

Quantitative Analysis of Volatile Organic Compounds (VOCs)
in Soil via Passive Sampling:
Polyethylene Sampler Design and Optimization

by

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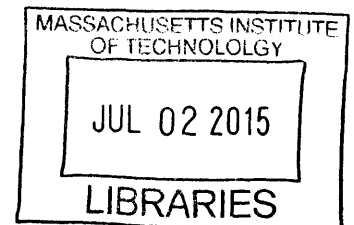
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ABSTRACT

The potential for the release of volatile organic compounds (VOCs) to our natural environment is pervasive. However, the ability to accurately measure and predict VOC soil vapor concentrations is still limited. A polyethylene (PE) quantitative passive sampler using performance reference compounds and deployed via a hand driven probe is proposed as a solution. Additionally, a 1D diffusion mass transfer model was developed in MATLAB to predict the mass uptake into the PE sampler over time. The model was then implemented to investigate the effects of PE size and deployment time on the detection limit of BTEX compounds.

Preliminary testing of the deployment probe indicates that a design to secure the PE around the outside of a driven rod must include a protective cover over the PE during insertion. A perforated pipe design is suggested. After deployment and recovery, the PE is extracted into water. The extraction water is then analyzed by direct aqueous injection to GC/FID. The minimum concentration detectable in soil vapors, by this PE passive sampling method, was determined to be the product of the target compound's air-water partitioning coefficient and the analytical detection limit. Assuming a 5 ng/mL analytical detection limit, the minimum soil vapor detection limit for toluene was approximately 1.25 mg/m³. This limit would be similar for all BTEX compound and is above sub-slab vapor intrusion screening levels for the more toxic compounds such as benzene. This indicates that direct aqueous injection provides insufficient sensitivity and that purge and trap concentrations of VOCs is likely needed. It was also determined that a PE sampler, with dimensions as small as 5"x5/8"x0.0005", could theoretically reach 10 mg/m³ sensitivity within a 1 h deployment time. This result suggests potential applications of the sampler for rapid and accurate site characterization of BTEX compounds.

Thesis Supervisor: Philip M. Gschwend

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1 INTRODUCTION

1.1 VOLATILE ORGANIC COMPOUNDS (VOCs) IN SOIL VAPORS: A PERVASIVE PROBLEM

In 1986 the United States started a program dedicated to the regulation of underground storage tanks (USTs). As of September 2014 there were over 570,000 active USTs, most of which contain petroleum products for service stations. These USTs could not be designed to last forever and thus each of them will eventually leak petroleum into the soil unless they are replaced with new tanks on regular basis. In fact since 2009 the EPA has reported between 6000 and 7000 confirmed releases of contaminants by registered USTs each year. Furthermore these USTs are spread throughout the United States. The state of Massachusetts contains approximately 10,000 active USTs, equivalent to almost 1 potential release site every square mile of the State. (Office of Underground Storage Tanks, 2014)

The potential for the release of volatile organic compounds (VOCs) to our natural environment is pervasive in our modern world. Leaking USTs is an example of only one of the ways that a single type of contaminant can be released to the environment. Chemical contaminants exist in many modern day products and manufacturing processes where accidental spills and leaks are to be expected. While contaminants are entering the environment at a decreased rate due to improved regulation, the only way to completely prevent their releases is to stop using them altogether. Since this is not likely to occur in the near term, it is important to be prepared to evaluate the impact of leaks and spills as they occur.

1.2 THE RISK OF VOCs IN SOIL VAPORS: VAPOR INTRUSION

Though the discharge of contaminants to the environment is inevitable, not all of these discharges necessarily present an unacceptable risk to humans and the environment. The EPA describes three pieces of information that are needed in order to conduct an assessment of the risk posed at a contaminated site: inherent toxicity of the chemical, the amount of exposure a receptor has with the contaminated medium, and the quantity of the chemical present in an environmental medium (soil, water, air)(USEPA, 2012).

When chemical contaminants spill into the environment, there are several processes that can occur depending on properties of the contaminants and properties of the soil. For a non-aqueous phase liquid (NAPL), such as petroleum products, the bulk free phase will flow down through the unsaturated zone by gravity, leaving residual free phase product in the soil pores. If there is a significant volume, the NAPL can reach the water table where it will partially dissolve into the groundwater and be transported down gradient by advection. Another possible process is that the contaminant volatilizes from the NAPL or from the contaminated groundwater and is transported largely by diffusion to the ground surface.

Vapor intrusion is an important exposure pathway in risk assessment analysis and occurs when contaminants in the soil vapor are transported up to the ground surface and enter overlying buildings (Figure 1.1)(Office of Solid Waste and Emergency Response, 2012). Most vapor intrusion does not result in high concentrations of contaminants in indoor air. However, because humans can spend a significant portion of their day inside buildings and

breathe a large volume of air, relatively low concentrations of toxic chemicals can result in unacceptable levels of risk (Provoost *et al.*, 2009).

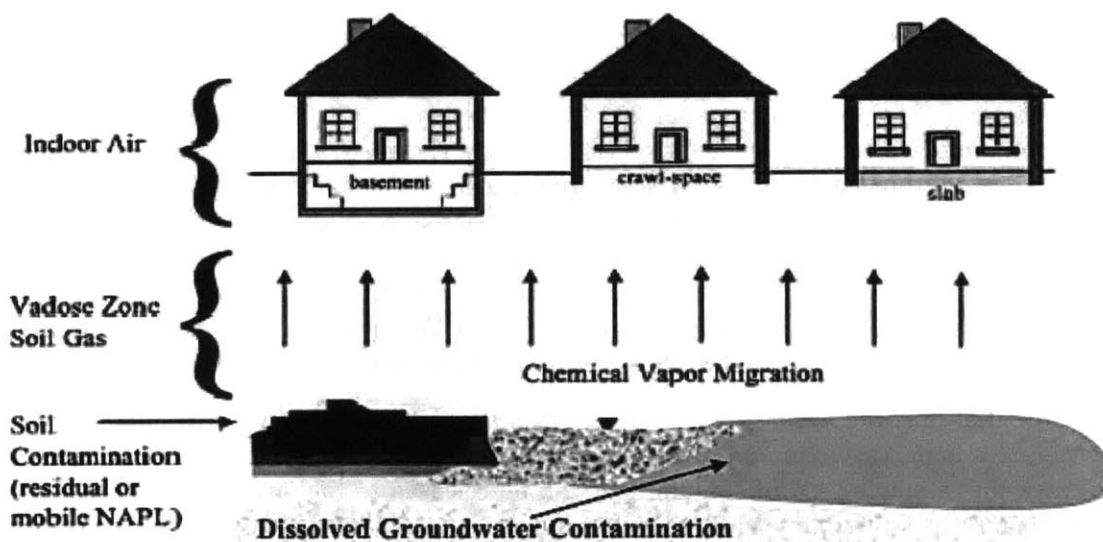


Figure 1.1: A conceptual model of potential vapor intrusion pathways (Office of Solid Waste and Emergency Response, 2002)

1.3 ACCURATE MEASUREMENTS OF SOIL VAPOR CONCENTRATION FOR MODELING

Several models have been developed which attempt to estimate the risk that subsurface contaminants pose to inhabitants of overlying buildings through vapor intrusion. While it is generally preferred to directly measure indoor air or sub-slab vapor concentrations, if access to a building is not possible or if the building is to be constructing in the future, vapor intrusion models can predict potential health risks. These screening models rely on solutions to contaminant partitioning and soil vapor transport with one of the most important inputs being reliable soil gas concentrations. Vapor concentration measurements are significant in modeling because mass transport is largely influenced by molecular diffusion, which is governed by concentration gradients (Wang *et al.*, 2003). Furthermore additional soil vapor measurements can help to confirm model accuracy.

Unfortunately there is a discrepancy between current screening models and direct measurement methods of soil gas concentration. In a comparison of seven commonly used vapor intrusion algorithms, Provoost *et al.* determines that most algorithms overestimate the observed soil gas concentrations (Provoost *et al.*, 2009). The deviation tended to be, on average, less than an order of magnitude, but was sometimes as much as four orders of magnitude or greater (Figure 1.2). This discrepancy in soil gas concentration draws into question both whether the screening algorithms correctly model the soil environment and whether current direct measurement techniques of soil gas concentration are accurate. To improve site and risk assessment accuracy, a sampling technique and model must be developed which better align predicted and observed soil vapor concentrations.

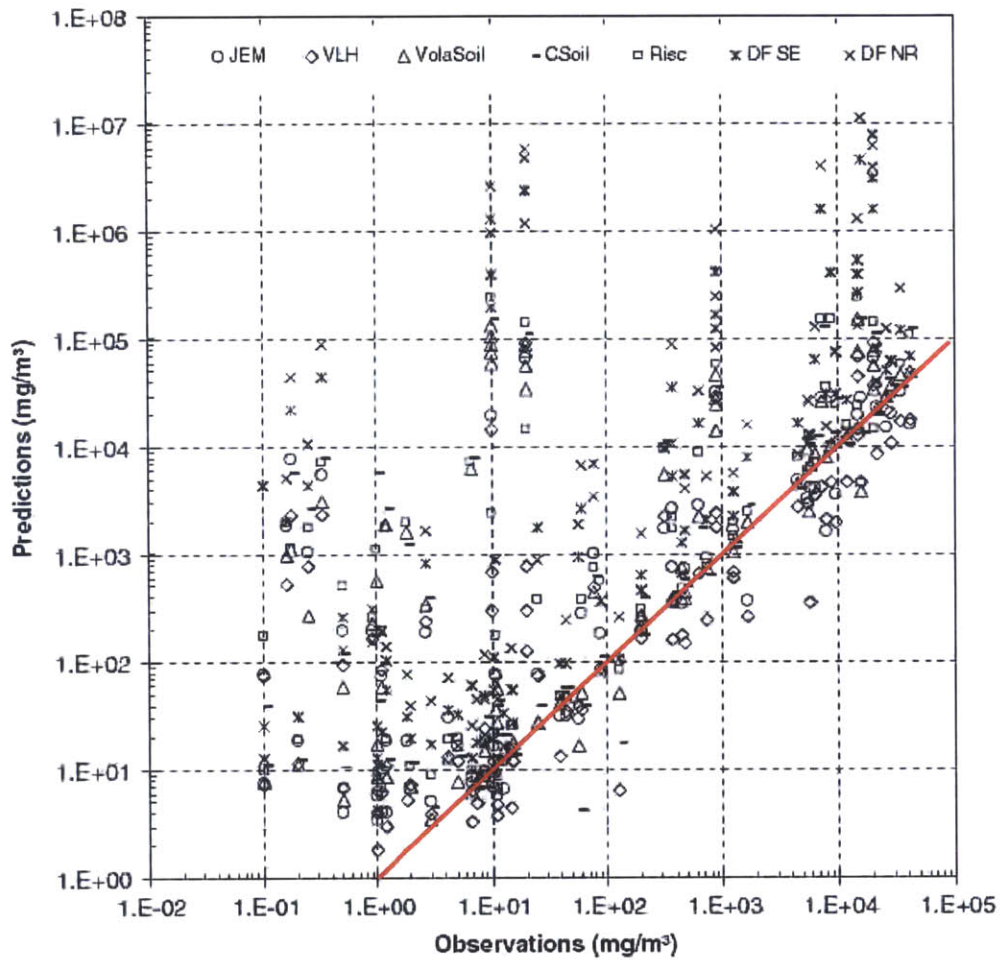


Figure 1.2: Scatter plot of observed and predicted soil gas concentration from several sites using 7 different vapor intrusion models. Models, on average, over predict the observed by one order of magnitude however they can over predict as much as 4 orders of magnitude or greater (Provoost et al., 2009)

2 SOIL VAPOR MEASUREMENT TECHNOLOGY

2.1 SOIL PARTITIONING ESTIMATE

The review by Provoost *et al.* (2009) suggests that vapor intrusion screening models, in general, predict higher soil gas concentrations than what is observed by direct soil gas measurement techniques. The models investigated in this review predict soil vapor concentration based on estimations from laboratory data of bulk soil concentrations. This method assumes that the majority of partitioning to solids is through absorption to organic carbon. The solid-water partitioning coefficient (K_d) can then be estimated by the organic carbon-water partitioning coefficient (K_{OC}) and scaled by the fraction of solid mass that is organic carbon (f_{OC}) (Schwarzenbach *et al.*, 2003). Assuming equilibrium conditions, the compound's air-water partitioning coefficient (K_{AW}) is used to determine the concentration in the soil vapor.

$$\frac{C_{solids}}{C_{water}} = K_d = f_{OC}K_{OC} \quad \frac{C_{air}}{C_{water}} = K_{AW}$$
$$C_{air} = K_{AW}C_{water} = K_{AW} \frac{C_{solids}}{f_{OC}K_{OC}}$$

This method makes several assumptions that can lead to errors in certain situations. The first is that only organic carbon absorption is driving solid-water partitioning. Sorption is not yet well understood and in many cases other factors may become significant. In these cases a simple $f_{OC}K_{OC}$ estimation of K_d would be inappropriate. For example the presence of black carbon is known to cause non-linearities in sorption isotherms due to a finite number of sorption sites and non-uniform sorbate affinity to adsorption sites (Schwarzenbach *et al.*, 2003). These properties of black carbon cause the sorption isotherms of soils to asymptote with increasing water concentrations. Because of these problems, as well as challenges with laboratory loss of gas phase product during analysis, a push was made to develop technology that directly measures contaminants in the soil vapor (ASTM Standard D7663, 2012).

2.2 ACTIVE SOIL GAS SAMPLING

Currently the most common method of direct soil vapor sampling is active gas extraction. In active gas sampling, a hollow probe is inserted into the soil to the desired depth. The soil gas is next pumped through the probe tip and into a sampling container. The sample is then sent to a lab for analysis or to a portable lab onsite. This method has the advantage of allowing direct measurement of the soil gas and it can be done relatively quickly (10-30 samples/day)(ASTM Standard D7663, 2012). Furthermore regulators already accept the method as a reliable means of measuring soil gas concentration.

There are, however, some disadvantages to the method. Active soil gas sampling requires the initial removal of soil vapor in order to purge the system. The removal of soil gas prior to sampling means that the sampled air may originate from an unknown distance away from the probe. This becomes especially significant if there are preferential pathways in the soil. Additionally, active soil gas sampling applies a vacuum to the subsurface, which may

disturb equilibrium conditions, causing contaminants to partition out of other phases and yielding an inaccurate measurement of soil vapor concentration (Office of Solid Waste and Emergency Response, 2008). Finally active soil vapor sampling requires a relatively complicated mechanical setup with the potential for leaks. Therefore the method requires several quality control procedures during sampling and a trained operator to run the system (ASTM Standard D7663, 2012).

2.3 PASSIVE SAMPLING: NON-QUANTITATIVE

An alternative sampling method involves the use of passive samplers. This method takes advantage of the chemical potential difference between the sampler phase and the surrounding environment to collect contaminant mass. Depending on the sampler and target chemicals, the sampler may be deployed in the soil for a day to a couple weeks. After the sampler is collected, it is sent to a lab where contaminants are extracted and analyzed. This method has distinct advantages over active gas sampling because it does not forcefully remove soil gas, it works well in a wide range of soil types for a wide range of VOCs, and it can be inexpensive. Furthermore passive samplers measure a time averaged concentration, thus removing the potential collecting unrepresentative extreme variances in concentration (Hodny *et al.*, 2009; Pyron, 1995). The notable challenges are that passive sampling can require long deployment times, and depending on the sampler type, this approach may not provide a quantitative result (Office of Solid Waste and Emergency Response, 2008).

There are two main types of passive sampling technologies currently in use. The first contains an adsorbent, such as black carbon, and is mainly used in air environments. The adsorbent is separated from the environment by a barrier, which allows soil vapor to pass through, but prevents solids and sometimes liquids from penetrating. These samplers were originally, and still are used, as semi-quantitative passive samplers. Recently, however, work has been conducted to demonstrate their potential as quantitative samplers (Hodny *et al.*, 2009; McAlary *et al.*, 2014). The second type of technology uses either a single absorbent phase or an absorbent phase surrounded by a membrane. Target chemicals partition from the soil into the single phase or diffuse through the membrane and into the absorbent. This method has been mostly commonly used in surface water and sediment porewater sampling such as with semi-permeable membrane devices. These samplers consist of lipid filled polyethylene tubes and are thought to better measure the bioavailability of contaminants (Kot-Wasik *et al.*, 2007; Seethapathy *et al.*, 2008; Zabiegała *et al.*, 2010).

While there are two main type of passive sampling technology, Hodny *et al.*, (2009) identify three different classes of passive samplers for use in soils based on the type of laboratory results the sampler can provide. The classes are qualitative, semi-quantitative, and quantitative. The qualitative class is the simplest sampler design and provides only a binary response indicating either the presence or absence of a contaminant to a certain sensitivity.

The semi-quantitative sampler does not report the exact concentrations in the soil vapor, but instead reports total mass collected during the deployment time. A single semi-quantitative sampler does not provide more information than the qualitative sampler class. However, if several semi-quantitative samplers are deployed over the same time period at different locations on a site, then the total mass data can create a map of relative magnitudes. This map is useful to identify “hot spots” of contaminant concentration that can

identify the potential location of residual source material in the soil and guide further site investigation (ASTM Standard D7758-11, 2012; Hodny *et al.*, 2009).

2.4 PASSIVE SAMPLING: QUANTITATIVE

The final passive sampler class described by Hodny *et al.* (2009) is a quantitative passive sampler. This class of sampler allows for the calculation of chemical concentrations in the target medium. In order for a passive sampler to be quantitative, some understanding of chemical uptake from the environment is required. While the exact kinetics is still debated, especially in porous media, the general profile is relatively well accepted (Figure 2.1).

After initial deployment, there exists a period of virtually linear uptake to the sampler. This requires that the sampler contain a near zero concentration of the target chemicals when deployed. Next, a curvilinear region begins as uptake substantially slows and the sampler approaches equilibrium. Finally, after a sufficient deployment time, the sorbent will reach equilibrium with the surrounding environment. The focus of most debate is at what deployment time the linear region ends and on how to model the entire concentration profile, specifically the curvilinear region (Fernandez *et al.*, 2009; Hodny *et al.*, 2009; Kot-Wasik *et al.*, 2007; Seethapathy *et al.*, 2008; Zabiegała *et al.*, 2010). Answers to these questions can be complex because they are dependent on properties of the chemical, the soil, and the sampler. However, most types of quantitative samplers try to take advantage of one of these regions in order to calculate the concentration of chemicals in soil vapor.

