DEVELOPMENT OF TESTBED FOR ASSESSMENT OF ENHANCED SOIL VAPOR EXTRACTION OF TRICHLOROETHYLENE IN UNSATURATED CLAYEY SOIL

by

Pedro X. Lorenzo Barreto

A Project submitted in fulfillment of the requirements for the degree of

MASTER OF ENGINEERING
in
CIVIL ENGINEERING

UNIVERSITY OF PUERTO RICO
MAYAGÜEZ CAMPUS
2014

Approved by:

_____	_____
Ingrid Y. Padilla Cestero, PhD President, Graduate Committee	Date
_____	_____
Eric Harmsen Truckenbrod, PhD Member, Graduate Committee	Date
_____	_____
Raúl E. Zapata López, PhD Member, Graduate Committee	Date
_____	_____
Ismael Pagán Trinidad, MSCE Director, Department of Civil Engineering and Surveying	Date
_____	_____
John Fernández Van Cleve, PhD Graduate Studies Representative	Date

ABSTRACT

Trichloroethylene (TCE) is a volatile organic compound (VOC) commonly found in many contaminated sites. It is a dense non-aqueous phase liquid (DNAPLs) considered harmful to human health. DNAPL pose particular threats because of their heterogeneous distribution and long-term perseverance in underground environments. Current remediation techniques for TCE in clay soil are extremely difficult and expensive. It is, therefore, necessary to develop an enhanced, cost-effective remediation technology that can be applied to those site contaminated clays.

This project involves: development and testing of a testbed; conducting soil vapor extraction (SVE) experiments in the testbed; using cycled injections, and evaluating of experimental data. A laboratory-scale SVE testbed was developed, consisting of a stainless steel column packed with fine clay soil, fourth (4) soil vents, two (2) injection wells, and an extraction system. It is instrumented with transducer pressure sensors, flow meters, and sampling port. To evaluate the enhancement of SVE for the removal of TCE from unsaturated clayey soils by the addition of a capillary-based delivery of alcohol and brine solutions (methanol / $CaCl_2$), SVE pilot study-experiments were conducted.

Results from the SVE experiments were analyzed to determine the performance of the SVE methods to induce airflow and extraction of TCE vapors from TCE-contaminated clay soils. According to the results, the hydraulic behavior and extracted mass show reproducibility and consistency. Capillary-based delivery

has proven to be a viable method to delivery reactant into clay soils of low permeability. Changes in pressure gradients suggest that the use of $CaCl_2$ brine may increase air permeability of the system. The results from all the tests show that SVE can be used to extract TCE contaminants from clay soil; however, the removal is subject to mass transfer limitations, which reduce the efficiency of the extraction. Removal efficiency is between 33% and 53%, indicating that a large amount of initial mass still resides in the system and that total removal would take a long time. Measured temperatures through the soil bed during the extraction process indicate a significant variation in temperature. Lower temperatures under the extraction process are attributed to cooling effect of water in the system and TCE volatilization.

RESUMEN

Tricloroetileno (TCE) es un compuesto orgánico y volátil comúnmente encontrado en muchos lugares contaminados. Este compuesto es clasificado como uno denso y en fase líquido no acuoso (DNAPL, por sus siglas en inglés) considerado dañino para la salud humana. DNAPL es considerado una amenaza particular, ya que su distribución es heterogénea y se preserva a largo plazo en ambientes subterráneos. Las técnicas de remedición para TCE que existen actualmente para lugares con suelos arcillosos, son extremadamente difíciles y costosas. Es por esto que es necesario desarrollar mejores tecnologías de remedición, de tal forma que sean más costo-efectivas y que puedan ser utilizadas en lugares con arcillas contaminadas.

Este proyecto consiste de: desarrollar y probar un banco de prueba; llevar a cabo experimentos utilizando extracción de vapores del suelo (SVE, por sus siglas en ingles) en el banco de prueba; usar ciclos de inyecciones de soluciones, y la evaluación de los datos experimentales. Un banco de prueba de SVE a una escala de laboratorio, fue desarrollado. Este banco consiste de una columna de acero inoxidable empacada con suelo arcilloso fino, cuatro (4) orificios de ventilación del suelo, dos (2) pozos de inyección, y un sistema de extracción. Además, este banco está equipado con sensores transductores de presión, medidores de flujo y puerto de muestreo. Todo esto es para evaluar el desempeño del estudio piloto de SVE propuesto para mejorar la eliminación de TCE en suelos arcillosos en

estado insaturados, por medio de la adición capilar de soluciones de alcohol y sal (metanol / $CaCl_2$).

Los resultados de los experimentos de SVE fueron analizados para determinar el desempeño de cada uno de los métodos establecidos para inducir el flujo de aire y extracción de vapores de TCE en los suelos arcillosos contaminados. Según los resultados, el comportamiento hidráulico y la cantidad de masa extraída muestran que los experimentos se pueden reproducir de una forma consistente. La entrega de solución por medio de tensión capilar ha demostrado ser un método viable para la entrega de reactivos en los suelos arcillosos de baja permeabilidad. Cambios en los gradientes de presión sugieren que el uso de $CaCl_2$ podría mejorar la permeabilidad del aire a través del sistema. Los resultados de todas las pruebas muestran que el SVE podría ser utilizado para extraer contaminantes de TCE en suelos arcillosos, pero la remoción está sujeta a limitaciones de transferencia de masa, la cual reduce la eficiencia de la extracción. La eficiencia de remoción está entre 33% y 53%, lo cual indica que gran cantidad de la masa inicial, se mantiene residente en el sistema, y que extraer la masa total, tomará un largo periodo de tiempo. Medidas de temperaturas a través del suelo en la columna durante el proceso de extracción, indican una variación significativa en la temperatura. Las reducciones en las temperaturas durante el proceso de extracción se atribuyen al efecto enfriamiento del agua en el sistema y la volatilización del TCE.

ACKNOWLEDGEMENTS

First of all, I would like to thank God for all the blessings received and for guiding me every step of the way and the decisions that I made. I want to express a sincere acknowledgement to my advisor Dr. Ingrid Padilla for the opportunity she has given to me to perform research under her guidance and supervision. She provided me constant motivation, encouragement and unconditional support. Also, I am grateful, and recognize her wise guidance during certain points of this research, because she believed in me when I most needed it and pushed me to believe in myself. I want to thank my committee members Dr. Raul Zapata and Dr. Eric Harmsen for their special assistance. I am deeply grateful to my family members and relatives for their emotional support, love, and for always believing in me and inspired me to finish this goal. Also, I would like to express my thanks to all of my friends for their support, constant motivation, housing and real friendship. I would like to thank my friends and partners at the Environmental Engineering Laboratory, for all the support, advice, transmitted knowledge and great experiences. I want to thank: Victor, Angel, Perla, Carlos for their collaboration in my graduate investigation. Also, I want to express my respect, gratitude and special acknowledgment to Amilcar and Maria, who put all their effort to help me finish my experimental procedures and for their technical support. Finally, I want to thank the United States Department of Energy (DoE)-Savannah River (Grant Award No.DE-FG09-07SR22571) who provided the funding and the resources for the development of this research.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

°C	-	degrees Celsius
µm	-	micrograms
$CaCl_2$	-	Calcium chloride
$CaSO_4$	-	Calcium sulfate
cm	-	centimeter
DNAPL	-	Dense Non-Aqueous Phase Liquid
EPA	-	Environmental Protection Agency
ESVE	-	Enhanced SVE
FID	-	Flame Ionization Detector
g	-	Gram
GC	-	Gas Chromatography
HPLC	-	High Performance Liquid Chromatography
L	-	Liter
mg/L	-	milligram(s) per liter
min	-	minute
mL	-	milliliter(s)
MOM	-	Method of Moments
NaCl	-	Sodium chloride
NAPL	-	Non-Aqueous Phase Liquid
S	-	Sensor
SPME	-	Solid Phase Micro Extraction
SS	-	Stainless Steel
SVE	-	Soil Vapor Extraction
TCE	-	Trichloroethylene
TDR	-	Time-Domain Reflectometer
USGS	-	United States Geological Service
VOC	-	Volatile Organic Compound
µV	-	milli volts

1 INTRODUCTION

1.1 Justification

Population growth, industrial and urban development, and the increasing production of energy supply have caused an increase on the release of organic contaminants into the environment (Irizarry, 2013). Contamination of soils and underground by accidental spills, poor storage facilities, and inadequate disposal practices may cause serious detriment to the environment and can pose a serious threat to human health.

Trichloroethylene (TCE) is a volatile organic compound (VOC) commonly found in many contaminated sites (NRC, 2000). It is a dense non-aqueous phase liquid (DNAPLs), and considered harmful to human health (USEPA, 2011). DNAPLs pose a particular threat because of their heterogeneous distribution and long-term persistence in underground environments. They are also very difficult to locate, characterize, and remediate (NRC, 2000).

Deep soil penetration of TCE has been confirmed by a large survey (in the US) conducted by the USGS between 1985 and 2001 that showed frequent detection of TCE in underground zones (USEPA, 2011). Many contaminated sites are underlain by clay layers that have the capacity to retain large quantities of DNAPLs and serve as a long-term source of contamination in both unsaturated and saturated zones at a site (NRC, 2000). As the DNAPL moves downward through porous media, it eventually encounters a low-permeability layer, such as compressed clays, where it may pool and/or move laterally (NRC, 2000). Their heterogeneous distribution and perseverance in the

environment poses particular threats and challenges in the detection, characterization, and remediation of DNAPL contamination (NRC, 2000).

Traditional remedial approaches for chlorinated solvents such as TCE include: pump and treat, bioremediation, soil vapor extraction (SVE), thermal technologies, in-situ chemical oxidation, and surfactant and co-solvent flushing (USACOE, 2002 and Kueper et al., 2003). Recent remediation technologies, such as surfactant or alcohol flushing, and in-situ thermal treatment, suggest significant mass removal and reductions in DNAPL (SERDP & ESTCP, 2004). Most of these technologies, however, have been designed for sand and high permeability media. Technologies that are applicable for low permeability zones (e.g., heating) are very expensive. It is, therefore, necessary to develop new technologies that will enhance our ability to remediate low permeability zones. SVE is one of the most effective and cost-efficient methods of removing volatile organic compounds (VOCs) from unsaturated soils (USACOE, 2002). Previous laboratory research has demonstrated enhanced remediation of TCE-contaminated sites through combined treatment technologies using surfactants and gravity-induced mobilization (increasing buoyancy forces), dense brine containment and collection, and vapor phase extraction in saturated heterogeneous soils (Wright, et al., 2010). Previous research has also shown that brine solutions have been used to induce volatilization, enhance detection and increase the efficiency of the extraction process of VOCs (Cassada, et al., 2000). This enhancement is based on the salting-out ability of the salts, which is a process that utilizes the reduced solubility of certain molecules in a solution of very high ionic strength. This

typically causes precipitation when the salt concentration vary. This salt effect may be used for removing organic components from contaminated sites (Salabat, 2007).

It has been hypothesized that cycled alcohol and brine in combination with SVE could enhance the remediation of unsaturated clayey soils (Irizarry, 2013). Using capillary-based delivery, a porous membrane is used to deliver the brine and alcohol solutions in unsaturated soil. The solutions are expected to move into smaller pores because of the stronger capillary forces in unsaturated media. Alcohols, such as methanol, may act as a co-solvent, and increase the NAPL-air interfacial area, thus inducing higher volatilization rates (Weber et al., 2002). The application of a brine solution is expected to change the structuring around soil particles, increase relative permeability, and enhance TCE volatilization through salting-out processes. Combining these technologies with vapor extraction, the TCE removal can be enhanced in areas with low permeability.

Preliminary work by Irizarry (2013) to assess the effect of NaCl salt and alcohol, particularly methanol, on TCE volatilization indicates that NaCl enhances TCE volatilization from water and saturated clays at NaCl concentrations of 0.6 M, but not at higher concentrations. Although the addition of NaCl to unsaturated clay does not show enhanced volatilization in batch reactors, it increases air permeability on unsaturated clays subjected to flow of NaCl solution (Irizarry, 2013). Because of potential dispersive effect of NaCl on clay, it was recommended that $CaCl_2$ be used instead of NaCl (Irizarry, 2013). The use of $CaCl_2$ has been shown to also enhance air permeability in clay soils. Indeed, clay soils treated with $CaCl_2$ solution (0.6 M) show higher air permeability than

those treated with NaCl at 0.6 M (Irizarry, 2013). The addition of methanol (10%) enhances volatilization from unsaturated clays, but for water and saturated clays, methanol only enhances TCE volatilization when it is combined with NaCl (Irizarry, 2013).

Current remediation techniques for TCE in low permeability sites are extremely difficult and expensive (Kosegi et al., 2000). It is, therefore, necessary to develop enhanced, cost-effective remediation technologies that can be applied to DNAPL-contaminated sites. In this research, a testbed was developed to evaluate the enhancement of SVE for the removal of TCE from unsaturated clayey soils by the addition of a cycled injection of alcohol and brine solutions. Frequent sampling and analysis provide the necessary information to evaluate the effectiveness of the combined treatment.

1.2 Objectives

The overall goal of the proposed research centers on developing an enhanced soil vapor extraction (ESVE) technology to remediate unsaturated clays contaminated with chlorinated solvents. In particular, this project assesses the effect of cycling alcohol and brine solution injection on the removal of TCE in unsaturated clay by SVE. Because of its ubiquitousness and potential for health impacts, the proposed project focuses on TCE.

It is hypothesized that TCE vapor extraction from clayey formations can be enhanced by cycled alcohol / salt (methanol / calcium chloride) injections. The use of small alcohol molecules allows enhanced penetration of reactant into the small-size pores (range size in µm) characteristics of clay formations. The alcohol can also enhance water drainage,

increase NAPL-air interfacial area, and increase vapor flow (Weber et al., 2002). It is expected that the addition of brine solution may cause water structuring around soil particles, increase relative air permeability, and enhance TCE volatilization through salting-out processes.

It is also hypothesized that delivery of reactant solutions to unsaturated clays can be accomplished through capillary-based injections. Enhanced delivery of reactants shall improve contaminant mass removal in low permeability regions.

These hypotheses are tested through experimental methods designed to attain specific objectives. These specific objectives are:

- Develop a testbed to assess the performance of enhance SVE in unsaturated clay media.
- Conduct SVE experiments in the testbed to determine the amount of TCE mass removed from a clay soil when subjected to cycled alcohol / salt capillary injections.

2 LITERATURE REVIEW

Extensive subsurface contamination with DNAPLs poses a major threat to public health and the environment (Schaerlaekens et al., 2006). According to the Records of Decision for sites on the National Priorities List, there is suspected DNAPLs contamination in approximately 22% of the List (EMS, 2004). Sites contaminated with DNAPLs pose special cleanup challenges because this type of contaminants can penetrate to great depths in the subsurface, releasing dissolved contaminants to the underground zones for very long time periods, and can be difficult to locate (ITRC, 2003). Commonly DNAPL contaminant releases are associated with industrial operations using chlorinated solvents, industry-specific materials (e.g. wood preservatives, coal tar) and industrial processes involving metal cleaning/machining (e.g. paint removal, underground storage of solvents, mixed chemical waste disposal in landfills) (EMS, 2004).

A large group of DNAPL contaminants are classified as chlorinated solvents or organic chemicals that contain chlorine (OEH-NSW, 2011). Chlorinated solvents, such as TCE, account for 10 of the top 20 organic contaminants detected most frequently at hazardous waste sites in the United States (OEH-NSW, 2011). They are found at approximately 80% of all Superfund sites with contamination and frequently detected in other types of contaminated sites around the country (SERDP & ESTCP, 2004). Similarly, more than 3,000 U.S. Department of Defense (DoD) sites have identified this type of contaminant (SERDP & ESTCP, 2004).

TCE is a chlorinated DNAPL contaminant (Moran et. al, 2007) commonly found in the environment. The physico-chemical and toxicological properties (see Table 1) of the TCE pose a serious health threat to humans and ecological receptors (Tsai et al., 2008). TCE is volatile and slightly soluble on water. Therefore, it exists in the vapor phase, dissolved on water, and as a separate fluid phase immiscible in both water and air (USEPA, 2011). The physical and chemical properties of TCE render high resilience and widespread contamination of subsurface environments. When it is released on sufficient quantities, TCE DNAPLs tend to move vertically downward until it is distributed as residual saturation on the form of globules or ganglia (ITRC, 2002). If a strata of finer grains are encountered as the TCE DNAPL move downward, it will spread laterally and may form pools.

Table 1 TCE Physico-chemical and toxicological properties

Property	Value	Reference
Specific gravity (Water = 1)	1.4649	(ScienceLab.com, 2010)
Vapor pressure	58 mm of Hg @ 20°C	
Solubility	Easily soluble in methanol, diethyl ether, acetone. Very slightly soluble in cold water.	
Aqueous solubility	1,100 mg/L	(USEPA, 2011)
Vapor density (Air = 1)	4.53	
Viscosity	0.571 mPa·s @ 20 °C	
Henry's law constant	9.85×10^{-3} atm-cu m/mol @ 25°C	
Density	1.4642 g/cm^3 at 20°C	

In unsaturated media, TCE DNAPL globules, ganglia, and pools are exposed to air. Because of its relatively high vapor pressure, TCE volatilizes into the soil air and form a volatile plume (Pantazidou and Sitar, 1993; and USEPA, 2011). The DNAPL globule, ganglia, and vapor can also dissolve into infiltrating water. When vertically moving, TCE DNAPLs encounter the water table (i.e. the saturated zone), they accumulate until there is enough gravity force to overcome capillary and hydrostatic forces to displace water

(Bedient et al., 1997). Because of the higher density than water, TCE DNAPL is able to penetrate deep below the water table, where they slowly dissolve to form plumes that can spread beyond the source of contaminant (Ellis and Rivett, 2007). Low TCE aqueous solubility and degradation rates (Pankow and Cherry, 1996), and slow water velocities in the subsurface results in very low removal rates of the residual TCE. Consequently, the residual TCE acts as a long-term source of contamination, and give rise to widespread contamination of groundwater (Sneddon et al., 2002).

Many sites contaminated with chlorinated solvents, such as TCE, throughout the world are underlined by low permeability zones (Jin and Fallgren, 2010). The fate and transport of DNAPLs in these zones is very complex, and the removal is very difficult and costly (Jin and Fallgren, 2010). Removal of this type of contaminant from these zones is difficult due to preferential flow, inducing channeling and low reaction areas, and mass transfer limitations. In-situ remediation of clays soils contaminated with DNAPLs, is a major challenge to remediation techniques at the present (Jin and Fallgren, 2010). The reason for this problem is that low media permeability reduces the effectiveness of most in situ treatments at the present state of knowledge.

2.1 Remediation Technology for DNAPL Contaminated Sites

Several remediation technologies have been developed for DNAPLs contaminated sites. These include: pump and treat, soil vapor extraction (SVE), air sparging, co-solvent/alcohol flooding, surfactants, in situ oxidation, electrical heating, electrokinetics, in-well stripping, biodegradation, reactive barriers and containment (Fountain, 1998).

Pump-and-treat has shown to be an ineffective and costly remediation technology for DNAPL source zones (Siegrist et al., 2010). A common and efficient alternative of treating unsaturated soils impacted by volatile organic chemicals (VOCs) is through the use of soil vapor extraction (SVE). SVE is an accepted, recognized, and cost-effective technology for remediating soils contaminated with volatile and semi volatile organic compounds (USACOE, 2002). VOCs with high vapor pressures (e.g., benzene, TCE), are expected to volatilize to a significant degree when released in the subsurface and will respond favorably to SVE technology (Suthersan, 1999).

SVE (see Figure 1) involves inducing air flow in the subsurface that causes external pressure gradients at the well (i.e. vacuum pressure), and thus enhancing the volatilization or contaminant vapor movement and consequent removal (Nobre and Nobre, 2004; ITRC, 2004). The SVE process takes advantage of the volatility of the contaminants to allow mass transfer from adsorbed, dissolved, and free phases in the soil to the vapor phase, where it is removed under vacuum and treated above ground (Suthersan, 1999; Albergaria et al., 2008). Consequently, SVE results in the removal of VOC vapor, NAPL, and aqueous phase contamination (AFCEE, 2001). It may also be used in association with bioremediation technology. SVE has a relative low cost, is relatively simple to install, requires minimal amount of equipment for system operation, and remediation is done in situ (Nobre and Nobre, 2004).

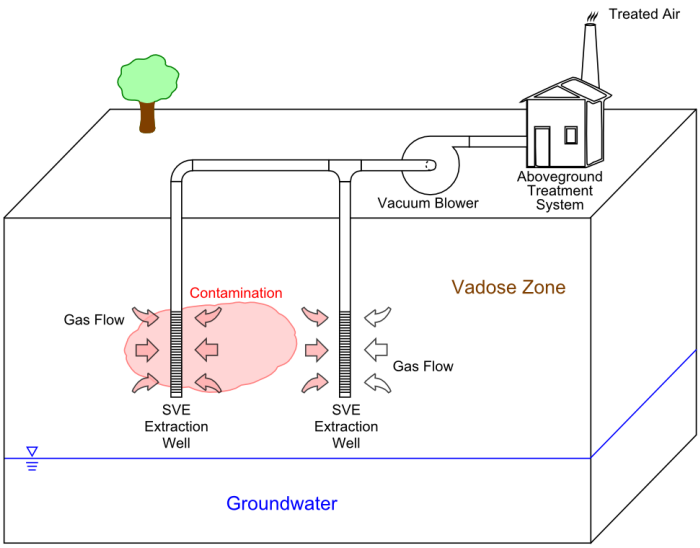


Figure 1 Soil Vapor Extraction system (Source: Gwremed, 2013)

An important limitation of the air flushing process is that once SVE removes a large portion of the VOC present in the soil gas, there is a significant decline in removal rate resulting from decreasing VOC concentrations in the soil gas phase (Sleep and McClure, 2001). The decreasing concentration in the gas phase is attributable to rate-limited dissolution, desorption, and diffusion across the water phase. Other potential limitations include: contaminant properties (e.g., volatility, solubility), soil characteristics and heterogeneities (e.g., air permeability, stratigraphy, porosity, organic matter, water content), and operational conditions, such as temperature and air flow rate (Albergaria et al., 2008).

Recently, other technologies (e.g. thermal treatment methods, surfactant enhanced recovery techniques, chemical degradation) have demonstrated their potential to accelerate underground zones cleanup and risk reduction in a cost-effective remediation (Siegrist et al., 2010). Surfactant/co-solvent fluids have been used for enhancement

removal of DNAPLs. When in contact with DNAPLs, these fluids lower the interfacial tension between DNAPLs and the aqueous phase, enhancing DNAPL solubility, or altering other physical properties. The primary appeal of surfactant/co-solvent flushing is its potential to quickly remove a large fraction of the total DNAPL mass as compared to other technologies (ITRC, 2003).

The most common co-solvents are alcohols (e.g. ethanol, methanol, isopropanol). They are similar to surfactants because they alter the properties of solution interfaces and are often combined with surfactants to improve flood performance (ITRC, 2000). The miscibility of the alcohols can be effective in lowering the interfacial tension between water and the DNAPLs contaminant and increasing its aqueous solubility (ITRC, 2004). Co-solvent flushing are used in DNAPL-contaminated zones to remove injected chemicals and mobilized DNAPL (ITRC, 2000). Alcohols have been used as co-solvents to enhance water drainage, and increase NAPL-air interfacial area or mobilization (e.g. reduced capillary forces), and volatilization rates (Christ et al., 2005). Also, several alcohols have been used to enhance solubilization. The heterogeneous characteristics of contaminated sites and DNAPL distribution are some of the greatest impediments to subsurface remediation using current flushing technologies. This is because numerous pore volumes of flushing solution are needed to ensure that at least one pore volume of flushing solution moves through the lower permeability regions. Consequently, the system must be designed to have a better sweep efficiency (ITRC, 2004).

