

# **ENHANCEMENT OF TCE VOLATILIZATION AND VAPOR EXTRACTION FROM VARIABLY-SATURATED CLAY USING SALT AND ALCOHOL SOLUTIONS**

by

María de Lourdes Irizarry Montalvo

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Approved by:

\_\_\_\_\_  
Ingrid Y. Padilla Cestero, PhD  
President, Graduate Committee

\_\_\_\_\_  
Date

\_\_\_\_\_  
Sangchul Hwang, PhD  
Member, Graduate Committee

\_\_\_\_\_  
Date

\_\_\_\_\_  
Eric Harmsen, PhD  
Member, Graduate Committee

\_\_\_\_\_  
Date

\_\_\_\_\_  
Luis R. Pérez Alegría, PhD  
Representative of Graduate Studies

\_\_\_\_\_  
Date

\_\_\_\_\_  
Ismael Pagán Trinidad, MS  
Chairperson of the Department

\_\_\_\_\_  
Date

## ABSTRACT

One of the most common dense non-aqueous phase liquids (DNAPLs) found in polluted underground systems in the U.S. is trichloroethylene (TCE). Most of the remediation technologies for chlorinated solvents like TCE have been designed for sands and high permeability media, therefore new technologies need to be developed to successfully remove these contaminants from tight formations. Previous research has demonstrated enhanced remediation of TCE-contaminated sites through the use of combined treatment technologies using surfactant- and gravity-induced mobilization, dense brine containment and collection, and vapor phase extraction in saturated heterogeneous soils. This research evaluates and develops the enhancement of TCE volatilization and vapor extraction from variably-saturated clay by the addition of salt and alcohol solutions. Enhanced volatilization of TCE is assessed in static and dynamic reactors. The effect of salt content on permeability is assessed through soil-air permeability measurements at different water contents and salt concentrations. Air permeability measurements indicate that the air permeability of Coto clay could be enhanced by the addition of NaCl at low moisture contents. Results for static batch experiments indicate that NaCl enhances vapor TCE extraction for reactors containing TCE-solution with TCE NAPL, for NaCl concentrations below 4.28 M. In the absence of TCE NAPL, for low TCE aqueous concentrations, a high NaCl concentration (4.28 M) yields higher TCE vapor concentrations, and suggests potential enhancement in vapor TCE extraction. Results for the dynamic flux experiments indicate that in TCE-solution with TCE NAPL, a NaCl concentration of 0.60 M yields higher TCE vapor concentrations than in absence of NaCl. NaCl also has a significant effect on TCE solution with saturated clay (i.e. Coto clay) in presence of MeOH. Results also indicate that in unsaturated clay (i.e. Coto clay) NaCl has a significant effect on TCE volatilization. MeOH has a significant effect on TCE solution with or without TCE NAPL.

In general, results show that there is a potential for enhanced vapor-phase extraction of TCE by using salt and methanol solution. The differences are, however slight for NaCl. Other salt solutions may show greater enhancement.

A test bed was designed to be tested as part of another project to determine if a cycled injection of brine and alcohol solutions enhances soil vapor extraction of TCE from clayey soils. The design integrated a soil column, liquid injection and vapor extraction points, vapor samplers, vacuum, and flow meters. The suggested experimental design involves the cycled application of an alcohol aqueous solution (10%), followed by a brine solution, both injected through reactant delivery membranes, and vapor extraction through extraction wells. Air pressures, flow rates, solution delivery rates, and changes in water content at the bottom boundary are to be monitored during the SVE enhancement experiments.

## RESUMEN

Uno de los líquidos densos en fase no acuosa (DNAPL) que más comúnmente se encuentran en sistemas subterráneos contaminados en los EE.UU. es el tricloroetileno (TCE). La mayoría de las tecnologías para remediación de solventes clorinados como el TCE, han sido diseñadas para arenas y medios de alta permeabilidad, por lo tanto, deben desarrollarse nuevas tecnologías que remuevan exitosamente estos contaminantes de formaciones poco permeables. Pasadas investigaciones han demostrado mejoras a la remediación de sitios contaminados con TCE a través del uso de tecnologías de tratamientos combinados usando movilización inducida por surfactantes y por la gravedad, la contención y colección por soluciones saladas densas, y la extracción en fase de vapor en suelos heterogéneos saturados. Esta investigación evalúa y desarrolla la mejora a la volatilización de TCE y la extracción de vapores de arcilla a saturación variable mediante la adición de soluciones de sal y alcohol. Se evalúa la mejora a la volatilización del TCE a través de reactores estáticos y de flujo dinámicos. El efecto del contenido de sal en la permeabilidad se evalúa a través de medidas de permeabilidad de aire en suelo a diferentes contenidos de humedad y diferentes concentraciones de sal. Las medidas de permeabilidad de aire indican que la permeabilidad de aire para la arcilla Coto se podría mejorar mediante la adición de cloruro de sodio (NaCl) a bajos contenidos de humedad. Los resultados para el experimento de reactores estáticos indican que el NaCl aumenta la extracción de TCE en vapor de los reactores que contienen solución de TCE con TCE en fase no acuosa, para concentraciones de NaCl menores a 4.28 M. En ausencia de TCE en fase no acuosa, para concentraciones acuosas de TCE bajas, una concentración alta de NaCl (4.28 M) resulta en concentraciones más altas de TCE en vapor, lo que sugiere una mejora potencial en la extracción de TCE en vapor. Los resultados para el experimento de reactores de flujo dinámico indican que en solución de TCE con TCE en fase no acuosa una concentración de NaCl de 0.60 M resulta en concentraciones de TCE en vapor más altas que en la ausencia de la sal. El NaCl también tiene un efecto significativo sobre la arcilla Coto saturada de solución de TCE en presencia de metanol (MeOH). Los resultados para el experimento de reactores de flujo dinámico también

indican que en arcilla Coto no saturada el NaCl tiene un efecto significativo sobre la volatilización del TCE. El MeOH tiene un efecto significativo en la solución de TCE con o sin TCE en fase no acuosa.

En general, los resultados muestran que hay potencial para la mejora de la extracción de TCE en fase de vapor al usar sal y solución de MeOH. Las diferencias son, sin embargo, leves para el NaCl. Soluciones de otras sales podrían resultar en una mayor mejora.

Una columna ha sido diseñada para ser evaluada como parte de otro proyecto, para determinar si una inyección cíclica de soluciones de sal y alcohol mejora la extracción de vapores de TCE del suelo. El diseño integra una columna de suelo, puntos de inyección líquida y de extracción de vapores, muestreadores de vapor, bomba de vacío y metros de flujo. El diseño experimental sugerido envuelve la aplicación cíclica de una solución de alcohol (10%), seguida por la aplicación de una solución de salmuera, ambas inyectadas a través de membranas de distribución de reactivos, y la extracción de vapores a través de pozos de extracción. Durante los experimentos de mejora a la extracción de vapores del suelo, se medirán las presiones de aire, razones de flujo, razones de distribución de soluciones, y los cambios en el contenido de humedad en el límite inferior de la columna.

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“To God for his guidance in every step I have taken.  
To my parents and my sister for their constant support.  
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## LIST OF SYMBOLS AND ABBREVIATIONS

°C	–	degrees Celsius
CaCl <sub>2</sub>	–	calcium chloride
CaSO <sub>4</sub>	–	calcium sulfate
CBD	–	Capillary-based delivery
DDL	–	Diffuse double layer
DNAPL(s)	–	dense non-aqueous phase liquid(s)
EPA	–	Environmental Protection Agency
FID	–	flame ionization detector
GC	–	gas chromatography
h, hr(s)	–	hour(s)
M	–	mol/L (molar concentration)
mg/L	–	milligram(s) per liter
mL	–	milliliter(s)
mL/min	–	milliliter(s) per minute
MOM	–	method of moments
NaCl	–	sodium chloride
[NaCl]	–	sodium chloride concentration(s)
NAPL	–	non-aqueous phase liquid
PTFE	–	polytetrafluoroethylene
SPME	–	solid phase micro extraction
SS	–	stainless steel
SVE	–	soil vapor extraction
TCE	–	trichloroethylene
TCE <sub>vc</sub>	–	TCE vapor concentration(s)
TDR	–	Time-Domain Reflectometry (water content reflectometer)
VOC	–	volatile organic compound
WC or wc	–	water content
TSSS	–	TCE saturated stock solution
g/m <sup>3</sup>	–	gram(s) per cubic meter

# 1 INTRODUCTION

The growth in use of chemicals and the development of new industrial processes and technologies in the early 20<sup>th</sup> century increased the potential for the entry of organic pollutants to groundwater systems. Soil and groundwater contamination caused by accidental spills, negligence in the disposal of hazardous waste, and unsafe storage is a risk to human health and the environment. Common contaminants in the subsoil and groundwater include dense non-aqueous phase liquids (DNAPLs), which are particularly dangerous because of their heterogeneous distribution and long-term perseverance in these environments (Reynolds & Kueper, 2004; NRC, 2004; Liang & Falta, 2008). They are also very difficult to locate, characterize, and remediate (NRC, 2004; EPA, 2007). Therefore, it is necessary to develop cost-effective alternatives that will help us in the cleanup of these contaminated areas.

## 1.1 Justification

One of the most common DNAPLs found in polluted underground systems in the U.S. is trichloroethylene (TCE) (Moran et al., 2007). TCE is a volatile organic compound (VOC) that has been widely used since the 1930's, when it was used as an anesthetic for surgery. Today, it is mostly used as a solvent to remove grease from metal parts, in dry-cleaning and in the manufacturing of other chemicals. It can also be found in some household products, including typewriter correction fluid, paint removers, adhesives, and spot removers. TCE has been identified as a central nervous system depressant, a hepatotoxin, and a carcinogen (Williams et al., 1997).

Traditional remedial approaches for chlorinated solvents like TCE include bioremediation, soil vapor extraction, thermal technologies, in-situ chemical

oxidation, and surfactant and cosolvent flushing (EPA, 2006a). Most of these technologies have been designed for sands and high permeability media. Technologies that are successful in remediating tight formations are thermal technologies, but they may not be cost effective (Kosegi et al., 2000). It is, therefore, necessary to develop new technologies that will enhance our ability to remediate tight (low permeability) zones.

Previous research has demonstrated enhanced remediation of TCE contaminated sites through the use of combined treatment technologies using surfactant- and gravity-induced mobilization, dense brine containment and collection, and vapor phase extraction in saturated heterogeneous soils (Johnson et al., 2004). In this study, dense brines are used to trap and vertically contain downward-moving DNAPLs. In general, poor results have been obtained when flushing through fractured rocks, clays, and sites with low permeability due to the inability to deliver the flushing solutions to where the contaminants are located (Lowe et al., 1999).

Brine solutions have also been used to induce volatilization and enhance detection of VOCs (Cassada et al., 2000). This enhancement is based on the salting-out effect (Salabat, 2007), which is the separation of an organic phase from an aqueous phase by the addition of a salt (Smith, 1996). This occurs when the weak intermolecular forces between organics (non-electrolyte) and water are disrupted by the hydration of electrolytes.

It is hypothesized that a combination of capillary-based delivery of cycled brine and alcohol in combination with soil vapor extraction (SVE) could enhance the remediation of unsaturated clayey soils. Capillary-based delivery relies on the application of the salt and alcohol solutions under capillary forces using porous membranes in unsaturated soil. The solutions are expected to move into smaller pores because of the stronger capillary forces in unsaturated media. The use of carefully selected porous membranes that compensate for capillary forces of the

media, water, and TCE shall improve the delivery of alcohol and salt solutions to low permeability areas. The use of an alcohol (e.g. methanol) is expected to increase TCE solubility in water, enhance water drainage, increase NAPL-air interfacial area, and thus induce higher volatilization rates (Weber et al., 2002). The application of a salt solution is expected to cause water structuring around soil particles, increase relative permeability, enhance TCE volatilization through salting out processes (Walworth, 2006; Cassada et al., 2000), and therefore enhance TCE removal through vapor extraction.

The proposed research evaluates the enhancement of SVE for the removal of TCE from unsaturated clayey soils by the addition of alcohol and salt solutions. Enhanced volatilization of TCE is assessed in static and dynamic reactors. The effect of salt content on permeability is assessed through soil-air permeability measurements at different water contents and salt concentrations. A SVE testbed to evaluate the effect of cycling salt and alcohol solutions on TCE vapor removal is designed, but tested in other studies (Lorenzo, 2014).

## 1.2 Hypothesis

Based on the previous discussion, it is hypothesized that:

- Salt solution enhances salting-out of TCE and NAPLs into the vapor phase.
- Capillary-based delivery of reactants enhances reactant spatial distribution in tight clay formations.
- Increase in salt water concentration enhances soil-vapor permeabilities.
- Addition of alcohol to NAPL-contaminated water and soil increases soil vapor concentrations and extraction.
- Combination of salt and alcohol solution enhances soil vapor extraction.

### 1.3 Objectives

The overall goal of this research centers on developing enhanced SVE technologies to clean up low-permeability zones contaminated with chlorinated solvents.

The specific objectives to attain this goal are to:

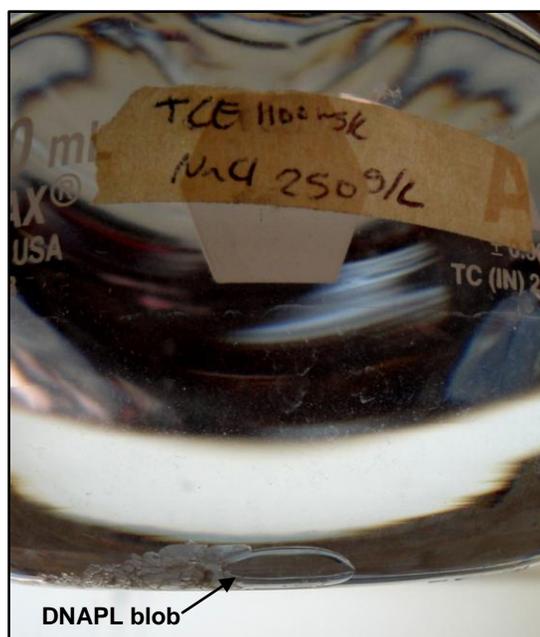
- Determine the effect of salt and alcohol on TCE volatilization and mass transfer from water and clay soils.
- Develop a method for capillary delivery of salt solution in unsaturated clay soil.
- Measure soil-air permeability as a function of salt water concentration.
- Design a SVE test bed.

## 2 LITERATURE REVIEW

The general objective of this study is to develop an enhanced soil vapor extraction (SVE) system to remediate dense non-aqueous phase liquids (DNAPLs) from low permeability soils. This section summarizes pertinent information about DNAPLs and their environmental fate and remediation technologies in soils.

### 2.1 Dense Non-Aqueous Phase Liquids

Non-aqueous phase liquids (NAPLs) are liquids that are immiscible with water. Light non-aqueous phase liquids (LNAPLs) have densities lower than water and, therefore float on water. Dense non-aqueous phase liquids (DNAPLs) are denser than water and, therefore, sink below the water surface (Figure 2.1). DNAPLs have been widely used since the beginning of the 20<sup>th</sup> century for a variety of industrial activities such as metal degreasing, paint stripping, chemical production, pesticide manufacturing, coal gasification plants, activities that involve chlorinated solvents, cleaning fluids and adhesives (Kueper et al., 2003; SWRCB, 2009). Their widespread use has resulted in the contamination of soils and groundwater resources for a long period of time. This contamination poses a major threat to public health (Schaerlaekens et al., 2004).



**Figure 2.1. DNAPL at bottom of flask containing TCE solution with [NaCl] of 4.28 M (or 250 g/L).**

Common DNAPLs include coal tar, creosote, oils containing polychlorinated biphenyls (PCBs) and chlorinated solvents like trichloroethylene (Liang & Falta, 2008). Most chlorinated solvent DNAPLs have densities in a range from 1,100 to 1,600 kg/m<sup>3</sup> and viscosities usually lower than water, generally ranging from approximately 0.57 to 1.00 cP. These properties generally result in relatively rapid movement of DNAPLs in the subsurface. They normally have low organic carbon distribution coefficient ( $K_{oc}$ ), meaning that they are not strongly sorbed into the organic carbon content of the solid phase (Kueper et al., 2003), and thus migrate readily within the subsurface. These compounds are volatile resulting in vapor contamination in the vadose zone (Kueper et al., 2003).

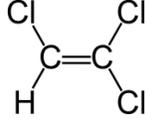
One of the most commonly found DNAPL in subsurface environments is trichloroethylene (TCE) (Moran et al., 2007; Weber et al., 2002). TCE has been widely found in the environment, including marine sediments, 59% of USEPA's Superfund sites, and in 9-34% of US drinking water supplies (ATSDR, 2003; Delinsky et al., 2005).

TCE, also known as acetylene trichloride, among other names (J.T. Baker, 2009) is a non-polar organic solvent. It is a nonflammable, colorless liquid with a somewhat sweet odor and a sweet, burning taste. TCE is a volatile organic compound (VOC) and has low water solubility and viscosity, and high volatility and toxicity (Williams et al., 1997; Kannepalli & Fennell, 2006). The physical and chemical properties of TCE are included in Table 2.1.

Many of the physical properties of TCE result in rapid movement in the subsurface and widespread contamination of the subsurface environments. High density and low viscosity facilitate downward transport in the subsurface. Its relatively low organic carbon distribution coefficient ( $K_{oc}$ ) and high volatility result in weak sorption attenuation and enhanced transport in the vapor phase. This also facilitates removal by vapor phase extraction (VPE).

A large number of TCE-contaminated sites exist in tight soil formations (Jin & Fallgren, 2010). Poor knowledge of the distribution of DNAPLs and of the fate and transport processes controlling their movement in these systems, and the difficulty of removing these contaminants from low-permeability zones makes remedial actions more difficult, less efficient, and costly (Kueper et al., 2003; NRC, 2004). Difficult removal of these contaminants from these zones is due to preferential flow, inducing channeling and low reaction areas, and mass transfer limitations (Jeong et al., 2002; NRC, 2004; Illangasekare et al., 2006).

**Table 2.1. Reported physical and chemical properties of TCE**

Property	Reported Value
Appearance	Clear, colorless liquid <sup>*2 *3</sup>
Odor	Chloroform-like <sup>*1 *3</sup>
Chemical formula and structure	C <sub>2</sub> HCl <sub>3</sub> <sup>*1 *3</sup> 
Molecular weight	131.39 g mol <sup>-1</sup> <sup>*1 *2 *3</sup>
Boiling point	86.7 °C (188.1 °F) <sup>*2 *3</sup>
Melting point	-87.1 °C (-124.8 °F) <sup>*2</sup>
Density	1.46 g mL <sup>-1</sup> (20 °C) <sup>*6</sup>
Vapor density	4.53 (air = 1.00) <sup>*1 *2 *3</sup>
Vapor pressure	9.737 x 10 <sup>-2</sup> atm (25°C) <sup>*6</sup> , 6.94 kPa(20°C) <sup>*14</sup>
Aqueous solubility	1100 mg L <sup>-1</sup> (20-25 °C) <sup>*1 *6 *15</sup>
Henry's Law constant	0.34 (20 °C) <sup>*4 *5</sup>
Absolute viscosity	0.57 cP (20 °C) <sup>*6</sup>
Gas-phase diffusion coefficient	7.8 x 10 <sup>-2</sup> cm <sup>2</sup> s <sup>-1</sup> <sup>*11</sup>
Aqueous-phase diffusion coefficient	8.8 x 10 <sup>-6</sup> cm <sup>2</sup> s <sup>-1</sup> <sup>*11</sup> 10.1 x 10 <sup>-6</sup> cm <sup>2</sup> ·s <sup>-1</sup> <sup>*7</sup>
Salting out constant	0.21 (±0.01) L·mol <sup>-1</sup> <sup>*8</sup>
Soil sorption coefficient (K <sub>oc</sub> )	126 L kg <sup>-1</sup> <sup>*9</sup>
Air-water surface tension	72.7 mN/m <sup>*12</sup>
Water-DNAPL interfacial tension	34.5-39.3 mN/m <sup>*10</sup> 34.9 mN/m <sup>*12</sup> 34.5 mN/m <sup>*13</sup>

Sources:

<sup>\*1</sup> Merck & Co., Inc., 2001

<sup>\*2</sup> Sciencelab.com, Inc., 2008

<sup>\*3</sup> J.T. Baker, 2009

<sup>\*4</sup> EPA, 2010a

<sup>\*5</sup> Peng & Wan, 1997

<sup>\*6</sup> NRC, 2004

<sup>\*7</sup> Pankow & Cherry, 1996

<sup>\*8</sup> Schwarzenbach et al., 2003

<sup>\*9</sup> Kueper et al., 2003

<sup>\*10</sup> Yoon et al., 2009

<sup>\*11</sup> Padilla, 1998

<sup>\*12</sup> Powers et al., 2004

<sup>\*13</sup> Powers et al., 2006

<sup>\*14</sup> Value calculated using the ideal gas law.

<sup>\*15</sup> EPA, 1996

## 2.2 DNAPL Environmental Fate and Transport

The fate and transport of DNAPLs in the subsurface is controlled by advection, dispersion, partitioning and degradation processes (NRC, 2004). These processes are further influenced by the type of soil, salinity, and temperature.

The migration and distribution of chlorinated solvents in the subsurface depends on factors like the permeability of the porous medium, the physical and chemical properties of the DNAPL, and the volume and concentration of the initial release (Reynolds & Kueper, 2004; NRC, 2004). After released into the surface, chlorinated DNAPLs tend to travel downward due to its density. Depending on its solubility and volatility, the contaminant will dissolve into the pore water or volatilize into the pore air. See Figure 2.2 for a visual summary of DNAPL migration and distribution. Many chlorinated DNAPLs, like TCE, are volatile, have some solubility and have viscosities smaller than water, thus partitioning to the water and gas phases and migrating more rapidly (NRC, 2004).

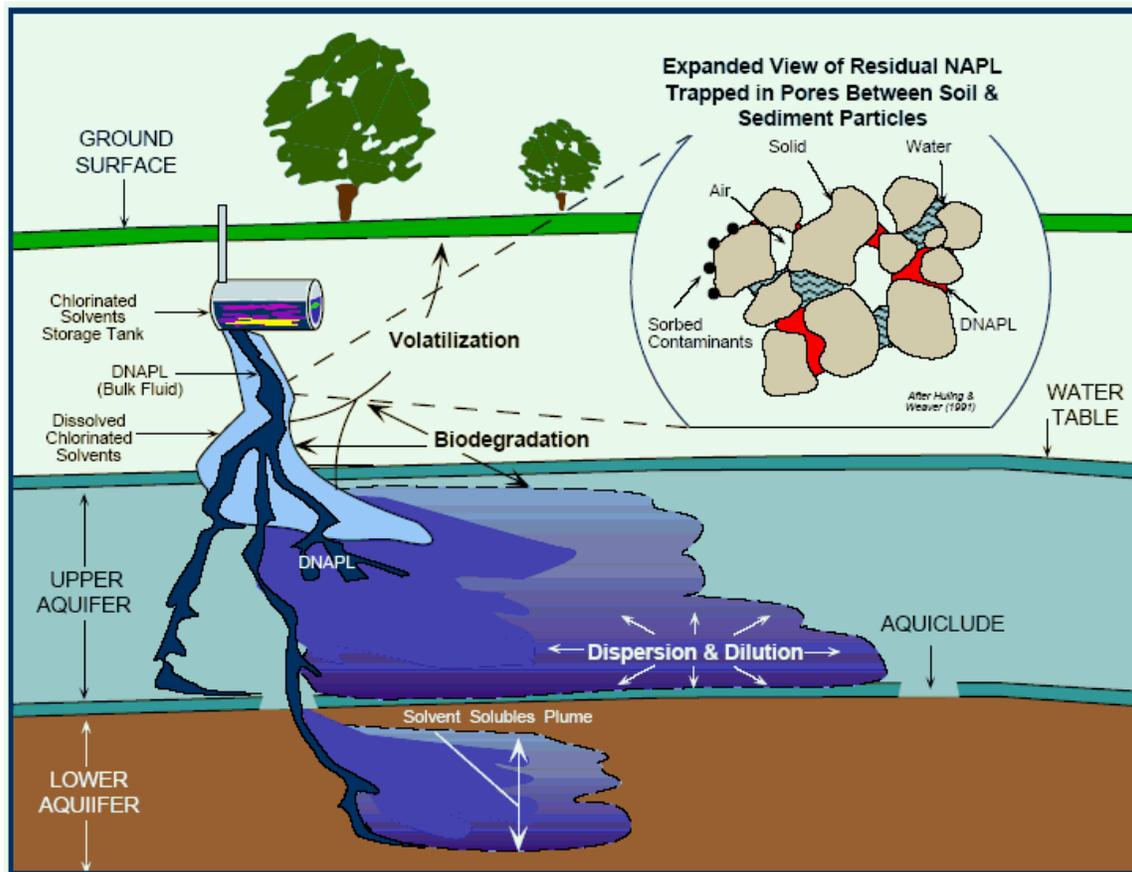


Figure 2.2. DNAPL migration and distribution below ground surface. Source: Stewart, 2008.

Another factor that affects the distribution of a DNAPL in the subsurface is the capillarity, which depends on the geometry of pores, interfacial tension and wettability (McClellan, 2012; SPE, 2012). The interfacial tension can be affected by the addition of other chemicals, and when reduced, it decreases the spread of a DNAPL perpendicular to its main direction of movement and decreases the force needed for it to displace water from pores (NRC, 2004). In terms of wettability, water is the wetting phase because it has a higher attraction to the solid surface, and therefore tends to occupy the smaller pores. DNAPLs, being a non-wetting phase, move downward in the unsaturated and saturated zones through larger wet pores.

The DNAPL moves downward until it reaches a low-permeability zone, where it may accumulate and form a pool (ITRC, 2004). It also may form discontinuous vertical veins and might remain sorbed to organic materials. Residual and pooled DNAPL together, form the DNAPL source zone, which is a source of continuous contamination for the groundwater system (NRC, 2004; EPA, 2007). The DNAPL then dissolves as groundwater passes through the contaminated zones, generating large plumes of contaminants (Guilbeault et al., 2005).

### 2.2.1 Partitioning Processes

The fate and transport of chlorinated VOCs, such as TCE, in the subsurface is controlled by several partitioning processes, including dissolution, volatilization, and sorption. Dissolution processes control the rate at which DNAPLs dissolve or partition into the groundwater or infiltration water forming a groundwater contaminant plume (Cohen & Mercer, 1993). Volatilization is the transfer of a contaminant from the aqueous phase, NAPL, or sorbed phase into the air. Sorption processes control the partitioning between water and the solid phase.

### 2.2.1.1 NAPL-Water Partitioning

When NAPL is composed of one chemical, its equilibrium concentration in water is limited by its aqueous solubility (Ramaswami et al., 2005). For DNAPLs, this is commonly a rate-limited process. Factors that affect the dissolution rate include the mass, distribution and surface area of the DNAPL in the subsurface, the solubility of the contaminant, the aqueous-phase diffusion coefficient, temperature, the porosity of the medium, and the effects of the presence of other chemicals. It is an important phase transfer process below the water table (Pankow & Cherry, 1996).

It has been observed that the presence of inorganic ionic species, such as  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ , usually decreases the aqueous solubility (or increases the aqueous activity coefficient) of non-polar organic compounds (Schwarzenbach et al., 2003). This effect is known as salting-out, which is the separation of an organic phase from an aqueous phase by the addition of a salt (Smith, 1996). This occurs when the weak intermolecular forces between organics (non-electrolyte) and water are disrupted by the hydration of electrolytes. The Setschenow formula (Schwarzenbach et al., 2003) relates organic compound solubilities in saline aqueous solutions ( $C_{iw,salt}^{sat}$ ) to the compounds' solubilities in pure water ( $C_{iw}^{sat}$ ):

$$\log \left( \frac{C_{iw}^{sat}}{C_{iw,salt}^{sat}} \right) = K_i^S [\text{salt}]_{tot} \quad 2.1$$

where  $K_i^S$  is the Setschenow or salting constant, with units of L/mol and  $[\text{salt}]_{tot}$  is the total molar salt concentration.

### 2.2.1.2 Air-Water Partitioning

The equilibrium between the NAPL and air phase is defined by the vapor pressure of the contaminant (Bedient et al., 1997). The distribution of a contaminant between the water and gas phase is described by Henry's Law,

$$K_H = \frac{C_v}{C_w} \quad 2.2$$

which is based on a local equilibrium and is shown in Equation 2.2, in which  $K_H$  is Henry's Law constant,  $C_v$  is the gas-phase concentration of the contaminant and,  $C_w$  is the contaminant's solubility in water. The rate of volatilization depends on a contaminant's physical and chemical properties (U.S. Army Corps of Engineers, 2008).

### 2.2.1.3 Soil-Water Partitioning

The partitioning of contaminants between soil and water occurs in two ways: sorption, which refers to the transfer of contaminants from fluids to solid surface, and desorption, which refers to the release of a sorbed contaminant from a particle (Chapra, 1997). The soil-water partition (or distribution) coefficient ( $K_d$ ) relates the equilibrium contaminant concentration in soil to that in water (Ramaswami et al., 2005) or air, and can be related to the organic carbon-water partition coefficient ( $K_{oc}$ ) (Schwarzenbach et al., 2003).

## 2.2.2 Transformation

Transformation processes by which contaminants are converted to other products, result from abiotic (chemical transformation) or biotic (biodegradation) processes. Abiotic reactions include hydrolysis, oxidation, and reduction. In

biodegradation the contaminant is converted to less harmful end products (i.e. CO<sub>2</sub>, H<sub>2</sub>O) through metabolism by living organisms and/or their enzymes (Margesin & Schinner, 2001). Chlorinated ethenes are generally resistant to hydrolysis, but for TCE, an important transformation reaction is reductive dechlorination. This biotransformation process transforms PCE to TCE to *cis*-1,2-dichloroethylene to vinyl chloride to ethene (ITRC, 2008; Pankow & Cherry, 1996). TCE can be degraded both aerobically and anaerobically (Ramaswami et al., 2005). TCE can also be degraded abiotically (e.g. oxidation). Abiotic transformation is significant because the transformation of chlorinated ethenes is often nearly complete (Tobiszewski & Namieśnik, 2012). The oxidation technique has been quite successful in remediating TCE groundwater contamination (Liang et al., 2008). In contrast with biological reductive dechlorination, which results in the accumulation of harmful intermediates, such as *cis* 1,2-dichloroethylene, abiotic mineral-mediated dechlorination of TCE usually results in complete transformation to non-toxic products, such as acetylene (Butler, et al., 2009). This work does not consider degradation.

### 2.3 DNAPL Remediation

A DNAPL-contaminated site may contain several zones of contamination. These include: a source zone with very high DNAPL concentrations with potential for movement; a residual zone where the contaminant has diffused or sorbed onto aquifer solids; and plumes of dissolved and/or volatilized contaminants (EPA, 2010b).

Some of the remedial actions applied in contaminated sites include: removal, stabilization, installation of multi-layer surface barriers (NRC, 2000); pump and treat systems, vacuum extraction, air and dynamic stripping, and bioremediation (EPA, 2010b). Some common remedial technologies used to clean up DNAPL contaminated areas are further described below and are grouped into three categories: containment, physical removal, and chemical/biological treatment.

### 2.3.1 Containment Technologies

Containment activities do not remove mass from the site, but reduce risks by minimizing contaminant migration and exposure (NRC, 2004). A typical system consists of impermeable barriers that are created on all sides of the source zone, a clay aquitard below the source and a low-permeability cap on top (EPA, 2010b). It is a simple and inexpensive technology but requires long-term monitoring to assure that contaminants are not migrating, because data is not available regarding the durability of the physical containment systems (EPA, 2010b)

### 2.3.2 Physical Removal Technologies

Physical removal technologies include excavation, pump and treat, soil heating, air sparging, chemical and biological treatment, and soil vapor extraction (SVE). All, but SVE are briefly described below. SVE is described in more detail in the next section, as this technology is the focus of this research.

Excavation is a technology that attempts to remove the source of contamination. Total removal may be impossible if it is too deep (i.e. deeper than 10 ft) (EPA, 2010b), below a building or if NAPLs are present (Bedient et al., 1997). Source materials are dug out and shipped to an appropriate site for treatment or disposal. This may be costly depending on the volume extracted. This technology requires backfilling with clean material, extensive physical access to the source area, and a rigorous zone characterization (NRC, 2004).

Pump-and-treat (P&T) is a system that involves contaminated groundwater being extracted with extraction wells and treated ex-situ. In most cases, it is not very effective because of the limited solubilities of NAPLs and large NAPL-water interfacial tensions (Soga et al., 2004). Decreases in contaminant concentrations have been observed, but cleanup targets are not necessarily met (NRC, 2004). These technologies, although still used, have proven to be ineffective to reduce

groundwater concentrations to drinking water standards (NRC, 2004). They are also more costly than other technologies and take decades or even more time to reduce contamination substantially (EPA, 2009). According to Voudrias (2001) the application of P&T is impractical and expensive and pumping may be limited at low permeability zones.

Surfactant/cosolvent flushing or enhanced soil flushing relies on the use of co-solvents or surfactants to enhance the solubility and/or mobility of DNAPLs in the soil. Surfactants are surface active agents present in soaps and detergents (ITRC, 2003). Co-solvents are solvents, such as acetone and methanol that modify the solvent properties of water (NRC, 2004) and may cause an increase in the solubility of organic contaminants (ITRC, 2000). They are both amphiphilic molecules, meaning that they have water-like and oil-like parts. Therefore, they accumulate at interfaces of multiphase systems, with the water-like part of the molecule in the polar water phase and the oil-like part of the molecule in the non-polar oil or less polar air phase (NRC, 2004). As water and co-solvents are flushed through a DNAPL-contaminated zone, more DNAPL can dissolve and be removed from the system (Illangasekare, et al., 2006). Pump-and-treat systems have been enhanced with the addition of surfactants by reducing their operation time and cost (Li & Hanlie, 2008). Using higher concentrations of surfactants and/or co-solvents will further enhance solubilization but could also increase a DNAPL's mobility by reducing the interfacial tension and decreasing the capillary forces responsible for its residual retention and the formation of pools (Brooks et al., 2004). An increase in the mobility of a DNAPL is not desirable because it could promote migration to deeper regions, which would be called mobilization. Poor results have been obtained when flushing through fractured rocks, clays, and sites with low-permeability, due to the inability to deliver the flushing solutions to where the contaminants are located (Strbak, 2000).

Soil heating technologies aim to augment organic chemical partitioning into the vapor phase that will then be extracted by vacuum (NRC, 2004). They rely on the application of heat to increase the vapor pressure of the contaminants, alter

fluid properties, and enhance the vapor flow through the media. It is a form of enhanced soil vapor extraction (SVE). Soil heating technologies have been applied successfully to remediate areas contaminated with DNAPL (Juhlin et al., 2004), even low permeability soils (ITRC, 2002), but they can have a relatively high cost (Geosyntec Consultants, 2004).

Air-sparging works by stripping volatile contaminants from the subsurface. It consists of injection wells that pump air below the water table removing contaminants by volatilization from the dissolved, sorbed and NAPL phases (EPA, 2010b). At the same time, oxygen that enters the subsurface while pumping air promotes biodegradation in the saturated and unsaturated zones. This technology is normally successful at removing dissolved VOCs and could potentially be applied for low levels of LNAPLs or DNAPLs (Batelle, 2001). But air-sparging is not reliable in low permeability zones because these units may not allow adequate air flow (EPA, 2010b).

Chemical transformation technologies involve the introduction of chemicals into the subsurface to react with contaminants, resulting in their degradation or transformation (NRC, 2004). For example, in situ chemical oxidation involves adding strong oxidants such as peroxide, persulfate, ozone or permanganate. It works with a wide variety of dissolved contaminants by oxidizing them to less harmful compounds and promoting mass transfer from sorbed or NAPL phases to aqueous phase (NRC, 2004). This technology has been quite successful in remediating TCE groundwater contamination (Liang et al., 2008). But contaminants in low permeability zones may not be contacted and destroyed by chemicals delivered (EPA, 2010b).

Biological technologies are techniques that directly or indirectly promote biodegradation of contaminants in situ. Bioremediation directly promotes contaminant degradation, which can occur under aerobic or anaerobic conditions in two different ways: Intrinsic biodegradation relies on microorganisms original from the contaminated area to degrade the contaminants without any added chemicals or pumped air (EPA, 2010b). Enhanced bioremediation includes any

in situ system where chemicals are introduced into the subsurface to stimulate microorganisms that can degrade or transform the contaminants, destroying them partially or completely. These chemicals can be substrates, electron acceptors (e.g. oxygen) and/or nutrients (e.g. nitrogen and phosphorus) that are injected. One advantage of this technology is that contaminants are destroyed mostly in place and do not need to be transported to the surface (NRC, 2004), even though this type of remediation takes longer time to complete. These technologies work mostly for the dissolved phase and not in the NAPL-phase pools. A condition of low hydraulic conductivity will limit substrate delivery and is therefore unfavorable to bioremediation (Moretti, 2005).

## 2.4 Soil Vapor Extraction

VOCs, such as TCE, could be effectively recovered from the unsaturated zone by enhancing air-phase transport as opposed to water-phase transport (Bedient et al., 1997). An alternative technology for remediating unsaturated soils contaminated with VOCs is soil vapor extraction (SVE), which results in the removal of contaminants in-situ, in the form of vapors (EPA, 2001), by pulling air through the contaminated zone into wells that are screened in the vadose zone (Figure 2.3). As air is drawn through the pores, it will carry away the existing vapors by advection. It removes contaminants by desorption from the surface of soil particles, volatilization of the dissolved contaminants and volatilization of NAPLs (EPA, 2006b). Extracted vapors may be discharged directly into the atmosphere at a certain permitted height, or treated and then released. Vapor extraction wells are designed very similar to ground-water wells. Air-vent wells are used as part of the system because fresh air needs to be circulated through the contaminated area. These wells have the upper end open to the atmosphere. SVE is a cost-effective technology that has been effective for remediation and has been widely used at contaminated sites (Stauffer et al., 2007). It is appropriate for remediating highly permeable soils but for low

permeability soils it is more difficult and often requires enhancements (EPA, 2006a).

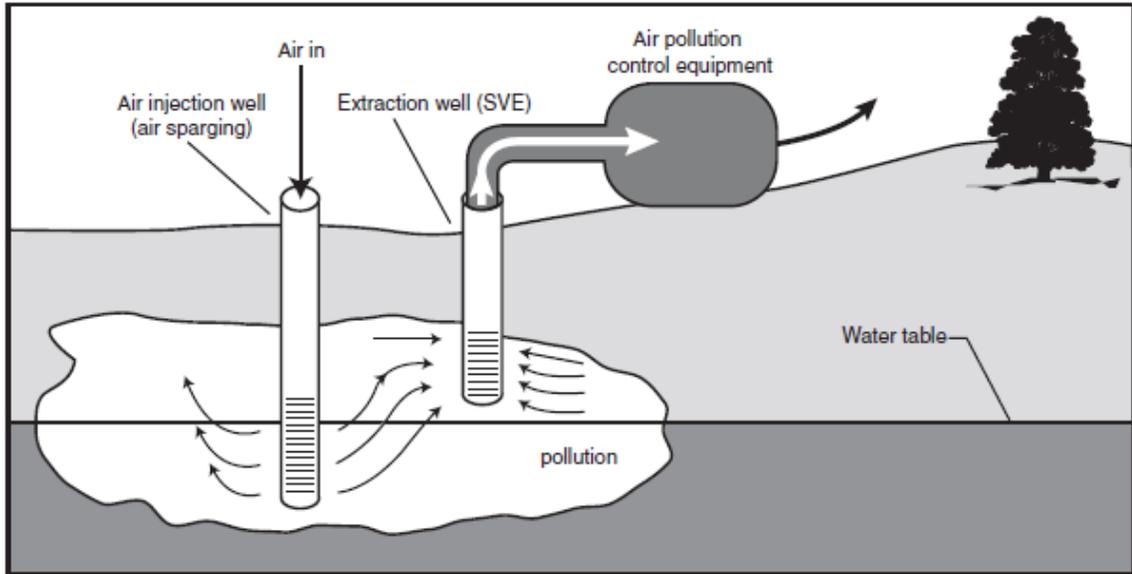


Figure 2.3. Soil vapor extraction system. Source: EPA, 2001.

## 2.5 Enhanced/Combined Remediation Technologies

Surfactants, dense brines, and SVE combined technologies have been used to enhance remediation of TCE-contaminated sites in saturated sandy soils (Johnson et al., 2004). In this study, the surfactant is used to mobilize DNAPL. The dense brine is used as a containment and collection barrier below the contaminated zone to prevent further migration of the DNAPL. SVE is used to remove residual DNAPL remaining after mobilization. The study concluded that the complexity of DNAPL flow and entrapment will increase as the heterogeneity of the media increases; roughly 85% removal is obtainable at the level of heterogeneity investigated (six different quartz sands, finer to coarser from bottom of cell). Vapor extraction showed to be effective in removing the remaining residual DNAPL (after surfactant injection and brine barrier collection) to levels of less than 1% of the original entrapped DNAPL mass.

Brine solutions have also been used to induce volatilization and enhance detection of VOCs (Cassada et al., 2000). Their method involves adding NaCl to environmental samples contained in a vial. This method induces salting out of VOCs and enhances their detection. The study concluded that the analysis of ethanol, MTBE, and related compounds in water at low microgram per liter levels has been accomplished by SPME extraction and GC/MS detection. The amount of salt (NaCl) added to the water sample and the length of extraction time increased the extraction efficiency for all analytes.

The use of salt solutions in soils has also been found to induce flocculation and restructuring of soil particles, and enhance soil permeability (Walworth, 2006). The introduction of salt solutions can cause either salinity or sodicity in a soil, both of which affect soil structure and permeability (Fukumura et al., 1996). Salts that contribute to salinity are for example calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ). Sodicity refers to the amount of sodium ( $\text{Na}^+$ ) present in water and it causes the opposite effect of salinity. Sodicity causes soil dispersion and clay platelet and aggregate swelling (Pearson, 2009). The flocculation or dispersion of clay particles is related to the thickness of the diffuse double layer (DDL) that surrounds clay particles. Most clay particles are negatively charged, therefore, they electrostatically attract cations to the particle surface (Walworth, 2006), which form the DDL. As the DDL of clay particles approach each other, electrostatic repulsion occurs and dispersion tends to occur. This repulsion increases as the thickness of the DDL increases (Clark et al., 2000). DDL thickness is greater in the presence of monovalent cations ( $\text{Na}^+$ ) than in the presence of divalent cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ). Therefore, high  $\text{Na}^+$  concentrations increase DDL thickness resulting in dispersion and reduced hydraulic conductivity (Clark et al., 2000). Dispersed clay particles plug soil pores reducing soil permeability. High concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  decrease DDL thickness, resulting in flocculation and increased hydraulic conductivity (Clark et al., 2000). Permeability reduction is dependent on soil type but it is more damaging in clayey soils (Fukumura et al., 1996). The more sodium a type

of clay can hold, the less the hydraulic conductivity will be (Pearson, 2009). Montmorillonite clays are more affected by sodium, therefore are more prone to swelling and dispersion, whereas kaolinites are the least affected and swell and disperse the least (Pearson, 2009).

Several alcohols have been used to enhance solubilization of chlorinated organic solvents, including methanol, ethanol and isopropyl alcohol (Chawla et al., 2001). In this study, these three alcohols were used separately as co-solvents with water in thoroughly-mixed batch systems to determine TCE solubility as a function of cosolvent concentration. Results from this study showed that the addition of each alcohol enhanced the solubility of TCE in aqueous phase. PCE solubility in a 70% ethanol solution has been reported to reach values ranging from approximately 70,000 mg/L to 100,000 mg/L, which are several orders of magnitude higher than its solubility in pure water (~200 mg/L) (Liang & Falta, 2008).

## 2.6 Delivery of Reagents

Some innovative remediation technologies, such as multiphase extraction, surfactant/co-solvent flushing, in situ chemical oxidation, and chemical reduction, have been applied, but their applicability for low permeable zone is limited by the ability to deliver the reactants into the zone. Commonly, fluids and injected reactants follow a path of preferential flow, inducing channeling and low reaction areas. This research addresses simple and cost-effective technologies based on capillary forces to deliver remediation reactants to unsaturated tight formations. If feasible, this would reduce the amount of energy and cost of the remediation operations.

Capillary-based delivery relies on the application of reagent solutions, such as salt and alcohol solutions, under capillary forces using porous membranes in

unsaturated soil. The solutions are expected to move into smaller pores because of the stronger capillary forces in unsaturated media. Capillary-based delivery relies on the movement of reactants from areas of low liquid tension (low capillary forces) to areas of high capillary forces. In unsaturated soil, liquid tension or capillary pressure ( $P_c$ ) depends on the surface tension of the solution-air interface ( $\theta$ ), the contact angle ( $\phi$ ), and the effective radius ( $r$ ) where the interface is located as given by the Young–Laplace equation (Jury and Horton 2004):

$$P_c = \frac{\theta \cos\phi}{r} \quad 2.3$$

For similar  $\theta$  and  $\phi$ ,  $P_c$  is therefore higher for solutions located in the smaller radius pores resulting in the movement of the liquid toward these pores.

### 3 METHODOLOGY

The main goal of this research, centers on developing enhanced soil vapor extraction (SVE) technologies for the removal of DNAPLs from tight clay soils with salt and alcohol solutions. The objectives of this research are accomplished through a systematic methodology that involves static and dynamic batch experiments, development of capillary-based delivery methods, pneumatic characterization of the soil, SVE testbed design and development, and integrated data analysis. This chapter describes the materials and methods used for the experimental work, as well as the analytical methods. The measurements were used to determine changes in TCE volatilization under different solutions.

#### 3.1 Soil Characteristics

Experiments with clay soil were conducted using Coto Clay soil collected from Isabela, PR. This soil is mainly composed of kaolinite and quartz mineralogy. Tables 3.1, 3.2 and 3.3 show its physical, chemical and hydraulic characteristics (Molina et al., 2006; Rodríguez et al., 2007). To eliminate roots, large aggregates and large particles, the clay soil was passed through a 0.71 mm (#25) sieve. Particles retained by the sieve were disposed of, and those passing through the sieve were used in the experiments.

**Table 3.1. Average physical characteristics of Coto Clay. Source: Molina et al., 2006.**

Soil	USCS Classification	Liquid Limit %	Plastic limit %	Plastic Index %	Specific Gravity (g/cm <sup>3</sup> )	Specific Surface Area (m <sup>2</sup> /g)	Mineralogy
Isabela Clay	CL	46.6	25.4	21.2	2.62	44.4	Quartz/kaolinite

CL → clay, as defined by the Unified Soil Classification System (USCS)

**Table 3.2. Chemical characteristics of Coto Clay. Source: Molina et al., 2006.**

Ca (ppm)	Mg (ppm)	Na (ppm)	HCO <sup>3-</sup> (mg/kg)	CO <sup>3</sup> (mg/kg)	Cl <sup>-</sup> (ppm)	FOC %	OM %	TFe (mg/kg)	TN (mg/kg)	pH	CEC (mg/100g)
307.9	42.3	42.3	1	<1.00	77	0.67	1.52	7938.8	914	5.1	25.7

**Table 3.3. Physical and hydraulic properties of Coto Clay in the field. Source: Harmsen et al., 2003.**

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Bulk Density (g·cm <sup>-3</sup> )	Porosity	Hydraulic conductivity (cm hr <sup>-1</sup> )
0-20	35.1	19.35	45.6	1.36	0.48	50.42
20-40	28.72	1.85	69	1.36	0.48	13.21
40-60	22.5	5	72.5	1.31	0.5	2.92
60-80	20	5.8	74.2	1.29	0.51	0.5

### 3.2 Chemical Reagents

The chemical reagents used for this research were trichloroethylene (TCE), sodium chloride (NaCl), calcium chloride (CaCl<sub>2</sub>), calcium sulfate (CaSO<sub>4</sub>), and methanol (MeOH). Also, distilled and deionized water was used, which was obtained from a water purification system (Barnstead/Thermolyne, Model D4741) in the Environmental Engineering laboratory at the University of Puerto Rico, Mayaguez.

#### 3.2.1 Trichloroethylene

TCE was purchased from Sigma-Aldrich, an ACS certified reagent 99.5+%. TCE standards (2000 µg/mL in Purge and Trap Methanol) were purchased from Restek Corporation (Bellefonte, PA).

TCE stock solutions were prepared by adding a TCE NAPL mass in excess of solubility and allowing the solution to reach solubility. Specifically, the solutions were prepared by adding 6 mL of TCE NAPL to 4 L of water in 4-L amber bottles. They are stirred for no less than 30 days using a Stirring Hot Plate (Thermolyne Cimarec ® 2) to enhance dissolution.

Measurements of the headspace above the stock solution (Table 3.4) yield an average TCE vapor phase concentration of  $196.5 \pm 67.7 \text{ g/m}^3$ , which is about 52% of the TCE saturated vapor pressure concentration ( $C_{vp} = 374 \text{ g/m}^3$ ) at 20°C. Lower vapor concentrations may be caused by losses to the atmosphere when the bottles are opened, and subsequent mass transfer limitations in the dissolution of the DNAPL (which sits on the bottom of the bottle) and volatilization of the aqueous TCE.

**Table 3.4. Stock solutions samples taken for dynamic equilibration reactor experiments: dissolution times, measured concentrations and equilibration time before sampling.**

Dynamic flux experiment ID	Stock solution dissolution time (days)	Stock solution sample vapor concentration ( $\text{g/m}^3$ )	Sample equilibrating time (hours)
D1	30	237.46	28.5
	-	233.52	125
	53	314.65	14
D2	77	156.87	4
	-	286.24	120.5
D3	92	201.26	58
	-	229.13	122
	-	170.05	36
	102	137.67	147
D4	131	75.13	8
D5			
D6	No stock solution sample was prepared/analyzed.		
D7	137/288	169.37	36
	-	146.42	144

### 3.2.2 Salts and Alcohol

The effect of salt injection on TCE volatilization was studied using NaCl solutions. NaCl solutions were selected because of its relative small molecular size, and ability to stay in solution (i.e. not precipitate) in the presence of carbonates. CaBr<sub>2</sub> has been used by other researchers in saturated media (Johnson et al., 2004), but Ca<sup>+2</sup> can precipitate in the presence of CO<sub>2</sub> from soil air in unsaturated media. Several NaCl concentrations were tested (0 M, 0.26 M, 0.60 M, 1.71 M or 4.28 M). A [NaCl] value of 0.26 M (15,000 mg/L TDS) is classified under brackish waters, which are significantly less saline than seawater ranging from 1000 to 20,000 mg/L. A [NaCl] value of 0.60 M (35,000 mg/L TDS, seawater) is classified under saline waters, which have salinities similar to or greater than that of seawater. [NaCl] values of 1.71 M (100,000 mg/L TDS) and 4.28 M (250,000 mg/L TDS) are classified under brines, which are waters that are significantly more saline than seawater (Drever, 1988). NaCl was purchased as sodium chloride crystalline certified ACS from Fisher Scientific.

CaSO<sub>4</sub> and CaCl<sub>2</sub> were also used, but only for air permeability tests. These salts were used because they contribute to salinity in soils, which may induce flocculation and restructuring of soil particles, therefore enhancing soil permeability (Walworth, 2006). On the contrary, high concentrations of NaCl may cause sodicity, which in turn causes soil dispersion and clay platelet and aggregate swelling (Pearson, 2009), therefore reducing soil permeability (Section 2.5). CaSO<sub>4</sub> was purchased as -325 mesh 99%, from Sigma Aldrich. It was used at a concentration of 0.005 M (680.67 mg/L) as suggested for hydraulic conductivity tests to prevent the test sample from getting clogged with entrapped air or migrating fine particles (Klute, 1986). CaCl<sub>2</sub> was purchased from Acros Organics (Fisher Scientific) as Anhydrous Powder 96% pure. It was used at two concentrations: 0.06 M (6,658.68 mg/L) and 0.60 M (66,586.80 mg/L).

Among the alcohols considered (Table 3.5), methanol was selected for the study as the testing alcohol because it is smaller than the other alcohols, readily biodegradable in soil and water with an ability to evaporate quickly from soil and has a low cost (Chawla et al., 2001). MeOH was purchased as HPLC Grade 0.2 micron filtered from Fisher Scientific.

