Direct Volatilization of Naphthalene at a Creosote-Contaminated Site with a Phytoremediation System

Elizabeth Claire Booth

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Linsey C. Marr, Chair
John T. Novak
Mark A. Widdowson

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by

Elizabeth Claire Booth

Committee Chair: Linsey C. Marr
Environmental Engineering

Abstract

In 1990, creosote contamination was discovered at a railroad tie yard in Oneida, Tennessee. A phytoremediation system that included over 1,200 hybrid poplar trees was installed between 1997 and 1998 for hydraulic control of the groundwater and enhancement of the natural biodegradation processes in the subsurface. Since then, Virginia Polytechnic Institute and State University has monitored eight polycyclic aromatic hydrocarbons (PAHs) in the soil and groundwater. They have found that concentrations of smaller and more volatile PAHs have decreased over the years as the DNAPL contamination has become more enriched with the larger PAHs. This thesis focuses on the movement of naphthalene through the subsurface because it comprises the majority of the creosote and evidence for its remediation exists.

Of the many mechanisms within the phytoremediation system that serve to remediate contaminated groundwater and soil, the most important are rhizosphere bioremediation and plant uptake. However, another mechanism, direct volatilization through the soil, was thought to have significant remediation capabilities at this site. Because naphthalene is a highly volatile PAH, it was hypothesized that naphthalene is volatilizing directly through the soil to the atmosphere and that the rate of volatilization may be enhanced by the presence of the phytoremediation system.

The goals of this research are to measure the amount of naphthalene that volatilizes from the subsurface and determine the factors that significantly influence this direct volatilization. A flux chamber was designed and constructed to measure naphthalene fluxes from the soil. Factors that influence direct volatilization include the groundwater level, soil moisture, precipitation, pressure changes, temperature and humidity, the most important of which we found to be the groundwater level through its

influence on naphthalene concentrations in the groundwater. We found that the presence of the trees significantly affects groundwater levels. As trees transpire and lower the groundwater table, concentrations in the uppermost portion of the groundwater increase, and under dry conditions, naphthalene fluxes from the soil are maximized.

To complement the field measurements of direct volatilization, we also investigated rates of volatilization and biodegradation in the laboratory. Column experiments were conducted to determine the importance of direct volatilization on biodegradation in the vadose zone. We hypothesize that the combined mechanisms of contaminant transfer to the vadose zone, followed by rapid biodegradation, speeds up remediation in contrast to biodegradation that occurs only in the saturated zone under high groundwater conditions. Several columns using contaminated and uncontaminated soil from the site were constructed with a naphthalene source. Vertical naphthalene vapor concentration profiles were measured, and first-order biodegradation rates were determined. We found that biodegradation rates in the bacterially active columns were small initially, but that the biodegradation rates of the contaminated soil dramatically increased at day 60, while the biodegradation rates of the uncontaminated soil did not begin to increase until day 150. By the end of the experiment, both soil types had approximately the same biodegradation rate, signifying that soil that had previously been exposed to naphthalene degrades naphthalene more efficiently in the early stages than soil that has not been exposed, but that over time the non-exposed soil degrades naphthalene as efficiently as the pre-exposed soil. We determined that the combined mechanisms of diffusion and biodegradation in the unsaturated zone have significant remediation capabilities.

Because long-term exposure risks are associated with inhaling indoor contaminant vapors, the Johnson and Ettinger vapor intrusion model was applied to the creosote-contaminated site, as outlined in Appendix C. This model takes into account soil, chemical, and building foundation characteristics to determine a dimensionless attenuation ratio, which is the ratio of contaminant vapor concentration in an enclosed space (i.e. basement) to the vapor concentration directly above the source. For a conservative case, the Johnson and Ettinger model without biodegradation was used. We found that if the land were developed, naphthalene vapor intrusion would not pose any

health risks based on regulatory standards and levels at which health effects have been recorded.

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Table of Contents

List of Figures

List of Tables

CHAPTER 1

1.0 Introduction

Phytoremediation, which is the use of plants (grasses and trees) to remediate contaminated soil and water, is a technique that is implemented at many hazardous waste sites to aid in the long-term clean-up of subsurface contaminants (Schnoor, 2002; Robinson et al., 2003). These types of projects take advantage of natural processes to stabilize and degrade organic compounds. Although the time required for phytoremediation systems to reduce contaminants can be long, there are clear advantages to this in situ remediation technique. Phytoremediation is environmentally friendly, economically feasible, requires little maintenance, and minimizes the risks associated with contaminant mobility.

The dominant mechanisms used by trees to remove hazardous compounds are rhizosphere bioremediation and plant uptake. These mechanisms both use the natural processes associated with the growth of trees and grasses to either biodegrade, biotransform, accumulate, or phytovolatilize contaminants. However, the trees also create physical changes within the subsurface that may lead to a reduction in contaminants. These physical processes include but are not limited to the fluctuating groundwater table with rain and seasonal events, the increased mass transfer rates of contaminants in the groundwater during periods of high transpiration rates, and the preferential pathways and air voids created by the roots within the soil matrix. Each of these physical processes directly influence the rate at which contaminants volatilize from the groundwater and soil to the atmosphere. This process is known as direct volatilization and may significantly influence subsurface remediation.

Both phytovolatilization, a natural process that occurs within the bark, stems and leaves, and direct volatilization, which occurs as a result of physical processes in the subsurface, serve to reduce the amount of contaminants in the groundwater and soil, and both release contaminants to the atmosphere. However, a thorough comparison of the remediation capabilities of these two mechanisms in the field has not yet been conducted. In addition, very little research has been documented on the enhancement of direct volatilization at phytoremediation sites.