Heterogeneous distribution of soil having zones of higher and lower permeabilities induce particular limitations to SVE because air flow occurs in the higher permeability regions, and the lower air permeability regions have limited treatment effectiveness (Switzer et al., 2004). Air by pass of low permeability areas leads to mass transfer limitations of the remediation (Høier et al., 2006).

The presence of low permeability zones in the subsurface increases SVE remediation time because of contaminant mass transfer limitations (USACOE, 2002). Also high moisture levels in the soil restrict the air flow through the soil pores, reduce its permeability and consequently the SVE may become less effective (Khan et al., 2004). Taking in consideration all of these restrictions; an emergent vapor extraction technique called pneumatic soil vapor extraction is proposed to enhance VOCs removal from low permeable areas in heterogeneous settings or areas subject to that diffusion limitation (Høier et al., 2006). Pneumatic SVE is based on enforcing a sequence of large pressure drop on the system to enhance the recovery from the low-permeable areas (Høier et al., 2006). These experiments demonstrate that depending on the air flow velocity and the composition of the contaminant (in this case TCE), the removal of contaminants from the low-permeable zone could be restricted by the flow velocity in the adjacent high-permeable zone (advective flow zone), diffusion within the low-permeable area, or controlled by liquid resistance in a phase mixture. They suggest that pulse pumping as a method to increase the efficiency of the venting. The purpose of this method is to pump and flush the TCE contaminated area until the mass transfer limitations constrain the recovery. Then, the pumping stops for some time to allow the mass transfer to take place

followed by the restarting of the pump to continue the cycle. The experiments results showed that using the traditional SVE, the removal of TCE from the low permeable lens is extremely slow and subject to diffusion limitations. Application of pneumatic venting enhanced removal rates by up to 77%. In general, the experiment confirms that recovery of the contamination is enhanced during the first tests, but at late stages of the first pneumatic period the removal rates decreased indicating that the pneumatic SVE cannot entirely overcome the problems of mass transfer limitations.

Research has shown that a combination of various remediation technologies could enhance reaction of combination in heterogeneous sites (Johnson et al., 2004). For instance, the use of combined surfactants, dense brines, and SVE have been applied to induce DNAPL mobilization, contain and collect the DNAPL, and remove the residual DNAPL remaining after mobilization (Johnson et al., 2004). During the surfactant flush, a percent of the injected TCE preferentially migrates downward through the coarser sands after interfacial tension was reduced. Dense brine is used to contain, and prevent further migration, and enhance removal of the DNAPL in collection barriers. Residual contaminants are thereafter recovered during the well and vapor-phase extraction phase. The combination of various technologies enhances removal depending on the level of heterogeneity of the system. The use of a brine barrier and surfactant-gravity mobilization in conjunction with SVE was shown to reduce over 90% of the contaminants with a zone of heterogeneous unsaturated sandy soils (Johnson et al., 2004). In low-permeability soils such as clay soils, the removal of VOCs through SVE suffers serious limitations as other commonly used remedial technologies. Taking into consideration these limitations (e.g.

contaminant channeling through preferential flow zones, rate limited mass transfer, low flow rates) and the advantages of each existing technology, a possible solution to this problem can be developed. Probably, combined remedial technology is the best way to achieve these goals.

Many of the commonly used remediation technologies have been developed for medium to high permeability soils, and are not efficient for low permeability soil formations. Thermal enhanced recovery (steam injection, electrical heating) offer promising alternatives for efficient remediation of TCE-contaminated clayey formations (e.g. enhanced rate of vapor transport from low permeability zones to regions of higher permeability, increased overall mass removal of contaminant), but are very expensive (e.g. increases the unit cost per mass removal). With continuously rising energy cost, they may not be feasible (AFCEE, 2001).

3 MATERIALS AND METHODOLOGY

This project aims at developing a testbed and methodology for enhanced soil vapor extraction (SVE) techniques for removal of TCE from clay formations. It relies on cycled injection of alcohol and brine solutions. The project involves: developing and testing the testbed; conducting SVE experiments in the testbed; using cycled injections, and evaluating of experimental data. This chapter describes the specific materials and methods used in the project.

3.1 Materials

Enhanced SVE (ESVE) is conducted in a soil column testbed packed with a clayey soil known as Coto Clay soil (USDA, 2012) from the northern part of Puerto Rico. ESVE experimental work involves extraction of vapor phase from a TCE-contaminated soil in the SVE testbed. For ESVE experiment, vapor is extracted after cycled injections of methanol and $CaCl_2$ brine solutions. Solutions are injected through a capillary-based delivery method using porous membranes. The materials used in this work, thus involve the Coto clay soil, and TCE, methanol, and $CaCl_2$ reagents. These are described in this section. Description of the testbed is given in section 3.2.

3.1.1 Soil Properties

The Coto Clay soil (see Figure 2) is used in this work. The soil is collected from the Isabela Experimental Station in Isabela, Puerto Rico (see Figure 3). Coto Clay soil is mainly composed of kaolinite and quartz mineralogy, and is classified as a very deep,

well drained, moderately permeable soil formed from weathered limestone (Rodriguez et al., 2007).

The physical and hydraulic properties of the Coto clay soil are shown in Table 2 and Table 3. Table 3 shows the physical and hydraulic properties of the clay in the field. The data shows that bulk densities in the field range from 1.29 g/cm^3 to 1.36 g/cm^3, and that hydraulic conductivity are relatively higher near the surface, but decrease with depth (Rodriguez et al., 2007).

Figure 2 Coto clay in the field (Source: Rodriguez et al., 2007)

Figure 3 Coto clay raw material extraction place; Isabela, Puerto Rico

Table 2 Physical characteristics of the Isabela Clay Soil (Rodriguez et al., 2007)

Soil	Isabela Clay
USCS Classification	CL
Liquid Limit %	46.6
Plastic limit %	25.4
Plastic Index %	21.2
Specific Gravity	2.62
Specific Surface Area m^2/g	44.4
Mineralogy	Quartz/kaolinite

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

Table 3 Physical and hydraulic properties of Coto clay in the field. (Rodriguez et al., 2007)

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Bulk Density ($g\ cm^{-3}$)	Porosity	Hydraulic conductivity ($cm\ hr^{-1}$)
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

3.1.2 Soil Preparation

The Coto clay soil collected from the field site shows large numbers of soil conglomerates (see Figure 4). To remove the bigger soil particles, the soil is manually sieved through # 18 (1 mm or 0.0394 in) mesh. These bigger particles are crushed, and re-sieved. All particles passing the mesh are used for soil packing.

Figure 4 Extracted Coto clay soil conglomerates

3.1.3 Soil Particle Size Distribution

Knowledge of the granular material gradation is essential for understanding the performance of the true material in remediation settings. Particle size distribution is conducted on the soil particles passing through the #18 (1 mm or 0.0394 in) mesh, which is the soil component used in the testbed. After passing through the #18 mesh, the soil is further sieved through #20 (0.841 mm or 0.0331 in) and #60 (0.250 mm or 0.0098 in) meshes. To accelerate the soils gradation test a mechanical sieve shaker is used in periods of (3) three minutes for each analysis. To obtain a uniform soil distribution sample, the particles that are retained in the first sieve (#18) and had passed the last (#60) are discarded (Vargas, 2011).

3.1.4 Reagents and Solutions

Experiments use TCE, Methanol, $CaSO_4$ and $CaCl_2$ reagents. Their specific use, preparation, and applied concentration are described below.

- TCE (Sigma Aldrich, ACS certified reagent 99.5+% pure) is used to contaminate the clay soil.
- Methanol (Fisher Scientific, HPLC Grade 0.2 micron filtered) is diluted at 10 % with distilled water. Methanol is used for the cycled injections to enhance TCE mass transfer into the vapor phase from clayey soil because it is small in size, not toxic, and have low viscosity (Irizarry, 2013).
- $CaCl_2$ (Fisher Scientific USA, Acros Organics: Anhydrous Powder 96% pure) is used to alternate salt injections with SVE and alcohol injections. A $CaCl_2$ concentration of 0.6 M (66.59 g/L) is used to enhance air permeability and induce

TCE volatilization during SVE. At this concentration, $CaCl_2$ is classified as a brine solution (Drever, 1988). Previous work (Irizarry, 2013) has shown that NaCl only enhances air permeability and volatilization slightly, and has recommended the use of $CaCl_2$.

- $CaSO_4$ (Sigma Aldrich, -325 mesh, 99%) at a concentration of 0.005 M (0.6807 g/L) is used as a background and control solution for the $CaCl_2$ cycled injection. This is the same salt and concentrations used in standard methods to measure hydraulic conductivity (Klute, 1986) and water characteristics curve (Klute, 1986) in soils.
- The $CaCl_2$ + $CaSO_4$ solution is prepared by adding 133.176 g of $CaCl_2$ and 1.3614 g of $CaSO_4$ to 2,000 mL distilled water (see Figure 5).

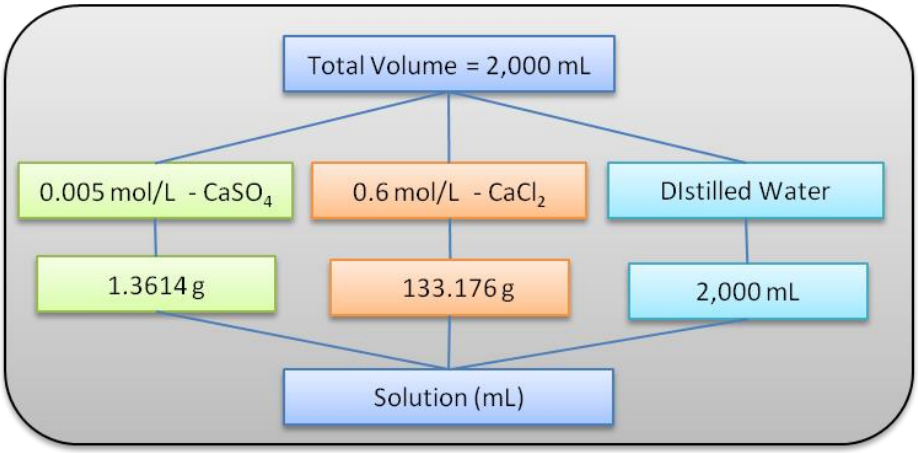


Figure 5 Diagram showing masses and water volume used for the preparation of $CaSO_4$ + $CaCl_2$ solution

- The brine solution and alcohol mixture is prepared by adding 1.3614 g of $CaSO_4$ and 133.176 g $CaCl_2$ to 1,800 mL of water and 200 mL of methanol (see Figure 6) to obtain the 10% diluted in distilled water. Each solution is placed in a bag and then, injected into the column through the injection wells. The injection process is explained in the Experimental Method (section 3.3).

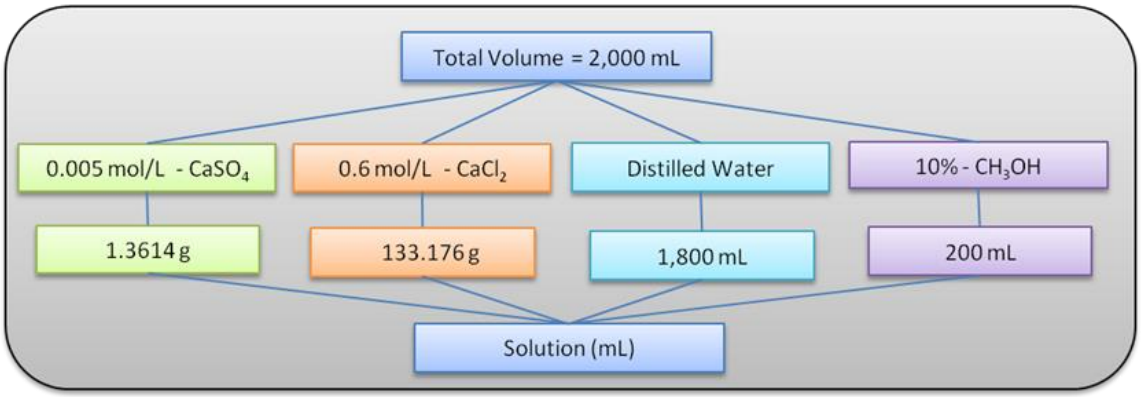
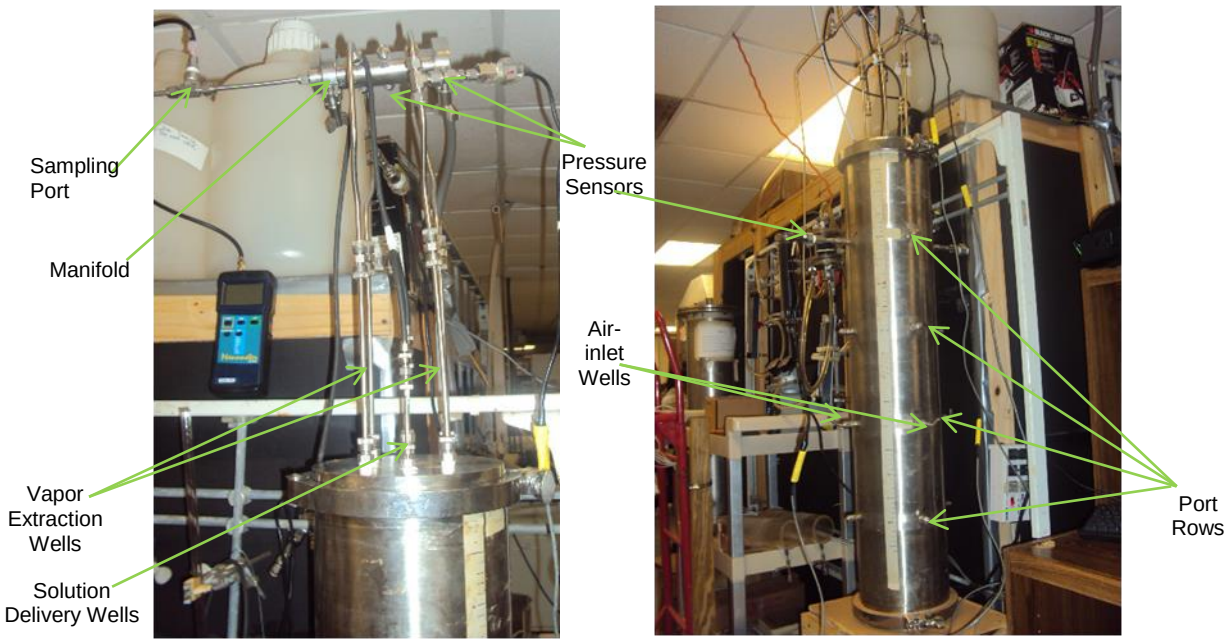


Figure 6 Diagram showing masses, and water and methanol volumes used for the preparation of the salt and methanol solution

3.2 Soil Testbed

Enhanced TCE vapor extraction from unsaturated clayey soils of low permeability is tested using cycled injections of alcohol/brine solutions. Experiments are conducted in a laboratory-scale testbed system consisting of a soil column (Figure 7a and 7b), a vapor extraction system, and a solution-delivery system. The column is packed with uncontaminated and TCE-contaminated soils, and integrates four vapor extraction wells, two solution delivery, and two air-inlet wells, pressure sensors, a Time-Domain Reflectometer (TDR), and a TCE vapor sampling port. The dimensions of the instruments are summarized in Table 4.



(a) **(b)**

Figure 7 Top of the soil column and manifold (a) and stainless steel column with sensors (b)

Table 4 Soil column and instruments dimensions

Item	Quantity	Length of Each Item (cm)	Diameter of Each Item (cm)	Occupied Area (cm^2)	Occupied Volume (cm^3)
Column	1	100	19	283.5	28,352.9
Extraction Wells	4	20	1	12.6	1,005.3
Injection Wells	2	35	0.5	0.8	55.0
Air-inlets (Venting wells)	2	52	1	3.1	326.7
Pressure Sensors (3- 5)	3	9	0.5	0.8	47.7

3.2.1 Soil Column

The soil column compartment consists of a uniform cylindrical stainless steel column (custom-made by Swagelok®), 100 cm height and 19 cm in diameter (see Figure 8). The column has sixteen (16) ports along fourth (4) vertical rows. Each port row is located 20 cm apart; with four (4) ports equally distributed around the row circumference. The column is packed with dry clay from the bottom to 50 cm above the bottom of column, followed by a 5 cm layer of TCE-contaminated soil, 40 cm of dry soil, and 5 cm of Bentonite. The

bottom cap of the column contains a 0.3175 cm perforation (see Figure 9) to install the TDR. A detail description of the packing and packing characteristics is given in section 3.2.1.1.

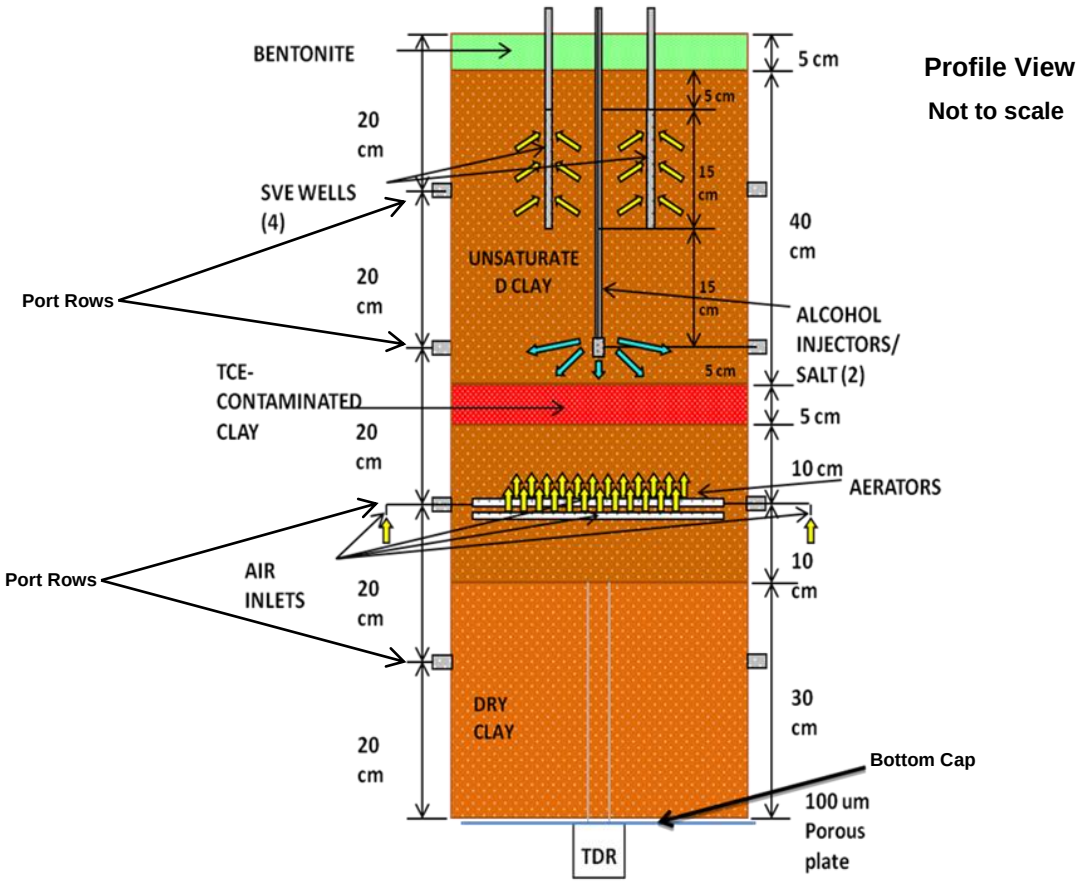


Figure 8 Test bed configuration (Source: Irizarry, 2013)

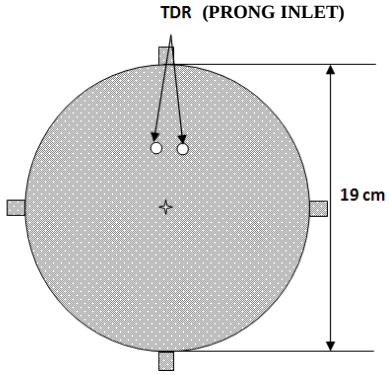


Figure 9 Lower cap of column. (Source: Irizarry, 2013)

3.2.1.1 Column Packing Method and Characteristics

The packing method does not follow particular standard methods because of the unique characteristics of the ESVE testbed; including the installation of SVE wells, sensors, and air-inlets. Soil packing is conducted using a piston (5.08 cm x 10.16 cm) weight attached to a 1.065 cm wooden stick (see Figure 10). The piston base is covered with an acrylic disc (0.635 cm thick) for a smoother surface. The total weight of the piston is 3.18 Kg and it has five (5) perforations in its base. The perforations allow packing the soil with the SVE wells in place. Packing is conducted by adding 5 cm of soil over the column area and dropping the piston tool onto the soil surface. This packing method produces reproducible packing configuration for the tests that performed in this research. A packing density goal of 1.28 g/cm^3 is set to represent field conditions.

Figure 10 Wooden piston used for soil packing

The soil packing is divided in seven (7) principal layers through the Testbed (see Table 5 and Figure 11). Those layers take in consideration all the instruments and sensor

mounted inside the column. The first step is to fill and pack the column 30 cm from bottom of the column. Using the piston, the soil is compacted with 29 blows in each 5.0 cm of soil. The air-inlets are then placed at 40 cm from the bottom and more soil is added. All the air-inlets joints, fitting and air vents are verified to be free of leak and obstacles. The air-inlets zone is filled with 15 cm of soil to prevent damage during the packing with the piston. The next soil layer (2nd layer) is filled and packed 5 cm from the top of the 1st layer up to the TCE-contaminated zone. The third layer consists of 5 cm of TCE-contaminated soil. The soil TCE mixture characteristics and packing condition for this zone are described in Section 3.2.1.2. The 4th layer is filled and packed 5 cm from the top of the TCE contaminated soil to the bottom of the solution injection wells. The injection wells are installed and more soil is added, and compacted up to the bottom of the extraction wells. This 5th layer has a thickness of 15 cm of soil. The last soil layer contains the extraction wells and has a thickness of 20 cm. To prevent leaks and a short circuit in the testbed a 5 cm Bentonite layer is placed on top of the last soil layer. Following this packing method, the general bulk density (without contaminated soil) is obtained (1.24 g/cm^3), which is slightly below the reported bulk density at the field.

