Demonstrating the Feasibility of Polyethylene Passive Samplers for Quantitative Assessment of Volatile Organic Compounds in Soil

by

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B.S. in Chemical Engineering
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Submitted to the Department of Civil and Environmental Engineering in partial fulfillment of the requirements for the degree of

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Abstract

A quantitative assessment of the nature and extent of volatile organic compounds (VOCs) in soil vapors is a valuable tool, as these chemicals are pervasive and a health concern at many contaminated sites. Motivated by the successful use of polyethylene (PE) passive samplers in sediments, this research focused on demonstrating the feasibility of PE samplers to accurately assess volatile organic compounds in soil vapors. Experimental values of PE-water partitioning coefficients (K_{pew}) for benzene, toluene, ethyl benzene, and *ortho*-xylene (BTEX) were determined. A benchtop experiment in a controlled environment was performed, which consisted of a jar of sand with known amounts of trichloroethylene (TCE) and tetrachloroethylene (PCE). The concentrations of the TCE and PCE were measured using the PE passive sampler and compared to mathematically estimated results. Finally, the PE passive samplers were tested in an actual site at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) and showed consistent results with the available data. The results of this thesis demonstrated that the PE passive sampling is a promising technique to measure VOCs in soil vapors.

Thesis Supervisor: Philip M. Gschwend
Title: Ford Professor of Civil and Environmental Engineering

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Chapter 1

Introduction

1.1 Volatile Organic Compounds in the Environment

In 1986 the United States Congress authorized the Environmental Protection Agency (EPA) to regulate underground storage tanks (USTs). Until the mid-1980s most of these tanks were made of plain steel. Over time, UST contents leaked into the environment due to corrosive nature of steel.[1] Flawed installation or inadequate operating and maintenance procedures also caused USTs to release their contents into the environment. As of September 2014, there were over 570,000 active USTs with potential hazard from a substance that can leak into the soil and contaminate groundwater, the source of drinking water for nearly half of all Americans. The EPA has reported between 6000 and 7000 confirmed releases of contaminants by registered USTs annually since 2009.[2] A leaking UST substance can present health and environmental risks, including the potential for fire and explosion. Thus, the potential for the release of volatile organic compounds (VOCs) to our natural environment is prevalent, and it is important to be able to quickly and accurately measure and evaluate the impacts of leaks and spills.

1.2 Migration of Volatile Organic Compounds via the Vapor Intrusion Pathway

Depending on properties of the contaminant and the soil, the bulk free phase the organic liquid flows down through an unsaturated zone by gravity leaving residual free phase product in the soil pores. Some of the spilled substances can reach the water table where they partially dissolve into the groundwater and get transported down gradient by advection. Low molecular weight volatile compounds evaporate from the original spill or from the contaminated groundwater and get transported largely by diffusion or advection to the ground surface.

The migration of these vapor chemicals from any subsurface source into overlying buildings is called vapor intrusion. Vapor-forming volatile organic compounds such as petroleum hydrocarbons and chlorinated solvents in soil, ground water, sewers and drain lines may transfer via a vapor intrusion pathway into buildings and other enclosed spaces and pose threats to indoor air quality (Figure 1-1).

The accumulated vapors in dwellings or occupied buildings may pose acute health effects or near-term safety hazards including explosions. Even though most vapor intrusions result in relatively low concentrations of contaminants in indoors air, because humans may spend a long time inside buildings and breathe a large volume of air, toxic chemicals can result in unacceptable levels of risk.[3]

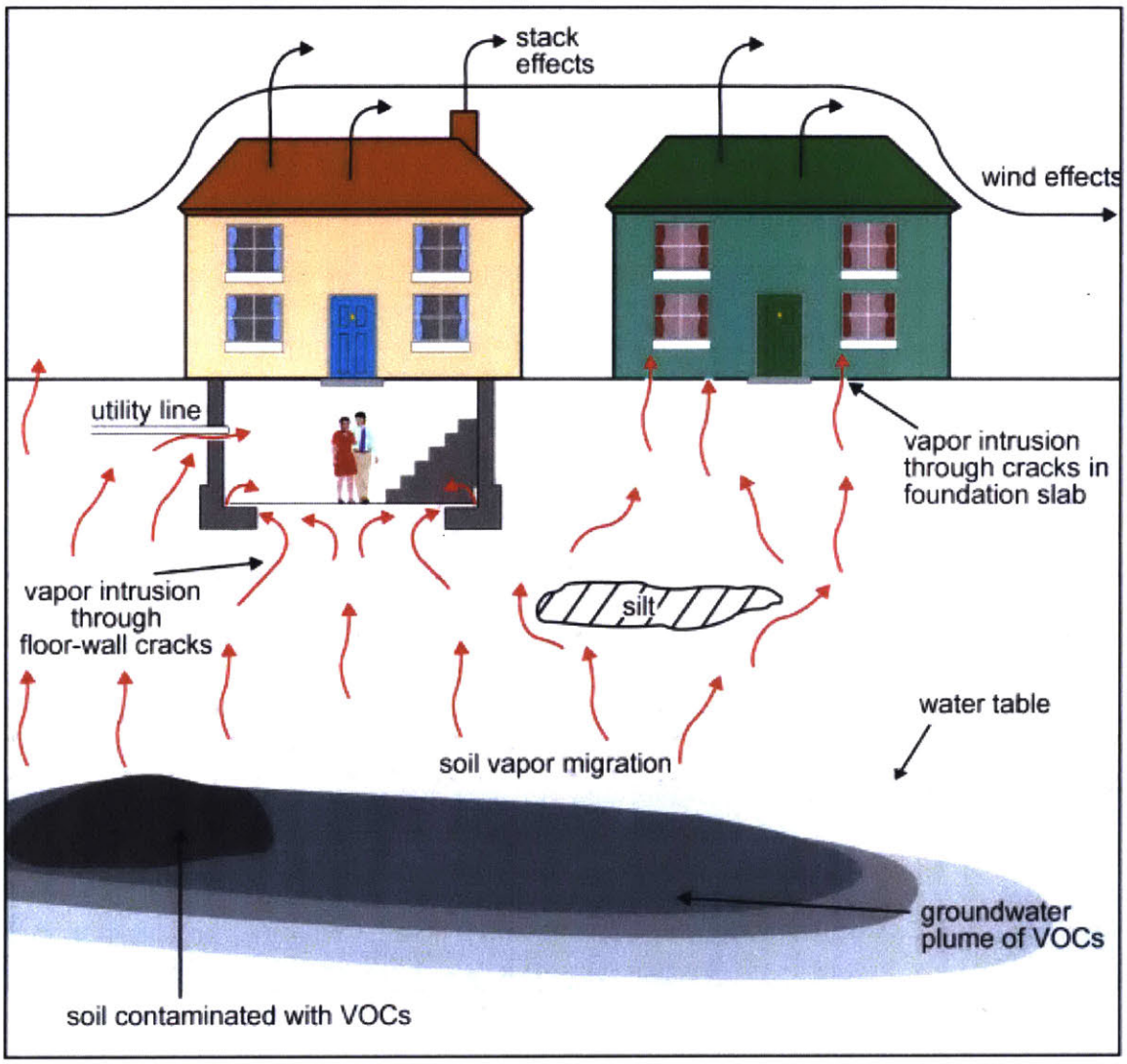

***Figure 1-1**: Illustration of soil gas migration through potential vapor intrusion pathways from contaminated soil and groundwater to indoor air. The process of vapor intrusion might be induced by atmospheric conditions and ventilation system of buildings.*[4]

1.3 Overview of an Environmental Risk Assessment of Volatile Organic Compounds and Its Current Limitations

Only some of these discharged substances in the soil present an intolerable risk to humans and the environment. According to the United States Environmental Protection Agency's policies, it is essential to measure: (a) the inherent toxicity of the spilled chemical, (b) the exposure a receptor has with the contaminated medium, and (c) the amount of the chemical present in an environmental medium to fully assess of the risk posed at a contaminated site. Many models have been developed as an attempt to estimate the risk that subsurface contaminants pose to people in overlying buildings through vapor intrusion. One method would be directly measuring indoor air or sub-slab vapor concentrations, but in this second case there would still be a need to estimate transport into the building. If there is no access to a building or if the building is to be constructed, then one must use a model that can estimate soil gas concentrations to predict potential health risks.

In most of the vapor intrusion models the mass transport of the soil gas is largely governed by molecular diffusion, which is driven by concentration gradients.[5] Provoost et al. states that inconsistency between current assessment models and direct measurement methods of soil vapor concentration is prevalent.[3] When seven approaches commonly used to translate total soil concentrations into corresponding soil vapor concentrations were compared, most of them were found to overestimate the observed soil gas concentrations.[3] On average the deviation was less than an order of magnitude, but sometimes it was nearly four orders of

magnitude or greater (Figure 1-2).

This inconsistency in soil gas concentrations shows inaccuracy either in the screening models or in current direct measurement techniques. This is not surprising as the individual complexities of each site make predicting soil gas concentrations imperfect. Nevertheless, this also shows the necessity of developing better sampling techniques to estimate soil vapor concentrations to improve risk assessment accuracy.