1.1 Research Overview

The overall goals of this research are to determine the magnitude and relative importance of direct volatilization through field measurements and to describe the mechanisms influencing direct volatilization at a phytoremediation site in Oneida, TN. It is hypothesized that direct volatilization may be a significant removal mechanism at contaminated subsurface sites and may be enhanced by phytoremediation. These research goals are achieved by answering two research questions: 1) how much naphthalene volatilizes from the ground and 2) do the trees enhance this volatilization? As a result of this research, the implications of removing hazardous compounds from the groundwater and soil through direct volatilization in the unsaturated zone followed by biodegradation will be discussed.

The specific objectives of this research are to (1) measure the rate of direct volatilization of naphthalene at the phytoremediation site, (2) identify the most influential factor affecting direct volatilization, (3) assess whether the trees at the site enhance naphthalene volatilization, (4) determine health risks associated with the use of land above the contaminated soil and groundwater, (5) estimate biodegradation rates for naphthalene in the unsaturated zone from experimental column studies, and (6) compare the mechanisms of direct volatilization and biodegradation of naphthalene in the unsaturated zone.

1.2 Review of Phytoremediation

At least ten different physiological processes that aid in subsurface contaminant management have been identified and are further detailed in Schnoor (2002). These processes include phytoextraction (phytoaccumulation), rhizofiltration (contaminant uptake), phytostabilization, phytocontainment, brine volume reduction, phytovolatilization, phytostimulation (rhizosphere bioremediation), phytodegradation, phytophotolysis, and phytoslurry. Once in the plant tissue, contaminants first undergo transformation by oxidation or reduction, then conjugation to detoxify or metabolize the contaminants, and lastly sequestration, which stores compounds in the metabolic tissues (Schnoor, 2002). Figure 1.1 and the following subsections describe the four

phytoremediation mechanisms addressed in this work: rhizosphere bioremediation, plant uptake, phytovolatilization, and direct volatilization.

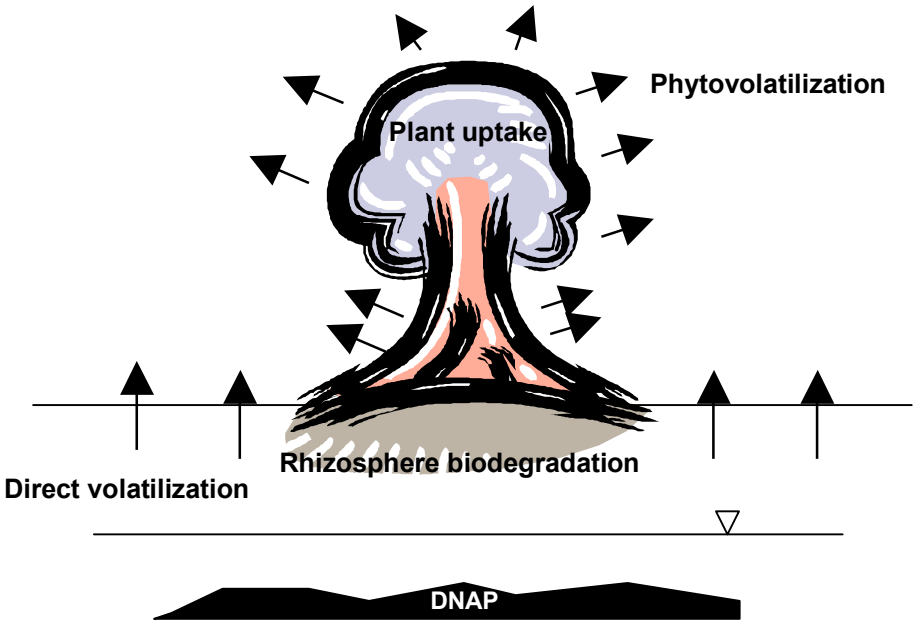

Figure 1.1 The main processes used in phytoremediation applications to remediate contaminated groundwater and soil. The contamination is in the form of a dense non-aqueous phase liquid (DNAPL) that resides between bedrock and the top of the water table.

1.2.1 Rhizosphere bioremediation

Plants, grasses and trees provide many natural processes that help remediate contaminated groundwater and soil. Rhizosphere bioremediation is a process by which trees greatly enhance the degradation of contaminants by providing an optimal environment for microbial growth within the root zone (Kruger et al., 1996). This process relies on the availability of nutrients in and around the root zones and has been shown to be quite effective in degrading contaminants such as pesticides, PAHs, and other synthetic chemicals (Kruger et al., 1996). Over the last ten years, the realization of enhanced degradation of chemicals in vegetated soils as compared to non-vegetated soils has proliferated.

1.2.2 Plant uptake

Plant uptake is comprised of many different mechanisms such as transformation, conjugation, and sequestration. The initial step in the metabolism of contaminants once in the plant tissue is transformation, in which oxidation or reduction reactions occur. Most oxidation reactions increase the solubility of the contaminant and allow conjugation to occur. After transformation, the contaminants are detoxified or metabolized through conjugation. Conjugates are usually more water-soluble and have reduced toxicity (Schnoor, 2002). In some cases, the toxicity of the pollutant is increased, such as when organic or inorganic mercury salts are converted to the more elemental form, which is highly toxic (Susarla et al., 2002). The last step is sequestration, in which compounds are stored in the plant tissue (Schnoor, 2003). However, this presents a danger for animals that eat these plants or when the contaminants are re-released to the environment through either burning or decomposition. Another plant uptake mechanism is phytovolatilization, which is the uptake of contaminants by the plant and release into the atmosphere through the plant's bark, stems, and leaves (Schnoor, 2002).