Table 5 Soil layers characteristics

Layer	Height (cm)	Volume (cm^3)
Bentonite seal zone	5	1,417.6
Six (up to the bottom of the Bentonite seal zone)	20	5,670.6
Fifth (up to the bottom of the SVE wells)	15	4,252.9
Fourth (up to the bottom of the delivery wells)	5	1,417.6
Third (TCE contaminated zone)	5	1,417.6
Second (from the top of the air-inlets to the bottom of TCE contaminated zone)	5	1,417.6
First (from the column bottom to the top of the air-inlets)	45	12,758.8

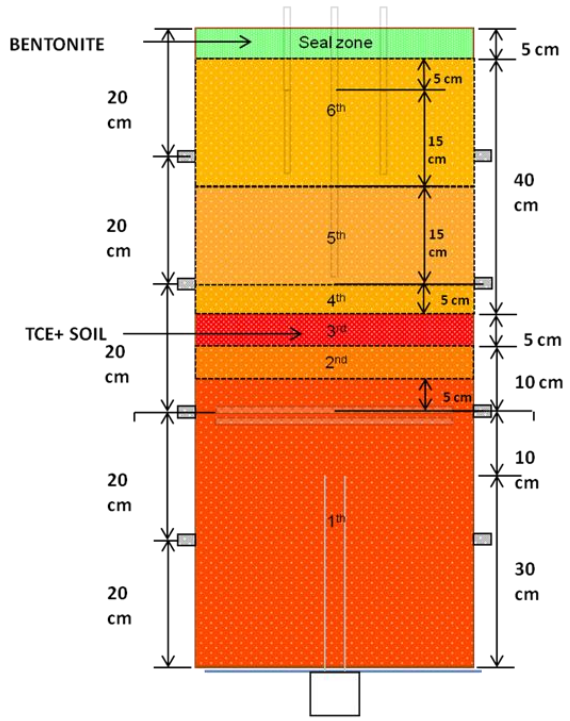


Figure 11 Soil layers configuration and Bentonite

3.2.1.2 TCE Contaminated Soil Layer

The TCE contaminated soil layer located between 55 and 60 cm from the bottom of the column is prepared. Is prepared by mixing 422.8 mL of TCE (617.3 g TCE) with a 2,268 g of soil. This yields a 40 % TCE saturated (22 % TCE content by volume, 27 % TCE by mass) for an average bulk density of 1.18 g/cm^3 (Vargas, 2011). The mixing is done in a 10 L glass bottle. Once mixed, the mixture is packed immediately to prevent losses by volatilization.

3.2.2 Air-inlet Wells

The air-inlet wells consist of two aerators ring tubes placed 40 cm above the bottom of the column and connected to air-inlets opened to the atmosphere (see Figure 12). They are used to enhance air entry through the soil during SVE. Each aerator ring

consists of two Teflon tubes (1.27 cm OD x 0.95 cm ID x 0.16 cm wall) sections, perforated with 0.079375 cm holes, 0.635 cm apart. The tube sections are connected through two stainless steel Swagelok® tees (0.635 cm tube size) and form an elliptical shape (see Figure 12 and Figure 13). The tees connect to stainless steel tubing (0.635 cm), which is used to connect to the air-inlet tube outside the column. A Swagelok Ultra-Torr connector (0.068 cm) is used to connect the tee-connected tube (see Figure 14) and avoid preferential air flow through the column walls. Results from the pneumatic tests show that the aerators respond according to the design specifications.

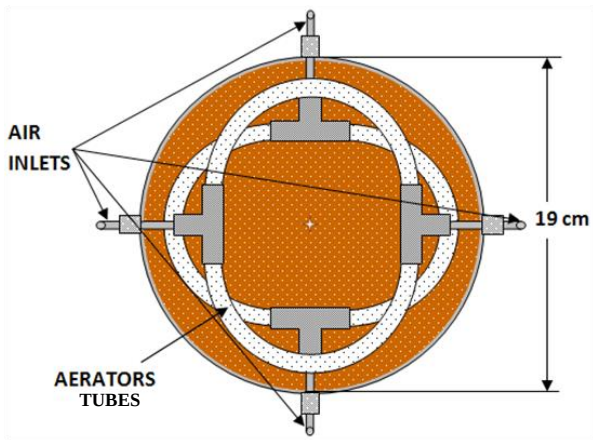


Figure 12 Cross-section at 40 cm from bottom where aerators are located

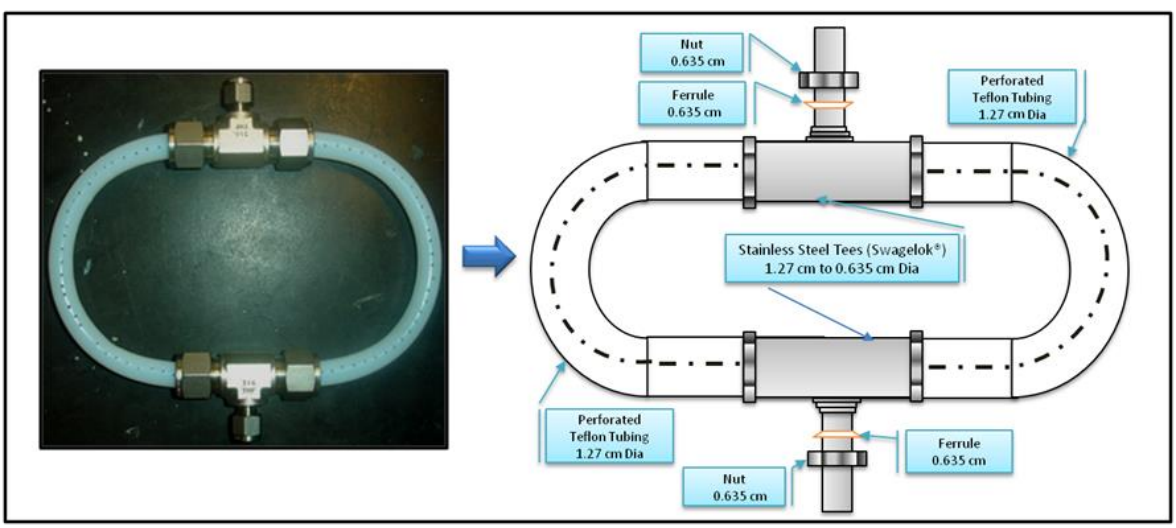


Figure 13 Aerator connections configuration

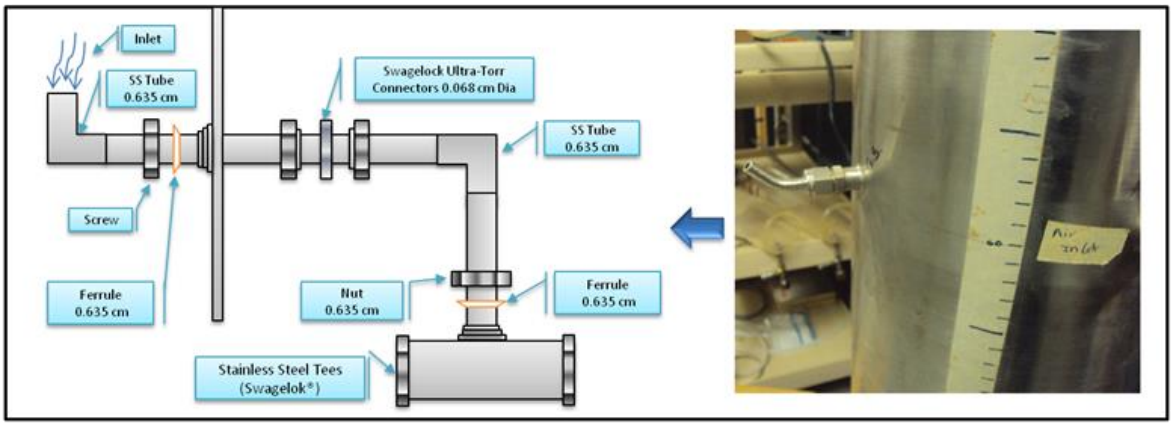


Figure 14 Aerator /air-inlet cross-section

3.2.3 Solution Delivery Wells

The delivery of the brine/alcohol solutions is conducted using two (2) capillary-based delivery wells. The delivery section in these wells is located 60 cm above the bottom of the column, 5 cm above the contaminated soil, and 15 cm below the SVE wells (see Figure 8). The capillary-based, solution delivery wells consist of a 40 µm stainless steel porous membranes (1.27 cm diameter, 2.54 cm long) (see Figure 15), having larger average pores than the clay so that the solution moves by capillary forces from the membrane into the clay.

Figure 15 Stainless steel porous membrane

3.2.4 Vapor Extraction Wells

TCE contaminated vapor is removed using four (4) vapor extraction wells located 75 cm above the bottom of the column and 20 cm above the contaminated zone (see Figure 8).The SVE wells consist of stainless steel tubing (0.635 cm) perforated with 0.237

cm diameter holes and lined with 400 µm stainless steel mesh (Type 304 Mesh #400 X 400, 0.00254 cm wire diameter, 30.48 cm width; Small Parts, Inc.) (see Figure 16). The tubes are perforated up to 6.05 cm from the bottom of the tube. SVE wells are connected to a manifold using stainless steel tubes and joints.

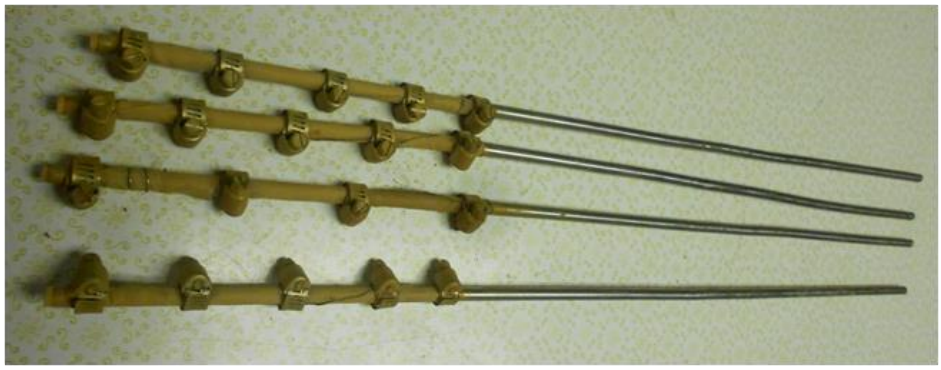


Figure 16 SVE vapor extraction wells

3.2.5 Test Instrumentation

The testbed is instrumented with pressure sensors, air flow meter and a TDR. The details of the instruments are given below.

3.2.5.1 Pressure Sensors

Pressure sensors are used to monitor pressure distribution in the system. The system integrates five (5) pressure sensors: three (3) sensors are connected inside the column to measure the differential pressure within the soil bed; and the others two (2) are connected to the SVE manifold to measure the pressure at the exit of the extraction wells. Figure 17 illustrates the specific location of the pressure sensors in the testbed. This configuration shows the pressure sensors distribution inside the soil bed and in the manifold. The sensors are identified with a letter (S) and a number. The sensors located inside the soil bed are S2, S5 and S6. Sensor S2 is placed in the port of 60 cm from the

bottom. Sensors S5 and S6 are placed in two (2) ports at 80 cm from the bottom of the soil bed. The other two sensors (S3 and S4) are located in the manifold at the top of the column. This configuration allows the measurement of the pressures in five (5) different places, when the pump applies vacuum to the system. Pressure-head tests are conducted to characterize the hydraulic/pneumatic behavior of the testbed (section 3.3.2.1), which rely on pressure measurement from these sensors.

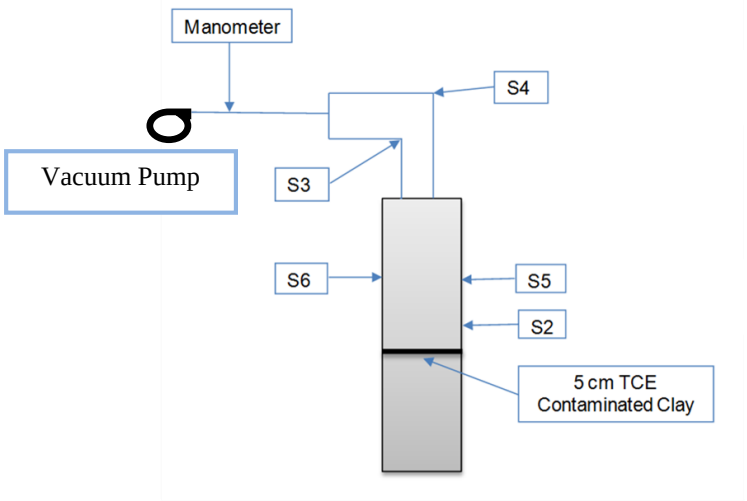


Figure 17 Sensor configuration (S # refers to the sensors number)

The pressure sensors connected to measuring points within the column consist of a pressure transducer (Model 236PC, Micro Switch) and a 100 µm stainless steel porous membrane (see Figure 18) to allow the air pass through. The sensors are connected with wires to a Campbell Scientific® CR23X Micrologger. This data logger is connected to a personal computer that has the LoggerNet 3.1.2 software (Cambell Scientific) and configuration to measure pressures. Each sensor provides a millivoltage measurement for each location. Using simple calibration curve, this measurement is changed to millibar using linear regression. Calibration curves for the pressure transducer sensors are show in Appendix A.

Figure 18 Pressure sensor with their components

3.2.5.2 Air Flow Meter

Air flow variations going through the system when the vacuum is applied are monitored using a flow meter with a control valve (see Figure 19). This flow meter is manufactured by ManoStat (Model - 36-541-305), and has a scale reading at center of float. It has two (2) balls with different material; one is in stainless steel and the other is in glass. The flow meter has the capability to measure air or liquid flow, depending on the fluid used. In this project the only fluid measured is air. The scale reading varies from a minimum level of 10 mm (1.086375 L/min) to the maximum of 150 mm (24.71175 L/min). The calibration data provided by the manufacturer (see Appendix B) is used to calculate the air flow rates during each experiment. The flow meter entrance is connected to the manifold and the exit is connected to the vacuum pump. The control valve of the flow meter is maintained open all the time in this project to obtain the maximum air flow applied by the vacuum pump. The air flow values measured during the experiments are used to calculate the average mass extracted in each sampling, explained later in section 3.4.

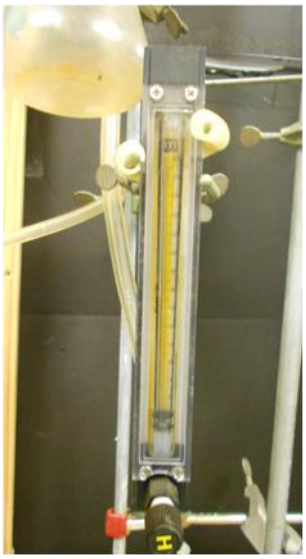


Figure 19 ManoStat (Model: 36-541-305) air flow meter

3.2.5.3 Time-Domain Reflectometer (TDR)

A Time-Domain Reflectometer (TDR) (CS616-L15 Water Content Reflectometer from Campbell Scientific, Inc.) is inserted through the bottom cap of the column. It is used to monitor the water content in the bottom clay layer of the testbed during the SVE experiments. This layer must be maintained dry to exert high water tension during the experiments. The value obtained from this instrument was constantly the same as the initial setup of the column.

3.2.5.4 Temperature Thermocouples

During each test, temperature is measured in the soil bed. Using a TEGAM Thermocouple (Model 821 Microprocessor Thermometer), the temperature is monitored through time in the area is between the bottom of the solution delivery membrane (65 cm from column bottom) and the center of the TCE contaminated layer (55 cm from column bottom), this temperature is identify as a T1 and T2, respectively. This area is selected

because it is where most of the volatilization occurs, which may induce changes in temperature. The extraction of VOCs in gas stream using SVE can cause condensation due to lowering of the temperature at constant pressure, increasing the pressure at constant temperature, or combination of both (Suthersan, 1999).

The calibration for this instrument was done using various equipments available in the laboratory (e.g. thermometer, oven, etc.). Results from this calibration are show in Appendix C.

3.2.6 Vapor Sampling Port

The vapor sampling port is located between the manifold outlet and the vacuum pump to allow sampling for TCE and alcohol (methanol) vapors. It consists of a stainless steel tee (0.653 cm) of which one of the sides (the one perpendicular to flow) is fitted with a 0.635 Thermo Green Septa (Alltech). TCE vapor samples are taken by introducing a Solid Phase Micro Extraction (SPME) fiber through the septa (details of sampling are given on section 3.3.2.3).

3.2.7 Vapor Integrated Extraction System

The extraction compartment integrates the four (4) extraction wells connected to a manifold, sampling port, pressure sensors, a flow meter, and a vacuum pump (see Figure 20).

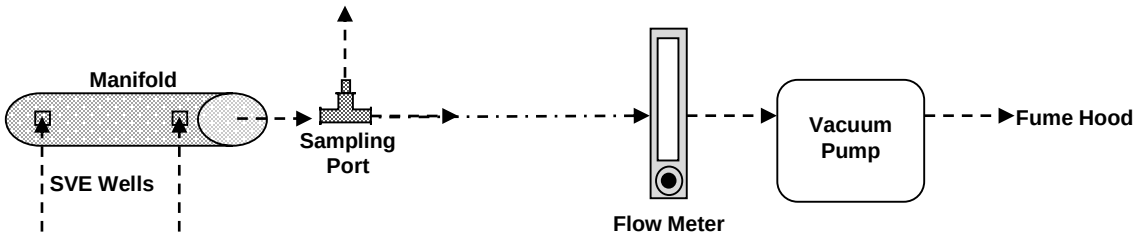


Figure 20 Testbed SVE system setup (Source: Irizarry, 2013)

3.2.8 Solution Delivery System

The solution delivery system integrates the solution delivery wells to a reactant solution sources. It consists of a volumetric burette, which feeds to another burette that is hydraulically connected to the porous membranes used for solution delivery by capillary injection during the injection of methanol solution. A Tedlar bag is used for solution delivery by capillary injection during injection of methanol solution. The development and testing of the solution delivery system is described in section 3.3.1.1.

3.3 Experimental Method

Experimental methods are applied to: (1) develop a capillary-based delivery method; (2) assess the testbed pneumatic performance; (3) develop and test the SVE technologies using cycled alcohol/ salt brine injections; and (4) determine optimal SVE parameters to maximize TCE removal from clay soils. Capillary-based delivery methods are developed in an acrylic column (0.91 m high and 7.62 cm ID) pack with the Coto clay soil (76.2 cm), and applied to the SVE testbed. All other experimental methods are conducted in the SVE testbed.

3.3.1 Capillary-based Delivery

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 (Pc) depends on the surface tension of the solution-air interface (θ), the contact angle (ϕ), and the effective radius (r) where the interface is located as given by the Young–Laplace equation (Jury and Horton 2004):

$$P_C = \frac{\theta \cos \emptyset}{r} \tag{1}$$

For similar θ and ϕ, P_c is higher for solutions located in the smaller radius pores resulting in the movement of the liquid toward these pores. For clay and other silicate minerals, ϕ is often assumed to be zero (0) (Shang et al., 2008).

3.3.1.1 Delivery Application Method

Results from previously capillary-based delivery 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 because the solution travels farther down, is more evenly distributed, and it does not take as much time (Delgado and Padilla, 2011, in Appendix D). For this project, similar approach was used and involves placing the alcohol or/and brine solution source at the same elevation as the delivery membrane to induce flow by capillary forces. The amount of solution delivered into the column is monitored over time by measuring the

change in solution level at the delivery burette or the bag. To obtain this condition the injection equipments need a specific configuration. A 40-μm 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 is selected because it does not react with organic contaminants. The 40-μm pore-size of the membrane maximizes delivery to low-permeability areas.

To deliver the solution under capillary conditions, a tygon tubing is connected to a stainless steel tube (0.32 cm) and then connected to the porous membrane (see Figure 15) to deliver the solution from the solution reservoir. The delivery tension tube and porous membrane are saturated and connected to the solution prior to placement in the soil. This delivery application method is the same for all of the tests, but the source container is different, and depends on which reagent is being delivered, brine solution only or brine solution mixed with alcohol. During the tests, 950mL of the solution is delivered to the clay media. Once this amount is injected, the tests are stopped and the time it takes to deliver the solution is recorded.

The delivery system for the brine solution consists of a 50 mL burette, a 265 mL laboratory-made graduated column, a stainless steel rod, 0.0635 cm hoses, and the injections wells (see Figure 21 and Figure 22). All of these are in series to maintain a constant-head solution level in the laboratory-made graduated column. The brine solution is delivered through the solution delivery system (section 3.2.8) by setting the level in the laboratory-made graduated column at the elevation as where the stainless steel porous

membrane (wells) is located inside the soil bed (see Figure 21 and Figure 22). The stainless steel rod is used as a reference line in both places (same elevation).

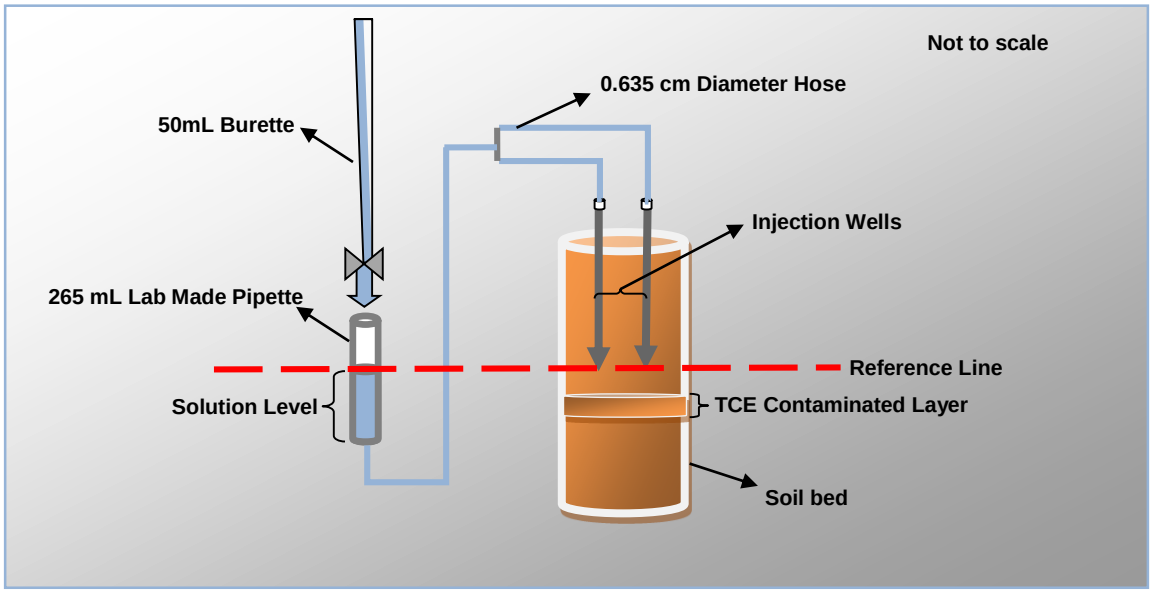


Figure 21 Capillary-based delivery configuration for brine solution

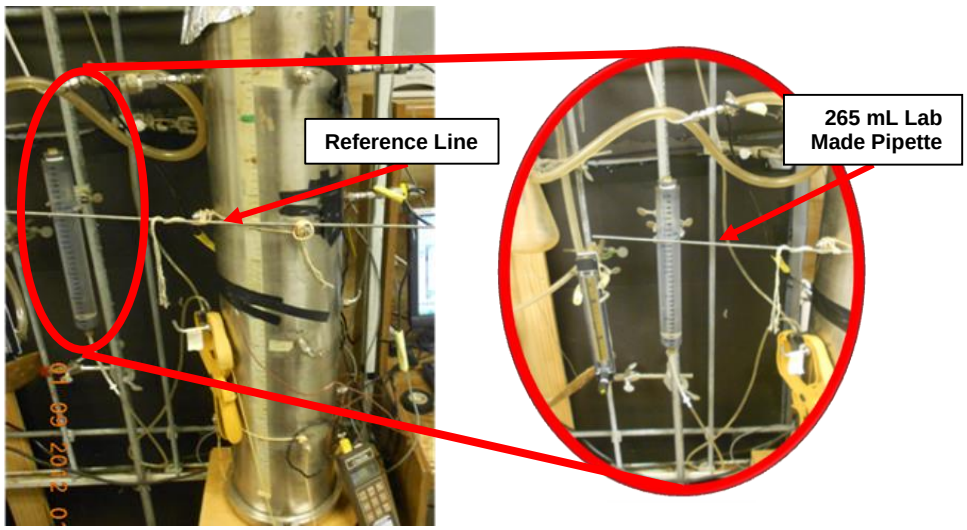


Figure 22 Example view of the capillary-based delivery configuration for brine solution

The alcohol/brine solution delivery method is partially the same as the brine solution only, but the source configuration is different. To prevent significant losses of alcohol concentration by volatilization (do to air headspace increases) during the delivery, a 2L

Tedlar® Gas Sample Bag 22.86 cm x 22.86 cm (Grace Discovery Sciences) is used to store and deliver the mixed solution. This bag collapses during the injection process, and eliminate any head space (see Figure 23). This bag is attached to the 0.635 cm diameter hose connected in series with the injection wells and is maintained at the same level of the reference line to maintain a capillary-based delivery configuration. Figure 24 shows an example view of the configuration for alcohol and brine solution delivery.