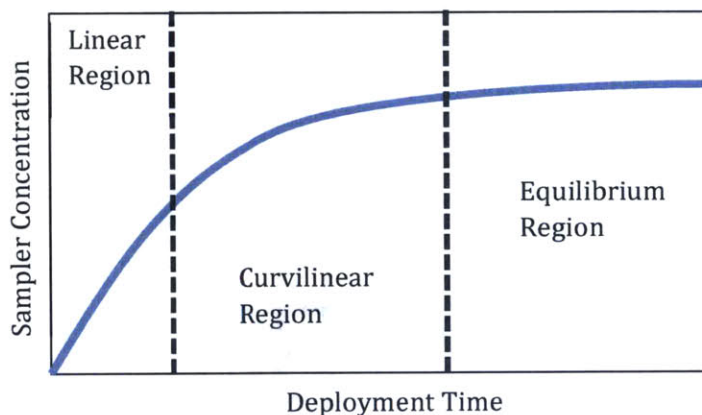


Figure 2.1: Depiction of a passive sampler concentration versus deployment time with initial linear uptake region, curvilinear regional, and a final constant equilibrium region.

2.4.1 Equilibrium Method

The simplest method of quantitative passive sampling is to wait for equilibrium conditions. When equilibrium is reached, the concentration in the target medium can be calculated from the measured concentration in the sampler and the chemical's partitioning coefficient between the two phases. Sampler testing or kinetic uptake information is essential in order to determine a deployment time that ensures equilibrium conditions are achieved. This method has all the benefits of a passive sampler, however it has the disadvantage of potentially requiring long deployment times in order to reach equilibrium conditions (Kot-Wasik *et al.*, 2007; Seethapathy *et al.*, 2008; Zabiegała *et al.*, 2010).

2.4.2 Linear Method: Constant Sampling Rate

The most common method being applied to determine soil vapor concentrations from passive sampler data is a sampling rate method. This method was originally developed for passive samplers measuring hydrophobic organic compounds in ambient air or water environments (Bartkow *et al.*, 2005; Booij *et al.*, 1998). In order to determine the potential utility of this method in soil environments a review of its development for ambient air is first discussed.

The sampling rate method requires a couple of simplifying assumptions. The first assumption is that the concentration inside the sampler remains close to zero over the entire deployment time. The second assumption requires that the distance between the zero-concentration environment inside the sampler and a turbulent well-mixed air concentration outside the sampler remains constant. This distance is defined as the length over which diffusion is the dominant mass transfer mode. With these assumptions the concentration profile at steady state, from the air to the sorbent, is approximated as a series of constant concentration gradients. Therefore, a constant overall diffusive flux into the sampler can be determined (Figure 2.2) (Bartkow *et al.*, 2005).

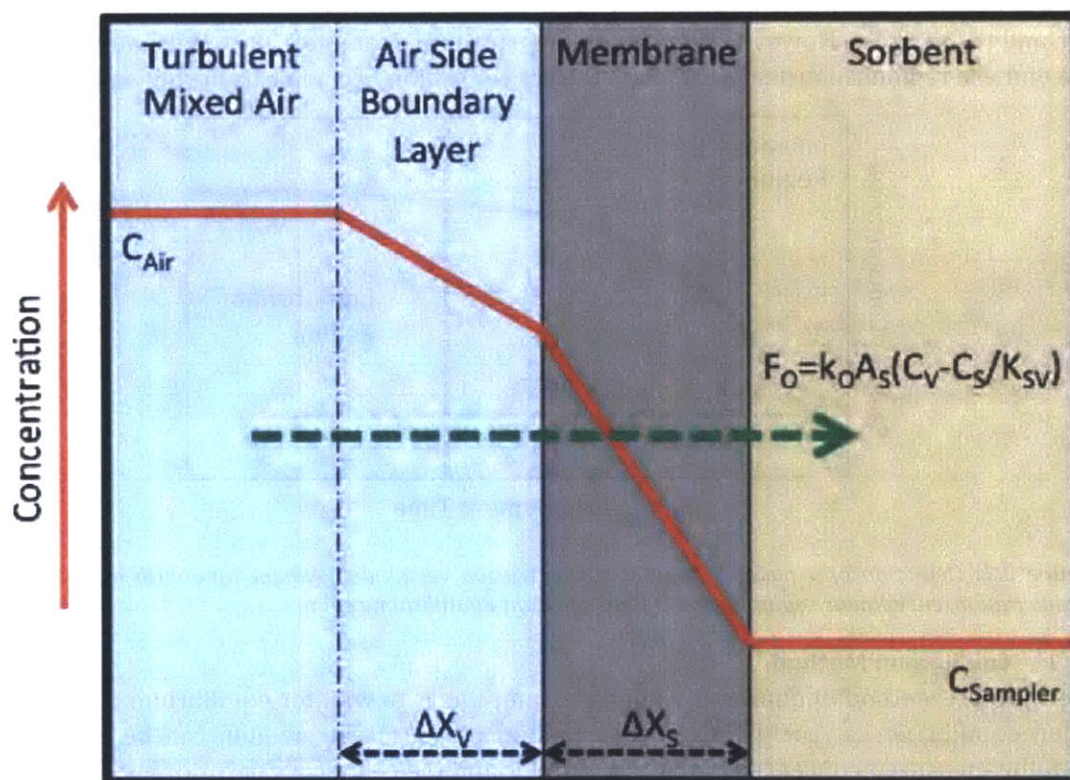


Figure 2.2: Depiction of sampling rate assumptions to calculate mass flux into passive sampler. Requires constant air concentration, a sampler concentration near 0, and constant diffusion path length over the entire deployment time.

Following the work of Bartkow *et al.* (2005) on passive air sampling theory, each individual mass flux may be calculated as

$$F_i = -k_i A \Delta C_i$$

where F is the mass transfer rate of the contaminant in units of mass/time, A is the cross-sectional surface area, and ΔC is the change in concentration over the diffusion length. The diffusion length Δx is the distance over which diffusion is the dominant mode of mass transfer for a constant diffusion coefficient D . Finally k is the diffusive velocity equal to the diffusion coefficient divided by the diffusion length.

$$k_i = -\frac{D}{\Delta x_i}$$

These individual mass fluxes can then be combined to define the overall mass transfer rate. For example a simplified model of a passive sampler in an ambient air environment would combine two diffusive velocities, one through a vapor boundary layer and a second through a membrane or barrier layer which results in the following overall mass transfer rate.

$$F_O = k_O A_S \left(C_{Air} - \frac{C_{sampler}}{K_{sampler-air}} \right)$$

where C_{vapor} is the constant turbulent mixed air concentration, $C_{sampler}$ is the concentration in the sampler, $K_{sampler-vapor}$ is the partitioning coefficient, and k_O is the overall diffusive velocity. The overall diffusive velocity can be derived and theoretically determined, however this assumes all diffusive velocities are identified and boundary layer thicknesses and diffusion coefficients are known. Instead of trying to calculate these values, k_O is typically combined with the sampler interfacial surface area into a sampling rate term (R_S). The sampling rate is then measured through laboratory experiments by observing chemical uptake over time with a constant free air concentration (Hodny *et al.*, 2009; McAlary *et al.*, 2014). Then, if the sampler is used in the initial linear uptake region, the concentration in the sampler is approximately zero, simplifying the above expression. Solving for C_{Air} yields the sampling rate equation:

$$F_O = \frac{M_{sampler}}{t} = k_O A_S C_{vapor} = R_S C_{Air}$$

$$C_{Air} = \frac{M_{sampler}}{R_S t}$$

where $M_{sampler}$ is the total mass collected of the target chemical, t is the deployment time, and R_S is the sampling rate of the target contaminant. The sampling rate constant is specific to a target chemical, sampler, and the laboratory environment where it was measured. Therefore use of this equation assumes that the variations between the laboratory and the sampling site have negligible impact on R_S . Furthermore, a sampling rate values must be tabulated for each sampler and every target compound to be collected by that sampler (e.g., the air boundary layer thickness is the same in both cases).

While the sampling rate method may provide reasonable estimates in ambient air conditions, its application to soils is questionable. The first concern is that if the sampler is

in direct contact with a porous medium then there is no turbulent mixing and therefore no traditional airside boundary layer. The diffusion length will therefore be from each chemical's location in the soil vapor to the sorbent. Fernandez *et al.* (2009) have shown that, in sediments, since there is no turbulent mixing, as the compounds in the immediate environment of the sampler are depleted, additional compounds have to diffuse from increasingly farther distances. This results in a curvilinear concentration profile, which lengthens over time.

Another concern is that the sampling rate is influenced by many factors including environmental and chemical properties. For example, diffusion through a porous medium is retarded due to partitioning between phases and tortuosity. These factors however are not considered if the sampling rate is determined in the laboratory using a constant ambient air concentration. Therefore the assumption that the sampling rate is translatable from the laboratory setting to all soil environments, and that it remains constant over the entire deployment, seems unlikely (Fernandez *et al.*, 2009; Hodny *et al.*, 2009; Seethapathy *et al.*, 2008).

2.4.3 Kinetic Method: Exponential

In an initial attempt to approximate the curvilinear region between the linear uptake and equilibrium, it was still assumed that the diffusion velocity remained constant over the entire sampler deployment, but that C_{Sampler} did not remain equal to zero (Booij *et al.*, 1998). Therefore the diffusion equation can be integrated to an exponential form

$$C_{PE,t=\infty} = \frac{C_{PE,t}}{1 - e^{-k_e t}}$$

where the diffusion rate k_e can be determined from laboratory studies and is related to the resistance of diffusion through the sampler. Several studies have demonstrated problems with this theory in sediments, because of the same issues described for constant sampling rate theory (Apell & Gschwend, 2014; Fernandez *et al.*, 2009). Additionally, over extended deployment times, there is a greater chance of error due to an almost guarantee change in diffusion length and thus diffusion velocity.

2.4.4 Kinetic Method: Performance Reference Compounds

The final method of quantitative passive sampling involves the addition of performance reference compounds (PRCs). While originally introduced for more accurate measurements of bioavailable contaminant concentrations in surface waters by Huckins *et al.* (2002), they also may have application in the measurement of soil vapors (Booij *et al.*, 1998; Kot-Wasik *et al.*, 2007; Seethapathy *et al.*, 2008). For example testing with PRCs and solid phase microextraction fibers to calculate soil vapor concentration has shown some promise (Chen *et al.*, 2004; Chen & Pawliszyn, 2004).

The PRC is a compound that has similar chemical and physical properties to the target contaminant; usually it is a deuterated or ^{13}C labeled species. The PRC is preloaded into the passive sampler to a known concentration before deployment. During deployment the PRC diffuses out of the sampler at the same rate as the target chemical diffuses in. When the sampler is removed and chemicals are extracted, the concentration of the remaining PRC is measured along with the target chemical. The fraction of PRC mass that has diffused out of

the sampler is then proportional to the fraction of the target chemical in the sampler (Figure 2.3). This method captures any changes in the sampling rate over the deployment time. The only assumption is that the sampling rate of the PRC is the same as that of the target compound (Adams *et al.*, 2007; Apell & Gschwend, 2014; Fernandez *et al.*, 2009).

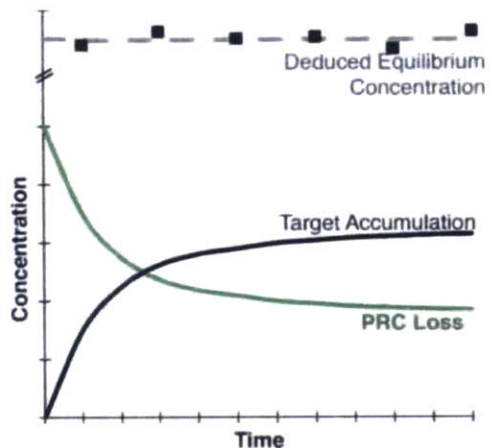


Figure 2.3: Diagram of target chemical and performance reference compound concentration in a passive sampler over the deployment time. If the PRC has the same chemical and physical properties as the target compound the equilibrium concentration of the target compound can be deduced at any deployment time (Apell & Gschwend, 2014).

3 PROJECT GOALS AND OBJECTIVES

3.1 SPACE FOR IMPROVING SOIL VAPOR PASSIVE SAMPLING TECHNOLOGY

Ultimately the interest of this work is investigating a passive sampling technology for soil vapor application, which can improve the agreement between predicted and measured concentrations. In order to accomplish this, the best solution seems to be furthering the advancement of performance reference compounds in passive samplers. By using PRCs the sampler will be accurate in any soil conditions, including changing environments, and for a variety of hydrophobic contaminants.

Recent work by Fernandez *et al.* (2009) and Apell and Gschwend (2014) demonstrates the utility of quantitative passive samplers with PRCs in porous medium. Their research focuses on a polyethylene (PE) sampler deployed in sediments and used to measure porewater concentrations of PAHs or PCBs. They also used a corresponding 1D diffusion model, governed by Fick's laws and solved through a Laplace transform with a numerical inversion solution. The model predicts the change in mass of a target chemical or PRC in the sampler with deployment time (Fernandez *et al.*, 2009).

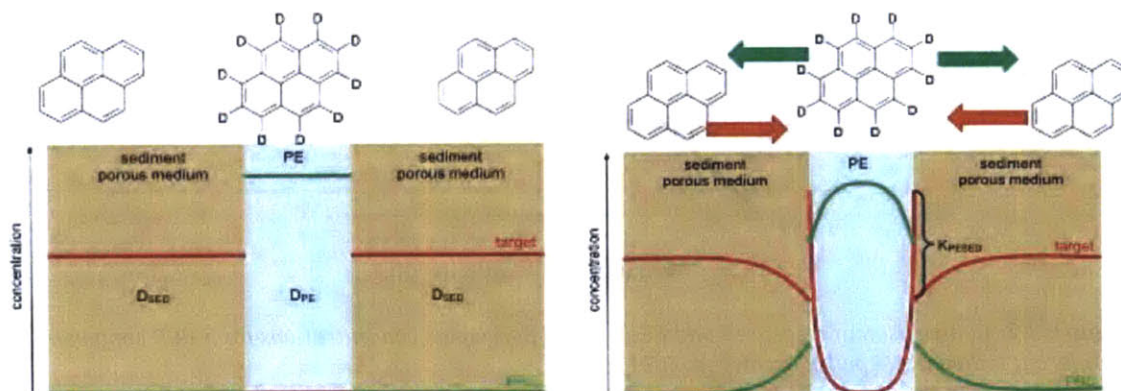


Figure 3.1: Diagram of target compound and PRC concentration profiles at initial deployment time and at some time later. The use of PRCs allows the sampling rate to change over the deployment time, as target chemicals diffuse from farther away before partitioning into the polyethylene (Fernandez *et al.* 2009.).

It is worth mentioning that without a method to interpolate sampling properties to other chemicals, it would be necessary to have a PRC for every compound to be sampled. Using a PRC for every target compound, however, will become expensive and cumbersome to measure. Therefore, Fernandez *et al.* (2009) proposed using their 1D diffusion mass transport model to generate a linear regression from a small number of PRCs. The diffusion model uses measured PRC data to determine a partitioning constant between the bulk sediment (including all phases) and water. This partitioning coefficient is then plotted against the PRCs octanol-water partitioning coefficient (K_{ow}) and a linear regression is determined. By then using the known K_{ow} of a target compound and the regression, one can calculate the sediment-water partitioning coefficient. From this partitioning value plus the target chemical diffusion in free water, diffusion in free PE, and its PE-water partitioning

coefficient, the model calculates a fraction to equilibrium based on deployment time for that specific chemical (Fernandez *et al.*, 2009; Gschwend *et al.*, 2014).

In a later study of PE quantitative passive sampling in sediments, Apell & Gschwend (2014) validated the PRC equivalent diffusion assumption for PCBs. They showed that equilibrium concentrations in sediment porewater could be accurately determined using PE removed at several different times prior to equilibrium (Figure 3.2). Furthermore they confirmed the ability to use a linear regression generated from the 1D diffusion mass transfer model to infer chemical transport properties. Using these inferred properties, they were able to calculate PE deduced concentrations that reasonably matched measured equilibrium values (Apell & Gschwend, 2014).

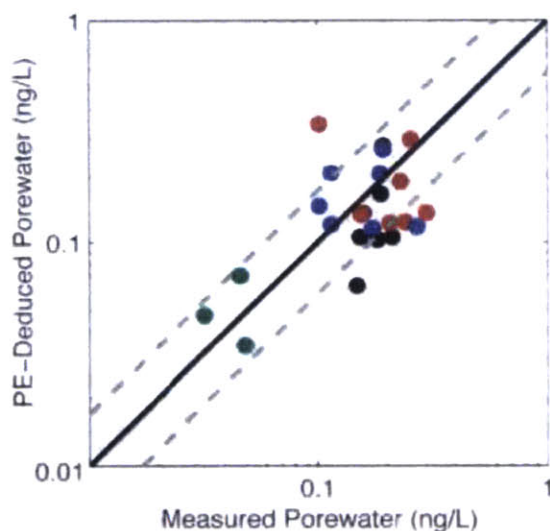


Figure 3.2: Comparison of measured and PE-deduced porewater concentrations for 3 PCB congeners in 7 different sediments (Apell & Gschwend, 2014).

Because of the success demonstrated in sediments and by following the lead of Fernandez *et al.* (2009), this research will be focused on investigating whether a polyethylene quantitative passive sampler will accurately assess volatile organic compounds in soil vapor.

3.2 OVERALL PROCESS DESCRIPTION

In order to investigate the PE quantitative passive sampler in soil, a 1D diffusion mass transfer model was developed by adjusting the MATLAB code from Fernandez *et al.* (2009). However to use the model effectively, accurate measurements of chemical and physical properties for target VOCs must be obtained. Specifically experimental values of polyethylene (PE)-water partitioning coefficients and PE diffusion coefficients must be determined. Using these values, the model will determine deployment times required to reach equilibrium conditions. These times will be used for bench tests of increasing soil environment complexity to confirm accuracy of polyethylene as a passive sampler at equilibrium conditions. Finally, a probe design must be developed with which to insert the

PE into the unsaturated zone. By using the mass transfer model, an optimal PE thickness and surface area versus deployment time can be determined.