1.2.3 Phytovolatilization

Many experiments have been conducted on the phytovolatilization of contaminants using different plant species and contaminant sources. During phytovolatilization, volatile contaminants are taken up by the plant and the gas vapors diffuse through the leaves when the stomata are open and through the stem tissue to enter the atmosphere (Schnoor, 2002). Due to the persistence of trichloroethylene (TCE) in groundwater and its carcinogenic effects, much attention has been placed on reducing this contaminant in the environment, and many studies have been conducted to determine the fate of TCE in plants. Burken and Schnoor (1998) found that transpiration through the leaves of hybrid poplar trees is a significant pathway for the contaminants benzene, TCE, toluene, ethylbenzene, and m-xylene. Newton et al. (1997) studied the fate of TCE in hybrid poplar trees and also concluded that plants are capable of transpiring contaminants through their leaves, but volatilization through the stems was not addressed. Ma and Burken (2003) studied TCE diffusion along the transpiration pathway and concluded that volatilization through the stems is a major pathway for TCE to enter the atmosphere.

Narayanan et al. (1999) found the concentrations of most volatile organic compounds (VOCs) introduced to the atmosphere by phytovolatilization unlikely to exceed gas phase concentration standards. The mass of most VOCs volatilized through the plant tissue is small relative to the amount transformed by rhizosphere biodegradation (Schnoor, 2002). Furthermore, the mass volatilized from plants is small in comparison to emissions to the atmosphere from other sources, such as industry and fuel emissions; and therefore phytovolatilization presents a potential remediation strategy for VOCs with very low risk to human health (Schnoor, 2002). Nonetheless, action levels may be exceeded with highly toxic and volatile substances that are present in groundwater at high levels and released from vigorously growing plants under hot and dry conditions (Narayanan et al., 1999). The type of plant, contaminant, and depth to contamination are all variables that must be considered when assessing the risk of human health from phytovolatilizing contaminants.

1.2.4 Direct volatilization

In addition to reducing contaminants through natural processes, certain physical processes also aid in subsurface remediation. Direct volatilization is the movement of volatile contaminants from contaminated groundwater and soil to the atmosphere. The physical processes influencing direct volatilization rates may include groundwater table fluctuations, transpiration rates, and preferential pathways created by the tree roots within the subsurface. These processes may enhance the rate at which contaminants are directly volatilized through the soil, with significant remediation implications. This mechanism is believed to be dependant on many environmental factors (pressure, rainfall, temperature), soil characteristics (permeability, moisture, porosity), and the presence of trees.

Trees act as a solar driven pump-and-treat system, increasing the flux of water through the vadose zone during high transpiration periods and lowering the groundwater table (Narayanan et al., 1999; Al-Yousfi et al., 2000; Robinson et al., 2003). When transpiration rates are large, such as in the early summer, hot conditions are prevalent, the groundwater table is high, and the trees use massive amounts of water per day. The increased flow rate of groundwater to the roots may provide more opportunity for mass transfer due to greater exposure of the contaminated water to the gas-phase, giving a larger mass of contaminants a chance to volatilize out of the water and into the gas-phase

pore space. Additionally, the trees pull contaminated water closer to the ground surface, where oxygen availability is higher and aerobic biodegradation in the rhizosphere can occur as well as volatilization to the atmosphere (Narayanan et al., 1999).

Narayanan et al. (1999) theorized that as trees transpire and act as pumps, there is an upward flux of water through the vadose zone. As the trees take up water and lower the groundwater table, the saturated zone becomes thinner, and more volatile compounds are exposed to air-filled spaces. This plant-induced drying of the soil increases gas-phase diffusion through the subsurface, and the presence of air-filled spaces allows the contaminants to diffuse and advect upwards (Narayanan et al., 1999). While in the vadose zone, contaminants are transported by diffusion through the soil, and while in the roots, contaminants travel through the tree and are volatilized through the leaves. Tree roots also create large voids in the unsaturated zone that serve as preferential pathways for volatile contaminants to migrate upwards. In addition to physical properties, the amount of contaminants directly volatilized depends largely on the groundwater table level, depth to groundwater, and contaminant source characteristics.

Direct volatilization at phytoremediation sites may be responsible for a significant portion of the overall remediation of soil and groundwater, and may indirectly increase the effectiveness of biodegradation. As volatilization rates increase, naphthalene concentrations throughout the soil column increase, thereby causing biodegradation rates to go up (ATSDR, 2003). Schnoor (2002) states that PAH degradation depends on the presence of lower molecular weight aromatic compounds to trigger enzyme stimulation. With increased biodegradation rates, the rate at which contaminants are degraded is much higher, and this causes contaminants to be removed from the ground more efficiently.

Contaminants moving upward through the soil may experience both advection and diffusion. Smith et al. (1996) studied the vertical diffusion flux of TCE in the unsaturated zone and found that advection may be the dominant mechanism contributing to an increase in measured fluxes during changes in atmospheric temperature and pressure. To test this theory, Choi et al. (2002) conducted field measurements and computer simulations to determine the relative magnitude of the diffusive versus advective fluxes of TCE at the same site. They found that TCE fluxes were sensitive to moisture content, porosity and weather. Soil moisture content had the largest effect on

diffusive fluxes while rapidly changing atmospheric pressure had the largest effect on advective fluxes. Fluxes were also dependent on time, and by studying a crude oil-contaminated aquifer at a 12 year interval, Chaplin et al. (2002) were able to determine that volatilization is dominant in the early stages of plume evolution, while biodegradation dominates in the later stages.

The effect of barometric pumping on contaminant transport was studied by Auer et al. (1996). Barometric pumping refers to variations in atmospheric pressure that result in subsurface motion of air in porous and fractured soils. Their study found that barometric pumping enhances transport and causes contaminants near the surface to mix with the atmosphere more quickly. Fractures in the earth cause the barometric pumping phenomenon to be enhanced as pressure variations move deeper into the subsurface, and thereby greatly affect the rate of contaminant transport. Contaminants in the gas phase may either be transported into the atmosphere or further into the subsurface by barometric pumping. Massmann and Farrier (1992) found that air can migrate several meters into the subsurface under fluctuating natural atmospheric conditions that include changes in pressure.