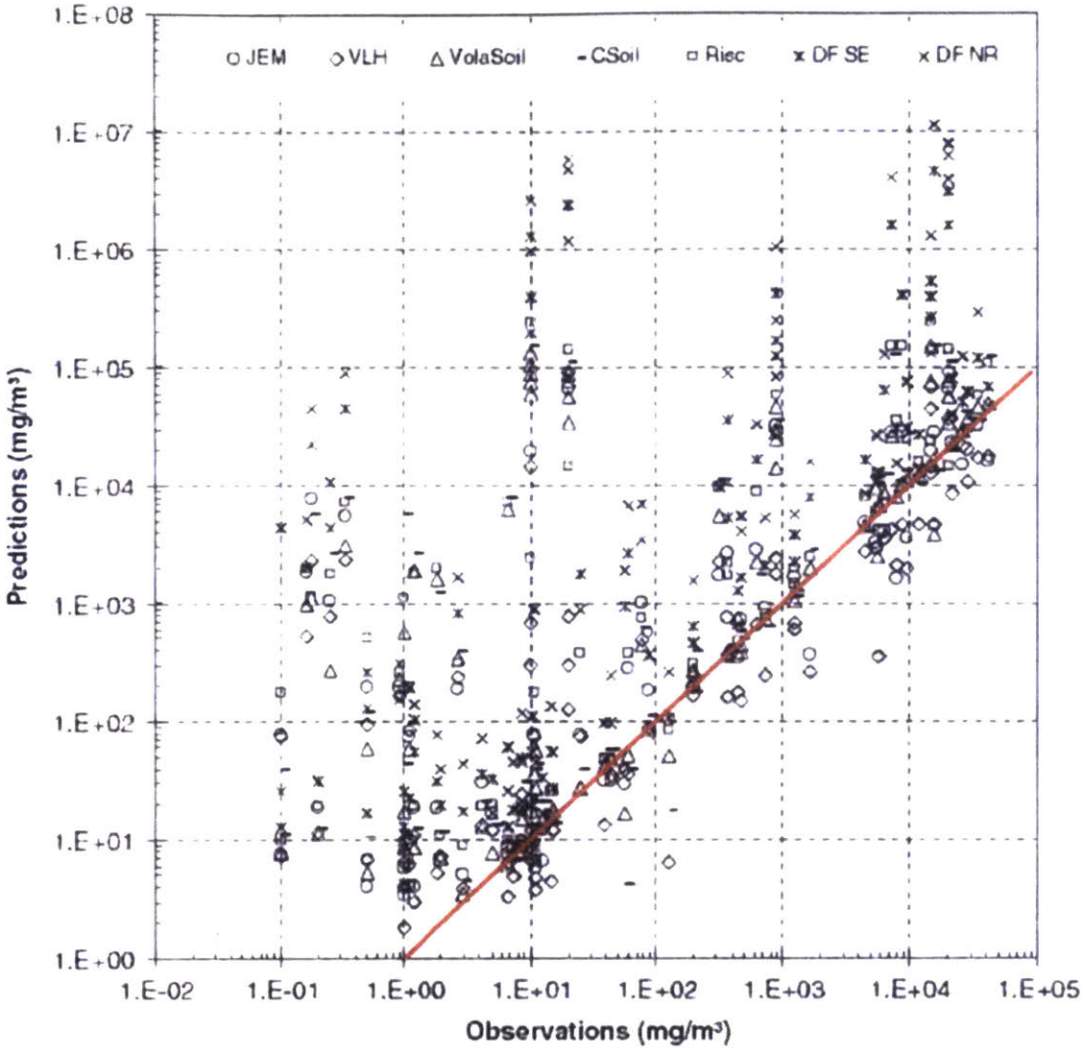

***Figure 1-2**: A plot of predicted soil vapor concentrations from seven commonly used models versus directly measured concentrations. Most of the models found to overestimate the observed soil gas concentrations.*[3]

1.4 Soil vapor measurement techniques

Commonly soil gas concentrations were found by extrapolating from bulk soil concentrations, but this technique often overestimated actual vapor concentrations. Also, there were significant losses of VOCs during the sampling process.[6] Consequently, a technique that directly samples the soil gas by pumping it out of the ground was developed. It is currently the most common used method as well as accepted by regulators as a reliable approach to measure soil gas concentrations.[6] Active gas extraction uses a hollow probe that is inserted into the soil to the desired depth. The soil gas gets pumped into a sampling container through the probe tip. An advantage of active sampling method is that the soil gas is measured directly and can be done as quickly as 10 to 30 samples per day.[6]

Nonetheless, active sampling has its own disadvantages, as the initial withdrawal of soil gas is essential for this technique in order to purge the system. The collected air may come from a distance far away from the probe tip leading to inaccurate sampling at the location of the prove. This limitation is particularly problematic for cases when there are preferential pathways in the soil. The vacuum needs to be applied to the subsurface while sampling, which in its turn may disturb equilibrium sorption or liquid-gas partitioning conditions. Contaminants might be forced to partition out of other phases leading to inaccurate measurement of soil gas concentration. Furthermore, active sampling has a fairly complicated mechanical setup, thus a trained operator and numerous quality control practices are needed throughout the sampling process.[7]

Passive sampling is an alternative method that utilizes the difference in chemical potential of the sampler phase and the environmental media. That difference is what moves contaminants into the passive samplers. These techniques have been quickly emerging for the past 20 years, and are widely used for monitoring pollutants in air, water, and sediment. Passive samplers have many significant advantages, including simplicity, low cost, no need for expensive and complicated equipment, no power requirements, unattended operation, and the ability to produce accurate results.

The deployment time of passive samplers in the soil may vary from a day to a couple weeks. Once the sampler is collected, the contaminants are extracted from the sampler and analyzed. A distinct advantage of this method over active gas sampling is that it does not forcefully remove soil gas. Passive samplers should work well in a wide range of soil types for various VOCs. Besides, passive samplers measure a time-averaged concentration of contaminants and avoid potential collecting of unrepresentative extreme variances in concentrations.[8]

An adsorbent such as activated carbon is used as a passive sampler in air environments.[9] The adsorbent has a barrier that allows vapors to penetrate through but prevents solids and sometimes liquids.[9] An absorbent phase surrounded by a membrane has been used in surface water and sediment pore water sampling.[10] Target chemicals partition from the soil into a single phase or diffuse through the membrane and into the absorbent. These samplers consist of lipid filled polyethylene tubes and are thought to better measure the bioavailability of contaminants.[10]

1.5 Quantitative Passive Sampling

The general profile of passive sampler's chemical uptake from the environment is relatively well understood. Once the sampler is deployed, there is a period of nearly linear uptake to the sampler (Figure 1-3), given that it contains a near zero concentration of the target chemicals.[16] A curvilinear region begins after this initial period and uptake considerably slows down as the sampler approaches equilibrium. Lastly, after a sufficient deployment time, the sorbent will reach equilibrium with the surrounding environment and the concentration in the sampler will remain constant.

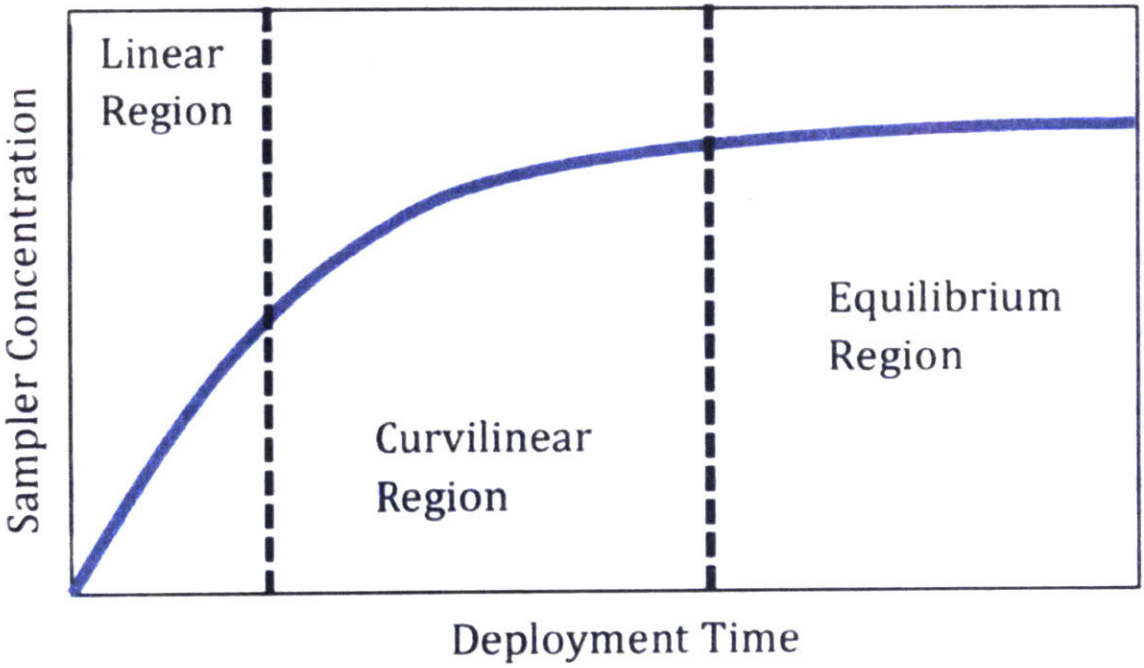

***Figure 1-3**: A passive sampler's uptake concentration over deployment time. The uptake starts almost linearly and reaches a plateau at an equilibrium region*[11]

Once equilibrium is reached, the concentration in the target medium is calculated from the measured concentration in the sampler and the chemical's partitioning coefficient between the sampler medium and the air. However, disadvantages are potentially long deployment times and the scarce of information on kinetics of the uptake.[12]

Another method of quantitative passive sampling involves impregnation of performance reference compounds (PRCs) in polyethylene (PE). It was originally introduced for measurements of bioavailable contaminant concentrations in surface waters and sediments.[13, 14] The PRC has similar chemical and physical properties to the target contaminant and is preloaded into the PE passive sampler at known concentration. Once the sampler is deployed in the target medium, the PRC diffuses out of it at the same rate as the target chemical diffuses in. When the sampler is removed and chemicals are extracted, the concentrations of both the remaining PRC and the target chemical are measured. The fraction of PRC mass that has diffused out of the sampler is then proportional to the mass of target chemical absorbed into the sampler (Figure 1-4). With an assumption that the sampling rates of the PRC and the target chemical are equal, this method captures any changes in the sampling rate over the deployment time.[15]