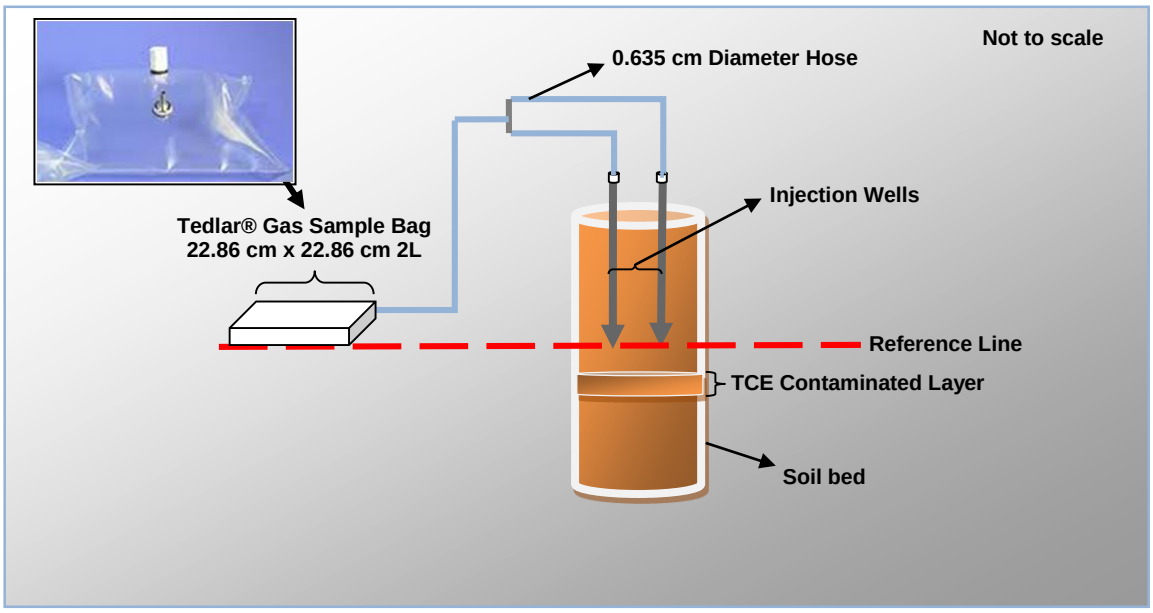


Figure 23 Capillary-based delivery configuration for alcohol + brine solution

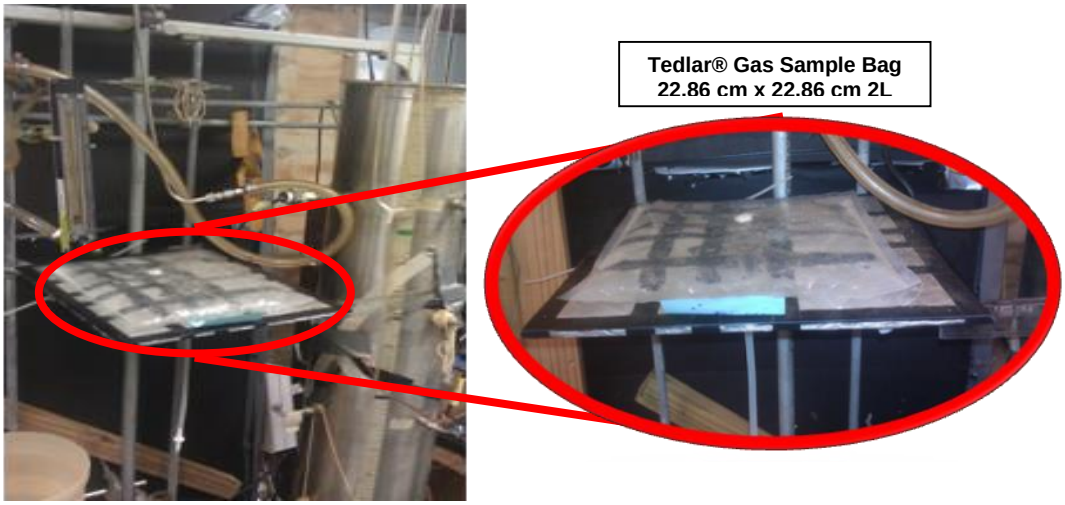


Figure 24 Example view of the capillary-based delivery configuration for alcohol + brine solution

Originally, the capillary-based delivery method was developed in an acrylic column (0.91 m high and 7.62 cm ID) pack with the Coto clay soil. This original test showed the injected solution flow path, distribution through the each layer of soil, and how much volume of solution is needed to reach the bottom of the contaminated layer. Based on the results obtained during the injections using this acrylic column (see Appendix E), the injection methodology was developed and applied to the SVE testbed. The results show that approximated 950 mL of solution are enough to reach the bottom of the TCE-contaminated layer. All reagent solution injections are conducted in the SVE testbed. Solution delivery rates are monitored one time by measuring changes in water levels during a period of time from the solution reservoir.

3.3.2 Soil Vapor Extraction

SVE experiments are conducted to evaluate the extraction performance of the system under several conditions. Generally, SVE experiments involve applying a given vacuum to the system to conduce air flow and extraction of TCE vapors through the SVE wells.

Initial pneumatic testing is conducted to evaluate the integrity if the system (i.e., system leaks, air flow short-circuits to atmospheric, and monitor pressure drops across the soilbed. TCE vapor extraction experiments are thereafter conducted to assess the efficiency of the system to extract TCE contamination from clay soils subjected to the delivery of different salt and alcohol solutions.

3.3.2.1 Pneumatic Performance

The pneumatic performance of the testbed is evaluated by applying vacuum and inducing air flow through the vapor extraction wells, while monitoring pressures through the system. Several extraction flows are evaluated by setting different extraction vacuum set point at the pump. Pressures are monitored at the pump manometer, and several locations throughout the system using a digital manometer and the pressure sensors connected to the data logger (see Figure 17 for the location of sensors). System's flow is measured using a flow meter located after the SVE well manifold. Pneumatic and air flow testing is conducted under two conditions: maximum and two thirds (2/3) of the maximum vacuum of the pump. These conditions provide a measure of the magnitude of pressure drops with the different vacuum applied. The measurements are performed during various days to assess if any change occurs during the pneumatic test. All pneumatic tests show that the pressure drops follows the expected pneumatic behavior for this type of configuration (see Appendix F). This behavior shows that those sensors are closer to the pump have a more negative pressure and those that are more distant from the vacuum source and closer to the air-inlet are less negative (see Figure 17).

3.3.2.2 TCE Vapor Extract from Soil

The efficiency of TCE vapor extraction from TCE contaminated clay soil subjected to different conditions is evaluated through a series of SVE experiments (see Figure 25). The SVE experiments involve preparing the system for the desired testing condition followed by vacuum extraction. During the extraction phase, vacuum is applied through the SVE wells to induce air flow through the contaminated soil into the extraction wells.

Air enters the soil column from the atmosphere through the air-inlet wells located below the TCE contaminated zone, move through the soli column above, and exit the system through the SVE wells. TCE vapor concentrations are monitored at the exit point of the SVE testbed (see Figure 7).

A series of SVE experiments are conducted under: dry soil at different vacuum (experiments M-E1, M-E2, H-E3, H-E4 and H-E5 is indicated in Figure 25); and capillary-based delivery of $CaSO_4$ background solution (experiment I-E6, in Figure 25), $CaSO_4$+$CaCl_2$ brine solution (experiment I-E7-9, in Figure 25), and brine + methanol solution (experiment I-E10-12, in Figure 25). Enhance SVE experiments involve applying cycles of capillary-based solution delivery followed by vacuum extraction. The capillary-based solution delivery is accomplished by placing the solution source at the same level (i.e., elevation) as the delivery membrane. Vacuum extractions are applied at a constant head by the vacuum pump connected to the manifold.

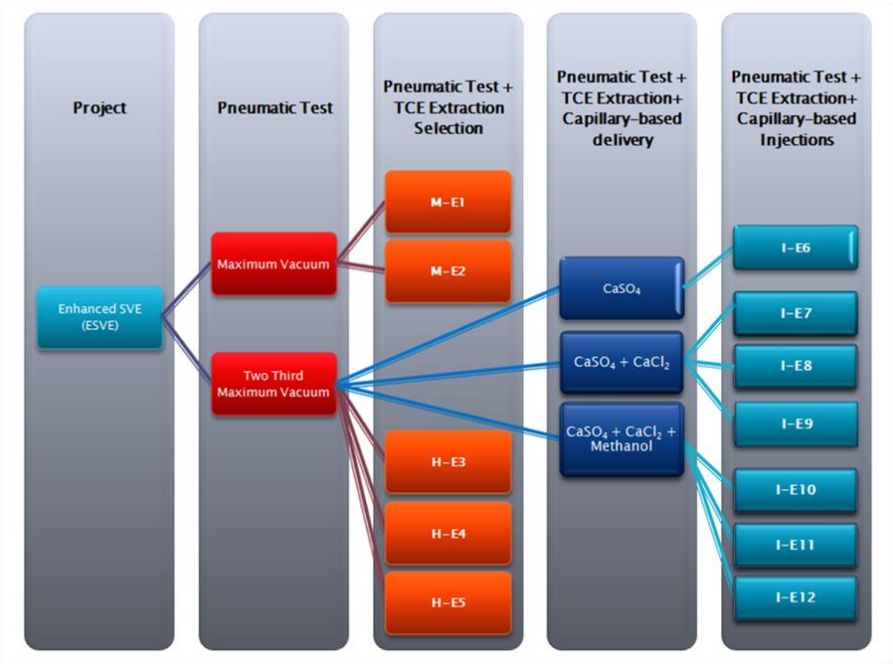


Figure 25 Experimental configuration flowchart

Prior to each experiment, the soil column is packed following the methodology described in sections 3.2.1.1 and 3.2.1.2 for the TCE contaminated soil layer. Once packed, the soil column is subjected to the selected treatment condition prior to activation of SVE:

- For dry SVE experiment (M-E1-2 and H-E3-5), no treatment is applied and SVE is started after a pre-determined vacuum extraction waiting period of 3 hours (approximate testbed assembly time), a TCE sample is taken right before the start of the vacuum extraction.
- For experiments involving capillary-based solution delivery (I-E6-12), the solution is delivered after packing, following the methodology described in section 3.3.1.1, and SVE is started after a pre-determine waiting period (approximate testbed assembly time and solution delivery). The waiting period for treatments involving solution delivery is longer under wet conditions than for the dry systems and vary between 19 and 22 hours for experiments without (I-E6-9) and with (I-E10-12) methanol. The longer waiting period allow distribution of the solution through the contaminated zone. Differences between treatment without and with alcohol are based on the capillary-based delivery process that takes more time (described in section 4.2). A TCE vapor sample is taken right before the start if the vacuum extract.

Vapor extractions for all experiments are conducted during three (3) consecutive days and each day has an extracting period of 6 hours. After the initial vacuum extraction of 6 hours, the vacuum pump is turned off for the day to allow for TCE concentration recovery. The recovery is necessary to compensate for rate-limits mass transfer process. The 16-

hour recovery period is followed by second 6-hours of vacuum extraction and a second 16-hour recovery period. This is finally followed by a third 6-hour vacuum extraction and its recovery period.

TCE vapor concentrations are sampled right before the start of the vacuum extraction periods, and every 20 minutes thereafter until the end vapor extraction period. Air flow, pump gage pressure, sensors pressure, water content at bottom of the column, and temperature are also monitored during the extraction period:

- Air pressures (i.e. vacuum) distribution and flow rates. Air pressures are monitored at the vacuum manifold and in the soil (see Figure 17). Flow rates are measured with a flow meter placed downstream of vapor sampler (see Figure 20).
- Solution delivery rates. Solution delivery rates are monitored one time by measuring changes in water levels over a period of time from the solution reservoir.
- Water content at bottom boundary. Water content is monitored using a water content Time-Domain Reflectometer (TDR) instrument.
- TCE and methanol vapors. Concentrations of TCE and alcohol vapors are monitored during SVE experiments at the sampling port located downstream of the SVE outlet manifold to monitor the behavior of TCE vapor concentration during vapor extraction test period. This data is used to: assess extracted and remaining TCE mass; quantify removal efficiencies of contaminants in clays; and develop optimal remedial technologies and parameters (e.g. delivery rates, imposed boundary conditions, contact times). Sampling frequency depends on flow rates applied but vary between 3 and 20 samples per day.

3.3.2.2.1 Maximum Vacuum Pressure – Dry Clay (M-E1 to M-E2)

These set of experimental SVE tests are conducted under dry soil conditions with the maximum vacuum pressure of 320 mbar provided by the pump. At this vacuum, the flow rates through the system are held at 6.0 mL / min, as measured in the flow meter. These experiments are labeled as M-E (for “Maximum Experiment”) and a number (1 and 2) of the test.

3.3.2.2.2 Two Third (2/3) Maximum Vacuum Pressure – Dry Clay (H-E3 to H-E5)

These set of experimental SVE tests are conducted under dry soil conditions with the vacuum set at two thirds (2/3) of the maximum pressure of the pump. A pump vacuum of 213 mbar, the flow rates through the system are maintained at 6.0 mL/min. These experiments are labeled as H-E (for “Two Third Maximum Experiment”) and a number (3, 4 and 5), identifying the test number.

3.3.2.2.3 Two Third (2/3) Maximum Vacuum Pressure – With Capillary-Base Injections (I-E6 to I-E12)

These set of SVE experiments sets a pump vacuum of 213 mbar and involves capillary-based delivery of three different reagents. Air flow is set 6.0 mL/min. These experiments are labeled as I-E, indicating that they are conducted at two third maximum pressure, and a number (6, 7-11 and 12), corresponding to the test identification number (see Figure 25).

- Experiment I-E6 applies a capillary-based delivery of 0.005 M $CaSO_4$ background solution. Because the solution wets the soil, this experiment is used to compare results with dry conditions (M-E1, M-E2 and H-E3 to H-E5) and serves as the experimental control for the treatments.

- I-E7, I-E8, I-E9 applies a brine of $CaSO_4$ and $CaCl_2$. Results from these experiments are compared to the control only having $CaSO_4$ (I-E6) background solution.
- Experiments I-E10, I-E11, and I-E12 applies brine and alcohol ($CaSO_4$, $CaCl_2$ and CH_3OH) prior to SVE. These experiments are performed to determine if the alcohol has any effect in the extraction process, compared to the others experiments.

Capillary-based delivery experiments start after the installation of the delivery wells (section 3.3.1). Once the delivery wells are installed, the head at the delivery-system graduated column or bag is set at the same level as the bottom of the membranes. The rest of the column is immediately packed with soil. The system is sealed and total volume of the solution is delivered.

Table 6 summarizes the primary experimental condition for the SVE experiments. They are classified according to the configurations, wetness condition and the capillary-based reagent delivery and it concentration.

Table 6 Summary of the experimental conditions

Experimental Arrangements	Experiment ID	Vacuum Pump Gage Pressure (mbar)	Clay Condition	Capillary-Based Delivery	$CaSO_4$ (0.005 M)	$CaCl_2$ (0.6 M)	CH_3OH (10%)
Max Vacuum Pressure – Dry*	M-E1	320	Dry				
	M-E2						
2/3 Max Vacuum Pressure – Dry*	H-E3	213					
	H-E4						
	H-E5						
2/3 Max Vacuum Pressure - With Capillary-Based Delivery*	I-E6		Wet	x	x		
				x	x		
				x	x		
				x	x		
				x	x		
	I-E7			x	x	x	
				x	x	x	
				x	x	x	
				x	x	x	
				x	x	x	
	I-E8			x	x	x	
				x	x	x	
				x	x	x	
				x	x	x	
				x	x	x	
	I-E9			x	x	x	
				x	x	x	
				x	x	x	
				x	x	x	
				x	x	x	
	I-E10			x	x	x	x
				x	x	x	x
				x	x	x	x
				x	x	x	x
				x	x	x	x
	I-E11			x	x	x	x
				x	x	x	x
				x	x	x	x
				x	x	x	x
				x	x	x	x
	I-E12			x	x	x	x
				x	x	x	x
				x	x	x	x
				x	x	x	x
				x	x	x	x

*All the tests perform: TCE extraction, soil packing and interval of sampling during 3 days.

3.3.2.3 Chemical Sampling and Analysis

Sample analysis is performed using an Autosystem Gas chromatograph with a Flame Ionization detector (GC/FID) from Perking Elmer® and PC software called Turbochrom Navigator (V.4.1<2.12F12>). This instrument works with three (3) different gases: Oxygen (Industrial Grade), Helium (Ultra high purity (UHP)) and Hydrogen (Ultra high purity (UHP)). The flows for each gas are 460, 5, and 45 mL/min, respectively. Analysis is performed using a Dimethylpolysiloxane (30 m x 0.53 mm x 5.0 μm) ValcoBond (VB-) column. Helium is used as the carrier gas through the column.

The GC analysis is conducted using an oven temperature program with an initial temperature of 40°C for 2 minutes, followed by a ramp of 20°C degree/minutes to 160°C, and holding for 0 minutes. A flow rate of 5 mL/min of Helium as the carrier gas is used. The complete analysis run time is 8 minutes. Table 7 shows data and instrument control configuration used in this method.

Table 7 SPME MIM method configuration

Parameter	Value	Units
Run Time	8	min
Delay Time	0	min
Sample Rate	25	Pts/s
Total Runs	7	
Segments Free	1	
Channel	A	
Injection	Manual	

Two of the principal components of this instrument are the detector and injector of the GC. The injector and detector temperatures for this method are set to 225°C and 250°C, respectively. The configuration for the data processing and reporting in this instrument take in consideration multiples parameters. Those parameters have scale

factor (1.0), offset (0.0 μV), and the scale (1000.0 μV). The instrument internal calibration has an outlier tolerance of 3%. This tolerance is established as a PC software input during the setup of the analysis method in the GC.

TCE vapor concentrations are measured in the sampling port located at the SVE exit point downstream of the manifold (see Figure 7). Sampling is conducted using a solid phase microextration (SPME) fiber (100 μm polydimethysiloxane coating) supported in a fiber holder (for use with manual sampling; both from Supelco, Inc.). The SPME fiber is introduced into the sampling port through a 11mm thermo green septa (Alltech) for a holding period of 3 minutes. This period allows for vapor to sorbs onto the fiber. After the holding period, the SPME fiber is removed from the port and introduced into the injection port of the analytical gas chromatograph (GC) for description and analysis. The fiber of the SPME is exposed inside the GC injection for a period of 5 minutes to allow for TCE desorption.

3.3.2.3.1 GC Analysis and Calibration

After a sample has been injected in the GC, a sample chromatograph is obtained (see Figure 26). A chromatograph shows a temporal response of the instrument to the chemical being injected that has a unique retention time associated with that chemical. This response yields an area, which is direct associated to the concentration of the sample. For direct qualification of the analyzer, it is therefore necessary to develop a calibration curve which relates GC area to sample concentration.

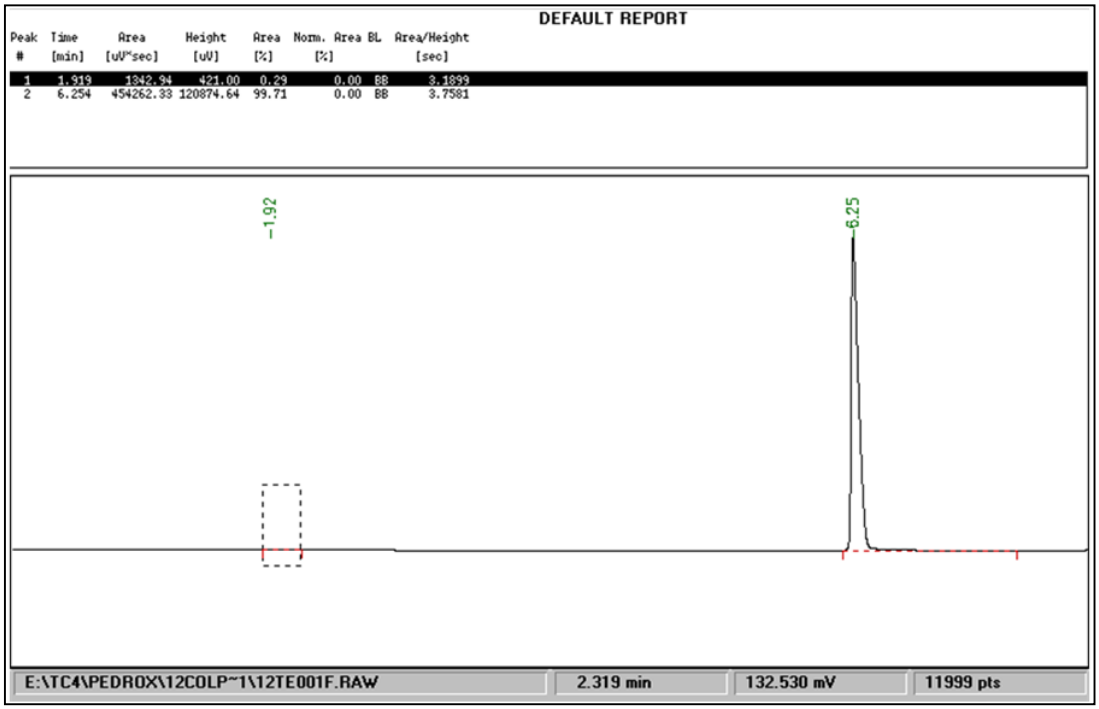


Figure 26 Example of the chromatograph and peak report obtained from the GC

TCE vapor standards are prepared and used for the development of the calibration curve. The standards are prepared by adding a predetermined volume of pure TCE into a one liter (1L) glass bottles (see Figure 27). Based on the TCE density (see Table 1), the predetermined amount used and associated TCE vapor concentration are given on Table 8. Once added to the bottle, the bottle is sealed and the TCE is allowed to volatilize. It is assumed that all mass is completely volatilized after (2 hours) since the mass added would yield a concentration below that expected for vapor pressure at 20°C and 1atm pressure (value of concentration at 336.6 mg/L), based at the universal gas law equation. Once volatilized, the SPME fiber is introduced into the sealed bottle for sampling and analyzing of the sample. The resulting areas are used in conjunction with the TCE vapor concentrations to develop the calibration curve (see Appendix G).

