | 4       | 50               | 100           | 554                                | 13 | 0.001  |       |
|                  | 4       | 100              | 100           | 11                                 | 1  | 0.002  |       |
|                  | Average |                  |               |                                    |    |  |       |
| 80               | 5       | 50               | 100           | 406                                | 7  | 0.000  | 0.000 |
|                  | 5       | 50               | 100           | 406                                | 7  | 0.002  |       |
|                  | 5       | 100              | 100           | 6                                  | 2  | 0.001  |       |
|                  | Average |                  |               |                                    |    |  |       |

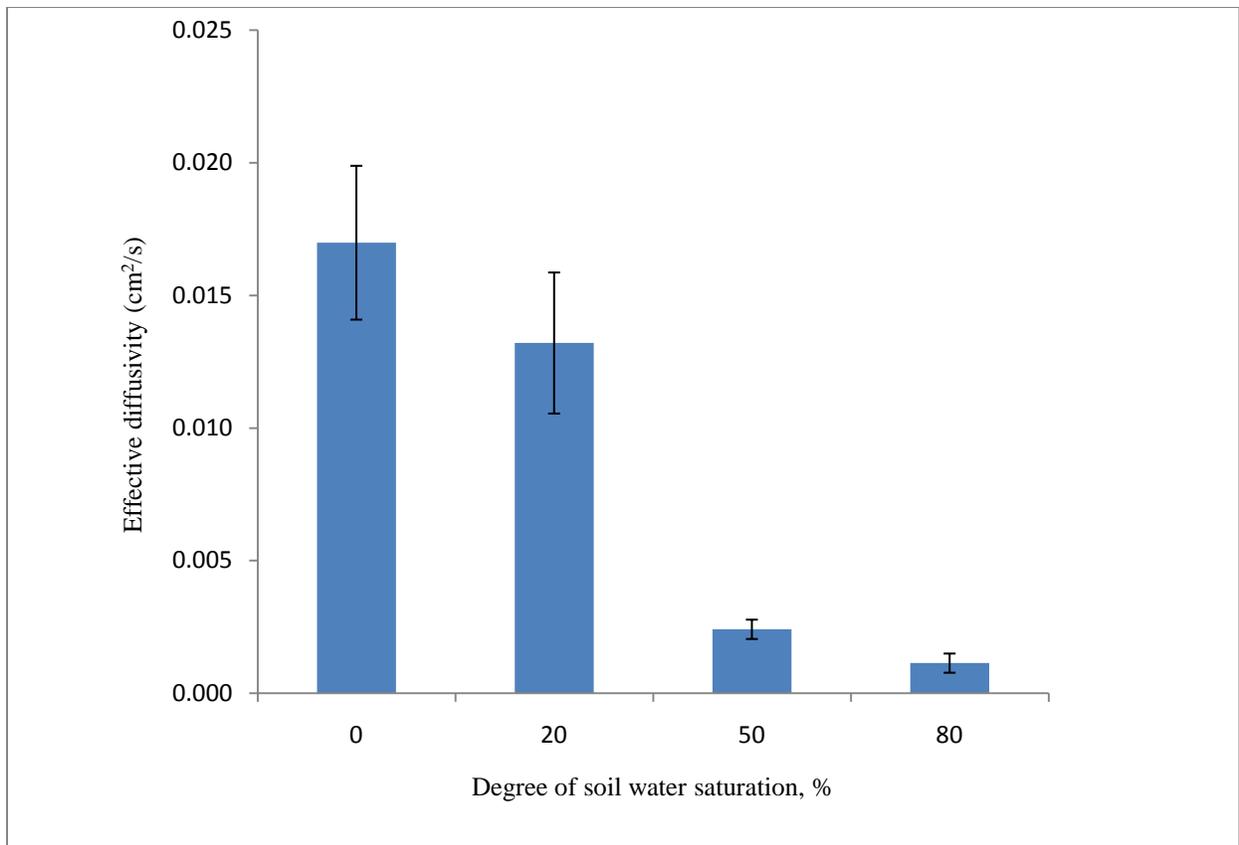


Figure 4.3 Effective MTBE diffusivity and its variation with different degrees of saturation (more detail in Tables 3.1 and B1).

## 4.2 INFLUENCE OF PARTICLE SIZE DISTRIBUTION ON MTBE GAS PHASE EFFECTIVE DIFFUSIVITY

Figures 4.4 and 4.5 show MTBE concentrations versus time at various clay contents of soil. Concentration profiles started to rise sharply during the initial hours of the test. MTBE concentrations in the gas phase varied from 575 to 623 ppm and from 70 to 87 ppm at 50 and 100 mm above the screen, for different clay contents of soil. Equilibrium was achieved after 5 to 15 hours, depending on the soil clay content, with concentrations remaining constant after this time. Effective diffusivity values calculated as explained in Section 4.1 are presented in Table 4.2. Figure 4.6 shows effective diffusivities of MTBE at various soil clay contents. Diffusivities varied from 0.014 to 0.018 cm<sup>2</sup>/s.

A slight reduction in concentration appeared to be caused by an increment in clay content of the soil. The effect of particle size distribution was not as significant as that of water content since it does not change the air filled porosity of soil significantly. This finding supports the results of Wang *et al.* (2002).

The most significant effect of soil particle size distribution was on the time to reach equilibrium. However, for soil samples were at the same porosity, samples with greater clay content required more time before establishment of steady state conditions.

The greater portion of finer aggregates, the more tortuous is the soil (Figure 4.7). The finer particles reduce straight path lines and cause greater tortuosity. Furthermore, finer aggregates clog more soil pores in comparison with coarser soil particles, cutting connectivity of pores. This leads to reduction of available diffusion pathways for MTBE migration.

Soil particle size varies from less than 0.002 mm for clay to 2-75 mm for gravel in real soil samples. Different regions have different distributions of particle size. Based on our studies, particle size distribution does not have a significant effect on diffusion flux when there is a continuous source of MTBE release to the soil. This situation can occur in practice when there is continuous leakage from an underground storage tank or an underground pipeline.

Our study also demonstrated that longer time is needed to reach equilibrium for finer soils regarding MTBE diffusion. This means at first stage of gas phase diffusion after release of MTBE in soil, it migrates faster in coarser aggregate soils. Hence, regions with coarser aggregates surrounding a contaminated site are at greater risk of exposure.

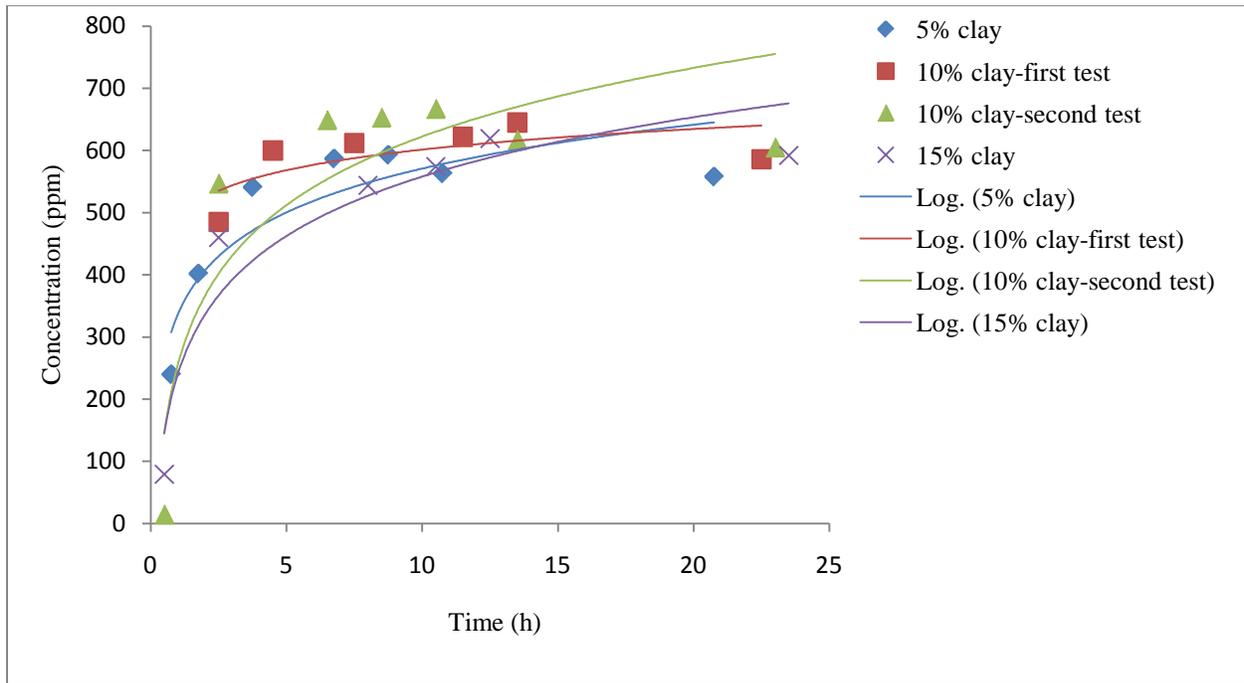


Figure 4.4 MTBE concentration in gas phase versus time at various clay contents of soil at 50 mm above the screen (more detail in Tables 3.1 and B1).