This thesis addresses the development of the MATLAB model, including its assumptions and limitations, how it can be used to aid in the design of a deployment probe, and how it can be used to evaluate the limits of the passive sampler. Information on the measurement of chemical properties can be found in H. Liu's thesis (2015) *Analysis of Volatile Organic Compounds (VOCs) in Soil via Passive Sampling: Measuring Partition and Diffusion Coefficients*. Information on the development of bench tests to demonstrate accuracy of the polyethylene sampler in soil vapor can be found in J. Soo's thesis (2015) *Benchtop Testing of Polyethylene Passive Sampling Towards a Quantitative Analysis of Volatile Organic Compounds (VOCs) in Soil Vapours*.

4 CONCEPTUAL MODEL OF MASS TRANSPORT IN THE UNSATURATED ZONE

4.1 CONCEPTUAL MODEL OF THE UNSATURATED ZONE

Predicting everything that will affect chemical transport from the soil into a sampler is difficult to near impossible. The environment is too heterogenous to allow a few parameters to capture everything. PRCs are the best solution to making accurate concentration measurements, especially in combination with a corresponding 1D diffusion model for soil mass transport. A mass transport model will allow the comparison of sampler measurements to theory and the estimation of the time required to reach equilibrium.

Contaminants in soil vapor are transported mainly by advective fluxes and diffusion processes. Previous studies however suggest that the most common method of transport through the unsaturated zone is diffusion (Office of Solid Waste and Emergency Response, 2008; Provoost *et al.*, 2009; Wang *et al.*, 2003). As previously discussed, diffusion is in most cases well described by Fick's Laws. When diffusion is through a porous medium, the free air diffusion coefficient must be reduced due to the tortuosity of the soil as well as partitioning to other phases. It is assumed that partitioning between phases occurs faster than diffusion, and therefore the retarded diffusion coefficient is proportional to the fraction of the compound in the air (Schwarzenbach *et al.*, 2003). In the unsaturated zone, it is assumed that there are three phases in which a contaminant will partition: soil vapor, water, and solids.

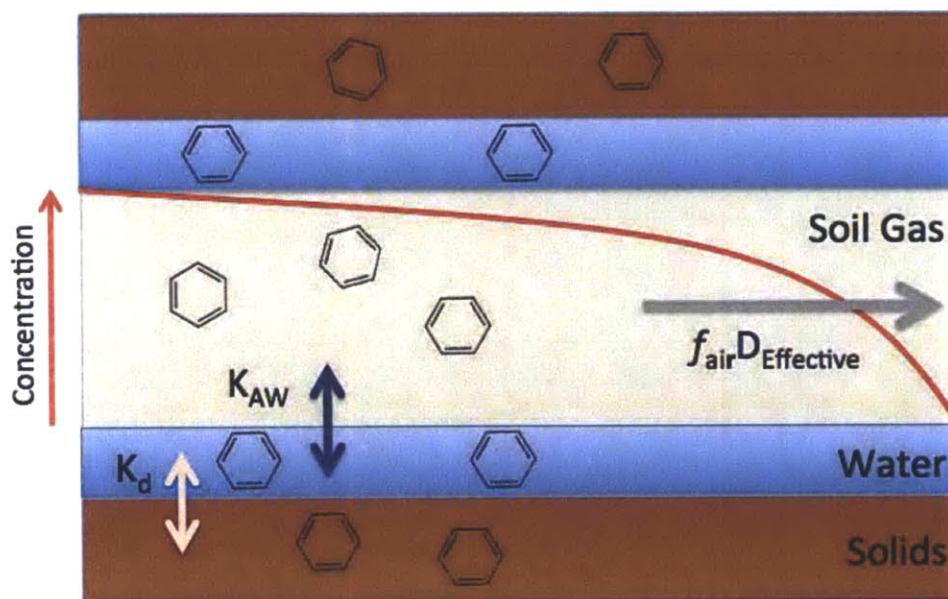


Figure 4.1: 3-phase conceptual model of contaminant diffusion through the unsaturated zone. The contaminant's free air diffusion is retarded due to partitioning between water, organic carbon, and air.

This 3-phase equilibrium partitioning assumption is commonly used in vapor intrusion transport models as a way to calculate effective diffusion (Provoost *et al.*, 2009). To simplify the model, it is assumed that all soil surfaces are covered with a thin layer of water such that the polar water molecules dominate the adsorption to mineral surfaces. Aside from very arid environments, this assumption is reasonable as studies have observed that even at low humidity a monolayer of water will tend to form on mineral surfaces (Unger *et al.*, 1996; Wang *et al.*, 2003). Therefore the partitioning to solids is considered proportional to the fraction of organic carbon in the soil. Furthermore lateral diffusion of chemicals in the water phase can be ignored such that contaminant transport is only through the vapor phase in this work (Figure 4.1).

4.2 1D MASS TRANSPORT MODEL USING MATLAB

The MATLAB code developed by Fernandez *et al.* (2009) for sediments assumes partitioning between phases to be faster than diffusion of the chemical and was developed for a polyethylene sampler with identical boundary conditions as it would in soil. Therefore the code was altered to generate a 1D diffusion mass transport model based on the basic 3-phase conceptual model for diffusion through soil. To adjust the sediment model for soil, an air phase was added and diffusion was transferred from the water to the vapor phase (Appendix A). The tortuosity calculation was also changed to a density-corrected formula developed by Deepagoda *et al.* for diffusion in soils (Deepagoda *et al.*, 2011). Similar to the original code described in section 3.1, the adjusted model predicts the amount a target chemical in the PE sampler over time as a fraction of equilibrium mass (Figure 4.2). Using the model, one can anticipate the timecourse for VOC uptake into a PE sampler (Figure 4.3). The model output shows that initial mass uptake is very rapid with the sampler reaching 90% of equilibrium in about 12 h. However, the uptake rate then decreases rapidly barely adding another 5% in the next 12 h. The MATLAB code can be found in Appendix B.

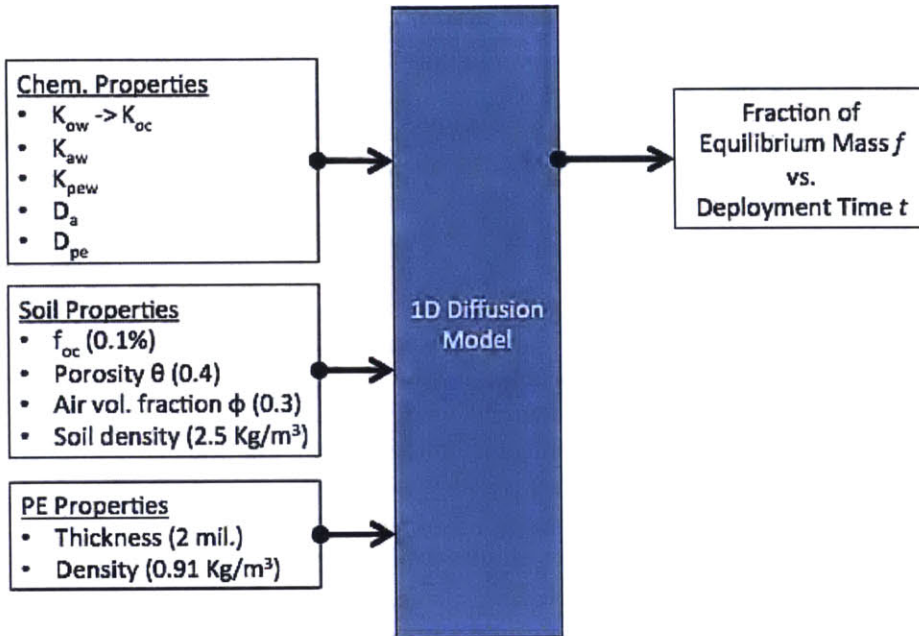


Figure 4.2: Parameters required for 1D diffusion mass transport model and its output. Default values for soil properties are shown in prentices.

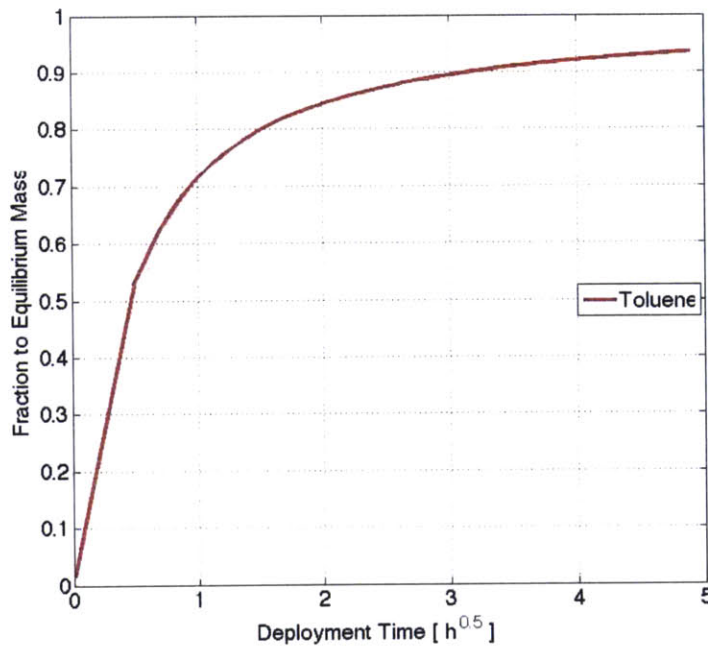


Figure 4.3: 1D diffusion mass transport model output of toluene, using a 0.002" (51 μm) thick PE sampler, as fraction of equilibrium mass vs deployment time. Assumes a 3-phase partitioning model, with partitioning to solids proportional to fractional of organic carbon (0.1%), in a soil with porosity of 0.4 and air volume content of 0.3.

4.3 ADDITIONAL COMPLEXITIES OF THE UNSATURATED ZONE

It is expected that there are additional complexities not currently captured in the 3-phase partitioning model. As Rivett *et al.* (2011) showed (Figure 4.4), the environment in the unsaturated zone can be extremely complicated. Potential complications are expected due to varying moisture content, the presence of free phase contaminant, adsorption to mineral surfaces, chemical reactions, and biodegradation. Previous studies have demonstrated the significance of soil moisture content in determining effective diffusion because of its influence on tortuosity (Rivett *et al.*, 2011; Unger *et al.*, 1996; Wang *et al.*, 2003). Some papers have also suggested that organic content in soils is a minor influence to sorption under certain conditions and that adsorption to minerals is the dominant process (Cabbar & McCoy, 1996). Additionally, others have indicated that black carbon in the soil will substantially influence sorption partitioning such that simple $f_{oc}K_{oc}$ models become inaccurate (Apell & Gschwend, 2014). Consideration of soil temperature, which can change partitioning coefficients, especially Henry's constant, is also of concern (Provoost *et al.*, 2009). Even the influence of a separate gas/water interface phase has been observed in literature and may need to be considered for accurate predictive modeling (Cabbar & McCoy, 1996; Wang *et al.*, 2003).

In this thesis, consideration will only be given to three phase partitioning between air, water, and solids. Where partitioning to solids is proportional to organic carbon content. This conceptual model is potentially an over simplification in some environments and as such its use in a predictive model without verification should be evaluated with some uncertainty.

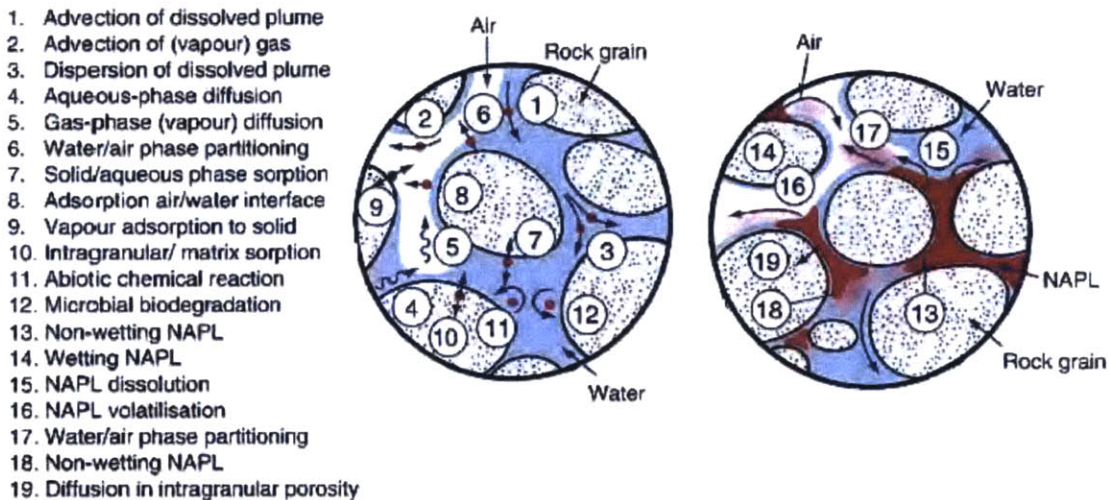


Figure 4.4: Conceptualization from Rivett *et al.* (2011) of potential phase partitions and reactions occurring in the unsaturated zone. Only dissolved contaminants are considered in the left figure and dissolved plus free phase NAPL contaminants are considered in the right.

5 PROBE DESIGN CRITERIA AND EXTRACTION METHOD

5.1 DESIGN CRITERIA

Design criteria for the soil vapor probe were selected in order to gauge the probe's effectiveness as a measurement tool, its practicality in the field, and its ability to be quickly implemented into current practice. The most important property of the sampler, however, is that it accurately measures the concentration of target chemicals in the soil vapor. In order to be accurate, the sampler should disturb equilibrium conditions as little as possible and minimize potential sources of error. Additionally, these accurate measurements must be at concentration levels of interest to regulators and landowners.

Furthermore for the passive sampler to be quickly accepted as a sampling method, it should use existing technology and methods where possible. By using existing probe equipment, field engineers investigating a site ideally need only to purchase the PRC impregnated polyethylene to begin using it. Moreover by taking advantage of existing approved laboratory analysis methods, the sampler can be analyzed for VOCs immediately at most environmental testing labs. Other design criteria were considered and all are summarized in Table 5.1.

Table 5.1: Design criteria that gauge a deployment probe sampler system's effectiveness, practicality in the field, and ability to be quickly implemented into current practice.

Design Considerations
1. Maximize accuracy – minimum disturbance of existing conditions
2. Detect concentrations below regulator screening levels for vapor intrusion
3. Use existing methods and analysis techniques
4. Deployable in vertical and horizontal profiles
5. Low cost
6. Robust and durable
7. Portable/minimize size requirements

5.2 CURRENT SOIL VAPOR SAMPLER PROBE DESIGNS

5.2.1 Passive Sampler Deployment

Current passive sampling devices are typically deployed by drilling a small diameter hole of about 2.5 cm in the ground to a depth between 15 cm and 1 m below land surface. The sampler is then suspended within the hole by a wire or string and the top of the hole is sealed (ASTM Standard D7758-11, 2012). This method has been successful at deploying samplers and making measurements at shallow depth; however the ideal probe design should also be able to make measurements at greater soil depths. By being able to deploy at depth greater than 1 m, both horizontal and vertical concentration profiles can be generated thereby providing greater information to site investigators. While this is not common in passive sampler deployment, many active gas sampling devices are able to deploy to significant depths.

5.2.2 Active Soil Gas Sampler Deployment

Current active gas sampling devices have two main deployment methods. The first method involves auguring a large diameter hole and placing screened implants throughout the hole at desired depths. The well hole is then backfilled with permeable material to encourage gas flow except for a layer of low permeability bentonite used to separate screened implants. Soil gas can then be pumped through the screened implants to containers and shipped for analysis (Figure 5.1 C). This setup can be useful for permanent or semi-permanent active gas sampling locations (ASTM Standard D7663, 2012). The auguring method however causes large disturbances to the equilibrium conditions underground, and it is not readily apparent that there is an easy way to retrieve the passive sampler after deployment.

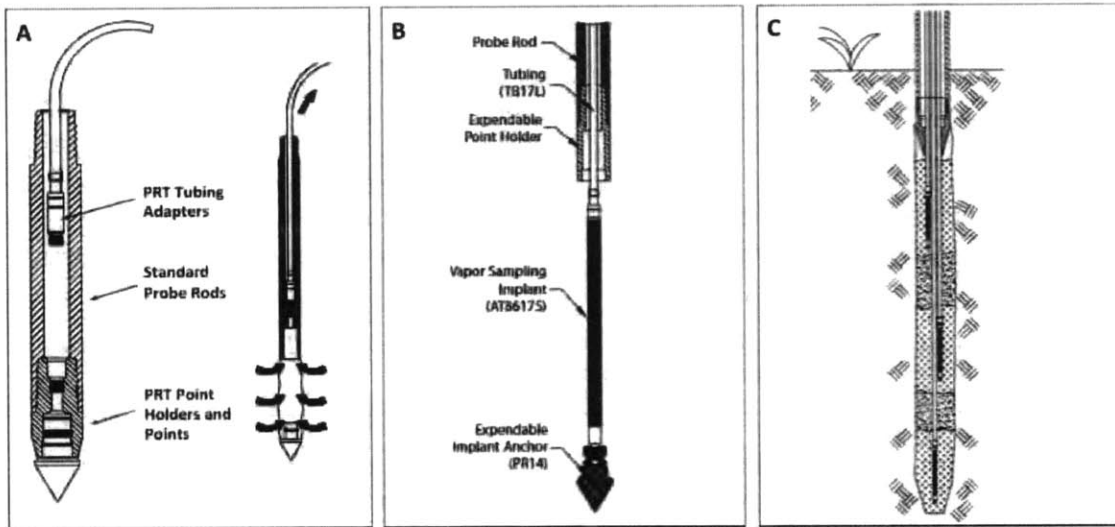


Figure 5.1 (A,B,C): Examples of current active gas sampling deployment methods. Image A shows a post-run tube sampler and image B shows a screen implantation device. Both of these devices can be installed by hand or direct-push technologies. Image C shows a common soil gas monitoring well installation with multi-level soil gas sampling. Bentonite layers separate the screened implants (Geoprobe Systems, 2006).

The other category is a probe design that is either driven into the soil by hand or inserted via direct-push technology. In both cases, the probe is pushed into the ground to the desired sampling depth and then pulled up slightly to expose the end of the pipe to the surrounding soil gas. When pulled back the probe tip either detaches or a screened implant is deposited and the hole is backfilled (Figure 5.1 A&B). However, in one design, a screened and perforated section of the rod is revealed and remains attached to the tooling string to be extracted and reused after decontamination (Figure 5.2).