(a) (b)

Figure 27 Views of: a) 1L bottle b) SPME in the bottle

Table 8 Calibration standards

Sample	Concentration in Air (mg/L)	TCE (uL)
Cal 0	0.00	0.00
Cal1	3.74	2.6
Cal2	37.4	25.6
Cal3	168.3	115.3
Cal4	224.4	153.7
Cal5	276.76	189.6
Cal6	336.6	230.5

3.4 Data Analysis

Results from the SVE experiments are analyzed to determine the performance of SVE methods to induce airflow and extraction of TCE vapors from TCE-contaminated clay soils. Pneumatic tests yield pressure and flow response data through the system. Vapor extraction experiments provide temporal concentration distribution data of TCE vapors exiting the testbed under imposed experimental conditions, which vary on soil wetness and type of solution delivered under capillary tension.

Pressure data from pneumatic experiments is used to determine airflow behavior and pressure drop across the system. Pressure drops is calculated as the difference in pressure from sensors measurements.

Temporal concentration distributions are used to determine the magnitude of TCE vapor concentration exiting the system and amount of mass eluted from the system. Qualitatively, TCE vapor concentrations are plotted against time to observe the effect of the treatments on TCE concentration and volatilization rates. The amount of mass eluted from the system and eluted characteristics are quantified by applying the Method of Moments to the TCE temporal concentration distribution. The first Moment (M_1) of a temporal concentration distribution is described by Padilla, 1998:

$$M_1 = \int C(t)tdt \tag{2}$$

where,

C= TCE Vapor Concentration (mg/L) at different time

t= Time(s), from t=0 up to $t=t_{max}$, where t_{max} is the time of the last data point.

Assume constant flow rates, the amount of mass removed from the soil is given by the Zeroth Moment (M_0) and the air flow rates (L/s):

$$\mathrm{M_0 = Q\int_{-\infty}^{\infty} C(t)dt = Q\sum_1^n \left(\frac{C_i + C_{i-1}}{2}\right)(t_i - t_{i-1})} \tag{3}$$

TCE vapor concentrations determined from GC results (using linear regression equation analysis of calibration curve) are used to calculate average TCE concentration in air (mg/L) between each time interval. The average concentration is multiplied by time

interval (20 minutes) and airflow rate to determine the amount of TCE vapor eluted at that time. The total amount of TCE extracted is obtained as the sum of all eluted mass through the extraction time. Total eluted mass for an experimental concentration is estimated as the summation of total mass eluted at each of the three 6-hours vapor extractions periods. Cumulative extracted mass is plotted against time to assess the change in mass extraction during each experiment.

The average time of travel ($\dot{t}$) for the removal of the center of mass is given by the first normalized moment:

$$\bar{t} = \frac{M_1}{M_0} = \frac{\int C(t)tdt}{\int C(t)dt} \quad (4)$$

This values provides a comparative parameter to assess how fast the mass is extracted under the different experimental conditions applied.

4 RESULTS AND DISCUSSION

The following chapter presents and discusses the results obtained from the experimental work designed to determine the feasibility for the enhancement of TCE removal from clay soils using enhanced SVE. Results are presented base on: soil packing and bulk density; capillary-based reagent delivery; pressure distribution, and TCE vapor extraction under different conditions.

4.1 Soil Bulk Density

The measured soil bulk densities obtained through the packing methodology described in section 3.2.1.1 show relative reproducible results with an average total bulk density of 1.30 ± 0.04 g/cm^3 (average of all columns ± one standard deviation) as showing in Table 9. Although the average ranges within the packing density goal of 1.28 g.cm^3, results shows that soil density varies with depth depending in the instrumentation/packing condition of the zones. For instance average soil densities within the different packing zone (see section 3.2.1.1) vary between 1.02 ± 0.09 and 1.61± 0.01 g/cm^3. Higher and lower values are associated worth the 2nd and 3th zones, respectively. Layer third that was contaminated with TCE have higher bulk density values, compared to the other layers. Differences are attributed to variation made in the weight of the piston and other parameters to maintain the compaction energy constant (e.g. instrument assembly process).

Table 9 Average bulk density values for the different soil layer. Average values are calculated using 12 data ports for each layer.

			Average Values/Standard Deviation Error		
Soil Layer	**Height (cm)**	**Volume (cm^3)**	**Weight (g)**	**Density (g /cm^3)**	**Porosity (%)**
Bentonite seal zone	5	1,417.6	-	-	-
Six (up to the bottom of the Bentonite seal zone)	20	5,670.6	6,676.8 ± 104.1	1.18 ± 0.02	0.50
Fifth (up to the bottom of the SVE wells)	15	4,252.9	5,468.7 ± 253.8	1.29 ± 0.06	0.46
Fourth (up to the bottom of the delivery wells)	5	1,417.6	1,444.7 ± 127.8	1.02 ± 0.09	0.39
Third (TCE contaminated zone)	5	1,417.6	2,280.17 ± 10.9	1.61 ± 0.01	0.61
Second (from the top of the air-inlets to the bottom of TCE contaminated zone)	5	1,417.6	2,002.8 ± 110.6	1.41± 0.08	0.51
First (from the column bottom to the top of the air-inlets)	45	12,758.8	16,835.0 ± 227.2	1.32 ± 0.02	0.55
General bulk density without TCE contaminated soil				**1.30 ± 0.04**	

4.2 Reagents Capillary-Based Delivery

Capillary-based delivery of reagents to clay soil delivers a reagent volume of 950 mL under low water tension. Delivery quantification is based on the time it takes for total delivery of this volume. Delivery times of 10, 8, 12, and 10 hours for experiments I-H6, I-H7, I-H8, I-H9, respectively, yield delivery rates varying between 79 and 119 mL/min. Therefore, delivery times and flow rates for salts solution average 10 ± 0.8 hours and 97 ± 8.2 mL/min, respectively. Delivery times of 11,16, and 13 hours for experiments I-H10, I-H11 and I-H12 yield delivery rates between 59 and 86 mL/min for delivery of brine solution + methanol. The average delivery times and rates of 13 ± 1.3 hours and 73 ± 6.7 mL/min for these experiments suggest slower delivery of the alcohol-brine solution. The differences are not significantly different when taking into account standard deviations of the amount groups.

The variations in the total delivery time and rates between each experiment are influenced by the delivery process, systematic error, and the soil packing. If each arrangement is grouped by delivery process and compared, the results are similar. This is because the system used to perform the capillary delivery varying between arrangements. As discussed in section 3.3.1.1, the delivery of brine solutions used a laboratory-made graduated column and a Tedlar bag that is used to deliver the mix of solution (brine/methanol). This difference in instruments is a potential source of systematic and delivery process errors.

4.3 Air flow Rate Monitoring

Air flow is monitored during the sampling interval for each experimental condition. The collected data is grouped by the experimental condition and the averaged. Average flow rates for each experimental arrangement (see

Figure 28), show similar values with small variations. Overall, flow rates ranged between 5.5 and 7.6 L/min, and averaged 6.5 ± 0.15 L/min for all experimental conditions, and thus support small flow rate variability's. Higher air flow rates are generally observed for cases in which the pump is working at maximum capacity (M-E1 and M-2). Higher flow rates are expected under these conditions because of the higher pressure differential. When the set point is at 2/3 of the maximum and don't have capillary-base delivery (H-E3 to H-E5), the air flow rate are one a specific range of values (6.0 ± 0.07 L/min). These three experiments are designed to have the same flowing conditions. In I-E6 an irregular peak is shown. The behavior of the air flow in this experimental condition should be the same as that for 2/3 of the maximum set point. This is because all the parameters are the

same, but with the exception that has capillary-based injection. Higher flow rates in these experiments are probably caused by changes in the vacuum pressure during the extraction process inside the soil column. Average flow rates in experiments I-E7 through I-E9, is maintained at a specific range of values 6.5 ± 0.15 L/min, but with a little tendency to increases. In experiments I-E10 through I-E12, the values of the air flow rate 6.7 ± 0.05 L/min are approximately the same.

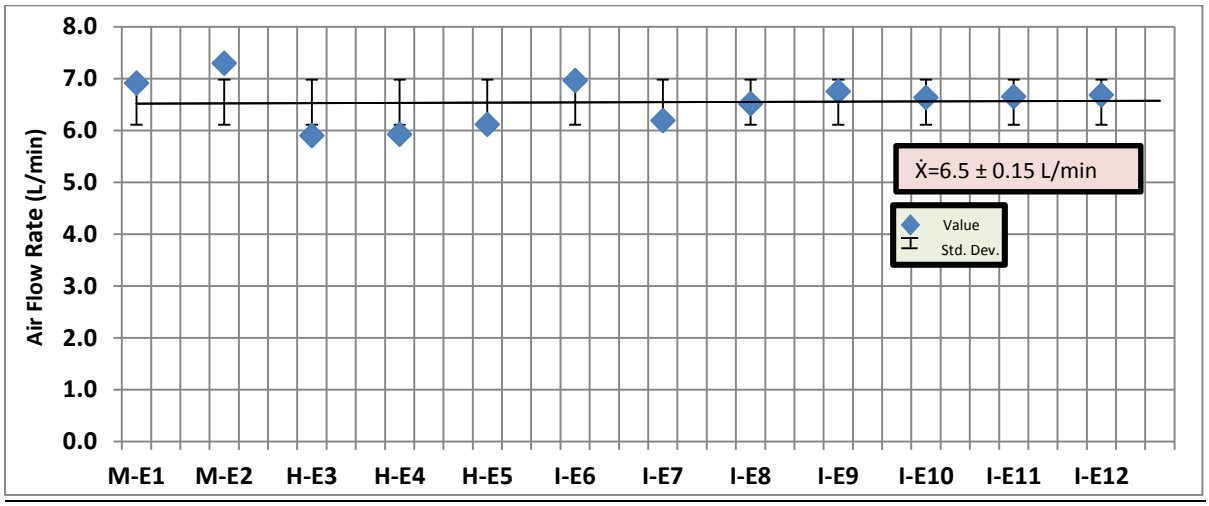


Figure 28 Experimental flow rates by experimental arrangement

4.4 Pneumatic Test Analysis

Pressure measurements through the testbed system are used to assess the pneumatic behavior, quantify pressure drop across the system, and identify significant changes. Pressure data is grouped by sensor location and experimental condition to calculate the average values. Sensor # 2 (S2) is located at 60 cm above the bottom of the column and is the closest to the air-inlet wells points, which are located at 40 cm above the bottom of the column. This port is located above the TCE contaminated and reagent delivery zones. Port S5 and S6 are located at 80 cm from the bottom of the

column. Ports S3 and S4 are located at the exiting manifold, and therefore are closest to the vacuum source.

Average pressure through the system for the different experimental condition (see Figure 30) show higher pressure (lower vacuum) in ports closer to the air-inlet ports (i.e., S2) and lower pressure (higher vacuum) in ports located at the exit point of the vapor extraction wells (i.e., S3 & S4) thus closer to the vacuum pump. This is expected as pressure conditions at air-inlets are expected to be near atmospheric values, and ports closer to the pump should have higher vacuum. Average pressure in dry clay are generally lower (high vacuum) for experiments M-E1-2 than H-E3-5 since the former are subjected to a higher vacuum source than the later. Average pressures tend to be lower for experiments with reagent delivery (H-E6-12) relative to there in dry clay (H-E3-5), indicating higher air pressure drop across clay soil. Pressure drops tend to be higher across the wetted and TCE contaminated zone (from 40-60 cm), but lower above this zone (see Figure 29). This behavior is expected because in the wetted zone, only a fraction of pores are available for air flow that result in higher resistance to flow and (theoretically) lower air permeability's. The zone above the wetted zone is dryer and more pores are available for air flow, resulting in lower resistance of flow and (theoretically) higher air permeability's. Experiments with brine injection (H-E7-9) tend to show lower air pressure drops across the soil, suggesting that the brine increasing air permeability across soils.

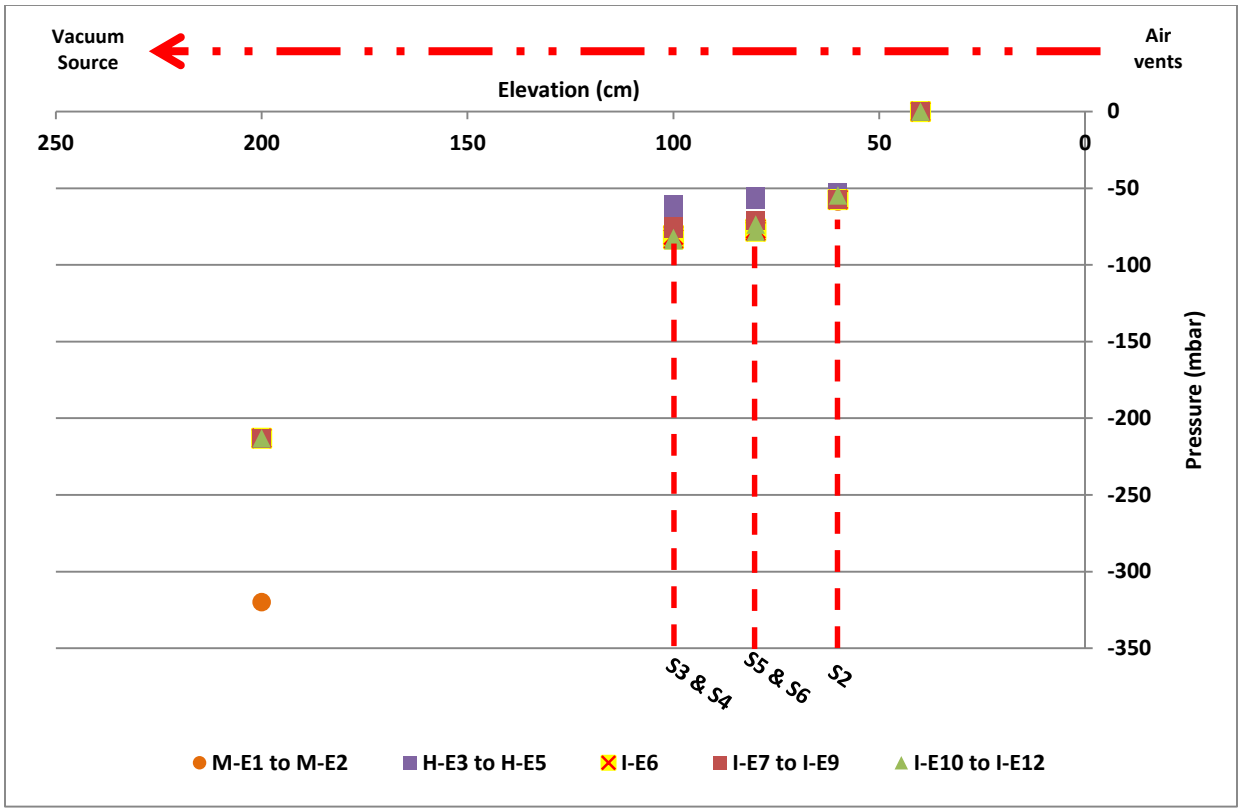


Figure 29 Average pressure measurements as function of sensor location and experimental condition

Analysis of pressure measurements indicate that values are consistent with the pneumatic behavior described in the methodology developed for these tests. More precisely, the obtained pneumatic behavior show (see Figure 30) that those sensors closer to the pump, have more negative pressure values (greater vacuum) and those that are more distant from the vacuum source are which are less negative. Their behavior under the different experimental conditions also reflect the proper response to the changes.

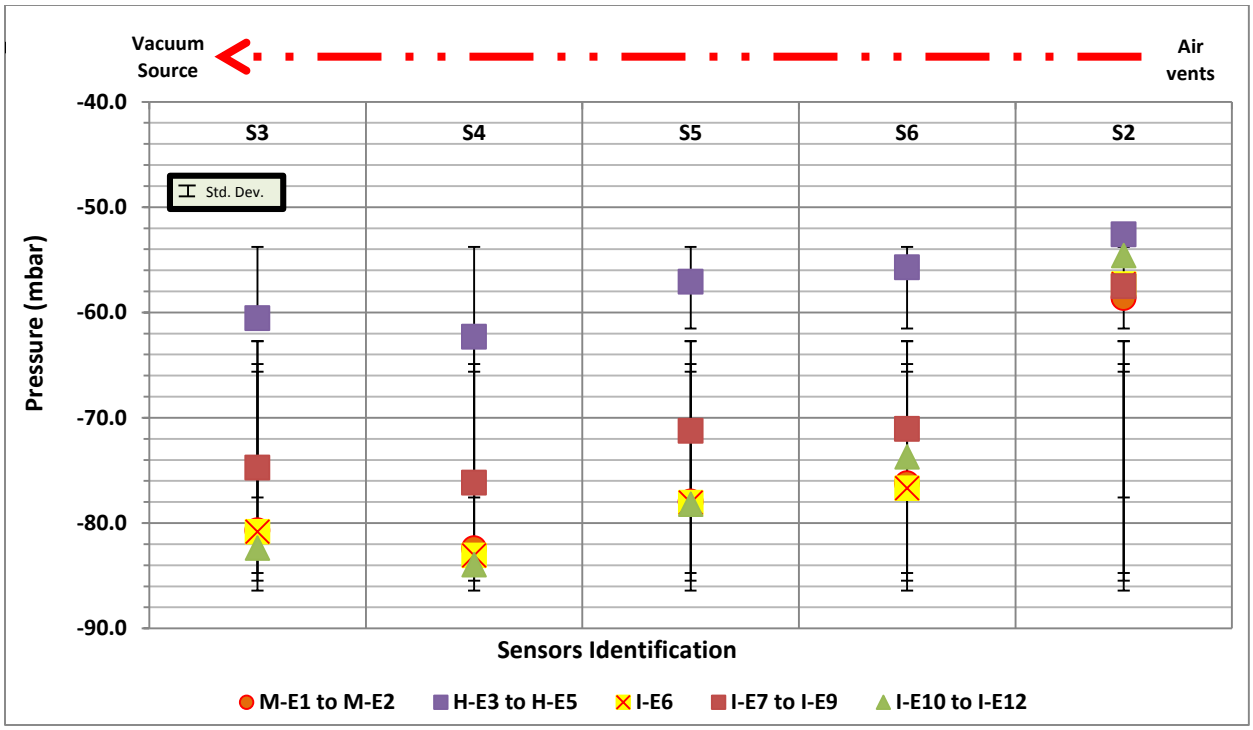


Figure 30 Average pressure measurements from sensors under the different experimental conditions

4.5 TCE Vapor Extractions

Temporal TCE vapor concentration distributions for all experiments are shown in Figure 31. All the experiments show that the TCE vapor concentration tend to reach the maximum value during the 1st extraction phase and then decrease. Maximum concentrations ranged from 771.91 mg/L in experiment H-E9 to 231.78 mg/L in experiment M-E1 (see Figure 32). Average maximum concentration suggest that maximum concentration are higher for experiments with $CASO_4$+$CaCl_2$ (H-E7-9), although the difference may not be significant.

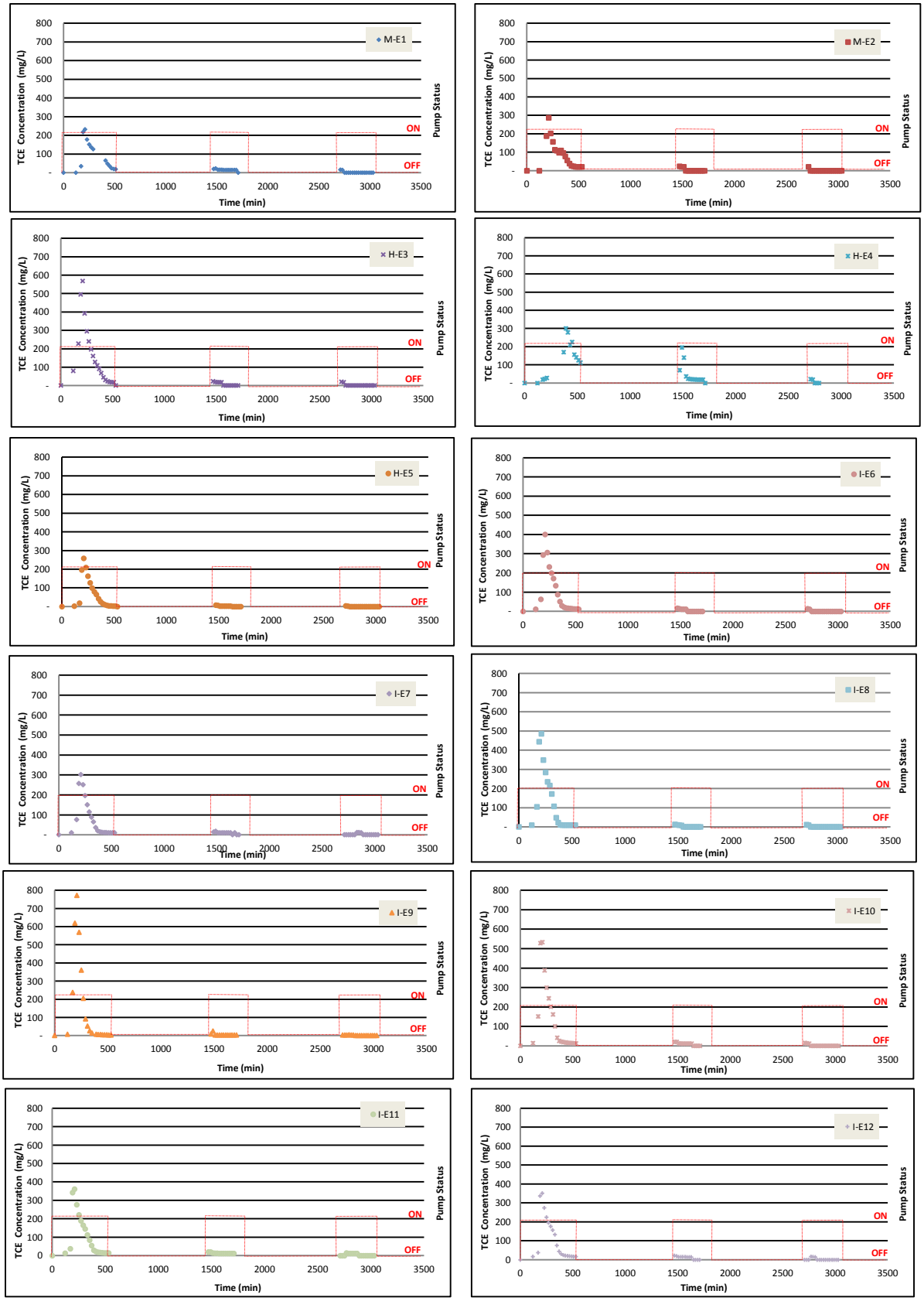


Figure 31 TCE concentration data by experimental arrangements

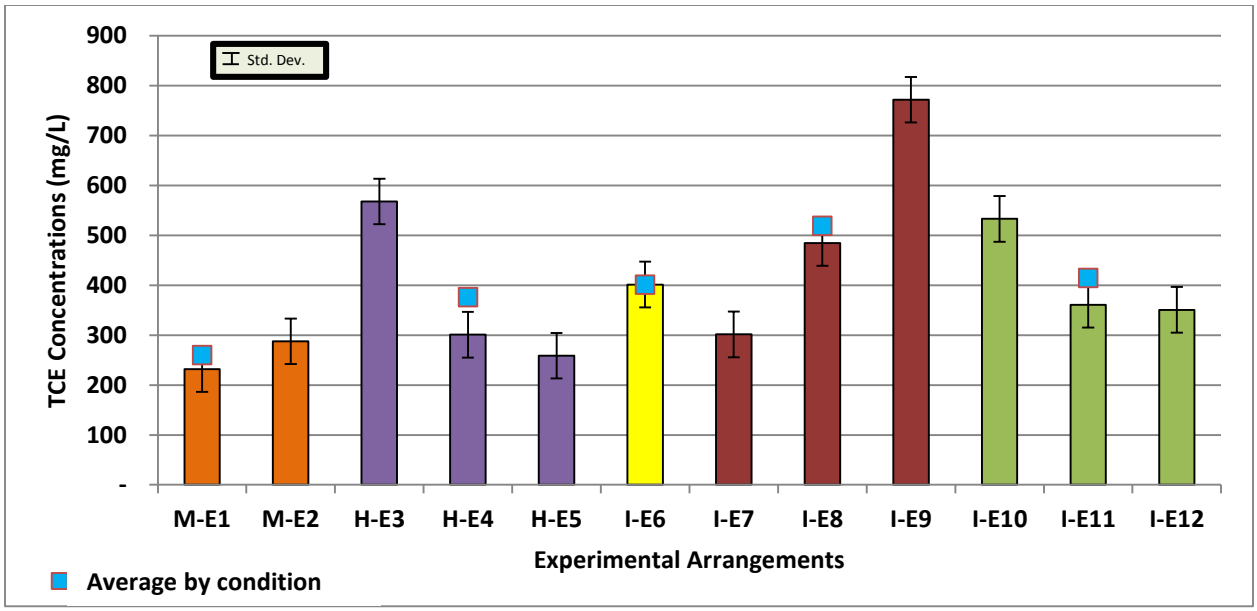


Figure 32 Maximum TCE concentration data by experimental arrangements (see Table 6 for experimental description)

Generally, the TCE concentration tends to increase slightly at the beginning of each extraction phase (until reach the maximum extraction concentration), but max concentration are much lower for the 2nd and 3rd extraction phases (see Figure 31) maximum concentration occur about 210 minutes for experimental except H-E4, which shows a maximum concentration at 390 minutes. The difference in this behavior is unknown, but potentially attributed to pump and GC problems during the initial extraction phase.