Pasteris et al. (2002) studied the vapor phase transport of fuel compounds and found that fuel compounds in the saturated zone accumulated in the groundwater while these same compounds volatilized from the unsaturated zone. Their study suggests that volatilization and biodegradation are effective processes for removing VOCs from the groundwater surface. Jellali et al. (2003) conducted experiments to assess the transport of TCE vapors in the unsaturated zone by using a vertical flux chamber, a device that is placed on top of the soil to trap contaminants volatilizing from the contaminant source. Their laboratory results showed that contaminants are mainly transported to the atmosphere instead of the groundwater, which significantly reduces the potential for groundwater pollution. Several other authors published papers on vertical flux chamber designs that were tested in the laboratory and/or field (Gao et al., 1997; Reichman and Rolston, 2002; Tillman et al., 2004).

1.2.5 Direct volatilization v. phytovolatilization

Few studies have compared the magnitude of contaminants that are directly volatilized versus phytovolatilized within phytoremediation systems. Of the studies that

are published, the results differ greatly in the magnitude of contaminants that are phytovolatilized and directly volatilized. Orchard et al. (2000) conducted experiments with TCE in hybrid poplar trees and discovered that 90% volatilized directly from the soil while an extremely low amount phytovolatilized from the plant tissue. Ramaswami and Rubin (2001) studied methyl-tertiary-butyl-ether (MTBE) uptake by poplar trees and developed a membrane jar unit to distinguish between how much MTBE is taken up by the plant and transpired versus how much is directly volatilized from the contaminated groundwater to the atmosphere. In their laboratory experiments, they determined that direct volatilization accounted for half of the reduction in mass and concentration of MTBE seen in the plant system. Conversely, Burken et al. (2001) studied the fate of benzene in poplar trees in reactor experiments and found that volatilization from plant tissues is not a major pathway for contaminant fate and direct volatilization from the soil served as an even smaller percentage.

The above examples show that laboratory studies can have varied and inconclusive results that depend on the plant growth environment, specific plant species, exposure duration, contaminant type, and soil type (Orchard et al., 2000). Because of the varying magnitude of the results, the importance of field measurements as a supplement to laboratory experiments should be emphasized.

1.3 Vertical Flux Chamber

There are a variety of techniques and designs that have been developed to measure the flux of vapors at the soil surface, and most of them involve placing a chamber over a small area of ground where clean air is introduced into the chamber and contaminated air is collected. These vertical flux chambers are dynamic sampling devices that use sorbents to trap contaminants that have volatilized from the soil. Although flux chambers have been found to provide accurate and precise measurements, site heterogeneities are not well represented due to the small area covered by each chamber.

Bekku et al. (1997) studied the importance of maintaining conditions in the chamber similar to ambient conditions and showed that when the headspace concentrations are close to ambient concentrations, accurate flux measurements can be

obtained. The importance of maintaining ambient conditions within a chamber was also investigated by Hutchinson et al. (2000), who found that air exchange rates in the chamber should mimic air exchange rates outside the chamber. Flux chambers that are closer to ambient conditions in terms of initial concentrations and air flow rates have also been determined to reach steady state and perform better within reasonable time periods (Gao and Yates, 1998b).

Gao et al. (1997) designed a flux chamber and tested its ability to maintain a uniform flow of air across the soil surface. They assumed that advective fluxes were negligible, the chamber was operating under steady-state conditions, and the incoming and outgoing gases were well-mixed. Laboratory studies were conducted to determine the distribution of the horizontal air velocity inside the chamber because areas of stagnant zones and vertical air flow components can cause spatially variable fluxes. Their laboratory tests consistently show a faster air flow through the middle of the chamber but no stagnant zones above the soil surface. After conducting field tests, they suggested that future chambers operate in conjunction with an anemometer.

Reichman and Rolston (2002) also designed a flux chamber to maintain a uniform distribution of air flow over the soil surface, but the air flow rate they chose to use caused some cooling of the ground. They discovered that the outflow rate must be carefully controlled to minimize pressure deficits across the soil, which can cause an under- or over-estimation of the measured flux. Their suggestions include outfitting chambers with pressure transducers to monitor and minimize pressure deficits. Pressure deficits within the chamber were also a concern for Tillman et al. (2003), who used an oil manometer to measure pressure changes in their chamber design. They conducted laboratory experiments to study contaminant transport, and in both cases, the chamber performed well without any measurable pressure differences. Jellali et al. (2003) also constructed a flux chamber and found negligible pressure deviations within the chamber using a low flow rate. In addition to reviewing different chamber types, Pumpanen et al. (2004) state the importance and difficulty in obtaining uniform mixing of air within the chamber that minimizes turbulence and concentration build-up.

Pressure deficits caused only by varying air flow rates were studied by Gao and Yates (1998a and 1998b). Gao and Yates (1998b) found that using very low flow rates

regardless of media type underestimates the flux, but low flow rates employed in flux chambers over less permeable soils allow pressure deficit effects to be neglected. Gao and Yates (1998a) also determined that the flux may be overestimated with high flow rates. They suggest creating a pressure deficit within the chamber to induce a flux to compensate for the depressed diffusive flux that occurs when gas concentrations build up in the headspace. However, they pointed out the difficulties present in determining the proper air flow rate and pressure deficit combination and that the actual flux would remain unknown. Their final suggestion was to operate at high flow rates while measuring and minimizing pressure deficits in the chamber headspace. In each case, the flux measurement depends largely on the design of the chamber, which includes the size of the chamber, the air flow rate through chamber, and air mixing within chamber, as well as the distance to source, contaminant type, and soil and meteorological conditions. Table 1.1 compares the flow rates and dimensions used by various references in their flux chamber designs.

Table 1.1 Chamber dimensions and flow rates used in various references.