Based on the background research into probe designs, it was determined that the PE passive sampler could be integrated with common active soil vapor extraction methods. By integrating with this existing technology, it is possible to generate horizontal and vertical concentration profiles. Additionally, if drillers already own the active gas equipment, the passive sampler method can easily be implemented with minimal additional costs.



Figure 5.2: Image of AMS "Retract-A-Tip" Gas Vapor Probe Tip (AMS, 2013)

In order to simplify a prototype design, it was decided that the probe should be initially hand driven into the ground. Direct-push technology is common in most site investigations and provides access to sampler deployments in a wider variety of soils and at greater depths. However, it also requires a trained operator to run and access for testing was not readily available. Therefore if a hand driven tool is proven successful, further investigation should be done into transferring the design to direct-push probe technology. In order to better investigate the active gas sampling equipment, hand tool versions of the Geoprobe and AMS samplers for soil vapor sampling were rented and inspected.

The provided Geoprobe system included 4' long interlocking segments of pipe with a 1.5" diameter. The interlocking pipe system offered a smooth exterior surface the entire length of the tooling string. After inserting the probe to the desired depth, air extraction tubing is run through the pipe and attached to an adapter near the tip. Finally by pulling up on the tooling string, the expendable tip is removed and soil vapor can be extracted through the end of the pipe by vacuum (Figure 5.1 A).

The AMS system consists of individual 4' lengths of pipe with a 5/8" diameter. The pipes are connected via couplings which protruded to a slightly greater width than the pipe. Different from the Geoprobe, which uses post-run tubing, the AMS system attaches the vapor extraction tubing to the probe end before insertion into the ground. Once the desired depth is reached the tooling string is pulled up slightly exposing the tip and soil vapor is extracted by vacuum. The probe tip can either be of an expendable or a retract-a-tip design (Figure 5.2).

5.3 PASSIVE SOIL VAPOR SAMPLER PROBE IDEAS

Based on consideration of the design criteria, several ideas were generated that would use the hand driven systems and provide direct exposure of the PE to the soil. Some conceptual ideas for a sampler deployment method included:

- PE, installed in the end of the pipe just above the tip, is securely attached to the tooling string and loosely attached to the expendable tip. Thus when the tooling string is pulled up and the expendable tip detached, the PE unravels and is exposed to the soil environment.

- PE is installed within a retract-a-tip system such that, when the tooling string is pulled back, PE wrapped around a smaller diameter pipe is exposed to the soil environment.
- PE is secured directly to the outside of the tooling string and if necessary can be protected during the driving by a perforated cover.

By heavily weighting the need for ease of implementation into current practice and low costs, it was decided to first try securing the PE around the circumference of the pipe. Because the couplings of the AMS system are slightly wider than the pipe segments, it was surmised that they could provide some protection to the PE as opposed to the smooth exterior of the Geoprobe system. The AMS system was therefore chosen for initial testing. Further investigation into the AMS samplers showed that the company also sells tile probes of the same design as the vapor probes, but as solid rods. This design is more amenable, as it provides greater strength to the tooling string. In order to integrate the passive sampler into the AMS tile probe system, short segments of 1 ft length and 5/8" diameter rod were machined to have threads compatible with the AMS couplings. Using these short segments was thought to provide better protection to the PE during driving and removal due to the closer proximity of the couplings. It also provides the flexibility to machine any additional features that may be required to secure the PE without altering the original AMS tools (Figure 5.3).

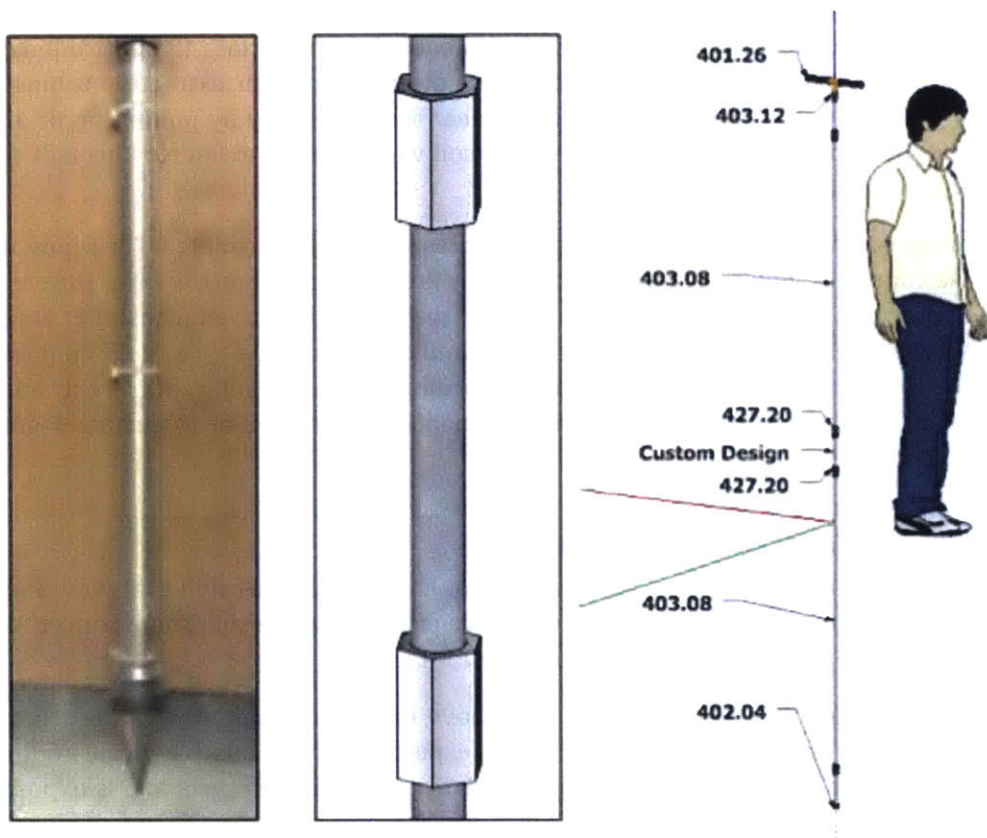


Figure 5.3: Diagram of initial probe design consisting of 1' sections of rod, on which PE sampler will be secured. Short sections are separated by 4' sections of rod. AMS Sampler part numbers are labeled.

Using this design, the PE would be fixed to the short segment of rod and driven into the ground separated by the long segments. This pattern of short PE covered pipes inserted between each 4' length provides the advantage of a discretized vertical soil profile in a single tooling string.

5.4 PRELIMINARY PROBE TESTING

All parts except the custom 1 ft length rods were purchased from AMS. Table 5.2 contains all the part numbers, descriptions, and costs of those items purchased. The overall costs for materials from AMS were relatively low for a complete probe. The unknown costs are associated with the custom 1 ft rods, which were machined from 304 stainless steel 5/8" diameter rod purchased from McMaster Carr. The rods were machined to add threads that match the AMS couplings, but as discussed below, these rods may need additional features. It is also presumed that any costs associated with this manufacturing would decrease with increased production.

Table 5.2: AMS Sampler parts purchased to make passive sampler probe. Additional probe extensions and couplings can be purchased to reach greater depth.

Description	Part #	Unit Price	Quantity	SubTotal
5/8" Extendible Tile Probe Complete Includes: Base extension (4'), tip, hammer adapter, 10" cross handle	403.09	\$102.90	1	\$102.90
5/8" Extendible Tile Probe Coupling	427.20	\$9.00	3	\$27.00
5/8" Tile Probe Extension	403.08	\$99.40	1	\$99.40
5/8" Threaded, Regular Slide Hammer	400.99	\$173.80	1	\$173.80
Removal Jack	211.05	\$186.70	1	\$186.70
Tee Jack Adapter	211.06	\$28.50	1	\$28.50
			TOTAL	\$618.30

Preliminary testing was conducted on the sampler to investigate different methods of securing the polyethylene to the rod and PE integrity during driving. As a simple test, a potting soil and gravel mix was added to a 4 1/2 ft tall by 1 ft diameter PVC pipe. The soil mixture had very low moisture content. After the soil mixture was added, the pipe was tapped with a rubber hammer to settle the material. The settling caused an approximate 4" drop in soil height within the PVC pipe. After securing PE to the probe, it was driven into the soil to an approximate depth of 4' using a small metal sledgehammer. After reaching the desired depth, the PVC pipe was lifted up allowing the soil mixture to fall out the bottom. This procedure allowed observation of the PE as it would exist at sampling depth instead of after extraction.

Two methods were used to secure the PE. The first was plastic cable ties and the second was with electrical tape. The probe was assembled such that two custom 1 ft sections followed the probe tip allowing a limited comparison between PE bordered by the tip and a coupling and PE bordered by two couplings. These custom rods were then coupled to a 4'

length, which was hit by the sledgehammer to drive the probe. After a single test of each securing method it was clear that a protective cover over the PE would be needed during the insertion of the probe. Observation of the PE after driving showed extensive damage as well as sliding on the rod (Figure 5.4). This damage to the PE would severely impact the ability to make accurate measurements and predict necessary deployment times. Additional pictures of preliminary testing are shown in Appendix C.

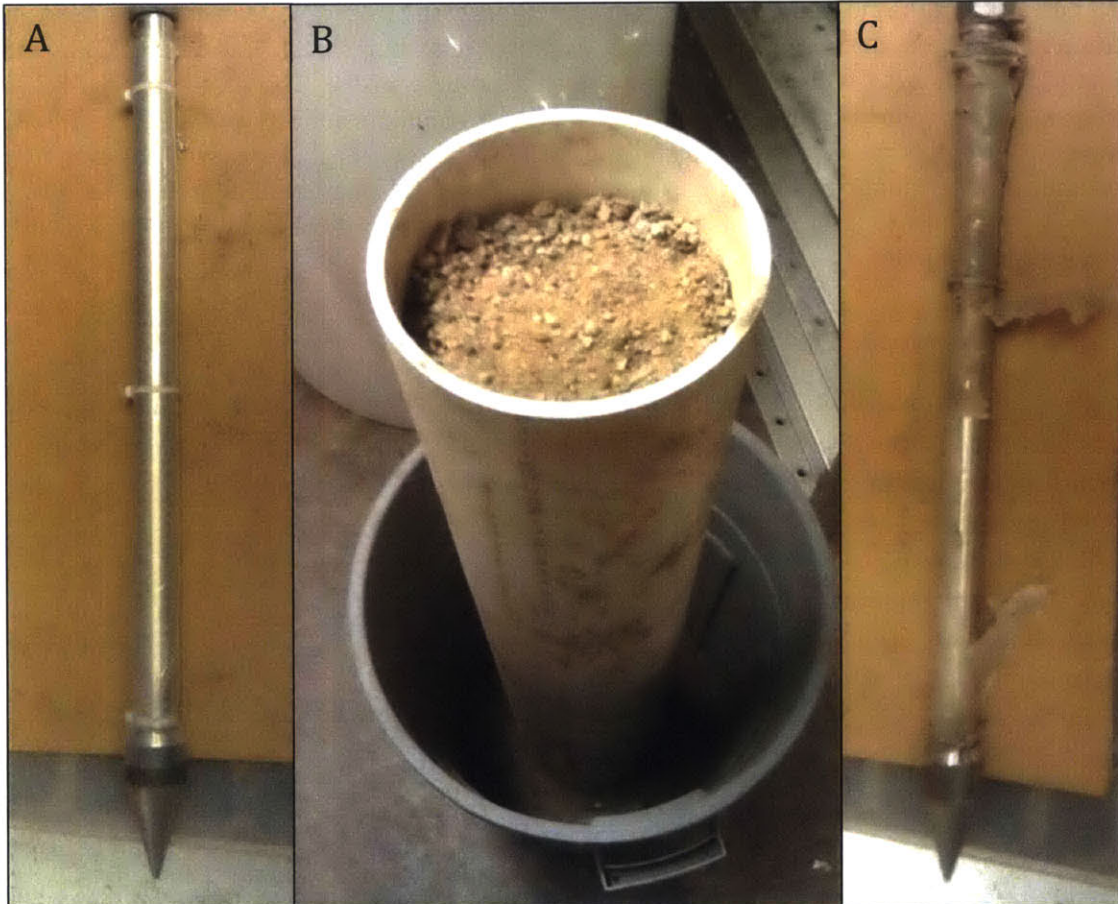


Figure 5.4(A,B,C): A) PE secured to custom 1' length and 5/8" diameter rod via plastic cable ties. B) Potting soil and gravel mixture in approximately 4' long and 1' diameter PVC pipe. C) PE was ripped and stretched during driving into soil mixture. Cable ties slid along rod length. A protective cover over the PE is needed, such as perforated pipe.

In order to address this problem, an investigation must be made into a design that protects the PE during driving of the probe. A possible solution is to add a perforated pipe that would slide over the PE once it was secured to the probe rod. If done correctly this design would provide sufficient protection to the PE while minimizing interference of soil vapor diffusion to the PE. If this method does not work then a design similar to the retract-a-tip system may need to be investigated (Figure 5.2).

5.5 POLYETHYLENE EXTRACTION METHOD

Finally the extraction method was selected to take advantage of existing laboratory analysis methods for VOCs. The EPA method of interest was 5030B for purge and trap analysis of aqueous samples, paired with EPA method 8015C for analysis of nonhalogenated organics by GC-FID. As such, after the probe is removed from the ground, the PE is wiped clean of solids, placed in a 60 mL BOD bottle of water, ensuring no headspace, and allowed to equilibrate (Figure 5.5). The extraction water can then be analyzed and the concentration related back to the initial PE concentration by a mass balance and the PE-water partitioning coefficient using the following equation:

$$C_{PE}^0 M_{PE} = C_{PE} M_{PE} + C_{W,Measured} V_W \quad C_{PE} = K_{PE-W} C_W$$

$$C_{PE}^0 M_{PE} = C_{W,Measured} K_{PE-W} M_{PE} + C_{W,Measured} V_W$$

$$C_{PE}^0 = (K_{PE-W} M_{PE} + V_W) \frac{C_{W,Measured}}{M_{PE}}$$

where C_{PE}^0 is the compound concentration in the PE prior to extraction in units of mass/mass PE, M_{PE} is the mass of PE, C_{PE} is the compound concentration in the PE after equilibration in units of mass/mass PE, $C_{W,Measured}$ is the compound concentration in the extraction water after equilibration in units of mass/length³, V_W is the volume of extraction water, and K_{PE-W} is the PE-water partitioning coefficient in units of length³/mass PE.

Additional information on the analysis methods and laboratory procedures can be found in theses by J. Soo (2015) and H. Liu (2015).

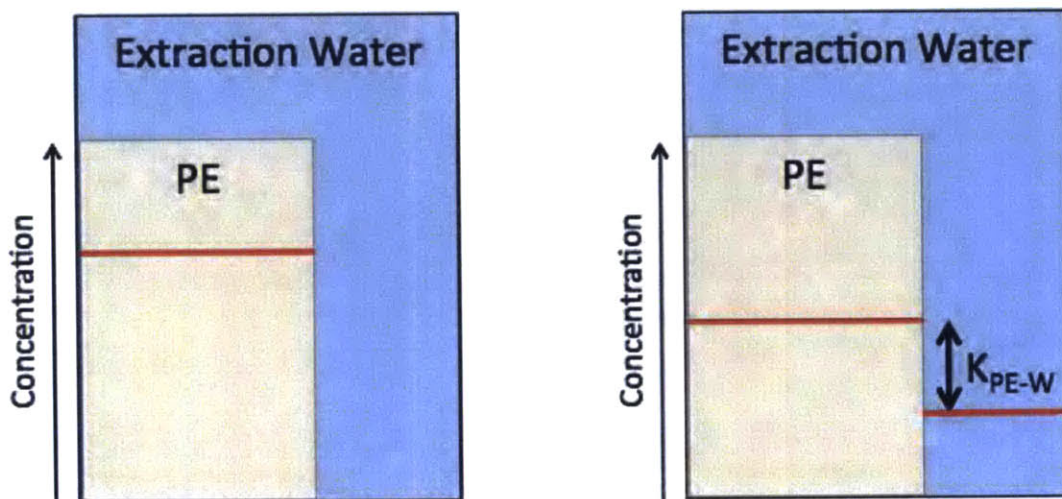


Figure 5.5: In order to utilize existing laboratory methods for VOC analysis the PE is extracted by water. The PE added to a BOD bottle, ensuring no headspace, and allowed to equilibrium with the water. The initial PE concentration can be determined by summing the measured extraction water concentration and PE equilibrium concentration, calculated by the PE-water partitioning coefficient.

6 POLYETHYLENE DIMENSION OPTIMIZATION

6.1 THE SOIL VAPOR DETECTION LIMIT

When sampling soil gas via active gas extraction, the collected vapor sample can be directly injected into an analytical instrument. This means that the lowest concentration of a chemical that can be measured in the vapor is equivalent to the detection limits of the instrument. However, in most cases, when using an absorptive passive sampler, contaminants partition into the sampler and then later into an extraction medium. Therefore the minimum soil vapor concentrations that can be measured are not the same as the detection limits of the analytical instrument. The detection limit of the passive sampler will be dependent, not only on the sensitivity of the analytical instrument, but also chemical properties of the contaminant, sampler properties, and deployment times. For example, a larger mass of PE (thicker or greater surface area) will increase the amount of contaminant that the sampler can collect at equilibrium. A larger quantity of contaminant in the sampler increases the mass that can partition into the extraction solvent (here it is water) to be detected by the analytical instrument.

For the purpose of this report, the analysis of VOCs is assumed to be by direct aqueous injection from PE-equilibrated water and then GC-FID separation and detection (EPA method 8015C). The detection limit for BTEX compounds using direct aqueous injection has been reported to be 5 µg/L (Potter, 1996). It is also possible to use purge and trap collection (EPA method 5030B) instead of direct aqueous injection. We expect the purge and trap concentration approach will be at least a factor of 100 lower. However, for the following, we will assume the VOC detection limits to be 5 µg/L (= 5 ng/mL) to be conservative.

Given the detection limit of the instrument and the defined extraction process, it is possible to determine an equivalent soil vapor concentration. For the rest of this report this concentration will be referred to as the Soil Vapor Detection Limit (SVDL). The SVDL is specific to the selected extraction and analysis method and is dependent on the properties of the target compound.