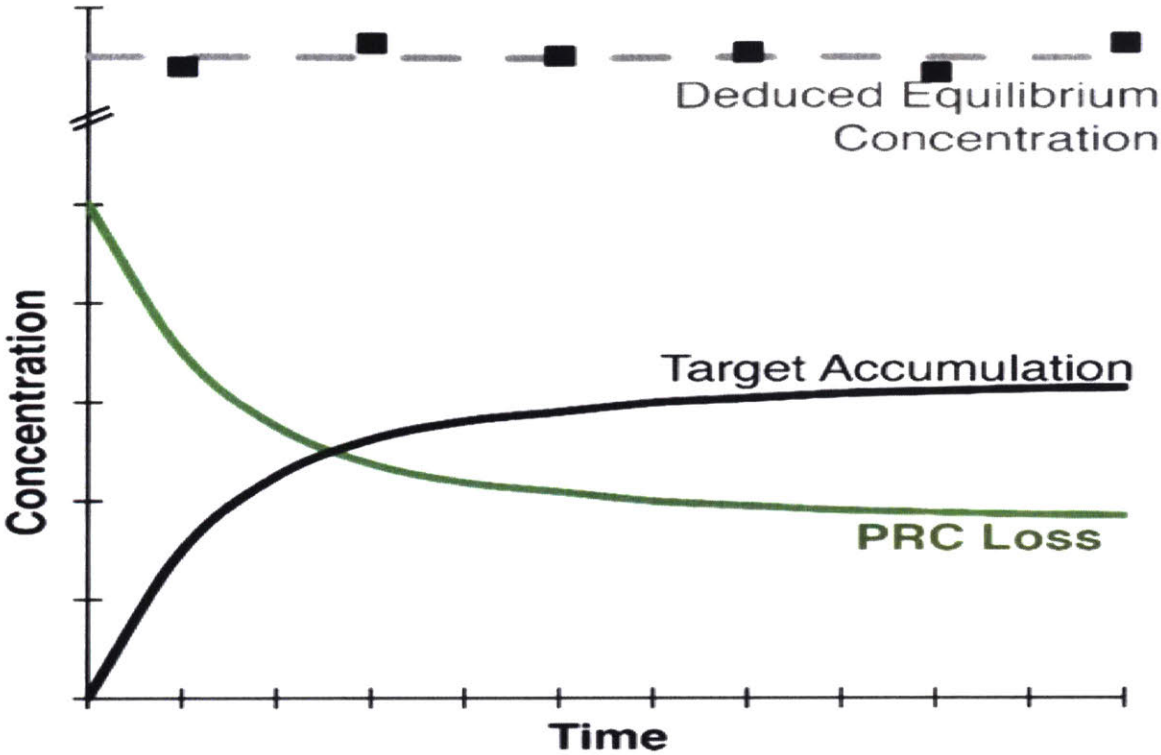

***Figure 1-4**: Concentrations of a performance reference compound and a target chemical in a passive sampler versus the deployment time. Graph shows that the equilibrium concentration of the target chemical can be found at any time given that the PRC has the similar chemical and physical properties as the target compound.*[15]

In light of this previous progress, the main objective of this project is to investigate a polyethylene passive sampling method for soil gas applications and to demonstrate that this method can improve the agreement between predicted and measured concentrations.

1.6 Project Motivation

The recent research validated an advantage of polyethylene (PE) passive samplers with performance reference compounds PRCs in porous media like water-saturated sediments. Porewater concentrations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediments were measured using PE sampler with a corresponding 1D diffusion model.

This model predicts the change in mass of a target chemical or PRC in the sampler with deployment time. Using a PRC for every target compound is expensive and cumbersome. Thus, the 1D diffusion mass transport model generated a linear regression from a small number of PRCs. This regression is used to infer necessary mass transfer properties for any other target chemicals.[15, 16]

To generate this regression, the diffusion model used measured PRC data to determine a partitioning constant between the bulk sediment and water, which was then plotted against the PRCs' octanol-water partitioning coefficient (K_{ow}). Thus, using a known K_{ow} value of a target compound and the regression, the sediment-water partitioning coefficient can be estimated.

Furthermore, later studies demonstrated that equilibrium concentrations in sediment porewater could be accurately determined using PE sampler removed at several different times prior to equilibrium (Figure 1-5). This research confirmed the ability to use a regression generated from the 1D diffusion mass transfer model to infer chemical transport properties. Using these inferred properties one can calculate PE deduced concentrations that reasonably matched measured

equilibrium values.[15]

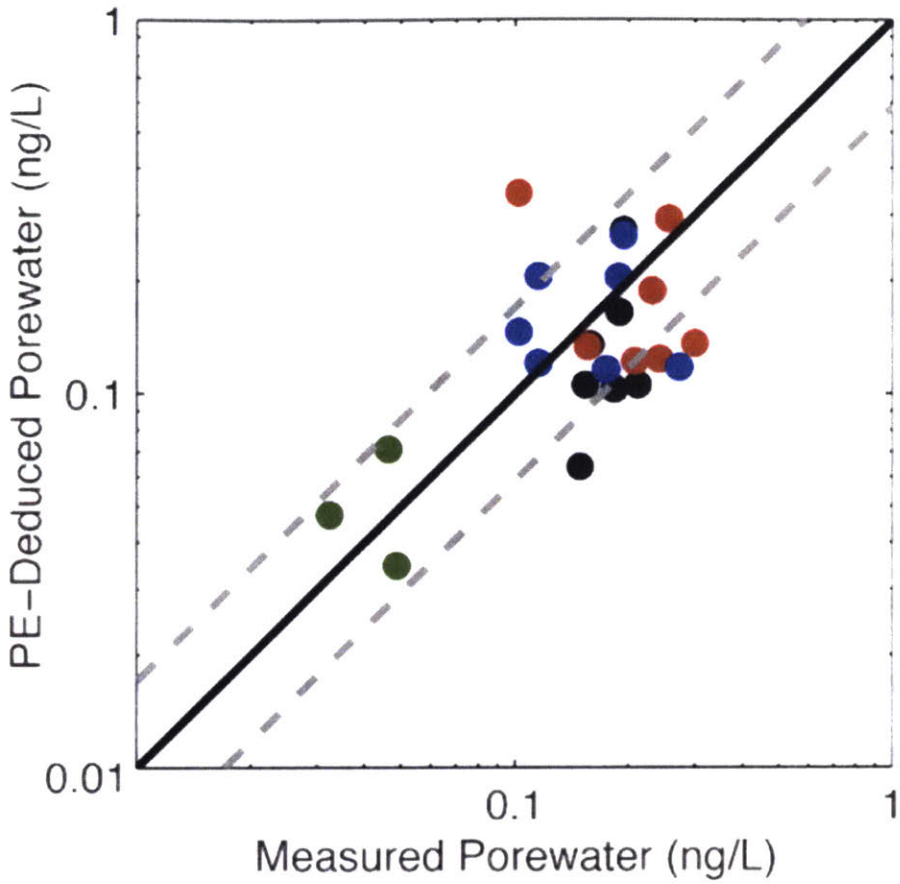

***Figure 1-5**: PE-deduced versus measured porewater concentrations for three PCB congeners in 7 different sediments from Lake Cochituate.[15]*

Motivated by the successful use of PE passive samplers in sediments, this research focused on demonstrating the feasibility of PE samplers to accurately assess volatile organic compounds in soil. First, the accurate measurements of experimental values of PE-water partitioning coefficients (K_{pew}) for target VOCs were determined. Second, a benchtop experiment in a controlled environment was performed. Last, the PE passive samplers were tested on an actual site.

1.7 Overall Description of Project Milestones

Passive sampling for soil vapor takes an absorptive polyethylene and places it underground for a period of time to allow the VOCs to diffuse into it. The PE-water partition coefficient (K_{pew}) is a key parameter for calculations, thus it is crucial to accurate K_{pew} for target VOCs. The experimental values of K_{pew} for benzene, toluene, ethyl benzene, and xylene (BTEX) were determined, detailed description of which will be in Chapter 2. To validate the results and to see how accurately these values can be measured in our lab, the our K_{pew} values were statistically compared with the K_{pew} values found by our Italian colleagues from Eni S.p.A., who use a somewhat different method of VOC measurement.

The next objective involved developing an experimental physical model for benchtop testing. A known mass of contaminant was added into a jar filled with sand. A piece of PE was inserted into the medium inside the jar and sealed for a specified length of time and then taken out for analysis. The benchtop testing was a way of conducting a small-scale experiment in a controlled environment before working in the field.

The final step was testing our PE passive samplers in an actual site at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL). The PE samplers loaded with a PRC, chlorobenzene, were inserted 5 feet (shallow) and 30 feet (deep) below the ground surface with a hydraulically powered GeoProbe drilling machine. Samplers were taken out of the ground the next day and brought to our lab for analysis.

Chapter 2

Polyethylene - Air Partition Coefficients

2.5 Concept Overview

In order to translate the concentration of contaminant in the PE to the concentration in soil vapor, the polyethylene-air partition coefficient (K_{pea}) for a target chemical needs to be determined:

$$Kpea = \frac{Cpe}{Cair}$$

where C_{pe} is the concentration of contaminant in the PE and C_{air} is the concentration in soil air. A related parameter the polyethylene-water partition coefficient K_{pew} can be determined:

$$Kpew = \frac{Cpe}{Cw}$$

where C_w is the chemical's concentration in water. Now, the K_{pew} can be related to K_{pea} by the following equation:

$$Kpea = \frac{Kpew}{Kaw}$$

where K_{aw} is the air-water partition coefficient of the same chemical. Since the K_{aw} values for volatile organic compounds (e.g. BTEX, TCE, etc.) are reported, finding the K_{pew} values will be enough to calculate the K_{pea} values.