Flow rate ($L\ min^{-1}$)	Soil surface area covered by chamber	Height of chamber headspace	Headspace volume	Reference
0.030	60 cm diameter	18 cm	51 L	Smith et al., 1996
24.5, 49.5, 74.5	40 x 40 cm	9.5 cm	15 L	Gao et al., 1997
20	40 x 40 cm	11.4 cm	18.24 L	Reichman and Rolston, 2002
1	30 x 30 cm	20 cm	18 L	Jellali et al., 2003
0.125	25 cm diameter	2.5 cm	1.2 L	Tillman et al., 2003; Tillman and Smith, 2004

1.4 Vertical Flux Theory

Flux chambers are designed to measure the advective and diffusive fluxes of contaminants that volatilize from a defined area of soil to the atmosphere. Even though advective fluxes are present due to atmospheric variations in pressure and temperature (Auer et al., 1996; Choi et al., 2002; Massmann and Farrier, 1992; Thorstenson and Pollock, 1989), these types of fluxes only account for a small percentage of the total flux,

as documented by Choi et al. (2002) and Tillman and Smith (2004). For this reason, one can assume that the only quantifiable fluxes from the soil are diffusive fluxes, which are driven by concentration gradients. In the work of Gao and Yates (1998a,b), the expression for the diffusive flux is derived and the resulting steady-state equation is given below

$$J_{steady} = Q/A\ (C_{out} - C_{in}) \quad (1)$$

such that J_{steady} [M L^{-2} T^{-1}] is the steady-state flux from the enclosed soil surface, $C_{in}(t)$ and $C_{out}(t)$ [M L^{-3}] are the vapor concentrations in the incoming and outgoing air, respectively, A [L^2] is the covered soil surface, and Q [L^3 T^{-1}] is the air flow rate. Assumptions within the above equations must be upheld in the design of the flux chamber as best as possible. These theoretical assumptions include (1) an air stream parallel to the enclosed soil surface, (2) a contaminant gas concentration in the chamber of zero before installation, (3) a constant subsurface source during sampling, and (4) a uniform flux caused only by diffusion.

1.5 Site Description and Background

The study area for this research is located in Oneida, Tennessee approximately 60 miles northwest of Knoxville, Tennessee. Beginning in the early 1950s, the tie yard was used by the Tennessee Railway Company to treat railroad ties with creosote, and treatment continued intermittently from 1960 to 1966 and from 1968 to 1973. In 1973, when the Southern Railway Company bought the Tennessee Railway Company, the cross-tie treatment stopped. The site originally had an above-ground storage tank for creosote, a pressurized wood treatment unit, and a spur track for transporting the treated railroad ties, with the majority of the treatment occurring about 100 feet north of Pine Creek. Figure 1.2 shows a plan view of the tie yard, including the suspected area of the holding pond and theorized locations of the treatment processes.

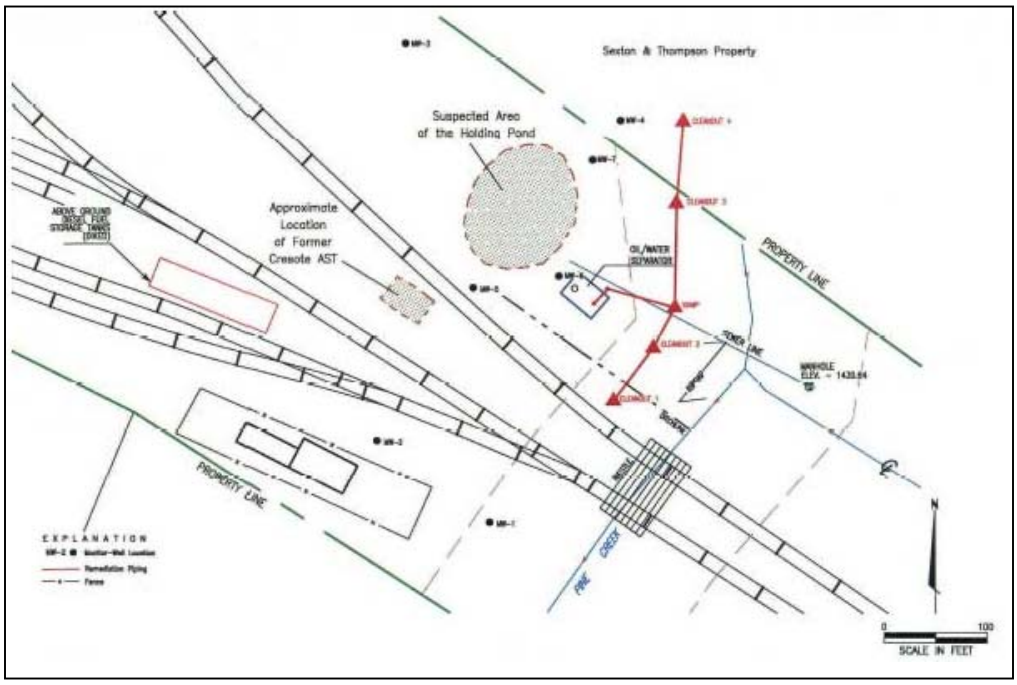

Figure 1.2 Oneida Tie Yard site layout.
(Geraghty & Miller, 1997)

Creosote is a brownish-black, oily liquid obtained from the distillation of coal tar, and coal tar is the by-product of the distillation of coal to coke, which is used to manufacture steel (Heikkila et al., 1987). Creosote is a mixture of hundreds of compounds, but only 100 have been identified and about 20 constitute the majority of the creosote with concentrations greater than 1%, representing 80% of the total amount of constituents in creosote (Heikkila et al., 1987). The major compounds consist of benzene, toluene, ethybenzene, xylene (BTEX), PAHs, and other petroleum byproducts. According to Heikkila et al. (1987), the creosotes used in Finland contain 15-21% PAHs and 0.03-0.12% benzo(a)pyrene (BaP).