The delivery of the temporal concentration distribution suggests solution sorption and mass transfer limitations in the transport process. As air move through the TCE-contaminated zone it carries TCE vapor residing in the air phase. As the TCE vapor moves through the initially clean clay zone overlying the contaminated zone, it is sorbed into the clay. Consequently, the peak concentration of the vapor residing in the TCE-

contaminated zone is retained with respect to the eluted volume of air. Assuming that the eluted of one (1) pore volume of air above the contaminated zone occurs at time T_{pv} = Vol $_{6th}$ / Q_{air}, when Vol_{6th} is the volume of pore in soil zone 6th (5,670.57 cm3 x 0.55 = 3,118.9 cm^3; Table 5), a Q_{an} in the air flow. For air flow between 7.1 and 6.0 L/min (see Figure 28), T_{pv} range from 6.44 to 0.52 minutes. These times are many orders of magnitude lower that the time to peak observed for TCE and indicating that the TCE vapor is retarded.

The decrease in TCE vapor concentration of the reaching maximum concentration is indicating that either the mass from the system has been completely removed or that mass transfer process are limiting (e.g. volatilization, desorption) the movement of TCE into the air phase. Slight increase in concentration after the beginning of the 2nd and 3rd extraction periods, and incomplete mass balance supports the mass transfer limitations. Strong tailing in the falling limb of the temporal concentration distribution is also indicating of mass transfer limitations. Estimation of total mass extracted (section 4.5.1) does not support complete removal.

4.5.1 TCE Vapor Extracted Mass

The amount of TCE extracted for each experimental condition is calculated by applying method of moments (equation 2 and 3) analysis to the temporal concentration distribution data (see Figure 33). The amount of mass remaining is calculated as the difference between the total mass of TCE packed in the contaminated zone (619,063.76 mg for all experiments) and the amount extracted. Results show slow removal of TCE during the three (3) vapor extraction periods. Long concentration tailing at low

concentrations after the initial extraction phase indicates that complete removal would take very long time. This is attributed to mass transfer limitations.

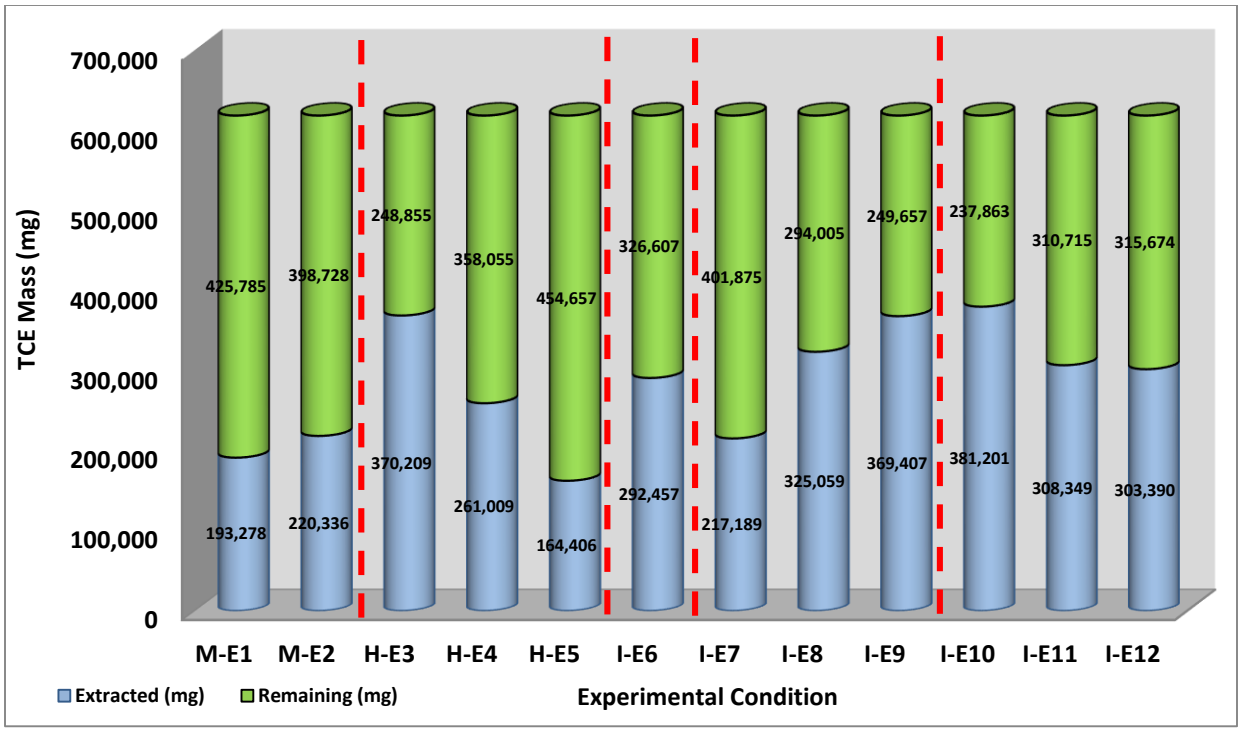


Figure 33 TCE vapor extracted mass by experimental arrangement

The amount of TCE extracted varies for the different experimental conditions. The highest and lowest mass extraction are measured for experiment I-E10 and H-E5, respectively. These experiments are from different experimental conditions (dry conditions at 2/3 max pump vacuum vs. wetted conditions at 2/3 max pump vacuum) and reflect a variability of the system. This variability is attributed to differences in soil density, porosity, flow rates and pressure gradients. The amount of extracted mass (see Figure 34) and percent removal of TCE (see Figure 35) are lower for the experiments conducted at maximum pump vacuum (experiments M-E1-2). Lower extraction mass at higher suction gradients flow rates supports that the extraction of TCE vapor is influenced by

mass transfer limitations. Although higher average extracted mass is observed for experiments with capillary injection of $CaSO_4$+$CaCl_2$+ methanol, there is a high variability in the extracted mass among the different experimental conditions.

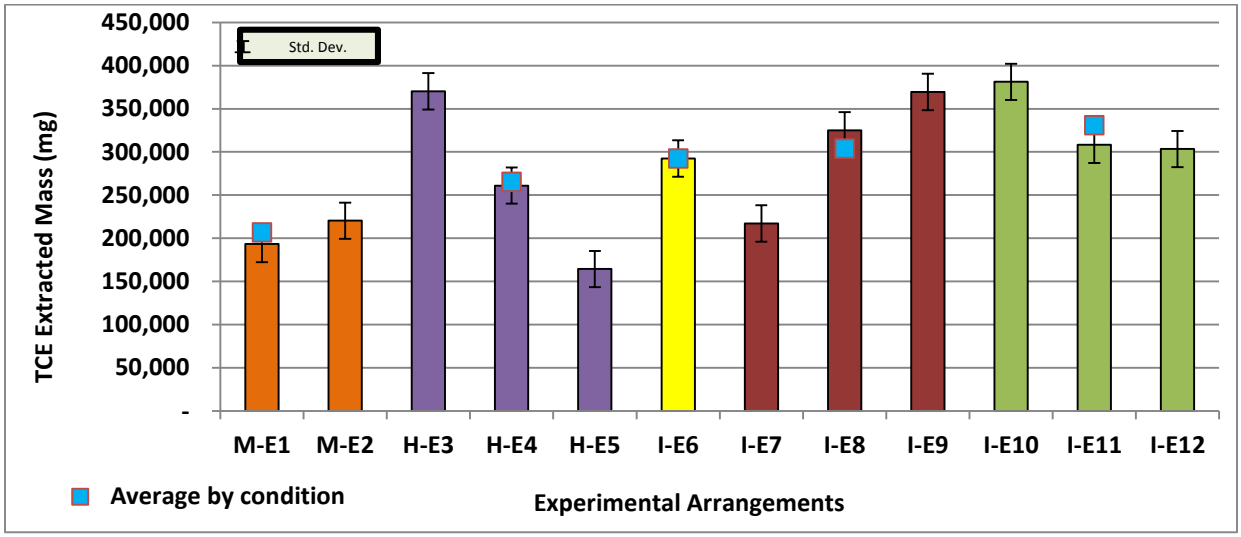


Figure 34 TCE Extracted Mass data by experimental arrangements

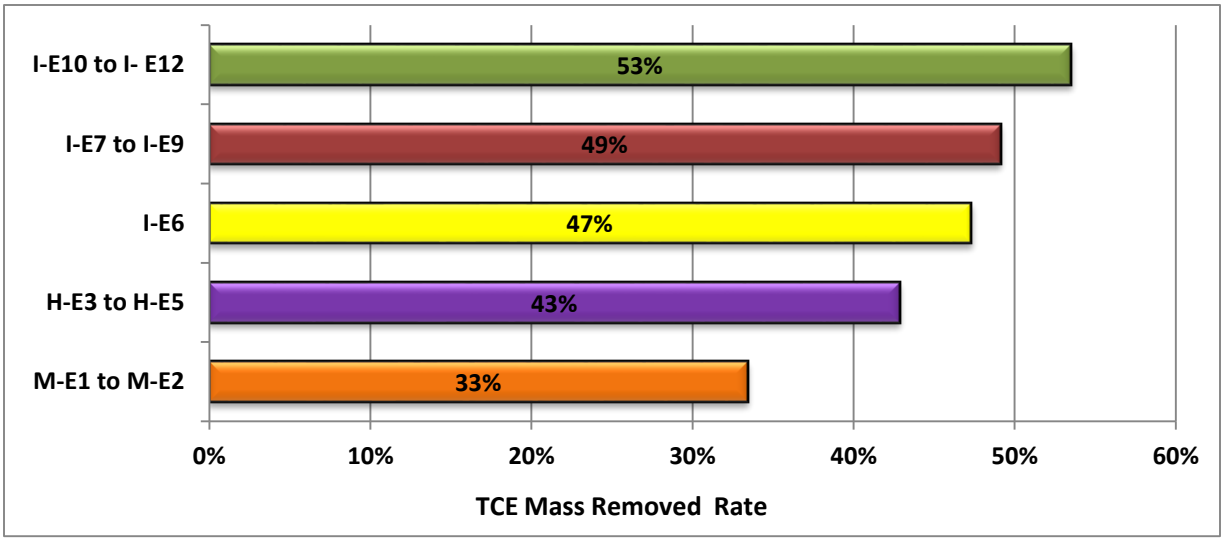


Figure 35 TCE mass extraction by experimental procedures

Average removal times for the initial extraction in each experimental arrangement suggest that the TCE vapor is extracted faster during the dry experiments at full vacuum

capacity (M-E) (see Table 10). Higher average removal times for experiments using the brine solution (I-E8-10), suggest slower removal under these conditions. High variability among average removal times, however, does not allow to discern any significant differences between treatments.

Table 10 Average removal time

	Experimental Arrangement											
	M-E1	**M-E2**	**H-E3**	**H-E4**	**H-E5**	**I-E6**	**I-E7**	**I-E8**	**I-E9**	**I-E10**	**I-E11**	**I-E12**
	Time (min)											
Average by Treatment	19.8	17.8	21.0	18.6	23.0	21.1	20.5	23.3	26.6	21.7	20.9	21.0
	18.8		20.9			21.1	23.5			21.2		

The time it takes to elude one pore volume from above the contaminated zone to the venting wells (t_e) can be estimated based on air-flow velocities (V_a):

$$t_{1pv} = \frac{Z}{V_a} \tag{4}$$

where,

V_a= $Q/A_c\ \Theta_a$ (Q= as previously defined, A_c= column area and Θ_a= air porosity and Z= distance).

These time provide an estimates of the time at which the mass would be eluted of instantaneously release into the air, with no sorption. Estimated t_{pv} (Table 11) shown that, based on air-flow velocities the TCE should be eluted much sooner (average t ≈ 0.54 ± 0.01 min) that what shown by the average removal times (Table 10). On fact, average removal times are about 40 times higher than the average times to elute one pore volume, indicating strong sorption, retardation and mass transfer limitation process.

Table 11 Estimates Removal times based on air-flow velocities

Experimental Arrangement											
M-E1	M-E2	H-E3	H-E4	H-E5	I-E6	I-E7	I-E8	I-E9	I-E10	I-E11	I-E12
Time (min)											
0.51	0.49	0.60	0.60	0.58	0.51	0.57	0.55	0.52	0.54	0.53	0.53

4.6 Additional Consideration during the Extraction Process

This section describes additional experimental variables measured during the extraction process. These include system temperature and methanol concentration during the H-E10-12.

4.6.1 Temperature Drop and Visible Condensation During the Extraction Process

Measured temperatures in the soilbed during the extraction process indicate that the average initial temperatures are between 30.7 ± 0.23 °C at the bottom of the solution delivery membrane (T1) and 23.1 ± 0.39 °C at the center of the TCE-contaminated zone (T2). All experiments show lower temperature at the TCE-contaminated zones than other area. During the first part of the extraction process (day 1), temperatures show a tendency to decrease through time, especially between 20 and 120 minutes from the onset of the experiment (see Figure 36). This variation shows that the average low temperature was 28.8 ± 1.50 °C for T1 and 20 ± 1.09 °C for T2.

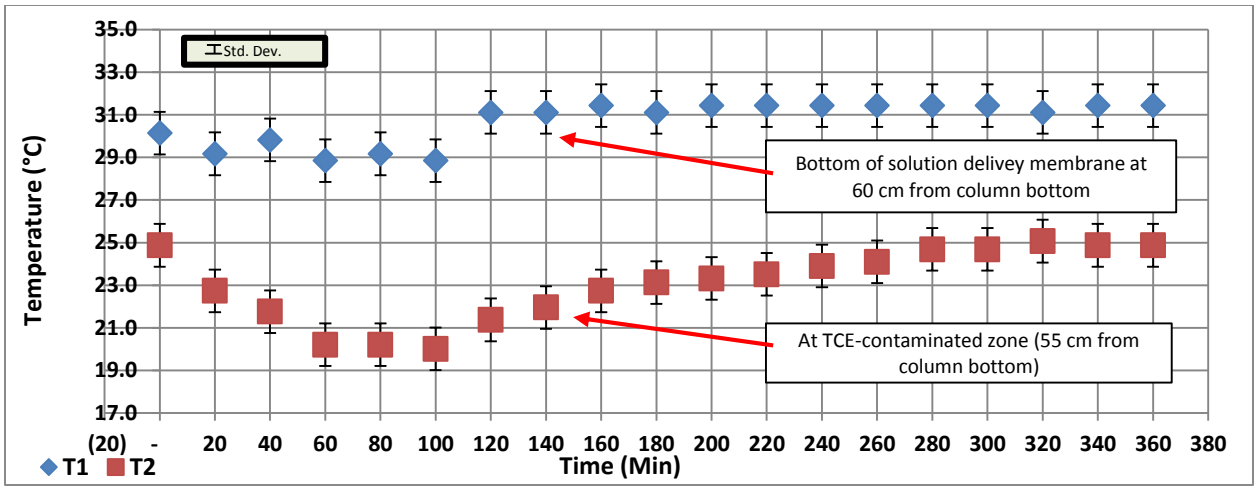


Figure 36 Temperature variation of the experiments by time (during day 1) at T1 and T2

The temperature drops significantly between layers 3 and 4 (55 to 60 cm from bottom) where the soil is contaminated with TCE and near the location where capillary-based injections are performed. At the time when the values of the thermocouples shows significant drop in temperature, the soilbed walls also show visible condensation (see Figure 37). Between the same layers that the temperature drops, the condensation is visible and maintained during the same period of time in the first day of the test. This condensation is probably caused by considerable changes in temperature and pressure inside the soil column. The drop in temperature is probably caused by heat transfer between cool air entering by the air vent and passing through the soil, and the volatilization of the TCE caused by the change in vapor pressure. In these cases the pressure was forced to drop by the applied vacuum during the extraction process (Suthersan, 1999). Lower temperature is also attributed to heat transfer from the surrounding media to cause volatilization of TCE. Both conditions described in this section (temperature drop and visible condensation) appear in all of the experiments.

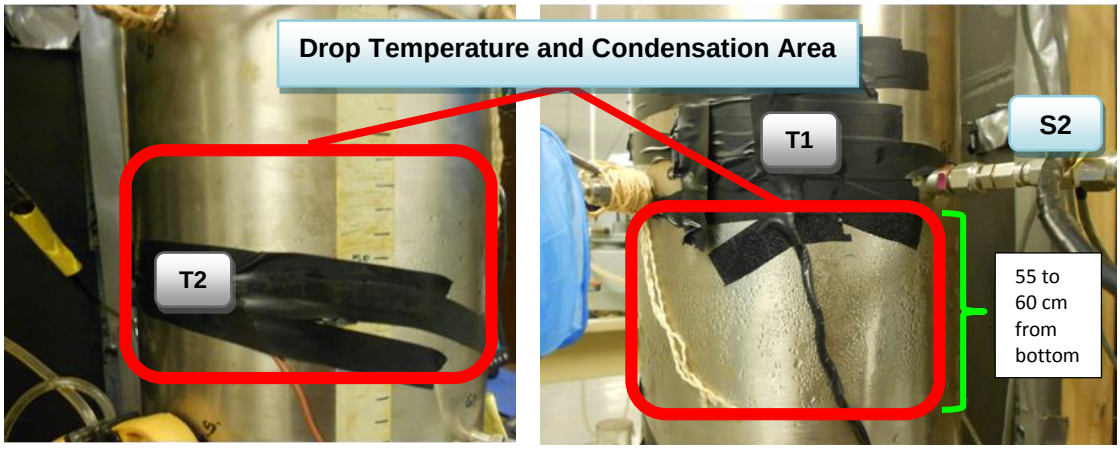


Figure 37 Examples of the area where the temperature drop and condensation was visible

4.6.2 Methanol Concentration in the TCE Extracted Sample

Methanol vapor is detected during the experiments in which methanol is delivered to the system (I-E10, I-E11and I-E12). The reason of this detection is attributed to volatilization and vapor transport of methanol during vapor extraction process. Assessment of the sampling concentration methanol is out of the scope of this project. For that reason no methodology was developed to determine this concentration quantity.

5 SUMMARY AND CONCLUSIONS

A laboratory-scale soil vapor extraction (SVE) testbed has been developed and a pilot study was conducted to assess the performance of SVE in unsaturated clay subjected to delivery of solutions. It was hypothesized that capillary delivery could improve reactant delivery into the soil and that the delivery of $CaCl_2$ and methanol solution could serves to improve air permeability, volatilization, and vapor extraction of TCE from these soils.

SVE experiments were conducted to determine the amount of TCE mass removed from a clay soil when subjected to cycled alcohol / salt capillary injections. Experimental results were used to evaluate the hypotheses that (1) TCE vapor extraction from clayey formations can be enhanced by cycled alcohol / brine solution injections, and (2) capillary injections through porous membranes results in more uniform delivery and lower preferential transport of reactants (alcohols/ salt) into low permeability media. The following conclusions were derived from various SVE experiments:

- The developed testbed is appropriated for SVE testing. The hydraulic behavior and extracted mass show it can be reproduced and show consistency.
    - Pressure data show that pressure drop is consistent and follow pneumatic behavior. The data indicates that no airflow short circuit occurs in the soil bed system.
    - TCE vapor extracted mass follow reproducible behavior, and show that mass removal increases up to a maximum and then decrease passing the

time. This behavior indicated that physical mass transfer limitations are related to volatilization and sorption/ desorption in the soil.

- Capillary-based delivery has proven to be a viable method to delivery reactant into clay soils of low permeability.
- Changes in pressure gradients suggest that the use of $CaCl_2$ brine may increase air permeability of the system.
- The results from all the tests show that SVE can be used to extract TCE contaminants from clay soil.
    - However, removal is subject to mass transfer limitations, which reduce the efficiency of the extraction.
- Removal efficiency between 33% and 53% were obtained during the extraction experiments, indicating that a large amount of initial mass still resides in to the system and that total removal would take a long time. Higher extraction mass was obtained for experiments conducted at 2/3 of the maximum pump vacuum, which tend to have lower flow rates. Although slight variations in the measurements are observed for experiments using $CaCl_2$ brine and methanol, the difference is not significant.
- Measured temperatures through the soilbed during the extraction process indicate a significant variation in temperature. That variation occurs between the top layer of the aerator and the injection wells layer. Temperatures show a tendency to decrease during a short periods, and then maintain a constant range of values. Lower temperatures under during the extraction process are attributed to cooling effect of water in the system and TCE volatilization.

- Average removal times for the initial extraction by experimental conditions, indicate that the TCE vapor is extracted faster for dry conditions at max pump vacuum (M-E1-2) and it is extracted slower in wetter conditions at 2/3 max pump vacuum (I-E7-9).
- The experimental results from the combination of: SVE and capillary-based delivery injection in clayey soil indicates that is an innovative remediation technology.
    - Commonly remediation technologies are developed for medium and high permeability soil, and not for low permeability zones, such a clayey soils.
    - Alcohol and brine solutions injections for this project, is classified as a state-of-the-art technology. The developed methodology allows the injection of a reagents and solutions through the soilbed (clayey soil) using a capillary-based delivery.