**Table 3.5. Alcohols considered and their properties.**

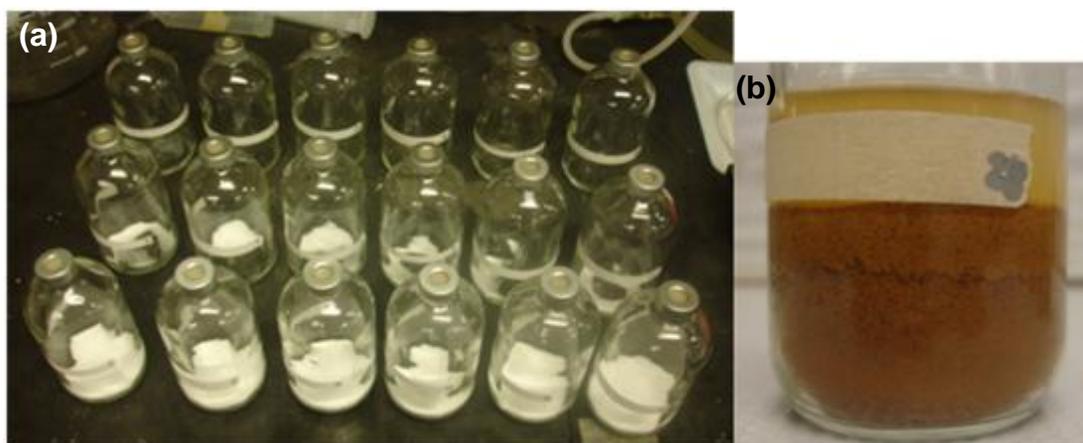
<b>Alcohol</b>	<b>M.W. (g/mol) <sup>1</sup></b>	<b>Vapor pressure @ 20°C (kPa) <sup>1</sup></b>	<b>Specific Gravity (Water = 1) <sup>1</sup></b>	<b>Viscosity @ 25°C (cP) <sup>2</sup></b>
<b>Isopropyl alcohol (99%)</b>	60.1	4.4	0.785	2.04
<b>Ethanol</b>	46.07	5.7	0.789	1.07
<b>Methanol</b>	32.04	12.3	0.792	0.54
<b>Acetone</b>	58.08	24	0.79	0.31

<sup>1</sup> ScienceLab.com, 2008

<sup>2</sup> Diversified Enterprises, 2008

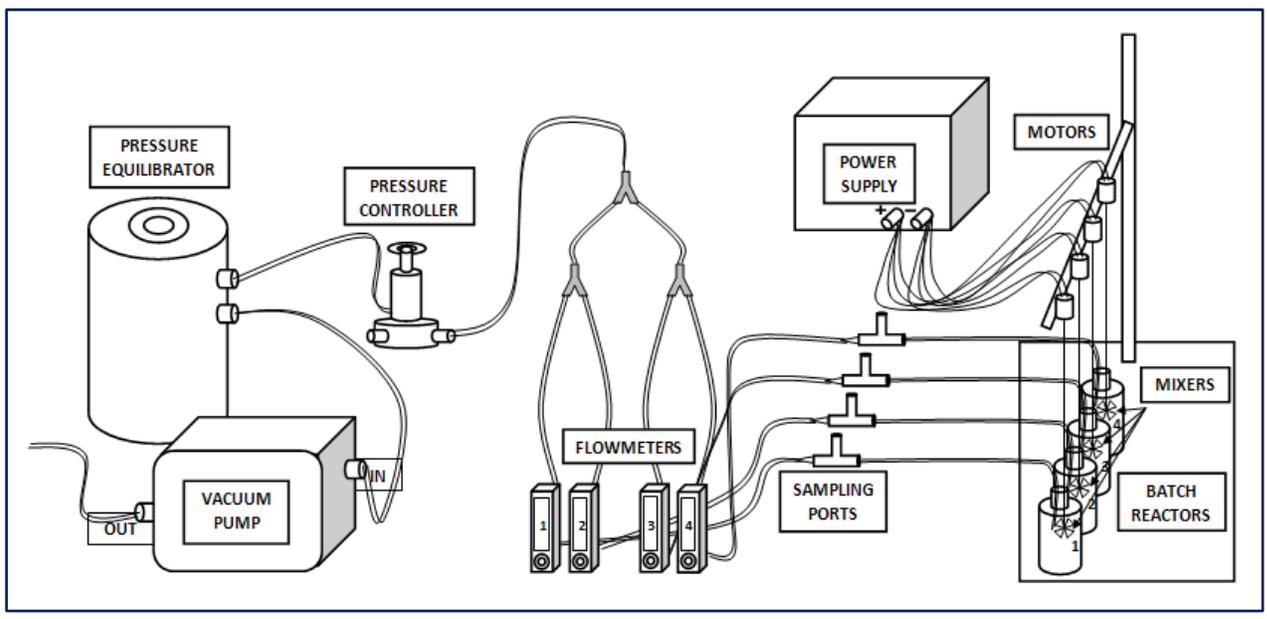
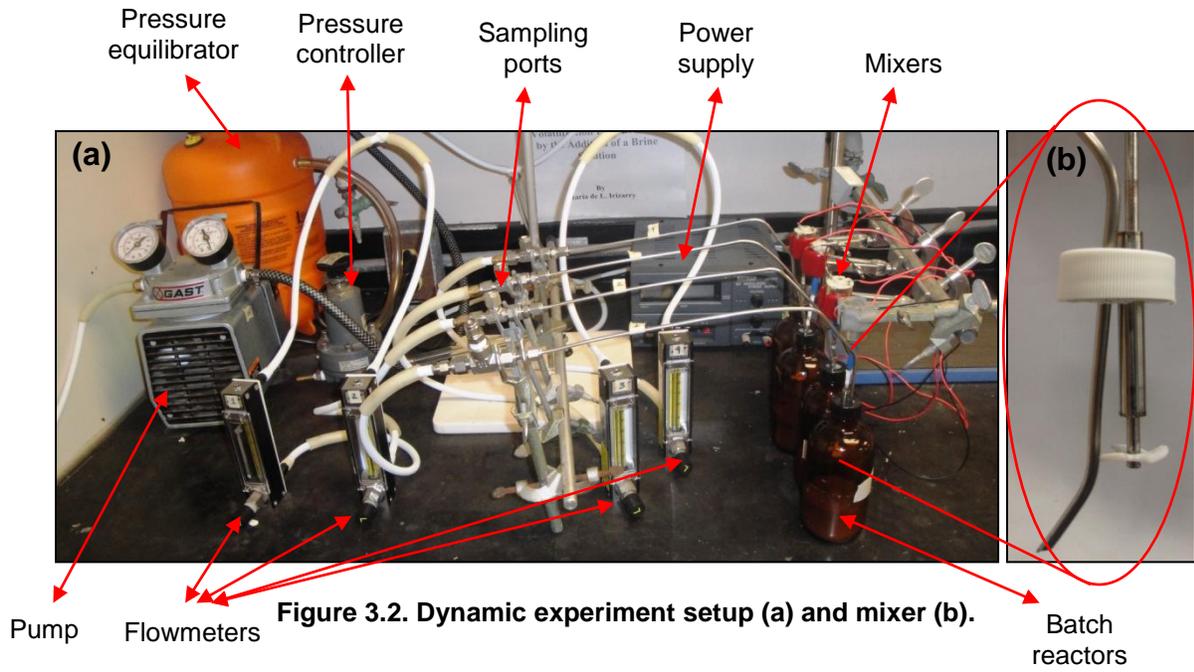
### 3.3 Batch and Flux Reactor Experiments

Static batch and dynamic flux reactors were used to determine the effect of brines and alcohols on the TCE equilibrium vapor concentrations and rates of volatilization. Static reactors were used to assess the volatilization levels under no-flow conditions. Dynamic flux reactors assessed volatilization mass transfer under vapor extraction conditions. Static batch reactors involve adding salt and TCE NAPL to a TCE aqueous solution in 150-mL closed crimp-top glass vials (serum clear-glass bottles made from Type I borosilicate glass and bought from Wheaton Science Products), and measuring the headspace concentration through time. After capping the vials, reactors were left still until sampling was done at specific times. These experiments were conducted without and with clays. The detailed procedure is explained in section 3.3.1.1. Static batch reactors are shown in Figure 3.1.



**Figure 3.1. Static batch experiment: Vials with measured amount of salt ready for tests without clay (a), vial from a test with clay (b).**

Dynamic flux reactors involved adding salt, alcohol and TCE NAPL to TCE aqueous solutions, TCE solution with saturated clay, or to unsaturated clay with 15% moisture content. These experiments involved sweeping the air within the headspace of the flux chambers and monitoring TCE concentrations in the sweeping air. Each flux chamber (Figure 3.2) was contained within a 250-mL amber bottle (amber Type III soda-lime glass bottles bought from Wheaton Science Products) fitted with a headspace mixer and an outlet tube. The mixer (Figure 3.2b) was made-up of handcrafted PTFE blades connected to a shaft and motor. The outlet tube was connected to a vacuum pump through flow controlled meters, a pressure regulator and a pressure equilibration tank (Figure 3.3). Air was swept through the headspace of the flux chamber at 7.5 mL/min and TCE vapors were extracted from an inline sampling port. These experiments provided information on the rate of TCE volatilization. The detailed procedure is described in section 3.3.1.2.



**Figure 3.3. Dynamic experiment diagram.**

### 3.3.1 Batch and Dynamic Flux Reactor Experiments Procedure

Several static and dynamic flux reactor experiments were conducted under different treatments (Table 3.6 and Table 3.7). These treatments included different salt concentrations, presence or absence of clay, methanol and TCE NAPL, and saturated clay TCE-solution.

**Table 3.6. Summary of experimental treatments for static batch experiments.**

Condition	Sample time (hours)	Experiment ID	# Reactors	NaCl (M)	TSSS <sup>1</sup>	Clay	Clay Condition <sup>2</sup>	NAPL (1 mL)	10% MeOH
Static kinetic	1, 3, 6, 12, 24, 48, 60, 72, 84, 96	S1	10	0.0	@			x	
			10	0.26	@			x	
			10	0.60	@			x	
			10	1.71	@			x	
			10	4.28	@			x	
		S2	10	0.0	@			x	
			10	0.26	@			x	
			10	0.60	@			x	
			10	1.71	@			x	
			10	4.28	@			x	
	1, 3, 6, 12, 24, 48, 60, 72, 84, 96, 120	S3	11	0.0	@			x	
			11	0.26	@			x	
			11	0.60	@			x	
			11	1.71	@			x	
			11	4.28	@			x	
Static kinetic with clay	1, 3, 6, 12, 24, 48, 60, 72, 84, 96, 120	S4 (1 & 2)	11	0.0	@	x	Sat	x	
			11	0.60	@	x	Sat	x	
			11	4.28	@	x	Sat	x	
Static equilibrium	120	E1	2	0.0	SV=110				
			2		SV=506				
			2		SV=990				
			2	0.60	SV=110				
			2		SV=506				
			2		SV=990				
			2	4.28	SV=110				
			2		SV=506				
			2		SV=990				

**Table 3.7. Summary of experimental treatments for dynamic flux experiments.**

Condition	Sample times (hours)	Experiment ID	# Reactors	NaCl (M)	TCE C <sub>0</sub> (g/m <sup>3</sup> )	Clay	Clay Condition <sup>2</sup>	NAPL (1 mL)	10% MeOH	
Dynamic flux	0, 0.33, 0.67, 1, 1.5, 2, 3, 6, 12, 24, 48, 60, 72, 84, 96, 120	D1	2	0.0	159.30			x		
			2	0.60	185.57			x		
			2	4.28	238.73			x		
		D2	2	0.0	263.35					
			2	0.60	103.60					
			2	4.28	76.35					
		D3	2	0.0	110.51	x	Sat	x		
			2	0.60	78.27	x	Sat	x		
			2	4.28	71.12	x	Sat	x		
		D4	2	0.0	65.30			x	x	
		D5	2	0.0	25.85				x	
		D6	2	0.0	73.87	x	Sat	x	x	
		D7	2	0.60	105.66	x	Sat	x	x	
		D8	2	0.0	120.98	x	Unsat	x		
			2	0.60	72.92	x	Unsat	x		
			2	4.28	63.96	x	Unsat	x		
D9	2	0.0	196.26	x	Unsat	x	x			
D10	2	0.60	159.66	x	Unsat	x	x			

<sup>1</sup>TSSS = TCE Saturated Stock Solution. @ = solution at TCE solubility ( $\approx 1100$  mg/L). Specific values (SV) refer to TCE solution concentration used by diluting the TSSS to 110, 506 and 990 mg/L.

<sup>2</sup>Sat = saturated, Unsat = unsaturated.

### 3.3.1.1 Static Batch Reactor Experiments

The reactors for these experiments (Figure 3.4) were prepared by weighting the required amount of NaCl in each 150-mL vial (headspace of 100 mL) to achieve the desired sodium chloride concentration (0 M, 0.26 M, 0.60 M, 1.71 M or 4.28 M), and adding 50 mL of the TCE saturated stock solution (TSSS). Vials were vibrated for 1 minute to mix the solution using a Vortex-Genie 2 with a pop-off cup from Scientific Industries, Inc. One milliliter (1 mL) of TCE NAPL was added. Vials were sealed with crimp caps and left still before sampling. The reactors were placed inside an

environmental chamber until sampling. The environmental chamber maintained a temperature of 20.5 °C ( $\pm$  0.5), using a NESLAB Digital One RTE 10 Chiller Recirculating Water Bath Circulator from Thermo Scientific Corporation. Changes in soil volatilization through time in static reactors were measured by sampling reactors at 1 hr, 3 hrs, 6 hrs, 12 hrs, 24 hrs, 48 hrs, 60 hrs, 72 hrs, 84 hrs and 96 hrs (S1-S2, Table 3.6). An experimental replicate in which the reactors were also sampled at 120 hours (S3, Table 3.6) was also conducted.



**Figure 3.4. Static batch reactors: Vials with measured amount of salt (a), reactors with three different sodium chloride concentrations during test (b).**

A set of static aqueous batch reactors at equilibrium was conducted using TCE solution concentrations below solubility (E1, Table 3.6). These experiments were similar to S1 – S3, except no TCE NAPL was added and the TSSS was diluted below solubility levels at three different concentrations (110 mg/L, 506 mg/L and 990 mg/L) and added to vials containing the required amount of NaCl to reach the following concentrations: 0 M, 0.60 M, and 4.28 M. Vials were closed with crimp caps and vibrated with Vortex-Genie 2 for 1 minute. The reactors were placed inside the environmental chamber. Samples were taken at 120 hours. Duplicates were prepared for each treatment, for a total of 18 vials.

Static batch reactors with clay (S4, Table 3.6; Figure 3.5) were prepared by packing 52.4 g of dry clay in 3 layers by vibration with Vortex-Genie 2 for 10 seconds each layer, adding 50 mL of TSSS (with [NaCl] = 0 M, 0.60 M or 4.28 M) and then injecting 1 mL of TCE NAPL at mid height of the solution-saturated clay. Vials were then sealed,

similarly to tests S1–S3 and left still before sampling. The reactors were placed inside an environmental chamber as explained above. Samples were taken at the same time intervals as for experiment S3.



**Figure 3.5. Static batch reactors with clay during test.**

### 3.3.1.2 Dynamic Flux Experiments

Dynamic flux reactors (Figure 3.6) were prepared by weighting the required amount of NaCl in each 250 mL-amber bottle to achieve the desired sodium chloride concentration (0 M, 0.60 M or 4.28 M) and adding 100 mL of the TSSS. The NaCl-TCE solution was shaken prior to the addition of 1 mL of TCE NAPL. Reactors were then connected to the extraction setup and the vacuum pump was started to begin with the air sweep. Samples were taken through the sampling port at: 0 hr, 0.33 hrs, 0.66 hrs, 1 hr, 1.5 hrs, 2 hrs, 3 hrs, 6 hrs, 12 hrs, 24 hrs, 48 hrs, 60 hrs, 72 hrs, 84 hrs, 96 hrs, and 120 hrs (Table 3.7).



**Figure 3.6. Dynamic flux reactors during test.**

Experiment varied in TCE NAPL presence, salinity concentrations, clay presence, methanol content, and clay saturation with TSSS (Table 3.7). For reactors containing saturated clay, the clay was first weighted (104.8 g) and added to the vial in 3 layers, each packed by vibration for 10 seconds, followed by TCE NAPL injection at mid height and TSSS addition at corresponding salt concentration (0 M, 0.60 M or 4.28 M). For reactors containing unsaturated clay, the clay (104.8 g) was first mixed with the TSSS having the corresponding salt concentration to attain 15% (V/V) moisture content, then it was weighted and packed and the TCE NAPL added. For reactors containing methanol (MeOH), the MeOH was mixed with the TSSS and NaCl to reach 10% concentration before adding it to the reactor.

### 3.4 Capillary-based Delivery

Capillary-based delivery (CBD) of reagents was tested in an acrylic column (91.44 cm long and 7.62 cm OD) sealed at the bottom by an acrylic plate assembly (Soil Measurements, Inc.). The acrylic column served as support to the compacted soil and granted clear visibility of the outer walls of the compacted soil, through which

observation data was collected while delivering the solution. The experiment setup is shown in Figure 3.7.



**Figure 3.7. Capillary-based delivery experimental setup.**

The column was packed with Coto Clay according to the compaction parameters on table 3.8. A circular piston was used to pack the soil by giving 4 blows from a height of 15.24 cm above the surface of the soil every 2.54 cm of soil and an additional blow from a height 13.97 cm above the surface of the soil. This was repeated until a height of 71.12 cm of compacted soil was reached. Between each 2.54-cm layer the soil was mixed thoroughly with a multi-nail hammer-head to enhance layer mixing and prevent the formation of horizontal heterogeneities. A CBD tension tube was placed in the center of the column at 71.12 cm, and the soil was packed using a similar packing hammer as the one used to pack the soil below 71.12 cm, but having a 2.54 cm-drilled hole in the center to accommodate the tension tube. A total packing height of 78.74 cm was attained. The densities attained in the tests are included in Table 4.4 in the results. The packing of the clay is expected to increase density relative to the density of an undisturbed sample, therefore, reducing its permeability.

**Table 3.8. Compaction parameters for CBD tests.**

Parameters	Value	Unit
# layers	31	-
# blows	4.83	-
Piston weight	3.05	kg
Free fall height	15.24	cm
Volume	$3.5 \times 10^{-3}$	$m^3$
Compaction energy	19634.02	$kg \cdot m/m^3$

The tension tube placed at 71.10 cm of the soil column was used to deliver the reagent solution to the clay soil. It was comprised of a 40- $\mu$ m stainless-steel porous membrane cup (0.32 cm OD x 2.53 cm length) attached to a 30-cm stainless steel tube (0.32 cm OD) (Figure 3.8). The 40- $\mu$ m membrane is used to compensate for capillary forces of the media, water, and TCE, and to improve the delivery of reagents to low permeability areas in unsaturated regions. A stainless steel porous membrane was selected because it does not react with organic contaminants, and the pore-size would maximize delivery to low-permeability areas having pores smaller than 40  $\mu$ m. Plastic tubing was connected to the stainless steel tube to deliver the solution from the solution reservoir. The source of the solution was set in a 25-ml burette (Figure 3.7)-. A constant solution level was always maintained at the 25-ml mark in the burette. The delivery tension tube was saturated and connected to the solution prior to placement in the soil.



**Figure 3.8. Tension tube.**

The distance between the 25-mL constant level mark and the solution outflow point at the porous membrane was varied to assess the effect of capillary and gravity forces on the uniformity of the solution delivery: Test A and D used a solution level at the same height as the bottom of the porous membrane (Figure 3.9 a); Test B used a solution level set at 10cm above the bottom of the porous membrane (Figure 3.9 b); Test C set the solution level at 10 cm below the bottom of the membrane cup (Figure 3.9 c). Test C

assessed the effect of capillary-based delivery, whereas Test B assessed the effect of gravity-fed delivery. Distilled water was used in experiments A, B and C. Test D was done using a 0.60 M solution of NaCl leveled at the same height as the porous membrane. Experiments for each condition were repeated 3 times.

(a)



(b)



(c)

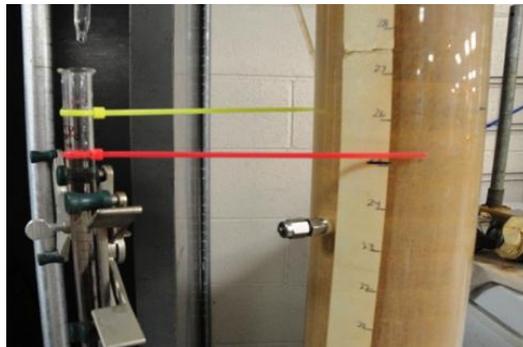
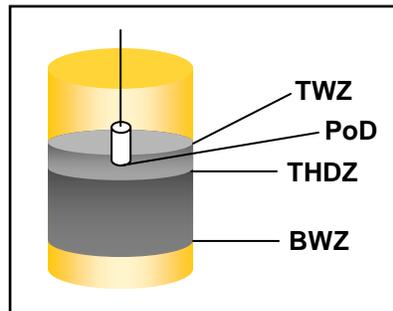


Figure 3.9. Capillary-based Delivery setup: Tests A and D (a), Test B (b), Test C (c).

Each test run used 175 mL of the solution. Once this amount was used, the tests were stopped and the time it took to deliver the solution was recorded. The dimensions of the wetted area were measured (Figure 3.10) and the water content within that area was measured gravimetrically. Other observations taken include: the time at which the solution reached the column wall, the volume of solution used up to this time, and the time and quantity of solution it took to complete a circumference. These observations were used to characterize the uniformity and homogeneity of the wetted distribution.



**Figure 3.10. Wetted distribution variables; TWZ = Top of wetted zone; PoD = Point of discharge; THDZ = Top of homogeneously distributed zone; BWZ= Bottom of wetted zone.**

### 3.5 Soil-Air Permeability Measurements

To assess the behavior of air flow in clay as a function of salt content, tests were designed and conducted to measure the air permeability of the clay. The method is modified from the Recommended Laboratory Method (Dane & Topp, 2002).

Air permeability of the clay was measured at different water contents, NaCl, CaSO<sub>4</sub> and CaCl<sub>2</sub> concentrations. The air-permeability testing setup (Figure 3.11) consisted of an air-delivery system and a soil compartment chamber. The air-delivery system supplied air from a pressurized air tank. The airflow is regulated by a pressure regulator (Siemens Moore, Model 44-50) and monitored through a flow meter (Manostat, Model 36-541-305). For wet soils, air was humidified by passing through an air-washing bottle to limit soil-water evaporation. Air was passed through a soil compartment chamber,

consisting of the soil sample (7.62 cm length, 7.62 cm ID) embedded in a large column (30.48 cm length on both sides of soil sample, 7.62 cm ID). The large columns on both sides of the soil sample served to eliminate radial pressure differential at the entrance and exit of the soil sample.

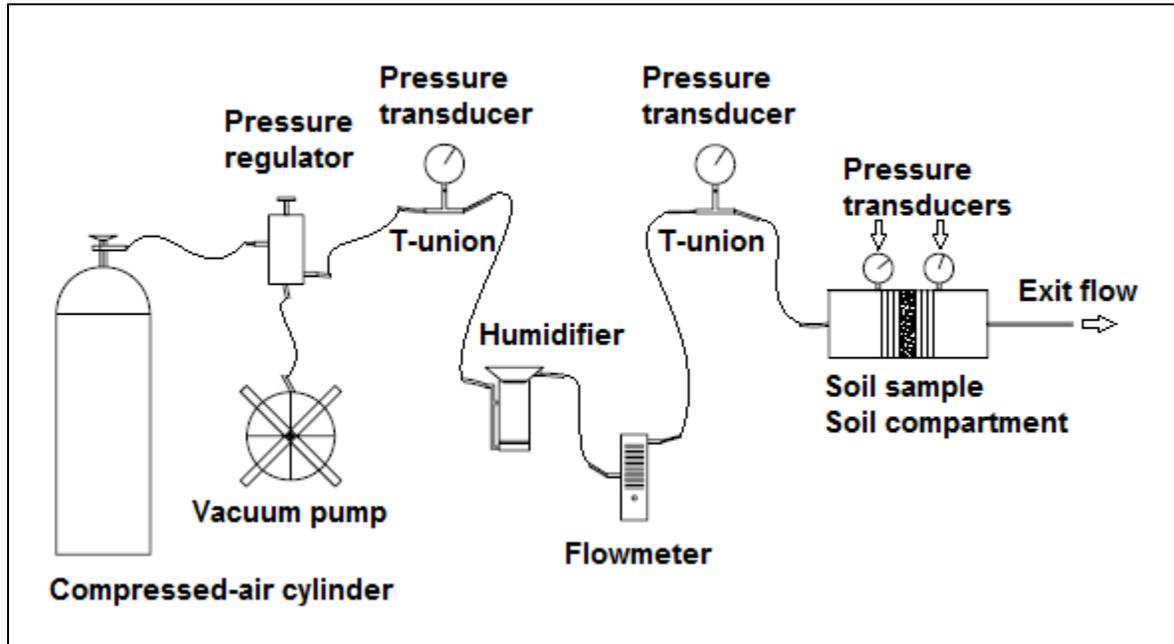


Figure 3.11. Air permeability testing setup diagram.

The soil sample was packed using the compaction parameters on Table 3.9, which were selected to maintain a compaction-energy of 19,634.02 kg-m/m<sup>3</sup>.

Table 3.9. Compaction parameters for air permeability tests.

Parameter	Value	Unit
# layers	3	-
# blows	14.53	-
Piston weight	1.05	kg
Free fall height	15.24	cm
Volume	$3.57 \times 10^{-4}$	m <sup>3</sup>
Compaction energy	19634.01	kg-m/m <sup>3</sup>

For the first tests (Tests 1 through 5) the clay was used dry or thoroughly mixed with distilled water or 4.28 M NaCl solution at desired moisture content before packing. For tests 6 through 13, the clay was packed and then saturated with the corresponding solution by connecting a hose to the bottom of the column, that was fed with a peristaltic pump (Cole Parmer-Masterflex 7553-70) at approximately 0.5 mL/min, and another hose to the top for exit of the saturating solution, with exit located above the top of the column to prevent negative pressure. Enough solution was prepared to supply 5 times the pore volume of the soil column. Solution was de-aerated with nitrogen. After saturation, each soil-core was de-saturated to reach two different moisture contents for two different tests. A 0.005 M CaSO<sub>4</sub> solution was used, as the suggested test fluid for hydraulic conductivity tests to prevent the test sample from getting clogged with entrapped air or migrating fine particles (Klute, 1986). Other solutions used included 0.005 M CaSO<sub>4</sub>, 0.60 M CaCl<sub>2</sub>, 0.60 M CaCl<sub>2</sub>, and 0.06 M CaCl<sub>2</sub>.

When the soil sample was packed to the desired bulk density and water contents, a constant air flow was passed through the soil, and pressure drops across the soil sample were monitored in pressure transducers (Model 236PC, Micro Switch) located upstream and downstream of the soil sample. The packing of the clay is expected to increase density relative to the density of an undisturbed sample, therefore, reducing its permeability.

Air permeabilities ( $K_a$ ) were estimated using:

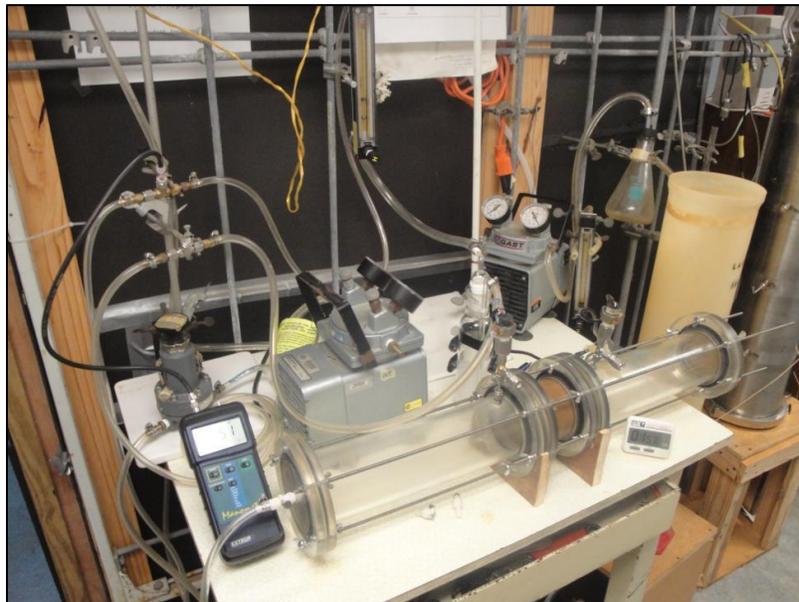
$$K_a = \frac{q_a \cdot \eta_a}{\nabla P_a} \quad 3.1$$

where  $q_a$  is the volumetric air flow rate per unit area ( $\frac{cm}{min}$ ),  $\nabla P_a$  is the pressure gradient ( $\frac{lb}{cm^3}$ ) across the soil sample, and  $\eta_a$  the dynamic air viscosity ( $\frac{lb \cdot min}{cm^2}$ ) at the tested temperature (Klute, 1986). It was assumed that pressure changes are small and that air densities remain constant at those pressure changes, therefore, the flow is described as incompressible (Munson et al., 2002).

Measurements were completed for dry soil and wet soil at five different flow rates (2897, 6469, 10227, 14257 and 18296 mL/min). Thirteen tests were run as detailed in Table 3.10. The test setup is shown in Figure 3.12.

**Table 3.10. Air permeability experiment treatments.**

Test	Treatments	% Moisture content	Bulk density (g/cm <sup>3</sup> )
1	Dry clay - original	0	1.14
2	Unsaturated clay with distilled water	15	1.30
3	Dry clay - replicate	0	1.16
4	Unsaturated clay with 4.28 M NaCl solution	11	1.29
5	Unsaturated clay with distilled water	12	1.26
6	Unsaturated clay with 0.005 M CaSO <sub>4</sub> solution	26	1.23
7	Unsaturated clay with 0.005 M CaSO <sub>4</sub> solution	14	1.23
8	Unsaturated clay with 0.005 M CaSO <sub>4</sub> 0.60 M CaCl <sub>2</sub> solution	32	1.25
9	Unsaturated clay with 0.005 M CaSO <sub>4</sub> 0.60 M CaCl <sub>2</sub> solution	27	1.25
10	Unsaturated clay with 0.60 M CaCl <sub>2</sub> solution	30	1.24
11	Unsaturated clay with 0.60 M CaCl <sub>2</sub> solution	27	1.24
12	Unsaturated clay with 0.06 M CaCl <sub>2</sub> solution	27	1.24
13	Unsaturated clay with 0.06 M CaCl <sub>2</sub> solution	23	1.24



**Figure 3.12. Air permeability test setup.**

### 3.6 SVE Testbed Design

Enhanced TCE vapor extraction from unsaturated clay soils of low permeability using cycled injection of brine/alcohol solution was tested in a laboratory-scale soil testbed packed with TCE-contaminated soil and instrumented with vapor extraction and venting wells, reactant delivery membranes, pressure sensors, a water content reflectometer, and a TCE vapor sampling port. Although the testing was the subject of another study (Lorenzo, 2014), experiments were conducted in a testbed designed and developed under this research.

The design of the SVE testbed was based on the need to develop a SVE extraction system that allows for cycled capillary-based delivery of reactants into unsaturated clay and extraction of the vapor phase from the soil. Because of equipment limitations, the system was designed in a cylindrical stainless steel column (100 cm long and 19 cm in diameter) that was available at the Environmental Engineering laboratory of UPRM. The column integrated stainless steel end caps, and contained 16 ports distributed along the length and circumference of the column. The ports were distributed in 4 rows located at 20 cm, 40 cm, 60 cm, and 80 cm above the bottom of the column (Figure 3.13). Each row accommodated 4 ports equally spaced around the circumference. The design integrates the following components:

- Unsaturated clay soil packed at similar densities as those used for air permeability and CBD experiments.
- SVE system
- Capillary-based delivery system
- Air-venting system
- Surface cap to prevent atmospheric short circuiting of air
- Constant head boundary at the bottom of the column
- TCE NAPL - contaminated soil
- Instrumentation to monitor concentration, pressure and flow rates

The final design and development of the testbed are described in the Results section.



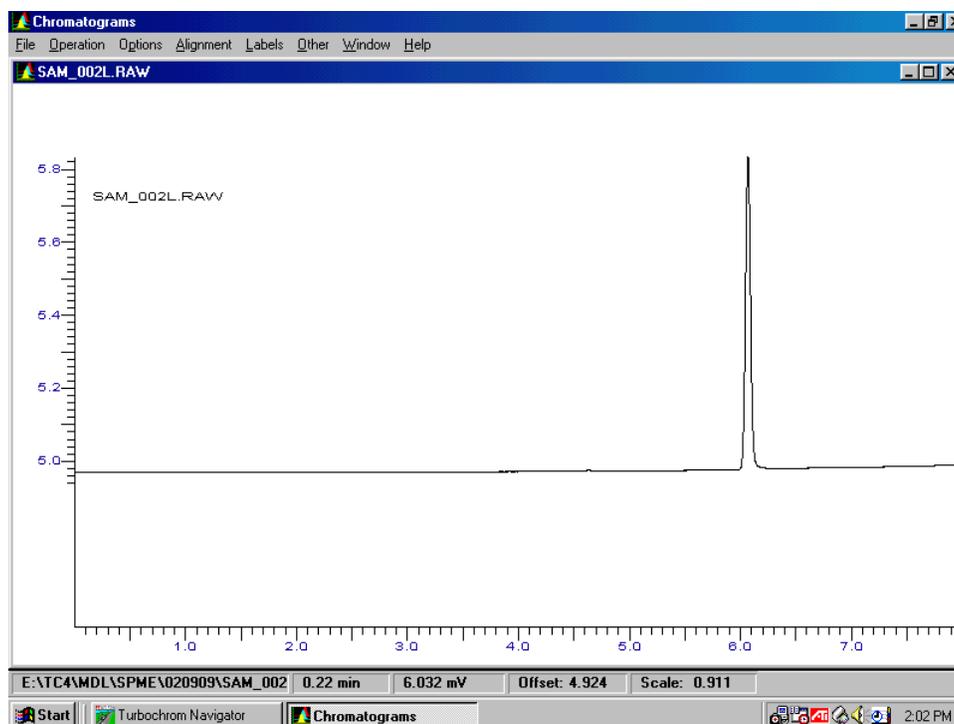
**Figure 3.13. Preliminary test bed setup: stainless steel column.**

### 3.7 Sampling and Analytical Methods

In the static batch reactors, samples were extracted through the septa located in the cap of the vials. In the dynamic flux reactors, samples were extracted through the septa in the union tee tube fitting located in the flow path between each reactor and the vacuum pump.

Vapor samples were extracted using a Solid Phase Micro Extraction (SPME) fiber (100  $\mu\text{m}$  polydimethylsiloxane coating) supported in a fiber holder (for use with manual sampling, both from SUPELCO). The sample extraction consisted of inserting the SPME fiber through the septa for 3 minutes to allow for vapor adsorption, followed by desorption into a Gas chromatograph (GC) for 5 minutes. A Perkin Elmer GC equipped with a flame ionization detector (FID) and a Dimethylpolysiloxane column (30 m x 0.53 mm x 5  $\mu\text{m}$ ) was used for the analysis. It was operated starting at a temperature of 40°C for 2 minutes, and increasing at a rate of 20°C/min to 160°C with helium as the

carrier gas (~4 mL/min). The analysis run time was 8 minutes. Under this analytical condition TCE showed a retention time of  $\pm 6.20$  minutes (Figure 3.14).



**Figure 3.14. Chromatogram showing a peak for TCE at  $\pm 6.20$  minutes.**

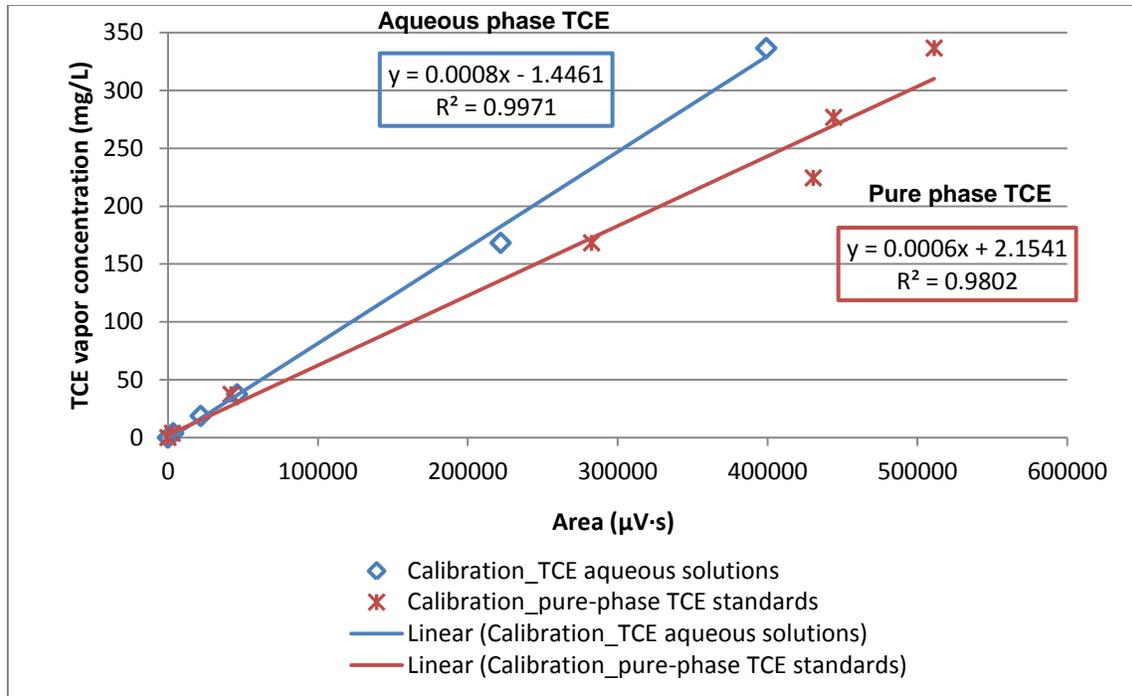
### 3.7.1 Vapor Standards Preparation and GC Calibration

Vapor standards were prepared from liquid standards, using the TCE saturated stock solution (TSSS) assumed to be near solubility (1100 mg/L). Vapor standards were prepared by diluting the TSSS in 100 mL (250 mL-vial) to the following aqueous concentrations: 0 mg/L, 11 mg/L, 55 mg/L, 110 mg/L, 495 mg/L and 990 mg/L. The vials were closed and left still for approximately 24 hours to equilibrate the gas and water phases. After equilibrium, the headspace (150 mL) was sampled and analyzed using the SPME method described above. Headspace concentrations ( $C_{\text{headspace}}$ ) in the vials were calculated using Equation 2.2 (in section 2.2.1.2) and solving for  $C_{\text{headspace}}$ :

$$C_{headspace} = \frac{C_{solution}V_w}{\frac{V_w}{K_h} + V_a} \quad 3.2$$

where  $C_{solution}$  and  $V_w$  are the aqueous TCE concentration and solution volume, respectively, added to the 250 mL-vial.  $K_h$  is Henry's constant and  $V_a$  is the headspace volume (150 mL). The  $K_h$  value used for TCE was 0.34 (Table 2.1). The TCE aqueous concentrations used above (0 mg/L, 11 mg/L, 55 mg/L, 110 mg/L, 495 mg/L and 990 mg/L) yielded the following TCE vapor concentrations (TCEvc): 3.74 g/m<sup>3</sup>, 18.70 g/m<sup>3</sup>, 37.40 g/m<sup>3</sup>, 168.30 g/m<sup>3</sup> and 336.60 g/m<sup>3</sup>, respectively.

Vapor standards were also prepared by volatilizing a certain volume of TCE NAPL in 1 L-glass bottles. Addition of 0 μL, 2.6 μL, 25.6 μL, 115.3 μL, 153.7 μL, 189.6 μL and 230.5 μL of TCE (density: 1.46 mg/L) yielded vapor phase concentrations of: 0 g/m<sup>3</sup>, 3.74 g/m<sup>3</sup>, 37.40 g/m<sup>3</sup>, 168.30 g/m<sup>3</sup>, 224.40 g/m<sup>3</sup>, 276.80 g/m<sup>3</sup> and 336.60 g/m<sup>3</sup>. Typical GC calibration curves for the methods using aqueous solutions and TCE NAPL (Figure 3.15) show that high response areas are generally observed for standards prepared using TCE NAPL. The higher-response areas for the pure-TCE standards are attributed to higher sorption capacity of SPME fiber in the absence of water vapor.



**Figure 3.15. Example of calibrations using TCE aqueous solution and TCE NAPL for preparation of standards.**

### 3.8 Data Analysis

Static and dynamic flux reactor experiments yielded temporal concentration data at equilibrium and non-equilibrium conditions under the different treatments tested. Temporal concentrations were analyzed comparatively, analytically, and statistically to determine the effect of the tested treatments on the TCE volatilization behavior and rates.

For dynamic flux reactors, TCE<sub>vc</sub> were plotted versus time to observe effects of treatments on TCE volatilization and to calculate percentage of extracted mass. To calculate the percentage of extracted mass we need to know the initial mass of TCE in the reactor. Given that the system's total TCE mass includes TCE mass in vapor and liquid phases, the total initial TCE mass can be expressed as:

$$M_{i\text{TCE total}} = M_{i\text{TCE gas}} + M_{i\text{TCE solution}} \quad 3.3$$

where  $M_{i\ TCE\ total}$  is the total initial TCE mass,  $M_{i\ TCE\ gas}$  is the initial TCE mass in vapor phase and  $M_{i\ TCE\ solution}$  is the initial TCE mass in solution. In terms of initial concentration it could be expressed as:

$$M_{i\ TCE\ total} = C_{i\ TCE\ gas} \cdot V_{headspace} + C_{i\ TCE\ solution} \cdot V_{solution} \quad 3.4$$

where  $C_{i\ TCE\ gas}$  and  $C_{i\ TCE\ solution}$  are TCE concentrations in vapor and liquid phases, respectively, and  $V_{headspace}$  and  $V_{solution}$  are, respectively, the volumes of the headspace and solution in the reactors.

Taking Equation 2.2 (Henry's Law) and substituting into Equation 3.4, we get:

$$M_{i\ TCE\ total} = C_{i\ TCE\ gas} \cdot V_{headspace} + \frac{C_{i\ TCE\ gas}}{K_H} \cdot V_{solution} \quad 3.5$$

where  $K_H$  is Henry's law constant for TCE.

Rearranging Equation 3.5 we get:

$$M_{i\ TCE\ total} = C_{i\ TCE\ gas} \left( V_{headspace} + \frac{V_{solution}}{K_H} \right) \quad 3.6$$

where the terms in parenthesis can be grouped in a constant factor:

$$M_{i\ TCE\ total} = C_{i\ TCE\ gas} \cdot f \quad 3.7$$

This factor ( $f$ ) is dependent on Henry's law constant for TCE and on the headspace and solution volumes in the flux reactors. Knowing that Henry's dimensionless law constant for TCE at 20°C is 0.34 (Table 2.1), and that the volume of solution added to the flux reactors is 100 mL or 0.10 L (Section 3.3.1.2) and the remaining volume of headspace is 150 mL (0.15 L), this factor is calculated as:

$$f = 0.15 L + \frac{0.10 L}{0.34} = 0.44 L \quad 3.8$$

By substituting this factor into equation 3.7, the initial total TCE mass in the flux reactors containing TSSS with no TCE NAPL is obtained as:

$$M_{i TCE total}(mg) = C_{i TCE gas} \left( \frac{mg}{L} \right) \cdot 0.44(L) \quad 3.9$$

For reactors that contained TCE NAPL, we add the mass of TCE in 1 mL of TCE NAPL, which is obtained by multiplying 1 mL by the density of TCE (1.46 g/mL) and converting to milligrams, to Equation 3.9 and get:

$$M_{i TCE total}(mg) = \left( C_{i TCE gas} \left( \frac{mg}{L} \right) \cdot 0.44(L) \right) + 1460 (mg) \quad 3.10$$

For unsaturated flux reactors the TCE initial mass is 1460 mg because only TCE NAPL is added.

Analytical assessment involved using the method of moment analysis of concentration distribution for calculating extracted mass. Equation 3.11 shows the formula used:

$$M_0 = \int_{-\infty}^{\infty} C(x, t) dt = \sum_1^n \left( \frac{C_i + C_{i-1}}{2} \right) (t_i - t_{i-1}) \quad 3.11$$

The cumulative extracted mass was plotted against time to assess the changes in mass extraction during the experiment.

A response time analysis was also conducted, in which response time represents the time it takes to extract a certain percentage of the initial concentration. It involved plotting TCEvc over time from 0 to 6 hours or until there was a notable change in slope. Assuming a first order process and a completely mixed system, an exponential regression was applied to the data yielding a curve of the form:

$$C = C_0 e^{-\lambda t} \quad 3.12$$

where  $C$  is concentration,  $C_0$  is initial concentration,  $\lambda$  is the eigenvalue, which is a characteristic value related to the pneumatic removal of mass from the system and mass transfer limitations between water and air, and  $t$  is time. From this equation, the time it takes for the system to reach a percent removal of the vapor (i.e. response time) can be estimated as (Chapra, 1997):

$$t_\varphi = \frac{1}{\lambda} \ln \frac{100}{100-\varphi} \quad 3.13$$

where  $t_\varphi$  is the response time,  $\lambda$  is the eigenvalue and  $\varphi$  is the fixed percentage of initial mass extracted (Chapra, 1997). Response time formulas for specific vapor removal percentages were obtained by substituting a fixed percentage of initial mass extracted (e.g. 50%) into Equation 3.13. The response time formulas used were included in Table 3.11.

**Table 3.11. Response time formulas.**

Response time (hours)	$t_{25}$	$t_{50}$	$t_{75}$	$t_{90}$	$t_{95}$	$t_{99}$
Formula	$0.288/\lambda$	$0.693/\lambda$	$0.139/\lambda$	$2.3/\lambda$	$3/\lambda$	$4.6/\lambda$

Mass transfer limitations were also analyzed assuming that the headspace of the dynamic flux reactors behaves as a completely mixed system. The temporal concentration response was analyzed using (Chapra, 1997):

$$\frac{dc_v}{dt} + c_v \lambda = \frac{W(t)}{V_a} \quad 3.14$$

where  $\lambda$  is the eigenvalue factor, and  $W(t)$  is the TCE loading function. The loading function ( $W(t)$ ) represents the mass transferred to the headspace from the contaminated matrix. This function is assumed to be related to mass transfer limitations. The loading function is assessed from the experimental data. Assuming there is no degradation in the vapor phase during the experimental period,

$$\lambda = \frac{Q}{V_a} - k \quad 3.15$$

where  $\lambda$  is the integrated eigenvalue,  $\frac{Q}{V_a}$  is the part of the eigenvalue related to the pneumatic mass removal from the system, and  $k$  is the water-air mass transfer coefficient, assuming a first order process and a completely mixed system. It is called an integrated eigenvalue because it involves two different processes: pneumatic mass removal and mass transfer from water to vapor phase. The integrated eigenvalue ( $\lambda$ ) was obtained from the equation of the exponential regression (Equation 3.12) that is applied to the TCEvc data over early time (0 hours to ~6 hours). The pneumatic mass removal term ( $\frac{Q}{V_a}$ ) was calculated from experimental parameters. The water-air mass transfer coefficient ( $k$ ) was subtracted because it is a mass loading into the vapor phase and not a mass removal process. It was calculated by subtracting the integrated eigenvalue ( $\lambda$ ) from the pneumatic mass removal term ( $\frac{Q}{V_a}$ ). Early and late times were determined by the change in slope observed in plotted TCE temporal data: 0 hours to 2, 6 or 12 hours and 2, 6 or 12 hours to 120 hours, respectively. Early and late times were used to identify two periods during vapor extraction: early time represents the period where vapor extraction is mostly influenced by the pneumatic sweeping of the completely-mixed headspace volume, while late time represents the period where vapor extraction is mostly influenced by the TCE mass transfer to vapor phase from water, NAPL and the soil matrix.

Air permeability measurements under the salt/alcohol injection conditions were used to determine the effect of these conditions on the pneumatic properties of compacted clay. Measured air permeabilities were analyzed as a function of water and salt content.

### 3.9 Statistical Analysis

Statistical analysis was performed on TCEvc values for static and dynamic batch experiments to determine the effect of treatments (e.g. NaCl presence). Minitab 15

(Minitab Inc., Version 15) was used to calculate basic statistics. Averages were calculated as a function of time (except for the equilibrium reactors since they were sampled at only 1 time). Comparative statistical analysis involved testing for normal distribution of the data by making a probability plot for each set of data. If the p-value was larger than an alpha ( $\alpha$ ) of 0.05 (corresponding  $\alpha$  to a confidence interval of 95%), the data was assumed to be normally distributed and the two-sample T-test was used to compare replicates of data for significant differences. If the data was non-normal ( $p < 0.05$ ), the average of the replicates were compared for significant difference using Mann Whitney test. If the replicates were statistically similar, an average was calculated, and a normality test is applied to the average data. The average data was then tested for normality. If normally distributed, the student T-test analysis was used to compare averages of the different treatments (time, [NaCl], [TCE], presence of methanol, presence of saturated or unsaturated clays and presence of TCE NAPL). If the averages were statistically different, the Kruskal Wallis or Mann Whitney tests were used to compare the averages of the treatments. The Mann-Whitney is a non-parametric test equivalent to the T-test, and Kruskal-Wallis is a non-parametric test equivalent to ANOVA. With either analysis, the difference between conditions is statistically significant if the p-value is below 0.05, which is the most commonly used  $\alpha$ -level (value between 0% and 100%) or level of significance (Minitab Inc., Version 17).

For statistical significance, p-values were evaluated following Table 3.12, modified from Hooper, 2002.

**Table 3.12. P-value analysis guide.**

$P > 0.05$	No evidence against the null hypothesis. The data appear to be consistent with the null hypothesis.
$0.01 < P < 0.05$	Weak/Moderate evidence against the null hypothesis in favor of the alternative.
$0.001 < P < 0.01$	Strong evidence against the null hypothesis in favor of the alternative.
$P < 0.001$	Very strong evidence against the null hypothesis in favor of the alternative.

## 4 RESULTS AND DISCUSSION

This chapter describes and discusses the results of this research. The discussion evolves from the results and centers on critical questions that led to the formulation of the research hypothesis and objectives (Sections 1.2 and 1.3, respectively). Results from static batch and dynamic flux experiments are evaluated to assess volatilization processes under different sodium chloride concentrations ([NaCl]), with and without non-aqueous phase liquid (NAPL) trichloroethylene (TCE), methanol (MeOH), and clay (saturated and unsaturated). Results from Capillary-based delivery (CBD) tests in compacted clay provide information on flow dispersal characteristics and delivery head optimization. Results from the air permeability tests are used to determine the effect of [NaCl] on the pneumatic properties of the clay and air-flow characteristics.