In 1990, the United States Army Corp of Engineers was working on the drainage channel along Pine Creek when they found creosote contamination. The contamination was reported to the Tennessee Department of Health and Environment, who investigated the site by analyzing soil and groundwater samples. In 1997, to prevent further contamination of Pine Creek, a consulting firm was hired to study the site and determine the appropriate remediation technique. In addition, Virginia Tech was chosen to do additional sampling and analysis.

The creosote contamination at the Oneida, TN site stemmed from an above-ground storage tank. The consultant was contracted to excavate the footings and foundation of the tank, ultimately removing 1147 tons of contaminated soil. According to the 1999 Source Removal Action Summary Report by the consultant, the mass of PAHs in the soil that was removed was 1.3 tons. The full extent of the contamination is unknown because it is not clear how much actually seeped into the ground, and an initial estimate would be very crude. Another source of contamination was the excess creosote that was placed in an unlined holding pond. This creosote migrated to bedrock over a long period of time.

Creosote is a dense non-aqueous phase liquid (DNAPL) and therefore sank to bedrock 8-12 feet below ground once it entered the subsurface. The soil is broadly characterized as consisting of three layers. A mixture of gravel and coal makes up the top layer and is approximately 2 feet thick. The next layer consists of silty clay that is 5-6 feet thick. Silty sand comprises the third layer, which is 4-5 feet thick and lies on top of the bedrock. Most of the contamination is located within this silty sand layer.

A phytoremediation system coupled with bioremediation that included over 1,000 poplar trees was installed in 1997 after extensive soil and groundwater samples were analyzed. The samples showed that most of the PAH contamination was located between the top of the water table, about 7 feet below the ground surface, and bedrock. A series of groundwater monitoring wells and over twenty multi-level samplers (MLSs) were installed with ports located every foot above bedrock. In addition to monitoring wells, piezometers and pressure transducers were installed. A full weather station was set up at the site to monitor hourly changes in temperature, humidity, wind, and precipitation.

Hybrid poplar trees were chosen because of their high evapotranspiration potential, rapid growth rate, depth and distribution of roots, biomass yield, degradative enzyme production, and their ability to bioaccumulate contaminants (Al-Yousfi et al., 2000). Narayanan et al. (1999) state that the ability of plants to draw up large quantities of water helps remediation by enhancing the upward movement of groundwater. Within this groundwater are contaminants that are drawn up to the rhizosphere, where oxygen availability is higher and the potential for aerobic biodegradation is increased. In 1998, an additional 120 poplar trees were planted down gradient of the original trees to increase

the barrier between the contaminants and the creek. The area that the trees cover is approximately 2.5 acres. Figure 1.3 shows the placement of the trees as well as the locations of the multi-level samplers, and Figure 1.4 is a picture taken October 2004 at the site.

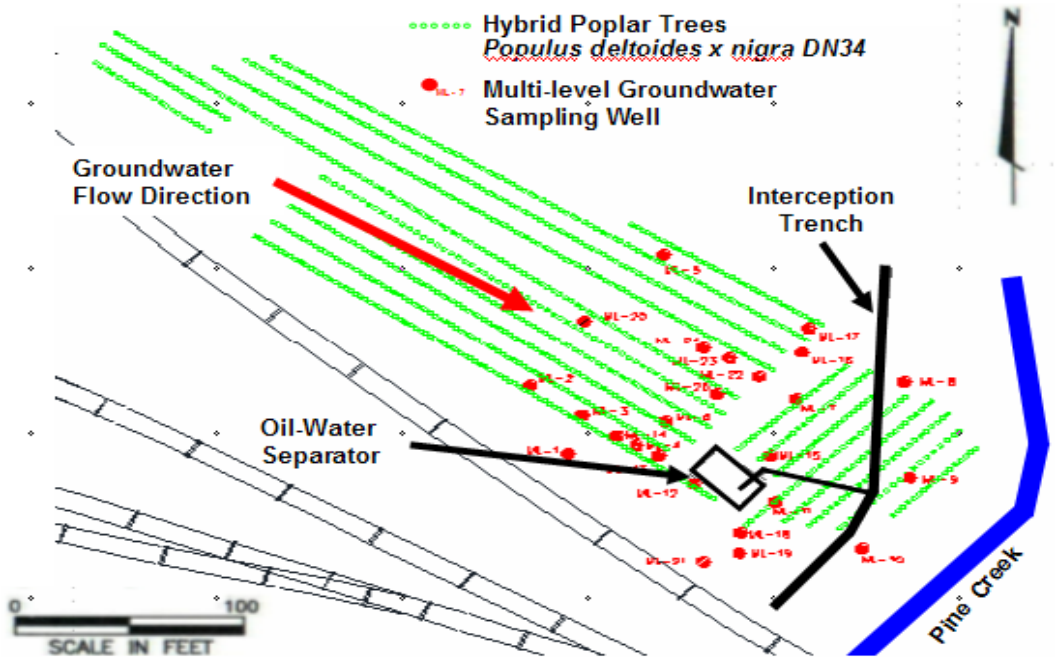

Figure 1.3 Location of trees and multi-level samplers.

Figure 1.4 Hybrid poplar trees at the Oneida Tie Yard site.

Since the phytoremediation system was implemented, Virginia Tech has been monitoring eight PAHs in the soil and groundwater. The concentrations of 2- and 3-ring PAHs monitored at the site such as naphthalene, acenaphthene, acenaphthylene and flourene are decreasing over time. These smaller PAHs are removed faster because they have a lower tendency to sorb and higher volatility. As these PAHs are removed, the DNAPL has become enriched with the 3- and 4-ring PAH compounds such as pyrene, floranthene, anthracene, phenanthrene, which are not removed as easily (Smartt, 2002). This research focuses on naphthalene since it comprises the majority of the creosote and is the most volatile.