2.6 Experimental Procedure

To find the polyethylene-water partition coefficients (K_{pew}) for benzene (Baker), toluene (Baker), ethyl benzene (Baker), and *ortho*-xylene (Aldrich Chemical Company), polyethylene samples were cut from stock supplies of 102 um (4 mil) thickness PE sheet obtained from the Ambicat hardware store. Then, the PE samples were cleaned by soaking in dichloromethane (Baker) for 1 day, in methanol (Baker) for 1 day, and in pure water for 1 day to leach out any residual organic solvent before use.

Each individual PE strips weighed about 220 mg or 500 mg. They were incubated in 65 mL water in glass biological oxidation demand (BOD) vessels for 1 day at a room temperature. These water samples contained benzene, toluene, ethyl benzene, and o-xylene (BTEX) between 50 and 200 ug/L for each compound. Each incubation was done in triplicate to assess the method reproducibility.

To measure the BTEX concentrations of water samples before and after the PE incubations, 5 mL aliquots were collected without headspace using syringes and were added to a Tekmar LSC 2000 Purge and Trap system for analysis. The aqueous solutions were purged for 5 min and the volatile organic compounds were collected. After purging, the BTEX were desorbed into a gas chromatograph (GC).

The GC was a Perkin Elmer Auto system XL Gas Chromatograph with a J&W Scientific capillary column, DB-624 (Agilent Technologies), 60 m length, 0.32 mm inner diameter, and used a flame ionization detector (FID) (Figure 2-1).

Sets of BTEX standards were analyzed to determine retention times and

establish the GC-FID response factors for each of the BTEX. Furthermore, each incubated PE test strip was transferred into a similar 65 mL BOD vial filled with pure water to desorb its accumulated BTEX concentrations. The advantage of using a stoppered BOD glass vessel is that water can be filled without any headspace left. After desorption of the BTEX, 5 mL aliquots were taken and analyzed similarly using the Tekmar Trap and Purge and GC-FID systems to establish PE-water equilibration.

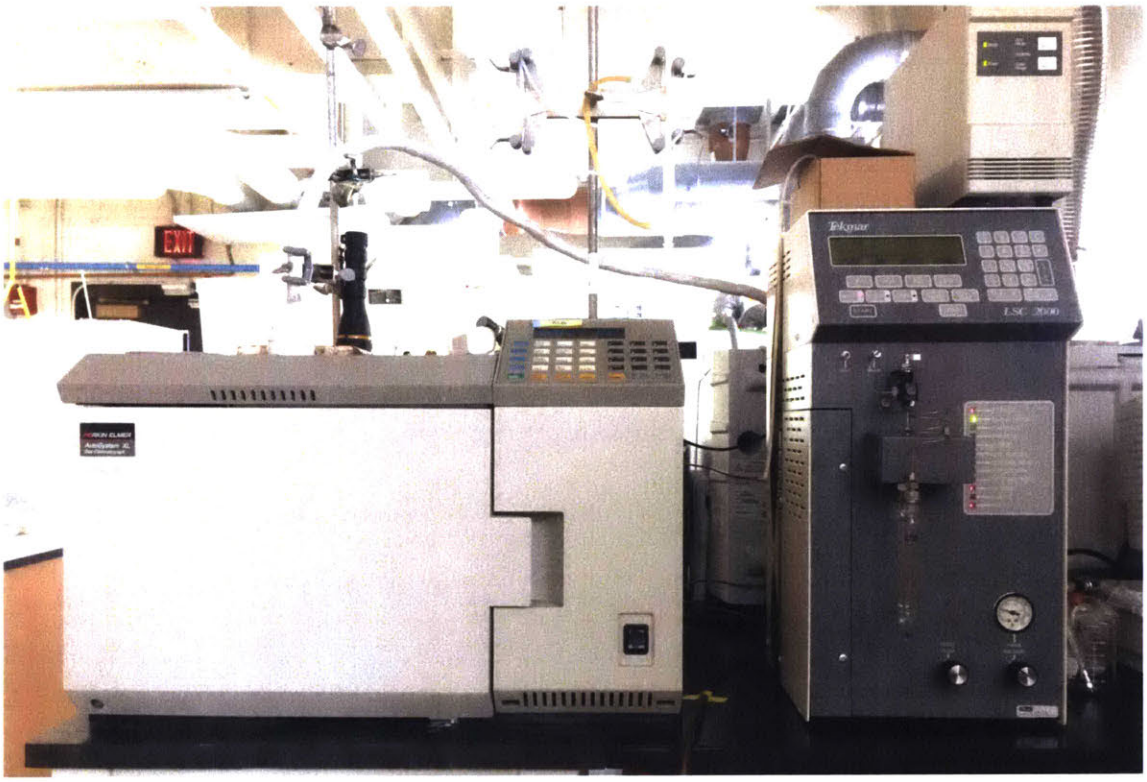

***Figure 2-1**: Perkin Elmer Auto system XL Gas Chromatograph (left) and Tekmar LSC 2000 Purge and Trap system (right)*

2.7 K_{pew} Calculation Methods

Polyethylene-water partition coefficients (K_{pew}) were calculated in one of two ways. If the PE absorbed a substantial fraction of initial BTEX concentrations from the water, then the following equation was used:

$$Kpew = \frac{Cpe}{Cend} = \frac{(C0 - Cend) * Vw / Mpe}{Cend}$$

where C_0 was the initial water concentration, C_{end} was the final water concentration, V_w was the volume of aqueous solutions in which the PE strips were incubated, and M_{pe} was the mass of PE used in each of the incubation.

If insufficient fractions of initial solute concentrations were absorbed into the PE, then there was not a statistically significant difference between the initial water concentrations (C_0) and the final water concentrations (C_{end}). Thus, the BTEX concentrations in the PE from post-incubation desorption into pure water (C_{des}) were used in an alternative equation:

$$Kpew = \frac{Cpe}{Cend} = \frac{(Cdes * Vdes + Kpew * Cdes * Mpe) / Mpe}{Cend}$$

where C_{des} was the measured concentration and V_{des} was the volume of the water into which BTEX were desorbed from the incubated PE.

Rearranging the last equation gives:

$$Kpew = \frac{Cpe}{Cend} = \frac{(Cdes * Vdes) / (Cend - Cdes)}{Mpe}$$

An important thing here was to have a statistically significant difference between the final water concentrations (C_{end}) and the post-incubation desorption concentrations (C_{des}). The second way of K_{pew} calculation was especially useful for benzene, as it is the most water-soluble compound among the BTEX system.

Our laboratory collaborated with Eni S.p.A., an Italian multinational oil and gas company. Researchers at Eni used a different method to calculate K_{pew}. After incubating in water with BTEX, a cut of the incubated PE was put into GC sampling vials, which were then heated to 80 °C. Concentrations of the BTEX initially absorbed from water into the PE (C_{pe}) almost completely desorb into the vials' headspaces. Then these headspace samples were analyzed on a gas chromatograph - mass spectrometer. Consequently, PE-water partitioning coefficients were found using a direct equation:

$$Kpew = \frac{Cpe}{Cend}$$

where C_{end} is the final water concentration.

2.8 Results and Statistical Comparison

Polyethylene sheets of 70 um and 102 um thicknesses were tested by both MIT and Eni laboratories to determine K_{pew} values for BTEX (Table 2-1). In each case, the triplicate results were used to deduce the $\pm 1\ \sigma$ errors.

Table 2-1: *Polyethylene-water partition coefficients K_{pew}, (g_{pe}/ml_w) for BTEX using polyethylene of 70 um and 102 um thicknesses*

	Tested at Eni		Tested at MIT		Geometric
BTEX	70 um	102 um	70 um	102 um	Mean
Benzene	50 ± 5	41 ± 1	18 ± 2	36 ± 6	**34**
Toluene	130 ± 18	116 ± 4	66 ± 12	140 ± 60	**110**
Ethyl Benzene	297 ± 57	285 ± 10	220 ± 80	320 ± 60	**280**
Ortho Xylene	195 ± 29	194 ± 6	290 ± 45	290 ± 60	**230**

Water solubility values decrease from benzene to toluene to ethyl benzene, thus, as can be seen from the table above the K_{pew} values increase in this order. The reproducibility of these BTEX analyses from MIT was ±18%.

Relatively large deviations in the results can be attributed to several factors. First, a small difference between the initial water concentrations (C_0) and the final water concentrations (C_{end}) makes the calculations less precise. To have a bigger difference, a ratio between a mass of PE and a volume of water in BOD vials

should have been higher. However, it was difficult to achieve as large PE sheets use up all the space inside the vials. Second, the measurement precision of about ±18% is relatively high and can lead to a significant variability in results. Lastly, as this was a long and multi step experiment there is a lot of room for experimental errors. For example, there could be air bubbles in the BOD bottles during desorption that caused a large fraction of chemical to partition into the air.

As can be seen from the table above, for some chemicals K_{pew} results noticeably vary for two different PE sources. Hence, a hypothesis that the two PE showed different K_{pew} values needed to be evaluated using a t-test. The question was whether there was a true difference between the two results, or whether the difference could be considered as statistical variation in results. The following equation was used to find test the hypothesis that there was no significant difference:

$$x_1 - x_2 = \pm \frac{t * s}{\sqrt{\frac{n_1 * n_2}{n_1 + n_2}}}$$

where x_1 and x_2 are the sample means of the two sets of values that are being compared, t is the value of Student's t for the 95% confidence level (t=3.182 for n=3), s is the mean standard deviation of the measurements, and n is the sample size or the number of replicates. Both n_1 and n_2 are equal to 3 as the test was done in triplicate.