### 4.1 Air Permeability

Results from air permeability tests (Table 4.1 and Table 4.2) show the magnitude and variability of air intrinsic permeability for different air flows, water contents and salt contents. Average air permeabilities vary from  $8.46 \times 10^{-8}$  ( $\pm 4.22 \times 10^{-9}$ )  $\text{cm}^2$  for an unsaturated soil sample with 0.005 M  $\text{CaSO}_4$  0.60 M  $\text{CaCl}_2$ -solution and water content of 27% to  $7.94 \times 10^{-7}$  ( $\pm 2.38 \times 10^{-7}$ )  $\text{cm}^2$  for an unsaturated soil sample with 0.005  $\text{CaSO}_4$ -solution and water content of 14% (Figure 4.1). Results show higher average air permeabilities for unsaturated soils ( $7.94 \times 10^{-7} \pm 2.38 \times 10^{-7}$   $\text{cm}^2$ ) with 0.005 M  $\text{CaSO}_4$ -solution at 14% wc. The next higher average air permeabilities are for unsaturated soils ( $6.92 \times 10^{-7} \pm 2.98 \times 10^{-8}$   $\text{cm}^2$ ) with 4.28 M NaCl-solution at 11% wc and dry soils ( $6.07 \times 10^{-7} \pm 8.94 \times 10^{-8}$   $\text{cm}^2$ ). Air permeabilities at 12% wc ( $5.31 \times 10^{-7} \pm 3.72 \times 10^{-8}$   $\text{cm}^2$ ) and 15% wc ( $3.65 \times 10^{-7} \pm 3.77 \times 10^{-8}$   $\text{cm}^2$ ) tend to decrease for higher water contents. For tests 11 and 12, both at 27% wc, a  $\text{CaCl}_2$  concentration of 0.60 M yields higher  $K_a$  ( $2.23 \times 10^{-7} \pm 2.57 \times 10^{-8}$   $\text{cm}^2$ ) than a  $\text{CaCl}_2$  concentration of 0.06 M ( $2.11 \times 10^{-7} \pm 3.98 \times 10^{-8}$   $\text{cm}^2$ ). Soils containing both  $\text{CaSO}_4$  and  $\text{CaCl}_2$  yielded the

lowest air permeability values (Test 8:  $9.78 \times 10^{-8} \pm 2.56 \times 10^{-9} \text{ cm}^2$ ; Test 9:  $8.46 \times 10^{-8} \pm 4.22 \times 10^{-9} \text{ cm}^2$ ). This is probably a result of the precipitation of calcium in the system, because this is the solution with the highest mass of calcium per liter. This precipitate clogs the clay pores therefore preventing air flow. The precipitation of calcium was observed on the membranes at the bottom of the soil sample after saturating the sample for tests 8 and 9 (Figure 4.2). The effect of flow rates in air permeabilities varies with water and salt contents. Higher flow rates yield slightly lower  $K_a$  for dry conditions, but tend to increase for higher water contents. For soil containing  $\text{CaSO}_4$  or  $\text{CaCl}_2$ , generally air permeability tends to increase for higher flow rates and decrease for higher water contents. No tendency is observed for soil containing  $\text{NaCl}$ . The slight variations in  $K_a$  as a function of flow may be attributed to air compression effects. Measured pressure changes and other parameters used in the air permeability calculations are included in Appendix A.

**Table 4.1. Intrinsic air permeability ( $\text{cm}^2$ ) for Coto clay with NaCl solution.**

Test		1	2	3	4	5
Treatment	Dry soil	x		x		
	NaCl (M)	0	0	0	4.28	0
	WC (%)	0	15	0	11	12
Flow (ml/min)	2897	$7.66 \times 10^{-7}$	$3.05 \times 10^{-7}$	$5.73 \times 10^{-7}$	$6.46 \times 10^{-7}$	$5.34 \times 10^{-7}$
	6469	$5.64 \times 10^{-7}$	$3.53 \times 10^{-7}$	$5.77 \times 10^{-7}$	$7.26 \times 10^{-7}$	$5.60 \times 10^{-7}$
	10227	$5.81 \times 10^{-7}$	$3.79 \times 10^{-7}$	$4.93 \times 10^{-7}$	$6.86 \times 10^{-7}$	$5.67 \times 10^{-7}$
	14257	$5.62 \times 10^{-7}$	$3.89 \times 10^{-7}$	$4.53 \times 10^{-7}$	$7.08 \times 10^{-7}$	$5.20 \times 10^{-7}$
	18296	$5.61 \times 10^{-7}$	$4.00 \times 10^{-7}$	$4.25 \times 10^{-7}$	$6.95 \times 10^{-7}$	$4.74 \times 10^{-7}$
Average		$6.07 \times 10^{-7} \pm 8.94 \times 10^{-8}$	$3.65 \times 10^{-7} \pm 3.77 \times 10^{-8}$	$5.04 \times 10^{-7} \pm 6.89 \times 10^{-8}$	$6.92 \times 10^{-7} \pm 2.98 \times 10^{-8}$	$5.31 \times 10^{-7} \pm 3.72 \times 10^{-8}$

\*WC = water content of soil

**Table 4.2. Intrinsic air permeability (cm<sup>2</sup>) for Coto clay with CaCl<sub>2</sub> solution.**

Test		6	7	8	9	10	11	12	13
Treatment	CaSO <sub>4</sub> (M)	0.005	0.005	0.005	0.005	0	0	0	0
	CaCl <sub>2</sub> (M)	0	0	0.60	0.60	0.60	0.60	0.06	0.06
	WC (%)	26	14	32	27	30	27	27	23
Flow (ml/min)	2897	2.11 × 10 <sup>-7</sup>	4.48 × 10 <sup>-7</sup>	9.39 × 10 <sup>-8</sup>	7.76 × 10 <sup>-8</sup>	1.52 × 10 <sup>-7</sup>	1.82 × 10 <sup>-7</sup>	1.44 × 10 <sup>-7</sup>	1.96 × 10 <sup>-7</sup>
	6469	1.97 × 10 <sup>-7</sup>	6.73 × 10 <sup>-7</sup>	9.70 × 10 <sup>-8</sup>	8.44 × 10 <sup>-8</sup>	1.85 × 10 <sup>-7</sup>	2.15 × 10 <sup>-7</sup>	2.06 × 10 <sup>-7</sup>	2.49 × 10 <sup>-7</sup>
	10227	1.95 × 10 <sup>-7</sup>	8.43 × 10 <sup>-7</sup>	9.79 × 10 <sup>-8</sup>	8.52 × 10 <sup>-8</sup>	1.95 × 10 <sup>-7</sup>	2.29 × 10 <sup>-7</sup>	2.23 × 10 <sup>-7</sup>	2.73 × 10 <sup>-7</sup>
	14257	1.98 × 10 <sup>-7</sup>	9.58 × 10 <sup>-7</sup>	1.00 × 10 <sup>-7</sup>	8.70 × 10 <sup>-8</sup>	2.04 × 10 <sup>-7</sup>	2.42 × 10 <sup>-7</sup>	2.36 × 10 <sup>-7</sup>	2.95 × 10 <sup>-7</sup>
	18296	2.01 × 10 <sup>-7</sup>	1.05 × 10 <sup>-6</sup>	9.97 × 10 <sup>-8</sup>	8.86 × 10 <sup>-8</sup>	2.09 × 10 <sup>-7</sup>	2.46 × 10 <sup>-7</sup>	2.44 × 10 <sup>-7</sup>	3.10 × 10 <sup>-7</sup>
Average		2.00 × 10 <sup>-7</sup> ± 6.28 × 10 <sup>-9</sup>	7.94 × 10 <sup>-7</sup> ± 2.38 × 10 <sup>-7</sup>	9.78 × 10 <sup>-8</sup> ± 2.56 × 10 <sup>-9</sup>	8.46 × 10 <sup>-8</sup> ± 4.22 × 10 <sup>-9</sup>	1.89 × 10 <sup>-7</sup> ± 2.24 × 10 <sup>-8</sup>	2.23 × 10 <sup>-7</sup> ± 2.57 × 10 <sup>-8</sup>	2.11 × 10 <sup>-7</sup> ± 3.98 × 10 <sup>-8</sup>	2.64 × 10 <sup>-7</sup> ± 4.46 × 10 <sup>-8</sup>

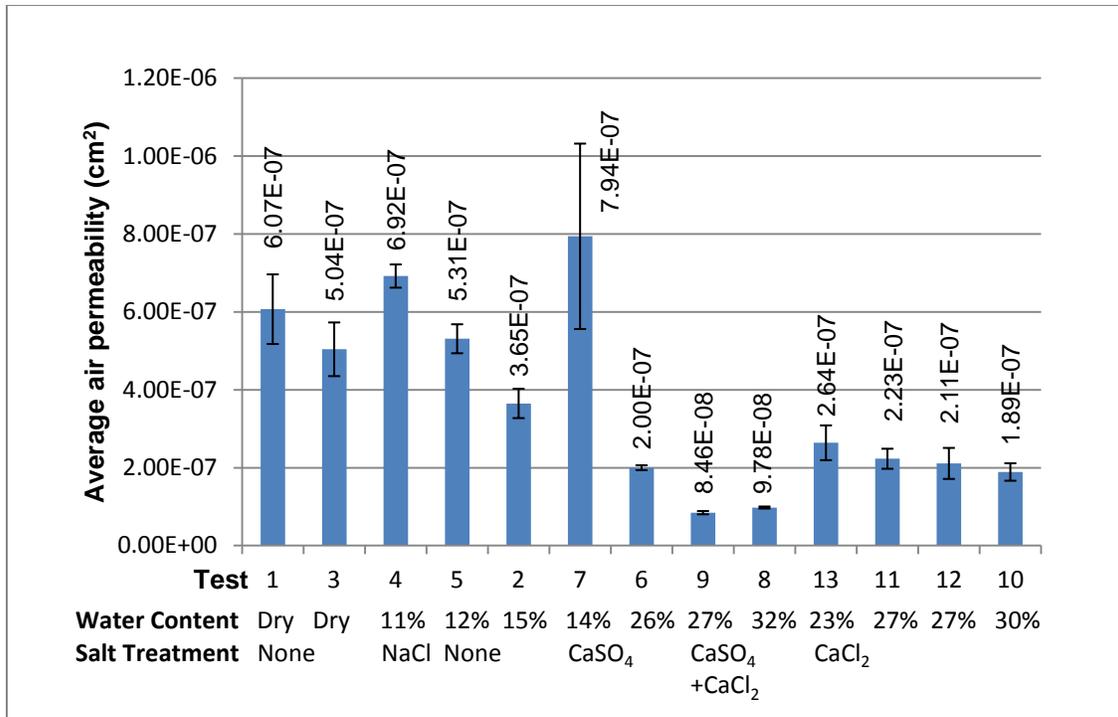


Figure 4.1. Average intrinsic air permeability for Coto Clay. Values shown are the average intrinsic air permeability for the test. Error bars represent 1 standard deviation.

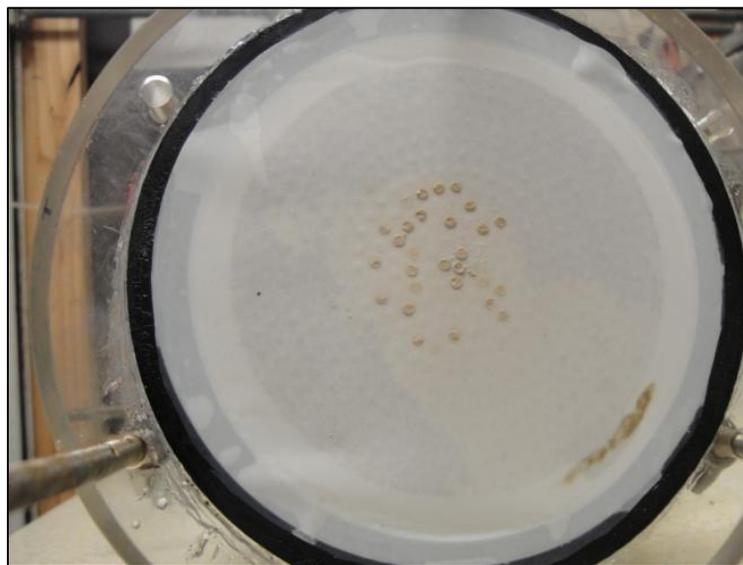


Figure 4.2. Calcium precipitates on membrane at bottom of soil sample (Tests 8 and 9).

Statistical comparison between results are conducted with Minitab Statistical Software (Versions 15 and 16) using the Kruskal Wallis Test, a non parametric test, because for some tests the data showed a non-normal distribution. A p-value smaller than 0.05, is indicative of significant statistical differences between compared data sets. A higher value indicates no significant statistical difference.

Results from the statistical analysis (Table 4.3) show that there is no significant difference between tests at dry conditions (Tests 1 and 3); therefore, the average of the air permeabilities for these two tests is used for further comparisons. There are significant differences ( $p$ -value < 0.05) between air permeabilities at dry (average of tests 1 and 3) and wet (Test 2) conditions indicating that air permeabilities are statistically higher at lower water contents. There is a significant difference when comparing air permeabilities at dry soil conditions (average of tests 1 and 3) to those at unsaturated soil with NaCl (Test 4), in which air permeabilities are higher in the presence of NaCl. There is no significant difference between air permeabilities at dry and wet conditions when comparing with a water content of 12% (Test 5). Comparison of air permeabilities at 11% wc without (Test 5) and with NaCl (Test 4, 12% wc) show significant differences between these treatments, and indicate that air permeabilities are higher in the presence of NaCl. Indeed, results indicate that air permeability for soil having NaCl is statistically higher than the air permeabilities estimated for any water or salt content, except for unsaturated soil with 0.005 M CaSO<sub>4</sub> at 14% wc (Test 7), which has the highest air permeability between all treatments. There is no significant difference between air permeabilities at dry soil conditions (average of tests 1 and 3) and unsaturated soil with 0.005 M CaSO<sub>4</sub> at 14% wc (Test 7). When comparing air permeabilities in unsaturated soil at 15% wc (Test 2) with air permeabilities in unsaturated soil at 14% wc but in presence of 0.005 M CaSO<sub>4</sub> (Test 7), there is a significant difference where air permeabilities are higher in presence of salt. But there are no significant differences when comparing air permeabilities from Test 7 with air permeabilities from Tests 4 and 5, which have 14% and 12% wc, respectively, and Test 4 has presence of 4.28 M NaCl.

**Table 4.3. Statistical comparison results between air permeability test treatments.**

Compared tests	N	P-value
1,3	5	0.175
1-3ave,2		0.009
1-3ave,4		0.016
1-3ave,5		0.602
1-3ave,7		0.117
2,4		0.009
2,5		0.009
2,7		0.009
4,5		0.009
4,7		0.465
5,7		0.117
6,7		0.009
6,9		0.009
6,11		0.117
6,12		0.175
8,9		0.009
8,10		0.009
9,11		0.009
10,11		0.076
11,12		0.602
12,13	0.076	

There is a significant difference when comparing unsaturated soils with 0.005 M CaSO<sub>4</sub> at 26% wc (Test 6) and 14% wc (Test 7), in which air permeabilities are higher with lower wc. When comparing air permeabilities for unsaturated soils with 0.005 CaSO<sub>4</sub> at 26% wc (Test 6) and 27% wc (Test 9), without and with 0.60 M CaCl<sub>2</sub>, respectively, there is a significant difference where air permeabilities are higher for soil without CaCl<sub>2</sub>. There is no significant difference between air permeabilities for unsaturated soils with 0.005 CaSO<sub>4</sub> at 26% wc (Test 6) when compared to unsaturated soils with 0.60 M CaCl<sub>2</sub> (Test 11) or 0.06 M CaCl<sub>2</sub> (Test 12), both at 27% wc. There is a significant difference between air permeabilities for unsaturated soils with 0.005 M CaSO<sub>4</sub> and 0.60 M CaCl<sub>2</sub> at 32% wc (Test 8) and 27% wc (Test 9) where it indicates that air permeabilities are higher for lower water contents. When comparing air permeabilities between soil with both salts (CaSO<sub>4</sub> and CaCl<sub>2</sub>) at 32% wc (Test 8) and soil with 0.60 M CaCl<sub>2</sub> at 30% wc (Test 10) there is a significant difference indicating that soil with less

salt (Test 10) yields higher air permeabilities. The same occurs when comparing air permeabilities for Tests 9 and 11. There is no significant difference when comparing air permeabilities for unsaturated soils with 0.60 M  $\text{CaCl}_2$  at 30% wc (Test 10) and 27% wc (Test 11). There is no significant difference between air permeabilities when comparing unsaturated soils with 0.60 M  $\text{CaCl}_2$  (Test 11) and 0.06 M  $\text{CaCl}_2$  (Test 12), both at 27% wc. When comparing air permeabilities for unsaturated soils with 0.06 M  $\text{CaCl}_2$  at 27% wc (Test 12) and 23% wc (Test 13), there is no significant difference.

In general, statistically, air permeabilities are higher at lower water contents. There is an increase in the air permeability of unsaturated soil in presence of NaCl. There is an increase in air permeability also in presence of  $\text{CaSO}_4$ . There is a decrease in the air permeability of unsaturated soil when in presence of  $\text{CaSO}_4$  and  $\text{CaCl}_2$ . For  $\text{CaCl}_2$ , it has no effect on air permeability if the salt concentration is 0.06 M or 0.60 M. For 0.60 M  $\text{CaCl}_2$ , a change in water content from 27% to 30% has no effect on air permeability. For 0.06 M  $\text{CaCl}_2$ , a change in water content from 23% to 27 % has no effect on air permeability.

## 4.2 Capillary-based Delivery

Capillary-based delivery tests generated images and dimensional parameters of the wetting front dynamics for the different experiments conducted (Test A through D) as described in section 3.4.

Images of the wetting front dynamics for test experiments A through D are shown in Figure 4.3. The distance from the bottom of the porous cup at which the water/solution is distributed around the circumference of the column (top of homogeneously distributed zone, THDZ) indicates the proximity between the point of delivery and the homogeneously-distributed wetted zone. This zone is located between the top of the wetted zone (TWZ) and the bottom of the zone (BWZ). The wetting distribution visual interpretations are characterized according to the variables given in Figure 3.10 and

summarized in Table 4.4. The images illustrate that the solution distribution is heterogeneous, but it becomes more homogeneous at later times (Figure 4.3).

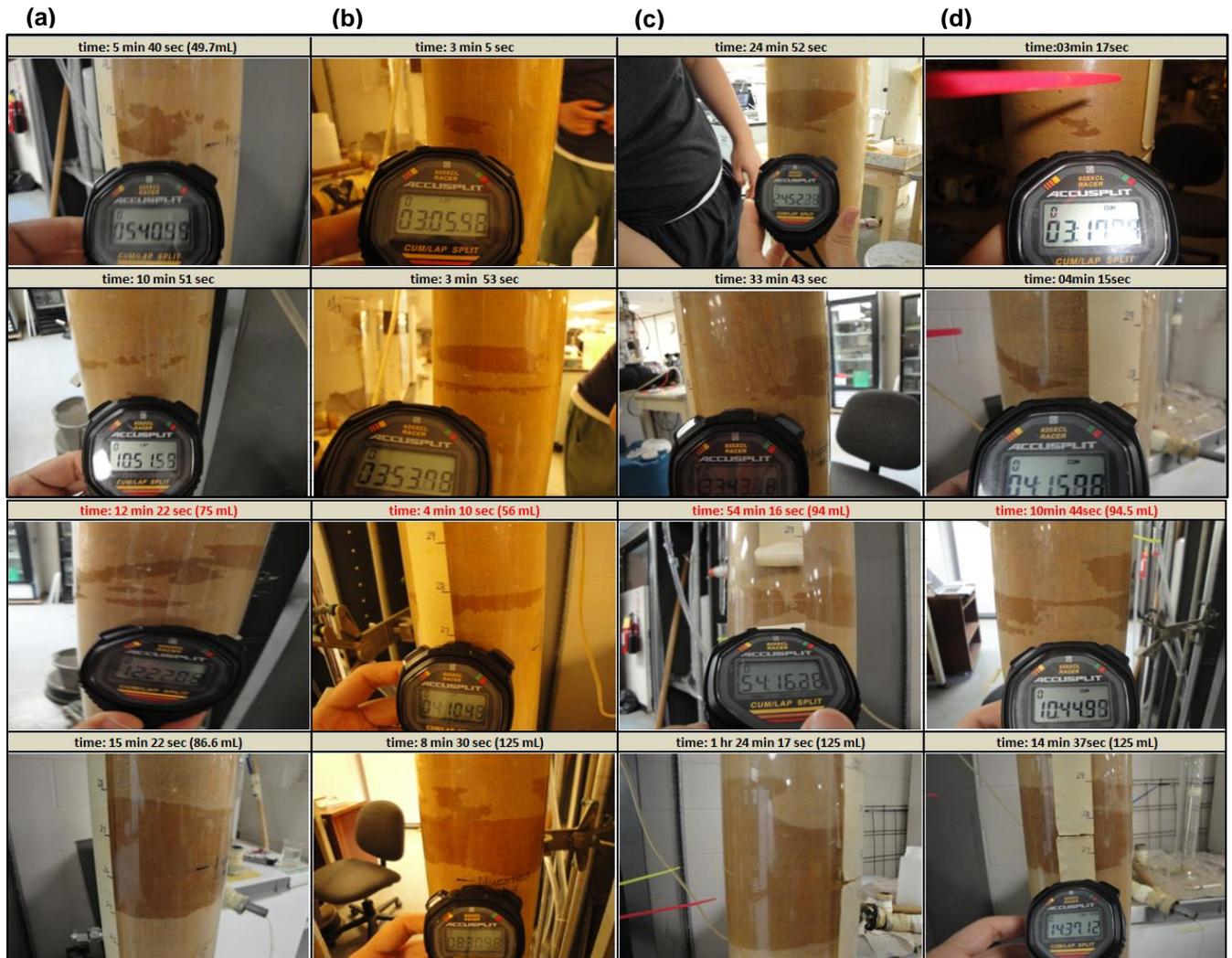


Figure 4.3. Distribution of solution in the clay during reagent delivery experiments: a) A1, b) B1, c) C1 and d) D1.

Comparisons of the preliminary results (Table 4.4) suggest that less water and time of delivery is used to form uniform wetted distribution when water level is above the point of delivery (Test B). The wetted zone is however, smaller than the other tested treatments. The faster times and higher flow rates to reach the circumference observed in testing indicates gravity-induced injection. Visual images of the wetting front at the end of the experiment (Figure 4.3 b) suggest preferential flow heterogeneities.

Having the water level at the same height as the point of delivery (Test A) induces greater water flow into the soil than the gravity-fed condition, but at a slower rate. As a consequence it takes longer to reach uniform distribution. It, however, takes much less time than when the water level is below the point of delivery (Test C). Flow rate into the soil for the latter case (Test C) is very slow, but results in a more uniform and larger wetted distribution (Figure 4.3 c) indicating that the wetted zone does not travel much vertically, and that the injection is influenced to a higher extent by capillary forces than gravity forces. This means that in a remediation process the reactant delivery point would have to be located near the contaminated area. The amount of solution delivered and the time to achieve a uniform wet circumference are lower with a saline solution (Test D) than with water (Test A). This suggests that the addition of NaCl may cause restructuring of the clay. The rate of delivery for the saline solution is, however, higher than for water. Closer proximity of the wetted zone and the point of delivery suggest greater influence of capillary forces for the saline solution. Total Capillary-based delivery test data is included in Appendix B.

The results show that capillary-based delivery can be used to preferentially deliver reagents to tight formations, and that the addition of NaCl for kaolinite clays may enhance the distribution of reagent solution.

**Table 4.4. Average values ( $\pm$  standard deviation) of experimental results variables for CBD tests.**

<b>Tests</b>	<b>A (at delivery point)</b>	<b>B (above delivery point)</b>	<b>C (below delivery point)</b>	<b>D (at delivery point + NaCl)</b>
<b>Solution added to achieve wet circumference (mL)</b>	98.00 $\pm$ 25.87	65.67 $\pm$ 15.04	70.83 $\pm$ 20.32	76.67 $\pm$ 16.66
<b>Time to achieve wet circumference (min)</b>	11.43 $\pm$ 0.98	5.19 $\pm$ 2.51	92.34 $\pm$ 76.29	8.64 $\pm$ 1.81
<b>Total solution added (mL)</b>	121.53 $\pm$ 33.34	125.00 $\pm$ 0	125.00 $\pm$ 0	125.00 $\pm$ 0
<b>Time to deliver total volume (min)</b>	14.57 $\pm$ 0.77	9.04 $\pm$ 1.39	203.24 $\pm$ 171.42	13.28 $\pm$ 1.29
<b>Delivery rate to achieve wet circumference (mL/min)</b>	8.64 $\pm$ 2.45	13.66 $\pm$ 3.46	1.33 $\pm$ 0.71	8.88 $\pm$ 0.88
<b>TWZ (cm)</b>	73.41 $\pm$ 2.17	73.66 $\pm$ 0	74.93 $\pm$ 1.27	74.51 $\pm$ 1.47
<b>BWZ (cm)</b>	64.77 $\pm$ 1.27	65.62 $\pm$ 0.73	66.04 $\pm$ 0	66.04 $\pm$ 0
<b>THDZ (cm)</b>	72.2 $\pm$ 1.4	71.4 $\pm$ 0.4	73.3 $\pm$ 0.6	72.1 $\pm$ 1.0
<b>Lenght of moist clay (cm)</b>	8.64 $\pm$ 0.39	8.04 $\pm$ 0.24	8.89 $\pm$ 0.73	8.47 $\pm$ 1.29
<b>Volume of wetted zone (cm<sup>3</sup>) from TWZ to BWZ</b>	393.83 $\pm$ 41.76	366.81 $\pm$ 33.44	405.42 $\pm$ 57.92	386.11 $\pm$ 66.88
<b>Density (g/cm<sup>3</sup>)</b>	1.08 $\pm$ 0.02	1.10 $\pm$ 0	1.10 $\pm$ 0	1.10 $\pm$ 0
<b>Water content (%)</b>	21.61 $\pm$ 1.34	21.55 $\pm$ 0.84	21.94 $\pm$ 0.94	22.23 $\pm$ 0.33

CBD = Capillary-based delivery

### 4.3 Batch Reactor Experiments

The batch reactor experiments include a static batch (S1) containing water solution and TCE, and replicates (S2 and S3), a static batch with clay (S4), and a static equilibrium batch (E1). Calibrations used for these experiments and all TCE<sub>vc</sub> data are included in Appendix C. The following subsections include experimental results and analysis for each experiment, and statistical analyses. Statistical analyses are performed to strengthen data analyses by assessing the reproducibility of the experiments with the comparison of replicates, and determining if there are statistically significant differences in measured TCE<sub>vc</sub> with the different treatments.

Normality tests for static experiments show that some data sets are normally distributed whereas other are not normally distributed (Table 4.5). Since several of the data sets are not normally distributed, comparisons among replicates are performed using the Mann-Whitney test. For statistically similar replicates, averages are estimated for comparison with averages of the different treatments. The average of the data sets are normally distributed (Table 4.6), and student T-tests are applied to compare the averages among treatments.

**Table 4.5. Data distribution for static experiments.**

Experiment (Table 3.7)	[NaCl] (M)	p-value	Distribution
<b>S1</b>	0	0.330	Normal
	0.26	0.638	Normal
	0.60	0.507	Normal
	1.71	0.008	Not Normal
	4.28	0.022	Not Normal
<b>S2</b>	0	0.579	Normal
	0.26	0.534	Normal
	0.60	0.808	Normal
	1.71	0.258	Normal
	4.28	0.044	Not Normal
<b>S3</b>	0	0.123	Normal
	0.26	0.005	Not Normal
	0.60	0.005	Not Normal
	1.71	0.252	Normal
	4.28	0.010	Not Normal
<b>S4_1</b>	0	0.122	Normal
	0.60	0.026	Not Normal
	4.28	0.005	Not Normal
<b>S4_2</b>	0	0.012	Not Normal
	0.60	0.026	Not Normal
	4.28	0.208	Normal

**Table 4.6. Data distribution for averages of static experiments.**

Experiment (Table 3.7)	[NaCl] (M)	p-value	Distribution
<b>S<sub>ave</sub></b>	0.00	0.448	Normal
	0.26	0.643	Normal
	0.60	0.760	Normal
	1.71	0.304	Normal
	4.28	0.082	Normal
<b>S4<sub>ave</sub></b>	0.00	0.292	Normal
	0.60	0.150	Normal
	4.28	0.094	Normal

### 4.3.1 Static Reactor Experiments

Static reactor experiments involve placing TCE stock solution with a [NaCl] (0 M, 0.26 M, 0.60 M, 1.71 M or 4.28 M) and TCE NAPL in a closed reactor for a period of time before sampling the headspace. Generally, measurements of TCE<sub>vc</sub> in static batch reactor at different times (Table 4.7; Figure 4.4) indicate lower concentrations at early times, with slight increase during the first 24 hours. After this initial period, TCE<sub>vc</sub> increase with a fluctuating behavior until reaching a relatively constant value. Higher TCE<sub>vc</sub> at the later stages are observed for reactors containing [NaCl] = 1.71 M, followed by those having [NaCl] = 0.60 M. Lowest late-time concentrations are generally observed for reactors with [NaCl] = 0 M. Among reactors with NaCl, TCE<sub>vc</sub> are the lowest for reactors with [NaCl] = 4.28 M. This suggests that NaCl enhances volatilization of TCE at NaCl concentrations below brine limits (Total dissolved solids ≤ 35,000 mg/L), but not for higher concentrations. Average TCE<sub>vc</sub> shown in Table 4.7 and used for Figure 4.4 are obtained by calculating the average of two experiments (i.e. S1 and S2). Further details are included in section 4.3.1.1.

**Table 4.7. Average TCE<sub>vc</sub> for S1-S2 tests.**

Time (hours)	Average TCE <sub>vc</sub> (g/m <sup>3</sup> )				
	[NaCl] M				
	0	0.26	0.60	1.71	4.28
1	344.75	305.73	599.03	584.36	205.70
3	337.05	263.51	239.25	262.35	429.46
6	443.44	521.12	196.78	466.09	253.59
12	400.20	491.45	359.90	430.88	241.76
24	431.81	495.65	518.91	1222.43	711.03
48	733.73	645.84	985.33	803.30	296.75
60	514.67	547.97	633.37	1248.03	400.10
72	613.58	847.58	993.26	1375.75	835.57
84	647.71	630.52	847.09	1211.83	726.06
96	626.10	806.40	775.84	869.80	765.16

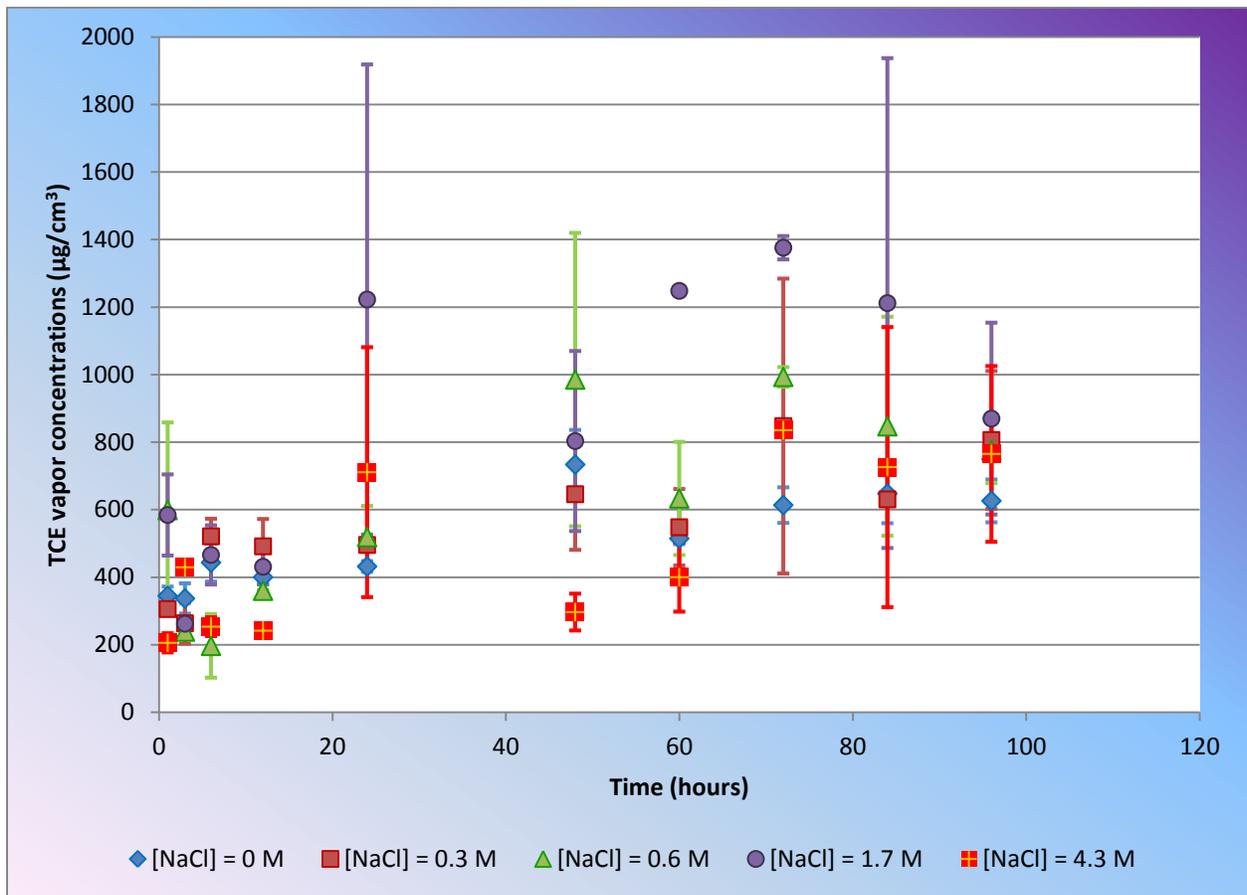


Figure 4.4. TCEv in S1 – S3.

#### 4.3.1.1 Statistical Analysis for S1-S3 Experiments

The S1-S3 experimental data reflects non-normal distributions. Reproducibility analysis of the static batch reactors and replicates using Mann Whitney reveals that the third test (S3) is statistically significantly different from the first two tests (S1 and S2). The average of the first two tests is, therefore, used for all comparisons. These average values reflect a normal distribution; hence two-sample t-test is used for comparisons. The p-values using two-sample t-test (Table 4.8) to compare treatments for late-time (>24 hrs) average TCEv, show a statistically significant difference for every treatment when compared with [NaCl] = 1.71 M, in which the mean is always higher for [NaCl] = 1.71 M, except for the comparison with [NaCl] = 0.60 M, in which there is no statistically significant difference. It also shows a statistically significant difference when comparing [NaCl] = 0 M and [NaCl] = 0.60 M, in which [NaCl] = 0.60 M has a higher mean.

Therefore, the statistical analysis for the late-time data validates the observed behavior over all sampling times, in which TCE<sub>vc</sub> are higher for reactors with [NaCl] = 1.71 M, followed by those having [NaCl] = 0.60 M.

**Table 4.8. Two-sample t-test results for average comparisons between treatments of S1-S2 experiments (t > 24 hrs).**

Compared treatments	N	P-value
0 M & 0.26 M NaCl	5	0.343
0 M & 0.60 M NaCl		<b>0.028</b>
0 M & 1.71 M NaCl		<b>0.016</b>
0 M & 4.28 M NaCl		0.852
0.26 M & 0.60 M NaCl		0.129
0.26 M & 1.71 M NaCl		<b>0.023</b>
0.26 M & 4.28 M NaCl		0.482
0.60 M & 1.71 M NaCl		0.100
0.60 M & 4.28 M NaCl		0.105
1.71 M & 4.28 M NaCl		<b>0.015</b>

N = sample size

#### 4.3.2 Static Aqueous Reactor Experiments at Equilibrium

Static aqueous reactor experiments measure the vapor concentrations of TCE after equilibrium with TCE solution at different aqueous concentrations (110 mg/L, 506 mg/L, and 990 mg/L) and each at three different sodium chloride concentrations (0 M, 0.60 M, and 4.28 M) without TCE NAPL. Experimental conditions for these experiments (E1) are summarized in Table 3.6.

Results show that average TCE<sub>vc</sub> in these experiments tend to increase with increasing TCE in solution and with higher sodium chloride concentrations (Figure 4.5). Statistical analysis (Table 4.9) using two-sample t-test indicates significantly higher TCE<sub>vc</sub> for the 0.60 M NaCl and 990 mg/L TCE solution when comparing with no NaCl. At a TCE solution concentration of 110 mg/L, [NaCl] = 4.28 M yields significantly higher TCE<sub>vc</sub> than [NaCl] = 0.60 M. No statistically significant difference between average TCE<sub>vc</sub> at

different TCE solution concentrations and different NaCl concentrations is observed among the other samples.

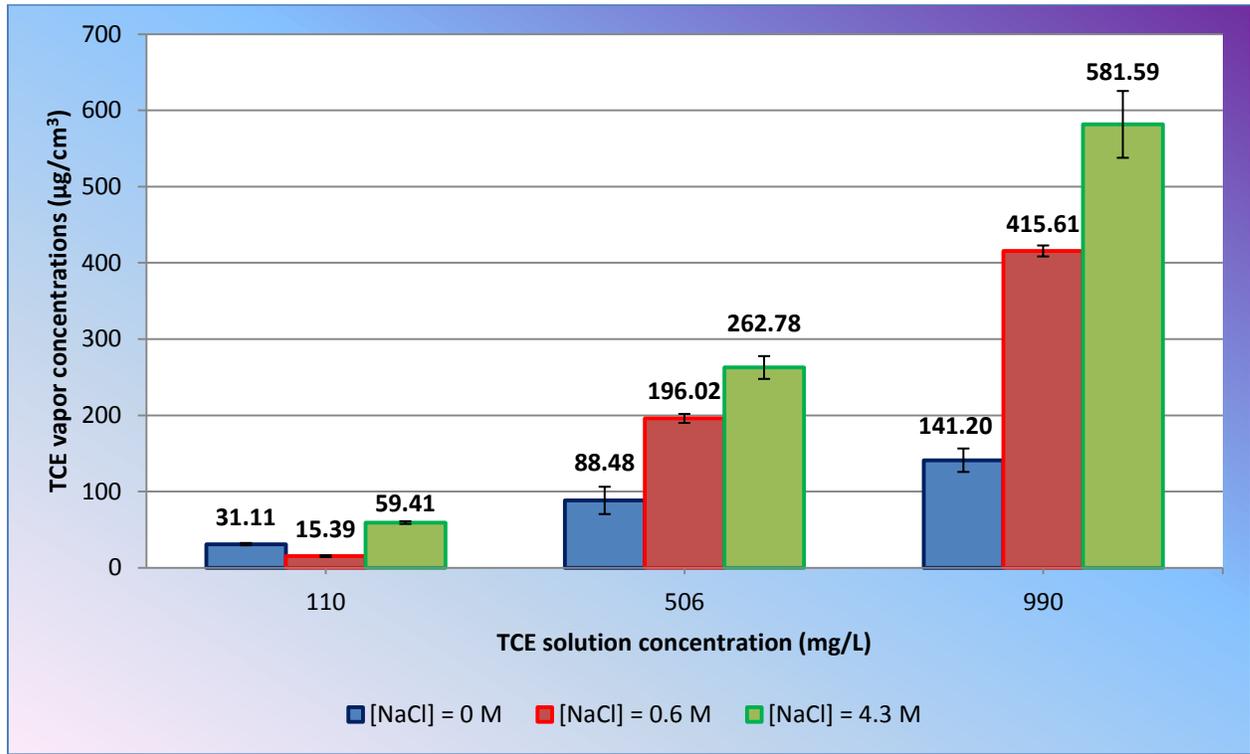


Figure 4.5. Average TCEvapor in E1. Values shown are the average TCEvapor for each test.

Table 4.9. Two-sample t-tests results for comparisons between treatments in experiment E1.

Compared treatments	N	P-value
0 M & 0.60 M NaCl (110 mg/L TCE solution)	2	0.077
0 M & 4.28 M NaCl (110 mg/L TCE solution)		0.052
0.60 M & 4.28 M NaCl (110 mg/L TCE solution)		<b>0.030</b>
0 M & 0.60 M NaCl (506 mg/L TCE solution)		0.111
0 M & 4.28 M NaCl (506 mg/L TCE solution)		0.085
0.60 M & 4.28 M NaCl (506 mg/L TCE solution)		0.151
0 M & 0.60 M NaCl (990 mg/L TCE solution)		<b>0.039</b>
0 M & 4.28 M NaCl (990 mg/L TCE solution)		0.067
0.60 M & 4.28 M NaCl (990 mg/L TCE solution)		0.166

N = sample size

### 4.3.3 Static Reactor Experiments with Clay

Static reactor experiments with clay are similar to the static reactor experiments (S1-S3), except that the reactors consist on TCE-solution saturated clay with a sodium chloride concentration (0 M, 0.60 M, or 4.28 M) and TCE NAPL. This experiment is labeled as S4 (Table 3.6). Generally, there is an increasing TCE<sub>vc</sub> with time for all the treatments (Table 4.10; Figure 4.6). Overall, TCE<sub>vc</sub> in reactor experiments with clay are higher compared to TCE<sub>vc</sub> in reactor experiments without clay. Initially, for reactor experiments with clay, TCE<sub>vc</sub> is higher for [NaCl] = 0 M, but from 84 hours to 96 hours concentrations are higher for [NaCl] = 0.60 M.

**Table 4.10. Average TCE<sub>vc</sub> for S4 tests.**

Average TCE <sub>vc</sub> (g/m <sup>3</sup> )			
Time (hours)	[NaCl] M		
	0	0.60	4.28
1	985.99	452.81	790.01
3	546.87	369.63	2613.49
6	693.85	447.90	2675.00
12	616.47	617.32	341.64
24	1568.52	980.24	649.02
48	4458.32	2763.30	578.36
60	2461.97	1387.01	612.53
72	2746.87	2391.76	1321.37
84	1326.66	3687.41	2997.69
96	3072.25	4003.06	1831.55
120	3023.97	1595.75	3370.43

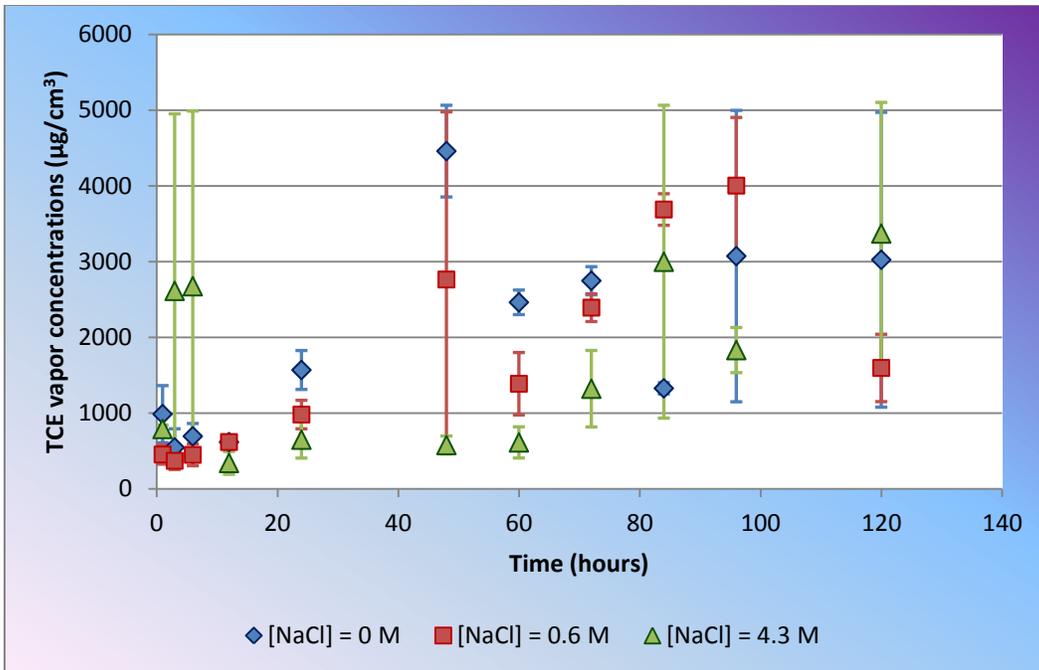


Figure 4.6. TCEvc in S4.

#### 4.3.3.1 Statistical Analysis for S4 Experiments

The S4 experiment and its replicate reflect a non-normal distribution, and they are, therefore, analyzed using the Mann-Whitney test. The test shows no statistically significant difference among replicates, and average values are therefore calculated. Average values reflect a normal distribution and two-sample T tests are run to test for statistical significant differences between late-time (>24 hrs) TCEvc at the different salt concentrations with and without clay. P-values lower than 0.05 (Table 4.11) indicate that there is a statistically significant difference between average TCEvc in reactors with and without clay at [NaCl] = 0 M and [NaCl] = 0.60 M, in which the mean is always higher for reactors with clay. There is no statistically significant difference at [NaCl] = 4.28 M.

**Table 4.11. Two-sample T-test results for late-time ( $48 \text{ hrs} \leq t \leq 96 \text{ hrs}$ ) comparison between static experiment with clay (S4) and without clay (S1-S3).**

Compared treatments	N	P-value
[NaCl] = 0 M with and without clay	5	0.013
[NaCl] = 0.60 M with and without clay		0.013
[NaCl] = 4.28 M with and without clay		0.134

N = sample size

Two-sample T tests are also run to test for statistical significant differences between the TCE<sub>vc</sub> at the different salt concentrations in reactor experiments with clay after 24 hours. P-values higher than 0.05 (Table 4.12) indicate that there is no statistically significant difference between average TCE<sub>vc</sub> in reactor experiments with clay at the three different NaCl concentrations.

**Table 4.12. Two-sample T-test results for late-time (>24 hrs) comparisons between NaCl treatments in static experiment with clay (S4).**

Compared treatments	N	P-value
[NaCl] = 0 M and [NaCl] = 0.60 M	6	0.735
[NaCl] = 0 M and [NaCl] = 4.28 M		0.130
[NaCl] = 0.60 M and [NaCl] = 4.28 M		0.223

N = sample size

#### 4.4 Flux reactor experiments

Normality tests for flux reactor experiments show that all data sets are not normally distributed (Table 4.13). Since the data sets are not normally distributed, comparisons among replicates are performed using the Mann-Whitney test. For statistically similar replicates, averages are estimated for comparison with averages of the different treatments. The average of the data sets are not normally distributed (Table 4.14), and

non-parametric tests (i.e. Kruskal Wallis test) are therefore applied to compare the averages between treatments.

**Table 4.13. Data distribution for flux reactor experiments.**

<b>Experiment (Table 3.7)</b>	<b>[NaCl] (M)</b>	<b>p-value</b>	<b>Distribution</b>
<b>D1_1</b>	0.00	<0.005	Not Normal
	0.60	<0.005	Not Normal
	4.28	<0.005	Not Normal
<b>D1_2</b>	0.00	<0.005	Not Normal
	0.60	<0.005	Not Normal
	4.28	<0.005	Not Normal
<b>D2_1</b>	0.00	<0.005	Not Normal
	0.60	<0.005	Not Normal
	4.28	<0.005	Not Normal
<b>D2_2</b>	0.00	<0.005	Not Normal
	0.60	<0.005	Not Normal
	4.28	<0.005	Not Normal
<b>D3_1</b>	0.00	<0.005	Not Normal
	0.60	<0.005	Not Normal
	4.28	<0.005	Not Normal
<b>D3_2</b>	0.00	<0.005	Not Normal
	0.60	<0.005	Not Normal
	4.28	<0.005	Not Normal
<b>D4_1</b>	0.00	<0.005	Not Normal
<b>D4_2</b>	0.00	<0.005	Not Normal
<b>D5_1</b>	0.00	<0.005	Not Normal
<b>D5_2</b>	0.00	<0.005	Not Normal
<b>D6_1</b>	0.00	<0.005	Not Normal
<b>D6_2</b>	0.00	<0.005	Not Normal
<b>D7_1</b>	0.60	<0.005	Not Normal
<b>D7_2</b>	0.60	<0.005	Not Normal
<b>D8_1</b>	0.00	<0.005	Not Normal
	0.60	<0.005	Not Normal
	4.28	<0.005	Not Normal
<b>D8_2</b>	0.00	<0.005	Not Normal
	0.60	<0.005	Not Normal
	4.28	<0.005	Not Normal
<b>D9_1</b>	0.00	<0.005	Not Normal
<b>D9_2</b>	0.00	<0.005	Not Normal
<b>D10_1</b>	0.60	<0.005	Not Normal
<b>D10_2</b>	0.60	<0.005	Not Normal

**Table 4.14. Data distribution for averages of flux reactor experiments.**

Experiment (Table 3.7)	[NaCl] (M)	p-value	Distribution
<b>D1</b>	0.00	<0.005	Not Normal
	0.60	<0.005	Not Normal
	4.28	<0.005	Not Normal
<b>D2</b>	0.00	<0.005	Not Normal
	0.60	<0.005	Not Normal
	4.28	<0.005	Not Normal
<b>D3</b>	0.00	<0.005	Not Normal
	0.60	<0.005	Not Normal
	4.28	<0.005	Not Normal
<b>D4</b>	0.00	<0.005	Not Normal
<b>D5</b>	0.00	<0.005	Not Normal
<b>D6</b>	0.00	<0.005	Not Normal
<b>D7</b>	0.00	<0.005	Not Normal
<b>D8</b>	0.00	<0.005	Not Normal
	0.60	<0.005	Not Normal
	4.28	<0.005	Not Normal
<b>D9</b>	0.00	<0.005	Not Normal
<b>D10</b>	0.00	<0.005	Not Normal

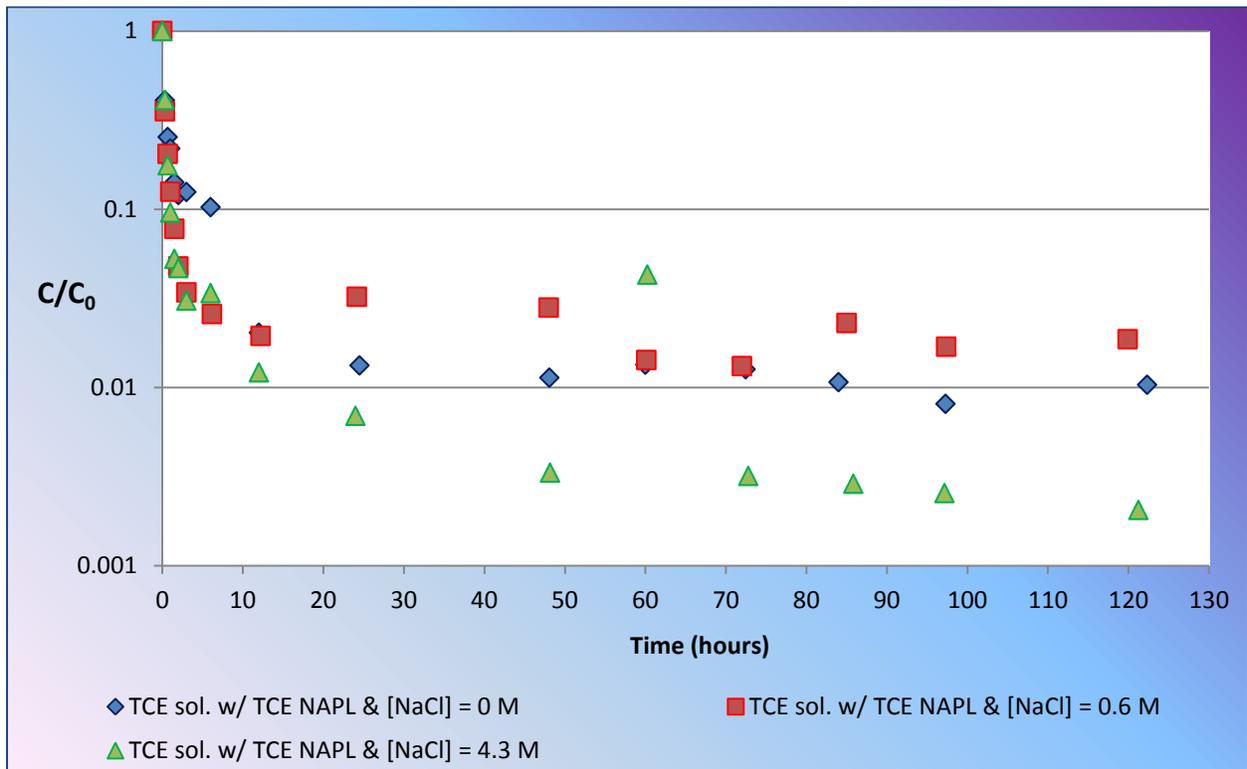
The flux reactor experiments involve measuring the TCE<sub>vc</sub> in an air stream passing through the headspace above the sample matrix (i.e. water, clay) in the flux reactor (Table 3.7). The following subsections present experimental results, and comparative, analytical and statistical analyses for each experiment (D1-D10, Table 3.7) and between experiments. Statistical analyses are done to assess the reproducibility of the experiments and to determine if there is a significant difference between the TCE<sub>vc</sub> with the different treatments (NaCl concentration, TCE NAPL presence and/or clay presence). Calibrations used for these experiments and all TCE<sub>vc</sub> data are included in Appendix D.