6 RECOMMENDATIONS

After the completion of this project, several recommendations are proposed to continue the study of ESVE. These include:

- Develop more experimental replicates to increase the reliability of the collected data. Although, it is known that this kind of experiments cannot be exactly replicated because of differences during the experimental setup, data collection and data analysis, the overall behavior can provide a basis for supporting or rejecting the given hypothesis.
- Measure temperature variations throughout the entire soil bed during each sampling.
- Quantify the concentration of the remaining TCE in soil layers.
- Vary the brine solution or/and alcohol to verify the effect during the extraction process.
- Perform experiments at different contaminant and/or water saturation (content by volume or by mass), air flow rates, and capillary delivery cycles.
- Develop design parameters (cycles, delivery paths, solutions injection, and vapor extraction rates) to obtain the optimums parameters for SVE enhancement.
- Install or use more water content and temperature sensors placed in the soil to better assess environmental conditions affecting the fate and transport of the contaminant.
- Consider the use of more sensitive pressure sensors.

- Develop a calibration methodology to establish the methanol residual concentration during each extract sampling.

7 REFERENCES

(AFCEE) Air Force Center for Environmental Excellence. 2001. Guidance on Soil Vapor Extraction Optimization- Final. Brooks AFB, TX: United States Air Force Environmental Restoration Program, Air Force Center for Environmental Excellence.http://www.clu-in.org/download/contaminantfocus/dnapl/Treatment_Technologies/SVE-optimization.pdf. Last date accessed on July 28, 2012. pp. 1.1-7.3.

Albergaria, J. T., M. da Conceição, M. Alvim-Ferraz, and C. Delerue-Matos. 2008. Soil vapor extraction in sandy soils: Influence of airflow rate. *Chemosphere, vol.* 73, pp. 1557–1560.

Bedient, P.B., H.S. Rifai, and C.J Newell. 1997. Ground Water Contamination Transport and Remediation. Prentice Hall, NJ. 1997.

Cassada, D. A., Y. Zhang, D. D. Snow, and R. F. Spalding. 2000. Trace Analysis of Ethanol, MTBE, and Related Oxygenate Compounds in Water Using Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry. Analytical Chemistry, vol. 72, No. 19, pp. 4654-4658.

Christ, J. A., C. A. Ramsburg, L. M. Abriola, K. D. Pennell, and F. E. Löffler. 2005. Coupling Aggressive Mass Removal with Microbial Reductive Dechlorination for Remediation of DNAPL Source Zones: A Review and Assessment. Environmental *Health Perspectives*, 113, no. 4: 465-477. http://dx.doi.org/10.1289/ehp.6932. Last date accessed on July 16, 2012.

Delgado, E., I. Padilla. 2011. Capillary Injection of Solutions in Compacted Clay Soil. Written communication, June 2011. University of Puerto Rico at Mayagüez. pp. 1-54.

Drever, J. I. 1988. The Geochemistry of Natural Waters, Second Edition Prentice-Hall, Englewood Cliffs, N.J.

Ellis, P.A., and M.O. Rivett. 2007. Assessing the impact of VOC-contaminated groundwater on surface water at the city scale. *Journal of Contaminant Hydrology,* vol. 91, pp. 107–127.

(EMS) Environmental Management Support, Inc. 2004. Site Characterization Technologies for DNAPL Investigations (EPA 542-R-04-017). Office of Solid Waste and Emergency Response (5102G). Cincinnati, OH: U.S. Environmental Protection Agency (EPA), Office of Superfund Remediation and Technology Innovation, National Service Center for Environmental Publications (NSCEP). http://www.epa.gov/tio. Last date accessed on July 16, 2012.

Fountain, J.C. 1998. Technologies for Dense Nonaqueous Phase Liquid Source Zone Remediation. Technology Evaluation Report, E Series: TE-98-02. State University of New York at Buffalo, Department of Geology. Pittsburgh, PA: Ground-Water Remediation Technologies Analysis Center. pp. 1-56.

Gwremed. 2013. Conceptual Diagram of Basic Soil Vapor Extraction (SVE) System for Vadose Zone Remediation: www.wikipedia.com. http://en.wikipedia.org/wiki/File:Conceptual_Diagram_of_ Basic_Soil_Vapor_Extraction_(SVE)_System_for_Vadose_Zone_Remediation.png#file history. Last date accessed on May 14, 2014.

Høier, C.K., T.O. Sonnenborg, K.H. Jensen, C. Kortegaard, and M.M. Nasser. 2006. Experimental investigation of pneumatic soil vapor extraction. *Journal of Contaminant Hydrology,* vol. 89, pp. 29–47.

ITRC) Interstate Technology & Regulatory Council. 2000. Dense Non-Aqueous Phase Liquids (DNAPLs): Review of Emerging Characterization and Remediation Technologies. Technology Overview: Interstate Technology and Regulatory Cooperation Work Group, DNAPLs/Chemical Oxidation Work Team. http://www.itrcweb.org/documents/DNAPLs-1.pdf. Last date accessed on July 18, 2012.pp. 1-79.

(ITRC) Interstate Technology & Regulatory Council. 2002. DNAPL Source Reduction: Facing the Challenge/Regulatory Guidelines: The Interstate Technology & Regulatory Council, Dense Nonaqueous-Phase Liquids Team. http://www.itrcweb.org/Documents/DNAPLs-2.pdf. Last date accessed on July 18, 2012. pp. 1-39.

(ITRC) Interstate Technology & Regulatory Council. 2003. Technical and Regulatory Guidance for Surfactant/Cosolvent Flushing of DNAPL Source Zones. Technical/Regulatory Guidelines: The Interstate Technology & Regulatory Council, Dense Nonaqueous-Phase Liquids Team. http://www.itrcweb.org/Documents/DNAPLs-3.pdf. Last date accessed on July 18, 2012.pp. 1-139.

(ITRC) Interstate Technology & Regulatory Council. 2004. Strategies for Monitoring the Performance of DNAPL Source Zone Remedies. Technical/Regulatory Guidelines: The Interstate Technology & Regulatory Council, Dense Nonaqueous-Phase Liquids Team. http://www.itrcweb.org/documents/dnapls-5.pdf. Last date accessed on July 18, 2012. pp. 1-205.

Irizarry, M. 2013. Trichloroethylene Volatilization Enhancement by Alcohol/Salt Cycled Injection in Unsaturated Clayey Soils. Written communication, October 2013. University of Puerto Rico at Mayagüez. pp. 1-124.

Jin, S., and P.H. Fallgren. 2010. Electrically induced reduction of trichloroethene in clay. *Journal of Hazardous Materials* vol. 173, pp. 200–204.

Johnson, D. N, J. A. Pedit, and C. T. Miller. 2004. Efficient, Near-Complete Removal of DNAPL from Three-Dimensional, Heterogeneous Porous Media Using a Novel Combination of Treatment Technologies. *Journal of Environmental Science and Technology,* vol.38, no. 19, pp. 5149-5156.

Jury, W.A.and R. Horton. 2004. Soil Physics, 6th Edition John Wiley & Sons, New York, pp. 390.

Khan, F.I., T. Husain, and R. Hejazi. 2004. An overview and analysis of site remediation technologies. *Journal of Environmental Management, vol.* 7, pp. 95–122.

Klute, A. 1986. Methods of Soil Analysis Part 1 Physical and Mineralogical Methods. Madison, Wisconsin. American Society of Agronomy, Inc., Soil Science Society of America.

Kosegi, J. M., Minsker, B. S., Member, A., ASCE, and Dougherty, D. E. 2000. Feasibility Study of Thermal in Situ Bioremediation. *Journal of Environmental Engineering*, pp. 601-610.

Kueper, B.H., G.P. Wealthall, J.W.N. Smith, S.A. Leharne, D.N. Lerner. 2003. An illustrated handbook of DNAPL transport and fate in the subsurface. R&D Publication 133. Environment Agency. Almondsbury, Bristol: Environment Agency Head Office.

Manager,I. 2006. Packed Bed Fluid Dynamics and CO2 Absorption Assignment. CBE Chemical Corporation, CE 428 Team. *Calibration curves for the air and liquid flowmeters in the gas absorption lab unit.* Spring 06 CO2 Absorption Assignment, Appendix 2, pp. 5.

Moran, M., J. S. Zagorski, and P.J. Squillage. 2007. Chlorinated Solvents in Groundwater of the United States, Environmental Science and Technology, vol. 41, no. 1, pp. 74-81.

National Research Council (NRC). 2000. Research Needs in Subsurface Science. Washington D.C: U.S. Department of Energy's Environmental Management Science Program, Board on Radioactive Waste Management Water Science and Technology Board. *National Academy Press*. pp. 1-186.

Nobre, M.M.M., and R.C.M. Nobre. 2004. Soil vapor extraction of chlorinated solvents at an industrial site in Brazil. *Journal of Hazardous Materials.* Vol. 110, pp.119–127.

(OEH-NSW) Office of Environment and Heritage of New South Wales. 2011. Management of Chlorinated Solvents. Strategic Environmental Compliance and Performance Review (OEH 2011/0642). Sydney, NSW: Office of Environment and Heritage of New South Wales in Australia, Compliance and Assurance Section. http://www.environment.nsw.gov.au/reso urces/licensing/110642chlorinatedsolvents.pdf. Last date accessed on July 28, 2012. pp. 1-27.

Padilla, I. 1998. Transport of Nonreactive and Voaltile Solutes in Unsaturated PorousMedia under Wetting and Draining Conditions. (Dissertation Thesis. University of Arizona).

Pankow J.F. and J.A. Cherry. 1996. Dense Chlorinated Solvents and Other DNAPLs in Groundwater, Waterloo Press, pp. 522.

Pantazidou, M., and N. Sitar. 1993. Emplacement of nonaqueous liquids in the vadose zone. *Water Resources Research,* vol. 29, pp. 705.

Rodriguez, S., I. Padilla, and S. Hwang. 2007. Development of a multi-scale packing methodology for evaluating fate and transport processes of explosive-related chemicals in clayey soils. *Detection and Remediation Technologies for Mines and Minelike Targets XII*, Proc. of SPIE, Vol. 6553, pp. 65531M-1.

Salabat, A. 2007. Liquid–liquid equilibria for the MTBE+water + salts systems at 298.15K, *Fluid Phase Equilibria, vol.* 257, pp. 1-5.

Schaerlaekens, J., J. Mertens, J.V. Linden, G. Vermeiren, J. Carmeliet, and J. Feyen. 2006. A multi-objective optimization framework for surfactant-enhanced remediation of DNAPL contaminations. *Journal of Contaminant Hydrology,* vol.86, pp. 176–194.

Shang, J., M. Flury, J.B. Harsh, R.L. Zollars. 2008. Comparison of different methods to measure contact angles of soil colloids. *Journal of Colloid and Interface Science*, vol. 328, pp. 299-307.

Sciencelab.com. 2010. Trichloroethylene MSDS, Material Safety Data Sheet. Houston, TX: Sciencelab.com, Inc. Last date accessed on July 16, 2012.

(SERDP & ESTCP) Strategic Environmental Research and Development Program and Environmental Security Technology Certification Program. 2004. DNAPL Source Zone Initiative. Annual Report. Alexandria, VA: U.S. Department of Defense, Strategic Environmental Research and Development Program & Environmental Security Technology Certification Program Annual Report. Meeting DOD's Environmental Challenges. pp. 1-15.

Siegrist, R., R. Oesterreich, L. Woods, and M. Crimi. 2010. Improved Monitoring Methods for Performance Assessment during Remediation of DNAPL Source Zones. Final Report Project ER-1490, v2. Department of Defense Strategic Environmental Research and Development Program (SERDP). pp. 1-101.

Sleep, B. E., P.D. and McClure. 2001. Removal of volatile and semivolatile organic contamination from soil by air and steam flushing. *Journal of Contaminant Hydrology, vol.* 50, pp. 21–40.

Sneddon, K.W., M.H. Powers, R.H. Johnson, and E.P. Poeter. 2002. Modeling GPR data to interpret porosity and DNAPL saturations for calibration of a 3-D multiphase flow simulation. USGS Open File Report 02–451. Denver, Colorado: U.S. Department of the Interior, U.S. Geological Survey. pp. 1-29.

Suthersan, S.S. 1999. Soil Vapor Extraction. Remediation engineering: design concepts. Boca Raton: CRC Press LLC. Ch. 3.

Switzer, C., T. Slagle, D. Hunter, and D.S. Kosson. 2004. Use of Rebound Testing for Evaluation of Soil Vapor Extraction Performance at the Savannah River Site. *Ground Water Monitoring & Remediation,* vol. 24, no. 4, pp. 106–117.

Tsai, T.T., C.M. Kao, A. Hong, S.H. Liang, and H.Y. Chien. 2008. Remediation of TCE-contaminated aquifer by an in situ three-stage treatment train system. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* vol. 322, pp. 130–137.

(USACOE) U.S. Army Corps of Engineers. 2002. Engineering and Design: Soil Vapor Extraction and Bioventing (EM 1110-1-4001). Engineering Manual, No. 1110-1-4001. Washington, DC: Department of the Army, US Army Corps of Engineers. pp. 1.1-11.7.

(USDA) U.S. Department of Agriculture. 2012. Natural Resources Conservation Service. Web soil Survey Interface. http://websoilsurvey.nrcs.usda.gov/app/WebSoilSurvey.aspx. Last date accessed on July 15, 2012.

(USEPA) U.S. Environmental Protection Agency. 2011. Toxicological Review of Trichloroethylene (CAS No. 79-01-6). (EPA/635/R-09/011F). Washington, DC: U.S. Environmental Protection Agency, In Support of Summary Information on the Integrated Risk Information System (IRIS). http://www.epa.gov/iris. Last date accessed on July 16, 2012.

Vargas, V. 2011. Development of testbed for assessment of enhanced soil vapor extraction of trichloroethylene in unsaturated clayey soil. Written communication, October 2011.University of PR, Mayagüez.

Weber, K., Braun, J., Greiner, P., Hofstee, C., Koschitzky, H. P., and Trotschler, O. 2002. Alcohol Flooding - An In-Situ Remediation Technology for the Saturated Zone (abstract). EGS XXVII General Assembly.

Wright, D. J. , J.A. Pedit , S.E. Gasda , M.W. Farthing , L.L. Murphy , S.R. Knight, G.R. Brubaker, and C.T. Miller. 2010. Dense, viscous brine behavior in heterogeneous porous medium systems. *Journal of Contaminant Hydrology,* vol. 115, pp. 46–63.

Appendix A: Pressure Transducer Sensors Calibrations

Calibration of Pressure Transducer Sensors

1. The Logger net 3.1.2 software and Data Logger CR23X Micrologger are used to obtain values of the difference in voltage in each Pressure Transducer (sensors). The procedure of calibration is explained, using the Figure 38 as reference. The list is show the number, in parenthesis, of the object mentioned in each step:
2. The sensors (4) are installed to manifold (3). The calibration setup shows 6 sensors, 3 of them are visible in the picture, but only 5 of them are used for the experimentation. For general knowledge, the main sensors for this calibration are the last 5 to the right.
3. Air vacuum (5) is applied to the manifold and the vacuum pump (1) controls the pressure in the system.
4. The valve of the system (6) regulates the pressure inside of the manifold creating a difference of voltage in the sensors.
5. Digital manometer (7) is connected to the sample port (2) of the system to corroborate the collected values.

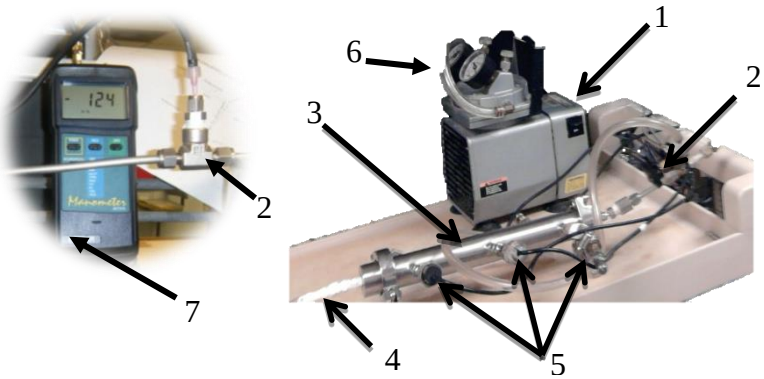


Figure 38 Sensors calibration instruments

The change in voltage data is collected by the sensor and sends to the Logger Net 3.1.2 in the computer, and then is analyzed in Excel. This calibration only takes in consideration the negative pressure because the pump in experiment is work in vacuum mode. Figure 39 provides the results obtained during the calibrations.

Results obtained during the calibration for Negative Pressure

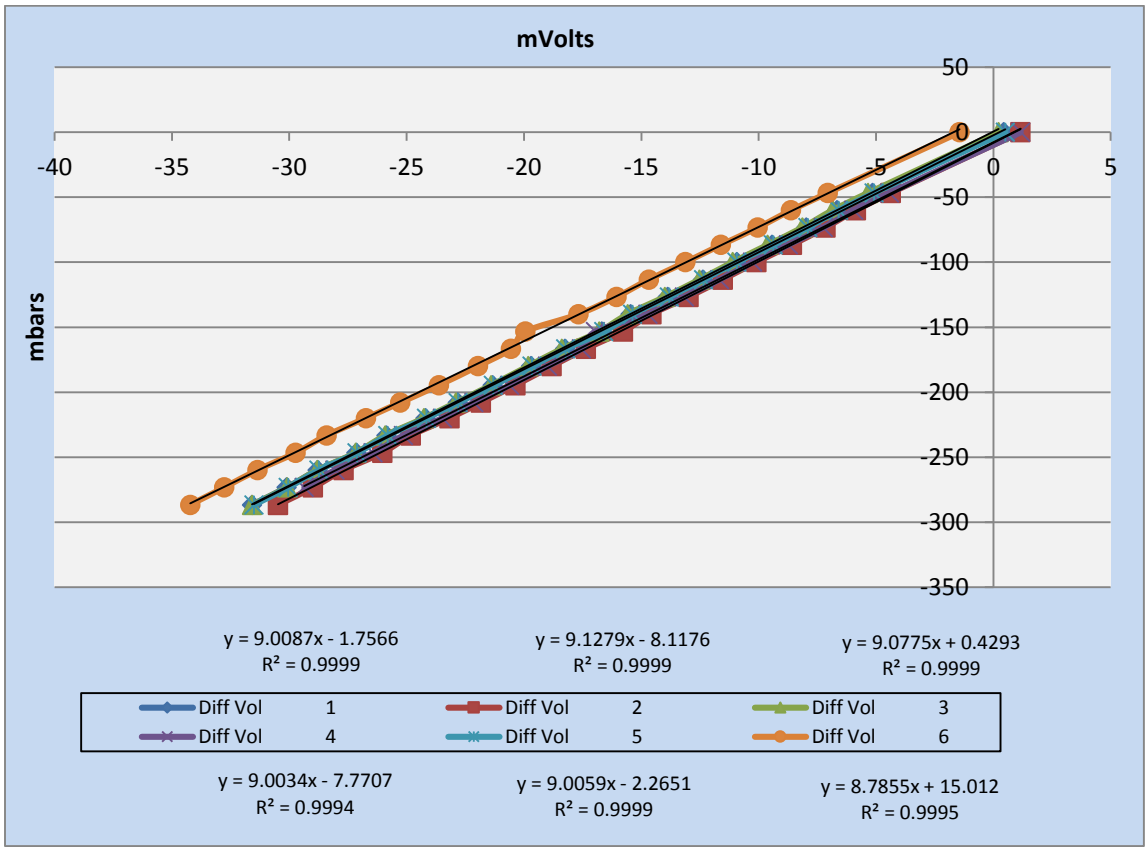


Figure 39 Sensors calibration chart for negative pressure

The Figure 39 show the results obtained for each sensor during the calibration. A linear pattern between pressure and difference in voltage are clearly illustrated in this graph. Due this linear pattern, a linear regression is applied to obtain the equations that describe the relationship between the pressure and difference in voltage. This equation gives the value of pressure of a particular voltage. Table 12 shows the correction factors for each

sensor during the calibration. Those factors are the equation slope and intercept from the linear regression in Figure 39.

Table 12 Correction factors for the sensors calibration

Factor	Sensor 1	Sensor 2	Sensor 3	Sensor 4	Sensor 5	Sensor 6
Multiplier	9.0087	9.1279	9.0775	9.0034	9.0059	8.7855
offset	-1.7566	-8.1176	0.4293	-7.7707	-2.2651	15.012

Appendix B: Air Flow Meter Calibration Data

The air flow meter calibration used the manufacturer conversion factor data sheet to convert the scale reading to a flow values (Manager, 2006). Table 13 shows the conversion factor to change from scale reading (mm) to flow (L/seg). This data was plotted to get the linear regression and its equation (see Figure 40). The flow was calculated using this equation and the corresponding unit conversion factor. Average air flow values obtained in each test are calculated using the linear regression equation and converted to L/min.

Table 13 Flow meter conversion factor

Calibration Curve for Gas Absorption Manostat 36-541-305 Flowmeters						
Scale reading (mm)	**Air Flow (cm^3/min)**		**Air Flow (ml/min)**		**Air Flow (L/seg)**	
	SS	Glass	SS	Glass	SS	Glass
150	65,898	23,564	65,898	23,564	0.4119	0.1473
140	60,615	21,997	60,615	21,997	0.3788	0.1375
130	55,146	20,247	55,146	20,247	0.3447	0.1265
120	50,086	18,425	50,086	18,425	0.3130	0.1152
110	44,897	16,751	44,897	16,751	0.2806	0.1047
100	40,051	14,970	40,051	14,970	0.2503	0.0936
90	35,557	13,153	35,557	13,153	0.2222	0.0822
80	31,086	11,452	31,086	11,452	0.1943	0.0716
70	26,848	9,793	26,848	9,793	0.1678	0.0612
60	22,505	8,080	22,505	8,080	0.1407	0.0505
50	18,296	6,494	18,296	6,494	0.1144	0.0406
40	14,257	4,973	14,257	4,973	0.0891	0.0311
30	10,227	3,512	10,227	3,512	0.0639	0.0220
20	6,469	1,976	6,469	1,976	0.0404	0.0124
10	2,897	545	2,897	545	0.0181	0.0034

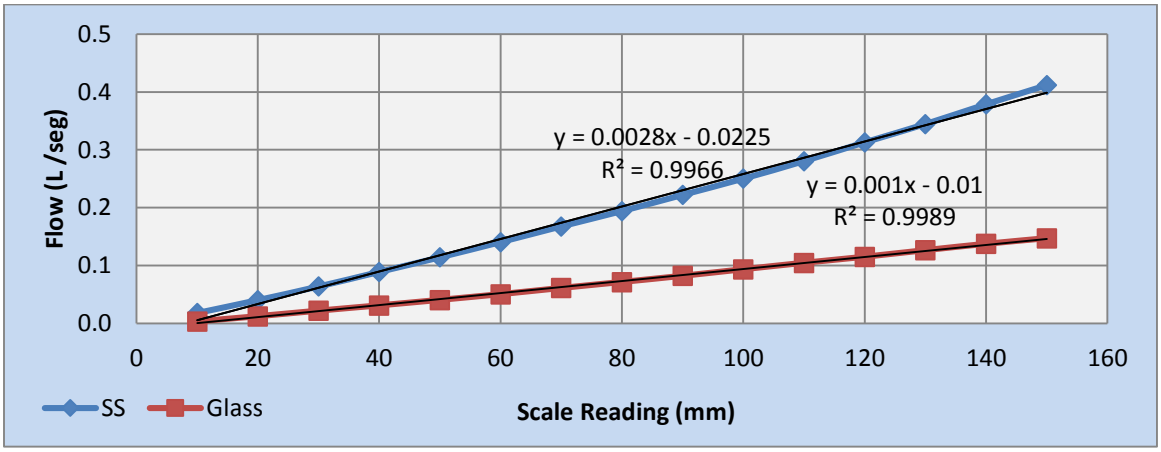


Figure 40 Flowmeter Calibration Curve for Air (Manostat 36-541-305)

Appendix C: TEGAM Thermocouples Calibration Data

The change in temperature data is collected by a thermometer, oven temperature display and the TEGAM Thermocouples later is analyzed in Excel. This information is used to create a graph, get the regressions and it equations. Using this equation and making simple computation, the real values of TI and T2 were obtained for each sample. This calibration only takes in consideration a short range of temperature measurements because the oven has a specific heat range capability. This is not the standard calibration methodology recommended by the manufacture. Due to the laboratory have limitations in equipments and materials availability, this alternative methodology is implemented.