While the left side (LS) of the equation shows the difference in the mean values for each compound partitioning into the two PE sources, the right side (RS) of the equation quantifies the precision of the estimates. If the right side (RS) of the equation is greater than the left side (LS), then the difference between two analytical results is not significant and with 95% certainty can be attributed to statistical variation in results. (Tables 2-2 and 2-3)

Some of the results of statistical testing of the hypothesis that BTEX partitioning into the two different PE types were significantly different at the 95% confidence level.

Table 2-2: *Statistical comparison between the data collected separately at MIT and at Eni using 70 um polyethylene versus 102 um polyethylene for BTEX* K_{pew}

BTEX	Tested at Eni			Tested at MIT		
	LS		RS	LS		RS
Benzene	18.6	>	8.8	9.5	>	6.1
Toluene	69.5	<	78.9	14.3	<	24.8
Ethyl Benzene	100.0	<	156.6	11.5	<	75.5
Ortho Xylene	0.8	<	119.3	0.8	<	39.6

The mean K_{pew} values for toluene, ethyl benzene, and *o*-xylene are not significantly different at the 95% confidence level for the two PE types tested at any

one lab, as the LS is smaller than the RS. This finding means that the difference can be attributed to the statistical variance in data, using only data generated at MIT or at Eni. In contrast, both labs separately found that the K_{pew} for benzene was significantly different for the two PE sources.

Next, using the same t-test, the hypothesis that partitioning of each BTEX to the same polyethylene was significantly different as measured at MIT versus as measured at Eni was tested. This would help to find out whether the uncertainty in K_{pew} values was from differences in PE or from methods used at both groups.

Table 2-3: *Statistical comparison between the data measured at MIT versus measured at Eni for partitioning of each BTEX to the same polyethylene*

	70 um PE			102 um PE		
BTEX	LS		RS	LS		RS
Benzene	32.4	>	7.1	4.3	<	7.8
Toluene	64.4	>	34.1	19.4	<	69.6
Ethyl Benzene	71.6	<	154.2	39.9	<	77.9
Ortho Xylene	90.9	>	83.3	92.5	>	75.5

In half of the comparisons the two collaborating laboratories observed significantly different K_{pew} values at 95% confidence level. Therefore, it is fair to assume that most of the uncertainty in K_{pew} values occurs because of two different methods used and not from differences in PE.

Outcomes of these statistical testing suggest that to determine environmental BTEX concentrations, the labs could use the geometric mean K_{pew} values (Table 2-1). Alternatively, each laboratory should use its own lab-specific K_{pew} values to get the most precise results or use the same methods to estimate polyethylene-water partition coefficients. Note, using the data (Table 2-1), one can find the K_{pea} values.

Chapter 3

Benchtop Testing of Polyethylene Passive Samplers

3.9 Overview of the Experiment

The benchtop experiment was a small-scale simulation of an actual field. The experiment was conducted in a controlled environment with preset conditions and parameters to see how accurate our polyethylene passive samplers worked. The idea was to mimic a spill of volatile organic compounds trichloroethylene (TCE) and tetrachloroethylene (PCE), both of which are toxic chemicals with human health concerns.[17]

A brief overview of the experiment is that the contaminant chemicals at known concentrations in an organic solvent would be introduced into a closed and humidified jar, which is filled up with sand and has a PE passive sampler inserted in it. A beaker with known volume of water would also be placed inside the jar.

After a specified length of time, the whole system would reach equilibrium, i.e. some of the TCE and PCE would partition into the air, the PE sampler, and the water. Next, the PE sampler and the beaker with water would be taken out of the system and analyzed for the TCE and PCE concentrations.

Since this is a controlled experiment with predetermined parameters, knowing the organic solvent – air, air – water, and air – PE partition coefficients for TCE and PCE, the concentrations in each phase can be estimated. Then, the

measured and estimated concentrations would be compared to see how well the process could be modeled. Furthermore, the water-based measurement would serve as an evaluation of the results attained by the PE passive sampler. A schematic diagram of the experimental jar is shown in Figure 3-1.

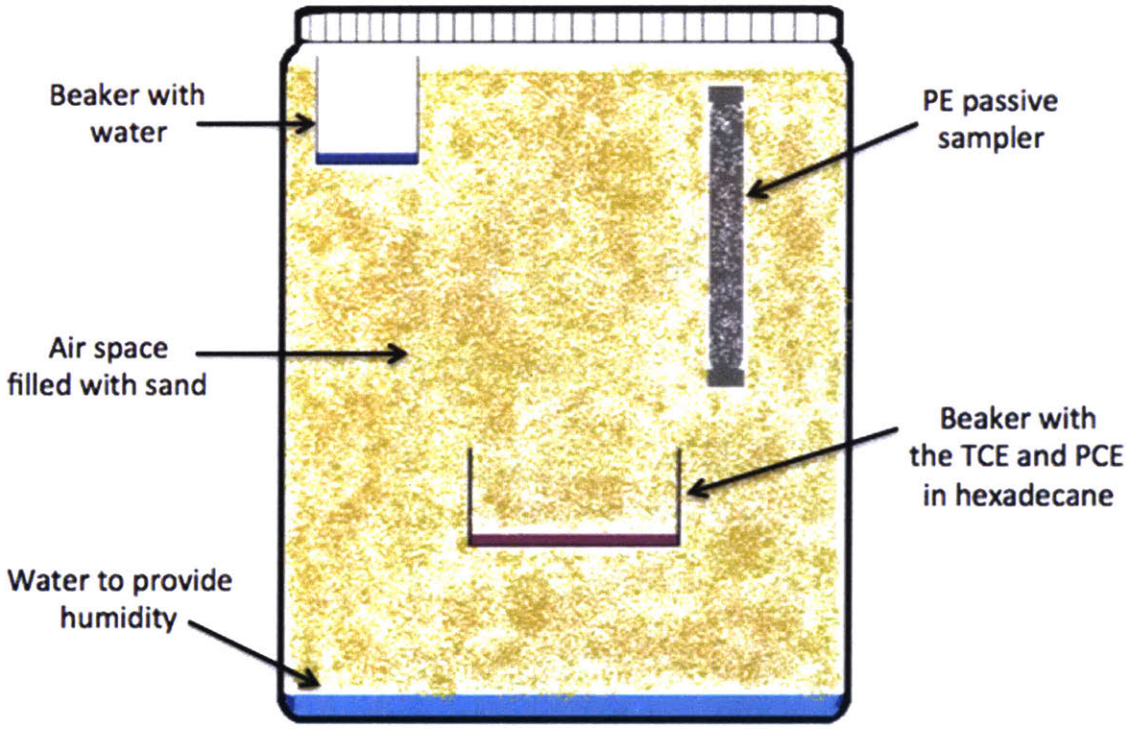

***Figure 3-1**: Schematic diagram of the experimental jar used for the benchtop testing*

3.10 Experiment Details

The experiment was conducted in a one-gallon jar sealed with a cap that was lined with an aluminum foil. In a closed system setup, the TCE and PCE could not diffuse into the open environment and eventually maintain equilibrium concentrations at all depths of the jar.

Hexadecane was chosen as an organic solvent as it has a low partial pressure and conserves its volume throughout the whole experiment. Thus, changes in concentrations of the TCE and PCE in pure phase hexadecane will be due to the partitioning of these chlorinated chemicals out to the gas phase, and not due to the change in volume of hydrocarbon. Moreover, the air – hexadecane partitioning coefficients for both TCE and PCE have already been well established in literature.[18]

Volume of the jar was 3.79 L, which was calculated gravimetrically by measuring the mass of water needed to completely fill up the jar. While doing the gravimetric analysis, a height at which 3.7 L of the jar was filled was marked. The marked line would serve as a limit up to which the sand will be filled, so that there is always a 90 mL headspace for the overlying air.

First, the jar was partially filled with sand and 50 mL of water was added to provide humidity. Then, 0.3 mL of each pure phase TCE and PCE were added to a beaker with 30 mL hexadecane, so that the volume ratios were 1 to 100. The TCE and hexadecane were obtained from J.T. Baker, and PCE was from ULTRA Scientific. The beaker then was placed on top of the sand inside the jar. Next, the jar was filled with sand up to the 3.7 L marked line, sealed with a cap, and left to be moisturized.

A time needed for the jar to be completely moisturized can be estimated using a simple back-of-the-envelope calculation, assuming diffusion is the only process affecting it. A length of the jar is about 30 cm and a diffusion coefficient at the room temperature is about 10^{-1} cm^2 per second, thus the time needed is equal to

$$\frac{(30\ cm)^2}{10^{-1} cm^2/sec} = 9000 \text{ sec} = 2.5\ hours.$$

The jar was left to equilibrate for a weekend, thus the medium was assumed to be fully humidified prior placing the PE sampler and the beaker of water.

Afterwards, the PE passive sampler and the beaker with 30 mL of water were introduced to the system. While the PE sampler was fully inserted into the sand, the beaker was partially left in the headspace (Figure 3-2). This prevented the water from being contaminated with sand, thus allowing the use of this water for VOC analysis by gas chromatography.

***Figure 3-2**: A top and perspective view of the PE sampler and the water beaker*

The sampler used for this experiment consisted of: (a) a metallic rod, (b) a hollow cylindrical piece of polyethylene of 102 um thickness that was inserted on that metallic rod, (c) a screen that protected the PE from damage while allowing the gas to penetrate through it, and (d) two screw-nuts that secured the PE (Figure 3-3).