The following process is a representative investigation into the utility of the PE quantitative passive sampler for a specific task using a developed MATLAB code (shown in Appendix B). However, depending on the needs of a site, the code may be adjusted to investigate different compounds, soils, or levels of sensitivity.

6.2 REGULATORY LEVELS OF SOIL VAPOR CONCENTRATION

In order to gauge sampler utility, predicted SVDLs were compared to state environmental agency sub-slab vapor intrusion screening values. Site investigators use screening concentrations to determine if soil vapor intrusion should be studied further as a potential exposure pathway. Therefore the ideal soil vapor sampler will be able to measure concentrations less than the screening values. Sub-slab screening is a method that is routinely used in vapor intrusion investigation and likely represents the lower bound of required soil vapor detection.

In 2002 the EPA issued vapor intrusion guidance documentation containing generic screening concentrations for chemicals of interest at varying degrees of health risk. Since then, state environmental agencies have issued their own guidance documents for vapor intrusion. These screening values are based on specific choices of acceptable risk and attenuation factors between the soil vapors and indoor air. State screening values will therefore differ depending on whether the site is located in a residential or an industrial setting. Screening levels from the Massachusetts Department of Environmental Protection (MassDEP) as well as those from the New Jersey Department of Environmental Protection (NJDEP) indicate target concentrations for BTEX between about 0.01 and 1000 mg/m³ (Table 6.1).

Table 6.1: Sub-slab screening levels [mg/m³] from MassDEP and NJDEP issued vapor intrusion guidance. Each agency uses a different method for determining acceptable risk and attenuation factors. (MassDEP, 2011; NJDEP, 2013).

VOC (mg/m ³)	Mass. DEP		NJDEP	
	Residential	Industrial	Residential	Industrial
Benzene	0.16	0.77	0.016	0.079
Toluene	3.8	310	260	1,100
Ethylbenzene	0.52	62	0.049	0.25
Xylenes (total)	1.4	62	5.2	22

Order of magnitude concentrations were then selected as reference values, to provide a quantitative method to analyze PE passive sampler utility in soil environments. The best sampler should be able to detect the highly toxic (e.g., benzene) compounds below their lowest screening levels thus requiring SVDLs in the 0.01 to 0.1 mg/m³ range. A sampler with sensitivity around 1 mg/m³ would not be able to screen for highly toxic VOCs at any site, but would be useful for screening lower toxicity compounds (e.g., toluene) at residential and industrial sites. A sampler with SVDLs around 10 mg/m³ is only applicable for less toxic VOCs at industrial sites. Finally, a sampler with 100 mg/m³ or greater sensitivity will only be useful for some low toxicity VOCs and therefore is not applicable as a sampler for sub-slab screening. These reference values are summarized in Table 6.2.

Table 6.2: Table of passive sampler sensitivity and its applicability to sub-slab screening of BTEX compounds based on concentrations from MassDEP and NJDEP vapor intrusion guidance documents (MassDEP, 2011; NJDEP, 2013). 'X' indicates sensitivity below the screening level and '-' indicates sensitivity above the screening level. The ideal sampler would be able applicable to all chemicals and sites.

Sampler Sensitivity (mg/m ³)	More Toxic (Benzene, Ethylbenzene)		Less Toxic (Toluene)	
	Residential	Industrial	Residential	Industrial
0.01mg/m³	X	X	X	X
1 mg/m³	-	-	X	X
10 mg/m³	-	-	-	X
100 mg/m³	-	-	-	X/-

6.3 EQUILIBRIUM CONDITION LIMITS OF DETECTION

In the limit where the PE sampler is allowed to come to equilibrium with the soil vapor, the influence of deployment time on the SVDL is removed. Furthermore PE dimensions are no longer significant, only the total PE volume is required. In this case the concentration in the PE is directly related to the concentration in the soil vapor by the PE-air partitioning coefficient

$$C_{PE}^0 = K_{PE-A} * C_{Air}$$

where C_{PE}^0 is the concentration in the PE upon removal from the soil in units of VOC/mass PE, C_{air} is the concentration in the soil vapors in units of VOC/length³, and K_{PE-A} is the partitioning coefficient for the target chemical between PE and air in units of length³/mass PE.

Substituting for the initial PE concentration (C_{PE}^0) in the equation developed in section 5.5, which relates extraction water concentration ($C_{W,Measured}$) to initial PE concentration, and rearranging, yields an equation for the soil vapor concentration.

$$C_{Air} = \left(K_{AW} + \frac{1}{K_{PE-A}} \frac{\left(V_{BOD} - \frac{M_{PE}}{\rho_{PE}} \right)}{M_{PE}} \right) C_{W,Measured}$$

where the volume of extraction water is calculated as the volume of the extraction bottle V_{BOD} less the volume of the PE, ρ_{PE} is the PE density, and M_{PE} is the mass of PE. K_{AW} is the air-water partitioning coefficient resultant from the quotient K_{PE-W}/K_{PE-A} .

If the extraction water concentration $C_{W,Measured}$ is the detection limit of the purge-and-trap instrument, then the soil vapor concentration C_{Air} is the equivalent soil vapor detection limit, for a specific chemical. The SVDL is a function of the extraction bottle volume and the PE volume. Furthermore, assuming the detection limit of the analytical instrument is constant, then in the limit where the mass of PE increases or the BOD volume decreases, the 2nd term will become negligible relative to K_{AW} , and C_{Air}^{min} will approach an asymptote equal to $K_{AW}C_{W,Measured}^{min}$.

$$\text{for } M_{PE} \rightarrow \infty, K_{AW} \gg \frac{1}{K_{PE-A}} \frac{\left(V_{BOD} - \frac{M_{PE}}{\rho_{PE}} \right)}{M_{PE}}$$

$$\text{and } C_{Air}^{min} = \left(K_{AW} + \frac{1}{K_{PE-A}} \frac{\left(V_{BOD} - \frac{M_{PE}}{\rho_{PE}} \right)}{M_{PE}} \right) C_{W,Measured}^{min} \approx K_{AW} C_{W,Measured}^{min}$$

Therefore at equilibrium, the smallest SVDL attainable by the passive sampler is dependent only on the air-water partitioning coefficient of the target chemical and the minimum detectable concentration of the analytical instrument. This is reasonably explained because if the amount of mass removed from the PE in the extraction process is small relative to the total contaminant mass in the PE, then the PE concentration doesn't change significantly. If the PE concentration doesn't change during extraction, then it's as if the soil vapor, PE, and extraction water are all in equilibrium. If the soil vapor and extraction water are in

equilibrium then they are related by their partitioning coefficient K_{AW} . Therefore the detection limit of the instrument translates to an air concentration limit simply by the partitioning coefficient.

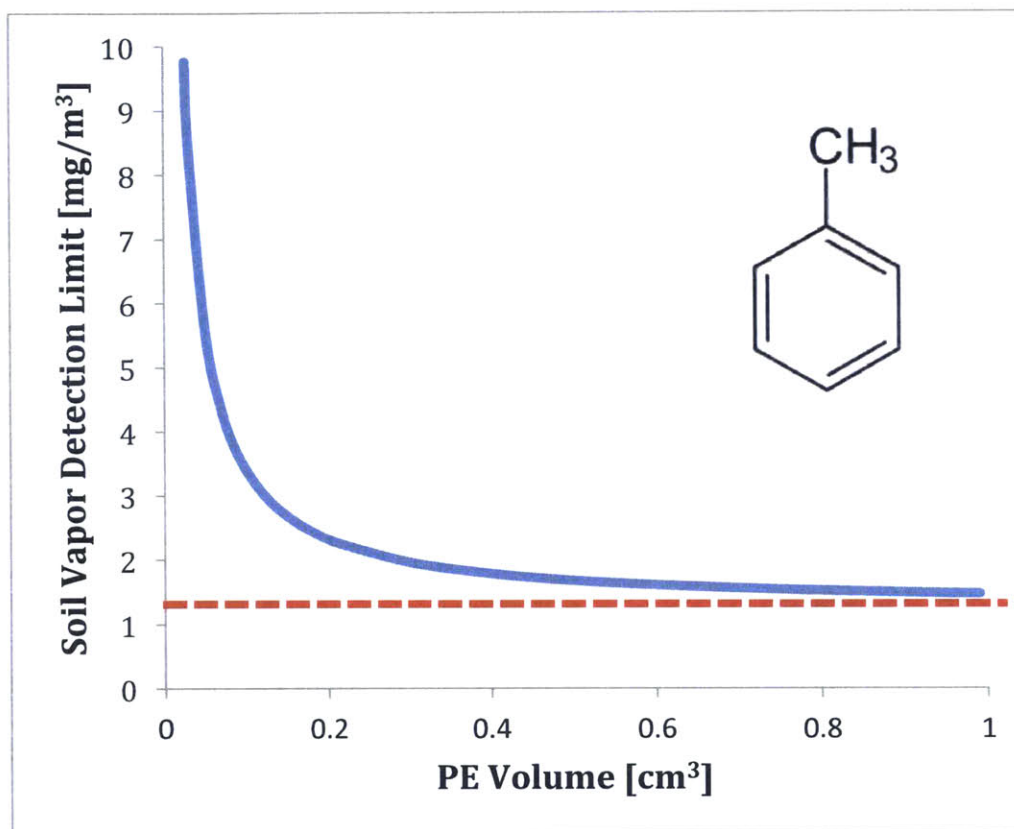


Figure 6.1: Plot of Toluene Soil Vapor Detection Limit with changing PE volume and an analytical sensitivity of 5ng/mL. The SVDL approaches an asymptote with increasing sampler volume equal to the detection limit of the analytical instrument multiplied by the chemical's air-water partitioning coefficient.

As an example, the soil vapor detection limit for toluene was plotted versus PE volume using an analytical instrument sensitivity of 5 ng/mL (based on direct aqueous injections). The resulting graph quickly approaches an asymptote with increasing PE volume (Figure 6.1). This minimum SVDL limit for toluene is equivalent to the air-water partitioning coefficient multiplied by the detection limit of the analytical instrument or approximately $(0.25\text{mL/mL}) \cdot (5\text{ng/mL})$, equal to 1.25 mg/m^3 .

A SVDL of 1.25 mg/m^3 , compared to the prepared outline of sampler sensitivity and vapor intrusion screening levels in Table 6.2, is too great to screen highly toxic VOCs at residential or industrial sites. It is, however, close to the 1 mg/m^3 magnitude level where lower toxicity chemicals can be screened at residential and industrial sites. Detecting below the screening level, however, will be dependent on the properties of the target compound and its related screening value. For example, toluene has a residential screening value of 3.6 mg/m^3 in Massachusetts, which may be too close to the sampler's theoretical limit given sampling and analytical uncertainties. However, the residential screening value of toluene is 260 mg/m^3

in New Jersey, which is easily attained by the sampler. Therefore, it would seem that the most practical use of the passive sampler for screening is for low toxicity compounds at industrial sites. At this level a sensitivity of only 10 mg/m³ is required.

Additionally, information about the required PE size can be attained from Figure 6.1. In the plot it appears that the SVDL asymptote for toluene is mostly achieved by around 0.5 cm³ of PE. Considering the selected probe design, described in section 5.3, it is possible to estimate the PE dimensions required to reach the minimum theoretical SVDL, given equilibrium conditions. Considering a typical PE thickness of 0.002", a probe diameter of 5/8", and a total volume of 0.5 cm³, the length of PE can be calculated.

$$PE \text{ Height} = \frac{PE \text{ Vol.}}{PE \text{ Thick} * PE \text{ Width}} = \frac{0.5 \frac{1in.^3}{(2.54cm)^3}}{0.002in. * \pi \frac{5}{8}in.} = 7.8in.$$

This PE height is within the 12 inches designed for the probe's short rod lengths that will hold the PE. Therefore the initial probe design is capable of achieving the minimum SVDL if equilibrium conditions are attained.

Finally, as observed from the theoretical calculations of SVDL in equilibrium conditions, increasing the size of the polyethylene cannot lead to greater sampler sensitivity than the air-water partitioning coefficient multiplied by the detection limit of the analytical instrument. Therefore in order to decrease the SVDL, the best approach is probably to improve the analytical instrument sensitivity to be less than 5 ng/mL. For example, purge and trap concentrations of VOCs from 5 mL samples are expected to be about 100x lower than direct aqueous injection. Using this method, the minimum SVDL for toluene would drop from 1.25 mg/m³ to about 10 µg/m³. No matter what approach is used, the new method must have an extraction medium/air partitioning coefficient and detection limit product ($K_{\text{Extract-Air}} \times C_{\text{Measure}}$) less than the current method's theoretical minimum SVDL.

6.4 NON-EQUILIBRIUM CONDITION LIMITS OF DETECTION

For some chemicals the time to wait for equilibrium may be longer than practical or the full sensitivity of the sampler may not be needed. Therefore if the sampler is removed when it is only at a fraction to equilibrium (f), there will be less mass in the sampler and the method sensitivity will decrease. Assuming the same water extraction process, the equation for equilibrium conditions can be altered to include the fraction to equilibrium such that the concentration in the PE prior to extraction is given by

$$C_{PE}^0 = f C_{PE,eq}^0 = f * K_{PE-A} * C_{Air}$$

Now the final equation for the soil vapor detection limit becomes

$$C_{Air}^{min} = \frac{1}{f} \left(K_{AW} + \frac{1}{K_{PE-A}} \frac{(V_{BOD} - \frac{M_{PE}}{\rho_{PE}})}{M_{PE}} \right) C_W^{min}$$

where f is a function of both deployment time and PE thickness for a specific contaminant and can be determined by the model described in section 4.2. As PE thickness increases, the

time to reach a given fraction of equilibrium also increases. This relation however is nonlinear, such that doubling the thickness of PE more than doubles the time to reach the same fraction of equilibrium (Figure 6.2). Therefore it is important to be able to visualize the relation between PE thickness, surface area, and deployment time on the SVDL for non-equilibrium condition.

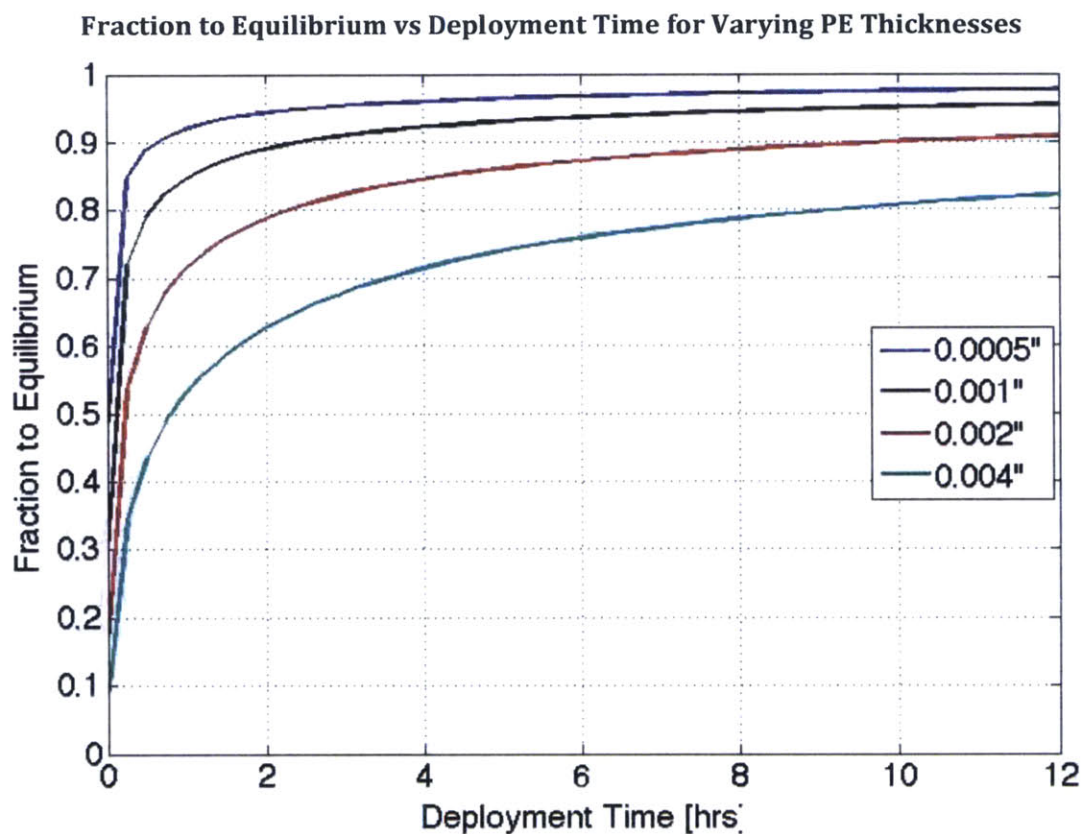


Figure 6.2: Nonlinear effects of PE thickness on fraction to equilibrium. Doubling PE thickness more than doubles the deployment time required to reach the same fraction to equilibrium.

By combining the 1D diffusion model with the equilibrium SVDL equation, it is possible to generate a 3D matrix of SVDL values for a target compound. The three matrix axes are PE thickness, PE surface area, and deployment time. Figure 6.3 (A) shows the required inputs for the model and Figure 6.3 (B) shows a representation of the 3D matrix output of SVDL data.