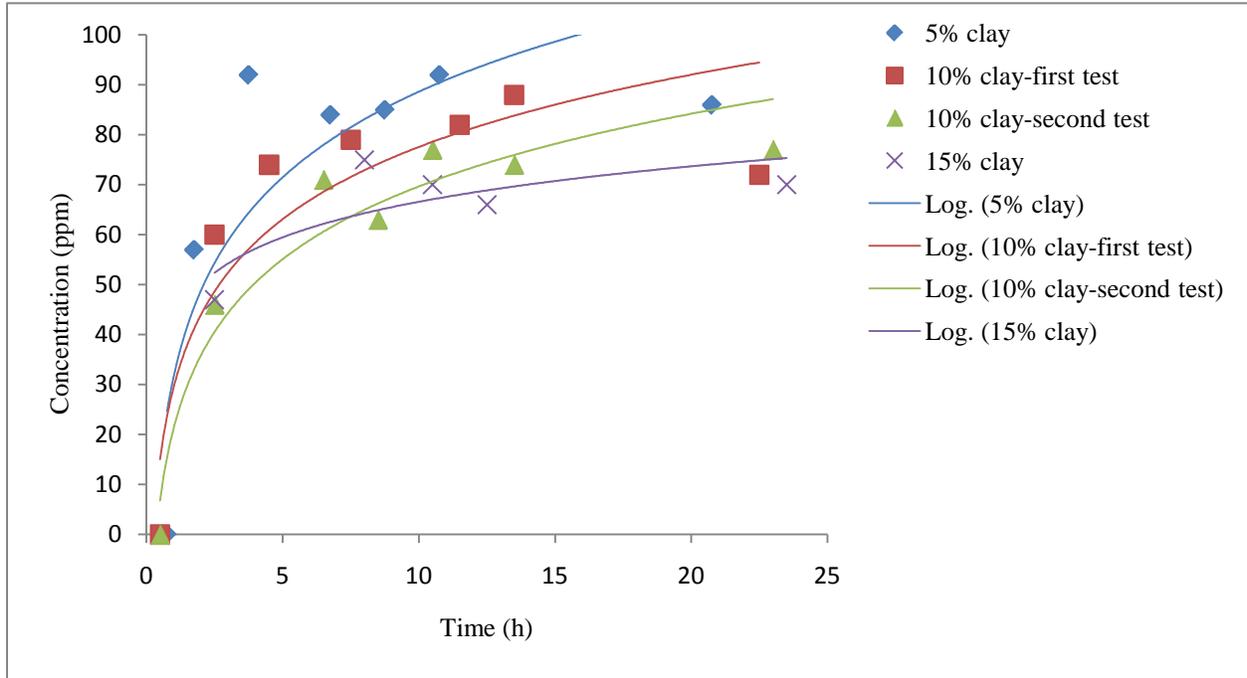


Figure 4.5 MTBE concentration in gas phase versus time at various clay contents of soil at 100 mm above the screen (more detail in Tables 3.1 and B1).

Table 4.2 Conditions and results of diffusion experiments showing influence of particle size distribution. (All tests were at 0% degree of saturation and a nitrogen head space flow rate of 100 mL/min).

| Clay content (%) | run no. | Soil height (mm) | Concentration ( $\mu\text{g/mL}$ ) |    | Effective diffusivity ( $\text{cm}^2/\text{s}$ ) |       |
|------------------|---------|------------------|------------------------------------|----|--|-------|
|                  |         |                  | av                                 | SD | av   | SD    |
| 5                | 6       | 50               | 575                                | 17 | 0.017  | 0.000 |
|                  | 6       | 50               | 575                                | 17 | 0.019  |       |
|                  | 6       | 100              | 88                                 | 4  | 0.018  |       |
|                  | Average |                  |                                    |    | 0.018  |       |
| 10               | 7       | 50               | 613                                | 22 | 0.018  | 0.001 |
|                  | 7       | 50               | 613                                | 22 | 0.016  |       |
|                  | 7       | 100              | 79                                 | 6  | 0.017  |       |
|                  | 8       | 50               | 623                                | 44 | 0.014  |       |
|                  | 8       | 50               | 623                                | 44 | 0.014  |       |
|                  | 8       | 100              | 72                                 | 6  | 0.014  |       |
|                  | Average |                  |                                    |    | 0.015  |       |
| 15               | 9       | 50               | 595                                | 18 | 0.015  | 0.000 |
|                  | 9       | 50               | 595                                | 18 | 0.014  |       |
|                  | 9       | 100              | 70                                 | 4  | 0.014  |       |
|                  | Average |                  |                                    |    | 0.014  |       |

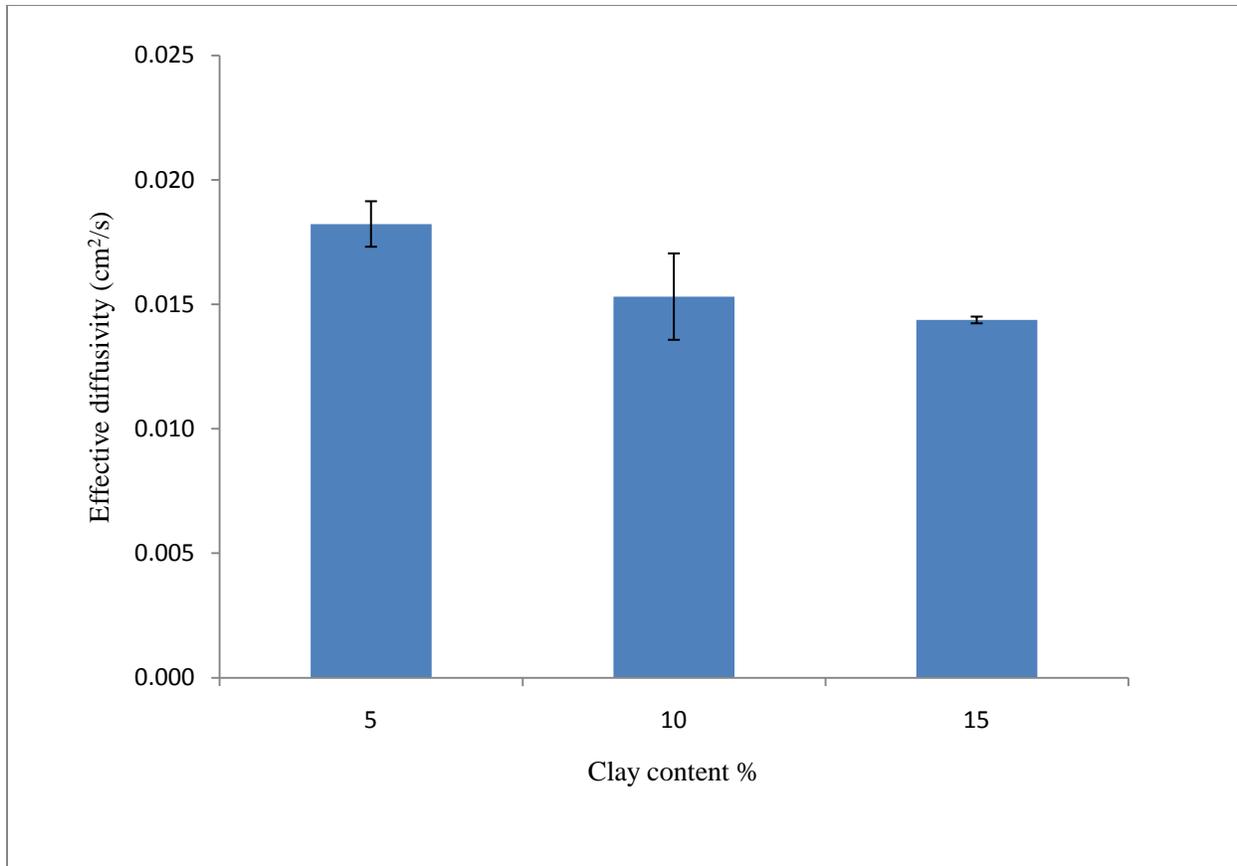


Figure 4.6 Effective MTBE diffusivity and its variation with different clay contents of soil (more detail in Tables 3.1 and B1).

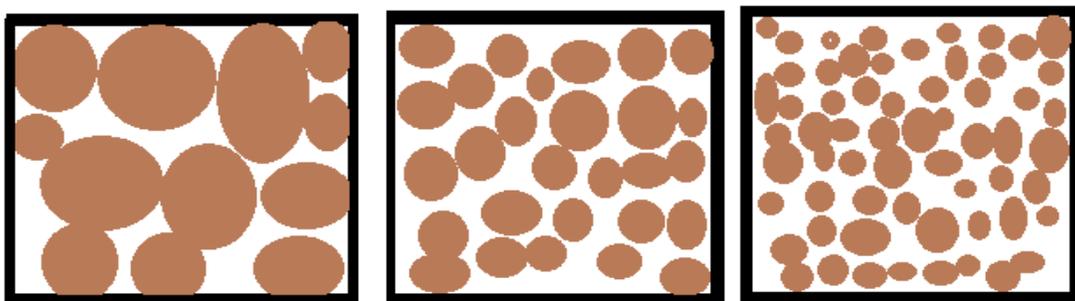


Figure 4.7 Schematic showing soil tortuosity changes due to smaller particles.

### **4.3 INFLUENCE OF ORGANIC CARBON CONTENT ON MTBE GAS PHASE EFFECTIVE DIFFUSIVITY**

Figures 4.8 and 4.9 present MTBE concentrations versus time at 50 and 100mm above the screen. The concentrations in soil gas started to rise sharply during the first hours of the test and appeared to reach steady state after 8 to 15 hours. The concentrations remained constant after this time. Increasing the soil organic content did not affect the MTBE concentration profile significantly along the soil column after equilibrium was achieved. MTBE concentrations were in the range of 600 to 657 ppm at 50 mm and 61 to 78 ppm at 100 mm above the screen at different organic carbon contents. Effective diffusivities calculated as explained in Section 4.1 are presented in Table 4.3. Figure 4.10 shows effective diffusivities of MTBE at various peat contents of the soil. Diffusivities varied from 0.014 to 0.012 cm<sup>2</sup>/s.

Increasing the carbon content of soil mainly influenced MTBE concentration profile in the initial hours of the test before equilibrium was reached. The higher the organic content of the soil, the longer the time needed to achieve equilibrium. It is clear that organic carbon content of the soil attenuated the vertical transport of MTBE through the soil column.

Organic carbon content of soil acts as a sorbent, adsorbing MTBE during the first hours of tests. (Before equilibrium is reached). This effect is later eliminated since adsorption of MTBE by organic matter of soil reduces with time (Figure 4.11). Water content of soil has the capacity to dissolve MTBE. This dissolution can be a reason for attenuation of MTBE migration. This effect also will be eliminated since soil water content become saturated with MTBE and cannot absorb more. Changing the particle size distribution of the soil by adding more peat also can be a reason for reduction in diffusivities.