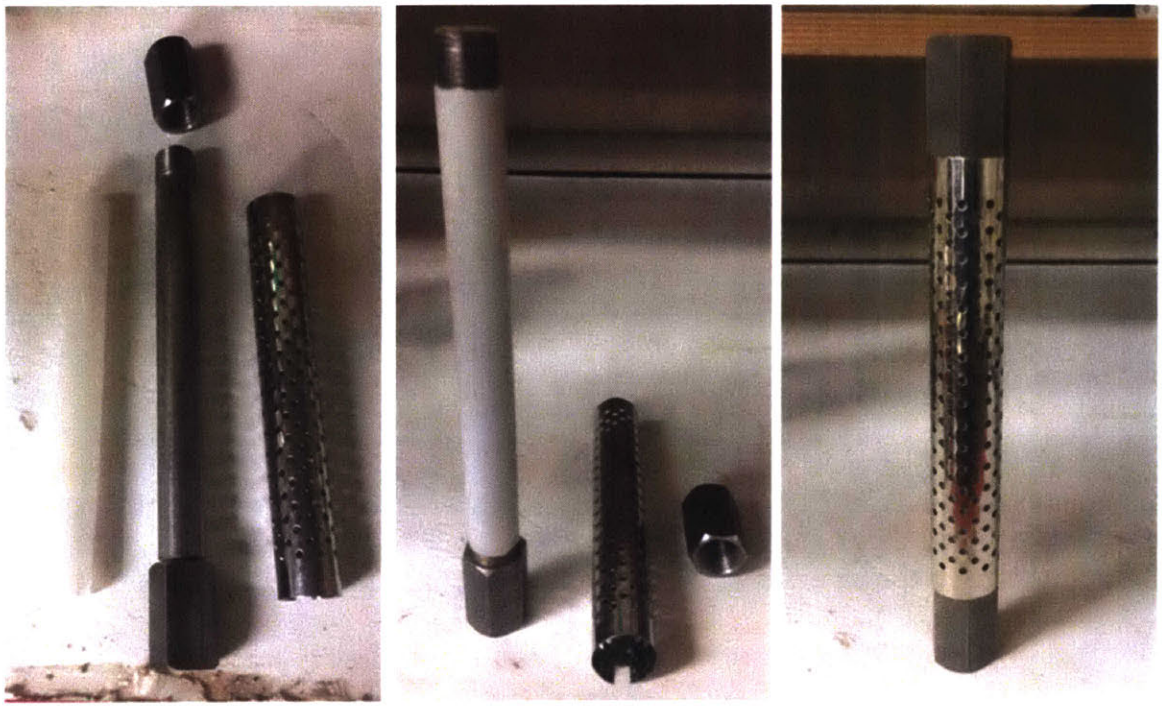

***Figure 3-3**: PE passive sampler used for the benchtop experiment*

Once these two means of measuring the vapor concentrations of TCE and PCE were placed into the experimental jar and the cap was closed, the system became exactly as the schematic diagram shown in Figure 3-1. The experimental setup was left to sit for 48 hours for the concentrations to reach the equilibrium between all phases (hexadecane, water, PE, and air) within the jar.

3.11 Phase Partitioning Coefficients of TCE and PCE

The TCE and PCE in hexadecane will partition into the pore space in sand. Once equilibrium is reached, the concentrations of TCE and PCE in the air can be calculated using the hexadecane-air partitioning coefficients (K_{ha}). Some of the TCE and PCE will then partition from the air into the PE in the sampler and into the water, which is present at the base of the jar and in the beaker on top. The Henry's law constants, or the air-water partitioning coefficients (K_{aw}), are used to determine the equilibrium concentrations in the aqueous phase. Similarly, the concentrations in the air and PE at equilibrium can be related by the PE-air partitioning constants (K_{PEA}).

While the values of K_{ha} and K_{aw} for both TCE and PCE can be are obtained from literature,[18] the values of K_{PEA} are not well established. Thus, they are calculated by dividing the experimentally determined PE-water partitioning constants (K_{pew}) by the K_{aw} obtained from literature.

The experimentally established values of K_{pew} for TCE and PCE were obtained through personal communication from the Gschwend Lab, Massachusetts Institute of Technology. These K_{PEW} values are also required for calculations in the water desorption analysis of the PE, which will be elaborated later in this chapter.

All of the partitioning coefficients required throughout the experiment are shown in Table 3-1.

Table 3-1: *TCE and PCE partitioning coefficients required for all the calculations throughout the benchtop experiment*

VOC	$K_{hex\text{-}air}$	$K_{air\text{-}wat}$	$K_{PE\text{-}wat}$	$K_{PE\text{-}air}$
Trichloroethylene	1000	0.49	76	155
Tetrachloroethylene	3802	1.20	560	467

3.12 Measurement of Quartz Porosity

Since TCE and PCE in hexadecane would partition into that pore space in sand, knowing its porosity is essential for the benchtop experiment. The value was obtained through couple simple steps:

1) Sand was filled into graduated cylinders of different volumes, so that the total volumes occupied by sand were known;
2) The masses of sand in graduated cylinders were weighed;
3) By dividing these measured masses by the quartz density of 2.65 g/cm^3 (the value at 25°C was readily available), the volumes of quartz were determined;
4) By subtracting the quartz volumes from the total volumes, the volumes of air in the pore spaces were calculated;
5) Finally, the porosity of sand in each cylinder was calculated by dividing the volume of air by corresponding total volume.

Table 3-2: *Porosity measurement for the sand used to fill up the experimental jar. The density of 2.65 g/cm³ was used to find quartz's volume using its mass*

Total Vol (mL)	Mass (g)	Quartz Vol (mL)	Air Vol (mL)	Porosity
100	166.8	62.9	37.1	0.37
300	504.4	190.3	109.7	0.37
400	666.1	251.4	148.6	0.37
500	788.3	297.5	202.5	0.41

Assuming a negligible difference between the quartz density value at 25°C and density at actual room temperature of 22°C, the porosity of the sand used in the experiment was calculated to be **38%**.

One thing to note is that this measurement neglected the possibility of sand rearranging itself in the experimental jar slightly different than in the graduated cylinder.

3.13 Fractions of TCE and PCE in different phases

As stated in the experiment overview, one of the benefits of the benchtop experiment is that it is a controlled system. Knowing the amount of TCE and PCE and the characteristics of all the phases where these VOCs will migrate, the fractions in each phase at equilibrium can be calculated. For example, the following equation is used to calculate the fraction of TCE in the air:

$$f_{TCE,air} = \frac{C_{TCE,air}}{C_{TCE,air} + C_{TCE,w} * \frac{V_w}{V_{air}} + C_{TCE,hex} * \frac{V_{hex}}{V_{air}} + C_{TCE,PE} * \frac{M_{PE}}{V_{air}}}$$

if both the numerator and the denominator are divided by $C_{TCE,air}$, the equation becomes:

$$f_{TCE,air} = \frac{1}{1 + \frac{1}{K_{TCE,air-w}} * \frac{V_w}{V_{air}} + K_{TCE,hex-air} * \frac{V_{hex}}{V_{air}} + K_{TCE,PE-air} * \frac{M_{PE}}{V_{air}}}$$

Equations to compute the fractions of VOCs in the hexadecane, water, and PE are derived similarly, and can be found in the Appendix. In addition to partition coefficients values given in Table 3-1, the various other parameters of the experiment that are needed to calculate the fractions are summarized in Table 3-2.

Table 3-2: *Volumes of different phases used in the experimental jar and a mass of PE*

V_{wat} (mL)	V_{air} (L)	V_{hex} (mL)	V_{TCE} (mL)	V_{PCE} (mL)	M_{PE} (mg)
80	1.5	30	0.3	0.3	646

Note, V_w is the volume of the water at the base for humidity and in the beaker for secondary measurement; V_{air} is the volume of the air in pore space of sand and in the headspace; M_{pe} is the mass of PE inserted into the passive sampler as shown in Figure 3-3.

Subsequently, using the equations and data from tables above, the percentage fractions of TCE and PCE at the equilibrium for each phase in the experimental jar can be calculated (Table 3-3). The vast majority of both TCE (95%) and PCE (98%) stayed in the pure phase hexadecane.

Table 3-3: *Percentage fractions of the total TCE and PCE introduced to the system in different phases at the equilibrium. Less than a percent of both TCE and PCE would partition into the water and PE*

VOCs	Phases			
	Hexadecane	Air	Water	PE
Trichloroethylene	94.61%	4.55%	0.51%	0.32%
Tetrachloroethylene	98.44%	1.25%	0.06%	0.26%

As it was stated in the previous section, the experimental setup with the PE sampler inserted into the medium in the jar was left to sit for 48 hours, so that the VOC concentrations reach the equilibrium between all phases within the jar. At the end of 48 hours, the PE sampler and the water beaker that absorbed the TCE and PCE from the soil gas were removed for further measurements.

Immediately after, the sampler was loaded with another PE sheet of the same thickness (102 um) and was inserted back into the sand. Similarly, another beaker with 30 mL of clean water that was placed on top of the sand just like in the first experiment. This was done to collect more data and to see how reproducible the results would be. The only difference this time was the mass of PE, which was 695 mg as opposed to 646 mg previously.

New percentage fractions of the original TCE and PCE in different phases were recalculated accounting the change in the mass of PE and almost negligible losses into the water beaker and PE sampler (Table 3-4). As one might have expected, the difference is insignificant and most of the TCE and PCE remain in the pure phase hexadecane.