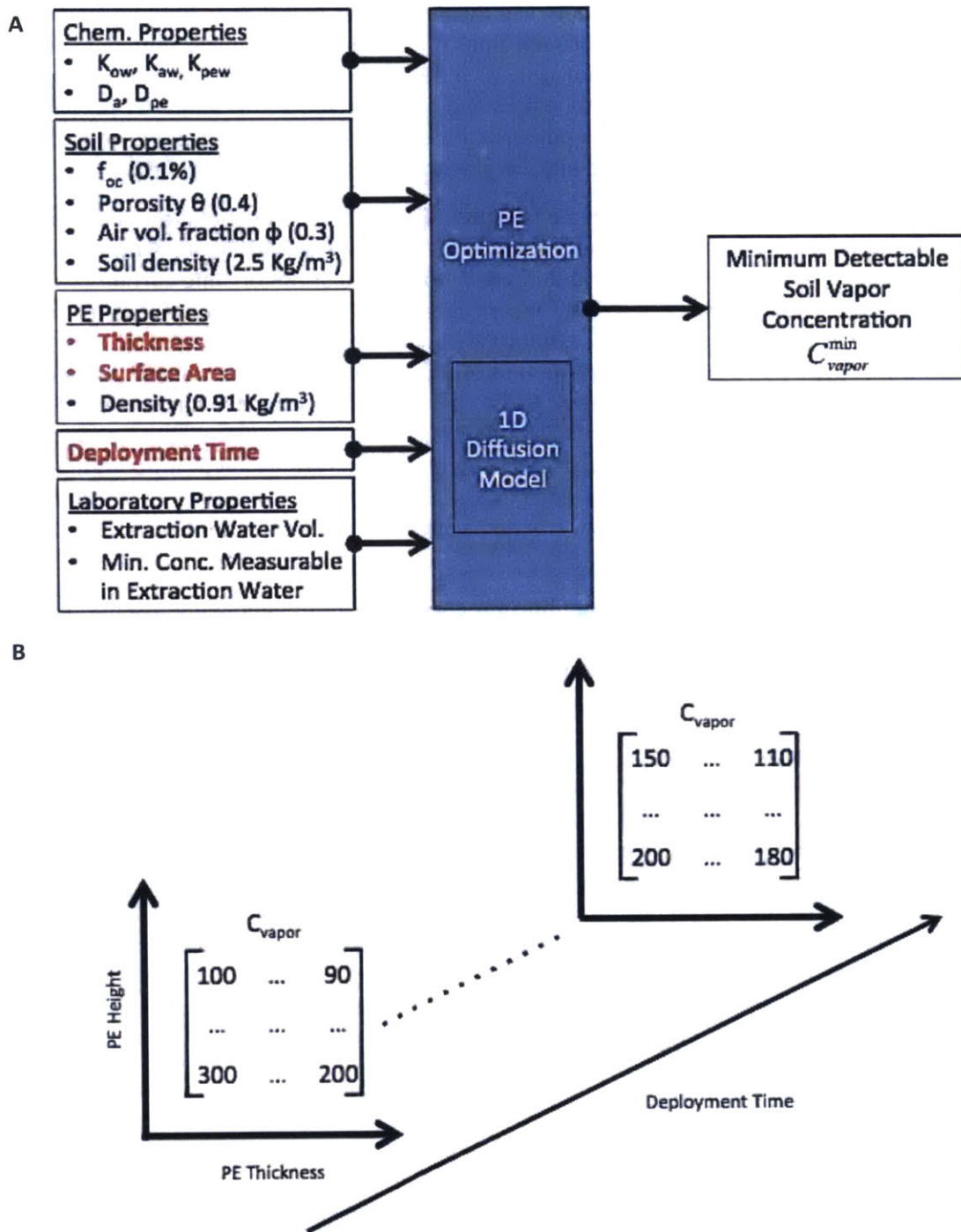


Figure 6.3: (A) Parameter inputs for MATLAB model of soil vapor detection limit. Variable parameters significant for the probe design are highlighted in red. (B) Diagram of 3D matrix output from model, where C_{vapor} is the soil vapor detection limit (mg/m³).

In order to visualize the relationship between these variables, it is best to hold one variable constant and create a contour plot showing lines of constant SVDL. For example, if the PE passive sampler is deployed for 12 hours, a 12 h deployment time contour plot will show the SVDLs for all combinations of PE thickness and height (given a 5/8" diameter pipe). The same analysis can be conducted for a constant PE thickness with changing PE height and deployment time or a constant height with varying thickness and deployment time.

Using typical soil properties, one can see how the PE sampling will depend on deployment time, PE surface area, and PE thickness (Figure 6.4, Figure 6.6, and Figure 6.6). Here the porosity was taken to be 0.4; the air volume fraction was 0.3; the organic carbon content was 0.1%; and the solids density was 2.5 kg/m³ (Figure 6.3 A). A GC/FID analysis by direct aqueous sample injection was assumed, with a detection limit of 5 ng/mL (Potter, 1996). A 60 mL BOD bottle was assumed for extraction of the PE by water. The chemical properties of toluene were used as a representative BTEX chemical. The parameter held constant and its value are labeled at the top of each contour plot. The contour lines show the combinations of the x & y variables that result in a specific SVDL value in units of mg/m³. Contour lines are only drawn and labeled at 2, 3, 4, 5, 10, 50, and 100 mg/m³. If the contour line is not present on the graph, then it is not achievable within the defined limits of the parameters.

Based on the analysis conducted at equilibrium conditions, in the following discussion the contour plots are used to determine the necessary PE thickness, PE height, and sampler deployment time to achieve a SVDL of 10 mg/m³. This sensitivity level would allow for the screening of low toxic chemicals at both residential and industrial sites.

6.4.1 Constant Deployment Time

Holding the deployment time constant allows for the determination of the PE height and thickness required to attain the 10 mg/m³ SVDL. Review of the four contour plots in Figure 6.4 shows that the 10 mg/m³ contour line does not change significantly between a 1 h deployment time and a 24 h deployment time. This suggests that a PE sampler with dimensions that fall on the 10 mg/m³ line is close to equilibrium within 1 h of deployment. This also means that the selected mass of PE is too small to absorb sufficient contaminant mass from soil vapor concentrations lower than 10mg/m³ to reach a water extraction concentration of 5 ng/mL. Therefore additional deployment time does not improve sampler sensitivity. This relationship is defined in Figure 6.1.

The pattern of time independent SVDL curves is observed for increasing smaller concentrations at each additional time step. For example between a 12 h and 24 h deployment time all the contour lines of SVDL greater than 3 mg/m³ barely change again suggesting the PE sampler is close to equilibrium and is thus limited by its dimensions. Referring back to Figure 4.3 shows that toluene has reach 90% of equilibrium after 12 h for a 0.002" thick sampler, confirming this assumption. Additionally these contour plots suggest that a larger piece of PE than that defined by the 10 mg/m³ line could be used to account for uncertainties in the model and not increase the required deployment time.

Soil Vapor Detection Limit (mg/m^3): Constant Deployment Time

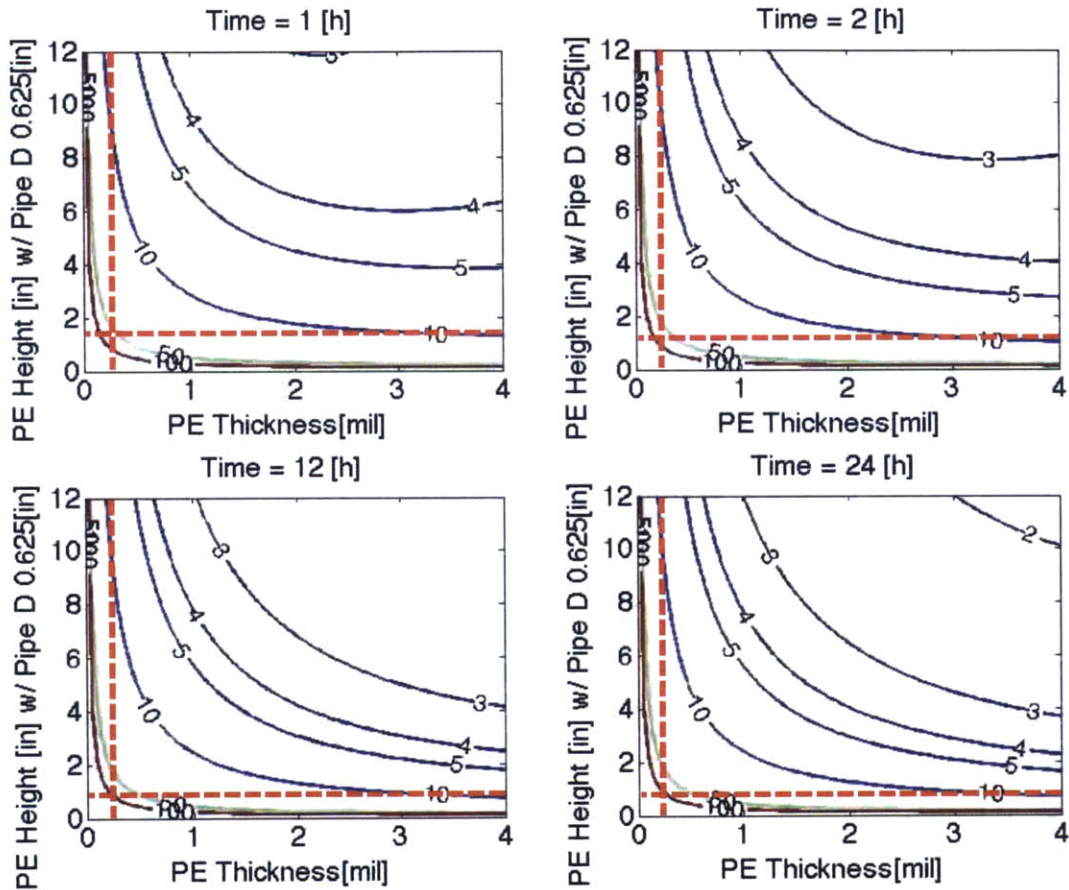


Figure 6.4: Contour plots of toluene soil vapor detection limit (mg/m^3) given constant deployment time. PE thickness of greater than about 0.005" and PE height of greater than 1.5" required for deployment times greater than 1 h to achieve 10 mg/m^3 SVDL.

6.4.2 Constant Polyethylene Thickness

From the contour graphs of constant PE thickness (Figure 6.5), the initial fast approach to equilibrium has an effect on sensitivity that is clearly visible. For the small PE thicknesses especially, deployment time has little impact on improving sensitivity. For example if a PE thickness of 0.002" is selected with a height of 5", after 5 h of deployment time the SVDL remains nearly constant at 4 mg/m^3 . Therefore to decrease the SVDL, the PE volume must be increased. With constant PE thickness, this is accomplished by increasing the PE height. To reach a sensitivity of 10 mg/m^3 , the PE thickness is relatively insignificant over 0.005", and the required deployment time is consistently only about 1 h. Similar observations were made from the constant deployment time plots (Figure 6.4). As expected, a constant SVDL near equilibrium conditions creates an inverse relation between PE thickness and PE length. This means that doubling the thickness of the PE nearly halves the required PE length. For example, a 0.0005" requires a 5" PE height and 0.001" thick PE only requires a 2.5" PE height to reach a 10 mg/m^3 SVDL.

Soil Vapor Detection Limit (mg/m^3): Constant PE Thickness

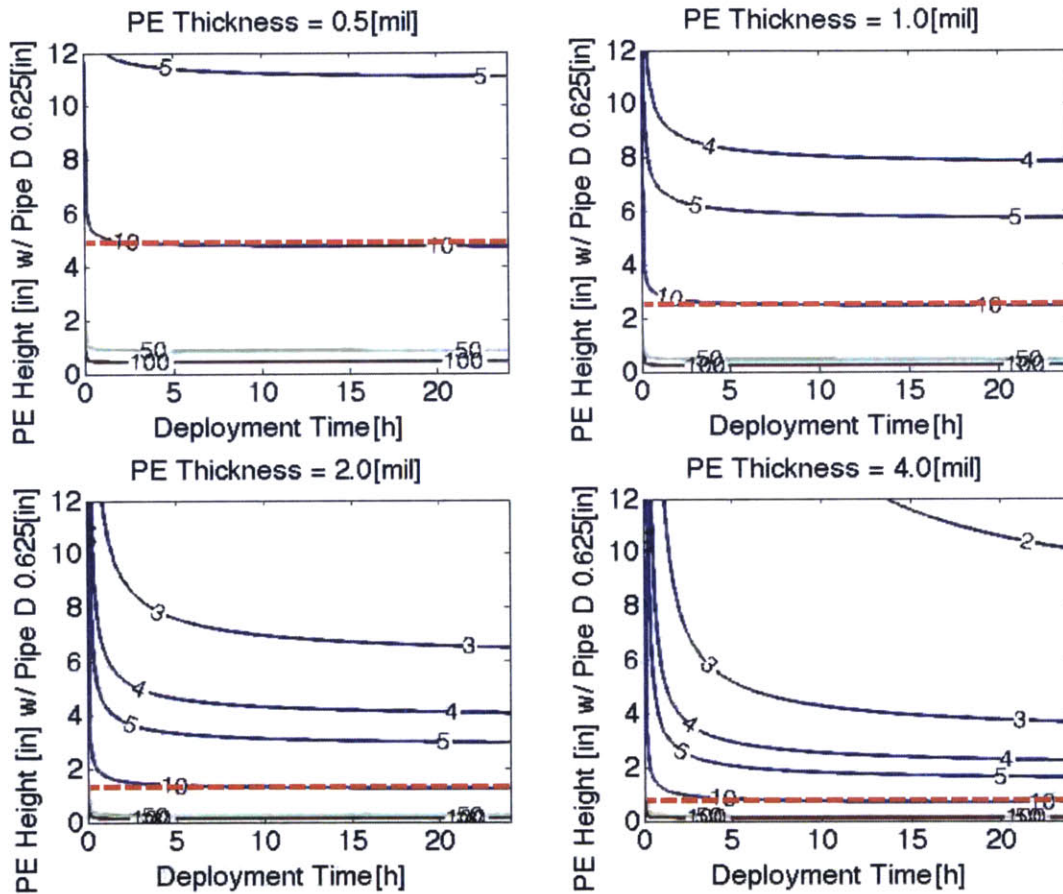


Figure 6.5: Contour plots of toluene Soil Vapor Detection Limit (mg/m^3) given constant PE thickness. As PE thickness increases, the required deployment time to achieve a $10 \text{ mg}/\text{m}^3$ SVDL stays the same at about 1h, but the required PE height decreases.

6.4.3 Constant Polyethylene Surface Area

Finally the 3D concentration matrix can be sliced into a 2D contour plot by holding the PE height constant (Figure 6.6). These plots can be useful in determining if a PE length can be divided in half, after sampling, and extracted separately to provide duplicates for a lab.

Many of the same observations can be made as were from the first two groups of contour plots. For example to reach a SVDL of $10 \text{ mg}/\text{m}^3$, a PE length of 1" or greater is required and as PE length increases the required PE thickness decreases. However it is more obvious in these plots that increasing sampler surface area decreases the required thickness and can significantly decrease deployment times for samplers not at equilibrium. For example, comparing the 3" length PE to the 6" length PE, the minimum deployment time, regardless of thickness, to reach a $4 \text{ mg}/\text{m}^3$ sensitivity drops from 5 h to less than 2 h. This analysis may be useful to determine when one can simply increase the PE height rather than have to wait for a longer deployment time to reach greater sensitivity.

Soil Vapor Detection Limit (mg/m^3): Constant PE Height

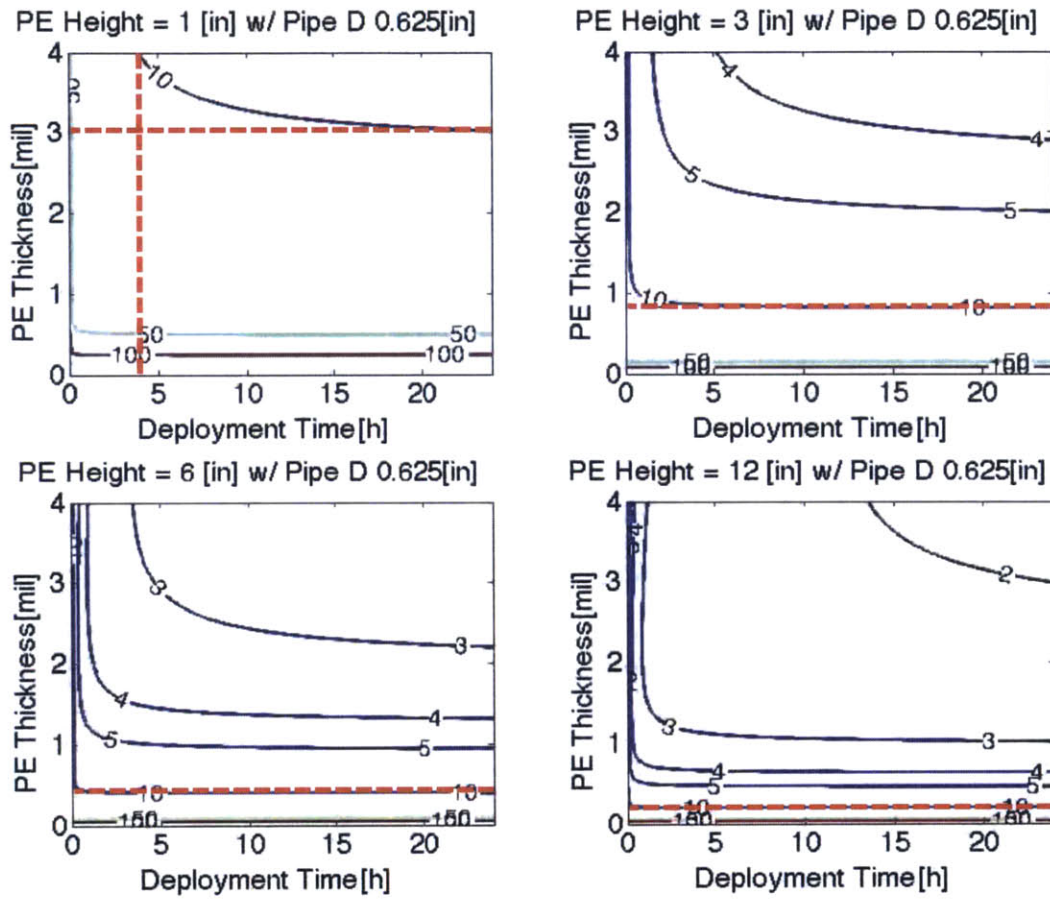


Figure 6.6: Contour plots of toluene soil vapor detection limit given constant PE surface area. The deployment time and PE thickness required to achieve a SVDL of $10 \text{ mg}/\text{m}^3$ both decrease as sampler surface area increases.

7 CONCLUSIONS AND FUTURE WORK

7.1 PE PASSIVE SAMPLERS AS SUB-SLAB VAPOR INTRUSION SCREENING DEVICES

From the analysis of the non-equilibrium soil vapor detection limit, it appears that this sampler design can be effective at measuring chemicals with screening levels in the 10 mg/m³ range within 1 h of deployment. This level of sensitivity, however, is only useful for vapor intrusion screening of low toxicity chemical, such as toluene, at residential or industrial sites. To achieve the sensitivities needed for more toxic chemicals, investigators must use methods such as purge and trap VOC concentrations before GC-FID analyses.

The results of the non-equilibrium model show that, given the default soil properties and direct aqueous injection method, chemicals with properties similar to toluene can be measured in soil vapors at concentrations of 10 to 4 mg/m³ in deployment times of 1 h. While this means sampling could occur very quickly it also raises concerns of quality control issues. Specifically if target chemicals are diffusing into and out of the sampler at such a rapid rate, how much mass is lost during the time it takes to remove the probe from the ground? This potential issue will need to be evaluated before or during field-testing.