High capacity of soil organic matters (as also found in previous studies, e.g. That of Batterman *et al.*, (1995); Michael and Bixler, (1961); Del Nobile *et al.*, (1995)) reduces risk of MTBE exposure in regions that have soils of high organic content. In contrast, people living in regions where soil contains less organic matter are at greater risk of exposure from a contaminated site. Furthermore, the capacity of organic content of soil adsorbing MTBE can be used for design of liners and barriers for waste pounds which contain MTBE, landfills and hazardous waste dumps. Definitely, more research is needed in this area to discover the feasibility of using organic matter as a component of these barriers.

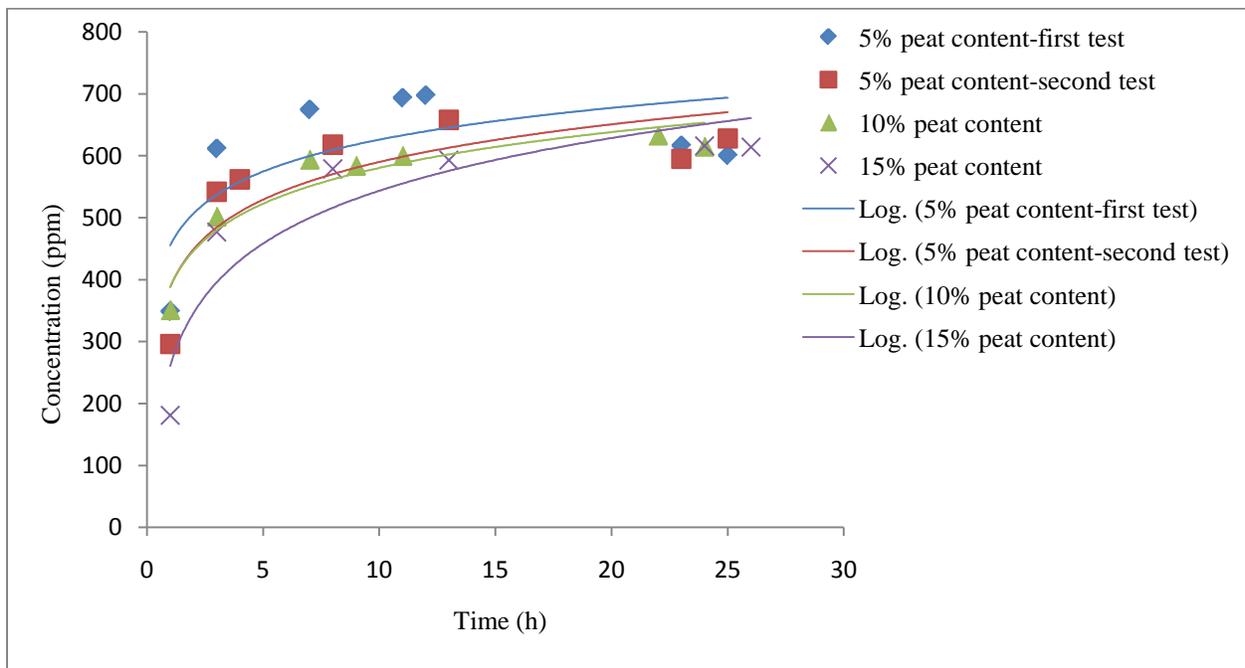


Figure 4.8 MTBE concentration in gas phase versus time at various organic contents of soil at 50 mm above the screen (more detail in Tables 3.1 and B1).

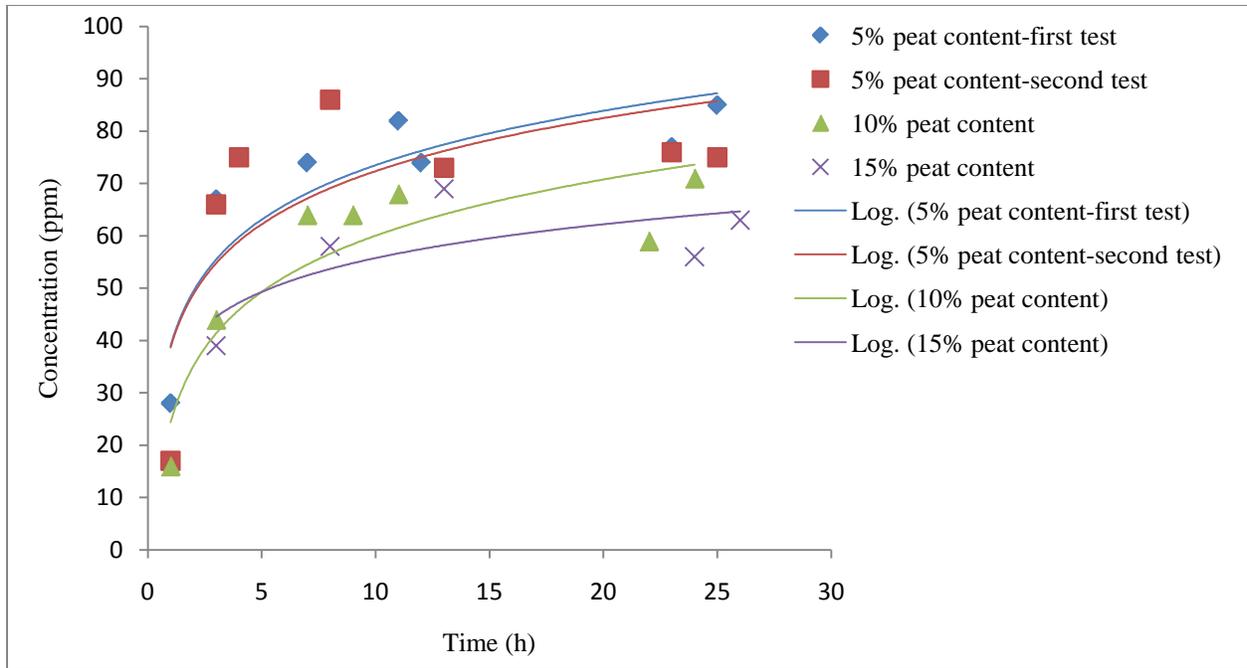


Figure 4.9 MTBE concentration in gas phase versus time at various organic contents of soil at 100 mm above the screen (more detail in Tables 3.1 and B1).

Table 4.3 Conditions and results of diffusion experiments showing influence of organic carbon content. (All tests were at 20% degree of saturation and a nitrogen head space flow rate of 100 mL/min).

| Peat content (%) | run no. | Soil height (mm) | Concentration ( $\mu\text{g/mL}$ ) |    | Effective diffusivity ( $\text{cm}^2/\text{s}$ ) |       |
|------------------|---------|------------------|------------------------------------|----|--|-------|
|                  |         |                  | av                                 | SD | av   | SD    |
| 5                | 10      | 50               | 657                                | 45 | 0.013  | 0.001 |
|                  | 10      | 50               | 657                                | 45 | 0.014  |       |
|                  | 10      | 100              | 78                                 | 5  | 0.014  |       |
|                  | 11      | 50               | 625                                | 26 | 0.015  |       |
|                  | 11      | 50               | 625                                | 26 | 0.015  |       |
|                  | 11      | 100              | 78                                 | 6  | 0.015  |       |
|                  | Average |                  |                                    |    |  |       |
| 10               | 12      | 50               | 605                                | 19 | 0.012  | 0.000 |
|                  | 12      | 50               | 605                                | 19 | 0.013  |       |
|                  | 12      | 100              | 65                                 | 5  | 0.012  |       |
|                  | Average |                  |                                    |    |  |       |
| 15               | 13      | 50               | 601                                | 15 | 0.011  | 0.000 |
|                  | 13      | 50               | 601                                | 15 | 0.012  |       |
|                  | 13      | 100              | 62                                 | 6  | 0.012  |       |
|                  | Average |                  |                                    |    |  |       |

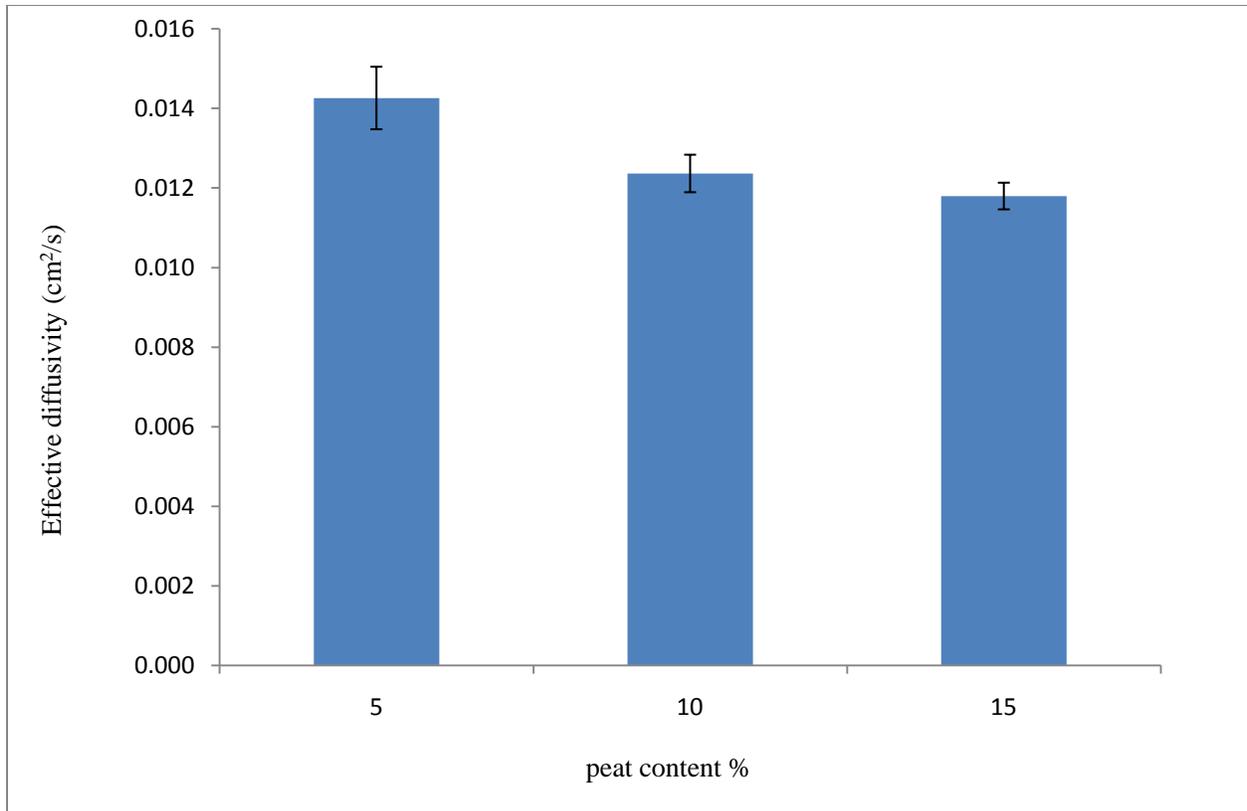


Figure 4.10 Effective MTBE diffusivity and its variation with different organic contents of the soil (more detail in Tables 3.1 and B1).