Table 3-4: *Percentage fractions of TCE and PCE in different phases at the equilibrium after the PE sampler and water beaker were replaced.*

VOCs	Phases			
	Hexadecane	**Air**	**Water**	**PE**
Trichloroethylene	94.59%	4.55%	0.51%	0.34%
Tetrachloroethylene	98.42%	1.25%	0.06%	0.28%

The PEs used in both experiments were soaked in dichloromethane for 24 h each, in methanol for 24 h, and then remained in water prior to the start of each experiment.

3.14 Analyses of the Collected PE and Water

At the end of the experiment, the PE passive sampler and the beaker with water were retrieved from the experimental jar (Figure 3-4). The water was carefully transferred into three 5-mL syringes with no headspace, which were then submerged into a container with water (Figure 3-5). This was done to minimize any risk of losing the TCE and PCE that was partitioned into the water during the experiment. The PE strips from the first and the second experiments were placed in 63.83 mL and 63.45 mL BOD vials respectively (Figure 3-6), the volumes of which were measured gravimetrically by adding water. The BOD vials were filled with water, capped ensuring no headspace air was present, and then similarly to syringes were submerged into water.

The PE strips desorbed collected TCE and PCE into the water inside the BOD vials for 48 hours to ensure the equilibrium between two phases was reached. Upon equilibration, the water from BOD vials was transferred into 5 mL syringes, which were used then used in gas chromatography analytical test to determine the concentrations of VOCs in the water.

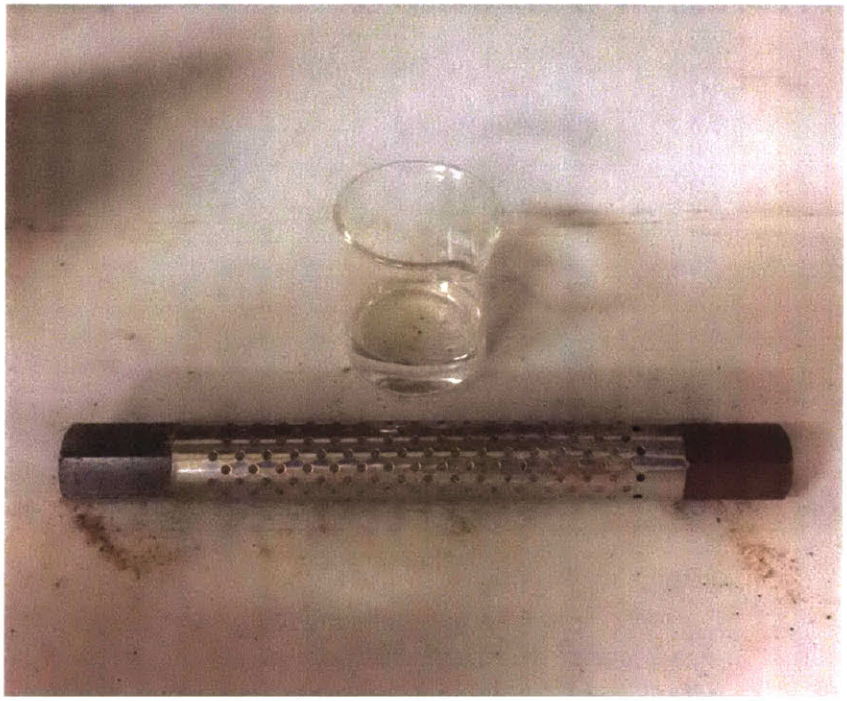

Figure 3-4: *The PE sampler and the water beaker retrieved from the experimental jar*

Figure 3-5: *The water from the beaker is collected into syringes*

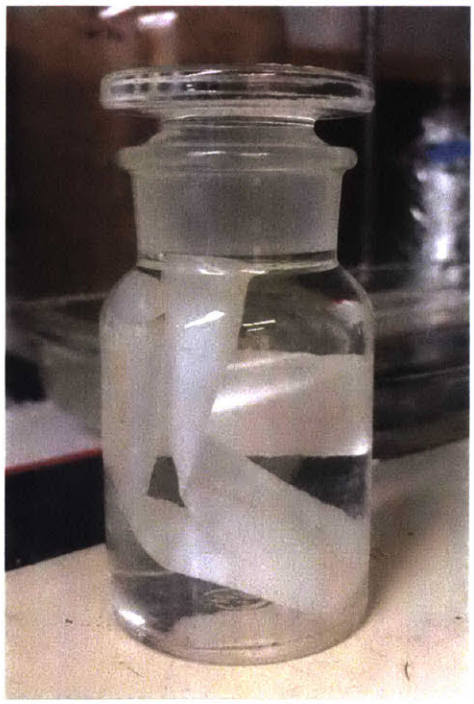

Figure 3-6: *The PE strip from the sampler placed in BOD vial to desorb*

The Perkin Elmer Auto system XL gas chromatograph with a J&W Scientific capillary column, DB-624 (Agilent Technologies), 60 m length, and with Flame Ionization Detector (FID) was used to analytically determine TCE and PCE concentrations. The temperature program started at 30°C without a hold time and was raised at 10°C/min rate until 100°C, followed by 20°C/min rate increase until 170°C, which was hold for 2 minutes. Both FID and injector were kept at 225°C.

The purge and trap system was a Tekmar LSC 2000 with a standby temperature of 35°C. Once an aqueous solution from 5 mL syringes was transferred into the system, it was purged for 5 minutes followed by a dry purge for 2 minutes. Desorb preheat temperature was at 245°C, while desorption was done for 1 minute at 250°C. The bake time was 8 minutes at 260°C. Both valve and line temperatures were kept at 225°C.

3.15 Calculations Overview

PE-based calculations of TCE and PCE (VOCs) concentrations in the gas phase (C_{air}):

Once the concentrations of VOCs in the BOD water (C_w) are measured using gas chromatography, the concentrations of VOCs in the PE (C_{PE}) are calculated:

$$C_{PE} = K_{PE-w} * C_w$$

Now, the initial concentrations of VOCs in the PE ($C_{PE,0}$) – the concentrations before the PE was placed into the water – are determined:

$$C_{PE,0} = \frac{C_{PE} * M_{PE} + C_w * V_{BOD}}{M_{PE}}$$

These initial concentrations of VOCs in the PE ($C_{PE,0}$) are the original VOC concentrations in the passive sampler that was inserted into the sand to equilibrate. Thus, the final step is:

$$C_{air} = \frac{C_{PE,0}}{K_{PE-air}}$$

Water-based calculations of TCE and PCE (VOCs) concentrations in the gas phase (C_{air}):

Unlike the PE-based case, this is one-step calculation. Once VOCs concentrations in the water from the beaker ($C_{w,\,beaker}$) placed inside the jar are measured using gas chromatography, the equation is:

$$C_{air} = K_{air-w} * C_{w,beaker}$$

Estimated calculations of TCE and PCE (VOCs) concentrations in the gas phase (C_{air}):

The volume of the air inside the jar and the fractions of total TCE and PCE in that air are already calculated (Tables 3-3 and 3-4). The mass of both TCE and PCE can be found using the known volumes and readily available densities. Thus, this equation can be used:

$$C_{air} = \frac{f_{air} * V * \rho}{V_{air}}$$

Note, the K_{PE-air} and K_{air-w} values for TCE and PCE are provided in Table 3-1.

3.16 Results and Discussion

The measured and estimated concentrations of TCE and PCE in the gas phase of the experimental jar were calculated as described in the previous section and are shown in the table below.

Table 3-5: *Calculated and analytically measured concentrations of TCE and PCE in the gas phase using the PE-based and water-based methods (mg/L_{air})*

Methods	1st experiment		2nd experiment	
	TCE	PCE	TCE	PCE
Measured C_{air} from the PE sampler	1.1	1.5	0.9	1.6
Measured C_{air} from the water beaker	1.6	0.4	1.6	2.2
Estimated C_{air} from partitioning constants and phase ratios	13	4.0	13	4.0

In both cases the measured soil gas concentrations were less than the mathematical estimated gas concentrations in experimental jar.

One possible explanation would be that less TCE and PCE were partitioning out of the pure phase hexadecane, i.e. the partitioning coefficients between the hexadecane and air ($K_{hex\text{-}air}$) were not representative at this concentrations, these coefficients assumed interactions between hexadecane and VOCs were in an infinite dilution condition. Calculation of the estimated C_{air} involves many parameters that could have measurements errors; for example, the value for the total volume of air was a product of the sand porosity and the volume of the jar, both of which were measured. Performing thorough error propagation calculations could possible

better relate the measured and estimated concentrations. Another possibility would be that the equilibrium between all phases has not been established when the samplers were taken out of the system. Despite the difference between the estimated and measured results, the water-based and PE-based measurements were relatively consistent with each other.

Chapter 4

Real World Testing of Polyethylene Passive Samplers

The last milestone of the project was to test our PE passive samplers in an actual site that was contaminated with volatile organic compounds. That became possible as our lab got a permission to work at the US Army Corps of Engineers' Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, New Hampshire.

In 1960s, CRREL had conducted comprehensive research in controlled refrigerated environments where trichloroethylene (TCE) was used as a cooling solvent in refrigeration systems.[19] Unfortunately, numerous major spills and leaks took place on CRREL property until 1987, when the use of TCE was discontinued.

Having an experience with testing our PE passive samplers with TCE in the lab, this was a great opportunity to try the sampler in the real world setting. Upon arrival to the field, suitable site was picked for two sample holes that were close together and near the monitoring wells. Prior to drilling, the monitoring wells were plugged to avoid exposure risks.

On the first day, the PE samplers (Figure 4-1) loaded with PRC chlorobenzene were inserted into the ground surface with a hydraulically powered GeoProbe drilling machine (Figure 4-2).