7.2 ADDITIONAL APPLICATIONS OF NON-EQUILIBRIUM PE OPTIMIZATION MODEL

The initial rapid uptake of toluene to around 70% of equilibrium in the passive sampler makes the kinetics considerations relatively insignificant. This means that the non-equilibrium MATLAB model provided little additional information on optimizing the PE dimensions to reach a 10 mg/m³ SVDL. However, the model was developed to be applicable to a variety of chemicals and sites. A chemical with a larger molar volume is expected to have lower diffusion coefficients thus will take longer to reach equilibrium. In this case kinetics will become significant and PE sampler dimensions and deployment time can be optimized.

Additionally the model can be used to observe the effects of different soil properties on sampler sensitivity, assuming a 3-phase partitioning model. For example one may want to investigate what happens to the sensitivity when the moisture content of the soil increases, such as after a rain event. Figure 7.1 shows the difference between two contour plots of toluene SVDL with constant PE surface area, where the air volume fraction decreases from 0.3 to 0.15. Though there is minimal change to the sampler properties required to reach the higher SVDLs (e.g., 10 mg/m³), the sampler properties required to reach lower sensitivities do change with moisture content. In this case, a PE thickness and deployment time that had a sensitivity of 5 mg/m³ in 0.3 air volume fraction soil may not be able to attain the same sensitivity in 0.015 air volume fraction soil. A sensitivity analysis of the different variables in the model should be run in the future to determine those variables that influence PE optimization the most and therefore those properties that must be entered with greater precision.

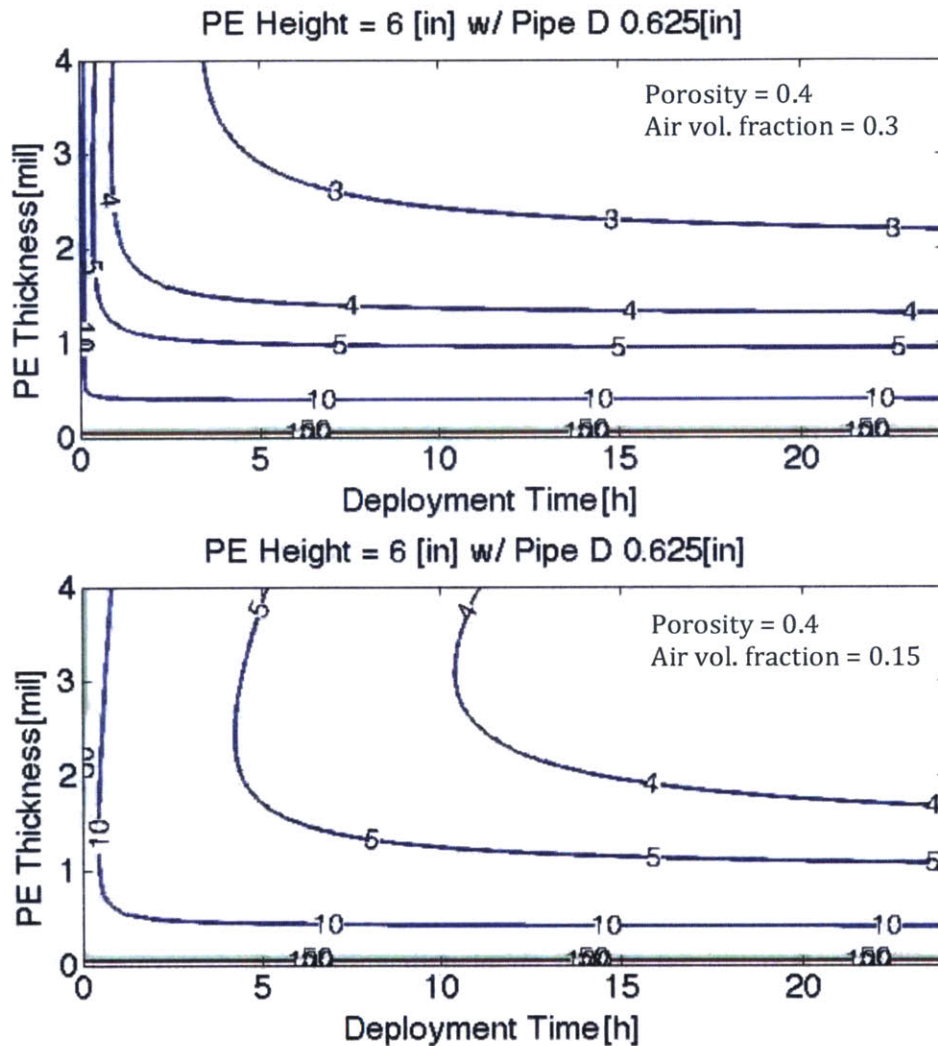


Figure 7.1: Contour plots of toluene soil vapor detection limits with a constant PE surface area. The top plot is for an air volume fraction of 0.3 and the bottom plot is an air volume fraction of 0.15 representative of increased soil moisture perhaps following a rain event.

7.3 FUTURE WORK

In an Environmental Security Technology Certification Program report Gschwend *et al.* (2014) describe a GUI that takes user inputs of PRC data from PE passive sampling in sediment porewater and generates the linear regression described by Fernandez *et al.* (2009). In the future a similar code could be developed, following their example, which calculates the regression line and is user friendly. The described model takes the chemical transport properties determined from an individual passive sampler's PRC data and captures them in a single partitioning coefficient K'_d (L water/L bulk soil). A regression is then made relating K'_d to another appropriate chemical property. In sediments this value was K_{ow} thus this would be the first property to investigate. As described in section 3.1, transport properties of target compounds can then be determined from the regression and

used to calculate soil vapor concentrations. These results might also be used to understand the mobility of specific VOCs in soil horizons of interest.

The 1D diffusion mass transfer MATLAB code described in section 4.2 can also have future application to research into soil vapor transport. A simple 3-phase conceptual model was initially coded for this thesis; however as identified in section 4.3 there is potential for significant additional complexities in the soil environment. Using an iterative process, it would be possible to develop a conceptual model, determine and measure necessary physical and chemical properties (Liu, 2015), adjust the diffusion model appropriately, and then compare the output to a bench test time course results (Soo, 2015). Depending on the comparison, the conceptual model can be adjusted or the bench testing made more complex and the process repeated (Figure 7.2).

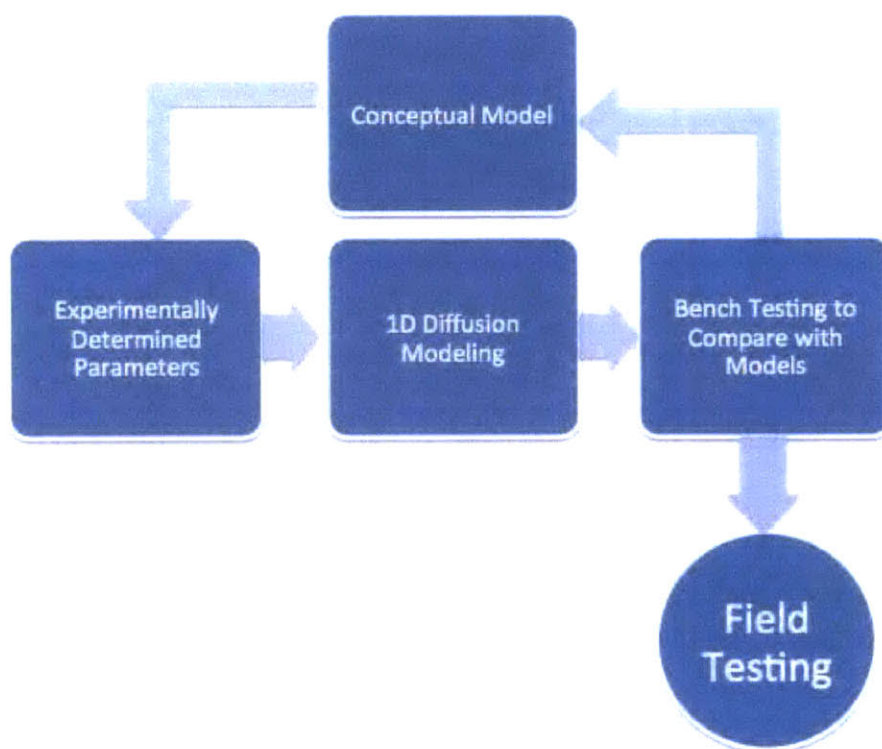


Figure 7.2: Flow diagram of process to investigate soil vapor transport. Initial conceptual model is developed, which determines the parameters that must be measured, to be use in the diffusion model, that can then be compared to bench tests results. The comparison between bench tests and the model is then used to adjust the original conceptual model and start the process again.

7.4 FINAL CONCLUSIONS

The MATLAB models developed for soil application of a PE passive sampler have a wide range of utility. In this thesis they were used to investigate and optimize the design of a sub-slab screening device for BTEX. It was determined that the use of a direct aqueous injection analysis method will likely not be sufficient to allow a PE passive sampler to be useful as a screening device. However, it is clear that BTEX chemicals can be easily measured at a 10 mg/m³ sensitivity in a deployment time of around 1 h. This could be useful for rapid and

accurate site characterization and vapor intrusion modeling. The MATLAB models can also be useful for future investigation of PE optimization for chemicals with slower approaches to equilibrium or soils with different physical properties.

Additionally it was determined that a deployment probe design, using the AMS tile probe system, could be purchased at a relatively low cost and provide the necessary PE volume to achieve the theoretical minimum soil vapor detection limits of BTEX compounds. Preliminary testing, though, shows that further design work is needed to protect the PE during driving of the probe rod. Investigation into a perforated pipe cover is suggested.

Finally the 1D diffusion mass transport model, when paired with bench testing could be used to better characterize soil vapor transport. By utilizing an iterative process, more complex conceptual model theories can be compared to experimental values and accepted, rejected or adjusting accordingly.

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Appendix A: DERIVATION OF EFFECTIVE DIFFUSION IN SOIL USING 3-PHASE MODEL

Assume major mass transport is through the air by molecular diffusion. Diffusion is based on fraction of the compound in the air at anytime and the physical characteristics of the soil - tortuosity.

$$D_{soil} = f_a \frac{D_{air}}{\tau}$$

$$f_a = \frac{\text{moles in air}}{\text{total moles in soil}} = \frac{C_{air}V_{air}}{C'_{soil}V_{soil}}$$

where C' indicates nontraditional units of mol/L soil instead of mol/kg because we are considering all phases in the soil not just the solid phase. Therefore we can rewrite C'_{soil} .

$$f_a = \frac{C_{air}V_{air}}{(C'_{water} + C'_{air} + C'_{solids})V_{soil}}$$

Again C' indicates that the concentration is per volume total soil such that

$$C'_{water} = C_{water} * (\phi - \theta)$$

$$C'_{air} = C_{air} * \theta$$

$$C'_{solids} = C_{solids} * \rho * (1 - \phi)$$

where C_{water} and C_{air} are in units of moles per volume water and air respectively. C_{solids} is concentration in moles per kg dry solids, ρ is the dry bulk density of the solids, ϕ is the porosity in volume of air and water per volume soil and θ is volume air per volume soil.

$$f_a = \frac{C_{air}V_{air}}{\{C_w(\phi - \theta) + C_a\theta + C_s\rho(1 - \phi)\}V_{soil}}$$

dividing the numerator and denominator by C_wV_w

$$f_a = \frac{K_{aw}r_{aw}}{\{(\phi - \theta) + K_{aw}\theta + K_d\rho(1 - \phi)\}r_{sw}}$$

where K_{aw} is Henry's constant in volume water/volume air, r_{aw} is the volume of air / volume water. K_d is the partitioning coefficient in volume water/Kg solids and r_{sw} is the volume of bulk soil/volume of water.

We can then define K'_d as the bracketed terms (exclude r_{sw}) or the concentration in the soil over the concentration in the water in units of volume.

$$K'_d = (\phi - \theta) + K_{aw}\theta + K_d\rho(1 - \phi)$$

therefore

$$f_a = \frac{K_{aw}r_{aw}}{K'_d r_{sw}}$$

but

$$r_{sw} = \frac{V_{soil}}{V_{water}} = \frac{1}{(\phi - \theta)} \qquad r_{aw} = \frac{V_{air}}{V_{water}} = \frac{\theta}{(\phi - \theta)}$$

$$\frac{r_{aw}}{r_{sw}} = \frac{\theta/(\phi - \theta)}{1/(\phi - \theta)} = \theta$$

therefore

$$f_a = \frac{K_{aw}}{K'_d} \theta$$

and

$$D_{soil} = f_{air} \frac{D_{air}}{\tau} = \frac{K_{aw} r_{aw}}{K'_d r_{sw}} \frac{D_{air}}{\tau} = \frac{K_{aw} \theta}{K'_d} \frac{D_{air}}{\tau}$$

Another way to define K'_d is if we distribute r_{sw} and assume 1 in denominator is negligible so as to approximate a new K'_d

$$f_a = \frac{K_{aw} r_{aw}}{1 + (K_{aw} \theta + K_d \rho (1 - \phi)) r_{sw}} \cong \frac{K_{aw} r_{aw}}{(K_{aw} \theta + K_d \rho (1 - \phi)) r_{sw}}$$

and

$$K'_d = K_{aw} \theta + K_d \rho (1 - \phi)$$

Appendix B: MATLAB CODE

MAIN GENERAL

Main general code used to generate a mass fraction curve for either performance reference compounds leaving the PE sampler or a target compounds entering the PE. Requires code to calculate effective diffusion Deffective.m, laplace formula for target compound entering PE (MassIn.m) or PRC leaving (MassOut), and laplace numerical inversion code (INVLAP.m).

```
%Adjusted from code developed by Fernandez et al. (2009)
%for 1D diffusion in sediment

%Calculates loss of PRC as a function of time from PE when
placed in a static soil bed
%uses function invlap.m to calculate the time domain
solution of the Laplace solution from:
% Hollenbeck, K. J. (1998) INVLAP.M: A matlab function
for numerical
% inversion of Laplace transforms by the de Hoog
algorithm,
% http://www.isva.dtu.dk/staff/karl/invlap.htm

clear all
clc
set(0,'DefaultAxesFontSize',20)

% deployment time in hours
time=24;
%sediment bed properties
foc=0.001; % fraction organic carbon
phi=0.4; % porosity (total water&air volume of bulk volume)
theta=0.3; % vol gas content of soil
rho_solids = 2.5; % density of soils Kg/L
% passive sampler properties
L=0.0051; % thickness of polymer (cm)
Den_PE = 0.91; % PE density [g/mL]
% properties of the chemical
ChemNames = {'Toluene','Chlorobenzene'};
V_array=[107 101]; % ENTER molar volume (cm^3/mol)
log10Kow=[2.7 2.78]; % ENTER log(Kow) for each chemical
Kaw_array = 10.^[-0.6 -0.8]; % ENTER Kaw for each chemical

% Convert Kaw to vol porous medium
Kaw_vol_soil = Kaw_array.*theta; % [vol water/vol air]*[vol
air/vol pm]=[vol water/vol pm]
% Estimate Kd from LLFER of Kow & foc and convert to vol pm
Kd = 10.^(0.72.*(log10Kow) + log10(foc) + 0.49);
%Schwarzenbach and Westall (1981)
```

```

[L_water/Kg_solid]=[cm3/g]
Kd_vol_soil = (1-phi)*rho_solids.*Kd; %
[cm3_solid/cm3_soil]
% Estimate Kpew from LLFER with Kow
Kpew_array= 10.^(0.96.*log10Kow)*Den_PE; % Kpew for each
chemical*density PE

% Estimate diffusivities from chemical molar volume
Dpe_array= 10.^(-V_array.*0.0145-6.1); % Diffusivity in
polymer (cm2/s)
Da_array=(2.35).*(V_array.^-0.73); % Diffusivity in
air (cm^2/s)

% Determine Kd' on volume/volume basis
Kd_prime_vol = ((phi-theta)+Kaw_vol_soil+Kd_vol_soil);

% plot information
linespec_array=['r','b','g','k','c','m','r','b','g'];
%matlab linespecs
t=linspace(0.0001,time); %hours

figure(1);
M=zeros(length(Kd_prime_vol),length(t));
for n=1:length(Kd_prime_vol) % for every chemical
    T=t*3600*Dpe_array(n)/(L^2); %unitless time

    K12=Kpew_array(n)/Kd_prime_vol(n);
% [Lw/Lpe] [Lsoil/Lw]=[Lsoil/Lpe]
    Dsoil=Deffective(Da_array(n), Kd_prime_vol(n),
Kaw_array(n),phi,theta);%cm^2/s
    Y=Dsoil/Dpe_array(n); %unitless ratio of diffusivities

    for i=1:length(t)
        M(n,i)=invlap('Mass_in', T(i),0,1e-9,Y,K12); %
invlap.m (2,3)
        % for calculating the fraction of target compound
diffusing out of PE,
        % you can take 1-M or run Mass_out instead of
Mass_in
    end

    plot(t,M(n,:), 'Color',linespec_array(n), 'LineWidth',3)
    xlabel('Deployment Time [ h ^{0.5} ]');
    ylabel('Fraction to Equilibrium Mass');
    legend('Toluene', 'location', 'e');
    grid on
    hold on
end

```

Effective diffusion coefficient (Deffective.m)

The D effective function is used to calculate the effective diffusion through the soil given a 3-phase partitioning model and tortuosity. This function is required for use of the

```
function F = Deffective(Da,Kd_prime,Kaw,phi,theta)
% Calculates effective diffusivity, Deff
% given:
% free air diffusivity Da,
% porosity phi & gas fraction theta
% air-water partitioning coefficient Kaw in Lw/La
% and water-soil partitioning coefficient Kd in Lw/Lsoil and
calc as:
% Kd_prime_vol = (phi-theta)+Kaw*theta+Kd*rho_solids*(1-
phi);

r_sw=1/(phi-theta);           % ratio of bulk soil to
water
r_aw= theta/(phi-theta);     % ratio of gas to water
fa=(Kaw*r_aw)/(Kd_prime*r_sw); % fraction in air assuming
Kd in (Lw/Lsoil)
tau_inverse = 0.1*(2*(theta/phi)^3+0.04*(theta/phi)); %
Deepagoda et al. 2010
Dpm=Da*tau_inverse; % Diffusivity in porous medium
F=fa*Dpm; % (cm^2/sec)
end

% Other possible calculation of tortuosity in soil
% tau_C=phi^(5/2)*theta^-4; % (eq 18-66) Currie(1970)
% tau_MQ=phi^2*theta^(-10/3); % Millington and Quirk (1961)
```

PE Optimization

The PE optimization code generates a 3D matrix of minimum concentrations detectable in soil vapors given a water extraction method for direct aqueous injection to a GC/FID. Three groups of 4 contour plots are generated holding either, PE height (given 5/8" diameter deployment rod), PE thickness, or deployment time constant.