#### 4.4.1 Temporal changes in relative TCE vapor concentrations

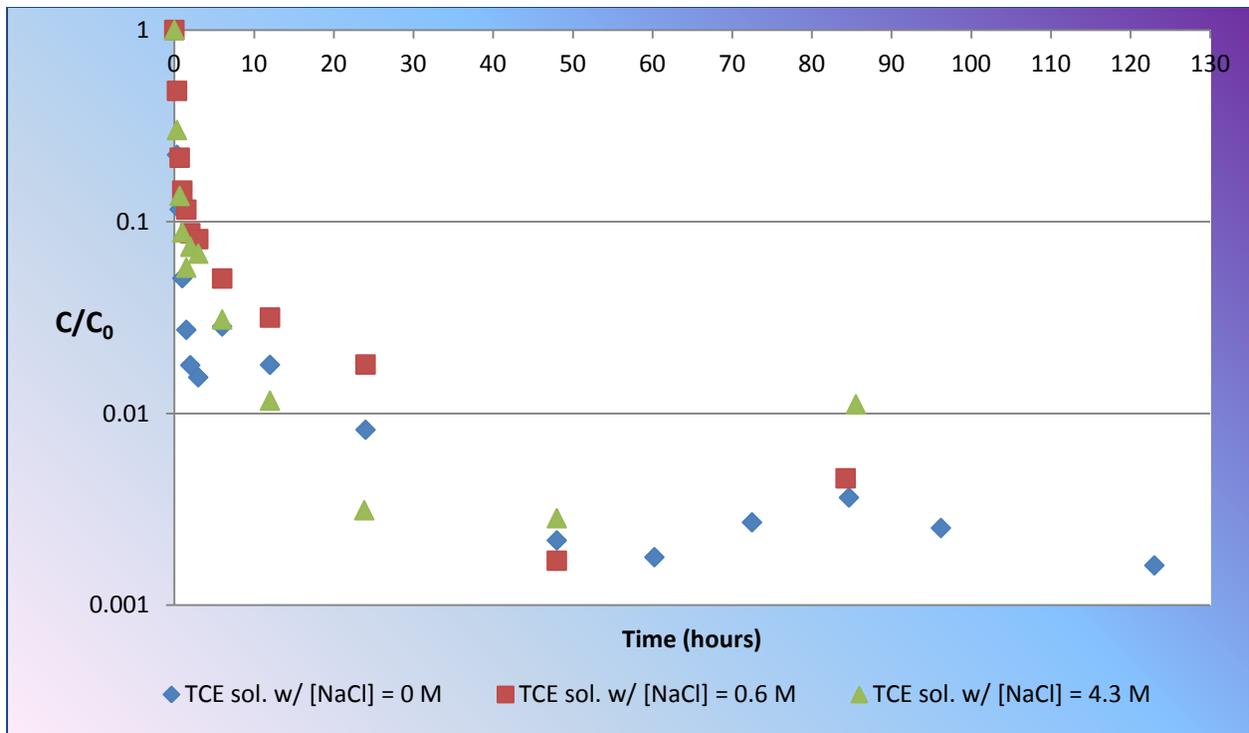
Temporal distributions of relative TCEvc in the dynamic flux reactors show that vapor concentrations are the highest at the onset of the experiments ( $t=0$ ) and tend to decrease with time toward constant values (Figures 4.7 through 4.14). Higher concentrations at the onset of the air stream reflect that the initial mass extracted is that residing in the headspace of the reactor. Lower concentrations at the later stages of the extraction reflect mass transfer limitations related to volatilization, diffusion, and dilution from the solution, clay, and NAPL present in the reactor. Initial concentrations in the reactors vary between  $25.85 \text{ g/m}^3$  and  $263.35 \text{ g/m}^3$  ( $\bar{X} = 120.62 \frac{\text{g}}{\text{m}^3}$ ;  $STDEV = 65.89 \frac{\text{g}}{\text{m}^3}$ ) and are considerably lower than the expected saturated vapor pressure concentration at  $20^\circ\text{C}$  ( $P_v = 6.94 \text{ kPa}$ ). Concentrations lower than the saturated vapor pressure concentration ( $C_{vp} = 374 \text{ g/m}^3$  at  $20^\circ\text{C}$ ) result from the lower concentrations in the stock solution (see section 3.2.1) and mass transfer limitation of TCE among the different phases. To account for varying initial concentrations in the reactor, TCEvc is normalized with respect to initial concentration ( $C_0 =$  concentration measured at  $t = 0$ ). The data used for the analysis is the average of the replicates, if no statistically significant difference is observed between replicates. If the replicates had a statistically significant difference, they are both plotted.

Temporal vapor concentration distribution of TCE suggests that higher relative concentrations are attained for  $[\text{NaCl}] = 0.60 \text{ M}$ , followed by  $0 \text{ M}$  and  $4.28 \text{ M}$   $[\text{NaCl}]$ , respectively, in the presence of TCE NAPL (D1: Figure 4.7). Similar behavior is observed at early times in the absence of TCE NAPL, but no major difference is observed at later times (D2: Figure 4.8). When saturated clay and TCE NAPL are present in the reactor, higher concentrations are obtained for the solution having  $0 \text{ M}$   $[\text{NaCl}]$ , followed by those having  $0.60 \text{ M}$  and  $4.28 \text{ M}$   $[\text{NaCl}]$  (D3: Figure 4.9). The presence of 10% methanol in water induces greater TCEvc in the presence of TCE NAPL, but much lower concentrations when TCE NAPL is not present (D4 & D5: Figure 4.10). The presence of saturated clays reduces the TCEvc in the 10% methanol-TCE system for the  $0 \text{ M}$   $[\text{NaCl}]$  (D6: Figure 4.11), but enhances the concentration when

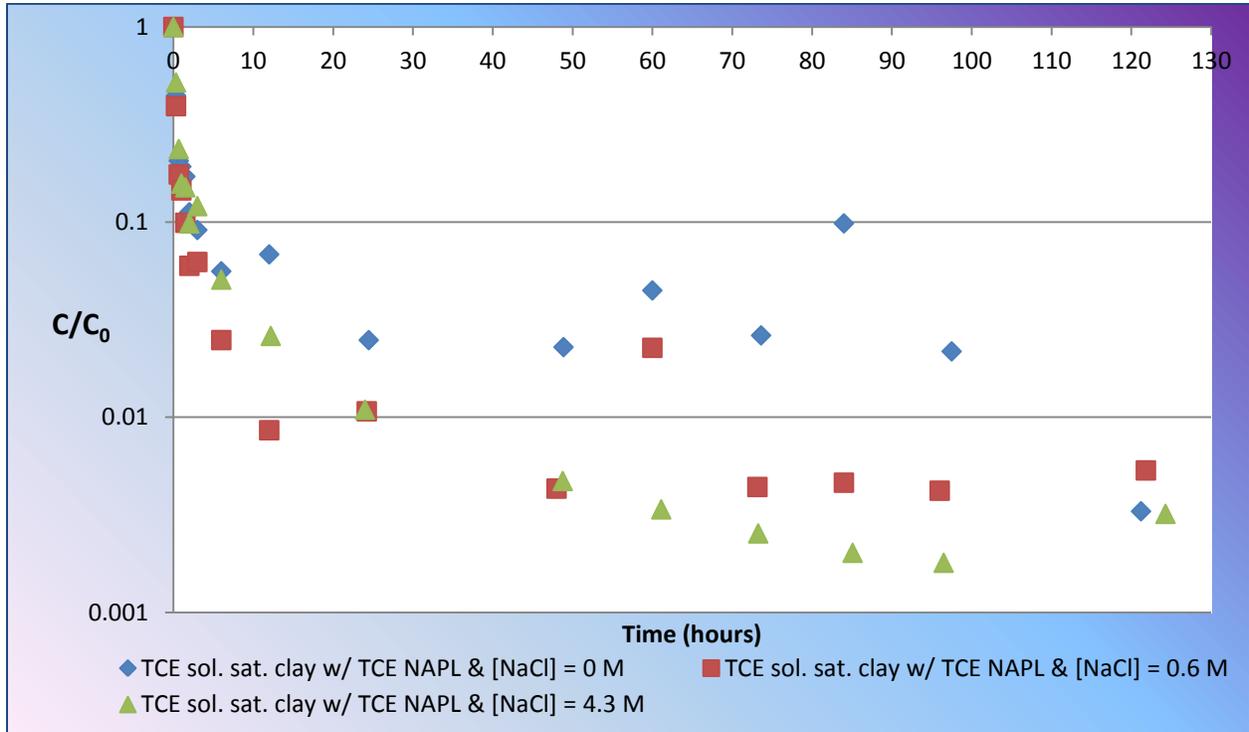
[NaCl] = 0.60 M (D7: Figure 4.12). TCEvc in unsaturated clay (D8: Figure 4.13) tend to be among the highest of all experiments, but no major difference is observed between the TCEvc measured under the different salt concentration treatments. It is interesting to note that TCEvc reach higher relative concentrations than 1, suggesting an enhanced initial transfer of TCE. Significant decrease in TCEvc is observed, however, when 10% methanol is added to the unsaturated clay (D9 & D10: Figure 4.14).



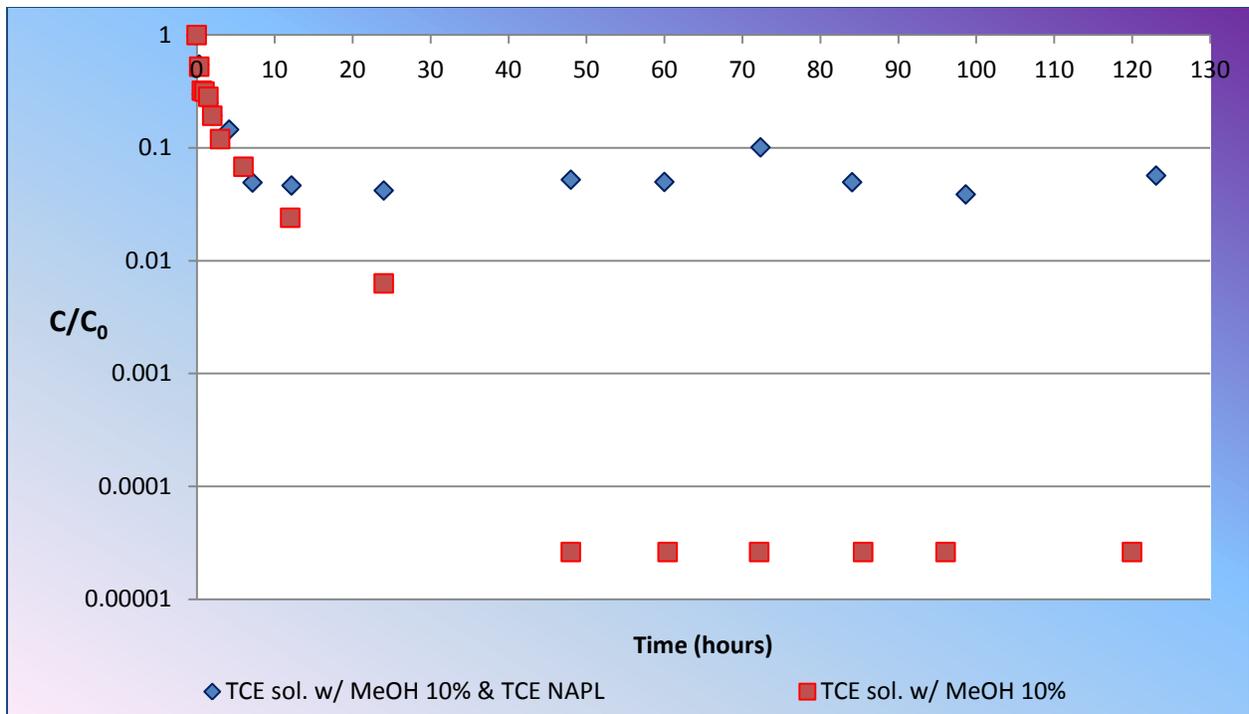
**Figure 4.7. Temporal changes in relative average TCEvc ( $C/C_0$ ) for D1: TCE solution with TCE NAPL and [NaCl] = 0 M, 0.60 M, 4.28 M.**



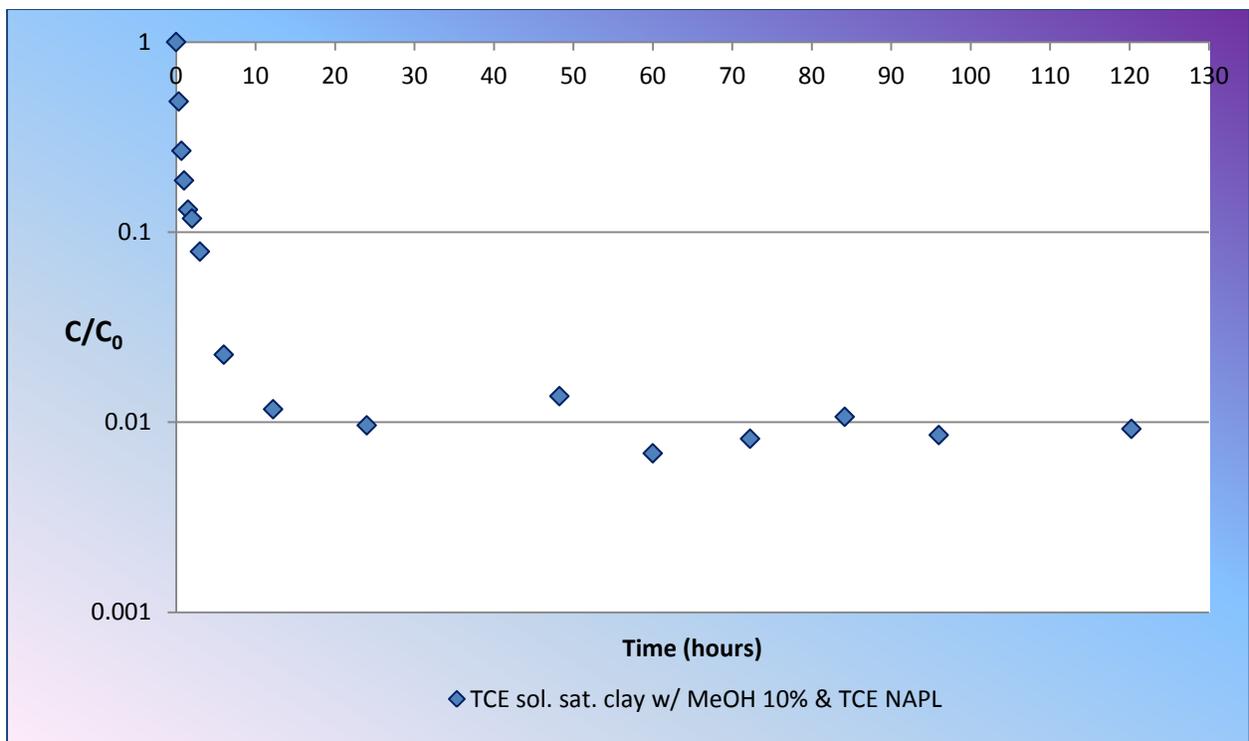
**Figure 4.8. Temporal changes in relative average TCEvc ( $C/C_0$ ) for D2: TCE solution with [NaCl] = 0 M, 0.60 M, 4.28 M.**



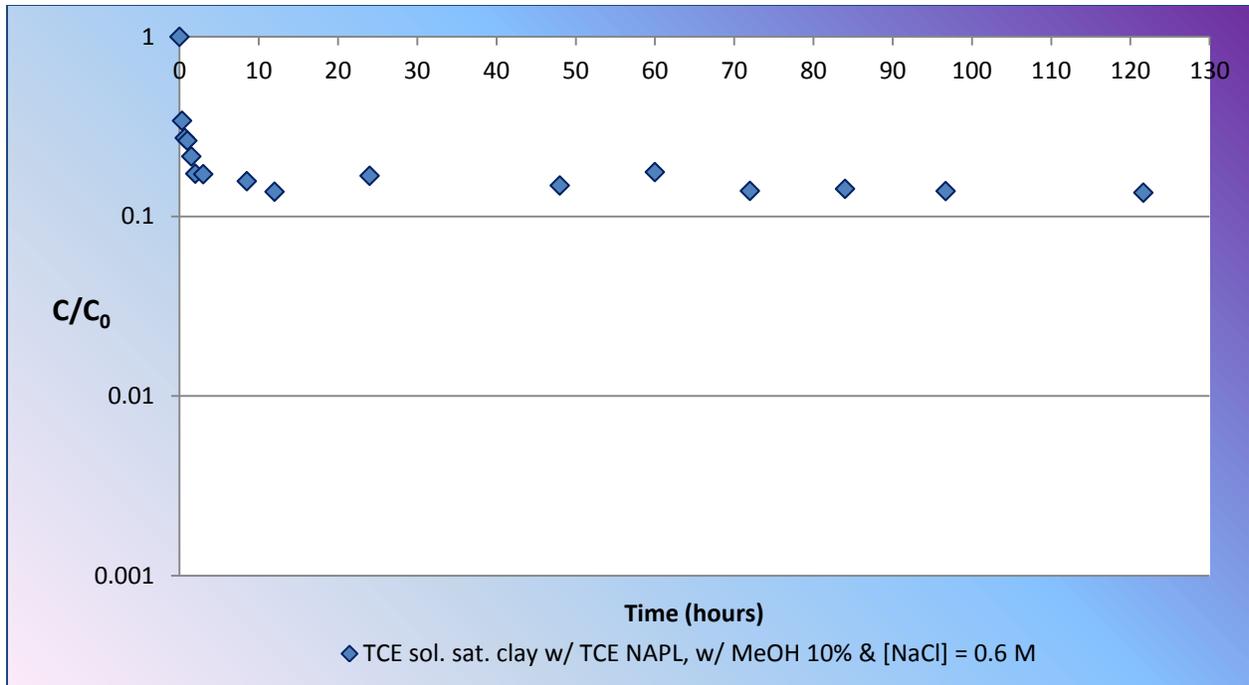
**Figure 4.9. Temporal changes in relative average TCEvc ( $C/C_0$ ) for D3: TCE solution and saturated clay with TCE NAPL and [NaCl] = 0 M, 0.60 M, 4.28 M.**



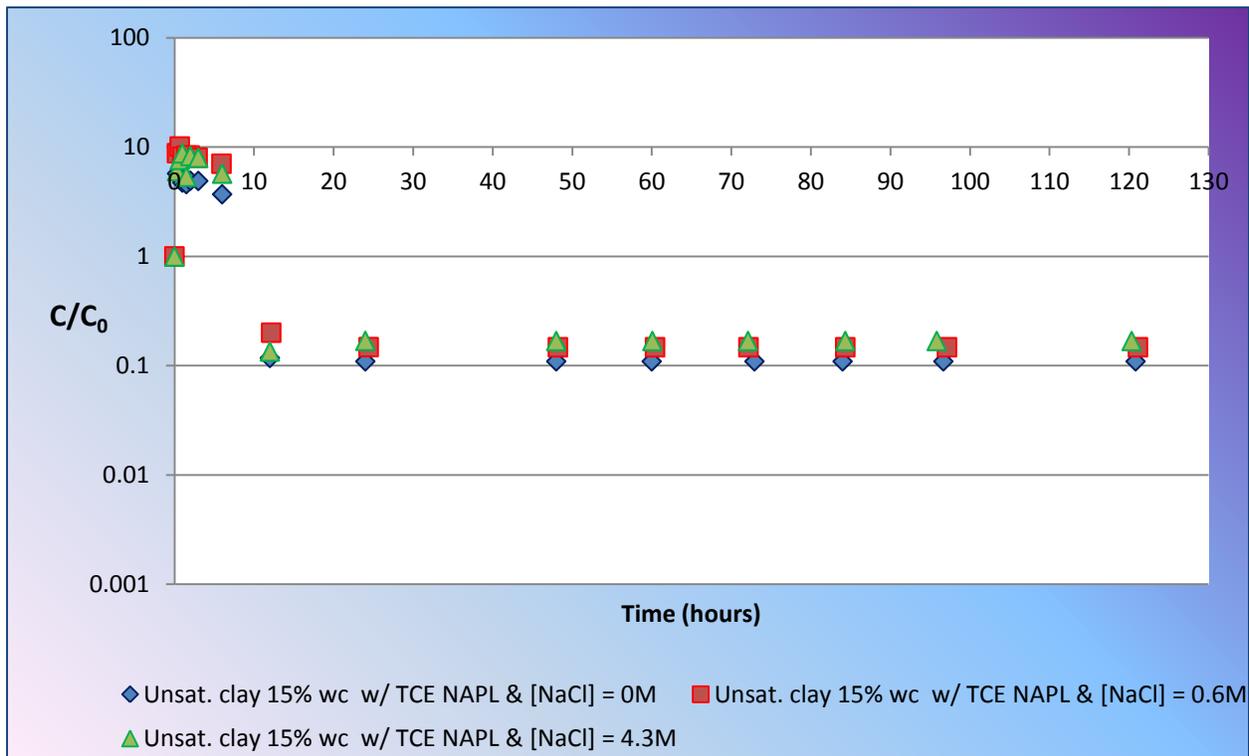
**Figure 4.10. Temporal changes in relative average TCEvc ( $C/C_0$ ) for D4 and D5: TCE solution with MeOH 10% with and without TCE NAPL, respectively.**



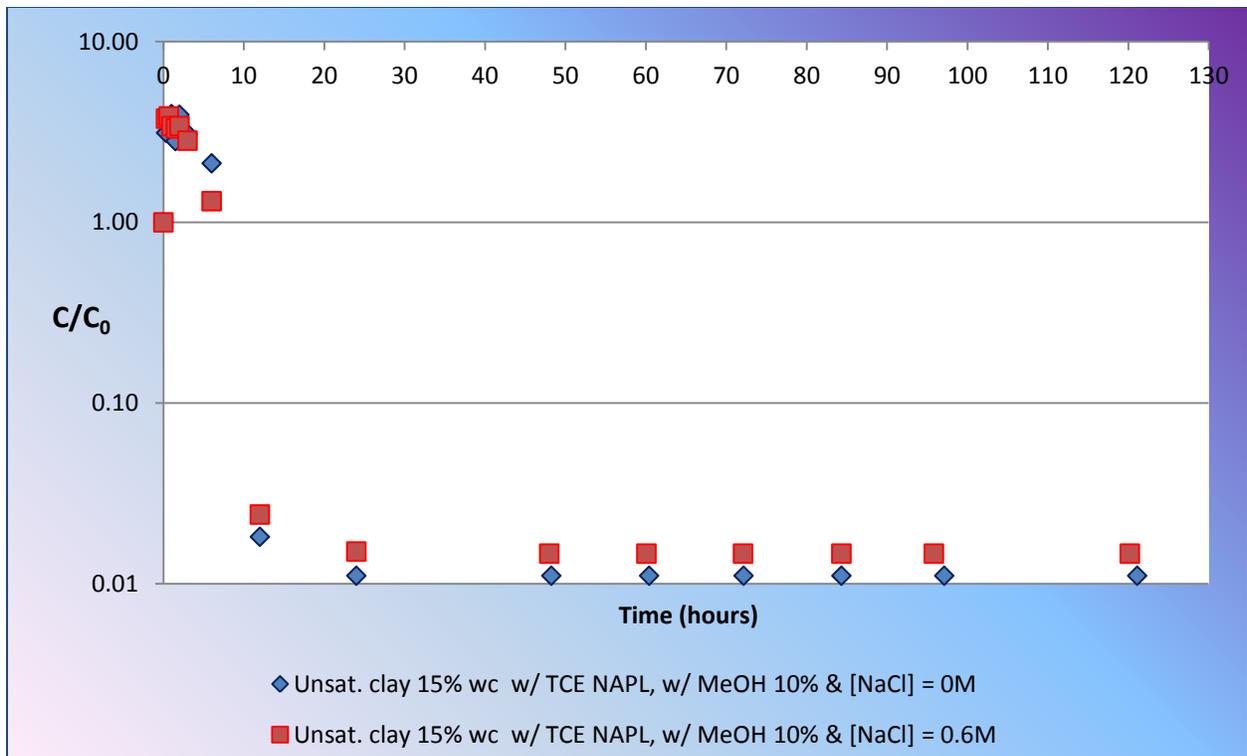
**Figure 4.11. Temporal changes in relative average TCEvc ( $C/C_0$ ) for D6: TCE solution and saturated clay with TCE NAPL and MeOH 10%.**



**Figure 4.12. Temporal changes in relative average TCEvc ( $C/C_0$ ) for D7: TCE solution and saturated clay with TCE NAPL, MeOH 10% and  $[NaCl] = 0.60$  M.**



**Figure 4.13. Temporal changes in relative average TCEvc ( $C/C_0$ ) for D8: Unsat. clay at 15% wc with TCE NAPL and  $[NaCl] = 0$  M, 0.60 M, 4.28 M.**



**Figure 4.14. Temporal changes in relative average TCEvc ( $C/C_0$ ) for D9 and D10: Unsaturated clay at 15% wc with TCE NAPL, MeOH 10% and  $[NaCl] = 0M$  and  $0.60 M$ , respectively.**

Analysis of the temporal distribution of TCEvc (Figures 4.7 to 4.13) suggests that the vapor extraction is influenced by two types of mass transport rates: a faster initial rate ( $t < 6$  hrs) and a slower rate observed at later times ( $t \geq 6$  hrs). Initial rates are associated to the removal of TCE from the completely-mixed headspace volume. The later rates are associated with the transport of TCEvc being volatilized from the water, and dissolved from the NAPL and soil matrix. Lower rates at the later times reflect rate-limited mass transfer into the flowing vapor phase.

The effect of reactor treatments (Table 3.7) in TCEvc is assessed through statistical comparison of the TCE concentration distribution at early and late times using the Kruskal Wallis non-parametric test. A statistically significant difference is assumed when  $p$ -values  $< 0.05$ . Table 4.15 summarizes the comparisons made to assess the reactor treatments effect.

**Table 4.15. Comparisons between flux reactor experiments.**

Experiment (Table 3.7)	Treatment condition						Statistical comparisons
	TCE solution	Clay	Clay condition	NAPL	MeOH	NaCl (M)	
<b>D1</b>	x			x		0, 0.60, 4.28	Between [NaCl] and each [NaCl] with conditions D2, D3, D4 (0M)
<b>D2</b>	x					0, 0.60, 4.28	Between [NaCl] and each [NaCl] with conditions D1, D5 (0M)
<b>D3</b>	x	x	Sat	x		0, 0.60, 4.28	Between [NaCl] and each [NaCl] with conditions D1, D6 (0M), D7 (0.60M), D8
<b>D4</b>	x			x	x	0	With conditions D1 (0M), D5, D6
<b>D5</b>	x				x	0	With conditions D2(0M), D4
<b>D6</b>	x	x	Sat	x	x	0	With conditions D3 (0M), D4, D7, D9
<b>D7</b>	x	x	Sat	x	x	0.60	With conditions D3 (0.60M), D6, D10 (0.60M)
<b>D8</b>		x	Unsat	x		0, 0.60, 4.28	Between [NaCl] and each [NaCl] with conditions D3, D9 (0M), D10 (0.60M)
<b>D9</b>		x	Unsat	x	x	0	With conditions D6, D8 (0M), D10
<b>D10</b>		x	Unsat	x	x	0.60	With conditions D7, D8 (0.60M), D9

Tables 4.16 and 4.17 summarize the statistical results for dynamic flux reactors (i.e. significant or not significant statistical difference) when comparing data before and after 6 hours of experiment, respectively. The diagonal shows the statistical results for the replicates. “S” means that the difference between the data is statistically significant; “NS” means that the difference is not statistically significant. The condition that yields the higher median will be denoted in the lower half of the cell containing the “S”. For example, a cell containing  $S_{/D5}$  means that the conditions that meet in that cell yield statistically significantly different results and D5 yields the higher median.

Table 4.16. Statistical analysis results summary for flux reactor experiments data up to 6 hours.

Replicates (diagonal)		Dynamic flux experiments (Table 3.7)																		
		D1 0	D1 0.6	D1 4.3	D2 0	D2 0.6	D2 4.3	D3 0	D3 0.6	D3 4.3	D4 0	D5 0	D6 0	D7 0.6	D8 0	D8 0.6	D8 4.3	D9 0	D10 0.6	
Dynamic flux experiments	D1_0	NS	NS	NS	NS			NS			NS									
	D1_0.6		NS	NS		NS			NS											
	D1_4.3			NS			NS			NS										
	D2_0				NS	NS	NS						S D5							
	D2_0.6					NS	NS													
	D2_4.3						NS													
	D3_0							NS	NS	NS				NS		S D8				
	D3_0.6								NS	NS					NS		S D8			
	D3_4.3									NS								S D8		
	D4_0										NS	NS	NS							
	D5_0											NS								
	D6_0													NS	NS				S D9	
	D7_0.6															NS				S D10
	D8_0															S	S 0.6	S 4.3	S D8	
	D8_0.6																S	S 0.6		S D8
	D8_4.3																	NS		
	D9_0																			NS
D10_0.6																				S D9&D10

Cells in this table represent the statistical results (i.e., significant or not significant difference) for comparisons between treatments of the dynamic flux reactor test data (t = 0 until t = 6 hrs). The diagonal shows the statistical results for comparisons between the replicates of each test. S = statistical difference is significant; NS = statistical difference is not significant. The condition that yields the higher median is denoted in the lower half of the cell containing the "S".

Table 4.17. Statistical analysis results summary for flux reactor experiments data after 6 hours.

Replicates (diagonal)	Dynamic flux experiments (Table 3.7)																		
	D1 0	D1 0.6	D1 4.3	D2 0	D2 0.6	D2 4.3	D3 0	D3 0.6	D3 4.3	D4 0	D5 0	D6 0	D7 0.6	D8 0	D8 0.6	D8 4.3	D9 0	D10 0.6	
D1_0	S D1_2	S 0.6	S 0	S D1			S D3			S D4									
D1_0.6		S D1_2	S 0.6		S D1			S D1&D3											
D1_4.3			NS			NS			NS										
D2_0				NS	NS	NS					NS								
D2_0.6					NS	NS													
D2_4.3						NS													
D3_0							NS	S 0&0.6	S 0		S D3	S D8							
D3_0.6								NS	S 0.6			S D7	S D8						
D3_4.3									NS						S D8				
D4_0									S D4_1	S D4	S D4								
D5_0										NS									
D6_0											NS	S D7					S D9		
D7_0.6												S D7_2						S D7	
D8_0													S D8_2	S 0.6	S 4.3	S D8			
D8_0.6														S D8_1	S 0.6&4.3			S D8	
D8_4.3															S D8_1				
D9_0																	S D9_2	S D9&D10	
D10_0.6																			S D10_1

Cells in this table represent the statistical results (i.e., significant or not significant difference) for comparisons between treatments of the dynamic flux reactor test data (t = 0 until t = 6 hrs). The diagonal shows the statistical results for comparisons between the replicates of each test. S = statistical difference is significant; NS = statistical difference is not significant. The condition that yields the higher median is denoted in the lower half of the cell containing the "S".

Statistical analyses between replicates during early times indicate that for most of the conditions, the replicates (diagonal cells) are statistically similar (i.e., NS = difference is not significant). There are significant differences (i.e., S = significant) between replicates in the case of D8, for [NaCl] of 0 M and 0.60 M and in the case of D10.

In general, statistical analyses between the different treatments (cells above the diagonal, not including the diagonal) during early times indicate that: initially TCE vapor extraction in TCE solution without TCE NAPL is enhanced in presence of MeOH; the addition of NaCl to unsaturated clay with TCE NAPL enhances TCE vapor extraction; there is a higher TCE vapor extraction in presence of unsaturated clay; TCE vapor extraction in unsaturated clay with or without NaCl is not enhanced by MeOH.

Statistical analyses between replicates during late times indicate that for half of the conditions, the replicates (diagonal cells) are statistically similar (i.e., NS = difference is not significant). There are significant differences (i.e., S = significant) between replicates in the case of D1 for [NaCl] of 0 M and 0.60 M, between D4 replicates, between D7 replicates, in the case of D8 replicates, for all [NaCl], and in the case of D9 and D10 replicates.

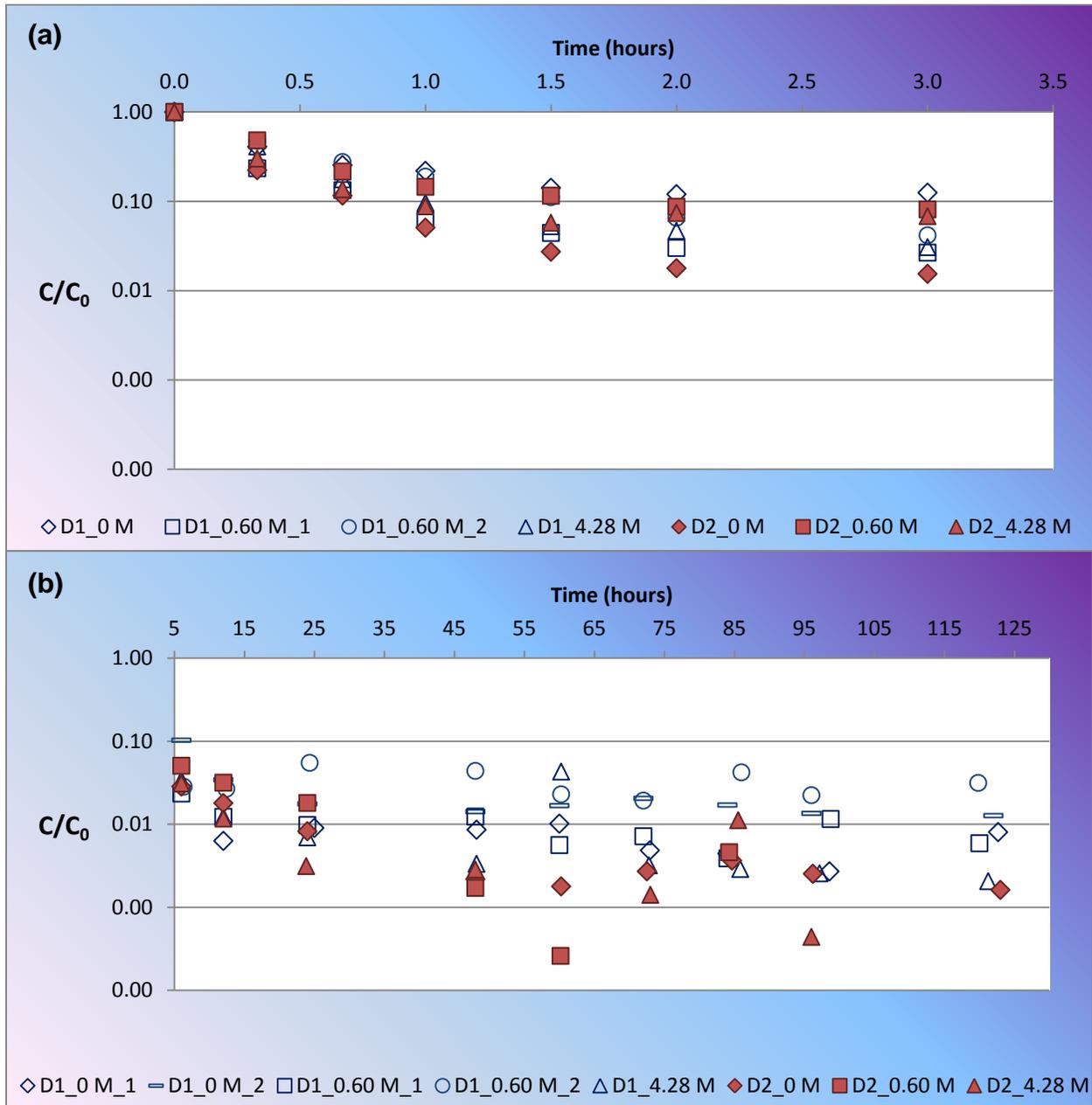
In general, statistical analyses between the different treatments (cells above the diagonal, not including the diagonal) at late times indicate that: a low NaCl concentration enhances TCE vapor extraction; TCE vapor extraction is higher in presence of TCE NAPL; TCE<sub>vc</sub> is higher in presence than in absence of saturated clay; TCE vapor extraction is enhanced by the presence of MeOH in TCE solution with TCE NAPL; a low NaCl concentration enhances TCE vapor extraction in saturated clay with TCE NAPL; TCE vapor extraction in saturated clay without NaCl is not enhanced by MeOH, but MeOH enhances the extraction in saturated clay with NaCl; TCE vapor extraction is higher in presence of TCE NAPL, in TCE solution with MeOH; TCE vapor extraction is higher in absence of clay, in TCE solution with MeOH without NaCl; TCE vapor extraction is enhanced in presence of NaCl, in saturated clay with TCE NAPL and MeOH; TCE vapor extraction is enhanced in presence of unsaturated clays than for

saturated clay, in presence of clay, TCE NAPL and NaCl; TCE vapor extraction is enhanced in presence of NaCl, in unsaturated clay with TCE NAPL; there is a higher TCE vapor extraction in presence of unsaturated clay than in saturated clay; TCE vapor extraction is higher in saturated than in unsaturated clay with TCE NAPL, NaCl and MeOH; TCE vapor extraction is higher in absence of MeOH, in unsaturated clay with or without NaCl.

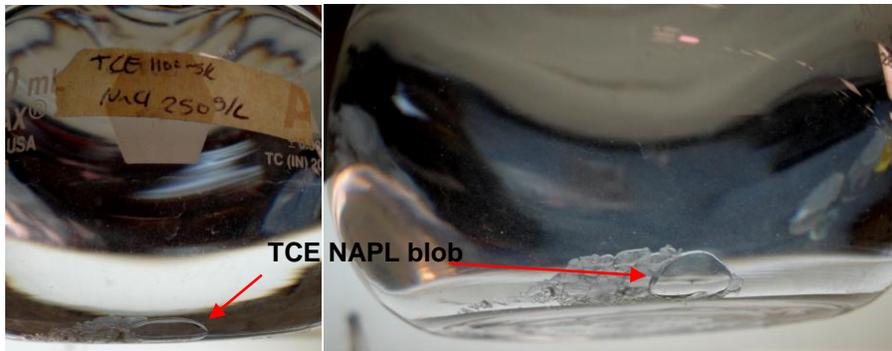
The effect of [NaCl] on TCE volatilization in the presence (experiment D1) and absence (experiment D2) of TCE NAPL is shown in figure 4.15. In general, TCE<sub>vc</sub> tend to be higher for reactors having TCE NAPL than those not having it. For those reactors with TCE NAPL, higher TCE<sub>vc</sub> are initially measured for solution with no NaCl ([NaCl] = 0 M), followed by those with [NaCl] = 0.60 M. Lowest TCE<sub>vc</sub> are observed for solutions with [NaCl] = 4.28 M. Lower TCE<sub>vc</sub> at higher [NaCl] in the presence of TCE NAPL may reflect changes in the partitioning behavior of the NAPL (i.e. dissolution), and/or the dissolved TCE (i.e. volatilization, partitioning into NAPL phase). The partitioning of TCE into NAPL phase was observed during the static batch experiments after mixing TSSS with NaCl to achieve a salt concentration of 4.28 M (See Figure 4.16). TCE NAPL was not visibly present before mixing and it appeared after mixing with NaCl. At later times TCE<sub>vc</sub> are higher for the reactors with [NaCl] = 0.60 M than those with no NaCl. In the case of reactors without TCE NAPL at early times, higher relative concentrations are observed for [NaCl] = 0.60 M, and those reactors with no NaCl ([NaCl] = 0 M) showed the lowest TCE<sub>vc</sub>. [NaCl] seems to have no effect on the TCE<sub>vc</sub> at late times in the absence of TCE NAPL. It is observed, however, that for later times ( $t \geq 6$  hrs) TCE<sub>vc</sub> for D2 is reduced. This may be due to the depletion of the TCE source which in these reactors is diluted TCE.

Statistically, there are significant differences at late times between treatments (0 M and 0.60 M, 0 M and 4.28 M, 0.60 M and 4.28 M) in D1 and between D1 and D2 at [NaCl] = 0 M and 0.60 M. In D1, [NaCl] = 0.60 M yields higher TCE<sub>vc</sub> than the other two treatments. At [NaCl] = 0 M and 0.60 M, D1 yields higher TCE<sub>vc</sub> because D2's TCE

source is being depleted while D1 has TCE NAPL that is still dissolving into solution to be later volatilized.

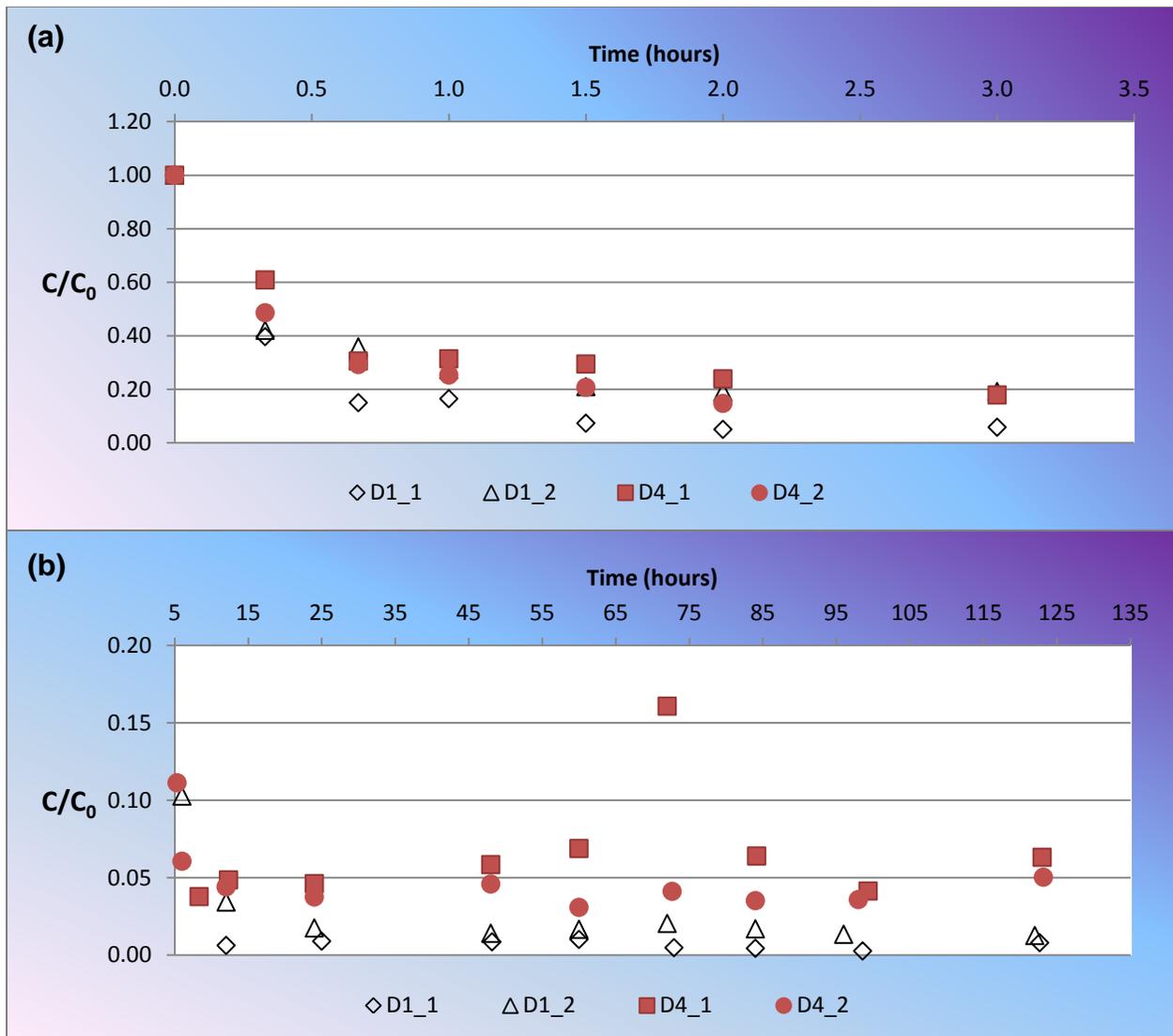


**Figure 4.15. Temporal changes in relative TCEvc ( $C/C_0$ ) for experiments D1 and D2 at (a) early times ( $t < 6$  hrs) and (b) late times ( $t \geq 6$  hrs). D1 reactors contain TCE solution, TCE NAPL and  $[\text{NaCl}] = 0$  M, 0.60 M or 4.28 M; D2 reactors contain TCE solution and  $[\text{NaCl}] = 0$  M, 0.60 M or 4.28 M; D1\_0 M\_1 and D1\_0 M\_2 are replicates for D1 containing  $[\text{NaCl}] = 0$  M; D1\_0.60 M\_1 and D1\_0.60 M\_2 are replicates for D1 containing  $[\text{NaCl}] = 0.60$  M.**



**Figure 4.16. TCE partitioning from TCE solution with high NaCl content into pure phase.**

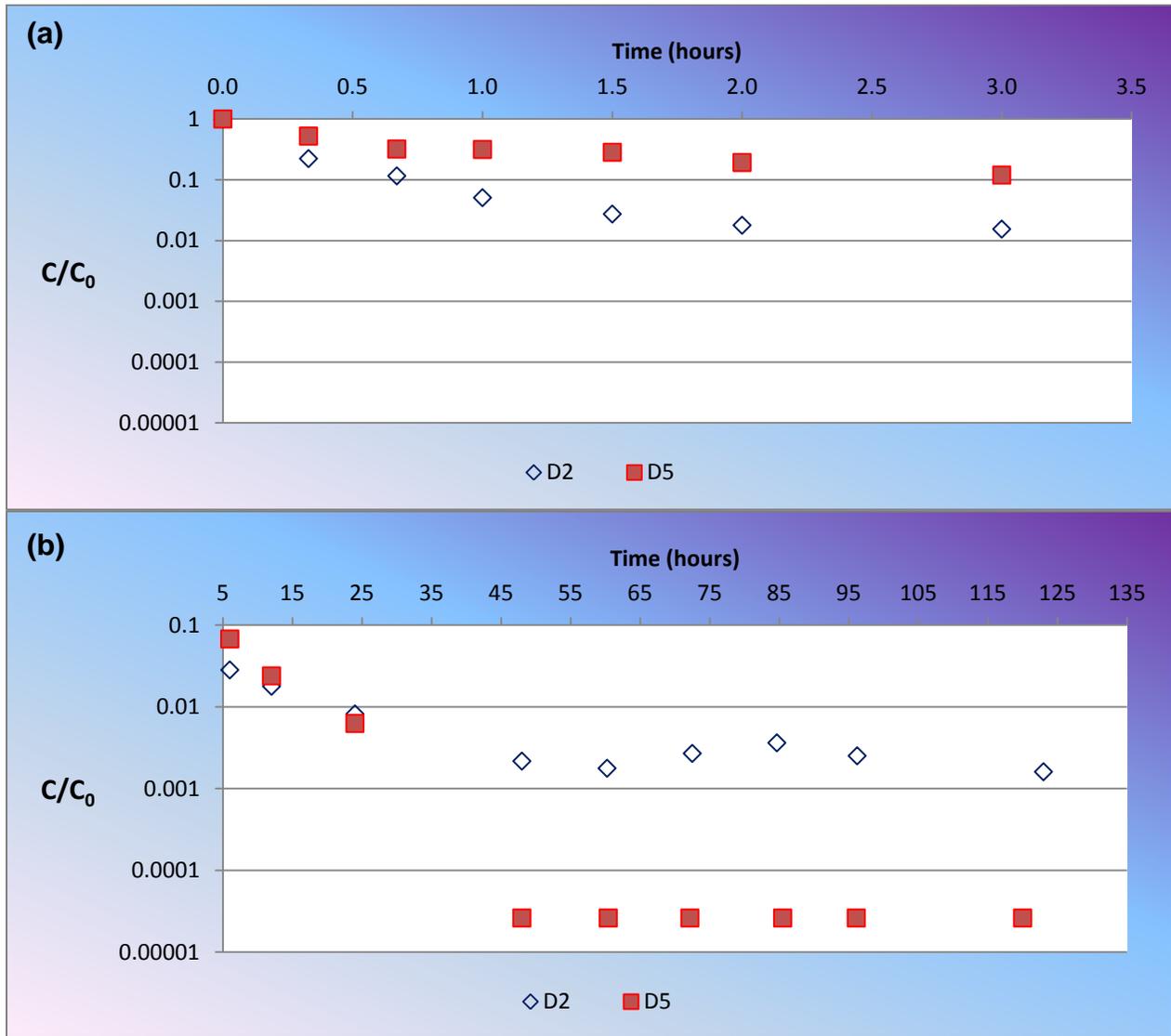
The effect of methanol (MeOH) on a TCE solution with TCE NAPL is assessed by comparing results from experiments D1 (NAPL, [NaCl] = 0 M) and D4 (NAPL, [NaCl] = 0 M, MeOH). Figure 4.17 shows that  $TCE_{vc}$  is higher for D4 at all times during the experiment. This suggests that MeOH may enhance dissolution of TCE NAPL, therefore making it more available for volatilization. Although, statistically, there was no statistically significant difference between D1 and D4 at earlier times ( $t < 6$  hrs), there is statistically significant difference at later times ( $t \geq 6$  hrs), in which the median is always higher for D4 suggesting that MeOH enhances TCE volatilization when added to a TCE solution with TCE NAPL.



**Figure 4.17. Temporal changes in relative TCEvc ( $C/C_0$ ) for experiments D1 and D4 at (a) early times ( $t < 6$  hrs) and (b) late times ( $t \geq 6$  hrs). D1 reactors contain TCE solution, TCE NAPL and  $[NaCl] = 0$  M; D4 reactors contain TCE solution, TCE NAPL and MeOH; D1\_1 and D1\_2 are replicates; D4\_1 and D4\_2 are replicates.**

The effect of MeOH on TCE solution without TCE NAPL is assessed by comparing results from experiments between D2 ( $[NaCl] = 0$  M) and D5 ( $[NaCl] = 0$  M, MeOH). From the plots in figure 4.18 it can be noted that in the first 3 hours of the experiments D5 yields higher TCEvc than D2. This suggests that MeOH enhances the volatilization of TCE even when there is no TCE NAPL present. Statistically, there is a significant

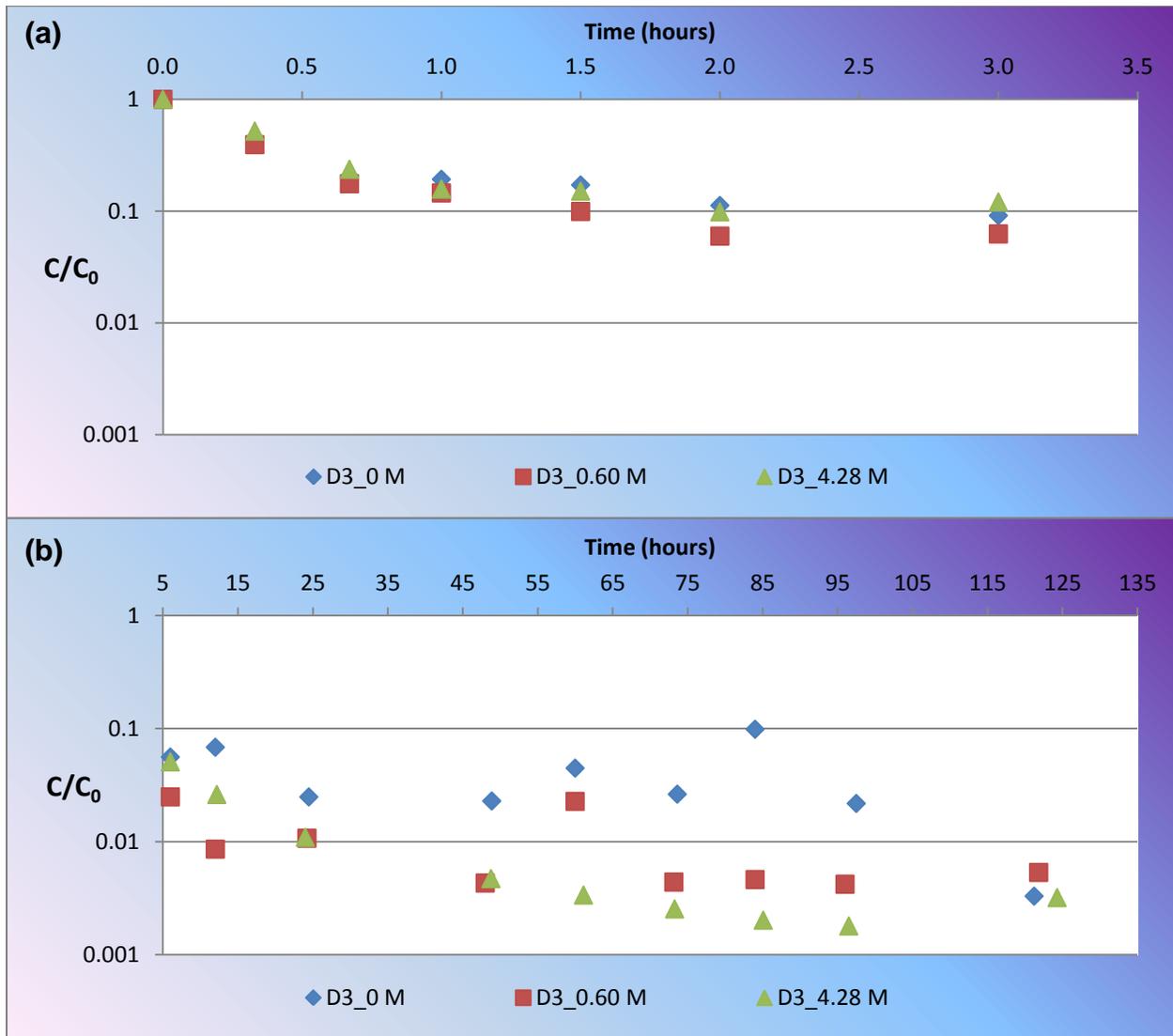
difference between D2 and D5 in the initial 3 hours, in which D5 has a higher median. For later times ( $t \geq 6$  hrs), there seems to be no difference until approximately 48 hours where D5 starts yielding TCEvc of zero, meaning that there is no more TCE in solution.