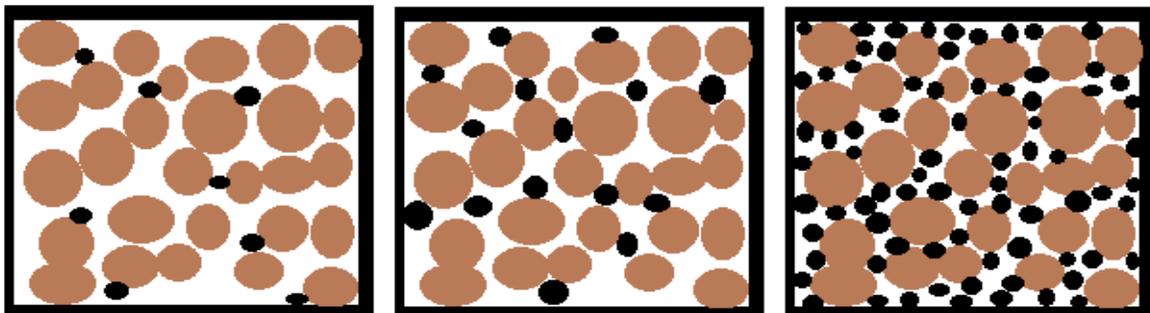


Figure 4.11 Schematic of organic matter in soil structure. (Brown ones are minerals and black ones represent organic matters).

## 4.4 COMPARISON OF RESULTS WITH THOSE OF PREVIOUS STUDIES

As mentioned in Section 2.1.3, a number of previous empirical equations have been developed for determination of effective diffusivity (see Table 2.2). These equations present the ratio of soil effective diffusivity to molecular diffusivity of compounds as a function of air-filled and total porosity of soil. Figure 4.12 shows the results of MTBE effective diffusivity along with some of these previous empirical equations. Table 4.4 also shows the calculation of effective diffusivities. Our results were in a good agreement with previous findings that a significant reduction in diffusivities occurred due to increment of degree of saturation.

Table 4.4 MTBE effective diffusivities calculated from empirical equations in the literature (assuming 1 cm<sup>3</sup> total volume of soil, 0.383 total porosity of soil and 0.09 cm<sup>2</sup>/s molecular diffusivity of MTBE).

| Deg. of sat. % | V <sub>A</sub> (cm <sup>3</sup> ) | V <sub>w</sub> (cm <sup>3</sup> ) | n <sub>c</sub> | n <sub>w</sub> | Penman<br>(1940)                      | Millington<br>(1959)                  | Marshal<br>(1959)                     | M-Q <sup>a</sup><br>(1960)            | M-Q <sup>a</sup><br>(1961)            | P-M-Q <sup>b</sup><br>(1997)          |
|----------------|-----------------------------------|-----------------------------------|----------------|----------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
|                |                                   |                                   |                |                | D <sub>eff</sub> (cm <sup>2</sup> /s) |
| 0              | 0.383                             | 0.000                             | 0.383          | 0.000          | 0.022                                 | 0.024                                 | 0.020                                 | 0.024                                 | 0.024                                 | 0.022                                 |
| 2              | 0.375                             | 0.008                             | 0.375          | 0.008          | 0.021                                 | 0.023                                 | 0.020                                 | 0.023                                 | 0.022                                 | 0.021                                 |
| 4              | 0.368                             | 0.015                             | 0.368          | 0.015          | 0.021                                 | 0.022                                 | 0.019                                 | 0.022                                 | 0.021                                 | 0.020                                 |
| 6              | 0.360                             | 0.023                             | 0.360          | 0.023          | 0.020                                 | 0.022                                 | 0.018                                 | 0.021                                 | 0.019                                 | 0.019                                 |
| 8              | 0.352                             | 0.031                             | 0.352          | 0.031          | 0.020                                 | 0.021                                 | 0.018                                 | 0.020                                 | 0.018                                 | 0.018                                 |
| 10             | 0.345                             | 0.038                             | 0.345          | 0.038          | 0.019                                 | 0.021                                 | 0.017                                 | 0.019                                 | 0.017                                 | 0.017                                 |
| 12             | 0.337                             | 0.046                             | 0.337          | 0.046          | 0.019                                 | 0.020                                 | 0.017                                 | 0.018                                 | 0.015                                 | 0.017                                 |
| 14             | 0.329                             | 0.054                             | 0.329          | 0.054          | 0.019                                 | 0.019                                 | 0.016                                 | 0.018                                 | 0.014                                 | 0.016                                 |
| 16             | 0.322                             | 0.061                             | 0.322          | 0.061          | 0.018                                 | 0.019                                 | 0.016                                 | 0.017                                 | 0.013                                 | 0.015                                 |
| 18             | 0.314                             | 0.069                             | 0.314          | 0.069          | 0.018                                 | 0.018                                 | 0.015                                 | 0.016                                 | 0.012                                 | 0.014                                 |
| 20             | 0.306                             | 0.077                             | 0.306          | 0.077          | 0.017                                 | 0.018                                 | 0.014                                 | 0.015                                 | 0.011                                 | 0.014                                 |
| 22             | 0.299                             | 0.084                             | 0.299          | 0.084          | 0.017                                 | 0.017                                 | 0.014                                 | 0.014                                 | 0.010                                 | 0.013                                 |
| 24             | 0.291                             | 0.092                             | 0.291          | 0.092          | 0.016                                 | 0.016                                 | 0.013                                 | 0.014                                 | 0.010                                 | 0.012                                 |
| 26             | 0.283                             | 0.100                             | 0.283          | 0.100          | 0.016                                 | 0.016                                 | 0.013                                 | 0.013                                 | 0.009                                 | 0.012                                 |
| 28             | 0.276                             | 0.107                             | 0.276          | 0.107          | 0.016                                 | 0.015                                 | 0.012                                 | 0.012                                 | 0.008                                 | 0.011                                 |
| 30             | 0.268                             | 0.115                             | 0.268          | 0.115          | 0.015                                 | 0.015                                 | 0.012                                 | 0.012                                 | 0.007                                 | 0.011                                 |
| 32             | 0.260                             | 0.123                             | 0.260          | 0.123          | 0.015                                 | 0.014                                 | 0.011                                 | 0.011                                 | 0.007                                 | 0.010                                 |
| 34             | 0.253                             | 0.130                             | 0.253          | 0.130          | 0.014                                 | 0.014                                 | 0.011                                 | 0.010                                 | 0.006                                 | 0.009                                 |

|     |       |       |       |       |       |       |       |       |       |       |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 36  | 0.245 | 0.138 | 0.245 | 0.138 | 0.014 | 0.013 | 0.010 | 0.010 | 0.005 | 0.009 |
| 38  | 0.237 | 0.146 | 0.237 | 0.146 | 0.013 | 0.013 | 0.010 | 0.009 | 0.005 | 0.008 |
| 40  | 0.230 | 0.153 | 0.230 | 0.153 | 0.013 | 0.012 | 0.009 | 0.009 | 0.004 | 0.008 |
| 42  | 0.222 | 0.161 | 0.222 | 0.161 | 0.013 | 0.011 | 0.009 | 0.008 | 0.004 | 0.007 |
| 44  | 0.214 | 0.169 | 0.214 | 0.169 | 0.012 | 0.011 | 0.008 | 0.007 | 0.003 | 0.007 |
| 46  | 0.207 | 0.176 | 0.207 | 0.176 | 0.012 | 0.010 | 0.008 | 0.007 | 0.003 | 0.006 |
| 48  | 0.199 | 0.184 | 0.199 | 0.184 | 0.011 | 0.010 | 0.008 | 0.006 | 0.003 | 0.006 |
| 50  | 0.192 | 0.192 | 0.192 | 0.192 | 0.011 | 0.009 | 0.007 | 0.006 | 0.002 | 0.005 |
| 52  | 0.184 | 0.199 | 0.184 | 0.199 | 0.010 | 0.009 | 0.007 | 0.005 | 0.002 | 0.005 |
| 54  | 0.176 | 0.207 | 0.176 | 0.207 | 0.010 | 0.008 | 0.006 | 0.005 | 0.002 | 0.005 |
| 55  | 0.172 | 0.211 | 0.172 | 0.211 | 0.010 | 0.008 | 0.006 | 0.005 | 0.002 | 0.004 |
| 56  | 0.169 | 0.214 | 0.169 | 0.214 | 0.009 | 0.008 | 0.006 | 0.005 | 0.002 | 0.004 |
| 58  | 0.161 | 0.222 | 0.161 | 0.222 | 0.009 | 0.007 | 0.006 | 0.004 | 0.001 | 0.004 |
| 60  | 0.153 | 0.230 | 0.153 | 0.230 | 0.009 | 0.007 | 0.005 | 0.004 | 0.001 | 0.003 |
| 62  | 0.146 | 0.237 | 0.146 | 0.237 | 0.008 | 0.007 | 0.005 | 0.003 | 0.001 | 0.003 |
| 64  | 0.138 | 0.245 | 0.138 | 0.245 | 0.008 | 0.006 | 0.004 | 0.003 | 0.001 | 0.003 |
| 66  | 0.130 | 0.253 | 0.130 | 0.253 | 0.007 | 0.006 | 0.004 | 0.003 | 0.001 | 0.002 |
| 68  | 0.123 | 0.260 | 0.123 | 0.260 | 0.007 | 0.005 | 0.004 | 0.002 | 0.001 | 0.002 |
| 70  | 0.115 | 0.268 | 0.115 | 0.268 | 0.006 | 0.005 | 0.003 | 0.002 | 0.000 | 0.002 |
| 72  | 0.107 | 0.276 | 0.107 | 0.276 | 0.006 | 0.004 | 0.003 | 0.002 | 0.000 | 0.002 |
| 74  | 0.100 | 0.283 | 0.100 | 0.283 | 0.006 | 0.004 | 0.003 | 0.002 | 0.000 | 0.001 |
| 76  | 0.092 | 0.291 | 0.092 | 0.291 | 0.005 | 0.004 | 0.002 | 0.001 | 0.000 | 0.001 |
| 78  | 0.084 | 0.299 | 0.084 | 0.299 | 0.005 | 0.003 | 0.002 | 0.001 | 0.000 | 0.001 |
| 80  | 0.077 | 0.306 | 0.077 | 0.306 | 0.004 | 0.003 | 0.002 | 0.001 | 0.000 | 0.001 |
| 82  | 0.069 | 0.314 | 0.069 | 0.314 | 0.004 | 0.002 | 0.002 | 0.001 | 0.000 | 0.001 |
| 84  | 0.061 | 0.322 | 0.061 | 0.322 | 0.003 | 0.002 | 0.001 | 0.001 | 0.000 | 0.001 |
| 86  | 0.054 | 0.329 | 0.054 | 0.329 | 0.003 | 0.002 | 0.001 | 0.000 | 0.000 | 0.000 |
| 88  | 0.046 | 0.337 | 0.046 | 0.337 | 0.003 | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 |
| 90  | 0.038 | 0.345 | 0.038 | 0.345 | 0.002 | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 |
| 92  | 0.031 | 0.352 | 0.031 | 0.352 | 0.002 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 |
| 94  | 0.023 | 0.360 | 0.023 | 0.360 | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 |
| 96  | 0.015 | 0.368 | 0.015 | 0.368 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 98  | 0.008 | 0.375 | 0.008 | 0.375 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 100 | 0.000 | 0.383 | 0.000 | 0.383 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |

<sup>a</sup> Millington-Quirk.

<sup>b</sup> Penman-Millington-Quirk.

$D_{eff}$  is the effective diffusivity,  $n_G$  is the gas-filled porosity,  $n_W$  is the water filled porosity,  $V_A$  is the volume of air, and  $V_W$  is the volume of water.

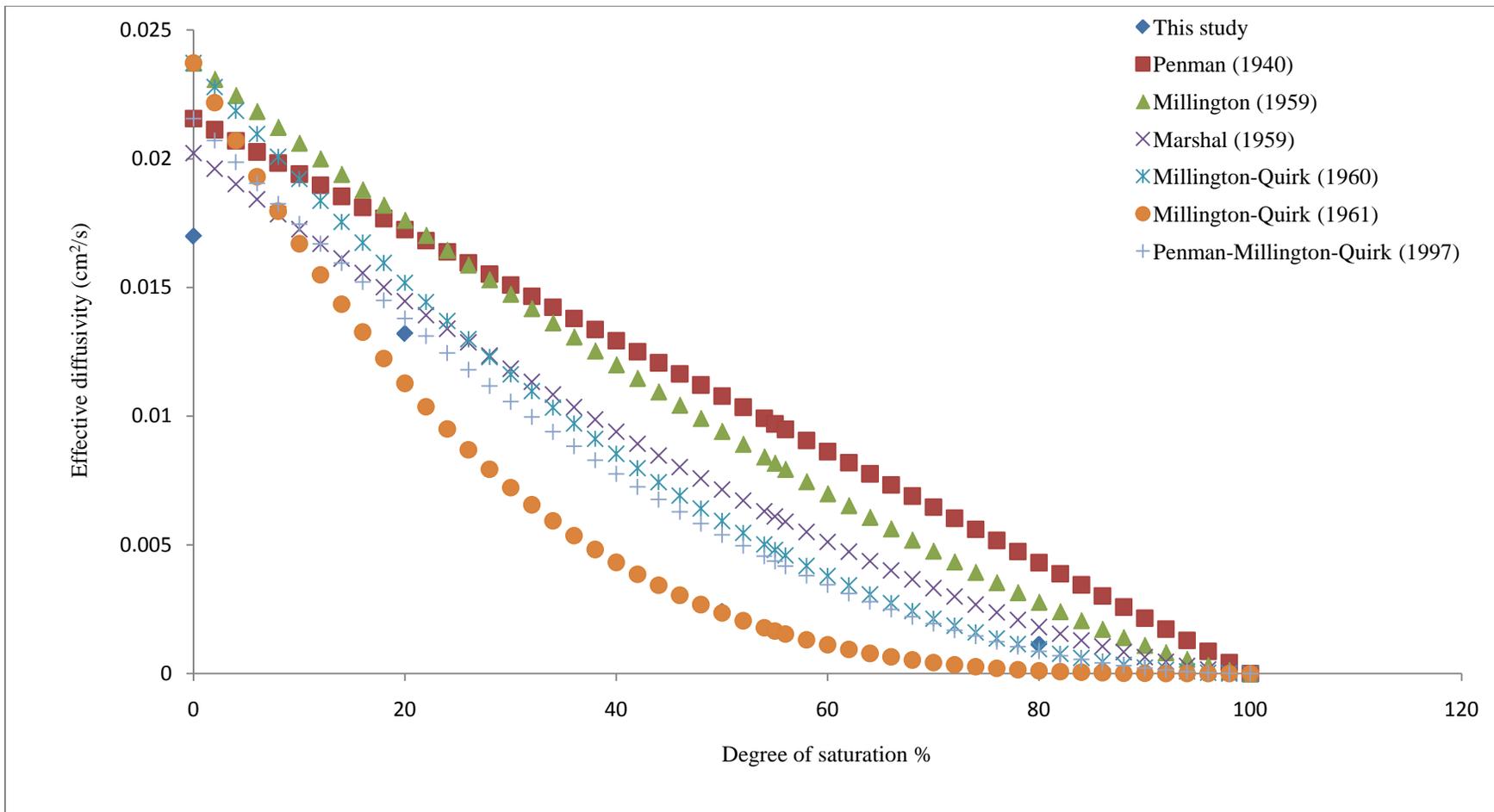


Figure 4.12 Results of MTBE effective diffusivity versus soil degree of saturation compared with predictions from some previous empirical equations.

The effect of particle size distribution of soil on effective diffusivity has not been studied systematically in previous works. Different soils were studied and tested for gas phase diffusivity. Figure 4.13 shows the calculated diffusivities versus average particle size of soil from our experiments along with some previous studies.

In our studies, it has been demonstrated that particle size distribution does not have a significant effect on MTBE effective diffusivity. This supports the results of Wang *et al.* (2002) on toluene, where toluene gas phase diffusivity did not show a meaningful change in coarse and fine sand for the same degree of water saturation. Based on literature review, in other previous gas phase diffusion studies, no other results (other than those of Wang *et al.*, (2002)) with different soil particle size distributions and other similar condition (VOC type, degree of saturation, etc) was found with which to compare our findings.

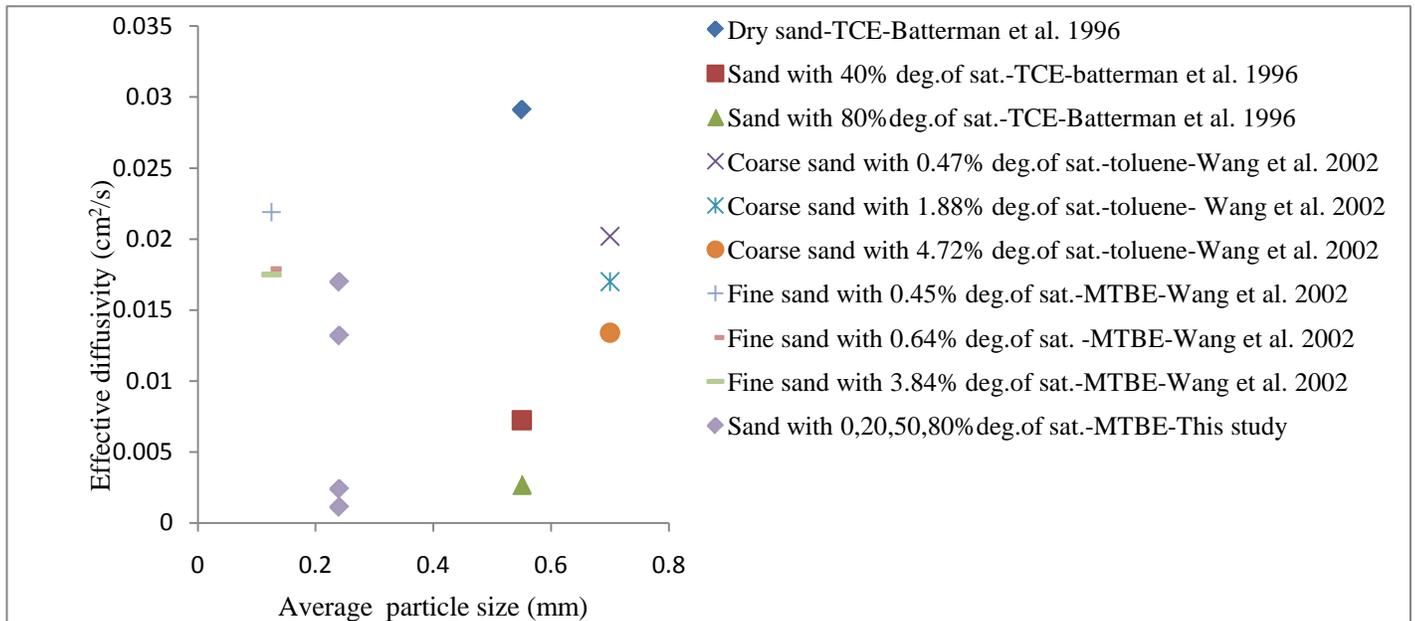


Figure 4.13 Effective diffusivity of TCE, toluene and MTBE in sands of different grain size and water contents based on this study and previous studies

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 CONCLUSIONS

This work developed a practical apparatus and method for determination of VOCs effective gas phase diffusivity in soil. Then experiments were conducted to discover the influence of soil degree of saturation, particle size distribution and organic carbon content on MTBE gas phase diffusion in soil.