Property inputs for the chemical, soil, sampler, and laboratory extraction are required. Soil properties must be entered in FractionMassIn.m or default values are foc=0.1%, porosity=0.4, vapor fraction=0.3, solids density=2.5Kg/L Uses FractionMassIn.m, Deffective.m, invalap.m, and MassIn.m

```
clc
clear all
set(0,'DefaultAxesFontSize',20)
```

```

C_w = 5000; %[ug/m3] %ENTER min measurable extract water
concentration
% For GC-FID using DAI analysis of BTEX in water
% Potter, T.L., (1996). Analysis of Petroleum-Contaminated
% Water by GC/FID with Direct Aqueous Injection

Den_PE = 0.91; %ENTER density of LDPE [kg/L]
BOD_vol = 60; %ENTER volume of extraction water
bottle [mL]
N = 24; %ENTER max deployment time [hrs]
Res = 200; %ENTER resolution of time steps
t=linspace(0.01,N,Res); %Deployment times[hrs]
dt=(N-0.01)/Res;

% Chem properties [default Toluene]
Kpew = 128; % ENTER Kpew in kg/L
% Or estimate Kpew from LLFER with Kow
% Kpew_array= 10.^(0.96.*log10Kow)*Den_PE; %
Kpew*density PE
Kaw = 10^-0.6; % ENTER Kpew in L/L for chemical
Kpea = Kpew/Kaw; % [L/Kg]
Kow = 10^2.7; % ENTER log(Kow) for chemical
V_mol = 107; % ENTER molar volume [cm^3/mol]

% Estimate diffusivities from chemical molar volume or
directly input
D_pe = 5.1*10^-7; % [cm2/s]
% D_pe= 10^(-V_mol.*0.0145-6.1); % Diffusivity in polymer
(cm2/s)
% D_a = ; % [cm2/s]
D_a=(2.35).*(V_mol.^-0.73); % D_a = diffusivity in air
(cm^2/s)

% PE properties
PE_Len_Max = 12; % ENTER PE maximum length [in]
PE_Len = linspace(0.01,PE_Len_Max);
dLen = (PE_Len_Max-0.01)/100;
Pipe_Diam = 5/8; % ENTER Diameter of pipe wrapping PE
around [in]
PE_SA = PE_Len.*(pi*Pipe_Diam*(2.54^2)); % calculate PE
SA and convert to cm2
b_mil_max = 4; % ENTER Maximum PE thickness [mil]
1mil=0.001"
b_mil = linspace(0.01,4);
db = (4-0.01)/100;
b = b_mil.*(2.54*10^-3); % convert thickness to cm

```

figure(1)

```

%initialize vectors
PE_vol = zeros(length(PE_SA),1);
C_air = zeros(length(PE_SA),length(b),length(t));
F = zeros(length(b),length(t));
counter=0; % counter variable for subplot index

ConLines = [1,2,3,4,5,10,50,100];
% loop through all times and lengths using SA vector
% generates 3D matrix of Soil Vapor Cocentration as
function of (PE_SA)X(PE_thickness)X(deployment time)
for j=1:length(t)
    for i=1:length(b)
        PE_vol = PE_SA.*b(i); % calc volume of PE cm^3
        % calculate volume of water in BOD bottle after
addition of PE
        Water_vol = BOD_vol.*ones(1,length(PE_vol))-PE_vol;
        % convert Kpe to units of L/L
        Kpew_prime = Kpew*Den_PE.*ones(1,length(PE_vol));
        % convert Kpea to units of L/L
        Kpea_prime = Kpea*Den_PE;
        % caculate fraction to equilibrium
        F(i,j) =
FractionMassIn(t(j),b(i),Kaw,Kow,Kpew_prime(1),D_pe,D_a);
        C_air(:,i,j) =
((Water_vol./PE_vol+Kpew_prime)'./(F(i,j)*Kpea_prime))*C_w/
1000; %mg/m3
    end

    % countour graph of C_air vs thickness & SA for
deployment times [1,2,12,48]h
    if j==round(1/dt)
||j==round(2/dt)||j==round(12/dt)||j==round(24/dt)
        counter=counter+1;
        subplot(2,2,counter)

[Z_1,h_1]=contour(b_mil,PE_Len,squeeze(C_air(:,:,j)),ConLin
es,'linewidth',2);
        clabel(Z_1,h_1,'fontsize',18);
        axis([0,b_mil_max,0,PE_Len_Max]);
        ylabel(['PE Height [in] w/ Pipe D ',
num2str(Pipe_Diam),' {[in]} '])
        xlabel('PE Thickness {[mil]} ')
        title(['Time = ', num2str(round(t(j))),' {[h]} '])
    end
end

% plot concentration change with thickness and time for a
single SA value

```

```

% 5/8"*pi*[1",3",6",12"]
figure(2)
counter=0;
for i = round([1,3,6,12]./dLen)
    counter=counter+1;
    subplot(2,2,counter)

[Z_1,h_1]=contour(t,b_mil,squeeze(C_air(i,:,:)),ConLines,'l
inewidth',2);
    clabel(Z_1,h_1,'fontsize',18);
    axis([0,N,0,b_mil_max]);
    xlabel('Deployment Time {[h]} ');
    ylabel('PE Thickness {[mil]} ');
    title(['PE Height = ',num2str(round(PE_Len(i))), ' [in]
w/ Pipe D ', num2str(Pipe_Diam), ' {[in]} '])
end

% plot concentration change with PE SurfaceArea and
Deployment time for
% thickness values [0.5,1,2,4]*0.001"
figure(3)
counter=0;
for i = round([0.5,1,2,4]./db)
    counter=counter+1;
    subplot(2,2,counter)

[Z_1,h_1]=contour(t,PE_Len,squeeze(C_air(:,i,:)),ConLines,'
linewidth',2);
    clabel(Z_1,h_1,'fontsize',18);
    axis([0,N,0,PE_Len_Max]);
    xlabel('Deployment Time {[h]} ');
    ylabel(['PE Height [in] w/ Pipe D ',
num2str(Pipe_Diam), ' {[in]} '])
    title(['PE Thickness = ',sprintf('%.1f',b_mil(i)), '
{[mil]} '])
end

% Fraction to equilibrium for changes in time and thickness
figure(4)
[Z_1,h_1]=contour(t,b_mil,F,[0.5:0.05:0.95],'linewidth',2);
clabel(Z_1,h_1,'FontSize',20);
xlabel('Deployment Time [hrs]')
ylabel('PE thickness [mil]')
axis([0.5,4,0,4]);
title('Fraction to Equilibrium')
grid on

```


Fraction to equilibrium mass (FractionMassIn.m)

Takes inputs of chemical and PE sampler properties and uses hardcoded soil vapor properties to calculate the fraction to equilibrium of a target chemical compound into the PE sampler. Similar to the Main General code, but it is called as a function and only for a single deployment time.

```
function [ M ] =
FractionMassIn(time,PE_thickness,K_aw,K_ow,K_pew,Diff_pe,Diff_a)
% Input variables
% time[hrs] = deployment time PE in soil
% PE_thickness[cm] = total thickness of PE
% K_aw [Lw/La] = Partitioning coefficient C_a/C_w
% K_ow [Lw/Lo] = Partitioning coefficient C_oct/C_w
% K_pew [Lw/Kg] = Partitioning coefficient C_pe/C_w
% Diff_pe [cm2/s] = diffusivity in PE
% Diff_a [cm2/s] = diffusivity in free air
%
% Adjusted from code provided by P.Gschwend for sediment
%
% Calculates fraction to equilibrium of target chemical as
a function of time when placed in a static soil bed
%
% uses function invlap.m to calculate the time domain
solution of the Laplace solution
% Hollenbeck, K. J. (1998) INV LAP.M: A matlab function
for numerical
% inversion of Laplace transforms by the de Hoog
algorithm,
% http://www.isva.dtu.dk/staff/karl/invlap.htm
%
% Sediment bed properties [ENTER values]
foc = 0.001; % fraction organic carbon
phi = 0.4; % porosity (total water&air volume vs
total volume)
theta = 0.3; % vol gas content of soil
rho_solids = 2.5; % density of solids Kg/L
%
% Passive sampler properties
L=PE_thickness; % thickness of polymer (cm)
% Properties of the chemical
Kaw = K_aw;
Kow = K_ow;
Kpew= K_pew;
D_pe = Diff_pe;
D_a = Diff_a;
%
% Convert Kaw to vol porous medium
```

```

    Kaw_vol_soil = Kaw.*theta; % [vol water/vol air]*[vol
air/vol pm]=[vol water/vol pm]

% Estimate Kd from LLFER of Kow & foc and convert to vol pm
%Schwarzenbach and Westall (1981)
[L_water/Kg_solid]=[cm3/g]
    Kd = 10.^(0.72.*(log10(Kow)) + log10(foc) + 0.49);
    Kd_vol_soil = (1-phi)*rho_solids.*Kd; %
[cm3_solid/cm3_soil]

% Calculate Kd' as ratio of Lw/L_bulk soil
    Kd_prime_vol = ((phi-theta)+Kaw_vol_soil+Kd_vol_soil);

    T=time*3600*D_pe/(L^2); % unitless time
    K12=Kpew/Kd_prime_vol; %
[Lw/Lpe] [Lsoil/Lw]=[Lsoil/Lpe]
    Dsoil = Deffective(D_a,Kd_prime_vol,Kaw,phi,theta); %
[cm^2/s]
    Y=Dsoil/D_pe; % unitless ratio of diffusivities

    M=invlap('Mass_in',T,0,1e-9,Y,K12); % invlap.m (2,3)

End

```

Mass In, Laplace space equation (Mass_in.m)

Laplace function used by invalap.m to solve differential equation of a target compound's fraction of equilibrium mass.

```

% Laplace-domain expression for the mass of target chemical
taken up by polymer from porous medium
% Modified by APT to include cases where the chemical
reacts in the sediment or in the PE
% K12 is partitioning coefficient between phase 1
(polymer) and phase 2 (porous medium)
% Y is ratio of diffusivities (D(porous
medium)/D(polymer))
% s is the Laplace parameter

```

```

function F = Mass_in(s,P1,P2)
Y = P1;
K12 = P2;
% no rxn
    F = (Y.^0.5)./((s.^1.5).*(K12+(Y.^0.5).*coth(sqrt(s))));
End

```

Mass out, Laplace space equation (MassOut.m)

Laplace function used by invalap.m to solve differential equation for a PRC's fraction of equilibrium mass as leaves PE

```
% Laplace-space expression for the mass of PRC transferred
from polymer to porous medium
% K12 is partitioning coefficient between phase 1
(polymer) and phase 2 (porous medium)
% Y is ratio of diffusivities (D(porous
medium)/D(polymer))
% s is the Laplace parameter

function F = Mass_out(s,P1,P2)

% no reaction
    Y = P1;
    K12 = P2;

    F = (1./(s))-
((sqrt(Y))./((s).^ (3/2) .* (K12)+ (s).^ (3/2) .*sqrt(Y) .*coth(sq
rt(s)))));
End
```

Inverse Laplace Transform (invalap.m)

Numerical solution to inverse laplace transform. Hollenbeck, K.J. (1998)

```
% INVLAP numerical inverse Laplace transform
%
% f = invalap(F, t, alpha, tol, P1,P2,P3,P4,P5,P6,P7,P8,P9);
% F laplace-space function (string referring to an m-
file), must have form F(s, P1,...,P9), where s is the
Laplace parameter, and return column vector as result
column vector of times for which real-space function values
are sought
% alpha largest pole of F (default zero)
% tol numerical tolerance of approaching pole (default
1e-9)
% P1-P9 optional parameters to be passed on to F
% f vector of real-space values f(t)
%
% example: identity function in Laplace space:
% function F = identity(s); % save these two lines
% F = 1./(s.^2); % ... as "identity.m"
% invalap('identity', [1;2;3]) % gives [1;2;3]
%
% algorithm: de Hoog et al's quotient difference method
with accelerated convergence for the continued fraction
expansion
% [de Hoog, F. R., Knight, J. H., and Stokes, A. N.
```

```

(1982). An improved
% method for numerical inversion of Laplace transforms.
S.I.A.M. J. Sci.
% and Stat. Comput., 3, 357-366.]
% Modification: The time vector is split in segments of
equal magnitude
% which are inverted individually. This gives a better
overall accuracy.

% details: de Hoog et al's algorithm f4 with modifications
(T->2*T and
% introduction of tol). Corrected error in formulation
of z.
%
% Copyright: Karl Hollenbeck
% Department of Hydrodynamics and Water
Resources
% Technical University of Denmark, DK-2800
Lyngby
% email: karl@isv16.isva.dtu.dk
% 22 Nov 1996, MATLAB 5 version 27 Jun 1997 updated 1 Oct
1998
% IF YOU PUBLISH WORK BENEFITING FROM THIS M-FILE, PLEASE
CITE IT AS:
% Hollenbeck, K. J. (1998) INVLAP.M: A matlab function for
numerical inversion of Laplace transforms by the de Hoog
algorithm, http://www.isva.dtu.dk/staff/karl/invlap.htm

function f = invlap(F, t, alpha, tol,
P1,P2,P3,P4,P5,P6,P7,P8,P9);

if nargin <= 2,
    alpha = 0;
elseif isempty(alpha),
    alpha = 0;
end
if nargin <= 3,
    tol = 1e-9;
elseif isempty(tol),
    tol = 1e-9;
end
f = [];

% split up t vector in pieces of same order of magnitude,
invert one piece at a time. simultaneous inversion for
times covering several orders of magnitudes gives
inaccurate results for the small times.

```

```

allt = t; % save full times vector
logallt = log10(allt);
iminlogallt = floor(min(logallt));
imaxlogallt = ceil(max(logallt));
for ilogt = iminlogallt:imaxlogallt, % loop through all
pieces

    t = allt(find((logallt>=ilogt) & (logallt<(ilogt+1))));
    if ~isempty(t), % maybe no elements in that
magnitude

        T = max(t)*2;
        gamma = alpha-log(tol)/(2*T);
        % NOTE: The correction alpha -> alpha-log(tol)/(2*T) is
not in de Hoog's paper, but in Mathematica's Mathsourc
(NLapInv.m) implementation of inverse transforms
        nt = length(t);
        M = 20;
        run = [0:1:2*M]'; % so there are 2M+1 terms in
Fourier series expansion
        % find F argument, call F with it, get 'a' coefficients
in power series
        s = gamma + i*pi*run/T;
        command = ['a = ' F '(s)'];
        if nargin > 4, % pass on parameters
            for iarg = 1:nargin-4,
                command = [command ',P' int2str(iarg)];
            end
        end
        command = [command ');'];
        eval(command);
        a(1) = a(1)/2; % zero term is halved

        % build up e and q tables. superscript is now row
index, subscript column
        % CAREFUL: paper uses null index, so all indeces are
shifted by 1 here
        e = zeros(2*M+1, M+1);
        q = zeros(2*M, M+1); % column 0 (here: 1)
does not exist
        e(:,1) = zeros(2*M+1,1);
        q(:,2) = a(2:2*M+1,1)./a(1:2*M,1);
        for r = 2:M+1, % step through columns
(called r...)
            e(1:2*(M-r+1)+1,r) = ...
                q(2:2*(M-r+1)+2,r) - q(1:2*(M-r+1)+1,r) + e(2:2*(M-
r+1)+2,r-1);
            if r<M+1, % one column fewer

```

```

for q
    rq = r+1;
    q(1:2*(M-rq+1)+2,rq) = ...
    q(2:2*(M-rq+1)+3,rq-1).*e(2:2*(M-rq+1)+3,rq-
1)./e(1:2*(M-rq+1)+2,rq-1);
    end
end

% build up d vector (index shift: 1)
d = zeros(2*M+1,1);
d(1,1) = a(1,1);
d(2:2:2*M,1) = -q(1,2:M+1).'; % these 2 lines changed
after niclas
d(3:2:2*M+1,1) = -e(1,2:M+1).'; % ...

% build up A and B vectors (index shift: 2)
% - now make into matrices, one row for each time
A = zeros(2*M+2,nt);
B = zeros(2*M+2,nt);
A(2,:) = d(1,1)*ones(1,nt);
B(1:2,:) = ones(2,nt);
z = exp(i*pi*t'/T); % row vector
% after niclas back to the paper (not: z = exp(-
i*pi*t/T)) !!!
for n = 3:2*M+2,
    A(n,:) = A(n-1,:) + d(n-1,1)*ones(1,nt).*z.*A(n-2,:);
% different index
    B(n,:) = B(n-1,:) + d(n-1,1)*ones(1,nt).*z.*B(n-2,:);
% shift for d!
end

% double acceleration
h2M = .5 * ( ones(1,nt) + ( d(2*M,1)-d(2*M+1,1)
)*ones(1,nt).*z );
R2Mz = -h2M.*(ones(1,nt) - ...
(ones(1,nt)+d(2*M+1,1)*ones(1,nt).*z/(h2M).^2).^5);
A(2*M+2,:) = A(2*M+1,:) + R2Mz .* A(2*M,:);
B(2*M+2,:) = B(2*M+1,:) + R2Mz .* B(2*M,:);

% inversion, vectorized for times, make result a column
vector
fpiece = ( 1/T * exp(gamma*t') .*
real(A(2*M+2,:)./B(2*M+2,:)) )';
f = [f; fpiece]; % put pieces together

end % if not empty time piece
end % loop through time vector pieces

```

Appendix C: ADDITIONAL PROBE TESTING PICTURES

PE was secured to the 5/8" diameter probe in 1 ft lengths using cable ties and electrical tape. The probe was then driven into a potting soil and gravel mixture contained in a 1' diameter PVC pipe. The PVC pipe was tapped after filling to settle the soil. Results show that PE integrity is severely compromised during insertion into the soil. A protective cover will need to be investigated.