1.6 Naphthalene

1.6.1 Naphthalene properties

Naphthalene ($C_{10}H_8$), also known as white tar and tar camphor, is a volatile organic compound (VOC) that is a widespread atmospheric contaminant. At room temperature, it is present as a water insoluble white solid or powder (U.S. EPA, 2003d). In the environment, its low solubility causes it to be mostly retained in sediments where it is more easily biodegraded than in water alone (U.S. EPA, 2003c). Naphthalene evaporates readily and has a strong mothball-like odor with an odor threshold of 84 ppb in air and 21 $\mu g\ L^{-1}$ in water (ATSDR, 2003). The Occupational Safety and Health Administration (OSHA) recommends occupational exposure limits not to exceed 10 ppm, and The National Institute for Occupational Safety and Health (NIOSH) considers naphthalene concentrations in air above 250 ppm to be life-threatening (U.S. EPA, 2003c). Table 1.2 summarizes the physical and chemical properties of naphthalene.

Table 1.2 Physical and Chemical Properties of Naphthalene

CAS Number	91-20-3
Molecular Formula	$C_{10}H_8$
Molecular Weight	128.19 g mol^{-1}
Melting Point	80.5˚C
Boiling Point	218˚C
Density at 20˚C	1.145 g mL^{-1}
Odor Threshold in Water	0.021 mg L^{-1}
Odor Threshold in Air	0.44 mg m^{-3} (0.084ppm)
Solubility in Water at 25˚C	31.7 mg L^{-1}
Log K_{OW}	3.29
Log K_{OC}	2.97
Vapor Pressure at 25˚C	0.087 mmHg
Henry's Law Constant	$4.6x10^{-4}$ atm m^{-3} mol^{-1}

Source: (ATSDR, 2003)

Naphthalene, whose principal commercial use is as an intermediate in producing plasticizers, resins, dyes, and insect repellents, is also used in moth repellants (mothballs and moth flakes), toilet deodorant blocks, leather tanning agents, and carbamate insecticides and fumigants (ATSDR, 2003). Naphthalene is described as a "hazardous inert ingredient" in insecticides and fumigants, and their use presents one of the many pathways for naphthalene to enter the environment (Journal of Pesticide Reform, 1999; EPA List of Inert Pesticide Ingredients, 2004).

Because naphthalene is used in a number of consumer products, it is portrayed as both an indoor and outdoor contaminant. Naphthalene is a natural component of fossil fuels such as coal and petroleum, constituting 11% of coal tar and 1.3% of crude oil (U.S. EPA, 2003d; OEHHA, 2004). A combustion byproduct that is also found in fuel oil and gasoline, naphthalene is emitted by wood and tobacco burning, industrial activities, and motor vehicles (U.S. EPA, 2003c; OEHHA, 2004). Another major source of naphthalene in the environment is spillage during the storage, transport and disposal of fuel elements (oil, coal tar). The U.S. EPA's Toxic Release Inventory (TRI) in 1998 estimated that

5,700,000 pounds of naphthalene were released through on-site and off-site releases in the United States, with 3,400,000 pounds as air emissions and the rest as land, surface water and underground discharges (U.S. EPA, 2003d). These numbers should be used with caution because only industries that meet certain criteria are required to report releases, such as industries that have greater than ten full-time employees and manufacture more than 25,000 lbs $year^{-1}$ or use more than 10,000 lbs $year^{-1}$ of naphthalene (U.S. EPA, 2003c).

1.6.2 Naphthalene health effects

It has been suspected that naphthalene causes cancer and other adverse health affects, and in 1993, naphthalene was added to the toxic air contaminant list. There have not been enough human toxicological studies completed to adequately describe the relationship between naphthalene and cancer, but it is known that adverse health effects are caused at high doses. Based on animal studies, the U.S. Department of Human Health and Human Services (DHHS) has concluded that naphthalene is reasonably anticipated to be a carcinogen, while the International Agency for Research on Cancer (IARC) concluded that naphthalene is possibly carcinogenic to humans (ATSDR, 2003; OEHHA, 2004). The Environmental Protection Agency (EPA) has classified naphthalene as a Group C possible human carcinogen, which means that inadequate human data is available (U.S. EPA, 2003d).

Table 1.3 Naphthalene Exposure Levels

NIOSH REL[a]	10 ppm TWA[d] (50 mg m^{-3})	15 ppm ST[e] (75 mg m^{-3})
OSHA PEL[b]	10 ppm TWA (50 mg m^{-3})	
IDLH[c]	250 ppm (1,310 mg m^{-3})	

[a]National Institute of Occupational Safety and Health Recommended Exposure Limit
[b]Occupational Safety and Health Administration Permissible Exposure Limit
[c] Immediately Dangerous to Life or Health
[d]Time weighted average
[e] Short-term exposure limit
Source: (NIOSH, 1997)

In Table 1.3, the NIOSH REL refers to the National Institute of Occupational Safety and Health's recommended exposure limit for an 8-10 hour time weighted average (TWA) and short-term exposure limit (ST), which is a 15-minute TWA that should not be

exceeded at any time during a workday. The OSHA PEL is the Occupational Safety and Health Administration's permissible exposure limit expressed as a time-weighted average. This is the concentration of a substance, averaged over an 8 hour workday or a 40 hour workweek, at which most workers can be exposed to without any adverse effects. NIOSH values only serve as advisory levels, whereas OSHA values are regulatory levels that are used in government regulations. The IDLH level is the immediately dangerous to life or health concentration. This concentration is the recommended exposure limit that allows a worker to escape from a situation that will likely cause death or permanent adverse health effects (U.S. EPA, 2003a).