**Figure 4.18. Temporal changes in relative TCEvc ( $C/C_0$ ) for experiments D2 vs D5 at (a) early times ( $t < 6$  hrs) and (b) late times ( $t \geq 6$  hrs). D2 reactors contain TCE solution and  $[\text{NaCl}] = 0 \text{ M}$ ; D5 reactors contain TCE solution and MeOH.**

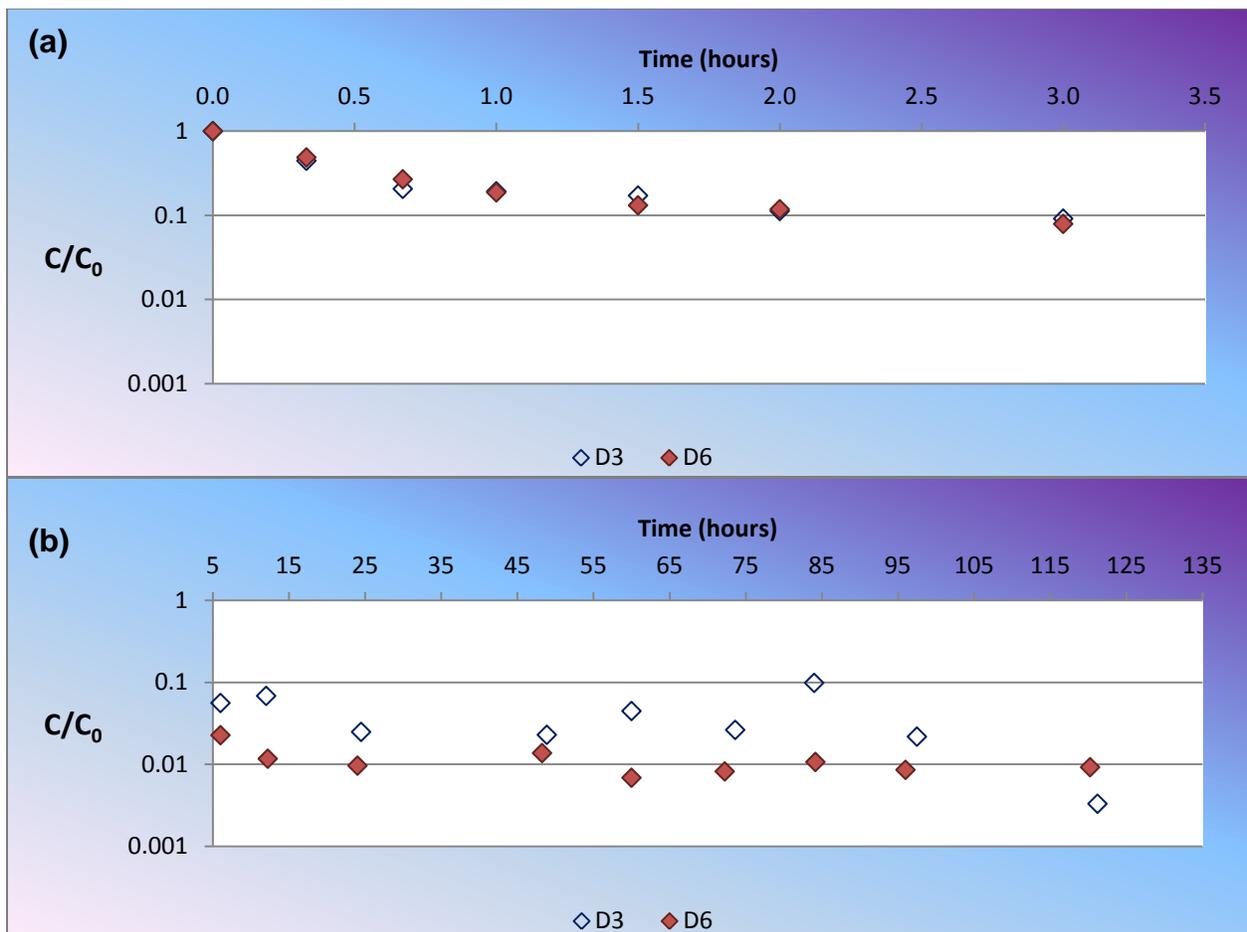
The effect of NaCl on TCEvc for TCE solution containing saturated clay with TCE NAPL is assessed by comparing different salt concentration treatments in D3. In the first 3 hours, reactors without NaCl yield the highest TCEvc, but statistically there is no

difference between the different treatments (Figure 4.19). For later times ( $t \geq 6$  hrs), the behavior stays the same with a more noticeable difference. Statistically, there is a significant difference where reactors without NaCl yield higher TCEvc than reactors with 0.60 M and 4.28 M NaCl. This indicates that higher salt concentrations do not yield higher TCEvc in the presence of saturated clays and TCE NAPL.



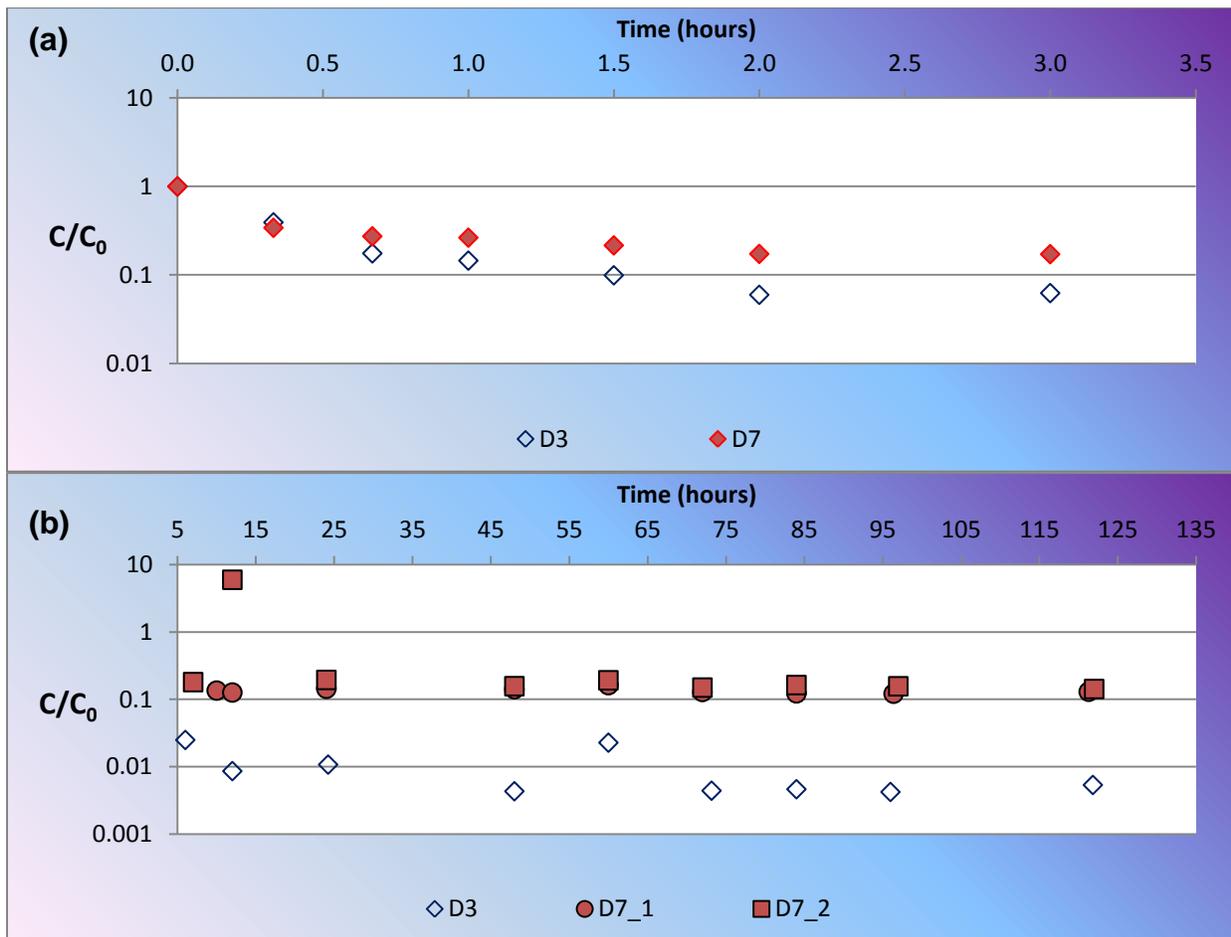
**Figure 4.19. Temporal changes in relative TCEvc ( $C/C_0$ ) for D3 at (a) early times ( $t < 6$  hrs) and (b) late times ( $t \geq 6$  hrs). D3 reactors contain TCE solution, saturated clay, TCE NAPL and  $[NaCl] = 0$  M, 0.60 M or 4.28 M.**

The effect of MeOH on TCEvc for a TCE solution containing saturated clay and TCE NAPL is assessed for solutions containing no [NaCl], with (D6) and without (D3) MeOH. Results show that during the first 3 hours (Figure 4.20), there is no difference between the TCEvc in the different treatments. Statistically, in the first 3 hours there is no significant difference. For later times ( $t \geq 6$  hrs), it seems that D3 yields higher concentrations than D6, suggesting that TCE is not more available for volatilization in the presence of MeOH, possibly due to TCE or methanol sorption onto clays. Statistically, there is a significant difference at later times, when D3 yields a higher median, indicating that MeOH does not enhance volatilization in the presence of saturated clay and TCE NAPL, in the absence of NaCl.



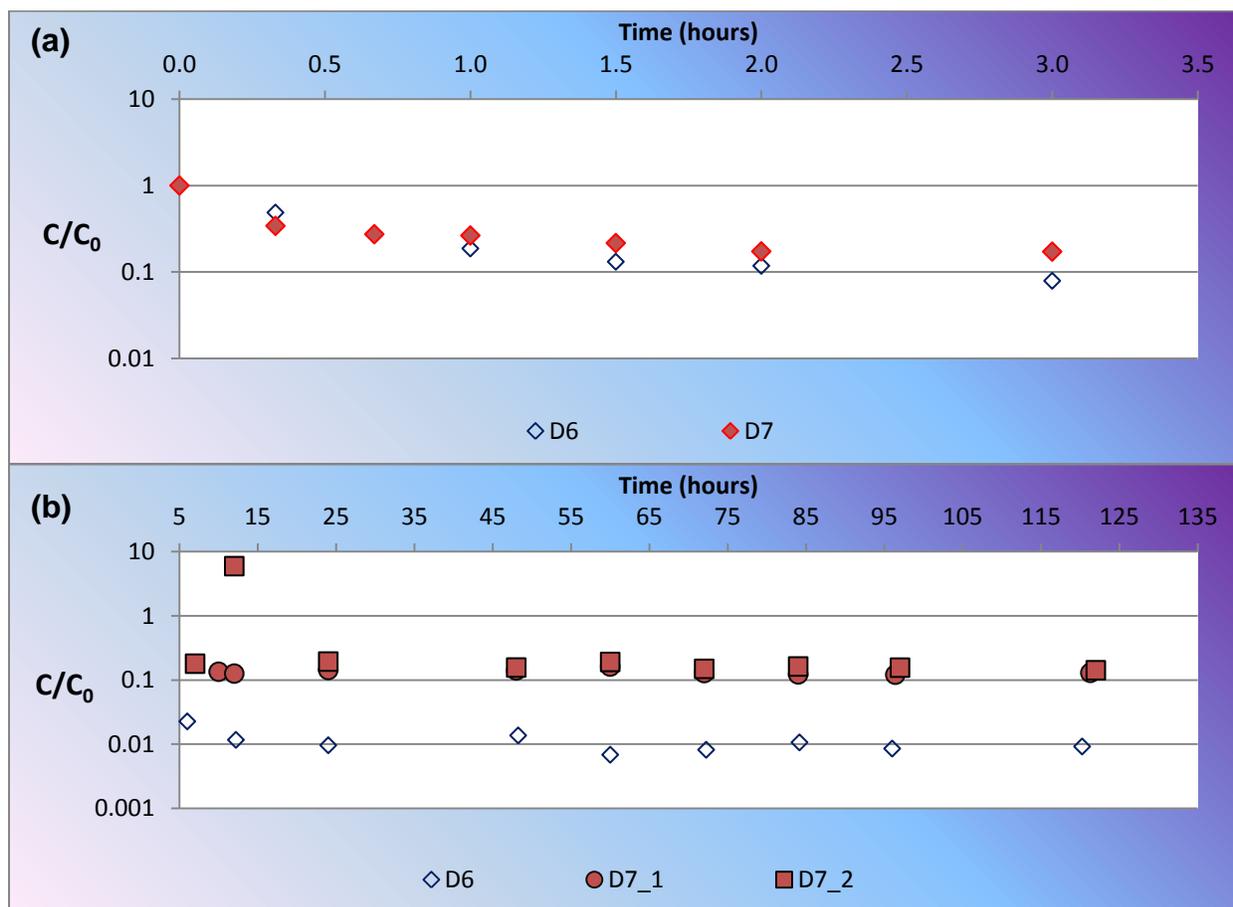
**Figure 4.20. Temporal changes in relative TCEvc ( $C/C_0$ ) for experiments D3 and D6 at (a)early times ( $t < 6$  hrs) and (b)late times ( $t \geq 6$  hrs). D3 reactors contain TCE solution, saturated clay, TCE NAPL and [NaCl] = 0 M; D6 reactors contain TCE solution, saturated clay, TCE NAPL and MeOH.**

The effect of MeOH on TCE solution containing saturated clay, TCE NAPL and a NaCl concentration of 0.60 M is assessed by comparing results from experiments D3 (TCE solution, TCE NAPL, clay and [NaCl] = 0.60 M) and D7 (TCE solution, TCE NAPL, clay, MeOH and [NaCl] = 0.60 M). Results (Figure 4.21) show that D7 yields a higher TCE<sub>vc</sub> during the first 3 hours than D3, which suggests that MeOH in the presence of 0.60 M NaCl increases the dissolution of TCE NAPL, therefore increasing TCE available for volatilization. Statistically, however, there is no significant difference. For later times ( $t \geq 6$  hrs), D7 yields higher TCE<sub>vc</sub> compared to D3 and the difference is statistically significant. Higher median in D7 suggests that at a [NaCl] of 0.60 M, the presence of MeOH enhances the volatilization of TCE from solution containing clay and pure phase.



**Figure 4.21. Temporal changes in relative TCE<sub>vc</sub> ( $C/C_0$ ) for experiments D3 and D7 at (a) early times ( $t < 6$  hrs) and (b) late times ( $t \geq 6$  hrs). D3 reactors contain TCE solution, saturated clay, TCE NAPL and [NaCl] = 0.60 M; D7 reactors contain TCE solution, saturated clay, TCE NAPL, MeOH and [NaCl] = 0.60 M.**

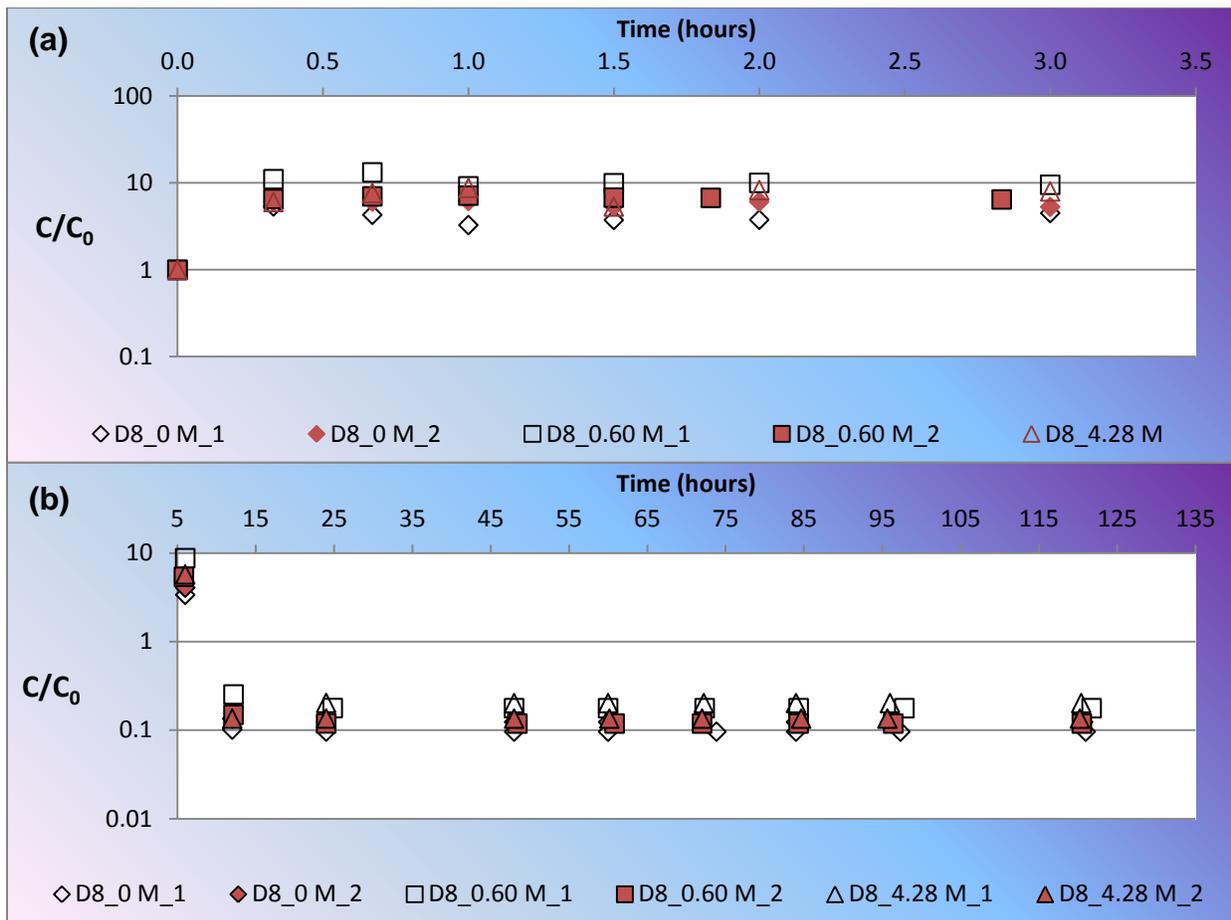
The effect of NaCl on TCEvc for solution containing clays, TCE NAPL and MeOH is assessed by comparing results from experiments D6 ([NaCl] = 0 M) and D7 ([NaCl] = 0.60 M). Results (Figure 4.22) show that D7 yields higher TCEvc than D6 during all the experiment. Statistically, in the first 3 hrs there is no significant difference but there is a significant difference after 6 hrs between the replicates of D7 and between D6 and D7, in which D7 yields a higher median. This suggests that NaCl may cause restructuring of the clay and/or the salting out of TCE, both of which could enhance TCE volatilization.



**Figure 4.22. Temporal changes in relative TCEvc ( $C/C_0$ ) for experiments D6 and D7 at (a) early times ( $t < 6$  hrs) and (b) late times ( $t \geq 6$  hrs). D6 reactors contain TCE solution, saturated clay, TCE NAPL and MeOH; D7 reactors contain TCE solution, saturated clay, TCE NAPL, MeOH and  $[\text{NaCl}] = 0.60$  M.**

The effect of  $[\text{NaCl}]$  on TCEvc in unsaturated clays ( $w_c = 15\%$ ) having TCE NAPL, is assessed by comparing results from experiment D8 using different  $[\text{NaCl}]$ . It is noted

that relative TCEvc are substantially higher in the experiments with unsaturated clay ( $C/C_0 \leq 10$ , Figure 4.23) than saturated clay ( $C/C_0 < 1$ , Figures 4.19, 4.20, 4.21 and 4.22). TCEvc tend to be slightly higher for clays having higher NaCl concentration during the first 3 hours, showing statistically significant difference between those having no NaCl ( $[NaCl] = 0$  M) and those having a 0.60 M or 4.28 M concentration. At later times ( $t \geq 6$  hrs), there is still a statistically significant difference in TCEvc between reactors having no NaCl and those having 0.60 M and 4.28 M. Results indicate that the TCEvc median is lower for reactors with no NaCl, than for those with higher concentrations, and suggest that NaCl enhances TCE volatilization in contaminated unsaturated clay.



**Figure 4.23. Temporal changes in relative TCEvc ( $C/C_0$ ) for experiment D8 at (a) early times ( $t < 6$  hrs) and (b) late times ( $t \geq 6$  hrs). D8 reactors contain unsaturated clay (15% wc), TCE NAPL and  $[NaCl] = 0$  M, 0.60 M and 4.28 M.**

The effect of MeOH on unsaturated clay (15% wc) with TCE NAPL and no NaCl concentration is assessed by comparing results from experiments D8 (unsaturated clay, NAPL and [NaCl] = 0 M) and D9 (unsaturated clay, NAPL and MeOH). Results (Figure 4.24) show that TCE<sub>vc</sub> is higher for treatments with no MeOH (D8) than with (D9) MeOH. This suggests the presence of MeOH in unsaturated clay enhances retention of TCE in the water and/or clay phase. Statistically, in the first 3 hours there is a significant difference between D8\_2 and D9, in which D8 yields a higher median. For later times (t ≥ 6 hrs), there is a statistically significant difference between both D8 reactors and both D9 reactors, in which D8 always yields a higher median.

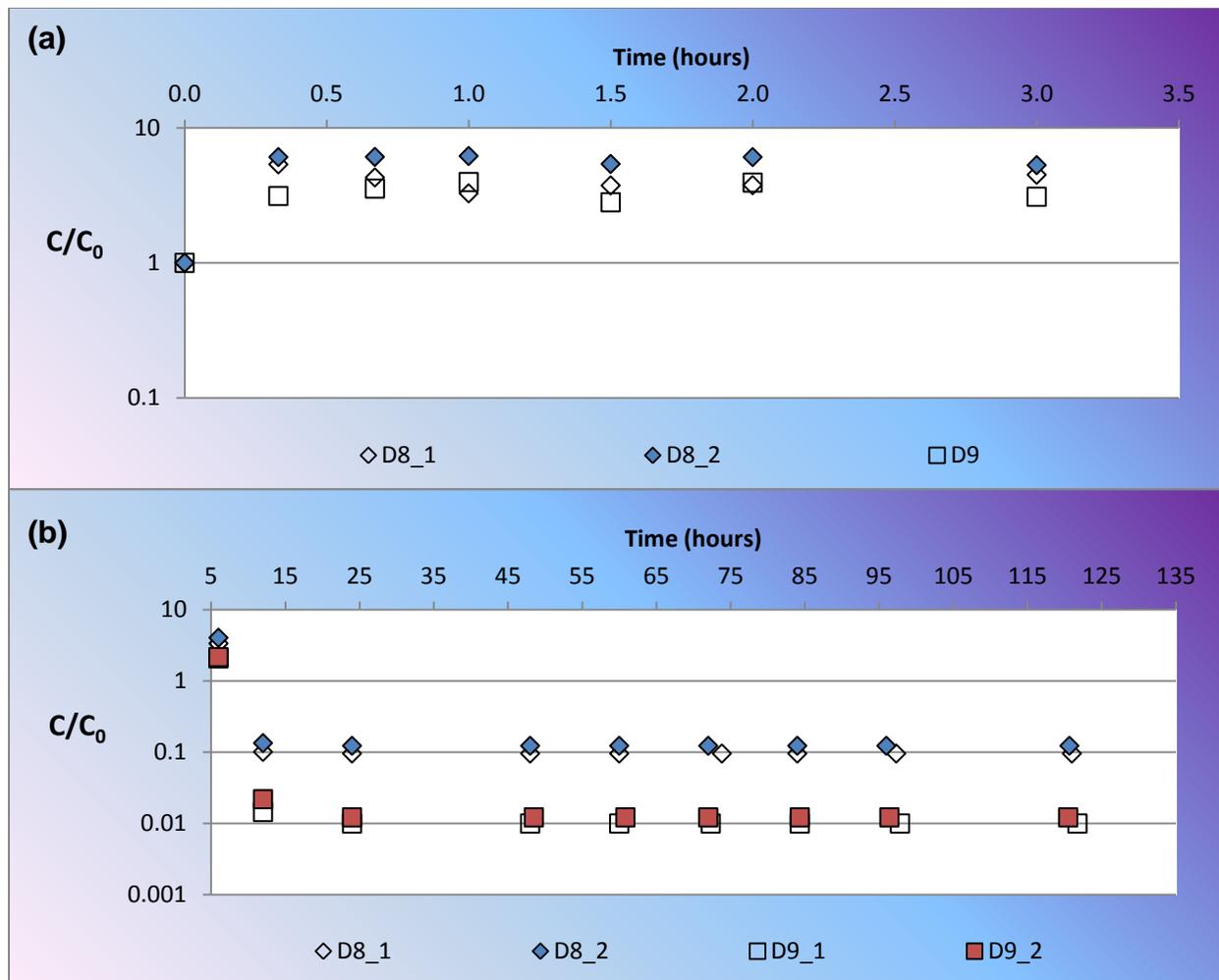
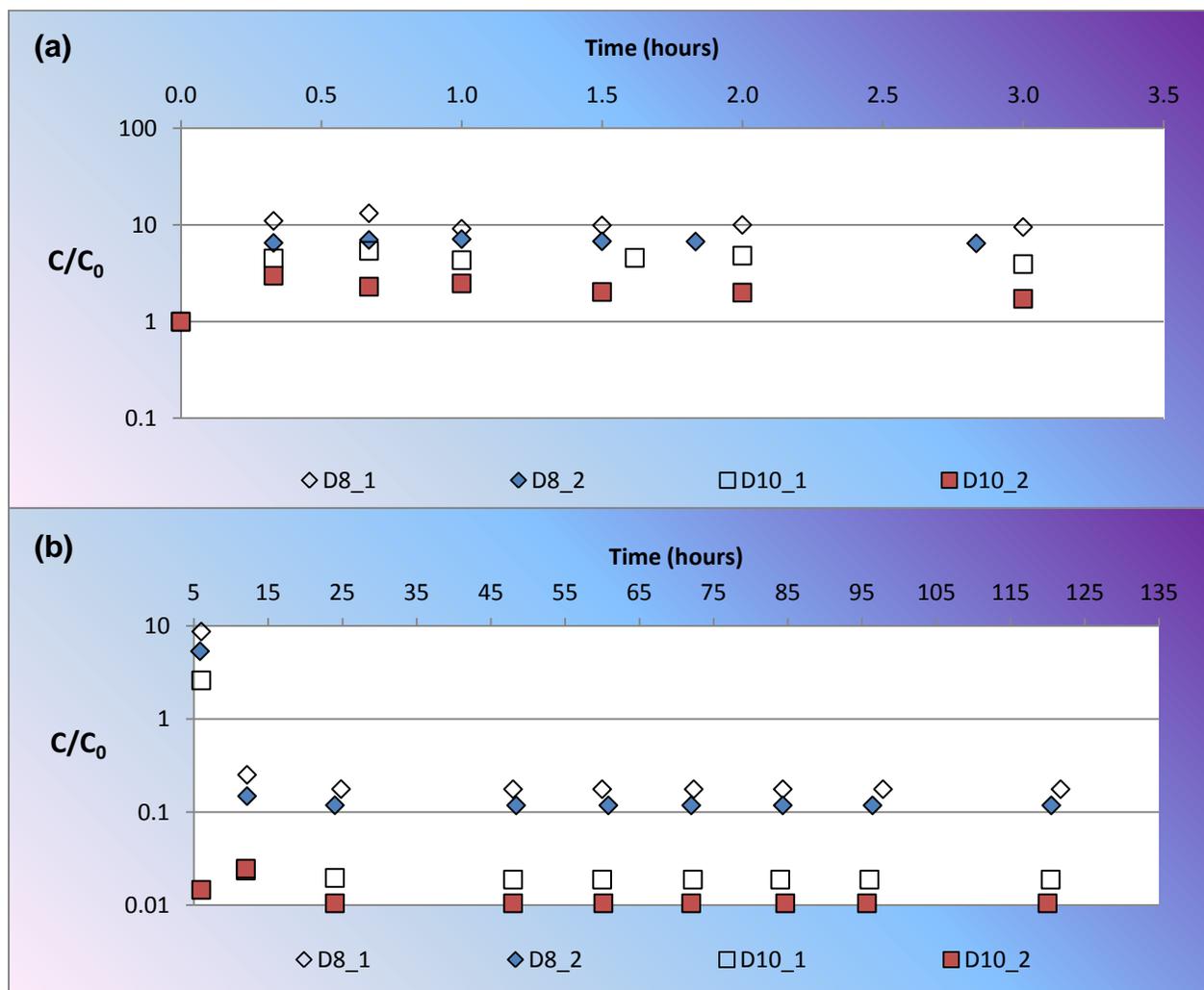


Figure 4.24. Temporal changes in relative TCE<sub>vc</sub> ( $C/C_0$ ) for experiments D8 and D9 at (a) early times ( $t < 6$  hrs) and (b) late times ( $t \geq 6$  hrs). D8 reactors contain unsaturated clay (15% wc), TCE NAPL and [NaCl] = 0 M; D9 reactors contain unsaturated clay (15% wc), TCE NAPL and MeOH.

The effect of MeOH on TCE volatilization from unsaturated clay (15% wc) with TCE NAPL and a NaCl concentration of 0.60 M is assessed through comparisons between D8 (unsaturated clay, NAPL and NaCl) and D10 (unsaturated clay, NAPL, NaCl and MeOH). Results show (Figure 4.25) that D8 yields higher TCE<sub>vc</sub> than D10 throughout the entire experiment. Statistically, there is a significant difference between D8 and D10 during the entire experiment, in which D8 always yields a higher median. Results indicate that MeOH does not enhance TCE volatilization when added to unsaturated clay containing NaCl and TCE NAPL.



**Figure 4.25. Temporal changes in relative TCE<sub>vc</sub> ( $C/C_0$ ) for experiments D8 and D10 at (a) early times ( $t < 6$  hrs) and (b) late times ( $t \geq 6$  hrs). D8 reactors contain unsaturated clay (15% wc), TCE NAPL and  $[NaCl] = 0$  M; D10 reactors contain unsaturated clay (15% wc), TCE NAPL, MeOH and  $[NaCl] = 0.60M$ .**

No observable difference between TCEvc in experiments D9 and D10 (Figure 4.26) may indicate that the presence of NaCl does not affect TCE volatilization in unsaturated clays having TCE NAPL and MeOH. There are, however, statistical differences at early times between D10 replicates and D10 and D9, in which D10\_1 yields a higher TCEvc than D9 but D10\_2 yields a lower TCEvc. There are also statistical differences at late times between the replicates for both D9 and D10, and between D9 replicates and D10 replicates, in which the result is not constant.

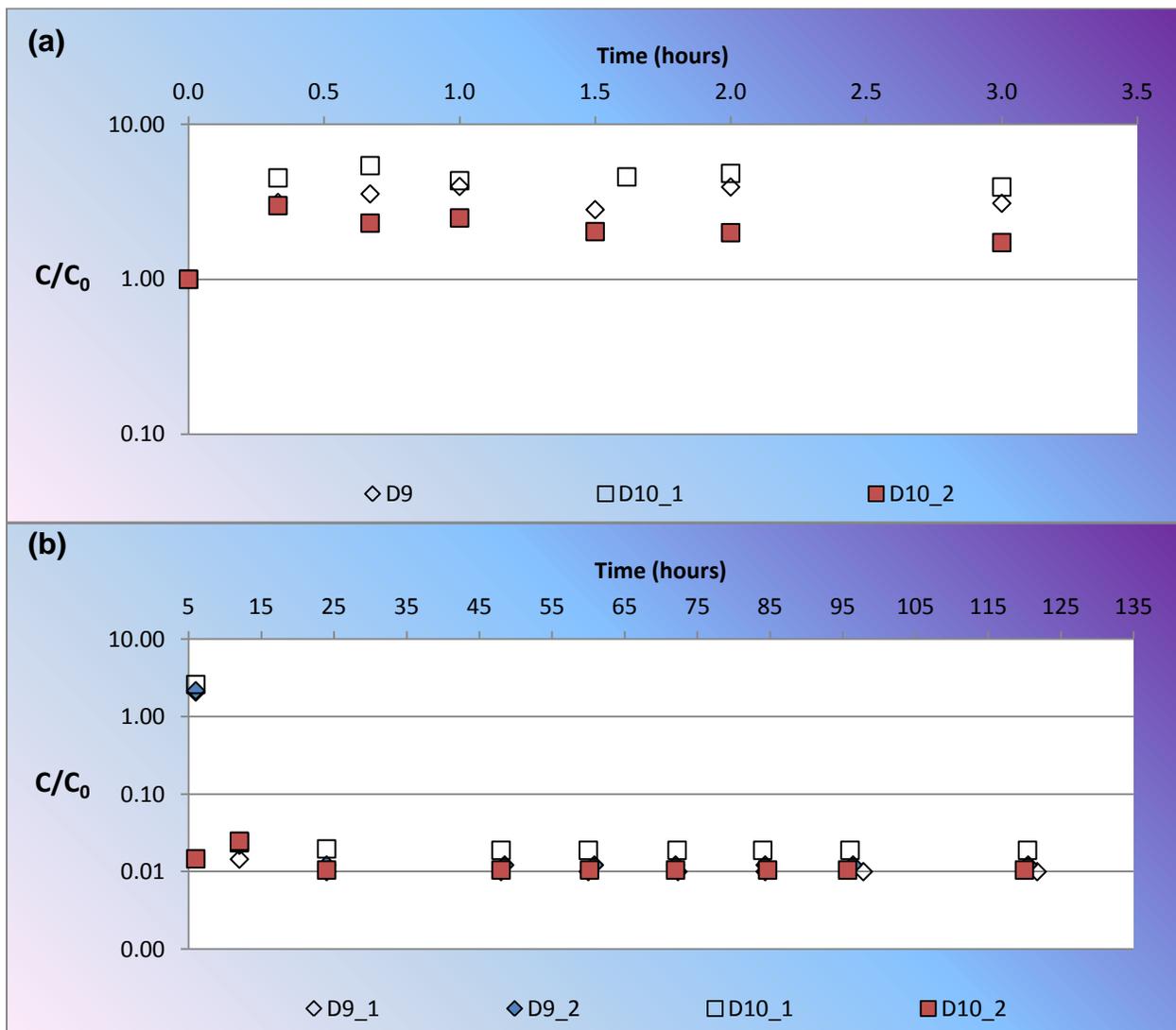


Figure 4.26. Temporal changes in relative TCEvc ( $C/C_0$ ) for experiments D9 and D10 at (a) early times ( $t < 6$  hrs) and (b) late times ( $t \geq 6$  hrs).

D9 reactors contain unsaturated clay (15% wc), TCE NAPL and MeOH; D10 reactors contain unsaturated clay (15% wc), TCE NAPL, MeOH and  $[NaCl] = 0.60M$ .

#### 4.4.2 Extracted mass

For the comparison of extracted mass values, experiment D1 with [NaCl] = 0 M was used as a control. Extracted mass results are shown in Table 4.18.

**Table 4.18. Extracted mass values.**

Condition (Table 3.7)	[NaCl] M	Extracted Mass (mg)	Initial Mass (mg)	% Mass Removal
<b>D1</b>	<b>0</b>	<b>162.84</b>	<b>1530.75</b>	<b>10.64</b>
	0.60	205.72	1542.41	13.34
	4.28	184.99	1566.02	11.81
<b>D2</b>	0	183.03	183.03	100.00
		50.88	50.88	100.00
	0.60	46.01	46.01	100.00
	4.28	44.72	44.72	100.00
		22.35	23.10	96.75
<b>D3</b>	0	249.04	1509.08	16.50
	0.60	57.97	1494.76	3.88
	4.28	49.85	1491.58	3.34
<b>D4</b>	0	220.26	1489.00	14.79
<b>D5</b>	0	17.35	17.35	100.00
		5.61	5.61	100.00
<b>D6</b>	0	66.28	1492.81	4.44
<b>D7</b>	0.60	876.84	1506.92	58.19
<b>D8</b>	0	1460.00	1460.00	100.00
	0.60	1460.00	1460.00	100.00
	4.28	1460.00	1460.00	100.00
<b>D9</b>	0	1460.00	1460.00	100.00
<b>D10</b>	0.60	1322.13	1460.00	90.56

From the data obtained of the extracted mass analysis the following results could be derived:

In reactors with TCE solution and TCE NAPL, extraction is higher for a [NaCl] of 0.60 M (13%), than for [NaCl] of 4.28 M (12%) and it is the lowest for reactors with no NaCl

(11%). This suggests that a [NaCl] of 0.60 M causes salting out of TCE, increasing TCE volatilization from solution.

Extraction is higher (97%-100%) at all NaCl concentrations in reactors with TCE solution without TCE NAPL (D2) compared to reactors with TCE NAPL (D1) (11%-13%). This is attributed to the lower mass to be extracted.

In reactors with TCE solution and TCE NAPL without NaCl, extraction is higher (15%) in presence of MeOH (D4) compared to D1 (11%). This is because MeOH increases NAPL dissolution which makes it more available for volatilization from solution. In reactors with TCE solution without TCE NAPL without NaCl, extraction is 100% in presence of MeOH (D5) but also in its absence (D2). This is attributed to the low mass to be extracted.

In reactors with TCE solution, saturated clay and TCE NAPL (D3), extraction is higher (17%) for reactors without NaCl and is the lowest (3%) for reactors with the highest NaCl concentration. Although speculative, this could be due to the effect sodium ions ( $\text{Na}^+$ ) may have on clay (Pearson, 2009), which can potentially enhance TCE sorption onto clay, limiting its availability for volatilization. This is also observed in reactors with NaCl, in which extraction is higher in solution (D1) than in the presence of saturated clay (D3). This supports the observation that the presence of clays limits volatilization of TCE.

In reactors having TCE-solution, saturated clay, TCE NAPL and no NaCl, extraction is higher (17%) in reactors without MeOH (D3) compared to those with MeOH (D6, 4%). It seems that MeOH does not increase TCE volatilization in reactors with saturated clay and no NaCl.

In reactors having TCE-solution, saturated clay, TCE NAPL and [NaCl] = 0.60 M, extraction is higher (58%) in reactors with MeOH (D7) compared to those without MeOH

(D3, 4%). This suggests that for a NaCl concentration of 0.60 M, MeOH enhances TCE volatilization in the presence of clays.

In reactors with clay, TCE NAPL and NaCl, extraction for all three NaCl concentrations is higher (100%) in unsaturated clay (D8) compared with D3 (3-17%). This could be because in unsaturated clay volatilization is not limited by dissolution as in saturated clay. Also the contact area between TCE NAPL and air may be larger. These results may be due to the difference in vapor phase measurements under saturated (with water) and unsaturated (no water) conditions. It is suspected that TCE vapor sorption in the sampling SPME fiber is higher in the absence than in the presence of water. Higher sorption of TCE in unsaturated than saturated soils has been attributed to lower competition for sorption sites on soil in the absence of water (i.e. water molecules preferentially adsorb onto soil) (Ong & Lion, 1991). If this phenomenon occurs for the SPME fiber, the calibration used to determine vapor phase concentration would be different in the presence or absence of water. Thus, the high extracted mass may be due to higher sorption capacity into the SPME fiber, and not really reflect higher extracted mass. To determine if this was due to measurement differences in saturated and unsaturated environments, or to volatilization processes, TCE<sub>vc</sub> were measured in reactors only containing TCE NAPL. One (1) mL of TCE NAPL was added to a 1 L bottle (this is the amount of TCE NAPL added to the reactors). After 4 hours, vapor concentrations were measured in the headspace. TCE<sub>vc</sub> in the headspace were found to be higher than for a reactor containing 1 mL of TCE NAPL in 100 mL of water. This suggests that the TCE<sub>vc</sub> measurement is affected by the amount of water vapor in the reactor, but it needs to be further investigated. For reactors with no water (i.e. very low water vapor), there is more sorption into the SPME fiber, loading a higher mass into the GC during the analysis. For reactors with water (i.e. having high water vapor in the headspace), there is less sorption into the SPME fiber. This is presumably caused by the sorption of water molecules onto the fiber at high relative humidities, which compete for sorption sites for the TCE (Ong & Lion, 1991).

In reactors with TCE solution and MeOH, extraction is higher in terms of percent when there is no TCE NAPL present (D5>D4). In the reactors without TCE NAPL (D5) all mass is extracted (100%) in contrast to reactors with TCE NAPL (D4) in which only 15% is extracted. In terms of extracted mass (mg), the amount extracted in D4 was more than 12 times larger (220 mg) than the mass extracted in D5 (6-17 mg). This is because the initial mass in D4 is larger than the initial mass in D5. The available mass in D5 was depleted completely.

In reactors with TCE solution, TCE NAPL, MeOH and no NaCl, extraction is higher in reactors with no clay (D4, 15%) compared to reactors with saturated clay (D6, 4%). This could be due to limited dissolution of TCE into solution in presence of clay.

In reactors with TCE-solution, saturated clay, MeOH, and TCE NAPL, extraction is higher in reactors with a NaCl concentration of 0.60 M (D7, 58%) compared to reactors without NaCl (D6, 4%). This is attributed to NaCl causing restructuring of clay particles and/or producing the salting out effect, both of which enhance TCE volatilization from clay.

In reactors with clay, MeOH, TCE NAPL and no NaCl, extraction is higher in reactors with unsaturated clay (D9, 100%) compared to reactors with saturated clay (D6, 4%). This is attributed to TCE being volatilized directly into air without prior dissolution into water phase, or to vapor concentration measurement differences due to the presence or absence of water vapor in the headspace, as explained above.

In reactors with clay, MeOH, TCE NAPL and [NaCl] = 0.60 M, extraction is higher in unsaturated clay (D10, 91%) than in saturated clay (D7, 58%). This could be due to TCE NAPL being more in contact with air in unsaturated clay than in saturated clay.

In reactors with unsaturated clay, TCE NAPL and [NaCl] = 0 M, extraction is the same for reactors without MeOH (D8, 100%) and reactors with MeOH (D9, 100%). In reactors with unsaturated clay, TCE NAPL and [NaCl] = 0.60 M, extraction is higher in reactors

without MeOH (D8, 100%) compared to reactors with MeOH (D10, 91%). In unsaturated clay, a combination of MeOH and NaCl does not enhance TCE volatilization.

#### 4.4.3 Cumulative extracted TCE mass

The cumulative extracted TCE mass (temporal summation of extracted mass) is calculated and plotted for each experiment. Comparison among the cumulative extracted TCE mass for the different experiments is discussed below.

The comparison between reactors with (D1) and without (D2) TCE NAPL (Figure 4.27), shows as expected, a higher cumulative extracted mass for those with TCE NAPL. This is because there is a higher mass to extract. In reactors with TCE NAPL (D1) cumulative extracted mass is higher at first for reactors without NaCl but later it is higher for reactors with  $[\text{NaCl}] = 0.60 \text{ M}$ . Reactors without TCE NAPL plateau after 40 hours, indicating that the total mass in the reactor has been removed. Similar to the reactors with TCE NAPL, reactors with  $[\text{NaCl}] = 0.60 \text{ M}$  show highest cumulative extracted mass (Figure 4.27). Statistically, there are no significant differences between cumulative mass extractions at the different  $[\text{NaCl}]$  for D1, but there are statistically significant differences between the extractions at all  $[\text{NaCl}]$  for D2. Statistically significant differences among replicates are also observed for D2 experiments. In general, cumulative extracted TCE for TCE solution without TCE NAPL is lowest for reactors with highest  $[\text{NaCl}]$ . Solutions with  $[\text{NaCl}] = 0.60 \text{ M}$  yield the highest cumulative extracted mass. Figure 4.27 shows that the curve for replicate 1 of D2 at  $[\text{NaCl}] = 0 \text{ M}$  (D2\_0 M\_1) does not plateau as expected, if as calculated, the TCE initial mass was extracted completely. This is due to a higher initial TCE mass than calculated due to human error, when TCE NAPL was added to this reactor during preparation and was removed 6.5 hours into the test. The temporal TCE data shows that at 120 hours mass is still being extracted because  $\text{TCE}_{\text{vc}}$  values have not reached zero.

Reactors with TCE solution and TCE NAPL without NaCl show an initial higher cumulative extracted mass for reactors without MeOH (D1), but higher for reactors with MeOH (D4) at later times ( $t > 70$  hours) (Figure 4.28). This suggests that some time is required for MeOH to have an effect on the solubility and volatility of TCE NAPL. Statistically, there is no significant difference between replicates or between D1 and D4.

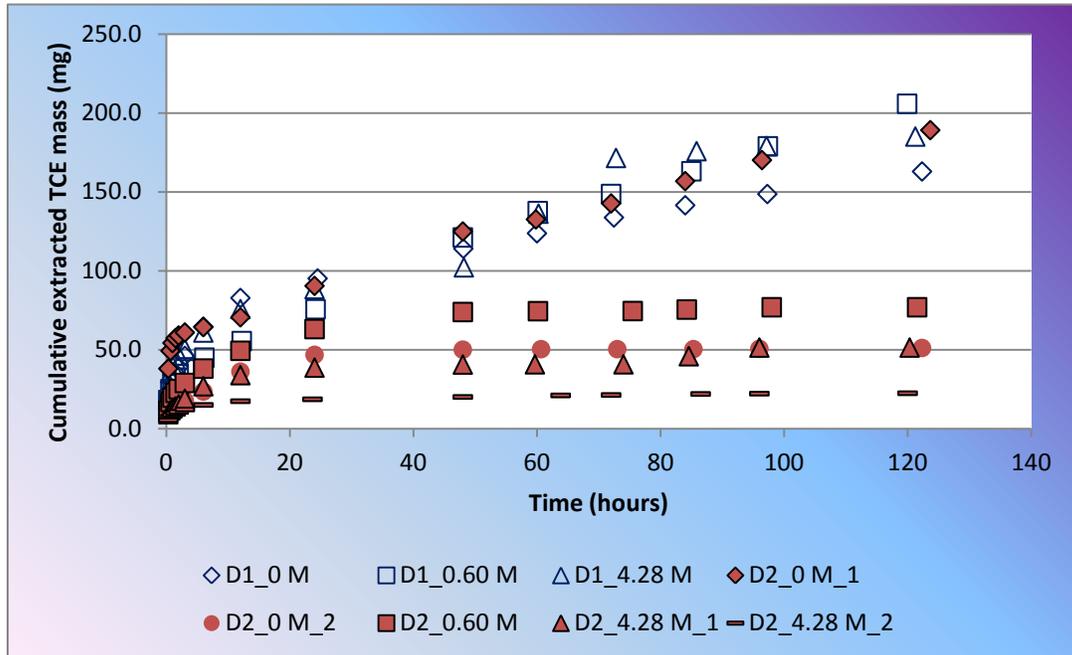


Figure 4.27. Cumulative extracted TCE mass comparison between conditions D1 and D2.

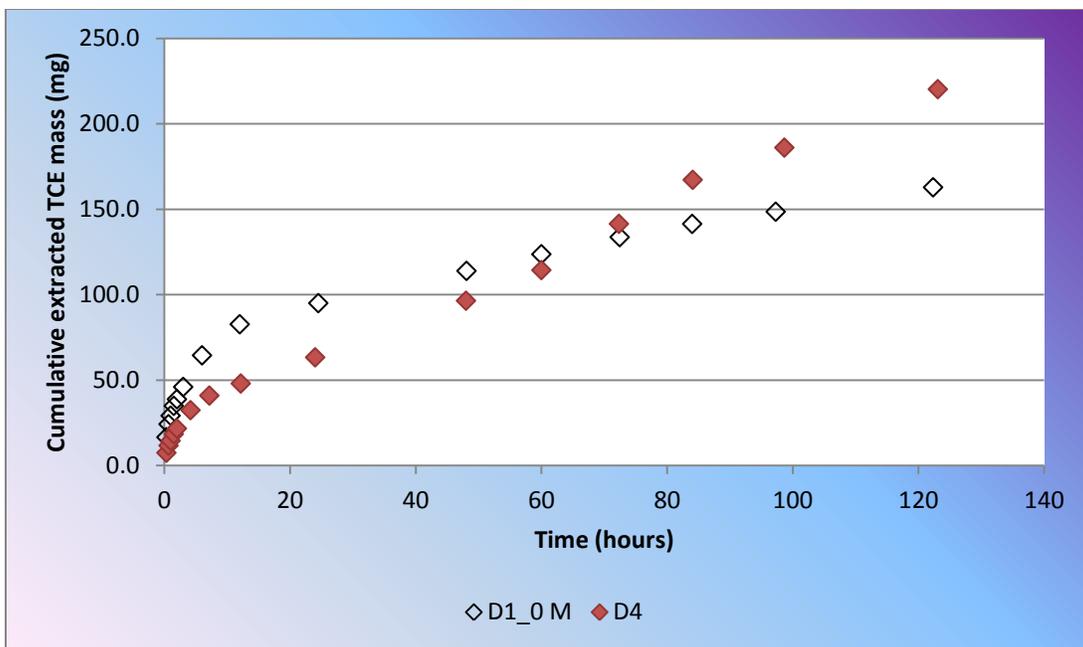


Figure 4.28. Cumulative extracted TCE mass comparison between conditions D1 and D4.

In the absence of TCE NAPL and NaCl, the addition of MeOH to TCE solution does not seem to enhance TCE volatilization. On the contrary, it lowers volatilization (Figure 4.29a). Statistical analysis between TCE<sub>vc</sub> in reactors with (D5) and without (D2) MeOH show a significantly higher median for D2 than D5, indicating that there is higher volatilization when MeOH is not added. This suggests that MeOH is enhancing the retention of TCE in the aqueous phase, thus limiting its volatilization. The large difference observed between replicates for D2 and D5 (Figure 4.29a) is caused by different initial masses in the reactors, and the initial mass in D2 reactors was much higher than that in D5 reactors (Table 4.18). Also, as explained earlier, it is observed that the curve for replicate 1 of D2 at [NaCl] = 0 M (D2\_0 M\_1) does not plateau as expected, which is due to a higher initial TCE mass than calculated due to human error, when TCE NAPL was added to this reactor during preparation and was removed 6.5 hours into the test. TCE<sub>vc</sub> relative data was added to Figure 4.29b to aid in analysis.