The modified reservoir-based one-flow diffusivity apparatus performed well during the experiments. The system for adjustment of nitrogen relative humidity had the capability of providing an appropriate mixture of dry and saturated nitrogen, depending on the soil degree of saturation. Pressure transducers guided the relative flow rates to prevent vertical advection through the column. Load cell results allowed the MTBE mass fluxes to be compared with those calculated based on nitrogen flow rates and MTBE mass concentrations at the top. Having three sections of column body made it possible to compact the soil samples without disassembling the whole apparatus.

Water content of soil showed a major effect, with more water content resulting in lower MTBE diffusive flux through soil. (The effective diffusivities decreased from 0.02 to 0.001  $\text{cm}^2/\text{s}$  when degree of saturation increased from 0 to 80%). This means that variation in the soil

degree of saturation due to seasonal changes in precipitation, transpiration and temperature in the environment are likely to drastically influence MTBE migration in soil.

Particle size distribution did not seem to have a major effect on MTBE diffusive flux in soil at steady state conditions for the range of conditions studied; however it can considerably change the time needed to reach equilibrium. (Effective diffusivities decreased from 0.018 to 0.014  $\text{cm}^2/\text{s}$  when the clay content of soil increased from 0 to 15%). This suggests that regions with coarse soil aggregates, such as sand and gravel, tend to have more rapid MTBE diffusive movement.

Organic content of soil showed a high capacity to absorb MTBE. Adsorption of MTBE into organic content of soil attenuates its migration. This means MTBE migrates more slowly in regions containing soils with higher organic contents until saturation occurs.

## 5.2 RECOMMENDATIONS FOR FUTURE STUDIES

Below are some recommendations for future studies in this area,

- Improving the experimental system (longer column length, more sampling ports along the column, etc) for better estimation of diffusivity under transient conditions.
- Curve-fitting transient data of this study to Fick's second law of diffusion and comparing diffusivity with steady state values.
- Modeling the experimental system with a transient diffusion model and solving it numerically (by finite-difference or finite-element methods).
- Developing a model for VOCs migration and fate prediction with consideration of advection, sorption and bio-degradation.
- Using the apparatus to determine effective diffusivities for gases other than MTBE, including other VOCs, CO<sub>2</sub>, O<sub>2</sub>, etc.

## REFERENCES

- Agency for Toxic Substances and Disease Registry. (1997). "Toxicological profile for trichloroethylene (update)." U.S. Department of Health and Human Services Public Health Service, U.S.
- Arocha, M. A., Jackman, A. P., and McCoy, B. J. (1996). "Adsorption kinetics of toluene on soil agglomerates: soil as a biporous sorbent." *Environ.Sci.Technol.*, 30(5), 1500-1507.
- Baehr, A. L., and Bruell, C. J. (1990). "Application of the Stefan–Maxwell equations to determine limitations of Fick’s law when modeling organic vapor transport in sand columns." *Water Resour. Res.*, 26 1155-1163.
- Bartelt-Hunt, S., and Smith, J. A. (2002). "Measurement of effective air diffusion coefficients for trichloroethene in undisturbed soil cores." *J. Contam. Hydrol.*, 56(3), 193-208.
- Batterman, S., Kulshrestha, A., and Cheng, H. (1995). "Hydrocarbon vapor transport in low moisture soils." *Environ.Sci.Technol.*, 29(1), 171-180.
- Batterman, S., Padmanabham, I., and Milne, P. (1996). "Effective gas-phase diffusion coefficients in soils at varying water content measured using a one-flow sorbent-based technique." *Environ.Sci.Technol.*, 30(3), 770-778.
- Bird, R. B. (2002). "Transport phenomena." *Appl.Mech.Rev.*, 55(1), R1-4.
- Braida, W., and Ong, S. K. (2000). "Modeling of air sparging of VOC-contaminated soil columns." *J.Contam.Hydrol.*, 41(3-4), 385-402.
- Cabbar, C. (1999). "Effects of humidity and soil organic matter on the sorption of chlorinated methanes in synthetic humic-clay complexes." *J. Hazard. Mater.*, 68(3), 217-226.
- Cabbar, C., Dogu, G., Dogu, T., McCoy, B. J., and Smith, J. M. (1994). "Analysis of diffusion and sorption of chlorinated hydrocarbons in soil by single-pellet moment technique." *Environ.Sci.Technol.*, 28(7), 1312-1319.
- Campagnolo, J. F., and Akgerman, A. (1994). "Investigation of normal hexane and nitrogen adsorption onto soil constituents and constituent mixtures." *J. Hazard. Mater.*, 37(3), 415-430.
- Carslaw, H. S., and Jaeger, J. C. (1948). *Conduction of heat in solids*. Oxford University Press, England.
- Chang, M., Wu, S., and Chen, C. (1997). "Diffusion of volatile organic compounds in pressed humic acid disks." *Environ.Sci.Technol.*, 31(8), 2307-2312.

Chiou, C. T., Lee, J. F., and Boyd, S. A. (1990). "The surface area of soil organic matter." *Environ.Sci.Technol.*, 24(8), 1164-1166.

Chiou, C. T., and Shoup, T. D. (1985). "Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity." *Environ.Sci.Technol.*, 19(12), 1196-1200.

Conklin, M. H., Corley, T. L., Roberts, P. A., Davis, J. H., and Van, D. W. (1995). "Nonequilibrium processes affecting forced ventilation of benzene and xylene in a desert soil." *Water Resour.Res.*, 31(5), 1355-1365.

De Vries, D. A. (1952). "A nonstationary method for determining thermal conductivity of soil in situ." *Soil Science*, 73(2), 83-90.

Del Nobile, M. A., Mensitieri, G., Nicolais, L., and Weiss, R. A. J. (1995). "Gas transport through ethylene-acrylic acid ionomers." *Journal of Polymer Science*, 33(8), 1269-1280.

Dogu, G., and Smith, J. M. (1976). "Rate parameters from dynamic experiments with single catalyst pellets." *Chemical Engineering Science*, 31(2), 123-135.

Gierke, J., Hutzler, N. J., and Crittenden, J. C. (1990). "Modeling the movement of volatile organic chemicals in columns of unsaturated soil." *Water Resources Research*, 26(7), 1529-1547.

Gierke, J. S., Hutzler, N. J., and McKenzie, D. B. (1992). "Vapor transport in unsaturated soil columns: Implications for vapor extraction." *Water Resour.Res.*, 28(2), 323-335.

Hers, I., Atwater, J., Li, L., and Zapf-Gilje, R. (2000). "Evaluation of vadose zone biodegradation of BTX vapours." *J. Contam. Hydrol.*, 46(3-4), 233-264.

Kalender, M., and Akosman, C. (2004). "Dynamic analysis of diffusion and adsorption of water-miscible and water-immiscible organic vapors in soil." *Chemical Engineering & Technology*, 27(4), 440-446.

Karickhoff, S. W. (1980). *Contaminants and sediments*. Ann Arbor Science, U.S.

Kleineidam, S., Rugner, H., Ligouis, B., and Grathwohl, P. (1999). "Organic matter facies and equilibrium sorption of phenanthrene." *Environ.Sci.Technol.*, 33(10), 1637-1644.

Lawrence, S. J. (2006). "Description, properties, and degradation of selected volatile organic compounds detected in ground Water - a review of selected literature." U. S. Geological Survey (USGS), U.S.

Leenheer, J. A., and Ahlrichs, J. L. (1971). "A kinetic and equilibrium study of the adsorption of carbaryl and parathion upon soil organic matter surfaces." *Soil Science Society of America Journal*, 35(5), 700-705.

Lin, T. F., Little, J. C., and Nazaroff, W. W. (1994). "Transport and sorption of volatile organic compounds and water vapor within dry soil grains." *Environ.Sci.Technol.*, 28(2), 322-330.

Lugg, G. A. (1968). "Diffusion coefficients of some organic and other vapors in air." *Anal.Chem.*, 40(7), 1072-1077.

Lyman, W. J., Reehl, W. F., and Rosenblatt, D. H. (1982). "Solubility in various solvents." *Handbook of chemical property estimation methods*, McGraw-Hill, U.S., .

Marshall, T. J. (1959). "The diffusion of gases through porous media." *J. Soil Sci.*, 10 79-82.

Mendell, M. J. (2007). "Indoor residential chemical emissions as risk factors for respiratory and allergic effects in children: a review." *Indoor Air*, 17 227-259.

Mendoza, C. A., Johnson, R. L., and Gillham, R. W. (1996). "Vapor migration in the vadose zone." *Dense chlorinated solvents and other DNAPLs in ground water: History, behavior, and remediation*. J. F. Pankow, and J. A. Cherry, eds., Waterloo Press, U.S., 179-201.

Michaels, A. S., and Bixler, H. J. (1961). "Solubility of gases in polyethylene." *Journal of Polymer Science*, 50(154), 393-412.

Millington, R. J. (1959). "Gas diffusion in porous media." *Science*, 130 100-102.

Millington, R. J., and Quirk, J. M. (1960). "Transport in porous media." 7th International Congress of Soil Science, SSSA, Madison, 97-106.

Millington, R. J., and Quirk, J. M. (1961). "Permeability of porous solid." *Trans. Faraday Soc.*, 57 1200-1207.

Minnesota department of health. (2005). "Drinking water standards for contaminants- volatile and synthetic organic chemicals." Rep. No. IC 141- 0795, Minnesota Department of Health, U.S.

Moldrup, P., Olesen, T., Rolston, D. E., and Yamaguchi, T. (1997). "Modeling diffusion and reaction in soil: predicting gas and ion diffusivity in undisturbed and sieved soil." *Soil Sci.*, 162 632-640.