Figure 41 shows two curves obtained from the data recollected during the TEGAM Thermocouples calibration test. A linear pattern is clearly illustrated in this graph for the thermometer vs. T2 temperature. Due this linear pattern, a linear regression is applied to obtain the equations that describe the relationship between the thermometer temperature and T2. In the case of T1 vs. thermometer the behavior doesn’t follow an exactly linear pattern, but a linear regression is applied also. The inconsistency of the temperature in this thermocouple (T1) is caused by systematic error due to the thermocouple wires are not exactly the same type and insulation.

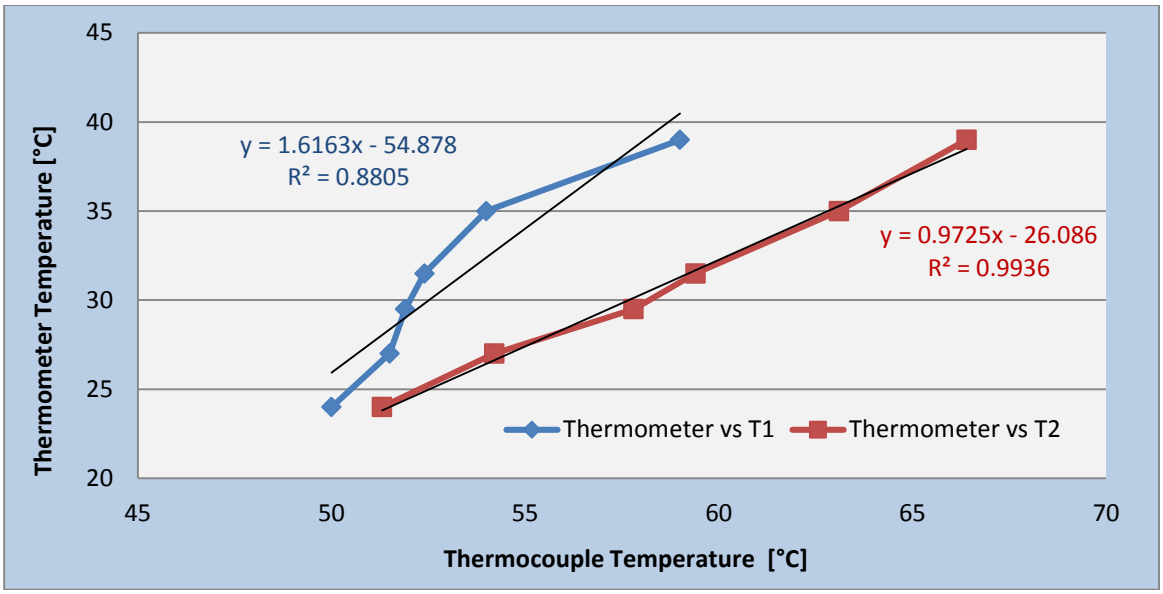


Figure 41 Thermocouples calibration curves

Appendix D: Copy of Written Communications

University of Puerto Rico at Mayaguez Campus
Civil Engineering and Surveying Department

Capillary Injection of Solutions in Compacted Clay Soil

Evian J. Delgado Santana
Inci 4998
Undergraduate Research
Prof. Ingrid Padilla

Executive Summary/ Abstract:

Capillary Injection of Solutions in Compacted Clay Soil

Evian Delgado[1] and Ingrid Padilla[1]
[1]Department of Civil Engineering and Surveying
University of Puerto Rico, Mayagüez, PR

Remediation of contaminated in low permeability zones is extremely difficult and costly due to mass transfer limitations of contaminants in the zone. 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. Capillary-based delivery is quantified by placing stainless steel porous membranes (40 and 100 µm) in compacted clay columns. Water was delivered at positive, atmospheric, and negative pressures at point of entry, while measuring cumulative volume injected, and time and depth of water to diffuse a radial distance of 3.6 centimeters. Delivery homogeneity was assessed through visual methods. Preliminary results indicate that the water preferentially enters zones of low permeability. The water distribution initially follows a heterogeneous distribution, but it becomes more homogeneous at later times. The results show that capillary-based delivery can be used to preferentially deliver reactants to tight formations. Further work is being conducted to optimize delivery conditions.

Appendix E: Examples of the Capillary Injections Results

Example the $CaSO_4$ + $CaCl_2$ Injection Procedure

To prepare the brine solution concentration simples calculations are done. Table 14 shows an example of the data used to calculate the concentrations of each salt. Table 15 are shows the instruments and it characteristics used to perform this capillary injection.

Table 14 Data and Calculation to prepare the brine solution concentrations

Solution:	$CaCl_2$	
MW:	110.98	g/mol
Concentration	0.6	(M) mol /L
Distilled Water	2	L

$$\frac{110.98\,g}{mol} \text{ x } \frac{0.6\,mol}{L} = \frac{66.588\,g}{L} \text{ x2L} = 133.176\,g\,CaCl_2$$

Solution:	$CaSO_4$	
MW:	136.14	g/mol
Concentration	0.005	(M) mol /L
Distilled Water	2	L

$$\frac{136.14g}{mol} \text{ x } \frac{0.005mol}{L} = \frac{0.6807g}{L} \text{ x2L} = 1.3614gCaSO_4$$

Table 15 Characteristics of the instruments used during the injection process

Burette:	50	ml
Hoses:	-	cm
Pump:	-	ml/m
Speed Controller:	3	level
HM Pipette:	265	ml

The injection process follows the methodology described previously in this report. This procedure consists in fill a burette and a HM Pipette with an initial volume, and adds an additional quantity of solution during a period of time (see Table 16). The initial solution volume is 45 mL to the burette and 65 mL to the HM Pipette. This initial volume is delivery in a certain period of time. When the last 45 mL are close to the line of reference, more solution is added. To maintain a control rate of the solution delivery and keep the level of the fluid very close to the reference line, the burette constantly fill the HM Pipette. This process is performed during a specific period of time. This add volume vary between 45

to 60 mL and depend in which period of time is added. The solution is added constantly until the fluid reach the bottom of the TCE contaminated layer.

The result show that approximated 950 mL of solution are enough to reach the bottom of the TCE contaminated layer. In other words, when the volume added reach 950 mL the injection process can be stopped.

Table 16 Example of the brine solution injection process

Initial Solution Volume in Burette (ml)=	45	**Initial Solution Volume in HM Pipette (ml)=**	65
Period	**Time**	**Solution Volume (ml)**	**Add Volume (ml)**
1	11:35 AM	65	45
2	11:36 AM	110	45
3	12:10 PM	155	45
4	12:40 PM	200	45
5	1:05 PM	245	33
6	1:40 PM	278	45
7	2:05 PM	323	45
8	2:40 PM	368	45
9	3:15 PM	413	45
10	3:25 PM	458	19
11	4:05 PM	477	45
12	4:45 PM	522	55
13	5:20 PM	577	50
14	6:00 PM	627	60
15	6:35 PM	687	65
16	7:20 PM	752	65
17	8:00 PM	817	60
18	8:25 PM	877	55
19	9:00 PM	932	18
20	9:30 PM	950	-
Total Time (hr):	**10**	**Total Add Volume (ml):**	**950**

Example of the $CaSO_4$ + $CaSO_2$ + Methanol Injection Process

This injection process follows the same methodology describe in the brine solution capillary delivery procedure with a few modifications. Table 17 shows an example of the data used to calculate the concentrations of the brine solution and the alcohol. In Table 18 are shows the instruments and it characteristics used to perform this capillary injection.

In this case, a Tedlar bag of 2,000 mL is filled with only 950 mL of solution. The air inside the bag is taking out to prevent methanol volatilization due to the air head space. This bag is connected to the injection wells as the same way of the brine solution process. When the system setup is done, the capillary delivery start and the solution is drain from the bag to the injection wells (see Table 19). To maintain a control rate of the solution delivery and keep the level of the fluid very close to the reference line, the bag is placed over a flat surface and constantly moved. This process is performed during a specific period of time. The solution is added from the bag until the fluid reach the bottom of the TCE contaminated layer.

Table 17 Data and calculation to prepare the brine solution and methanol concentrations

Solution:	CH_3OH	
MW:	32.04	g/mol
Diluted	10%	
Distilled Water	2	L

10 % of Methanol = 200 Ml
90 % of distilled water = 1800 mL

Solution:	$CaCl_2$	
MW:	110.98	g/mol
Concentration	0.6	(M) mol /L
Distilled Water	2	L

$$\frac{110.98\,g}{mol} x \frac{0.6\,mol}{L} = \frac{66.588\,g}{L} x2L = 133.176\,g\,CaCl_2$$

Solution:	$CaSO_4$	
MW:	136.14	g/mol
Concentration	0.005	(M) mol /L
Distilled Water	2	L

$$\frac{136.14g}{mol} x \frac{0.005mol}{L} = \frac{0.6807g}{L} x2L = 1.3614gCaSO_4$$

Table 18 Characteristics of the instruments used during the injection process

Tedlar Gas Sample Bag	2000	ml
Hoses:	-	cm
Pump:	-	ml/m
Speed Controller:	3	level

Table 19 Example of the brine solution and methanol injection process

Initial Solution Volume in Tedlar Gas Sample Bag (ml)=	950	**Initial Solution Volume in Burette (ml)=**	0

Period	Time	Solution Volume (ml)	Add Volume (ml)
1	11:35 AM	950	0
-	-	-	-
2	10:30 PM	950	-
Total Time (hr):	**11.0**	**Total Add Volume (ml):**	**950**

Appendix F: Example of the Pneumatic Data

During each tests a few pneumatic parameter are monitored periodically. This pneumatic data is collected from the pressure transducer sensors, TDR, potable digital manometer; vacuums pump pressure gage and flow meter scale reading.

Before the vacuum pump start to extract, the initial values of the pressures transducer sensors are obtained (see Table 20). These values are used to normalize the values obtained from the data logger. Once the extraction began, the values of the pressure sensors drop instantly. This pressure drop is caused by the applied vacuum. The values obtained in each sensor during the test maintain a consistency pattern. Table 20 shows an example of how the pressures values vary according to the location of the sensors. The variation between each sensor is calculated to monitored if inside the column have irregular pressure drop behavior (see Table 21).

Another parameter monitored during each test are the; pressure using a potable manometer and pump pressure gage, and air flow using a flowmeter. An example of this recollected data are show in Table 22.

Table 20 Example of the data provide by the pressure transducer sensors and TDR

Sensors	Initial Value(mbar)	Data logger (mbar)	Results (mbar)	TDR	
2	-42.4	-105.9	-63.5	**VW**	**PA**
3	-2.2	-78.7	-76.5	-0.1	0.6
4	-4.2	-80.4	-76.2		
5	-8.7	-82.3	-73.6		
6	0.8	-73.4	-74.2		

Table 21 Example of the pressure differences provided by the transducer sensors

ΔP Sensor 2 & Sensors 5-6 (mbar)	-10.4
ΔP Sensor 2 & Sensors 3 (mbar)	-13.0

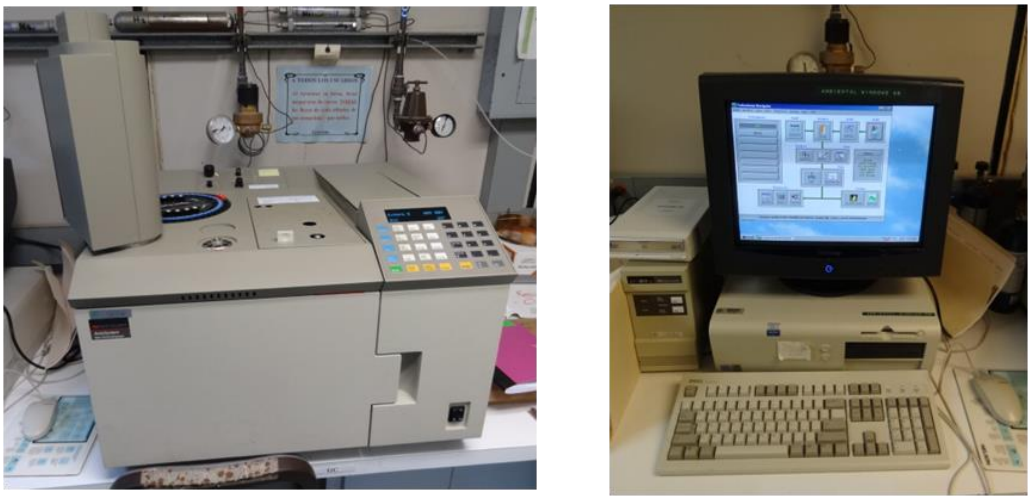
ΔP Sensor 2 & Sensors 4 (mbar)	-12.7
ΔP Sensor 5-6 & Sensors 3 (mbar)	-2.6
ΔP Sensor 5-6 & Sensors 4 (mbar)	-2.3

Table 22 Example of the data provide by the digital manometer, vacuum pump gage and flowmeter

Manometer (mbar):	-70			
Pump (mm/Hg):	-160	=	-213.3	mbar
Flowmeter (mm):	48	135		

Appendix G: TCE Calibrations

To have standards and ensure quality control, sample control calibration will be performed before and after each test in the GC Equipments (see Figure 42 and Figure 43). Figure 44 shows an example of the data obtained from the GC to perform the sample control calibration process. This calibration guarantee that the GC is running properly and the sampling in each test respond appropriately. Also this information is used to calculate the concentration of the extracted sample during each test.



(a) (b)

Figure 42 (a) Gas chromatograph (b) PC software

Figure 43 ValcoBond (VB-) Column

Table 23 shows an example of the data recollected during the calibration tests. This information is used to create a graph, get the regression and it equation (see Figure 45). Using this equation and making simple computation, the concentration for each sample can be obtained.

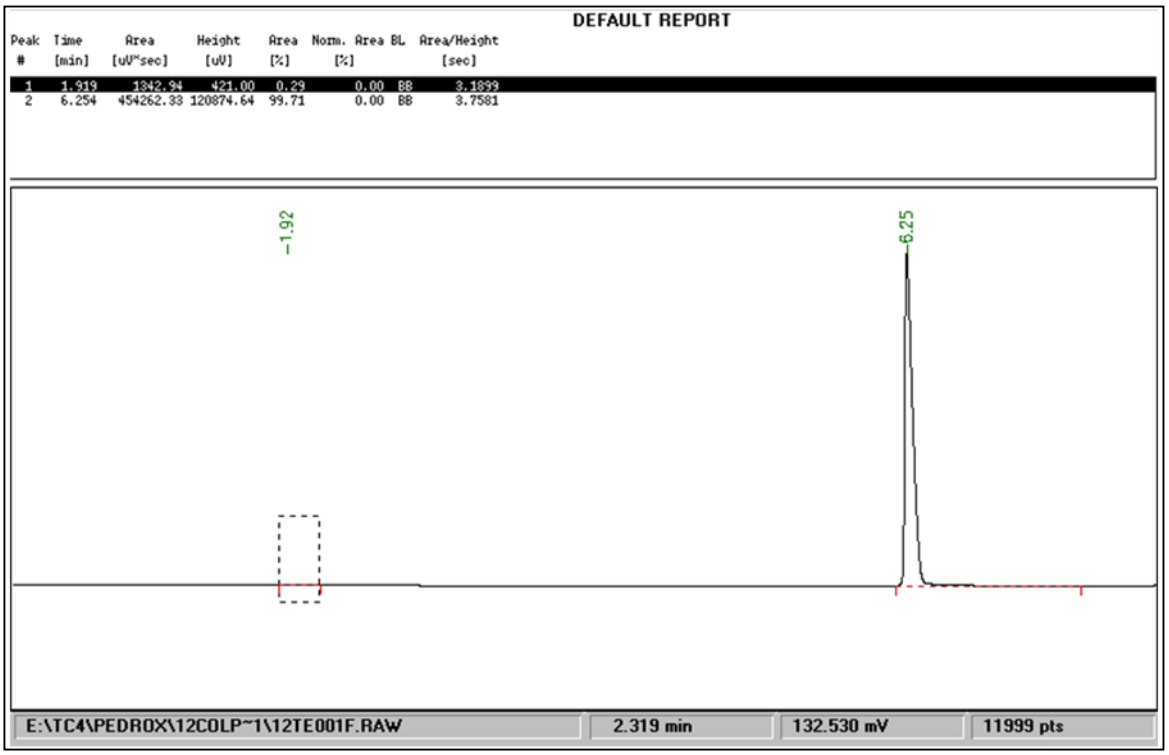


Figure 44 Example of the peak report obtained from the GC

Table 23 Example of a control calibration data

	Concentration in Air (mg/L)	TCE (uL)	Time in the Bottle (hr:min)	Time of the Peak (min)	Area (uV.s)
Cal 0	0.00	0.00	1:00	0	0
Cal1	3.74	2.6	1:20	6.257	19,252.97
Cal2	37.4	25.6	1:40	6.256	57,916.23
Cal3	168.3	115.3	2:00	6.246	287,608.00
Cal4	224.4	153.7	2:20	6.234	402,158.26
Cal5	276.76	189.6	2:40	6.236	537,931.33
Cal6	336.6	230.5	3:00	6.227	735,634.97

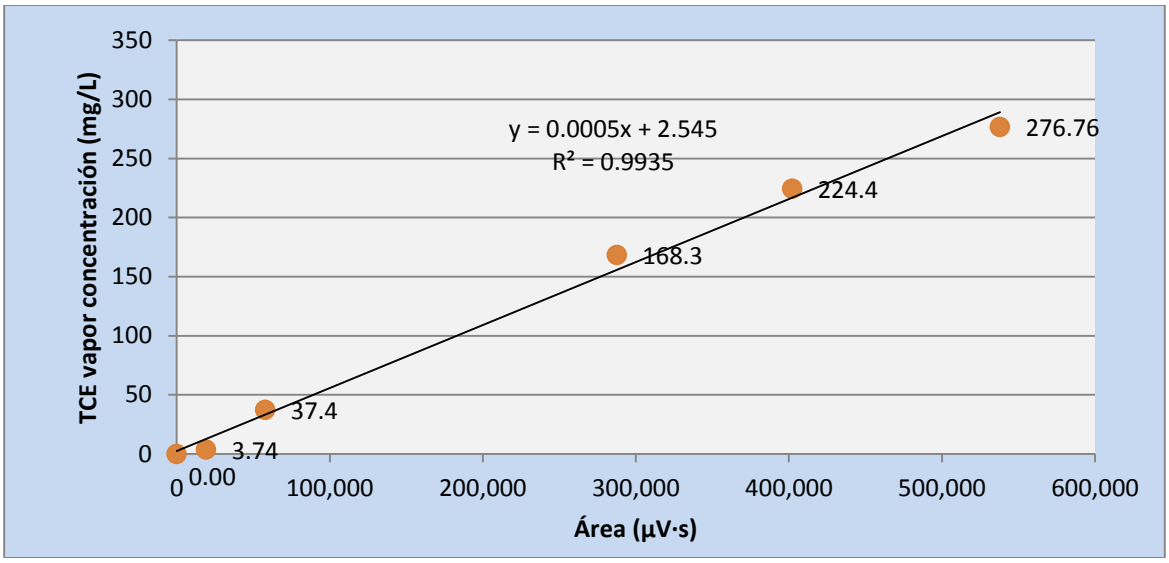


Figure 45 Example of the TCE vapor concentration calibration curve

The results obtained during all the calibration tests are plotted in the same graph to compare each sampling. Figure 46 shows the results of all the calibration curves obtained during this project. These curves provide an idea how good is the calibration data between each experiment and it linear behavior.

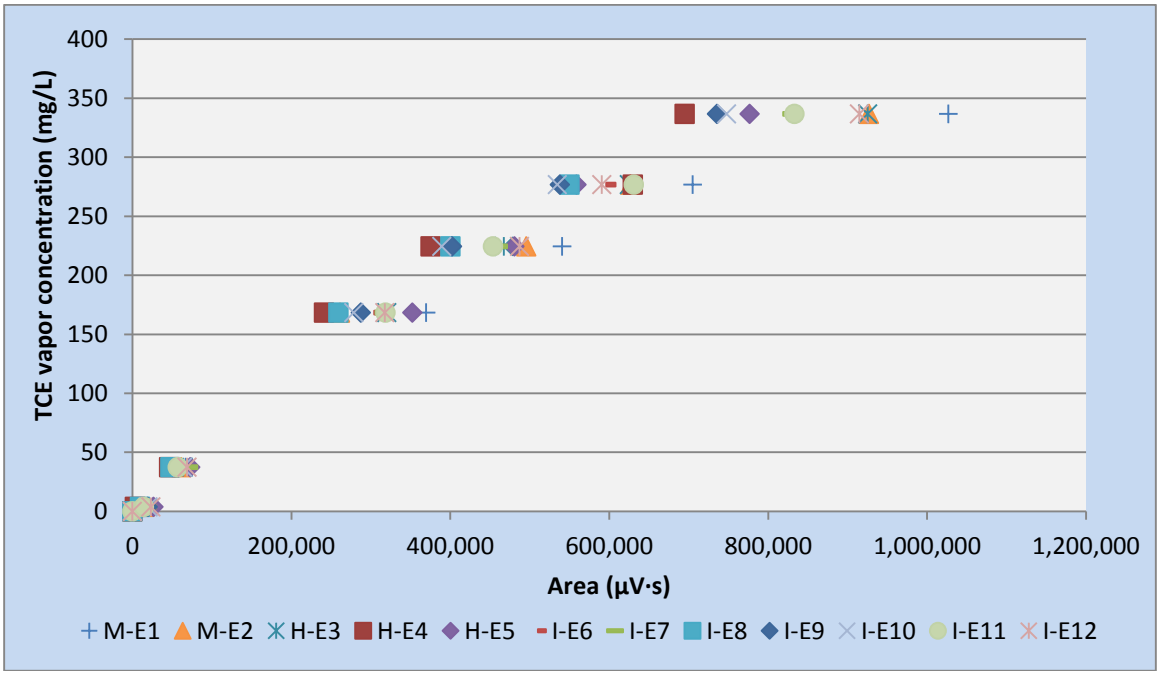


Figure 46 Results obtained during the TCE calibration testsm