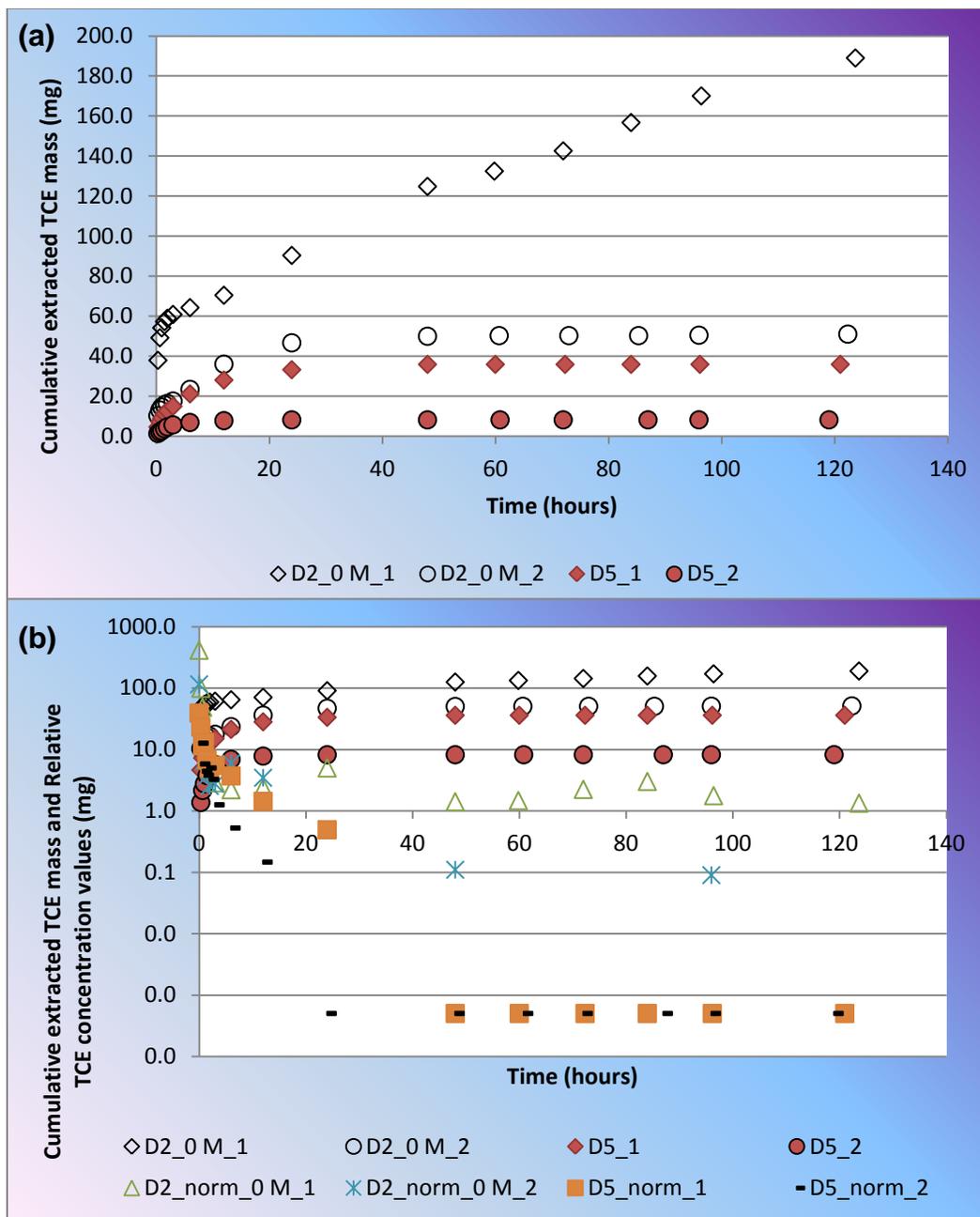


Figure 4.29. (a) Cumulative extracted TCE mass comparison between conditions D2 and D5. (b) Relative TCEvc values. 'norm' means that these are relative concentrations or concentrations that have been normalized with the initial concentration.

In the presence of saturated clay and TCE NAPL, cumulative extraction tends to be higher for solutions with no NaCl (Figure 4.30). This suggests that the presence of NaCl enhances sorption onto the clays, thus reducing the amount of TCE available for volatilization. This indicates that NaCl does not enhance, indeed it reduces, the TCE mass extraction in the presence of saturated clays. Statistically, there are significant differences between cumulative extracted mass for  $[\text{NaCl}] = 0 \text{ M}$  and  $0.60 \text{ M}$  and  $0 \text{ M}$  and  $4.28 \text{ M}$ , in which the median is always higher for  $[\text{NaCl}] = 0 \text{ M}$ .

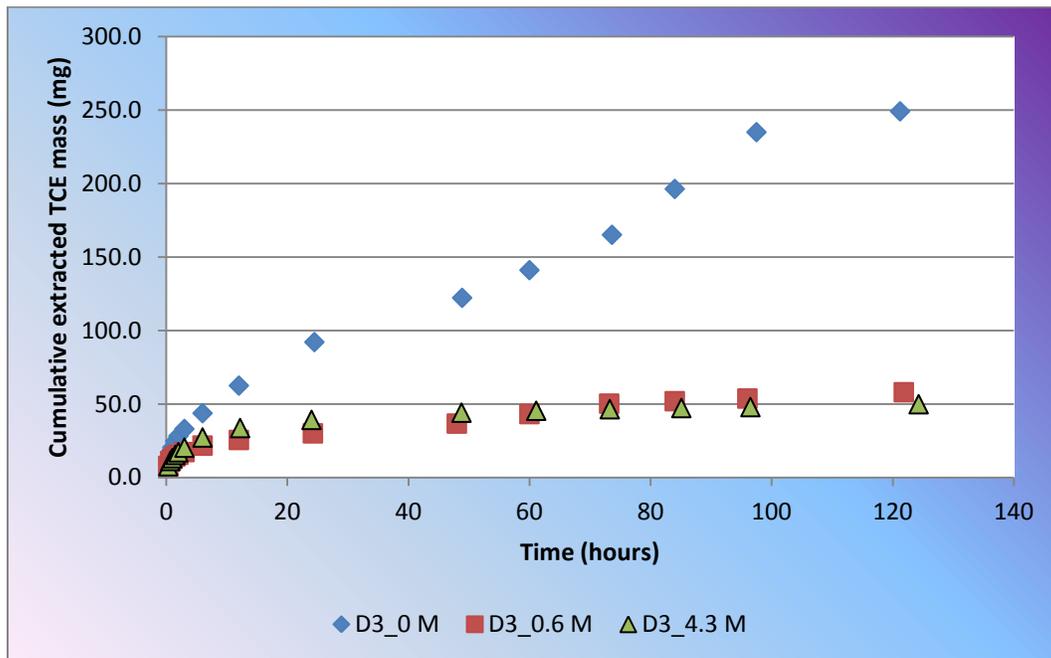


Figure 4.30. Cumulative extracted TCE mass comparison for D3 experiments.

The cumulative extracted mass for TCE vapor over solutions containing saturated clay and TCE NAPL depends on the [NaCl] (Figures 4.31 and 4.32). For solutions with no NaCl, the cumulative extracted mass is higher for reactors without MeOH (D3 > D6). For reactors with [NaCl] of 0.60 M, cumulative extracted mass is higher for reactors with MeOH (D7 > D3). Statistically, there is no significant difference between D3 ([NaCl] = 0 M) and D6 initially, but there is a difference after 6 hours, in which D3 yields a higher median. There is also a statistically significant difference between D3 ([NaCl] = 0.60 M) and D7, in which D7 yields a higher median. These results suggest that in saturated clay MeOH enhances solubilization of TCE in water, but volatilization is enhanced only in the presence of NaCl (Figure 4.33). Indeed, cumulative extracted mass for reactors with TCE solution, saturated clay, TCE NAPL and MeOH is higher for reactors with [NaCl] of 0.60 M (D7) (Figure 4.33). Statistically, there is a significant difference between D6 and D7 where D7 yields a higher median. It is suggested that the presence of MeOH with no NaCl enhances retention in water but in the presence of NaCl, TCE is forced out into gas phase. This also suggests that enhancement of TCE vapor extraction would work only with the presence of both, MeOH and NaCl.

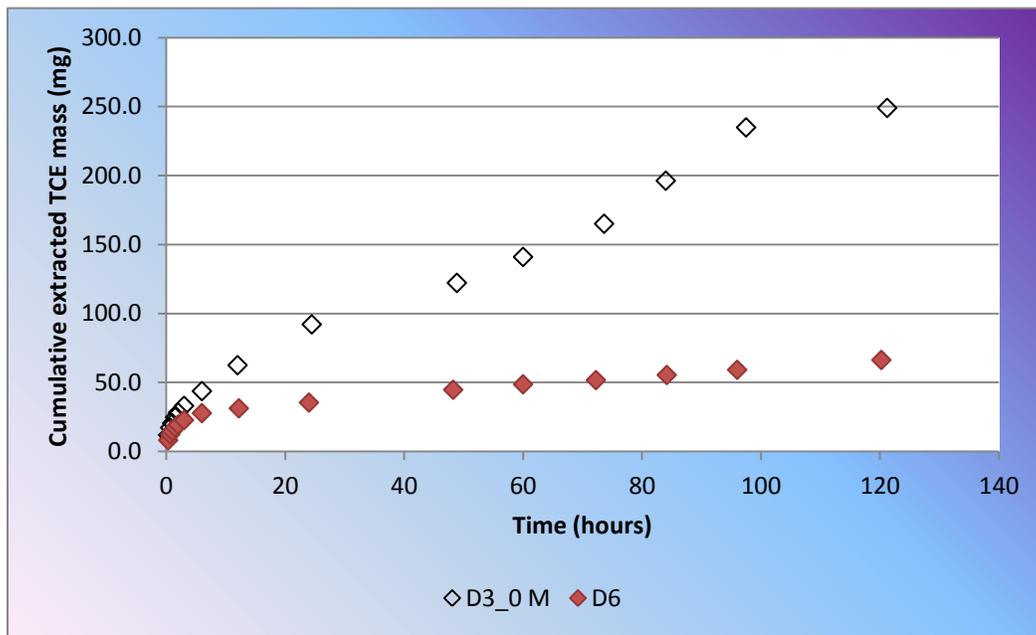


Figure 4.31. Cumulative extracted TCE mass comparison between conditions D3 and D6.

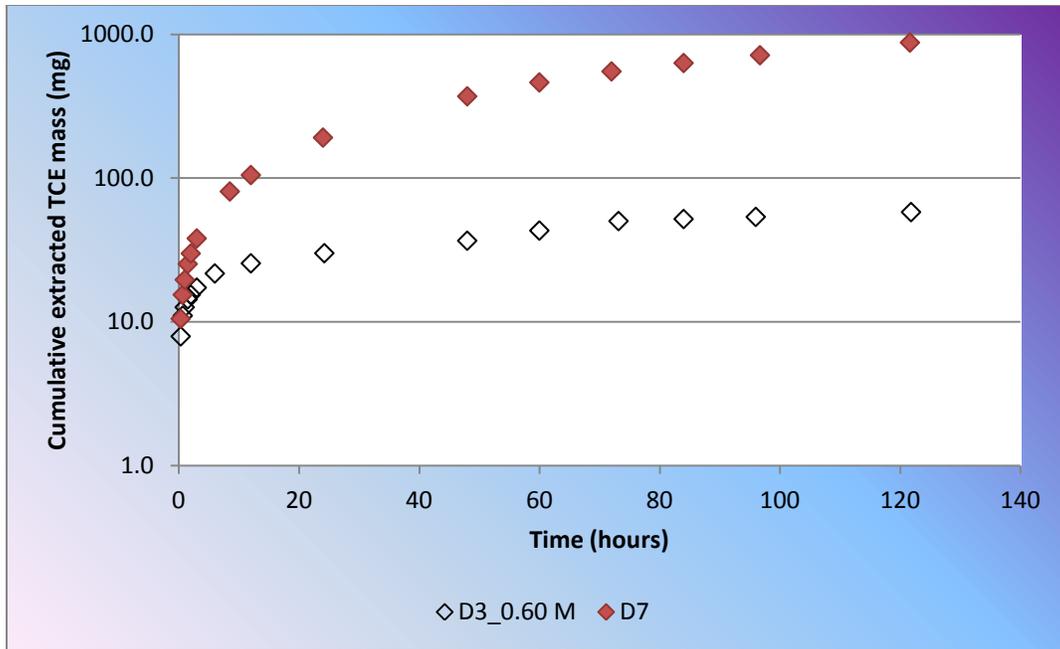


Figure 4.32. Cumulative extracted TCE mass comparison between conditions D3 and D7.

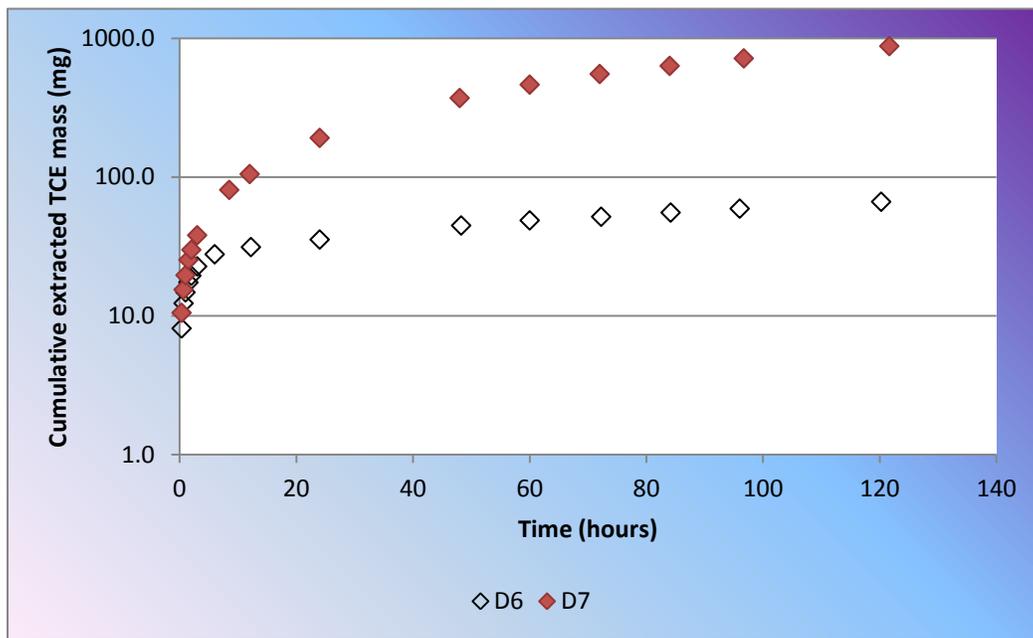


Figure 4.33. Cumulative extracted TCE mass comparison between conditions D6 and D7.

In unsaturated clay with TCE NAPL (Figure 4.34), cumulative extraction is much higher for unsaturated clays (Figure 4.34) than for saturated clays (Figures 4.30, 4.31 and

4.32). Cumulative mass extraction for unsaturated clays (Figure 4.34) is lower for reactors with the highest NaCl concentration (4.28 M). For reactors without NaCl and with  $[NaCl] = 0.60\text{ M}$ , at first TCE<sub>vc</sub> are higher for  $[NaCl] = 0.60\text{ M}$  but later seem to be lower than for reactors without NaCl. This is attributed to higher sorption of TCE onto the clay at the higher  $[NaCl]$ . At early times, there are no statistically significant differences between cumulative extracted mass at the different  $[NaCl]$  for D8 experiments. However, there are statistically significant differences between cumulative extracted mass at later times (after 6 hours) between  $[NaCl] = 0\text{ M}$  and  $[NaCl] = 4.28\text{ M}$ , and between  $[NaCl] = 0.60\text{ M}$  and  $[NaCl] = 4.28\text{ M}$ , in which  $[NaCl] = 4.28\text{ M}$  always yields the lowest median.

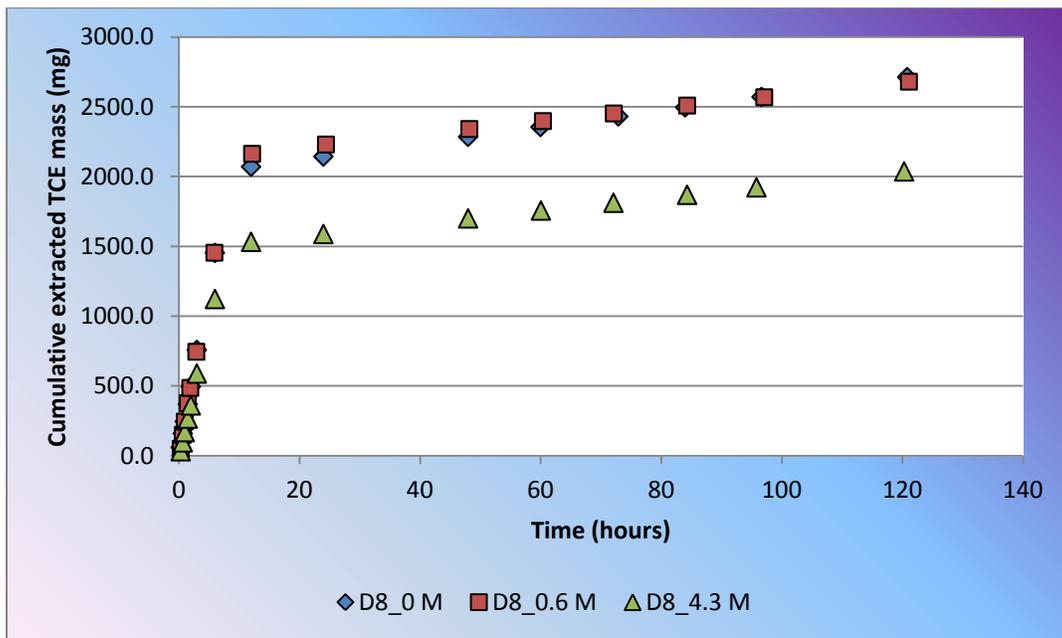


Figure 4.34. Cumulative extracted TCE mass comparison between D8 experiments.

In unsaturated clay containing TCE NAPL, cumulative extracted mass is higher for reactors without (D8) than with MeOH (D9, D10) (Figures 4.35, 4.36). Higher  $[NaCl]$  reduces even further the mass extraction (Figure 4.37). Statistically, at early times there are no significant differences, but after 12 hours there is a statistically significant difference in cumulative extracted mass between D8 and D9 (Figure 4.35), in which reactors without MeOH yield a higher median. There are also statistically significant

differences after 6 hours between D8 and D10 and D9 and D10, in which D8 and D9 yield higher medians than D10, respectively. These results suggest that for unsaturated clays, the presence of MeOH reduces the mass volatilization into the gas phase, this because there is greater sorption or because the presence of MeOH reduces the vapor pressure of TCE.

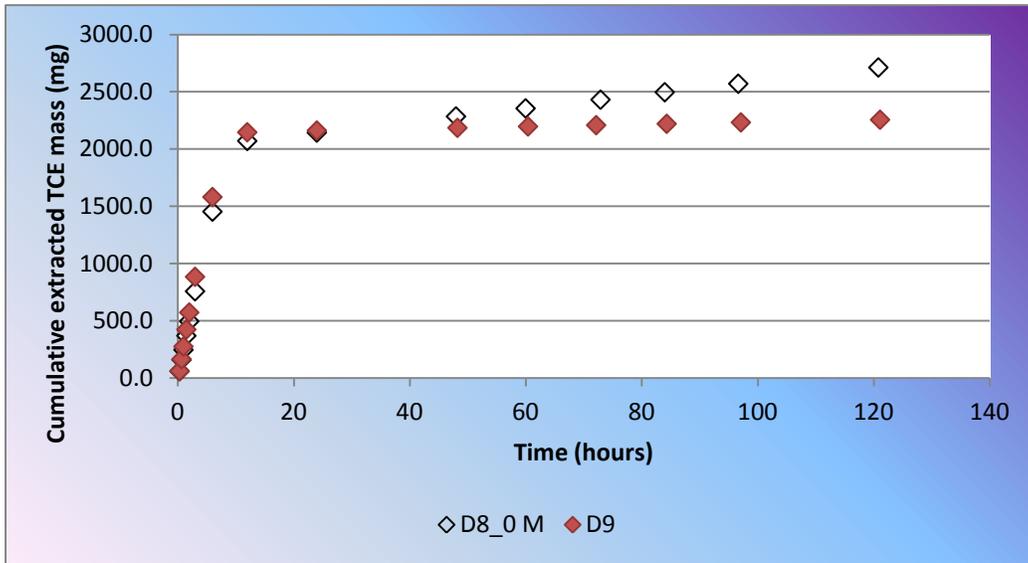


Figure 4.35. Cumulative extracted TCE mass comparison between conditions D8 ([NaCl] = 0 M) and D9.

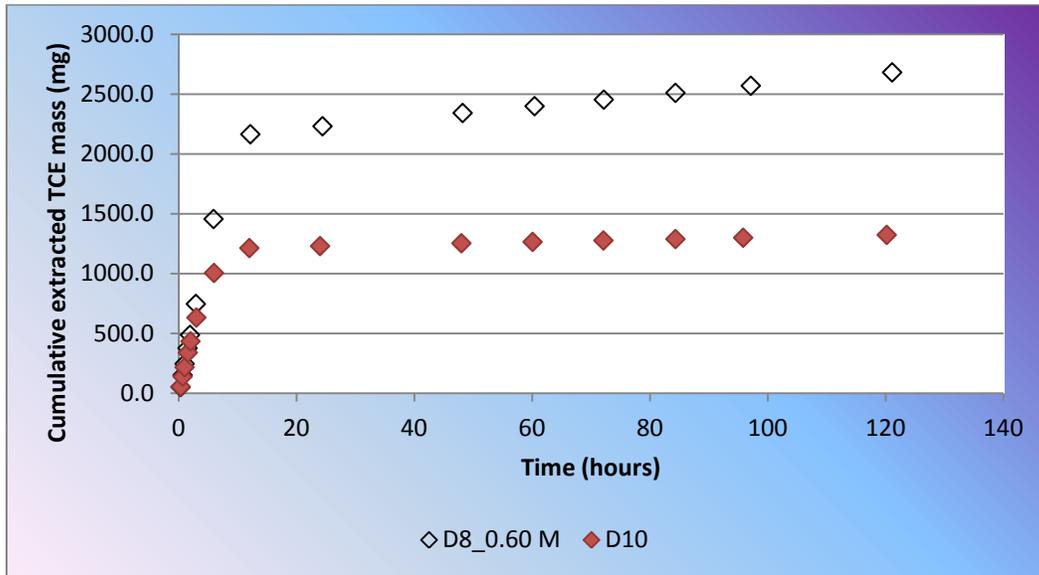


Figure 4.36. Cumulative extracted TCE mass comparison between conditions D8 ([NaCl] = 0.60 M) and D10.

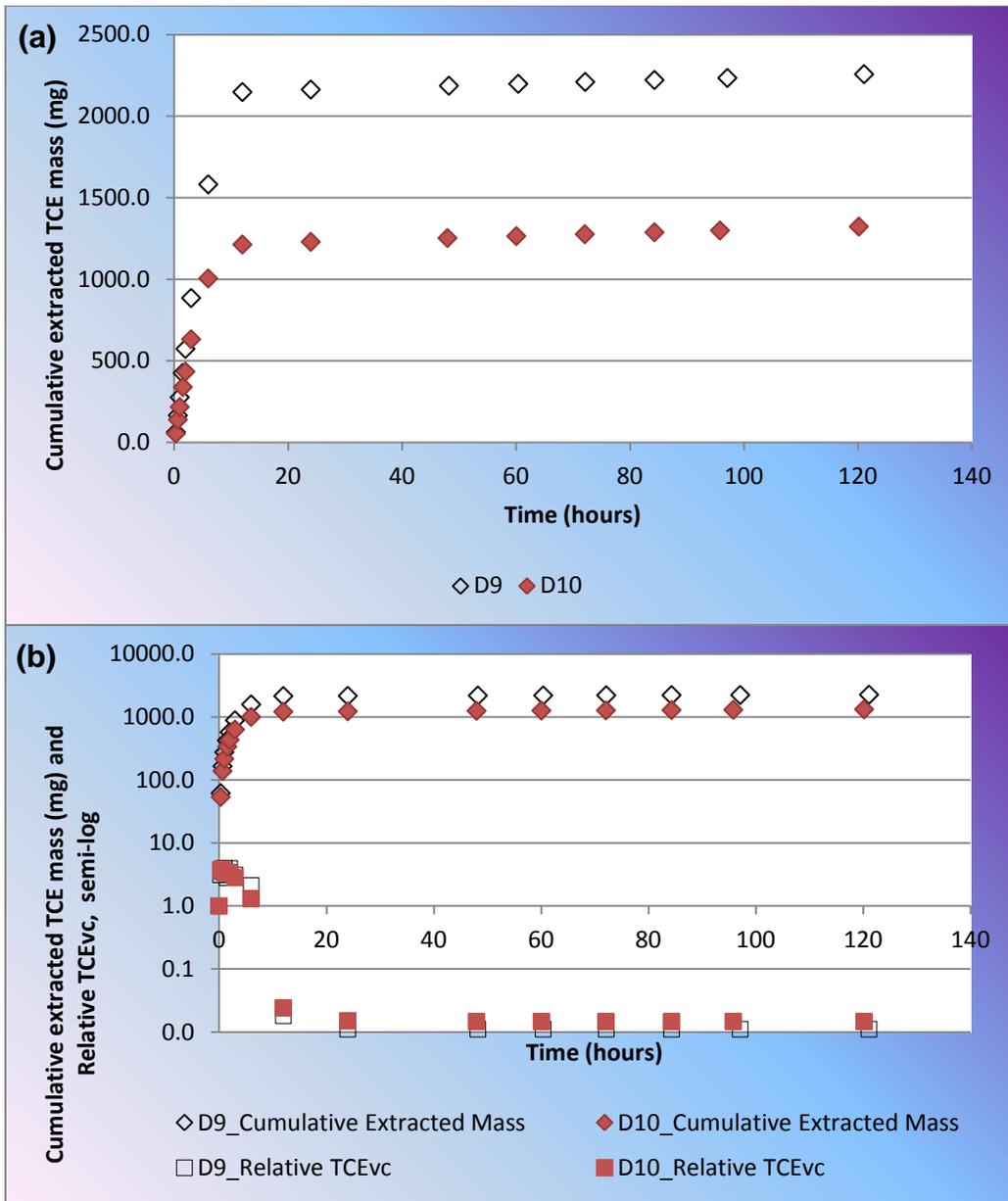


Figure 4.37. (a) Cumulative extracted TCE mass comparison between conditions D9 and D10. (b) Semi-log plot for cumulative extracted TCE mass including relative TCEvc.

Table 4.19 summarizes the statistical analysis for cumulative mass extraction data. “NS” means that the difference between the conditions that connect in that cell is not statistically significant, while “S” means it is statistically significant. The condition that yielded the higher median will be denoted in the lower half of the cell containing the “S”. For example, a cell containing  $S_{/D1}$  means that regarding cumulative extracted mass, the conditions that meet in that cell yield statistically significantly different results and D1 yields the higher median. The diagonal shows the statistical results for the replicates.

The statistical analyses indicate that most of the comparisons between the replicates of each test (diagonal cells) do not yield significant differences (i.e., NS = not significant). There are significant differences (i.e., S = significant) between replicates in the case of D2 for [NaCl] of 0 M and 4.28 M, and between D5 replicates.

Statistical analyses between the different treatments (cells above the diagonal, not including the diagonal) indicate that: there is a higher cumulative extracted mass in TCE solution in presence of TCE NAPL than in its absence; in TCE solution without TCE NAPL, a low NaCl concentration or no salt yield a higher cumulative extracted mass than a higher NaCl concentration; in TCE solution without TCE NAPL MeOH does not increase cumulative extracted mass; in saturated clay with TCE NAPL, NaCl does not increase cumulative extracted mass; in saturated clay with TCE NAPL without NaCl, MeOH does not increase cumulative mass extraction, but it increases it in presence of NaCl; in TCE solution with MeOH cumulative mass extraction is higher in presence of TCE NAPL; in presence of clay, TCE NAPL and NaCl, cumulative mass extraction is higher for unsaturated clays than for saturated clay; in unsaturated clay with TCE NAPL, cumulative mass extraction is higher for a low NaCl concentration or no salt; in presence of clay with TCE NAPL and MeOH, with or without NaCl there is a higher cumulative mass extraction in unsaturated clay; in unsaturated clay with TCE NAPL with or without NaCl MeOH does not increase cumulative mass extraction; in unsaturated clay with TCE NAPL and MeOH, NaCl does not increase cumulative mass extraction.

Table 4.19. Statistical analysis results summary for cumulative mass extraction data.

Replicates (diagonal)		Dynamic flux experiments (Table 3.7)																		
		D1 0	D1 0.6	D1 4.3	D2 0	D2 0.6	D2 4.3	D3 0	D3 0.6	D3 4.3	D4 0	D5 0	D6 0	D7 0.6	D8 0	D8 0.6	D8 4.3	D9 0	D10 0.6	
Dynamic flux experiments	D1_0	NS	NS	NS	S <sub>D1</sub>						NS									
	D1_0.6		NS	NS	S <sub>D1</sub>															
	D1_4.3			NS		S <sub>D1</sub>														
	D2_0				S <sub>D2,1</sub>	S <sub>0</sub>	S <sub>0</sub>					S <sub>D2</sub>								
	D2_0.6					NS	S <sub>0.6</sub>													
	D2_4.3						S <sub>D2,1</sub>													
	D3_0							NS	S <sub>0</sub>	S <sub>0</sub>			S <sub>D3</sub>	S <sub>D8</sub>						
	D3_0.6								NS	NS				S <sub>D7</sub>	S <sub>D8</sub>					
	D3_4.3									NS								S <sub>D8</sub>		
	D4_0										NS	S <sub>D4</sub>	NS							
	D5_0											S <sub>D5,1</sub>								
	D6_0												NS	S <sub>D7</sub>					S <sub>D9</sub>	
	D7_0.6													NS						S <sub>D10</sub>
	D8_0														NS	NS	S <sub>0</sub>	S <sub>D8</sub>		
	D8_0.6															NS	S <sub>0.6</sub>		S <sub>D8</sub>	
	D8_4.3																	NS		
	D9_0																		NS	S <sub>D9</sub>
	D10_0.6																			NS

Cells in this table represent statistical comparisons between conditions for the cumulative mass extraction data. The diagonal shows the statistical results for the replicates of each test. S = statistical difference between the data is significant; NS = statistical difference between the data is not significant. The condition that yields the higher median is denoted in the lower half of the cell containing the "S".

#### 4.4.4 Response time analysis

Response time represents the time it takes to reach a certain percent of the initial TCEvc. For the response time analysis, the results are presented below (Tables 4.20 to 4.25) for each experiment and the following response times:  $t_{25}$ ,  $t_{50}$ ,  $t_{75}$ ,  $t_{90}$ ,  $t_{95}$ , and  $t_{99}$ . The results also include the integrated eigenvalue ( $\lambda$ ), obtained from the equation of the exponential regression (Equation 3.12) that is applied to TCEvc data over early time, which includes the pneumatic mass removal from the system  $\left(\frac{Q}{V_a}\right)$  and the transfer of mass ( $k$ ) that is entering the system by volatilization from water to air. The pneumatic mass removal component  $\left(\frac{Q}{V_a}\right)$ , knowing that  $Q = 7.5$  mL/min and  $V_a = 150$  mL, yields a value of  $3.0 \text{ h}^{-1}$ . There may have been variability in the flow during the tests but this variability is not measured, therefore the flow ( $Q$ ) is assumed to be constant. The mass transfer component is then calculated as  $k = \frac{Q}{V_a} - \lambda$ , and the values are included in the resulting tables (Tables 4.20 – 4.25) below.

For reactors containing TCE solution, TCE NAPL and NaCl (D1), the shortest response time is always at [NaCl] of 0.60 M followed closely by 4.28 M (Table 4.20). Highest response time is observed for [NaCl] = 0 M. This indicates that initial volatilization rates are higher for solution containing NaCl, suggesting that NaCl enhances volatilization rates. The mass transfer component is the lowest (i.e., slowest) for reactors at [NaCl] of 0.60 M, followed by those at [NaCl] of 4.28 M, and the highest being for reactors with [NaCl] = 0 M.

**Table 4.20. Response times for D1 experiments having TCE solution, TCE NAPL and NaCl (up to 6 hours).**

[NaCl] M	$\lambda$ ( $\text{h}^{-1}$ )	$k$ ( $\text{h}^{-1}$ )	Response times (hours)					
			$t_{25}$	$t_{50}$	$t_{75}$	$t_{90}$	$t_{95}$	$t_{99}$
0	0.289	2.711	0.997	2.398	4.810	7.958	10.381	15.917
0.60	0.512	2.488	0.563	1.354	2.715	4.492	5.859	8.984
4.28	0.481	2.519	0.599	1.441	2.890	4.782	6.237	9.563

For reactors with TCE solution (no TCE NAPL) and NaCl (D2), the shortest response time is always at  $[\text{NaCl}] = 0 \text{ M}$ , followed by  $4.28 \text{ M}$  (Table 4.21). Response times for reactors with NaCl but without TCE NAPL are still higher than the response times for the reactors containing TCE NAPL. In the case of reactors containing no NaCl, the shortest response times are observed for those having no TCE NAPL. This is because it takes less time to remove less mass. For D2, reactors without NaCl have the lowest mass transfer component, also when comparing to the D1 reactors with no NaCl. But reactors with TCE solution (no TCE NAPL) and NaCl (D2) have higher (i.e., faster) mass transfer components than reactors with TCE NAPL. This may be due to TCE not having to go through dilution prior to volatilization.

**Table 4.21. Response times for D2 experiments having TCE and NaCl solution (up to 6 hours).**

[NaCl] M	$\lambda \text{ (h}^{-1}\text{)}$	$k \text{ (h}^{-1}\text{)}$	Response times (hours)					
			$t_{25}$	$t_{50}$	$t_{75}$	$t_{90}$	$t_{95}$	$t_{99}$
0	0.467	2.533	0.617	1.484	2.976	4.925	6.424	9.850
0.60	0.409	2.591	0.704	1.694	3.399	5.623	7.335	11.247
4.28	0.426	2.574	0.676	1.627	3.263	5.399	7.042	10.798

Similar to the reactors having TCE NAPL (D1), reactors with saturated clay in the presence of TCE NAPL (D3) show shorter response times for  $[\text{NaCl}]$  of  $0.60 \text{ M}$ , followed by those with  $[\text{NaCl}]$  of  $4.28 \text{ M}$  (Table 4.22). Those with no NaCl show the longest response time (Table 4.21). Response times for  $[\text{NaCl}] = 0.60 \text{ M}$  are very similar for reactors with (D3) or without (D1) saturated clays, but tend to be shorter for those having no NaCl concentrations in the presence of clays (D3). This suggests that clay enhances, at least initially, the volatilization rates of TCE when there is no NaCl. Longer response times for reactors having  $[\text{NaCl}]$  of  $4.28 \text{ M}$  in the presence of saturated clays suggest that the NaCl at high concentrations is enhancing the sorption capacity of the clays, thus decreasing the rate at which TCE is volatilized. Enhanced sorption capacity may be attributed to swelling of the clay in the presence of high NaCl concentrations. Mass transfer component is the lowest (i.e., slowest) for reactors at  $[\text{NaCl}]$  of  $0.60 \text{ M}$ , followed by those at  $[\text{NaCl}]$  of  $4.28 \text{ M}$ , and the highest (i.e., fastest) being for reactors with  $[\text{NaCl}] = 0 \text{ M}$ .

**Table 4.22. Response times for D3 experiments having TCE solution, TCE NAPL, NaCl and saturated clays (up to 6 hours).**

[NaCl] M	$\lambda$ (h <sup>-1</sup> )	k (h <sup>-1</sup> )	Response times (hours)					
			t <sub>25</sub>	t <sub>50</sub>	t <sub>75</sub>	t <sub>90</sub>	t <sub>95</sub>	t <sub>99</sub>
0	0.393	2.607	0.733	1.763	3.537	5.852	7.634	11.705
0.60	0.514	2.486	0.560	1.348	2.704	4.475	5.837	8.949
4.28	0.404	2.596	0.713	1.715	3.441	5.693	7.426	11.386

For reactors with TCE solution and MeOH at [NaCl] = 0 M (Table 4.23), the shortest response times are always for reactors without TCE NAPL (D5). In comparison to those reactors under same conditions but containing no MeOH (D1 & D2), however, the reactors containing MeOH with TCE NAPL (D4) show shorter response times than those without MeOH (D1 at [NaCl] = 0 M). Those having MeOH but without TCE NAPL (D5), show longer response times than those without MeOH (D2 at [NaCl] = 0 M). Shorter response times in the presence of TCE NAPL and MeOH suggest that MeOH enhances the solubility of the TCE NAPL and increases the concentration gradient between water and gas phase. This enhances the volatilization rates. In the absence of TCE NAPL, however, the enhancement of solubility does not increase gradients, but rather retains TCE in water and reduces volatilization rates. In the presence of saturated clays (D6), MeOH decreases even more the response times of the reactors containing TCE solution and NAPL (Table 4.23). This indicates that MeOH enhances TCE vapor extraction rates in saturated clay when there is no NaCl. Relative to reactors containing no clay (D4), the presence of clays (D6) decreases the response times indicating that MeOH further enhances volatilization rates in the presence of clays. In the presence of saturated clays with TCE NAPL (no NaCl), response times and mass transfer components are higher in absence (D3) than in the presence (D6) of MeOH. Mass transfer component is the lowest (i.e., slowest) in presence of saturated clays with TCE NAPL, MeOH and 0.60 M NaCl.

**Table 4.23. Response times for D4, D5, D6 and D7 experiments having MeOH (up to 2 (D7) or 6 hrs).**

Condition	$\lambda$ (h <sup>-1</sup> )	k (h <sup>-1</sup> )	Response times (hours)					
			t <sub>25</sub>	t <sub>50</sub>	t <sub>75</sub>	t <sub>90</sub>	t <sub>95</sub>	t <sub>99</sub>
TCE solution w/ NAPL, no NaCl (D4)	0.341	2.659	0.845	2.032	4.076	6.745	8.798	13.490
TCE solution w/o NAPL, no NaCl (D5)	0.396	2.604	0.727	1.750	3.510	5.808	7.576	11.616
TCE solution and NAPL, saturated clay, no NaCl (D6)	0.554	2.446	0.520	1.251	2.509	4.152	5.415	8.303
TCE solution and NAPL, saturated clay, [NaCl] = 0.60 M (D7)	0.707	2.293	0.407	0.980	1.966	3.253	4.243	6.506

Response times are further decreased in the presence of saturated clays and MeOH when [NaCl] is 0.60 M (D7, Table 4.23). When comparing D3 experiments having TCE solution, TCE NAPL, saturated clays and [NaCl] at 0.60 M, with similar reactors containing MeOH (D7), it is observed that the shortest response time is always for D7, which probably means that MeOH enhances TCE vapor extraction rates from saturated clay with TCE NAPL at [NaCl] of 0.60 M. When comparing D6 with D7, the shortest response time is always for [NaCl] of 0.60 M (D7), which could mean that NaCl enhances TCE vapor extraction rates in saturated clay with NAPL and MeOH.

Reactors containing unsaturated clays and TCE NAPL (D8) show the longest response times of any condition at all tested NaCl concentrations (Table 4.24). They also show the highest mass transfer components (2.742 – 2.759 h<sup>-1</sup>). The response times are lower for a [NaCl] of 4.28 M, but the rest of the values are not that different. When comparing with D3 experiments having the same conditions but saturated clays, the presence of unsaturated clays show much larger response times, suggesting that unsaturated clays retain (by sorption or capillary forces) more TCE and reduce volatilization rates.

**Table 4.24. Response times for D8 experiments having unsaturated clay, TCE NAPL and NaCl (up to 12 hours).**

[NaCl] M	$\lambda$ ( $\text{h}^{-1}$ )	$k$ ( $\text{h}^{-1}$ )	Response times (hours)					
			$t_{25}$	$t_{50}$	$t_{75}$	$t_{90}$	$t_{95}$	$t_{99}$
0	0.255	2.745	1.129	2.718	5.451	9.020	11.765	18.039
0.60	0.241	2.759	1.195	2.876	5.768	9.544	12.448	19.087
4.28	0.258	2.742	1.116	2.686	5.388	8.915	11.628	17.829

The addition of MeOH to unsaturated clays having TCE NAPL (D9 and D10), decreases the response time at [NaCl] of 0 M and 0.60 M (Table 4.25) relative to similar conditions without MeOH (D8), indicating that MeOH enhances volatilization rates from unsaturated clays. Relative to saturated clays (D6 and D7, Table 4.23), response times are still slower for unsaturated clays suggesting greater retention of the TCE under unsaturated conditions. Greater retention is attributed to strong sorption in unsaturated soil (Constanza-Robinson, 2001). Greater sorption has been reported for unsaturated than saturated soils (Ong & Lion, 1991). The results, therefore, indicate that MeOH enhances TCE solubility in saturated clay better than in unsaturated clay. Response times for experiments having unsaturated clay, TCE NAPL, and MeOH at different [NaCl] (D9 and D10, Table 4.25) show very similar results, but those having no NaCl yield slightly faster times. Results show that the effect of MeOH on response times in the presence of saturated (D6, D7) or unsaturated clays (D9, D10) depends on the level of saturation and [NaCl]. In the case of saturated clays, the addition of MeOH reduces response time at higher [NaCl] of 0.60 M (D7) relative to no NaCl (D6), suggesting that NaCl may be affecting the clay structure so as to reduce sorption and enhance volatilization rates. Slower response times in unsaturated clays in the presence of MeOH at an [NaCl] of 0.60 M (D10) relative to no NaCl (D9), suggest that MeOH and NaCl together may increase sorption of TCE in unsaturated clays. This is attributed to the lower amount of water available under unsaturated conditions for restructuring of the clay particles.

**Table 4.25. Response times for D9 and D10 experiments having unsaturated clay, TCE NAPL, MeOH and NaCl (up to 12 hours).**

[NaCl] M	$\lambda$ (h <sup>-1</sup> )	k (h <sup>-1</sup> )	Response times (hours)					
			t <sub>25</sub>	t <sub>50</sub>	t <sub>75</sub>	t <sub>90</sub>	t <sub>95</sub>	t <sub>99</sub>
0 (D9)	0.381	2.619	0.756	1.819	3.648	6.037	7.874	12.073
0.60 (D10)	0.376	2.624	0.766	1.843	3.697	6.117	7.979	12.234

Because a completely mixed system is assumed, it would be acceptable to say that TCE vapor residency in the headspace is the same as for air. Therefore, a residence time was calculated for the air being flushed (at Q = 7.5 mL/min) from the headspace (V = 150 mL) as  $\tau_{air} = \frac{V_{headspace}}{Q}$ , which yielded a value of 0.33 hrs. This value is lower than all response times, thus indicating that there are other processes affecting TCE extraction and residency besides the pneumatic removal. A residence time for TCE is then calculated as  $\tau_{TCE} = \frac{V_{headspace}}{Q - k \cdot V_{headspace}}$ , where k is the mass transfer component of the integrated eigenvalue. Equations are derived from the residence time equations in Chapra (1997). Calculated residence times for TCE are included in Table 4.26. Residence time values range from 1.414 hrs to 4.149 hrs ( $\bar{X} = 2.628$  hrs;  $STDEV = 0.771$  hrs), the lowest being for reactors in D7 and the highest for reactors in D8 with [NaCl] = 0.60 M. This suggests that TCE resides for the shortest time in the headspace of the reactors containing saturated clay, TCE NAPL, [NaCl] = 0.60 M and MeOH (D7), which are also the reactors with the smallest mass transfer component (k) value. Also, that TCE resides the longest in the reactors containing unsaturated clay, TCE NAPL and [NaCl] = 0.60 M (D8), which are the reactors with the highest mass transfer component (k) value. Residence times are higher than t<sub>25</sub> and t<sub>50</sub> for all tests but lower than all other response times.

**Table 4.26. Residence times for TCE in dynamic flux reactor experiments.**

<b>Test</b>	<b>[NaCl] M</b>	<b>MeOH 10%</b>	<b>TCE residence time (hours)</b>
<b>D1</b>	0		3.460
	0.60		1.953
	4.28		2.079
<b>D2</b>	0		2.141
	0.60		2.445
	4.28		2.347
<b>D3</b>	0		2.545
	0.60		1.946
	4.28		2.475
<b>D4</b>	0	x	2.933
<b>D5</b>	0	x	2.525
<b>D6</b>	0	x	1.805
<b>D7</b>	0.60	x	1.414
<b>D8</b>	0		3.922
	0.60		4.149
	4.28		3.876
<b>D9</b>	0	x	2.625
<b>D10</b>	0.60	x	2.660

#### 4.5 Test bed design

A test bed for the enhanced TCE vapor extraction from low permeability unsaturated clay soils, was designed using a cylindrical stainless steel column (custom-made by Swagelok®) 100 cm tall and 19 cm in diameter, with 16 ports (divided into 4 columns and equally-spaced around the circumference). The design and development of the test bed is described in the following subsections.

#### 4.5.1 Soil Packing

The packing of clay in the test bed is a variation of the Induced Settling Method (ISM) (Rodríguez et al., 2007) at a water content of 15% by weight. For the ISM, a 1-3 kg load is placed on top of each 2-3 cm layer of soil at 22, 24 or 30% gravimetric water content. In the developed method the soil was packed in layers of varied thickness depending on the type of test, followed by repetitive tapping with a piston of a weight that varied from test to test. Constant densities were achieved by applying a constant energy of compaction, as estimated with the compaction energy equation:

$$E_c = \frac{(L \times B \times W_p \times H_B)}{V} \quad 4.1$$

where  $E_c$  is the compaction energy, with units of lb·ft/ft<sup>3</sup>,  $L$  is the number of layers,  $B$  is the number of blows applied,  $W_p$  is the piston weight in pounds (lbs),  $H_B$  is the height of the blows in feet (ft) and  $V$  is the volume to be packed with soil with units of ft<sup>3</sup>.

The weight of the piston and other parameters varied for the different experimental setups by maintaining the compaction energy constant at 19,634.02 kg·m/m<sup>3</sup>. This method yielded reproducible packing densities of 1.278 (+- 0.0010) g·cm<sup>-3</sup>, which is similar to the bulk density of the Coto clay at 60-80 cm of depth. The compaction parameters to be used are shown in Table 4.27. The Coto clay is to be packed in 19 layers (5 cm each) followed by a 5 cm-layer of a bentonite seal added on top.

**Table 4.27. Compaction parameters for test bed preliminary tests.**

Parameter	Value	Unit
# layers	19	-
# blows	29	-
Piston weight	3.20	kg
Free fall height	30.48	cm
Volume	0.03	m <sup>3</sup>
Compaction energy	19913.89	kg·m/m <sup>3</sup>

#### 4.5.2 Boundary conditions and other design parameters

Original boundary conditions for the test bed included a high constant suction under unsaturated conditions at the bottom of the column. To attain this, a layer of very dry clay is to be packed in the lower 30 cm of the column. The clay water content is to be monitored during the testing phase to make sure that the boundary condition does not change. A no-water flow boundary condition is incorporated at the top of the column by capping the top clay layer (5 cm) with bentonite. Constant head boundary conditions are imposed for the gas phase during the vapor extraction activities. The constant head at the top of the column is attained through a vacuum pump, at the air entry level (60 cm below the top of the column); the constant head is to be maintained at atmospheric pressure.

Reactant delivery results from the CBD tests suggest that the best way to deliver reactants to the soil is by locating the level of the solution at the same height as the porous cup (A tests, section 3.4) because the solution travels farther down and it does not take as much time as to complete a wet circumference as the case in which the solution is below the porous cup (C test, section 3.4). In the B tests (gravity dominated delivery), the width of wet clay is the smallest, showing less uniformity and more heterogeneous water distribution. Therefore, the delivery of reactants will not be by a pumped injection or gravity induced.

The reactant delivery membranes are to be located approximately 15 cm below the vapor extraction wells to prevent an upward flow on the delivered solutions and to prevent the saturation of the soil where the vapor extraction wells are located. This distance will actually depend on other installed equipment and their respective locations.

### 4.5.3 Designed setup

The designed testbed setup is shown in figure 4.38. The testbed is to contain a TCE NAPL-contaminated zone at about 55 cm from the bottom. Four (4) vapor extraction wells are to be placed at about 20 cm above the contaminated zone. SVE wells are to be connected to a manifold (Figure 4.39) and to a vacuum pump. A vapor sampling port located at the manifold exit (Figure 4.39) is to allow sampling for TCE and alcohol vapors. A filter, made at the laboratory with pieces of High-Efficiency Particulate Air (HEPA) filters, is to be located after the sampling port and before the flow meter and vacuum pump to clean the extracted air from clay particles and other particulate (Figure 4.39). Two (2) reactant delivery membranes are to be located 5 cm above the contaminated zone. These delivery membranes are comprised each of a 40  $\mu\text{m}$  stainless steel porous membrane (Figure 3.8) with larger average pores than the clay so that the solution moves from the membrane into the clay. Venting wells are to be located below the contaminated zone at 40 cm from the bottom and will be connected to aerators (perforated rings made from PTFE tubing) on the inside to maximize air entry into the soilbed (Figure 4.40). Cross sections for the top and bottom of the column and for the venting wells location are shown in figure 4.41.

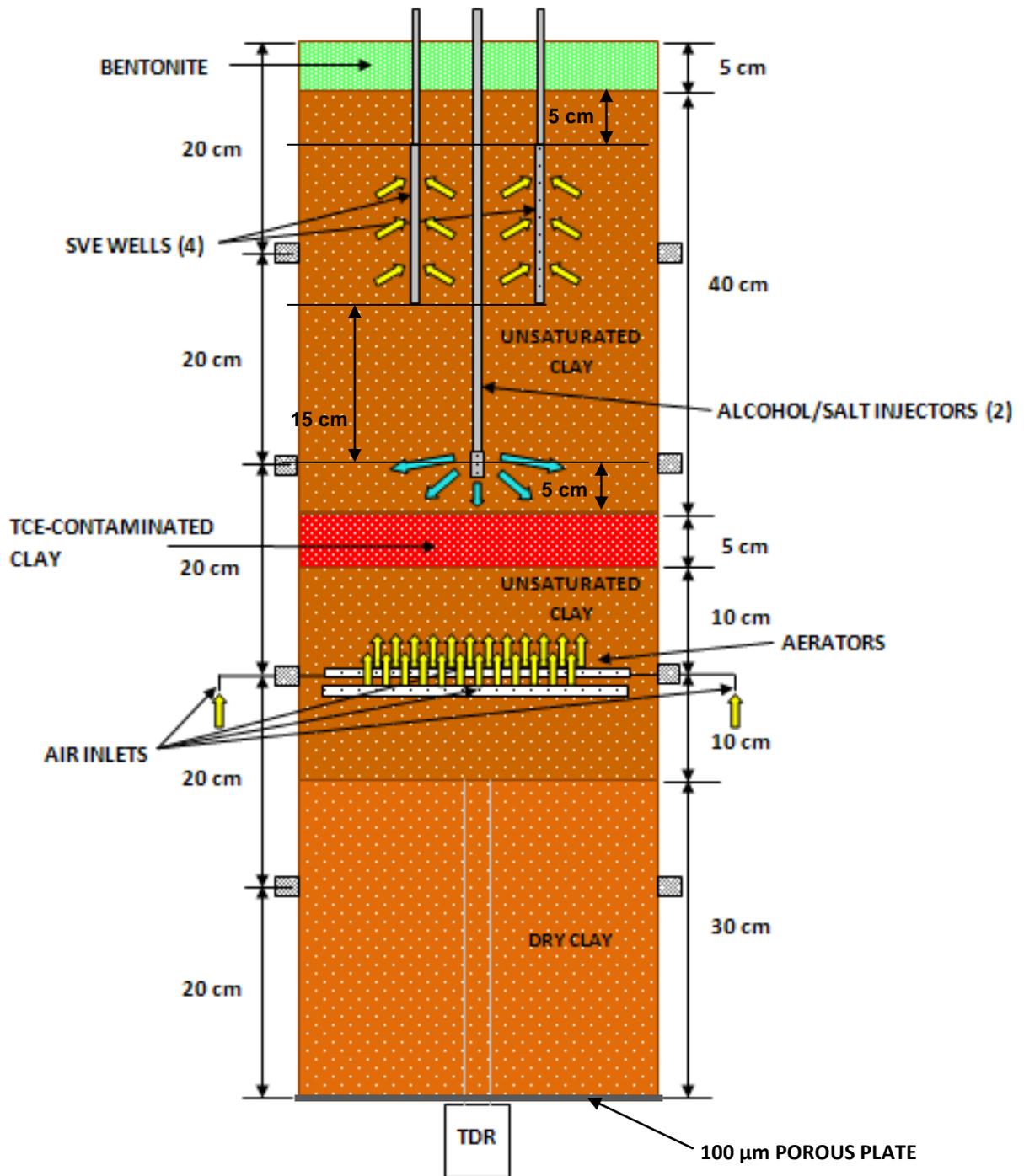


Figure 4.38. Soilbed setup design profile.