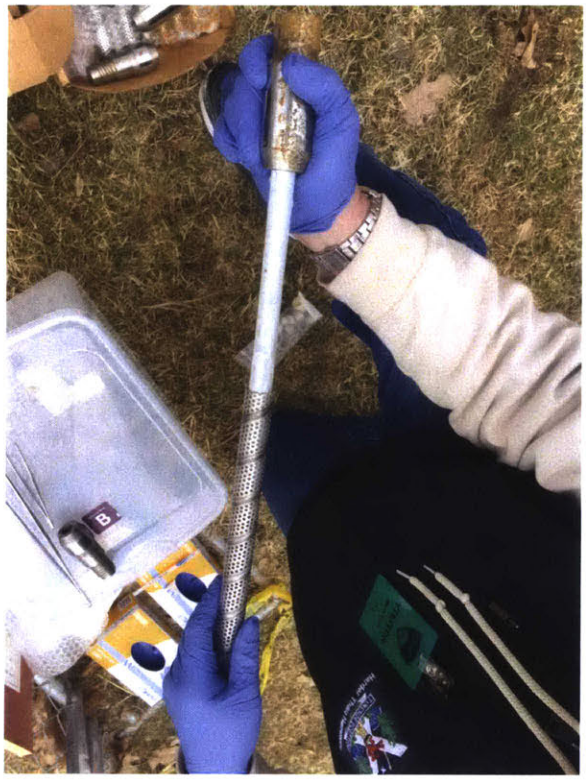

***Figure 4-1**: A preparation of the PE sampler prior to drilling. An adapter assembly with screened PE that was preloaded with PRC chlorobenzene.*

Two samplers into first hole and two samplers into second hole were drilled. Both holes had the PE samplers at about the same depths. The deep ones were at approximately 823 and 884 centimeters depth, while the shallow ones were around 46 and 61 centimeters deep in the ground. The samplers were left underground for one day to absorb the chemicals of that environmental.

***Figure 4-2**: On the left is a photo of a hydraulically powered GeoProbe drilling machine marking the hole. Metallic rods on the ground are used to push penetrate through the ground. One the right, the PE passive sampler attached the metallic rod is being drilled into the ground.*

The same cascade drilling team worked the next day to recover the samplers from the ground. From the first hole, both the surface sampler and the deep sampler were removed and cleaned. Each PE from both of the samplers was cut in half and placed in a separate 60 mL vial with water. Only the surface sampler was recovered from the second hole, the PE of which was also cut in half and placed in 60 mL water. However, a coupling had failed at top joint and the deep sampler was lost. A severe angle of remaining AMS thread indicated that the sampler penetration was not vertical.

The PE sheets from two shallow and one deep collected samplers were analyzed on Carlo Erba, HRGC 5300, Mega Series Gas Chromatograph fitted with on-column injector J&W Scientific, 60m DB-624 capillary column, 1.40μm film thickness Electron Capture Detector, Model ECD 400. Carrier gas helium was at 2 ml/min rate and the makeup gas was 5% Methane balanced with Argon (P-5 mixture).

PE sheets placed in BOD bottles were desorbing collected TCE and other chemicals into the water. By analyzing these water samples in gas chromatography, the concentration of TCE in BOD bottle was determined. Since concentrations the PE and water were at equilibrium, using PE-water partition coefficients ($K_{TCE, PEW}$) of TCE, the equilibrium concentration in the PE was found. Then, knowing the dry weight of PE and the volume of water used for desorption, the initial concentration in the PE was calculated. Finally, knowing the PE-air partition coefficient for TCE ($K_{TCE, PEA}$), the concentration of TCE in the soil gas at the PE sampler deployed location was determined.

Prior the testing the PE was loaded with Cl-Benzene PRC (2.8μg/g PE), and after 24 hours of in situ exposure the PRC was completely gone from the PE. While both of the shallow PE samplers did not detect any TCE, the analysis of the deep PE sampler resulted in large concentrations of TCE. Our findings were consistent with the CRREL data collected using active sampling methods. They also detected large concentrations at 25-30 feet and negligible concentrations of TCE at 5 feet depths. This consistency showed that the PE passive sampling is a promising method of measuring volatile organic compounds in soil vapors.

Reference:

(1) US EPA. *Underground Storage Tanks (USTs)* https://www.epa.gov/ust/learn-about-underground-storage-tanks-usts

(2) US EPA. Semiannual Report of UST Performance Measures: End of Fiscal Year 2014; 2014.

(3) Provoost, J., Bosman, A., Reijnders, L., Bronders, J., Touchant, K., & Swartjes, F. Vapour intrusion from the vadose zone - seven algorithms compared. *Journal of Soils and Sediments*, 2009, 10(3), 473-483.

(4) US EPA. Vapor Intrusion https://www.epa.gov/vaporintrusion/what-vapor-intrusion

(5) Wang, G., Reckhorn, S. B. F., & Grathwohl, P. Volatile Organic Compounds Volatilization from Multicomponent Organic Liquids and Diffusion in Unsaturated Porous Media. *Vadose Zone Journal,* 2003, 2(4), 692-701.

(6) US EPA. Brownfields Technology Primer: *Vapor Intrusion Considerations for Redevelopment*, 2008.

(7) ASTM Standard D7663. *Standard Practice for Active Soil Gas Sampling in the Vadose Zone for Vapor Intrusion Evaluations*, 2012 http://www.astm.org/doiLink.cgi?D7663

(8) Hodny, J. W., Whetzel Jr, J. E., Anderson, H. S. Quantitative Passive Soil Gas and Air Sampling in Vapor Intrusion Investigations. *In Proceedings of Vapor Intrusion*; Air and Waste Management Association, 2009

(9) McAlary, T., Wang, X., Unger, A., Groenevelt, H., & Gorecki, T. Quantitative passive soil vapor sampling for VOCs - part 1: theory. *Environmental Science: Processes & Impacts*, 16(3), 482-490. 2014 http://doi.org/10.1039/C3EM00652B

(10) Zabiegala, B., Kot-Wasik, A., Urbanowicz, M., & Namiesnik, J. Passive sampling as a tool for obtaining reliable analytical information in environmental quality monitoring. *Analytical And Bioanalytical Chemistry*, 396(1), 273-296, 2010 http://doi.org/10.1007/s00216-009-3244-4

(11) Jensen, D. G. Analysis of Volatile Organic Compounds (VOCs) in Soil via Passive Sampling: Polyethylene Sampler Design and Optimization, MEng Thesis submitted to the Department of Civil and Environmental

Engineering, Massachusetts Institute of Technology, 15, 2015

(12) Kot-Wasik, A., Zabiegata, B., Urbanowicz, M., Dominiak, E., Wasik, A., & Namiesnik, J. Advances in passive sampling in environmental studies. *Analytica Chimica Acta*, 602(2), 141-163, 2007 http://doi.org/10.1016/j.aca.2007.09.013

(13) Huckins, J. N., Petty, J. D., Lebo, J. A., Almeida, F. V., Booij, K., Alvarez, D. A., Mogensen, B. B. (2002). Development of the Permeability / Performance Reference Compound Approach for In Situ Calibration of Semipermeable Membrane Devices. *Environmental Science & Technology*, 36(1), 85-91. http://doi.org/10.1021/es010991w

(14) Seethapathy, S., Gorecki, T., & Li, X. (2008). Passive sampling in environmental analysis. *Journal of Chromatography A*, 1184 (1-2),234-253 http://doi.org/10.1016/j.chroma.2007.07.070

(15) Apell, J. N., & Gschwend, P. M. (2014). Validating the Use of Performance Reference Compounds in Passive Samplers to Assess Pore water Concentrations in Sediment Beds. *Environmental Science & Technology*, 48(17), 10301-10307. http://doi.org/10.1021/es502694g

(16) Fernandez, L. A., Harvey, C. F., &Gschwend, P. M. (2009). Using Performance Reference Compounds in Polyethylene Passive Samplers to Deduce Sediment Porewater Concentrations for Numerous Target Chemicals. *Environmental Science Technology*, 43(23), 8888-8894. http://doi.org/10.1021/es901877a

(17) U.S. Department of Health and Human Services. *Health effects linked with trichloroethylene and tetrachloroethylene* https://www.atsdr.cdc.gov/sites/lejeune/tce_pce.html

(18) Schwarzenbach, Rene P., Gschwend P. M.; Imboden, D. M. *Environmental Organic Chemistry*; 2nd Editio.; John Wiley & Sons, Inc.: Hoboken, NJ, 2003.

(19) US Army Corps of Engineers, *CRREL Environmental Restoration Project* http://www.nae.usace.army.mil/Missions/Projects-Topics/CRREL-Environmental-Restoration-Program/

Appendix

Equations used to compute fractions of TCE (i) in hexadecane, water, and polyethylene:

- In pure phase hexadecane:

$$f_{i,hex} = \frac{1}{1 + \frac{1}{K_{i,air-w} * K_{i,hex-air}} * \frac{V_w}{V_{hex}} + \frac{1}{K_{i,hex-air}} * \frac{V_{air}}{V_{hex}} + \frac{K_{i,PE-air}}{K_{i,hex-air}} * \frac{M_{PE}}{V_{hex}}}$$

- In water:

$$f_{i,w} = \frac{1}{1 + K_{i,air-w} * K_{i,hex-air} * \frac{V_{hex}}{V_w} + K_{i,air-w} * \frac{V_{air}}{V_w} + K_{i,PE-w} * \frac{M_{PE}}{V_w}}$$

- In polyethylene:

$$f_{i,PE} = \frac{1}{1 + \frac{K_{i,hex-air}}{K_{i,PE-air}} * \frac{V_{hex}}{M_{PE}} + \frac{1}{K_{i,PE-air}} * \frac{V_{air}}{M_{PE}} + \frac{1}{K_{i,PE-w}} * \frac{V_w}{M_{PE}}}$$