Morrissey, F. A., and Grismer, M. E. (1999). "Kinetics of volatile organic compound sorption/desorption on clay minerals." *J. Contam. Hydrol.*, 36(3), 291-312.

Nazaroff, W. W. (1992). "Radon transport from soil to air." *Rev.Geophys.*, 30(2), 137-160.

Norback, D., Bjornsson, E., Janson, C., Widstrom, J., and Boman, G. (1995). "Asthmatic symptoms and volatile organic compounds, formaldehyde, and carbon dioxide in dwellings." *Occup. Environ. Med.*, 52(6), 388-395.

- Olson, D. A., and Corsi, R. L. (2001). "Characterizing exposure to chemicals from soil vapor intrusion using a two-compartment model." *Atmos. Environ.*, 35(24), 4201-4209.
- Ong, S. K., and Lion, L. W. (1989). "Trichloroethylene vapor sorption onto soil minerals." *Soil Science Society of America Journal*, 55(6), 1559-1568.
- Ong, S. K., Culver, T. B., Lion, L. W., and Shoemaker, C. A. (1992). "Effects of soil moisture and physical-chemical properties of organic pollutants on vapor-phase transport in the vadose zone." *J. Contam. Hydrol.*, 11(3), 273-290.
- Ostendorf, D. W., Moyer, E. E., X., Yuefeng, and Rajan, R. V. (1993). "Hydrocarbon vapor diffusion in intact core sleeves." *Ground Water Monitoring & Remediation*, 13(1), 139-150.
- Park, G. S., and Crank, J. (1968). *Diffusion in polymers*. Academic Press, England.
- Patwardhan, A. S., Nieber, J. L., and Moore, I. D. (1988). "Oxygen, carbon dioxide, and water transfer in soils: mechanisms and crop response." *American Society of Agricultural and Biological Engineers*, 31(5), 1383-1395.
- Peat, J. K., Dickerson, J., and Li, J. (1998). "Effects of damp and mould in the home on respiratory health: a review of the literature." *Allergy*, 53(2), 120-128.
- Penman, H. L. (1940). "Gas and vapor movement in the soil." *J. Agric. Sci.*, 30 437-462.
- Poulsen, T. G., Moldrup, P., Yamaguchi, T., Massmann, J. W., and Hansen, J. A. (1998). "VOC vapor sorption in soil: soil type dependent model and implications for vapor extraction." *Journal of Environmental Engineering*, 124(2), 146-155.
- Rathbun, R. E. (1997). *Transport, behavior, and fate of volatile organic compounds in streams*. Taylor & Francis, England.
- Rehfeldt, S., and Stichlmair, J. (2007). "Measurement and calculation of multicomponent diffusion coefficients in liquids." *Fluid Phase Equilib.*, 256(1), 99-104.
- Robinson, A. L., Sextro, R. G., and Fisk, W. J. (1997). "Soil-gas entry into an experimental basement driven by atmospheric pressure fluctuations- Measurements, spectral analysis, and model comparison." *Atmos. Environ.*, 31(10), 1477-1485.
- Ruiz, J., Bilbao, R., and Murillo, M. B. (1998). "Adsorption of different VOC onto soil minerals from gas phase: influence of mineral, type of VOC, and air humidity." *Environ.Sci.Technol.*, 32(8), 1079-1084.
- Ruthven, D. M. (1984). *Principles of adsorption and adsorption processes*. John Wiley & Sons, Inc., U. S.

Scanlon, B. R., Nicot, J. P., and Massmann, J. W. (2001). "Soil gas movement in unsaturated systems." *Soil physics companion*, A. W. Warrick, ed., CRC Press LLC, U.S., 297-341.

Schneider, N. S., Moseman, J. A., and Sung, N. H. (1994). "Toluene diffusion in butyl rubber." *Journal of Polymer Science*, 31(3), 491-499.

Sciences international, I. (1995). "Tetrachloroethylene, draft for public comment (update)." U.S. Department of Health and Human Services. Agency for Toxic Substances and Disease Registry, U.S.

Shonnard, D. R., Bell, R. L., and Jackman, A. P. (1993). "Effects of nonlinear sorption on the diffusion of benzene and dichloromethane from two air-dry soils." *Environ.Sci.Technol.*, 27(3), 457-466.

Silka, L. R. (1988). "Simulation of vapor transport through the unsaturated zone - interpretation of soil-gas surveys." *Ground Water Monitoring & Remediation*, 8(2), 115-123.

Squillace, P. J., Moran, M. J., Lapham, W. W., Price, C. V., Clawges, R. M., and Zogorski, J. S. (1999). "Volatile organic compounds in untreated ambient groundwater of the united states, 1985-1995." *Environ. Sci. Technol.*, 33 4176-4187.

Technology Planning and Management Corporation. (1998). "Report on carcinogens background document for methyl tertiary- butyl ether." Rep. No. NOI-ES-85421, U.S. Department of Health and Human Services Public Health Services, U.S.

Troeh, F. R., Jabro, J. D., and Kirkham, D. (1982). "Gaseous diffusion equations for porous materials." *Geoderma*, 27(3), 239-253.

United States Environmental Protection Agency. (2009). "National primary drinking water regulations." Rep. No. EPA 816-F-09-004, USEPA, U.S.

Voudrias, E. A., and Li, C. (1993). "Benzene vapor transport in unsaturated soil: Adequacy of the diffusion equation." *J. Hazard. Mater.*, 34(3), 295-311.

Wallace, L. A. (1987). "The total exposure assessment methodology (TEAM) study." Rep. No. EPA/600/6-87/002a, U.S. Environmental Protection Agency, U.S.

Wang, G., Reckhorn, S. B. F., and Grathwohl, P. (2003). "Volatile organic compounds volatilization from multicomponent organic liquids and diffusion in unsaturated porous media." *Vadose Zone Journal*, 2(4), 692-701.

Weaver, J. W. (2004). "On-line tools for assessing petroleum releases." Rep. No. EPA 600/R-04/101, Ecosystems Research Division National Exposure Research Laboratory, U.S.

Weaver, J. W., Skaggs Sheldon A., Spidle David L., and Stone Guthrie C. (2009). "Composition and behavior of fuel ethanol." Rep. No. EPA/600/R-09/037, Ecosystems Research Division National Exposure Research Laboratory- United States Environmental Protection Agency, U.S.

Wieslander, ,G., Norback, ,D., Bjornsson, ,E., Janson, ,C., and Boman, ,G. (1996). "Asthma and the indoor environment: the significance of emission of formaldehyde and volatile organic compounds from newly painted indoor surfaces." *Int. Arch. Occup. Environ. Health*, (2), 115-124.

World Health Organization. (1989). "Indoor air quality: organic pollutants." World Health Organization (WHO)- Regional Office for Europe, Denmark.

## Appendix A Flow meter calibration curves

Figure A.1 shows calibration curves for the flow meters. Different known air flow rates (by a digital flow meter-AMD 1000, Agilent Technology) passed through each flow meter and the values were read. The known flow rates (vertical axle) and flow meter readings (horizontal axle) were used to produce the calibration curve for each flow meter.

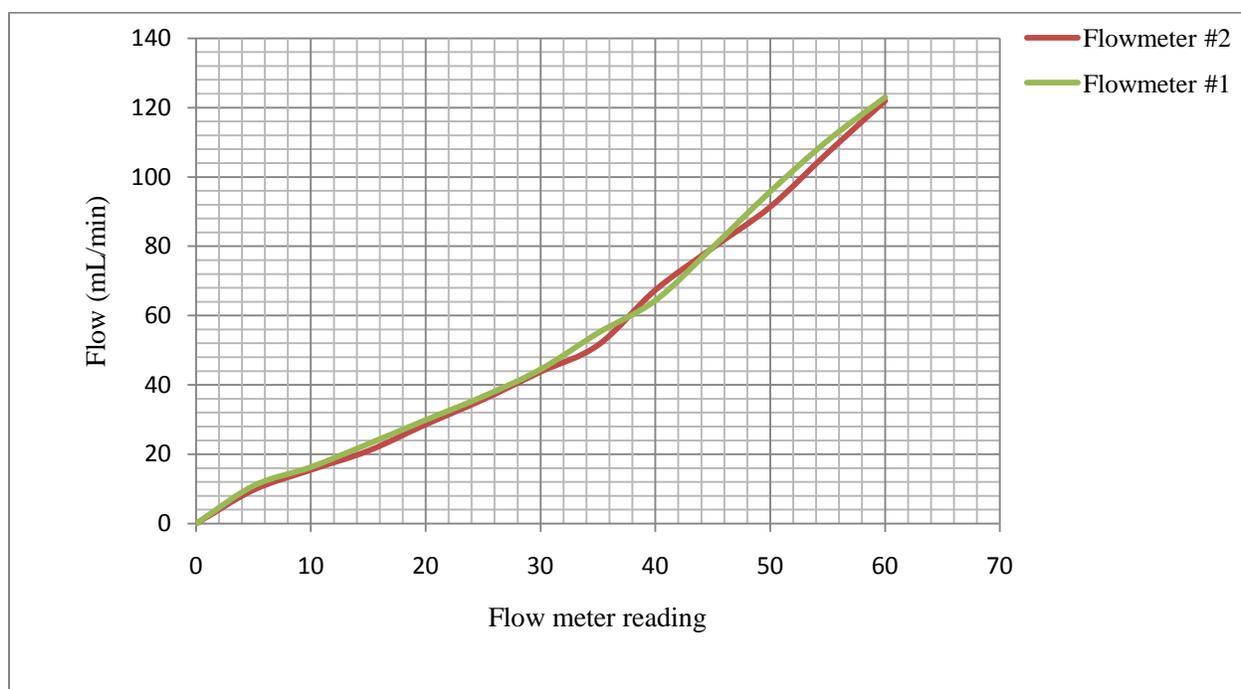


Figure A.1 Flow meter calibration curves.

## Appendix B Soil static compaction

Figure B.1 shows the compression unit used for soil samples static compaction. It basically is comprised of (1) a stationary rigid and heavy steel body attached to the work desk, (2) a vertically mobile and solid jaw and (3) a handle to move the jaw up and down to assign load to samples. It is completely manually operative and has a loading capacity up to 2000 kg.