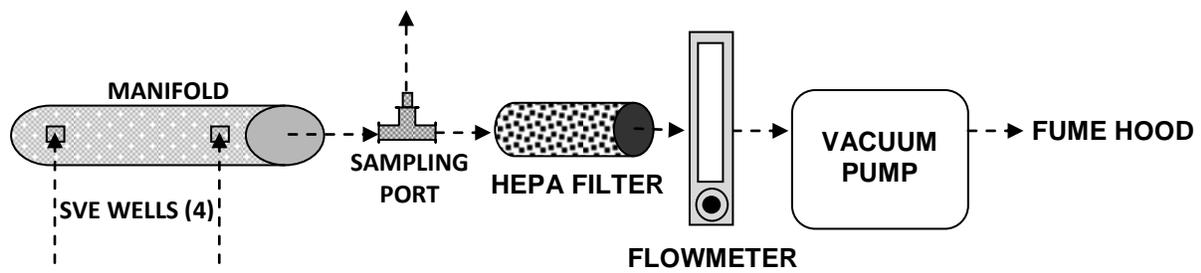


Figure 4.39. Soilbed SVE system.

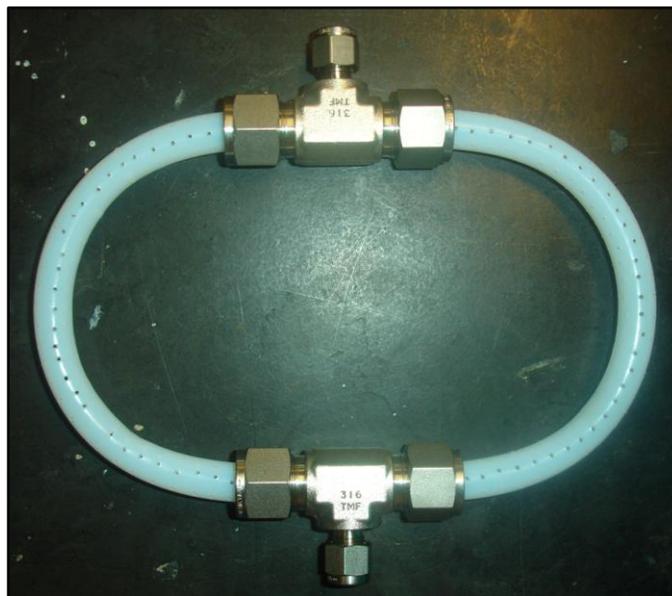
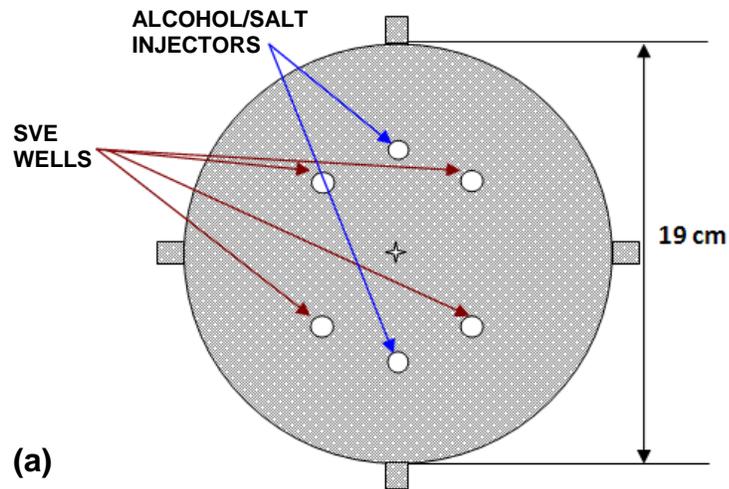
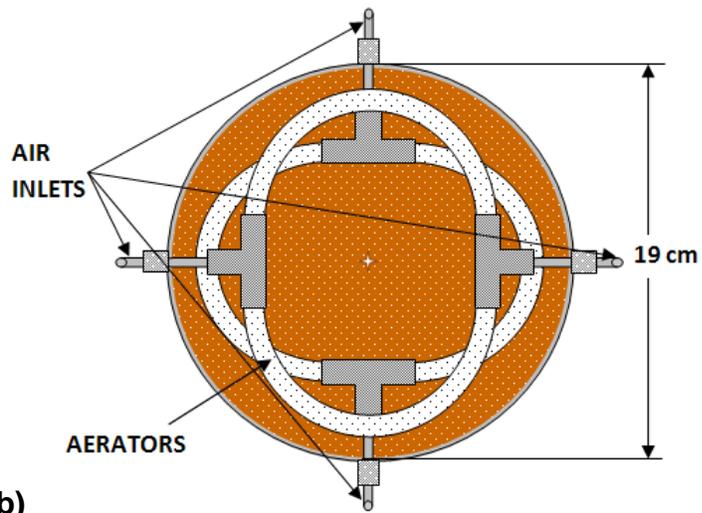


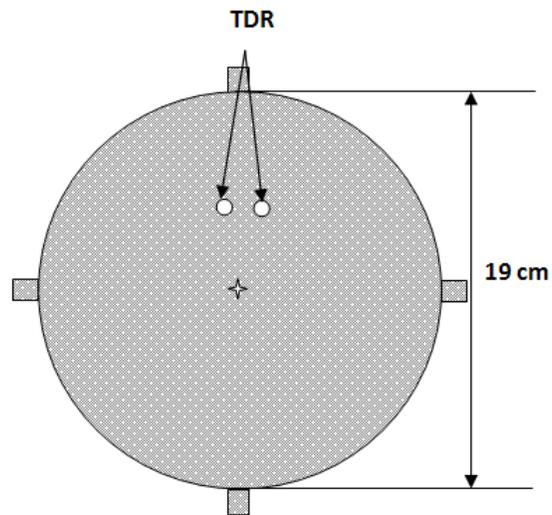
Figure 4.40. Aerator for testbed.



(a)



(b)



(c)

Figure 4.41. Cross section for the (a) top of the column, (b) location of the aerators (40 cm above the bottom of the column), and (c) bottom of the column.

## 4.6 Integrated discussion of results

This section integrates the results from the air permeability, reagent delivery, batch reactor and flux reactor experiments to evaluate the feasibility of using a concentration of salt and cosolvent solutions to enhance SVE of TCE in tight clay soils. It is important to note that the results from tests using clay apply only to the type of soil used (i.e. Coto clay, a kaolinite clay).

### 4.6.1 Air permeability

Air permeability experiments were designed and executed to assess the behavior of air flow in clay with different moisture contents and to test if salt restructures the clay increasing its permeability. This information is necessary for future experiments involving the enhanced extraction of TCE vapors from clayey soil. As expected, results indicate that with increasing moisture content the air permeability is lower. The permeability of dry clay averaged is higher than that of unsaturated clay at 12% and 15% water content. The addition of NaCl proved to increase air permeability in unsaturated clay (11% wc) by yielding an air permeability value similar to that of dry clay but higher than for unsaturated clay (12% wc) without NaCl. This is attributed to the restructuring effect salinity has on soils by inducing the flocculation of clay particles, therefore, increasing permeability. Although slightly higher air permeability is observed in the presence of NaCl, it is suspected that the use of divalent salts (such as  $\text{CaCl}_2$ ) may result in higher air permeability. This is because sodium ions, present in NaCl, disrupt the forces that bind together clay particles causing the expansion of clay particles, which results in soil swelling and dispersion, and, consequently, reduced soil permeability (Pearson, 2009). Further tests were conducted using  $\text{CaCl}_2$  to verify this. The air permeability for unsaturated clay (14%), containing 0.005 M  $\text{CaSO}_4$  was overall the highest. Tests with 0.005 M  $\text{CaSO}_4$  0.60 M  $\text{CaCl}_2$ -solution yielded the lowest air permeabilities. This is attributed to the precipitation of calcium in the system which

clogs the clay pores therefore preventing air flow. Therefore, the combination of 0.005 M  $\text{CaSO}_4$  and 0.60 M  $\text{CaCl}_2$ , proved unsuccessful in enhancing air permeability of clay. Air permeabilities for unsaturated clays at 23-30% wc with 0.06 M  $\text{CaCl}_2$  or 0.60 M  $\text{CaCl}_2$ , yielded low air permeabilities, which are among the lowest air permeabilities measured. The addition of  $\text{CaCl}_2$  at soil water contents above 23% does not increase air permeability of clay, but instead reduces it. In dry clays, increasing air flow slightly reduces air permeability. In unsaturated clay without salt, air flow increases air permeability. For soil containing  $\text{CaSO}_4$  and/or  $\text{CaCl}_2$ , generally air permeability tends to slightly increase for higher flow rates. No tendency is observed for soil containing  $\text{NaCl}$ . The slight variations in air permeability as a function of flow are attributed to air compression effects. The effect of  $\text{MeOH}$  solution on the air permeability of clays is assumed negligible, but this assumption needs to be tested.

#### 4.6.2 Reagent delivery

Reagent delivery experiments indicate that the fastest way to deliver a large volume of reagents is by gravity, although this is not the desired method because it does not provide a homogeneous distribution. Faster delivery results in preferential flow and heterogeneous water distribution. This is not desired because it would result in lack of reagent contact in areas not subject to preferential flow. Capillary delivery method, in which the solution level is below the delivery point, takes the longest time to achieve an apparent homogeneous distribution. This could be the best way to achieve the desired reagent distribution but it is slower. Based on time response and spatial water distribution, the ideal method for delivery of reagents during the TCE enhanced vapor extraction experiments is when the solution level is at the same height as the delivery point. This results in evenly distributed water content and does not take as long as the capillary-based method.  $\text{NaCl}$  reduced the time to achieve wet circumference for this setup, which means  $\text{NaCl}$  could have restructured the clay making it more permeable.

#### 4.6.3 Static experiments

The static kinetic reactors with and without clay results indicate that NaCl has either a slight or no effect on TCE volatilization. In the presence of TCE NAPL, TCE<sub>vc</sub> tend to be higher for [NaCl] of 1.71 M, followed by 0.60 M. For reactors having no TCE NAPL, highest TCE<sub>vc</sub> are observed for [NaCl] = 0.60 M. In the presence of clays and TCE NAPL, TCE<sub>vc</sub> are initially higher for [NaCl] = 0 M, but, although not statistically significantly different, TCE<sub>vc</sub> are higher for reactors containing [NaCl] = 0.60 M at late times. TCE<sub>vc</sub> were higher for reactors with clay. Results from the static equilibrium experiment indicate that at high TCE-solution concentrations, a low NaCl concentration may cause salting out, yielding higher TCE<sub>vc</sub>, but at lower TCE-solution concentrations, a higher NaCl concentration is more effective.

#### 4.6.4 Flux experiments

Flux experiments show higher TCE<sub>vc</sub> at the onset of the vapor extraction. Lower concentrations at later times reflect mass transfer limitations related to volatilization, dispersion, and dissolution of the NAPL. As expected, reactors with TCE NAPL show higher TCE<sub>vc</sub> than those without pure phase. This occurs because the TCE NAPL serves as a continuous source that is available for dilution and further volatilization. NaCl does not seem to have a significant effect on TCE<sub>vc</sub> when in absence of TCE NAPL. There is a statistically significant difference for reactors with TCE NAPL, in which a [NaCl] of 0.60 M yields higher TCE<sub>vc</sub> than when there is no NaCl and when [NaCl] = 4.28 M; the amount of extracted mass tends to also be higher for [NaCl] of 0.60 M. Response time for reactors with TCE solution and TCE NAPL is the shortest for all times at [NaCl] of 0.60 M, but for reactors without NAPL, the shortest response time for all times is always in absence of NaCl. NaCl does not seem to have a significant effect on TCE-solution with saturated clay and NAPL, which shows that NaCl does not enhance TCE volatilization in saturated clay. Even though, the shortest response time for all times is always at NaCl concentration of 0.60 M. The addition of MeOH

enhances TCE<sub>vc</sub> and increases the amount of mass extracted in the presence of TCE NAPL, but lowers the concentration in the absence of pure TCE. In the presence of saturated clays and TCE NAPL, the addition of MeOH enhances the vapor concentration of TCE, reduces response time, and increases the amount of TCE extracted when [NaCl] = 0.60 M, but reduces volatilization at [NaCl] = 0 M. For reactors with unsaturated clay and NAPL, higher TCE<sub>vc</sub> were measured for reactors with NaCl. The shortest response time is for 4.28 M NaCl. Higher cumulative mass extraction in unsaturated clays occurred at [NaCl] = 0 M and 0.60 M, with significantly less cumulative mass extracted at [NaCl] = 4.28 M. The addition of MeOH to unsaturated clays decreased TCE<sub>vc</sub>, the amount of TCE extracted, the response times and the mass transfer, indicating slower volatilization.

Table 4.28 summarizes the observed effect caused by NaCl presence. The effects of MeOH on measured TCE<sub>vc</sub> are summarized on Table 4.29. Results indicate that higher TCE<sub>vc</sub> are measured in presence of MeOH in reactors with TCE solution and TCE NAPL. The shortest response time is in presence of MeOH. This is attributed to MeOH increasing TCE solubility, therefore making it more available for volatilization. In absence of TCE NAPL, there is a slight difference where reactors with TCE solution yield higher TCE<sub>vc</sub> in presence of MeOH than in absence of MeOH. The shortest response time is in absence of MeOH. MeOH does not seem to enhance TCE vapor extraction by increasing TCE solubility in TCE-solution saturated clay with NAPL without NaCl, but higher TCE<sub>vc</sub> are measured when in combination with 0.60 M NaCl. For reactors with TCE-solution saturated clay, TCE NAPL and 0 M or 0.60 M NaCl the shortest response time is always in presence of MeOH. MeOH does not seem to enhance TCE vapor extraction in unsaturated clay with or without NaCl. But the shortest response time for both NaCl concentrations is in presence of MeOH.

Table 4.28. Summary of statistical analyses of NaCl effect on TCE volatilization.

Tests	NaCl hypothesized effect on TCEvc			Comments/explanation
	Big difference	Slight difference	No difference	
S1-S3		<b>Total time:</b> 1.71 M > 0M & 1.71 M > 4.28 M <b>Late time:</b> 1.71 M > 0M & 0.26 M & 4.28 M & 0.60 M > 0 M	x	Measured concentrations above vapor pressure.
S4			x	Measured concentrations above vapor pressure concentration. No difference between NaCl treatments.
E1		<b>At 990mg/L TCE solution:</b> 0.60 M > 0M.  <b>At 110mg/L TCE solution:</b> 4.28 M > 0M.	x	Measured concentrations above vapor pressure.
D1		<b>Late time:</b> 0.60 M > 0 M, 0.60 M > 4.28 M, 0 M > 4.28 M		
D2			x	0.60 M & 4.28 M NaCl seem to have helped deplete TCE mass.
D2 vs D1		<b>Late time:</b> D1 > D2 at 0 M & 0.60 M.		Reactors with NAPL yield higher TCEvc.
D3			x	Higher TCEvc in reactors without NaCl at later time.
D6 vs D7	<b>Late time:</b> D7 > D6			In saturated clay with MeOH, higher TCEvc are measured in presence of NaCl.
D8	<b>Late time:</b> 0.60 M > 0 M & 4.28 M > 0 M.	<b>Early time:</b> 0.60 M > 0 M, 4.28 M > 0 M & 0.60 M > 4.28 M.		Measured concentrations above vapor pressure. Higher TCEvc for unsaturated clay with NaCl.
D10 vs D9		<b>Early time:</b> D10_1 > D9 > D10_2 <b>Late time:</b> No conclusive effect		Measured concentrations above vapor pressure.

**Table 4.29. Summary of statistical analyses of MeOH effect on TCE volatilization.**

Tests	MeOH hypothesized effect			Comments/explanation
	Big difference	Slight difference	No difference	
D4 vs D1	Late time: D4 > D1			MeOH seems to enhance TCE solubility.
D5 vs D2		Early time: D5 > D2		D5 reaches a concentration of zero.
D3 vs D6	Late time: D3 > D6			MeOH does not increase TCE <sub>vc</sub> in saturated clay without NaCl.
D3 vs D7	Late time: D7 > D3			MeOH enhances TCE <sub>vc</sub> in saturated clay in combination with 0.60 M NaCl.
D8 vs D9 D8 vs D10	Late time: D8 > D9 D8 > D10	Early time: D8 > D9 D8 > D10		TCE <sub>vc</sub> is higher in unsaturated clay without MeOH.

The dynamic flux reactor experiments were also analyzed according to the percentage of mass removal. Results indicate that percentage of mass removal was higher than 97% or 100% in reactors without TCE NAPL because all TCE in solution was removed. In reactors with TCE NAPL percentage of mass removal was very low. In saturated clay, TCE vapor removal is very low even with the addition of MeOH. On the other hand, in saturated clay, when NaCl is added together with MeOH, TCE mass removal seems to be higher. In unsaturated clay, TCE mass removal percentage was near to or 100% independently of the [NaCl]. NaCl and MeOH together do not seem to improve TCE mass extraction in unsaturated clay.

From cumulative TCE extracted mass analysis it can be said that a [NaCl] of 0.60 M enhances TCE mass extraction when there is TCE solution without NAPL phase TCE. MeOH has no conclusive effect on TCE solution with TCE NAPL, but has no enhancing effect on TCE solution without TCE NAPL. In TCE-solution saturated clay NaCl does not enhance TCE vapor extraction. In TCE-solution saturated clay, MeOH and NaCl

seem to enhance TCE vapor extraction when used together. Experiments with unsaturated clay show that a [NaCl] of 4.28 M reduces cumulative mass extraction and that MeOH does not enhance mass extraction in unsaturated clays in presence or absence of NaCl.

## 5 CONCLUSIONS

As part of this investigation it was hypothesized that salt would cause salting-out of NAPL and would cause clay particle flocculation, therefore enhancing clay permeability. It was hypothesized that the addition of an alcohol solution would increase contaminant water solubility and together with salt would enhance vapor phase extraction of TCE. It was also hypothesized that the capillary delivery of reactants would enhance reactant entrance to smaller and difficult-to-reach pores, therefore enhancing contact with NAPL present in tight formations.

Based on the experimental results and hypotheses, the following conclusions are deduced from the experimental data analysis and statistical analyses:

From air permeability tests it can be concluded that air permeability of clay could be enhanced using NaCl solutions. It is also concluded that higher air permeabilities can be obtained using a CaSO<sub>4</sub> solution, but the addition of CaCl<sub>2</sub> reduces the air permeability of clay.

From reagent delivery tests it can be concluded that the delivery of reagent solutions is more efficient when the level of the reagent source is leveled with the point of delivery. Also, capillary-based delivery of reagents can be used to preferentially deliver reagents to tight formations in a more homogeneously distributed manner. However, the delivery would take longer than at the same level. It is also concluded that the use of saline water improves the wetted distribution of clay and yields a shorter delivery time.

From the static batch reactors containing TCE solution with TCE NAPL, NaCl brine (~1.71 M) and saline water (0.60 M) enhance TCE vapor extraction, but a highly concentrated brine (4.28 M NaCl) may be too high, causing the reverse of the desired effect. NaCl has no significant effect on TCE solution with saturated clay, but measured TCE<sub>vc</sub> are higher in reactors with clay. For reactors containing TCE solution at different

aqueous concentrations (110 mg/L, 506 mg/L, and 990 mg/L) but no TCE NAPL, NaCl enhances TCE vapor extraction at [NaCl] of 0.60 M. At low TCE-solution concentration, a higher NaCl concentration yields higher TCE extraction.

From the dynamic flux batch, NaCl has a significant effect at late times on reactors with TCE solution and TCE NAPL. It has no significant effect on reactors with TCE solution in absence of TCE NAPL. MeOH has a significant effect, increasing measured TCE<sub>vc</sub> on reactors with TCE solution and TCE NAPL at late times, but not without TCE NAPL. NaCl has no significant effect on TCE-solution saturated clay, although, when combined with MeOH, TCE vapor extraction is enhanced. MeOH has no significant effect on TCE-solution saturated clay without NaCl. In reactors with unsaturated clay, NaCl has a significant effect on TCE volatilization. MeOH has no significant effect on unsaturated clay with or without NaCl.

In general, results indicate that TCE vapor extraction is higher in the presence of [NaCl] = 0.60 M. It is also higher in presence of MeOH when there is water and TCE NAPL present. A combination of MeOH and NaCl may be appropriate for remediating saturated clays containing TCE NAPL. The addition of NaCl to unsaturated clays, increases air permeability and enhances the vapor extraction of TCE.

It is important to note that the conclusions from tests using clay apply only to the type of soil used (i.e. Coto clay, a kaolinite clay).

## 6 RECOMMENDATIONS

Several recommendations are offered to further advance research for the enhancement of TCE vapor extraction from unsaturated clayey soils:

- Assess effect of a salt that does not contain sodium on TCE volatilization. A different salt may prevent soil dispersion and aggregate swelling effects on the clay.
- Develop a TCE dilution method to attain TCE saturated solution to ensure the same initial TCE concentration for all experiments.
- Assess vapor sampling dynamics in presence and absence of water vapor.
- Study the effect of a MeOH solution on the air permeability of clays.
- Study the TCE loading function. Using the data from these tests the loading function can be explored and analyzed. A first order mass transfer process was assumed but it could be different (e.g. exponential). This is out of the scope of this thesis.
- Evaluate mass transfer processes at later vapor extraction times.
- Assess effect of salt and alcohol treatments in other types of soil, because results of these tests apply only to the type of clay used (i.e. Coto clay).

## 6.1 SVE Testbed Suggested Experimental Design

The following is a suggested experimental design for the SVE enhancement experiments:

Column reactor experiments involve the application of alcohol/brine cycles followed by vacuum extraction. Enhanced SVE is to be tested following this initial cycle: alcohol aqueous solution (10%) injection through reactant delivery membranes, brine solution injection through reactant delivery membranes and, vapor extraction through extraction wells. Cycles, delivery rates, and solution concentrations should be modified between experiments to determine optimum parameters for SVE enhancement. Reactant delivery involves placing the alcohol or brine solution at the same level (elevation) as the delivery membrane, to induce flow by capillary forces. Vacuum extraction should be applied at a constant head by the vacuum pump connected to the manifold.

Several variables are to be monitored during the SVE enhancement experiments:

- Air pressures and flow rates. Air pressures are to be monitored at the vacuum manifold and at the first 20 cm from the top of the soil. Flow rates are to be measured with a flow meter placed downstream of vapor sampler.
- Solution delivery rates. Solution delivery rates are to be monitored by measuring changes in water levels from the solution reservoir.
- Changes in water content at the bottom boundary are to be monitored using a water content reflectometer.

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## **APPENDIXES**

## Appendix A: Air Permeability Tests: Pressures and other parameters used

Test 1: Dry soil

$\Delta P$ : Pressure change,  $q_a$  = volumetric flux rate,  $\eta$ : air dynamic viscosity,  $K_a$ : soil air permeability

**Table A.1. Measured pressure for air permeability test 1.**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	321	9	6	5.1	2	3.06	4	2.04
6469	208	37	23	22	15	15.81	8	6.19
10227	224	77	48	46.57	36	37.08	12	9.49
14257	250	145	87	85.76	70	72.08	17	13.68
18296	311	232	139	137.04	117	119.44	22	17.6

**Table A.2. Air permeability and parameters used for the calculation for test 1.**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>f</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	64.38	6.89E-12	4	2.04	0.01	0.00	3.91E-07	7.66E-07
6469	143.76		8	6.19	0.02	0.01	4.36E-07	5.64E-07
10227	227.28		12	9.49	0.03	0.02	4.60E-07	5.81E-07
14257	316.84		17	13.68	0.04	0.03	4.53E-07	5.62E-07
18296	406.60		22	17.6	0.05	0.04	4.49E-07	5.61E-07

Test 2: Unsaturated clay with distilled water at 15% wc

**Table A.3. Measured pressure for air permeability test 2.**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	54	10	7	4.35	3	-0.77	4	5.12
6469	93	37	25	20.58	15	10.69	10	9.89
10227	152	82	51	46.2	38	31.64	13	14.56
14257	227	142	88	82.5	70	62.71	18	19.79
18296	338	228	141.5	134.12	118.5	109.42	23	24.7

**Table A.4. Air permeability and parameters used for the calculation for test 2.**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	64.38	6.89E-12	4	5.12	0.01	0.01	3.91E-07	3.05E-07
6469	143.76		10	9.89	0.02	0.02	3.49E-07	3.53E-07
10227	227.28		13	14.56	0.03	0.03	4.24E-07	3.79E-07
14257	316.84		18	19.79	0.04	0.04	4.27E-07	3.89E-07
18296	406.60		23	24.7	0.05	0.06	4.29E-07	4E-07

Test 3: Dry soil

**Table A.5. Measured pressure for air permeability test 3.**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	23	7	5	5.79	1	3.06	4	2.73
6469	54	25	15	15.46	6	9.41	9	6.05
10227	100	50	32	30.34	17	19.15	15	11.19
14257	158	89	54	52.23	33	35.23	21	17
18296	228	141	84	79.75	55	56.53	29	23.22

**Table A.6. Air permeability and parameters used for the calculation for test 3.**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	64.38	6.89E-12	4	2.73	0.01	0.01	3.91E-07	5.73E-07
6469	143.76		9	6.05	0.02	0.01	3.88E-07	5.77E-07
10227	227.28		15	11.19	0.03	0.03	3.68E-07	4.93E-07
14257	316.84		21	17	0.05	0.04	3.66E-07	4.53E-07
18296	406.60		29	23.22	0.07	0.05	3.40E-07	4.25E-07

Test 4: Unsaturated clay with 4.28 M NaCl solution at 11% wc

**Table A.7. Measured pressure for air permeability test 4.**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	50	7	4	5.25	1	2.83	3	2.42
6469	75	20	11	12.52	6	7.71	5	4.81
10227	118	46	28	26.28	18	18.24	10	8.04
14257	166	77	44	42.07	32	31.21	12	10.86
18296	236	126	69	66.32	54	52.11	15	14.21

**Table A.8. Air permeability and parameters used for the calculation for test 4.**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>f</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	64.38	6.89E-12	3	2.42	0.01	0.01	5.21E-07	6.46E-07
6469	143.76		5	4.81	0.01	0.01	6.98E-07	7.26E-07
10227	227.28		10	8.04	0.02	0.02	5.52E-07	6.86E-07
14257	316.84		12	10.86	0.03	0.02	6.41E-07	7.08E-07
18296	406.60		15	14.21	0.03	0.03	6.58E-07	6.95E-07

Test 5: Unsaturated clay with distilled water at 12% wc

**Table A.9. Measured pressure for air permeability test 5.**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	41	6	4	4.8	2	1.87	2	2.93
6469	69	20	11	14.16	6	7.93	5	6.23
10227	110	45	26	28.6	17	18.86	9	9.74
14257	163	78	44	49.18	32	34.38	12	14.8
18296	241	130	73	79.92	55	59.08	18	20.84

**Table A.10. Air permeability and parameters used for the calculation for test 5.**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	64.38	6.89E-12	2	2.93	0.00	0.01	7.82E-07	5.34E-07
6469	143.76		5	6.23	0.01	0.01	6.98E-07	5.6E-07
10227	227.28		9	9.74	0.02	0.02	6.13E-07	5.67E-07
14257	316.84		12	14.8	0.03	0.03	6.41E-07	5.2E-07
18296	406.60		18	20.84	0.04	0.05	5.48E-07	4.74E-07

Test 6: Unsaturated clay with 0.005 M CaSO<sub>4</sub> solution at 26% wc

**Table A.11. Measured pressure for air permeability test 6 (first test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	52	12	10	10	1	1	9	9
6469	91	37	28	25.9	6	5.9	22	20
10227	146	69	48	46.3	16	15.3	32	31
14257	216	114	73	71.6	30	29.7	43	41.9
18296	302	170	104	101.9	49	49.4	55	52.5

**Table A.12. Air permeability and parameters used for the calculation for test 6 (first test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	9	9	0.02	0.02	1.79E-07	1.79E-07
6469	147.95		22	20	0.05	0.04	1.64E-07	1.8E-07
10227	233.90		32	31	0.07	0.07	1.78E-07	1.83E-07
14257	326.07		43	41.9	0.10	0.09	1.84E-07	1.89E-07
18296	418.45		55	52.5	0.12	0.12	1.85E-07	1.94E-07

**Table A.13. Measured pressure for air permeability test 6 (second test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		ΔP	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	50	11	9	8.9	1	1.8	8	7.1
6469	90	35	26	24.5	6	6.7	20	17.8
10227	144	68	46	44.6	15	15.8	31	28.8
14257	213	112	70	69.1	29	29.4	41	39.7
18296	302	170	102	99.5	49	48.9	53	50.6

**Table A.14. Air permeability and parameters used for the calculation for test 6 (second test).**

Flow (ml/min)	q <sub>a</sub> (cm/min)	η (lb <sub>f</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, ∇P (lb/cm <sup>2</sup> /cm)		K <sub>a</sub> (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	8	7.1	0.02	0.02	2.01E-07	2.27E-07
6469	147.95		20	17.8	0.04	0.04	1.80E-07	2.02E-07
10227	233.90		31	28.8	0.07	0.06	1.83E-07	1.98E-07
14257	326.07		41	39.7	0.09	0.09	1.93E-07	2E-07
18296	418.45		53	50.6	0.12	0.11	1.92E-07	2.01E-07

**Table A.15. Measured pressure for air permeability test 6 (third test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		ΔP	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	48	11	8	8.9	1	1.8	7	7.1
6469	86	34	25	23.8	5	6.5	20	17.3
10227	140	65	43	42.8	14	15	29	27.8
14257	206	107	68	66.8	29	28.3	39	38.5
18296	292	162	98	95.9	47	47.1	51	48.8

**Table A.16. Air permeability and parameters used for the calculation for test 6 (third test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>f</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	7	7.1	0.02	0.02	2.30E-07	2.27E-07
6469	147.95		20	17.3	0.04	0.04	1.80E-07	2.08E-07
10227	233.90		29	27.8	0.07	0.06	1.96E-07	2.05E-07
14257	326.07		39	38.5	0.09	0.09	2.03E-07	2.06E-07
18296	418.45		51	48.8	0.11	0.11	2.00E-07	2.09E-07

Test 7: Unsaturated clay with 0.005 M CaSO<sub>4</sub> solution at 14% wc

**Table A.17. Measured pressure for air permeability test 7 (first test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	42	3	1	4.6	0	0.8	1	3.8
6469	73	16	7	12.1	3	5.9	4	6.2
10227	113	39	20	23	14	15.1	6	7.9
14257	170	68	36	38.5	27	28.5	9	10
18296	240	110	58	59.2	48	47.5	10	11.7

**Table A.18. Air permeability and parameters used for the calculation for test 7 (first test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>f</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	1	3.8	0.00	0.01	1.61E-06	4.24E-07
6469	147.95		4	6.2	0.01	0.01	9.00E-07	5.8E-07
10227	233.90		6	7.9	0.01	0.02	9.48E-07	7.2E-07
14257	326.07		9	10	0.02	0.02	8.81E-07	7.93E-07
18296	418.45		10	11.7	0.02	0.03	1.02E-06	8.7E-07

**Table A.19. Measured pressure for air permeability test 7 (second test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		ΔP	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	44	4	2	4	1	0.5	1	3.5
6469	73	17	9	10.7	6	5.6	3	5.1
10227	115	38	20	21.1	15	14.5	5	6.6
14257	170	68	36	36.3	30	28.2	6	8.1
18296	239	109	56	56.7	49	47.2	7	9.5

**Table A.20. Air permeability and parameters used for the calculation for test 7 (second test).**

Flow (ml/min)	q <sub>a</sub> (cm/min)	η (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, ∇P (lb/cm <sup>2</sup> /cm)		K <sub>a</sub> (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	1	3.5	0.00	0.01	1.61E-06	4.6E-07
6469	147.95		3	5.1	0.01	0.01	1.20E-06	7.06E-07
10227	233.90		5	6.6	0.01	0.01	1.14E-06	8.62E-07
14257	326.07		6	8.1	0.01	0.02	1.32E-06	9.79E-07
18296	418.45		7	9.5	0.02	0.02	1.45E-06	1.07E-06

**Table A.21. Measured pressure for air permeability test 7 (third test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		ΔP	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	42	3	2	3.7	1	0.2	1	3.5
6469	73	17	8	10.5	6	5.6	2	4.9
10227	115	39	19	20.5	16	14.5	3	6
14257	173	69	34	35.6	30	28.4	4	7.2
18296	241	110	53	54.5	48	46	5	8.5

**Table A.22. Air permeability and parameters used for the calculation for test 7 (third test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>f</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	1	3.5	0.00	0.01	1.61E-06	4.6E-07
6469	147.95		2	4.9	0.00	0.01	1.80E-06	7.34E-07
10227	233.90		3	6	0.01	0.01	1.90E-06	9.48E-07
14257	326.07		4	7.2	0.01	0.02	1.98E-06	1.1E-06
18296	418.45		5	8.5	0.01	0.02	2.04E-06	1.2E-06

Test 8: Unsaturated clay with 0.005 M CaSO<sub>4</sub> 0.60 M CaCl<sub>2</sub> solution at 32% wc

**Table A.23. Measured pressure for air permeability test 8 (first test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	60	20	18	19.6	1	1.3	17	18.3
6469	108	51	43	43.7	6	6.5	37	37.2
10227	171	94	74	74.8	16	15.7	58	59.1
14257	247	146	110	109.6	31	29.5	79	80.1
18296	344	213	154	153.3	51	49.6	103	103.7

**Table A.24. Air permeability and parameters used for the calculation for test 8 (first test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>f</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	17	18.3	0.04	0.04	9.48E-08	8.81E-08
6469	147.95		37	37.2	0.08	0.08	9.72E-08	9.67E-08
10227	233.90		58	59.1	0.13	0.13	9.81E-08	9.62E-08
14257	326.07		79	80.1	0.18	0.18	1.00E-07	9.9E-08
18296	418.45		103	103.7	0.23	0.23	9.88E-08	9.81E-08

**Table A.25. Measured pressure for air permeability test 8 (second test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	60	17	16	16.5	1	0.4	15	16.1
6469	107	49	42	42.4	5	5.3	37	37.1
10227	168	91	72	72.6	15	14.3	57	58.3
14257	240	140	106	106.2	30	27.3	76	78.9
18296	338	207	150	149.7	50	47.5	100	102.2

**Table A.26. Air permeability and parameters used for the calculation for test 8 (second test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	15	16.1	0.03	0.04	1.07E-07	1E-07
6469	147.95		37	37.1	0.08	0.08	9.72E-08	9.7E-08
10227	233.90		57	58.3	0.13	0.13	9.98E-08	9.76E-08
14257	326.07		76	78.9	0.17	0.18	1.04E-07	1.01E-07
18296	418.45		100	102.2	0.22	0.23	1.02E-07	9.96E-08

**Table A.27. Measured pressure for air permeability test 8 (third test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	60	17	16	17.6	1	0.4	15	17.2
6469	107	49	42	42.4	6	5.4	36	37
10227	164	88	70	71	14	14.1	56	56.9
14257	237	138	106	105.7	30	27.8	76	77.9
18296	331	200	149	147.9	50	47.6	99	100.3

**Table A.28. Air permeability and parameters used for the calculation for test 8 (third test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	15	17.2	0.03	0.04	1.07E-07	9.37E-08
6469	147.95		36	37	0.08	0.08	9.99E-08	9.72E-08
10227	233.90		56	56.9	0.13	0.13	1.02E-07	1E-07
14257	326.07		76	77.9	0.17	0.18	1.04E-07	1.02E-07
18296	418.45		99	100.3	0.22	0.23	1.03E-07	1.01E-07

Test 9: Unsaturated clay with 0.005 M CaSO<sub>4</sub> 0.60 M CaCl<sub>2</sub> solution at 27% wc

**Table A.29. Measured pressure for air permeability test 9 (first test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	60	17	16	16.8	1	1.6	15	15.2
6469	103	46	38	38.4	7	7.1	31	31.3
10227	160	83	63	63.4	16	15.3	47	48.1
14257	231	130	95	94.4	31	29.2	64	65.2
18296	324	194	132	131.5	50	48.4	82	83.1

**Table A.30. Air permeability and parameters used for the calculation for test 9 (first test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	15	15.2	0.03	0.03	8.09E-08	7.98E-08
6469	147.95		31	31.3	0.07	0.07	8.38E-08	8.3E-08
10227	233.90		47	48.1	0.11	0.11	8.59E-08	8.39E-08
14257	326.07		64	65.2	0.14	0.15	8.73E-08	8.56E-08
18296	418.45		82	83.1	0.18	0.19	8.81E-08	8.69E-08

**Table A.31. Measured pressure for air permeability test 9 (second test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	60	16	13	16.2	0	1	13	15.2
6469	101	44	36	36.1	6	5.6	30	30.5
10227	157	81	61	61.6	14	14.4	47	47.2
14257	228	127	93	92	30	27.9	63	64.1
18296	318	187	130	129	49	47.6	81	81.4

**Table A.32. Air permeability and parameters used for the calculation for test 9 (second test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	13	15.2	0.03	0.03	9.34E-08	7.98E-08
6469	147.95		30	30.5	0.07	0.07	8.65E-08	8.51E-08
10227	233.90		47	47.2	0.11	0.11	8.59E-08	8.55E-08
14257	326.07		63	64.1	0.14	0.14	8.86E-08	8.71E-08
18296	418.45		81	81.4	0.18	0.18	8.92E-08	8.87E-08

**Table A.33. Measured pressure for air permeability test 9 (third test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	60	16	13	17.3	0	0.7	13	16.6
6469	100	43	35	35.5	5	5	30	30.5
10227	156	80	60	60.8	14	14	46	46.8
14257	226	125	91	90.9	30	27.6	61	63.3
18296	314	184	127	127	49	46.9	78	80.1

**Table A.34. Air permeability and parameters used for the calculation for test 9 (third test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	13	16.6	0.03	0.04	9.34E-08	7.31E-08
6469	147.95		30	30.5	0.07	0.07	8.65E-08	8.51E-08
10227	233.90		46	46.8	0.10	0.11	8.77E-08	8.62E-08
14257	326.07		61	63.3	0.14	0.14	9.15E-08	8.82E-08
18296	418.45		78	80.1	0.18	0.18	9.26E-08	9.02E-08

Test 10: Unsaturated clay with 0.60 M CaCl<sub>2</sub> solution at 30% wc

**Table A.35. Measured pressure for air permeability test 10 (first test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	57	13	10	10.6	1	0.1	9	10.5
6469	93	34	25	24.6	6	4.8	19	19.8
10227	142	62	44	43.4	15	13.6	29	29.8
14257	204	102	67	66.1	30	26.7	37	39.4
18296	287	155	97	95.4	49	45.8	48	49.6

**Table A.36. Air permeability and parameters used for the calculation for test 10 (first test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2182	66.26	6.89E-12	9	10.5	0.02	0.02	1.79E-07	1.53E-07
4668	147.95		19	19.8	0.04	0.04	1.89E-07	1.82E-07
7256	233.90		29	29.8	0.07	0.07	1.96E-07	1.91E-07
10040	326.07		37	39.4	0.08	0.09	2.14E-07	2.01E-07
12988	418.45		48	49.6	0.11	0.11	2.12E-07	2.05E-07

**Table A.37. Measured pressure for air permeability test 10 (second test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	57	11	9	9.7	1	-0.9	8	10.6
6469	90	32	23	23.1	6	3.6	17	19.5
10227	140	61	43	41.9	15	12.6	28	29.3
14257	204	101	66	65.1	30	25.9	36	39.2
18296	284	152	95	93.8	48	44.6	47	49.2

**Table A.38. Air permeability and parameters used for the calculation for test 10 (second test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure changes (mbar)		Pressure gradient (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2182	66.26	6.89E-12	8	10.6	0.02	0.02	2.01E-07	1.52E-07
4668	147.95		17	19.5	0.04	0.04	2.12E-07	1.85E-07
7256	233.90		28	29.3	0.06	0.07	2.03E-07	1.94E-07
10040	326.07		36	39.2	0.08	0.09	2.20E-07	2.02E-07
12988	418.45		47	49.2	0.11	0.11	2.17E-07	2.07E-07

**Table A.39. Measured pressure for air permeability test 10 (third test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	56	11	9	9.6	1	-1	8	10.6
6469	90	32	23	23.2	6	4	17	19.2
10227	139	61	42	41.4	16	13	26	28.4
14257	203	102	65	64.6	30	26.6	35	38
18296	285	155	94	93.6	49	46	45	47.6

**Table A.40. Air permeability and parameters used for the calculation for test 10 (third test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2182	66.26	6.89E-12	8	10.6	0.02	0.02	2.01E-07	1.52E-07
4668	147.95		17	19.2	0.04	0.04	2.12E-07	1.87E-07
7256	233.90		26	28.4	0.06	0.06	2.19E-07	2E-07
10040	326.07		35	38	0.08	0.09	2.27E-07	2.09E-07
12988	418.45		45	47.6	0.10	0.11	2.26E-07	2.14E-07

Test 11: Unsaturated clay with 0.60 M CaCl<sub>2</sub> solution at 27% wc

**Table A.41. Measured pressure for air permeability test 11 (first test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	53	9	7	9.7	1	1.5	6	8.2
6469	89	31	22	23.4	6	6.5	16	16.9
10227	137	57	40	40.6	14	15.2	26	25.4
14257	196	93	60	60.9	28	27.4	32	33.5
18296	276	142	87	87.6	46	45.2	41	42.4

**Table A.42. Air permeability and parameters used for the calculation for test 11 (first test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	6	8.2	0.01	0.02	2.69E-07	1.97E-07
6469	147.95		16	16.9	0.04	0.04	2.25E-07	2.13E-07
10227	233.90		26	25.4	0.06	0.06	2.19E-07	2.24E-07
14257	326.07		32	33.5	0.07	0.08	2.48E-07	2.37E-07
18296	418.45		41	42.4	0.09	0.10	2.48E-07	2.4E-07

**Table A.43. Measured pressure for air permeability test 11 (second test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	52	10	8	11.1	1	1.9	7	9.2
6469	86	30	21	23.3	6	6.5	15	16.8
10227	134	57	38	39.3	14	14.5	24	24.8
14257	196	94	58	59.9	28	26.9	30	33
18296	275	142	84	85.4	45	44.2	39	41.2

**Table A.44. Air permeability and parameters used for the calculation for test 11 (second test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	7	9.2	0.02	0.02	2.30E-07	1.75E-07
6469	147.95		15	16.8	0.03	0.04	2.40E-07	2.14E-07
10227	233.90		24	24.8	0.05	0.06	2.37E-07	2.29E-07
14257	326.07		30	33	0.07	0.07	2.64E-07	2.4E-07
18296	418.45		39	41.2	0.09	0.09	2.61E-07	2.47E-07

**Table A.45. Measured pressure for air permeability test 11 (third test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	53	10	7	10.7	1	1.5	6	9.2
6469	87	30	20	23	6	6.4	14	16.6
10227	134	56	37	38.7	14	14.5	23	24.2
14257	194	92	57	58.7	28	26.7	29	32
18296	274	144	84	85.7	46	45.2	38	40.5

**Table A.46. Air permeability and parameters used for the calculation for test 11 (third test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	6	9.2	0.01	0.02	2.69E-07	1.75E-07
6469	147.95		14	16.6	0.03	0.04	2.57E-07	2.17E-07
10227	233.90		23	24.2	0.05	0.05	2.47E-07	2.35E-07
14257	326.07		29	32	0.07	0.07	2.73E-07	2.48E-07
18296	418.45		38	40.5	0.09	0.09	2.68E-07	2.51E-07

Test 12: Unsaturated clay with 0.06 M CaCl<sub>2</sub> solution at 27% wc

**Table A.47. Measured pressure for air permeability test 12 (first test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	57	13	9	12.8	1	1.4	8	11.4
6469	87	30	21	23.2	6	5.6	15	17.6
10227	136	59	38	40.8	14	15	24	25.8
14257	199	97	62	62.5	31	28.2	31	34.3
18296	276	146	89	88.7	49	46.5	40	42.2

**Table A.48. Air permeability and parameters used for the calculation for test 12 (first test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	8	11.4	0.02	0.03	2.01E-07	1.41E-07
6469	147.95		15	17.6	0.03	0.04	2.40E-07	2.04E-07
10227	233.90		24	25.8	0.05	0.06	2.37E-07	2.2E-07
14257	326.07		31	34.3	0.07	0.08	2.56E-07	2.31E-07
18296	418.45		40	42.2	0.09	0.09	2.54E-07	2.41E-07

**Table A.49. Measured pressure for air permeability test 12 (second test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		ΔP	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	56	12	9	11.8	2	1	7	10.8
6469	87	29	21	22.9	6	5.5	15	17.4
10227	134	58	39	39.8	16	14.4	23	25.4
14257	195	94	60	60.7	29	27.3	31	33.4
18296	273	144	87	87.4	48	45.8	39	41.6

**Table A.50. Air permeability and parameters used for the calculation for test 12 (second test).**

Flow (ml/min)	q <sub>a</sub> (cm/min)	η (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, ∇P (lb/cm <sup>2</sup> /cm)		K <sub>a</sub> (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	7	10.8	0.02	0.02	2.30E-07	1.49E-07
6469	147.95		15	17.4	0.03	0.04	2.40E-07	2.07E-07
10227	233.90		23	25.4	0.05	0.06	2.47E-07	2.24E-07
14257	326.07		31	33.4	0.07	0.08	2.56E-07	2.37E-07
18296	418.45		39	41.6	0.09	0.09	2.61E-07	2.45E-07

**Table A.51. Measured pressure for air permeability test 12 (third test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		ΔP	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	57	12	9	12.1	1	0.8	8	11.3
6469	87	30	20	22.7	6	5.2	14	17.5
10227	135	58	38	39.5	15	14.2	23	25.3
14257	198	97	59	60.7	30	27.5	29	33.2
18296	278	148	87	87.7	48	46.4	39	41.3

**Table A.52. Air permeability and parameters used for the calculation for test 12 (third test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>f</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	8	11.3	0.02	0.03	2.01E-07	1.43E-07
6469	147.95		14	17.5	0.03	0.04	2.57E-07	2.06E-07
10227	233.90		23	25.3	0.05	0.06	2.47E-07	2.25E-07
14257	326.07		29	33.2	0.07	0.07	2.73E-07	2.39E-07
18296	418.45		39	41.3	0.09	0.09	2.61E-07	2.46E-07

Test 13: Unsaturated clay with 0.06 M CaCl<sub>2</sub> solution at 23% wc

**Table A.53. Measured pressure for air permeability test 13 (first test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	51	8	5	9.1	0	0.7	5	8.4
6469	86	28	18	20.7	5	5.6	13	15.1
10227	132	55	34	35.8	13	13.7	21	22.1
14257	194	91	53	55.2	28	26.6	25	28.6
18296	275	140	77	78.8	45	43.9	32	34.9

**Table A.54. Air permeability and parameters used for the calculation for test 13 (first test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>f</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	5	8.4	0.01	0.02	3.22E-07	1.92E-07
6469	147.95		13	15.1	0.03	0.03	2.77E-07	2.38E-07
10227	233.90		21	22.1	0.05	0.05	2.71E-07	2.57E-07
14257	326.07		25	28.6	0.06	0.06	3.17E-07	2.77E-07
18296	418.45		32	34.9	0.07	0.08	3.18E-07	2.92E-07

**Table A.55. Measured pressure for air permeability test 13 (second test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	51	7	5	8.7	0	0.5	5	8.2
6469	84	26	17	19.6	5	5.3	12	14.3
10227	128	52	33	34.2	13	13.7	20	20.5
14257	190	87	52	53	28	26.4	24	26.6
18296	265	134	75	76.6	45	44.2	30	32.4

**Table A.56. Air permeability and parameters used for the calculation for test 13 (second test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
2897	66.26	6.89E-12	5	8.2	0.01	0.02	3.22E-07	1.97E-07
6469	147.95		12	14.3	0.03	0.03	3.00E-07	2.52E-07
10227	233.90		20	20.5	0.04	0.05	2.84E-07	2.77E-07
14257	326.07		24	26.6	0.05	0.06	3.30E-07	2.98E-07
18296	418.45		30	32.4	0.07	0.07	3.39E-07	3.14E-07

**Table A.57. Measured pressure for air permeability test 13 (third test).**

Flow (ml/min)	Pressure (mbar)							
	Before Flowmeter	After Flowmeter	Before soil chamber		After soil chamber		$\Delta P$	
			Manometer	Sensor 5	Manometer	Sensor 6	Manometer	Sensors
2897	49	7	5	8	0	-0.1	5	8.1
6469	83	25	16	18.7	5	4.7	11	14
10227	128	51	32	33.1	14	13	18	20.1
14257	186	85	50	50.7	28	25	22	25.7
18296	262	130	73	73.5	44	42	29	31.5

**Table A.58. Air permeability and parameters used for the calculation for test 13 (third test).**

Flow (ml/min)	$q_a$ (cm/min)	$\eta$ (lb <sub>r</sub> .min/ cm <sup>2</sup> ) at 23.8 °C	Pressure change (mbar)		Pressure gradient, $\nabla P$ (lb/cm <sup>2</sup> /cm)		$K_a$ (cm <sup>2</sup> )	
			Manometer	Sensors	Manometer	Sensors	Manometer	Sensors
<b>2897</b>	66.26	6.89E-12	5	8.1	0.01	0.02	3.22E-07	1.99E-07
<b>6469</b>	147.95		11	14	0.02	0.03	3.27E-07	2.57E-07
<b>10227</b>	233.90		18	20.1	0.04	0.05	3.16E-07	2.83E-07
<b>14257</b>	326.07		22	25.7	0.05	0.06	3.60E-07	3.09E-07
<b>18296</b>	418.45		29	31.5	0.07	0.07	3.51E-07	3.23E-07

## **Appendix B: Capillary-based Delivery Tests**

Table B.1. Capillary-based delivery test data.

Solution used	Distilled water												[NaCl] = 0.6 M			
Experiment	A				B				C				D			
	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>ave</sub>	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	B <sub>ave</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>ave</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>	D <sub>ave</sub>
Time to achieve wet circumference (min)	12.22	11.31	10.25	<b>11.26</b>	4.17	3.22	7.56	<b>4.98</b>	54.27	42.55	182.17	<b>92.99</b>	10.65	7.48	7.60	<b>8.58</b>
Total distilled water/solution added (mL)	75.00	126.00	93.00	<b>98.00</b>	56.00	58.00	83.00	<b>65.67</b>	94.00	56.00	62.50	<b>70.83</b>	94.50	74.00	61.50	<b>76.67</b>
Distance between porous cup and center of wet circumference column (in)	1.50	0.50	0.13	<b>0.71</b>	0.69	0.50	0.50	<b>0.56</b>	0.25	0.25	0.63	<b>0.19</b>	0.25	0.25	0.50	<b>0.33</b>
Width of moist clay (in)	3.00	3.00	3.38	<b>3.13</b>	3.13	3.00	3.00	<b>3.04</b>	3.50	3.50	3.38	<b>3.46</b>	3.50	3.50	3.00	<b>3.33</b>
Density (g/cm <sup>3</sup> )	1.06	1.09	1.10	<b>1.08</b>	1.09	1.10	1.10	<b>1.10</b>	1.10	1.10	1.10	<b>1.10</b>	1.10	1.10	1.10	<b>1.10</b>
Water content (%)	0.22	0.23	0.20	<b>0.22</b>	0.23	0.21	0.21	<b>0.22</b>	0.23	0.22	0.21	<b>0.22</b>	0.23	0.22	0.22	<b>0.22</b>

# Appendix C: Static batch reactor experiments: Calibrations and TCEvc

Static batch reactor experiments S1 & S2:

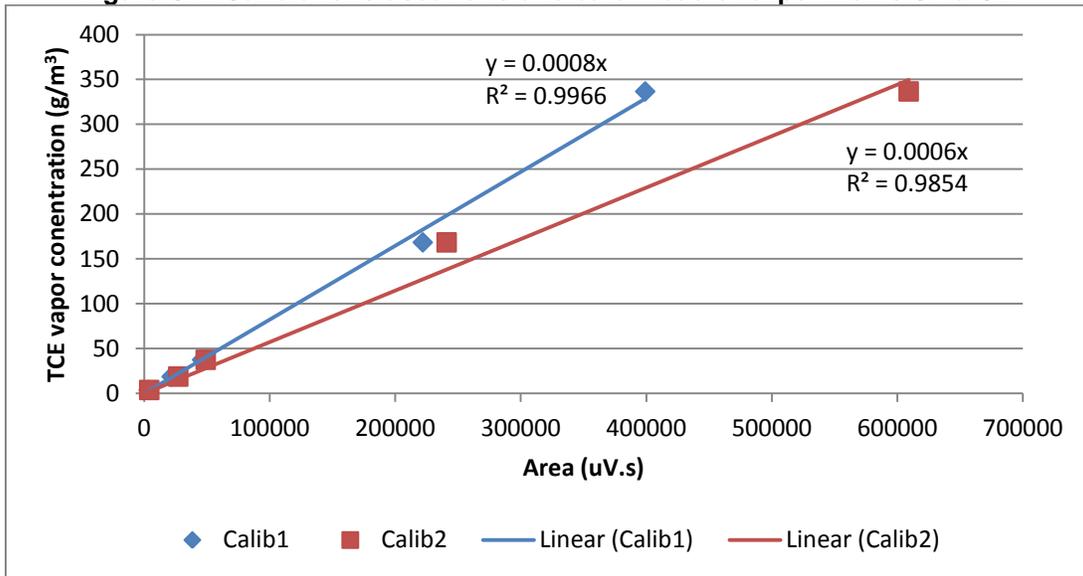
Table C.1. Calibration parameters for static batch reactor experiments S1 & S2.

C <sub>w</sub> (mg/L)	C <sub>a</sub> (g/m <sup>3</sup> )	Area (uV.s)	
		Calibration 1	Calibration 2
11	3.74	3543.67	4037.16
55	18.70	21850.54	27148.20
110	37.40	46101.22	49032.14
495	168.30	221985.41	240987.32
990	336.60	399175.65	609088.64

C<sub>w</sub>: TCE concentration of solution in liquid standards.

C<sub>a</sub>: TCE vapor concentration of standards.

Figure C.1. Calibrations used for static batch reactor experiments S1 & S2.



**Table C.2. TCE vapor concentrations for static batch reactor experiment S1.**

TCE vapor concentrations (g/m <sup>3</sup> )					
Time	[NaCl] (M)				
	0	0.26	0.60	1.71	4.28
<b>1</b>	372.3406	320.8554	858.2794	704.5188	177.2924
<b>3</b>	381.9218	323.9526	260.6603	267.9083	410.6233
<b>6</b>	499.8188	468.9792	290.9405	378.4747	281.4346
<b>12</b>	380.7980	410.4071	361.8464	483.1718	261.1895
<b>24</b>	415.9783	509.3474	426.7334	1918.5307	340.9285
<b>48</b>	631.1059	481.1758	551.0101	536.6810	351.2605
<b>60</b>	531.3082	661.1889	465.8178		297.9775
<b>72</b>	666.2597	410.8863	964.2664	1410.3031	829.0016
<b>84</b>	559.9545	624.3281	522.8058	486.5002	311.3072
<b>96</b>	562.6071	602.1142	678.3367	585.7839	504.9612

**Table C.3. TCE vapor concentrations for static batch reactor experiment S2.**

TCE vapor concentrations (g/m <sup>3</sup> )					
Time	[NaCl] (M)				
	0	0.26	0.60	1.71	4.28
<b>1</b>	317.1616	290.6145	339.7833	464.1944	234.1072
<b>3</b>	292.1812	203.0661	217.8497	256.8015	448.2869
<b>6</b>	387.0648	573.2680	102.6216	553.7042	225.7415
<b>12</b>	419.6003	572.5007	357.9505	378.5933	222.3325
<b>24</b>	447.6507	481.9533	611.0905	526.3383	1081.1262
<b>48</b>	836.3499	810.5099	1419.6554	1069.9134	242.2449
<b>60</b>	498.0268	434.7555	800.9158	1248.0309	502.2243
<b>72</b>	560.8905	1284.2808	1022.2609	1341.1985	842.1427
<b>84</b>	735.4666	636.7176	1171.3740	1937.1664	1140.8224
<b>96</b>	689.6011	1010.6856	873.3453	1153.8258	1025.3564

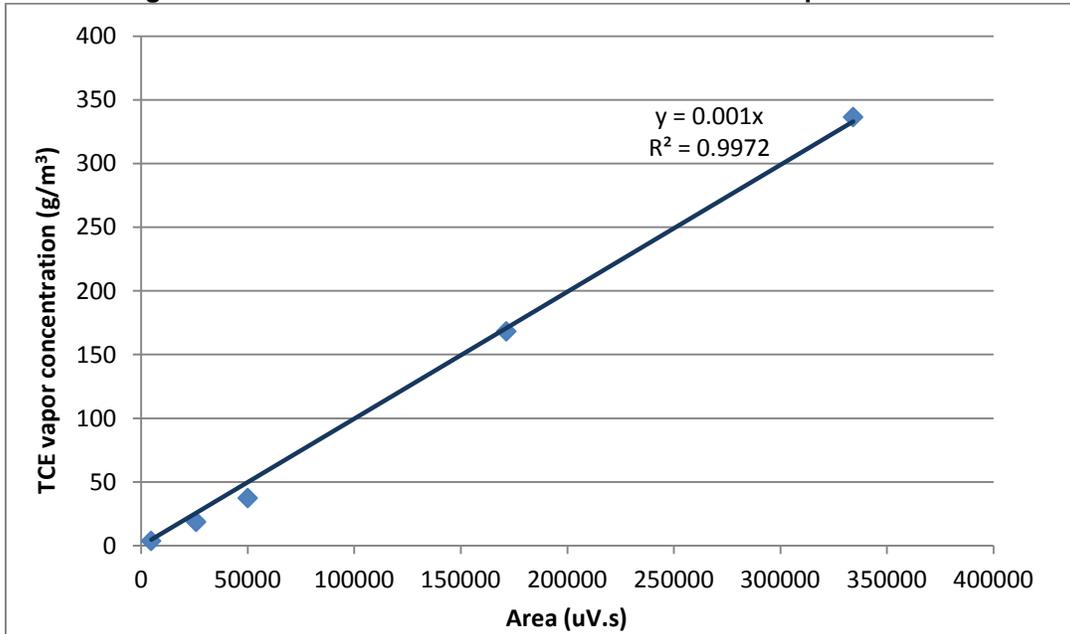
Static batch reactor experiment S3:

**Table C.4. Calibration parameters for static batch reactor experiment S3.**

$C_w$ (mg/L)	$C_a$ (g/m <sup>3</sup> )	Area (uV.s)
11	3.74	4662.01
55	18.70	25801.93
110	37.40	50014.37
495	168.30	171400.22
990	336.60	334200.34

$C_w$ : TCE concentration of solution in liquid standards.  
 $C_a$ : TCE vapor concentration of standards.

**Figure C.2. Calibration used for static batch reactor experiment S3.**



**Table C.5. TCE vapor concentration for static batch reactor experiment S3.**

TCE vapor concentrations (g/m <sup>3</sup> )					
Time	[NaCl] (M)				
	0	0.26	0.60	1.71	4.28
<b>1</b>	604.4691	614.5313	3423.87	944.7052	251.4055
<b>3</b>	524.2529	474.106	416.2008	984.278	209.8589
<b>6</b>	729.7545	508.3567	502.1302	2998.581	3438.169
<b>12</b>	281.0754	800.8705	861.9225	2392.083	3447.105
<b>24</b>	626.3682	614.8888	775.341	1127.883	3490.227
<b>48</b>	1132.574	988.1331	820.7433	663.7687	973.7449
<b>60</b>	424.3453	1899.624	587.2854	2098.544	517.3223
<b>72</b>	1260.375	861.6209	780.1066	1852.994	1394.264
<b>84</b>	447.1401	679.7488	1110.602	1425.119	948.0862
<b>96</b>	1599.645	2791.853	2235.834	967.2628	776.3061
<b>120</b>	2195.389	1311.81	782.1371	1593.534	2745.47

Static batch reactor experiments with clay, S4\_1 and S4\_2:

**Table C.6. Calibration parameters for static batch reactor experiments with clay S4\_1 and S4\_2.**

C <sub>w</sub> (mg/L)	C <sub>a</sub> (g/m <sup>3</sup> )	Area (uV*s)
<b>11</b>	3.74	6137.03
<b>55</b>	18.70	16430.46
<b>110</b>	37.40	31391.18
<b>495</b>	168.30	128269.33
<b>660</b>	224.40	159783.07
<b>814</b>	276.76	177344.72
<b>990</b>	336.60	232553.37

C<sub>w</sub>: TCE concentration of solution in liquid standards.

C<sub>a</sub>: TCE vapor concentration of standards.

Figure C.3. Calibration used for static batch reactor experiments with clay S4\_1 and S4\_2.

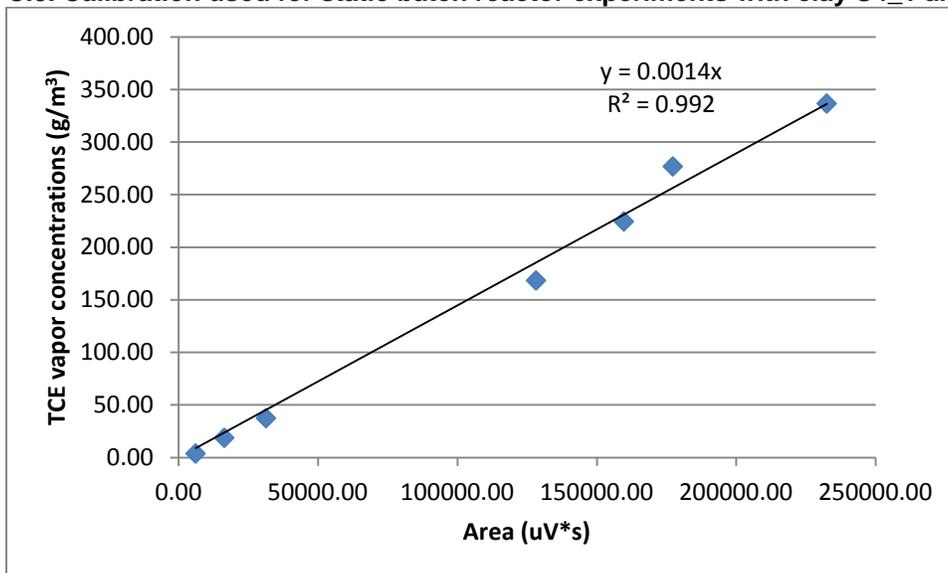


Table C. 7. TCE vapor concentration for static batch reactor experiment with clay S4\_1.

TCE vapor concentrations (g/m <sup>3</sup> )			
[NaCl] (M)			
Time	0	0.60	4.28
<b>1</b>	1362.74	325.22	840.60
<b>3</b>	301.23	255.28	4950.69
<b>6</b>	525.30	303.98	4987.69
<b>12</b>	530.64	541.75	190.93
<b>24</b>	1311.57	792.08	405.17
<b>48</b>	3853.10	4976.51	459.30
<b>60</b>	2299.91	974.88	406.21
<b>72</b>	2561.07	2208.03	816.34
<b>84</b>	1401.92	3895.92	5063.23
<b>96</b>	4995.57	4903.12	2129.85
<b>120</b>	4970.63	2040.55	5101.01

**Table C.8. TCE vapor concentration for static batch reactor experiment with clay S4\_2.**

TCE vapor concentrations (g/m <sup>3</sup> )			
[NaCl] (M)			
Time	0	0.60	4.28
1	609.24	580.40	739.43
3	792.51	483.98	276.29
6	862.41	591.82	362.30
12	702.29	692.88	492.36
24	1825.48	1168.41	892.86
48	5063.53	550.09	697.42
60	2624.04	1799.15	818.85
72	2932.66	2575.50	1826.40
84	1251.40	3478.90	932.15
96	1148.94	3102.99	1533.25
120	1077.31	1150.95	1639.85

Static aqueous reactor experiment E1:

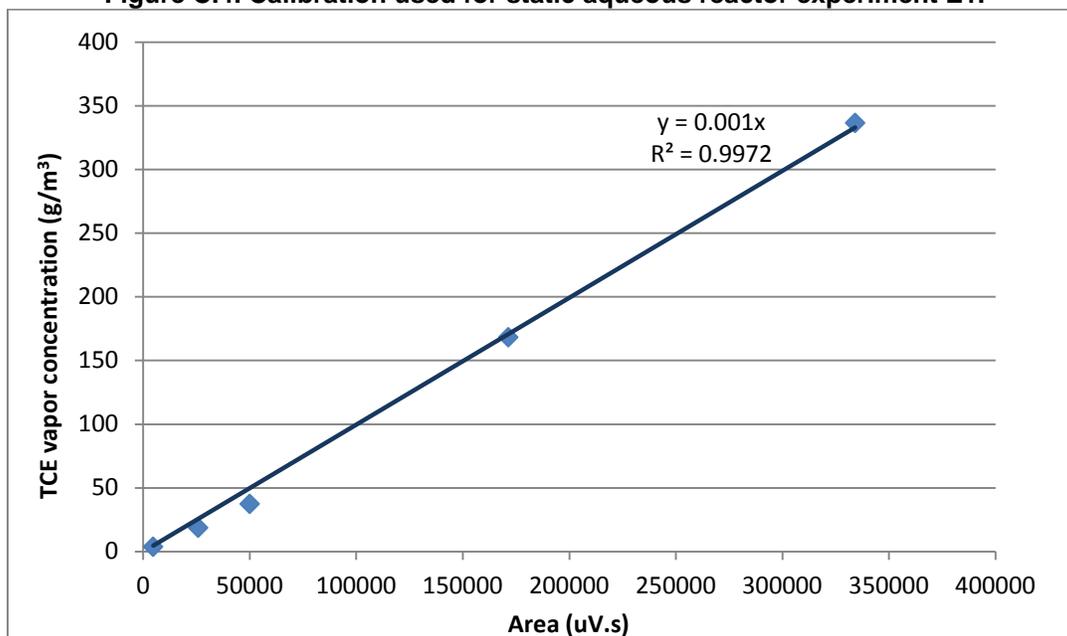
**Table C.9. Calibration for static aqueous reactor experiment E1.**

C <sub>w</sub> (mg/L)	C <sub>a</sub> (g/m <sup>3</sup> )	Area (uV.s)
11	3.74	4662.01
55	18.70	25801.93
110	37.40	50014.37
495	168.30	171400.22
990	336.60	334200.34

C<sub>w</sub>: TCE concentration of solution in liquid standards.

C<sub>a</sub>: TCE vapor concentration of standards.

**Figure C.4. Calibration used for static aqueous reactor experiment E1.**



**Table C.10. TCE vapor concentration for static aqueous reactor experiment E1.**

TCE vapor concentrations (g/m <sup>3</sup> )			
[TCE sol] mg/L	[NaCl] (M)		
	0	0.60	4.28
110	32.64	16.53	61.14
	29.58	14.24	57.68
506	106.41	190.13	247.80
	70.55	201.91	277.76
990	125.82	408.40	625.41
	156.58	422.82	537.78

**Table C.11. Average TCE vapor concentration for static aqueous reactor experiment E1.**

Average TCE vapor concentrations (g/m <sup>3</sup> )			
[TCE sol] mg/L	[NaCl] (M)		
	0	0.60	4.28
110	31.11	15.39	59.41
506	88.48	196.02	262.78
990	141.20	415.61	581.59

## Appendix D: Dynamic Flux Batch Reactor Experiments: Calibrations and TCEvc

Data for D1:

Table D.1. TCE vapor concentrations for dynamic flux reactor experiment D1.

TCE vapor concentrations (g/m <sup>3</sup> )						
Time (hours)	[NaCl] M					
	0		0.60		4.28	
	1	2	1	2	1	2
<b>0</b>	211.74	106.85	256.68	114.45	203.08	274.38
<b>0.33</b>	84.03	44.94	60.13	54.40	102.16	87.30
<b>0.67</b>	31.79	38.31	34.30	31.55	44.29	37.08
<b>1</b>	34.92	29.24	15.85	21.66	24.17	20.00
<b>1.5</b>	15.51	22.44	11.37	12.73	11.52	13.36
<b>2</b>	10.64	20.33	7.72	7.49	8.96	13.57
<b>3</b>	12.35	20.48	6.84	4.77	6.60	7.94
<b>6</b>	-	10.98	6.01	3.24	7.18	8.88
<b>12</b>	1.33	3.67	3.15	3.06	2.05	3.91
<b>24</b>	1.91	1.88	2.51	6.28	1.08	2.35
<b>48</b>	1.82	1.51	3.17	5.02	0.56	1.08
<b>60</b>	2.15	1.78	1.44	2.62	0.60	22.80
<b>72</b>	1.02	2.19	1.83	2.20	0.42	1.18
<b>84</b>	0.94	1.82	0.99	4.83	0.72	0.60
<b>96</b>	0.57	1.44	2.96	2.56	0.49	0.74
<b>120</b>	1.70	1.36	1.51	3.60	0.38	0.61

Table D.2. Relative TCE vapor concentrations for dynamic flux reactor experiment D1.

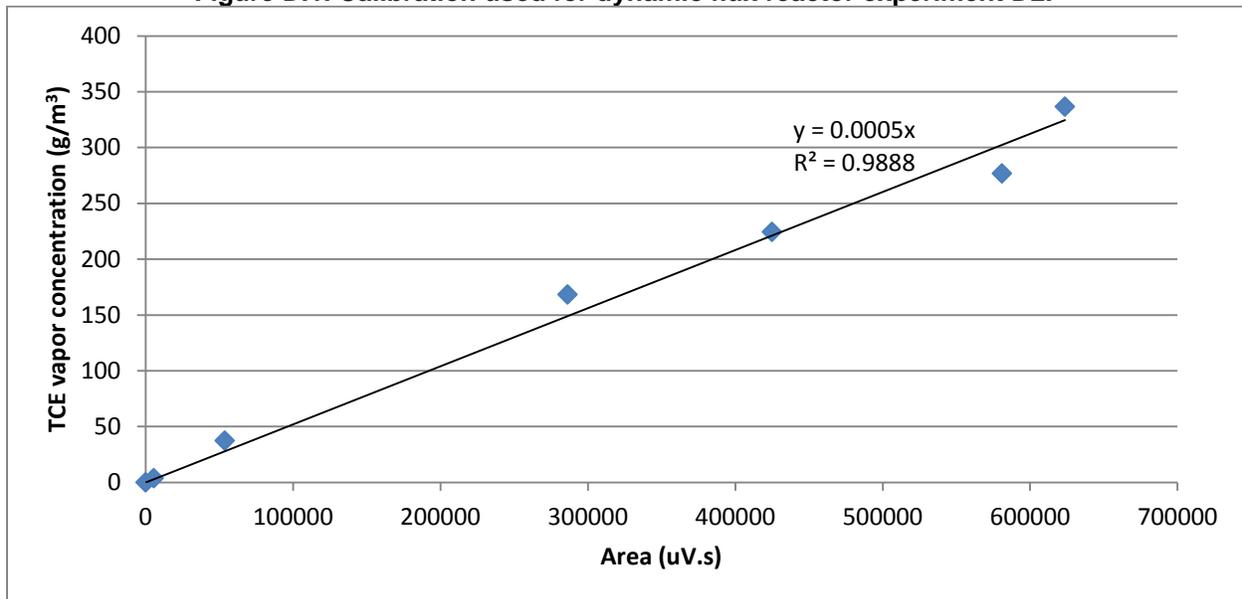
TCE vapor concentrations (Relative to initial concentration: $C/C_0$ )						
Time (hours)	[NaCl] M					
	0		0.60		4.28	
	1	2	1	2	1	2
<b>0</b>	1.00	1.00	1.00	1.00	1.00	1.00
<b>0.33</b>	0.40	0.42	0.23	0.48	0.50	0.32
<b>0.67</b>	0.15	0.36	0.13	0.28	0.22	0.14
<b>1</b>	0.16	0.27	0.06	0.19	0.12	0.07
<b>1.5</b>	0.07	0.21	0.04	0.11	0.06	0.05
<b>2</b>	0.05	0.19	0.03	0.07	0.04	0.05
<b>3</b>	0.06	0.19	0.03	0.04	0.03	0.03
<b>6</b>		0.10	0.02	0.03	0.04	0.03
<b>12</b>	0.01	0.03	0.01	0.03	0.01	0.01
<b>24</b>	0.01	0.02	0.01	0.05	0.01	0.01
<b>48</b>	0.01	0.01	0.01	0.04	0.00	0.00
<b>60</b>	0.01	0.02	0.01	0.02	0.00	0.08
<b>72</b>	0.00	0.02	0.01	0.02	0.00	0.00
<b>84</b>	0.00	0.02	0.00	0.04	0.00	0.00
<b>96</b>	0.00	0.01	0.01	0.02	0.00	0.00
<b>120</b>	0.01	0.01	0.01	0.03	0.00	0.00

Data for D2:

Table D.3. Calibration parameters for dynamic flux reactor experiment D2.

	TCEvc (g/m <sup>3</sup> )	TCE NAPL (uL)	Area (uV.s)
Cal1	0	0.0	0
Cal2	3.74	2.6	5541.2
Cal3	37.4	25.6	53694.75
Cal4	168.3	115.3	286258.67
Cal5	224.4	153.7	424942.03
Cal6	276.76	189.6	580932.15
Cal7	336.6	230.5	623649.14

Figure D.1. Calibration used for dynamic flux reactor experiment D2.



**Table D.4. TCE vapor concentration for dynamic flux reactor experiment D2.**

TCE vapor concentrations (g/m <sup>3</sup> )						
Time (hours)	[NaCl] M					
	0		0.60		4.28	
	1	2	1	2	1	2
<b>0</b>	412.12	114.57	115.92	91.28	100.70	52.01
<b>0.33</b>	98.77	23.73	49.16	49.19	22.00	19.94
<b>0.67</b>	48.51	13.08	24.83	19.81	10.52	8.74
<b>1</b>	18.52	6.49	14.33	15.24	6.48	5.80
<b>1.5</b>	9.15	3.71	14.49	9.69	3.93	3.97
<b>2</b>	5.61	2.53	9.02	8.80	7.78	3.68
<b>3</b>	2.86	2.74	9.78	7.12	8.00	2.96
<b>6</b>	2.20	5.90	4.28	5.87	3.72	1.29
<b>12</b>	2.38	3.45	3.60	2.94	1.46	0.46
<b>24</b>	4.99	0.50	1.70	1.95	0.32	
<b>48</b>	1.40	0.11	0.18	0.17	0.05	0.27
<b>60</b>	1.47	0.00	0.00	0.05	0.00	0.00
<b>72</b>	2.23	0.00	0.00	0.00	0.00	0.15
<b>84</b>	3.00	0.00	0.52	0.43	2.15	0.05
<b>96</b>	1.76	0.09	0.00	0.00	0.00	0.05
<b>120</b>	1.33	0.00	0.00	0.00	0.00	0.00

**Table D.5. Relative TCE vapor concentration for dynamic flux reactor experiment D2.**

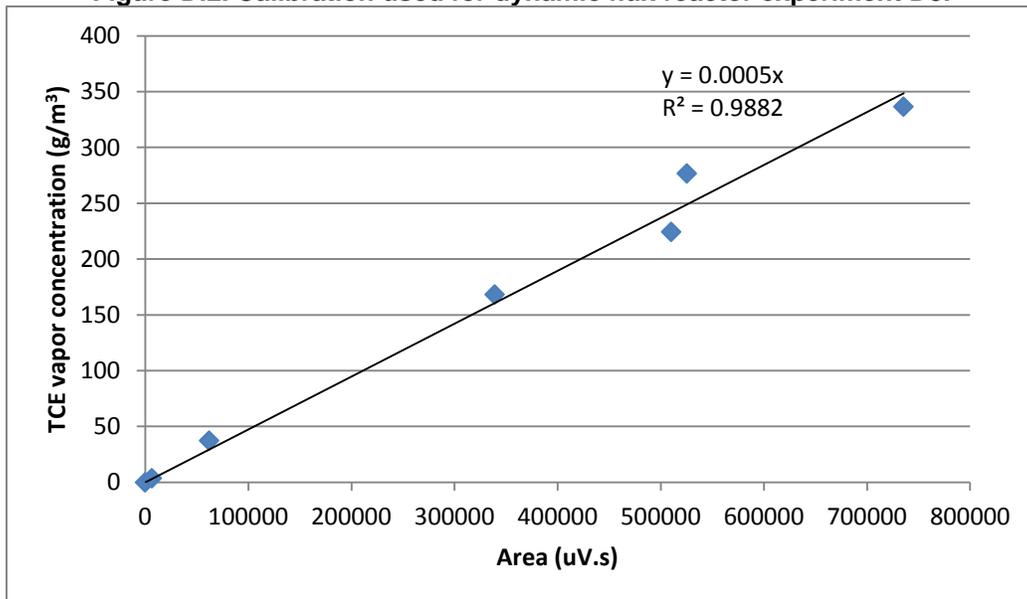
TCE vapor concentrations (Relative to initial concentration: $C/C_0$ )						
Time (hours)	[NaCl] M					
	0		0.60		4.28	
	1	2	1	2	1	2
<b>0</b>	1.00	1.00	1.00	1.00	1.00	1.00
<b>0.33</b>	0.24	0.21	0.42	0.54	0.22	0.38
<b>0.67</b>	0.12	0.11	0.21	0.22	0.10	0.17
<b>1</b>	0.04	0.06	0.12	0.17	0.06	0.11
<b>1.5</b>	0.02	0.03	0.13	0.11	0.04	0.08
<b>2</b>	0.01	0.02	0.08	0.10	0.08	0.07
<b>3</b>	0.01	0.02	0.08	0.08	0.08	0.06
<b>6</b>	0.01	0.05	0.04	0.06	0.04	0.02
<b>12</b>	0.01	0.03	0.03	0.03	0.01	0.01
<b>24</b>	0.01	0.00	0.01	0.02	0.00	
<b>48</b>	0.00	0.00	0.00	0.00	0.00	0.01
<b>60</b>	0.00	0.00	0.00	0.00	0.00	0.00
<b>72</b>	0.01	0.00	0.00	0.00	0.00	0.00
<b>84</b>	0.01	0.00	0.00	0.00	0.02	0.00
<b>96</b>	0.00	0.00	0.00	0.00	0.00	0.00
<b>120</b>	0.00	0.00	0.00	0.00	0.00	0.00

Data for D3:

Table D.6. Calibration parameters for dynamic flux reactor experiment D3.

	TCEvc (g/m <sup>3</sup> )	TCE NAPL (uL)	Area (uV.s)
Cal1	0	0.0	0
Cal2	3.74	2.6	6572.67
Cal3	37.4	25.6	62102
Cal4	168.3	115.3	339075.07
Cal5	224.4	153.7	510230.18
Cal6	276.76	189.6	525406.39
Cal7	336.6	230.5	735523.32

Figure D.2. Calibration used for dynamic flux reactor experiment D3.



**Table D.7. TCE vapor concentration for dynamic flux reactor experiment D3.**

TCE vapor concentrations (g/m <sup>3</sup> )								
Time (hours)	[NaCl] M							
	0		0.60		4.28		0	0.60
	1	2	1	2	1	2	3	3
<b>0</b>	68.62	117.40	103.23	42.86	94.30	47.94	103.62	53.30
<b>0.33</b>	45.91	39.93	30.86	23.89	28.50	35.33	56.91	25.95
<b>0.67</b>	17.22	16.51	11.77	7.78	14.99	15.08	28.13	12.63
<b>1</b>	14.30	7.98	6.61	7.23	11.03	9.51	32.87	12.08
<b>1.5</b>	4.47	10.11	2.50	30.03	8.90	9.94	26.59	9.29
<b>2</b>	4.12	4.39	2.56	6.88	8.45	5.15	19.41	5.05
<b>3</b>	3.00	3.37	4.50	6.03	5.43	8.82	15.92	4.34
<b>6</b>	3.13	7.16	3.28	3.54	2.81	3.44	5.29	0.96
<b>12</b>	1.10	10.25	1.04	3.87	0.91	2.04	5.11	0.38
<b>24</b>	0.64	4.91	1.45	4.53	0.38	0.86	0.82	0.39
<b>48</b>	1.60	4.18	0.37	2.28	0.16	0.37	1.05	0.27
<b>60</b>	0.41	4.71	3.57	2.54	0.17	0.24	5.10	0.58
<b>72</b>	0.40	3.67	0.38	2.77	0.22	0.13	2.21	0.27
<b>84</b>	0.74	3.61	0.43	2.37	0.12	0.14	17.24	0.27
<b>96</b>	0.57	0.74	0.38	1.15	0.17	0.09	3.86	0.25
<b>120</b>	1.40	0.20	0.57	3.29	0.14	0.24	0.50	0.28

**Table D.8. Relative TCE vapor concentration for dynamic flux reactor experiment D3.**

TCE vapor concentrations (Relative to initial concentration: $C/C_0$ )								
Time (hours)	[NaCl] M							
	0		0.60		4.28		0	0.60
	1	2	1	2	1	2	3	3
<b>0</b>	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
<b>0.33</b>	0.67	0.34	0.30	0.56	0.30	0.74	0.55	0.49
<b>0.67</b>	0.25	0.14	0.11	0.18	0.16	0.31	0.27	0.24
<b>1</b>	0.21	0.07	0.06	0.17	0.12	0.20	0.32	0.23
<b>1.5</b>	0.07	0.09	0.02	0.70	0.09	0.21	0.26	0.17
<b>2</b>	0.06	0.04	0.02	0.16	0.09	0.11	0.19	0.09
<b>3</b>	0.04	0.03	0.04	0.14	0.06	0.18	0.15	0.08
<b>6</b>	0.05	0.06	0.03	0.08	0.03	0.07	0.05	0.02
<b>12</b>	0.02	0.09	0.01	0.09	0.01	0.04	0.05	0.01
<b>24</b>	0.01	0.04	0.01	0.11	0.00	0.02	0.01	0.01
<b>48</b>	0.02	0.04	0.00	0.05	0.00	0.01	0.01	0.00
<b>60</b>	0.01	0.04	0.03	0.06	0.00	0.00	0.05	0.01
<b>72</b>	0.01	0.03	0.00	0.06	0.00	0.00	0.02	0.01
<b>84</b>	0.01	0.03	0.00	0.06	0.00	0.00	0.17	0.01
<b>96</b>	0.01	0.01	0.00	0.03	0.00	0.00	0.04	0.00
<b>120</b>	0.02	0.00	0.01	0.08	0.00	0.00	0.00	0.01

Data for D4 and D5:

Table D.9. Calibration parameters for dynamic flux reactor experiments D4 & D5.

	TCEvc (g/m <sup>3</sup> )	TCE NAPL (uL)	Area (uV.s)
Cal1	0	0.0	0
Cal2	3.74	2.6	4927.03
Cal3	37.4	25.6	41947.41
Cal4	168.3	115.3	248492.75
Cal5	224.4	153.7	365959.6
Cal6	276.76	189.6	494706.69
Cal7	336.6	230.5	717147.14

Figure D.3. Calibration used for dynamic flux reactor experiments D4 & D5.

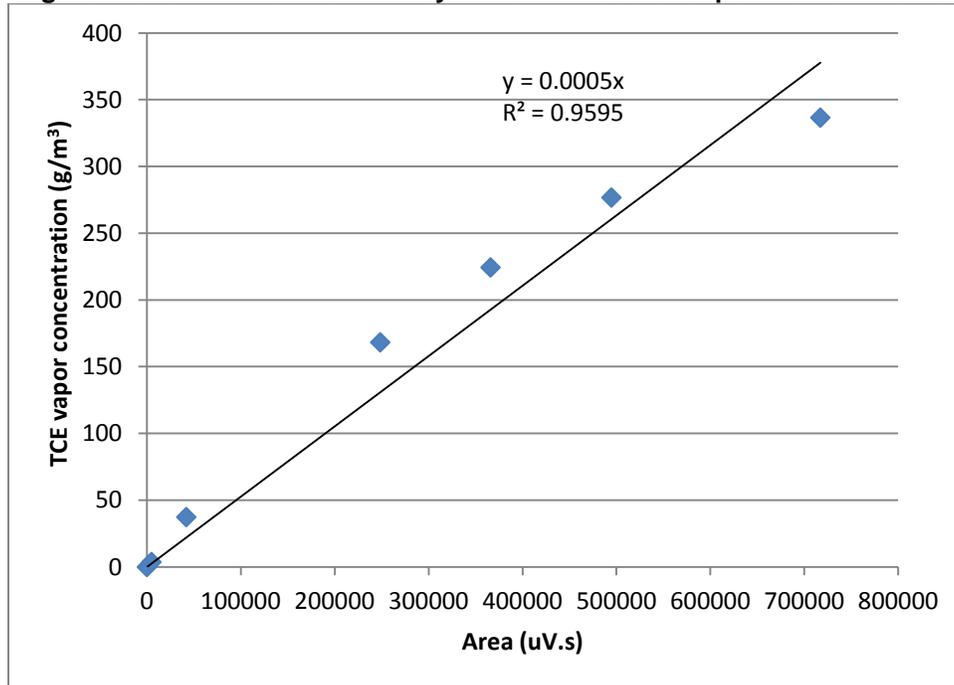


Table D.10. TCE vapor concentration for dynamic flux reactor experiments D4 & D5.

TCE vapor concentrations (g/m <sup>3</sup> )				
Time (hours)	[NaCl] = 0 M			
	D4 (with TCE NAPL)		D5 (without TCE NAPL)	
	1	2	1	2
0	63.96	66.64	39.07	12.62
0.33	38.94	32.39	23.12	5.77
0.67	19.57	19.50	11.47	4.40
1	20.08	16.88	12.92	3.79
1.5	18.84	13.80	6.76	4.98
2	15.30	9.82	5.01	3.24
3	11.45	7.42	5.48	1.25
6	2.42	4.05	3.69	0.52
12	3.11	2.94	1.43	0.15
24	2.96	2.51	0.4903	0.0005
48	3.74	3.06	0.0005	0.0005
60	4.41	2.06	0.0005	0.0005
72	10.29	2.75	0.0005	0.0005
84	4.10	2.35	0.0005	0.0005
96	2.65	2.39	0.0005	0.0005
120	4.04	3.36	0.0005	0.0005

Table D.11. Relative TCE vapor concentration for dynamic flux reactor experiments D4 & D5.

TCE vapor concentrations (Relative to initial concentration: C/C <sub>0</sub> )				
Time (hours)	[NaCl] = 0 M			
	D4 (with TCE NAPL)		D5 (without TCE NAPL)	
	1	2	1	2
0	1.00	1.00	1.00	1.00
0.33	0.61	0.49	0.59	0.46
0.67	0.31	0.29	0.29	0.35
1	0.31	0.25	0.33	0.30
1.5	0.29	0.21	0.17	0.39
2	0.24	0.15	0.13	0.26
3	0.18	0.11	0.14	0.10
6	0.04	0.06	0.09	0.04
12	0.05	0.04	0.04	0.01
24	0.05	0.04	0.01	0.00
48	0.06	0.05	0.00	0.00
60	0.07	0.03	0.00	0.00
72	0.16	0.04	0.00	0.00
84	0.06	0.04	0.00	0.00
96	0.04	0.04	0.00	0.00
120	0.06	0.05	0.00	0.00

Data for D6:

Table D.12. Calibration parameters for dynamic flux reactor experiment D6.

	TCEvc (g/m <sup>3</sup> )	TCE NAPL (uL)	Area (uV.s)
Cal1	0	0.0	0
Cal2	3.74	2.6	5764.19
Cal3	37.4	25.6	58050.72
Cal4	168.3	115.3	313494.65
Cal5	224.4	153.7	473404.12
Cal6	276.76	189.6	642333.82
Cal7	336.6	230.5	894184.36

Figure D.4. Calibration used for dynamic flux reactor experiment D6.

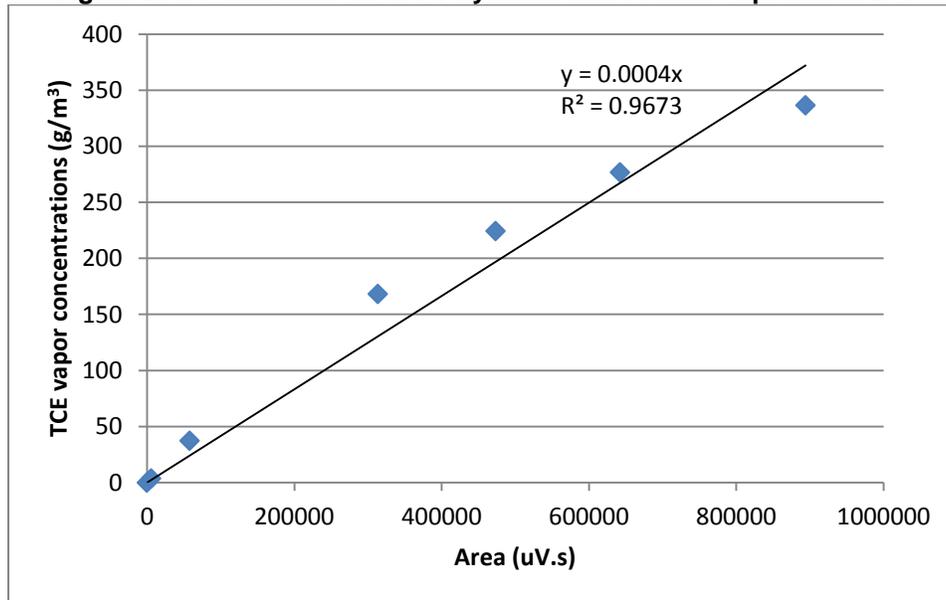


Table D.13. TCE vapor concentration for dynamic flux reactor experiment D6.

TCE vapor concentrations (g/m <sup>3</sup> )		
Time (hours)	[NaCl] = 0 M	
	Saturated clay	
	1	2
0	69.57	78.16
0.33	44.51	26.09
0.67	24.27	14.58
1	16.20	11.02
1.5	9.16	10.24
2	9.56	7.69
3	5.62	6.04
6	1.96	1.34
12	0.85	0.87
24	0.76	0.65
48	1.20	0.80
60	0.56	0.44
72	0.61	0.59
84	0.90	0.66
96	0.60	0.66
120	0.71	0.64

Table D.14. Relative TCE vapor concentration for dynamic flux reactor experiment D6.

TCE vapor concentrations (Relative to initial concentration: C/C <sub>0</sub> )		
Time (hours)	[NaCl] = 0 M	
	Saturated clay	
	1	2
0	1.00	1.00
0.33	0.64	0.33
0.67	0.35	0.19
1	0.23	0.14
1.5	0.13	0.13
2	0.14	0.10
3	0.08	0.08
6	0.03	0.02
12	0.01	0.01
24	0.01	0.01
48	0.02	0.01
60	0.01	0.01
72	0.01	0.01
84	0.01	0.01
96	0.01	0.01
120	0.01	0.01

Data for D7:

Table D.15. Calibration parameters for dynamic flux reactor experiment D7.

	TCEvc (g/m <sup>3</sup> )	TCE NAPL (uL)	Area (uV.s)
Cal1	0	0.0	0
Cal2	3.74	2.6	2247.06
Cal3	37.4	25.6	55199.84
Cal4	168.3	115.3	281359.41
Cal5	224.4	153.7	410209.85
Cal6	276.76	189.6	557251.5
Cal7	336.6	230.5	741980.7

Figure D.5. Calibration used for dynamic flux reactor experiment D7.

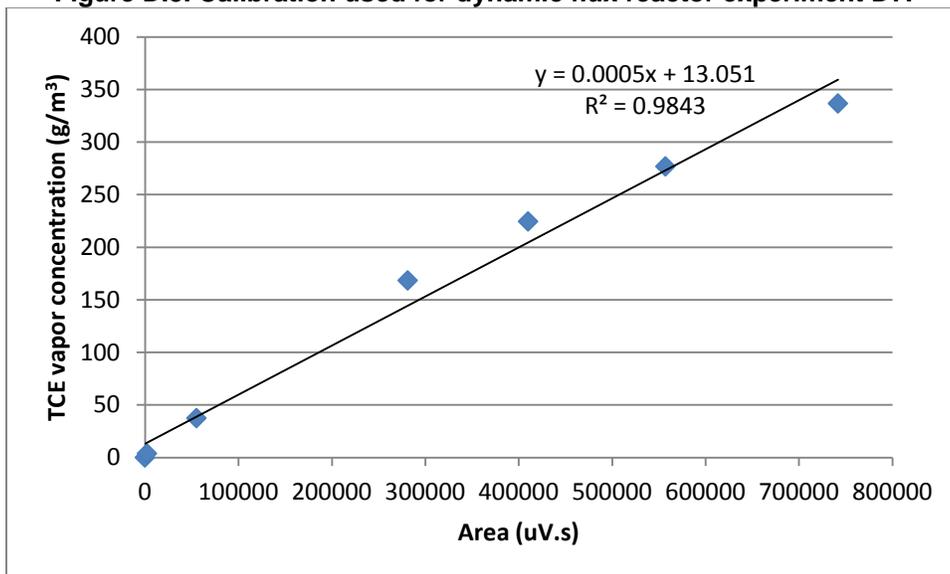


Table D.16. TCE vapor concentration for dynamic flux reactor experiment D7.

TCE vapor concentrations (g/m <sup>3</sup> )		
Time (hours)	[NaCl] = 0.60 M	
	Saturated clay	
	1	2
0	114.39	96.92
0.33	35.36	36.17
0.67	26.85	30.28
1	26.74	28.55
1.5	23.17	22.21
2	18.56	17.81
3	18.65	17.52
6	15.39	17.40
12	14.41	575.40
24	16.36	18.78
48	16.13	15.16
60	18.52	18.53
72	14.68	14.45
84	13.99	15.75
96	13.83	15.10
120	14.79	13.76

Table D.17. Relative TCE vapor concentration for dynamic flux reactor experiment D7.

TCE vapor concentrations (Relative to initial concentration: C/C <sub>0</sub> )		
Time (hours)	[NaCl] = 0.60 M	
	Saturated clay	
	1	2
0	1	1
0.33	0.309102	0.373192
0.67	0.234733	0.312424
1	0.233758	0.29454
1.5	0.202544	0.229181
2	0.162289	0.183748
3	0.16303	0.180747
6	0.134544	0.179568
12	0.125951	5.936572
24	0.14298	0.193722
48	0.140982	0.15636
60	0.161915	0.191178
72	0.128355	0.149091
84	0.122289	0.1625
96	0.120927	0.155779
120	0.129289	0.14195

Data for D8:

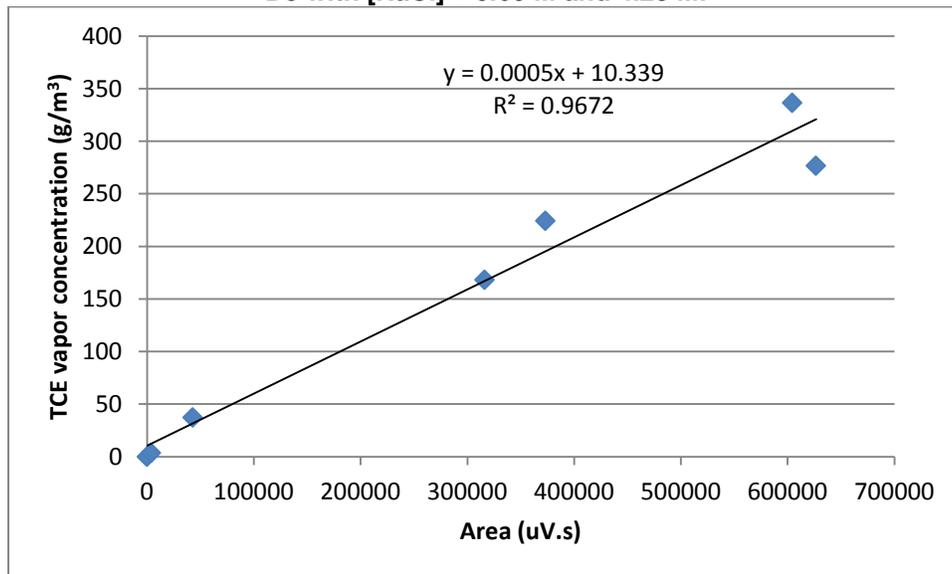
Calibration used for D8 with [NaCl] = 0 M is the same used for D7.

For D8 with [NaCl] = 0.60 M and 4.28 M the calibration used is the following:

**Table D.18. Calibration parameters for dynamic flux reactor experiment D8 with [NaCl] = 0.60 M and 4.28 M.**

	TCEvc (g/m <sup>3</sup> )	TCE NAPL (uL)	Area (uV.s)
Cal1	0	0.0	0
Cal2	3.74	2.6	3779.6
Cal3	37.4	25.6	42861.8
Cal4	168.3	115.3	316284.58
Cal5	224.4	153.7	373208.78
Cal6	276.76	189.6	626654.08
Cal7	336.6	230.5	604455.71

**Figure D.6. Calibration used for dynamic flux reactor experiment D8 with [NaCl] = 0.60 M and 4.28 M.**



**Table D.19. TCE vapor concentration for dynamic flux reactor experiment D8.**

TCE vapor concentrations (g/m <sup>3</sup> )						
Time (hours)	[NaCl] M					
	0		0.60		4.28	
	1	2	1	2	1	2
<b>0</b>	136.03	105.92	58.53	87.32	51.23	76.69
<b>0.33</b>	731.61	644.81	647.40	571.46	326.48	437.16
<b>0.67</b>	585.63	647.16	775.49	612.78	558.61	339.31
<b>1</b>	445.96	656.71	536.04	624.52	538.57	539.41
<b>1.5</b>	510.41	573.75	581.35	592.91	355.92	289.12
<b>2</b>	513.04	644.93	587.65	589.43	485.17	545.84
<b>3</b>	612.70	562.18	558.50	564.60	461.61	534.99
<b>6</b>	457.72	428.72	510.65	469.01	293.09	
<b>12</b>	13.77	14.23	14.76	13.00		10.34
<b>24</b>	13.05	13.05	10.37	10.37	10.37	10.38
<b>48</b>	13.05	13.05	10.34	10.34	10.34	10.34
<b>60</b>	13.05	13.05	10.34	10.34	10.34	10.34
<b>72</b>	13.05	13.05	10.34	10.34	10.34	10.34
<b>84</b>	13.05	13.05	10.34	10.34	10.34	10.34
<b>96</b>	13.05	13.05	10.34	10.34	10.34	10.34
<b>120</b>	13.05	13.05	10.34	10.34	10.34	10.34

**Table D.20. Relative TCE vapor concentration for dynamic flux reactor experiment D8.**

TCE vapor concentrations (Relative to initial concentration: $C/C_0$ )						
Time (hours)	[NaCl] M					
	0		0.60		4.28	
	1	2	1	2	1	2
<b>0</b>	1.00	1.00	1.00	1.00	1.00	1.00
<b>0.33</b>	5.38	6.09	11.06	6.54	6.37	5.70
<b>0.67</b>	4.31	6.11	13.25	7.02	10.90	4.42
<b>1</b>	3.28	6.20	9.16	7.15	10.51	7.03
<b>1.5</b>	3.75	5.42	9.93	6.79	6.95	3.77
<b>2</b>	3.77	6.09	10.04	6.75	9.47	7.12
<b>3</b>	4.50	5.31	9.54	6.47	9.01	6.98
<b>6</b>	3.36	4.05	8.73	5.37	5.72	
<b>12</b>	0.10	0.13	0.25	0.15		0.13
<b>24</b>	0.10	0.12	0.18	0.12	0.20	0.14
<b>48</b>	0.10	0.12	0.18	0.12	0.20	0.13
<b>60</b>	0.10	0.12	0.18	0.12	0.20	0.13
<b>72</b>	0.10	0.12	0.18	0.12	0.20	0.13
<b>84</b>	0.10	0.12	0.18	0.12	0.20	0.13
<b>96</b>	0.10	0.12	0.18	0.12	0.20	0.13
<b>120</b>	0.10	0.12	0.18	0.12	0.20	0.13

Data for D9 & D10:

Table D.21. Calibration parameters for dynamic flux reactor experiments D9 & D10.

	TCE (g/m <sup>3</sup> )	TCE NAPL (uL)	Area (uV.s)
Cal1	0	0.0	0
Cal2	3.74	2.6	2931.71
Cal3	37.4	25.6	42069.12
Cal4	168.3	115.3	282670.22
Cal5	224.4	153.7	430543.17
Cal6	276.76	189.6	444161.43
Cal7	336.6	230.5	511234.54

Figure D.7. Calibration used for dynamic flux reactor experiments D9 & D10.

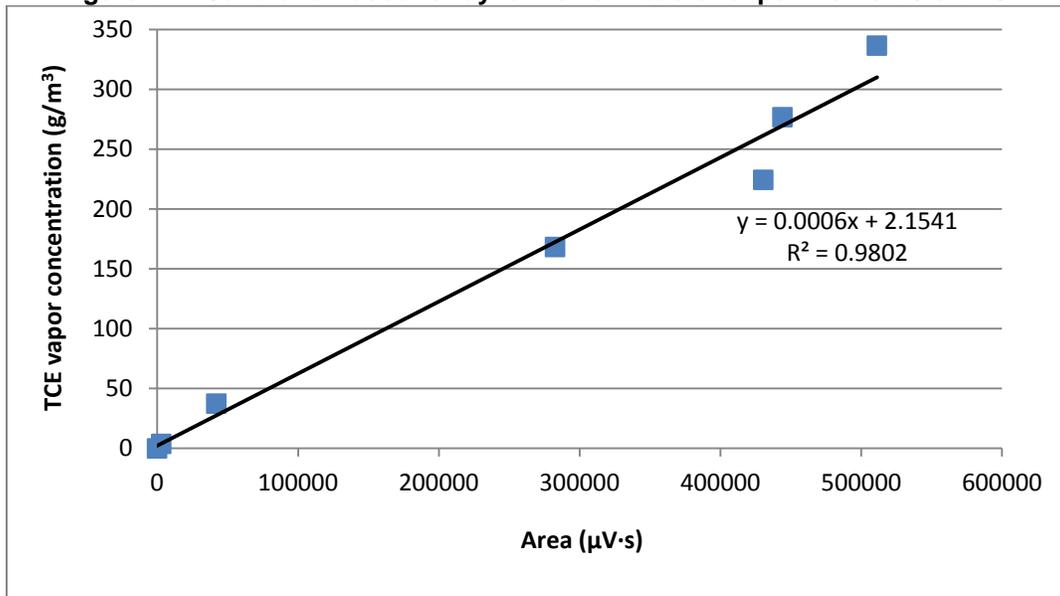


Table D.22. TCE vapor concentration for dynamic flux reactor experiments D9 & D10.

TCE vapor concentrations (g/m <sup>3</sup> )				
Time (hours)	[NaCl] M			
	0 (D9)		0.60 (D10)	
	1	2	1	2
<b>0</b>	215.50	177.02	114.12	205.21
<b>0.33</b>	914.46	357.53	514.94	613.34
<b>0.67</b>	961.75	469.28	617.82	472.74
<b>1</b>	759.01	784.18	494.07	510.65
<b>1.5</b>	577.90	522.15	522.69	416.79
<b>2</b>	802.19	736.11	550.77	410.11
<b>3</b>	769.51	463.15	449.71	354.04
<b>6</b>	448.23	383.15	297.46	3.01
<b>12</b>	3.12	3.88	2.69	5.07
<b>24</b>	2.15	2.15	2.24	2.15
<b>48</b>	2.15	2.15	2.15	2.15
<b>60</b>	2.15	2.15	2.15	2.15
<b>72</b>	2.15	2.15	2.15	2.15
<b>84</b>	2.15	2.15	2.15	2.15
<b>96</b>	2.15	2.15	2.15	2.15
<b>120</b>	2.15	2.15	2.15	2.15

Table D.23. Relative TCE vapor concentration for dynamic flux reactor experiments D9 & D10.

TCE vapor concentrations (Relative to initial concentration: $C/C_0$ )				
Time (hours)	[NaCl] M			
	0 (D9)		0.60 (D10)	
	1	2	1	2
<b>0</b>	1.00	1.00	1.00	1.00
<b>0.33</b>	4.24	2.02	4.51	2.99
<b>0.67</b>	4.46	2.65	5.41	2.30
<b>1</b>	3.52	4.43	4.33	2.49
<b>1.5</b>	2.68	2.95	4.58	2.03
<b>2</b>	3.72	4.16	4.83	2.00
<b>3</b>	3.57	2.62	3.94	1.73
<b>6</b>	2.08	2.16	2.61	0.01
<b>12</b>	0.01	0.02	0.02	0.02
<b>24</b>	0.01	0.01	0.02	0.01
<b>48</b>	0.01	0.01	0.02	0.01
<b>60</b>	0.01	0.01	0.02	0.01
<b>72</b>	0.01	0.01	0.02	0.01
<b>84</b>	0.01	0.01	0.02	0.01
<b>96</b>	0.01	0.01	0.02	0.01
<b>120</b>	0.01	0.01	0.02	0.01