Figure B.1 Compression unit for soil static compaction.

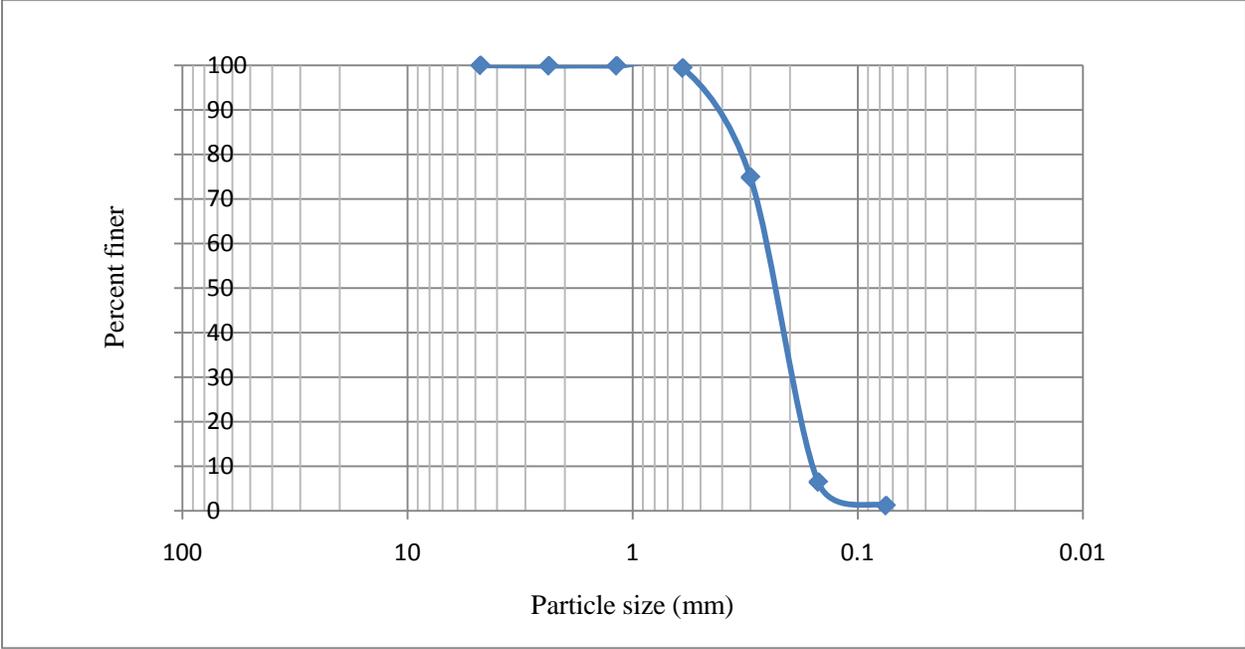
Soil samples were compacted in four layers in soil column. Vertical load was applying by a round stainless steel disk from the top to reach the desired volume. Table B.1 provides mass of soil components, water and porosity of samples after compaction.

Table B.1 Detailed information about soil samples.

| Run # | Sand mass (g) | Clay mass (g) | Peat mass (g) | Water mass (g) | Soil total porosity | Soil air-filled porosity |
|-------|---------------|---------------|---------------|----------------|---------------------|--------------------------|
| 1     | 1260          | 0             | 0             | 0              | 0.38                | 0.38                     |
| 2     | 1260          | 0             | 0             | 60             | 0.38                | 0.3                      |
| 3     | 1260          | 0             | 0             | 150            | 0.38                | 0.19                     |
| 4     | 1260          | 0             | 0             | 150            | 0.38                | 0.19                     |
| 5     | 1260          | 0             | 0             | 240            | 0.38                | 0.08                     |
|       |               |               |               |                |                     |                          |
| 6     | 1283          | 67            | 0             | 0              | 0.34                | 0.34                     |
| 7     | 1215          | 135           | 0             | 0              | 0.34                | 0.34                     |
| 8     | 1215          | 135           | 0             | 0              | 0.34                | 0.34                     |
| 9     | 1148          | 202           | 0             | 0              | 0.34                | 0.34                     |
|       |               |               |               |                |                     |                          |
| 10    | 1170          | 65            | 65            | 57             | 0.36                | 0.29                     |
| 11    | 1170          | 65            | 65            | 57             | 0.36                | 0.29                     |
| 12    | 1105          | 65            | 130           | 57             | 0.36                | 0.29                     |
| 13    | 1040          | 65            | 195           | 57             | 0.36                | 0.29                     |

# Appendix C Particle size analysis (ASTM D 421-85)

Particle size distribution curve of sand derived based on ASTM D 421-85 (dry sieving method) is provided in Figure C.1.



## Appendix D Organic carbon content test

Organic contents of sand, clay and peat were determined based on ASTM D 2974-87. Below is the test procedure.

- Soil samples (about 100 g) were completely dried in an oven at 104°C.
- Soil samples were burned in muffle oven at 440 °C until completely ashed (no mass change was observed).
- Ash content was calculated as,

$$\text{Ash content \%} = \frac{\text{Mass of ash (g)}}{\text{Mass of dried soil (g)}} \cdot 100 \quad (D.1)$$

- Organic matter were calculated by,

$$\text{Organic content \%} = 100 - \text{Ash content} \quad (D.2)$$

Table D.1 shows calculations.

Table D.1 Calculation of organic content.

| Soil type | Mass of dry soil (g) | Mass of ash (g) | Ash content (%) | Organic carbon content (%) |
|-----------|----------------------|-----------------|-----------------|----------------------------|
| Sand      | 100.96               | 100.56          | 99.60           | 0.40                       |
| Clay      | 98.95                | 97.34           | 98.37           | 1.63                       |
| Peat      | 100.43               | 46.54           | 46.34           | 53.66                      |

## Appendix E QA/QC results

QA/QC results are provided in Table E.1. For each test, four replicate samples (samples with known concentrations) were analyzed by GC and coefficient of variation and bias were calculated by equations 3.1 and 3.2

Table E.1 QA/QC results

| Run no | C <sub>Exp.</sub> | C <sub>m</sub> <sup>1</sup> | C <sub>m</sub> <sup>2</sup> | C <sub>m</sub> <sup>3</sup> | C <sub>m</sub> <sup>4</sup> | C <sub>m</sub> <sup>Mean</sup> | SD  | C.O.V. (%) | Bias (%) |
|--------|-------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|--------------------------------|-----|------------|----------|
| 1      | 170.1             | 171.5                       | 175.4                       | 180.2                       | 167.4                       | 173.6                          | 5.5 | 3.1        | 2.0      |
| 2      | 170.1             | 170.7                       | 178.3                       | 175.3                       | 183.5                       | 177.0                          | 5.4 | 3.0        | 3.9      |
| 3      | 170.1             | 176.7                       | 175.8                       | 171.6                       | 171.6                       | 173.9                          | 2.7 | 1.6        | 2.2      |
| 4      | 170.1             | 178.4                       | 181.5                       | 182.3                       | 179.4                       | 180.4                          | 1.8 | 1.0        | 6.1      |
| 5      | 271.5             | 275.5                       | 273.2                       | 275.2                       | 271.2                       | 273.8                          | 2.0 | 0.7        | 0.8      |
| 6      | 271.5             | 273.0                       | 263.6                       | 257.6                       | 261.9                       | 264.0                          | 6.5 | 2.5        | -2.7     |
| 7      | 170.1             | 159.1                       | 162.4                       | 162.3                       | 162.9                       | 161.7                          | 1.7 | 1.1        | -4.9     |
| 8      | 486.5             | 472.5                       | 484.6                       | 494.5                       | 485.2                       | 484.2                          | 9.0 | 1.9        | -0.5     |
| 9      | 271.5             | 227.8                       | 226.4                       | 221.5                       | 219.0                       | 223.7                          | 4.1 | 1.9        | 17.6     |
| 10     | 170.1             | 171.8                       | 165.5                       | 171.1                       | 174.0                       | 170.6                          | 3.6 | 2.1        | 0.3      |
| 11     | 170.1             | 177.0                       | 194.5                       | 187.6                       | 181.1                       | 185.1                          | 7.7 | 4.2        | 8.8      |
| 12     | 486.5             | 491.7                       | 510.7                       | 501.0                       | 499.8                       | 500.8                          | 7.8 | 1.6        | 2.9      |
| 13     | 259.5             | 282.0                       | 285.4                       | 296.6                       | 298.9                       | 290.7                          | 8.3 | 2.8        | 12.0     |

C<sub>Exp.</sub> = C<sub>Expected</sub>

C<sub>m</sub> = C<sub>Measured</sub>

SD = Standard deviation

C.O.V. = Coefficient of variation

## Appendix F Mass balance analysis

MTBE upward mass flux through the soil column were calculated for each test both by mass reduction of MTBE (liquid MTBE at the bottom section of column) and by multiplying the top head-space nitrogen flow rate and mass concentration under steady state conditions. Mass flux results and their relative errors are provided in Table F.1.

Table F.1 Mass balance analysis results of MTBE gas phase diffusion.

| run no | MTBE flux from mass loss<br>( $\mu\text{g/s.cm}^2$ ) | MTBE flux from nitrogen flow and concentration<br>( $\mu\text{g/s.cm}^2$ ) | Relative error (%) |
|--------|--|--|--------------------|
| 1      | 2.59   | 2.26   | -13                |
| 2      | 1.47   | 1.54   | 5                  |
| 3      | 0.37   | 0.3  | -19                |
| 4      | 0.34   | 0.24   | -29                |
| 5      | 0.17   | 0.13   | -24                |
|        |  |  |                    |
| 6      | 1.69   | 1.87   | 11                 |
| 7      | 1.59   | 1.68   | 6                  |
| 8      | 1.44   | 1.53   | 6                  |
| 9      | 1.35   | 1.49   | 10                 |
|        |  |  |                    |
| 10     | 1.74   | 1.66   | -5                 |
| 11     | 1.69   | 1.65   | -2                 |
| 12     | 1.27   | 1.38   | 9                  |
| 13     | 1.27   | 1.31   | 3                  |