Exposure to naphthalene in large amounts through ingestion, skin or eye contact, inhalation, or skin absorption can cause damage to red blood cells called hemolytic anemia, which results in fatigue, restlessness, lack of appetite, and a pale appearance. Naphthalene exposure can also cause headaches, nausea, liver damage, vomiting, eye irritation, and jaundice. Short-term (acute) exposure is linked to anemia, liver damage, and neurological damage, while long-term (chronic) exposure is associated with cataracts and retina damage (ATSDR, 2003). Animal studies have determined that when ingested, naphthalene exhibits a moderate to high toxicity, but a low to moderate toxicity when in contact with skin (RTECS online database, 1993). People at risk for high levels of naphthalene exposure include those who use moth repellants containing naphthalene, smokers and people near smokers, workers at naphthalene producing and naphthalene using industries, and those that live near hazardous waste sites.

In 1998, the EPA added naphthalene to the Contaminant Candidate List (CCL) as a priority contaminant, which is a list used by the EPA to determine new drinking water standards every five years. The 1996 amended Safe Drinking Water Act (SDWA) states that five or more contaminants must be selected from the list to determine if they should be regulated or not. On July 18, 2003, a final decision was made that no drinking water standards are to be set for nine contaminants on the list, one of which was naphthalene (U.S. EPA, 2003b). Based on the lack of available human toxicology data, the risk of naphthalene can not be well quantified, and the EPA could not justify regulating it. Along with naphthalene, the other contaminants that were denied regulatory action include acanthamoeba, aldrin, dieldrin, hexachlorobutadiene, manganese, metribuzin,

sodium, and sulfate (U.S. EPA, 2003b). The closest the EPA has come to regulating naphthalene was in 1990 when it issued a drinking water health advisory of 100 μg L^{-1} (U.S. EPA, 2003c).

1.6.3 Naphthalene in drinking water

Naphthalene has been detected in groundwater at relatively low levels, and naphthalene has been detected more often in urban wells than rural wells. The maximum values for naphthalene in runoff and groundwater have been well below the Health Reference Level (HRL), which is an exposure level that will not cause significant risks of noncancer health effects. The current HRL is 100 μg L^{-1} and the HRL to assess preliminary health effects is 140 μg L^{-1} (U.S. EPA, 2003c). In public drinking water supply samples collected under the SDWA, there was a low occurrence of naphthalene. Nationally, it is estimated that only 0.01% of the population (approximately 16,000 people) is exposed to naphthalene levels greater than the HRL in the public water supply (U.S. EPA, 2003c). When the EPA compared the average daily intake of naphthalene from public water supplies, they found that it only accounted for a very small percentage in comparison to the average daily intakes through the air, soil, and food, hence another reason why the EPA decided not to regulate naphthalene in drinking water.

1.6.4 Naphthalene in air

Approximately 90% of naphthalene enters the indoor environment through the air, most of which is from burning wood and fossil fuels in the home, with the second greatest release of naphthalene coming from moth repellants (U.S. EPA, 2003d; ATSDR, 2003). The most important removal mechanism for naphthalene while in the air is through reactions with hydroxyl radicals in the daytime to form 1- and 2-naphthol and 1- and 2-nitronaphthalene (ATSDR, 2003). At night, naphthalene reacts with NO_3 to form nitronaphthalenes (OEHHA, 2004). Calculated half-lives are generally less than 1 day, with some half-lives as low as 6 hours (ATSDR, 2003; OEHHA, 2004).

Typical outdoor air concentrations of naphthalene range from 0.076 to 32.5 ppb, while indoor concentrations of naphthalene in homes and office buildings range from 0.06 to 7.8 ppb. Houses near industrial sources and hazardous waste sites experienced concentrations ranging from 0.08-0.9 ppb (U.S. EPA, 2003d; ATSDR, 2003). In some cases, the concentration of naphthalene indoors exceeds the concentration outdoors. For

example, samples were taken in homes with smokers, and an average concentration of 0.42 ppb was detected in the indoor air with an outdoor concentration of 0.06 ppb. In homes with no smokers, the average indoor concentration was 0.19 ppb and the average outdoor concentration was 0.019 ppb. In addition, the average concentration of naphthalene in vehicles in traffic was 0.86 ppb (U.S. EPA, 2003d). Table 1.4 shows the typical concentrations of naphthalene in indoor and outdoor air within various types of buildings.

Table 1.4 Typical Concentrations of Naphthalene in Air

	Indoor Air	Outdoor Air	Reference
Houses	0.06 - 6 ppb	0.076 - 32.5 ppb	U.S. EPA, 2003d; ATSDR, 2003
Offices	0.95 - 7.8 ppb	-	U.S. EPA, 2003d
Laboratories	< 0.57 - 19 ppb	-	U.S. EPA, 2003d
Near Hazardous Waste Sites	-	0.08 – 0.9 ppb	U.S. EPA, 2003d; ATSDR, 2003
Vehicles in Traffic	0.86 ppb	-	U.S. EPA, 2003d
Houses with smokers	0.42 ppb	0.06 ppb	U.S. EPA, 2003d
Houses without smokers	0.2 ppb	0.02 ppb	U.S. EPA, 2003d

According to the Agency for Toxic Substances and Disease Registry (ATSDR), based on an average outdoor air concentration of 0.2 ppb (1.05 μg m^{-3}) and an inhalation rate of 20 m^3 day^{-1}, the average adult daily intake of naphthalene is estimated at 0.3 μg kg^{-1} day^{-1}, or 20 μg day^{-1} assuming 70 kg body weight (ATSDR, 2003). In contrast, the Health Effects Support Document for Naphthalene released by the U.S. EPA uses an average outdoor air concentration of 0.63 ppb (5.19 μg m^{-3}) and an inhalation rate of 15.2 m^3 day^{-1} to calculate an average daily intake of naphthalene for an adult of 1.1 μg kg^{-1} day^{-1}. For a 70 kg adult, this would correspond to 79 μg naphthalene per day. However, the average inhalation rate for a child is 8.7 m^3 day^{-1}, which results in an average daily intake of 4.5 μg kg^{-1} day^{-1}. With a body weight of 10 kg, a child is exposed to 45 μg naphthalene per day (U.S. EPA, 2003d). Based on the above results, it is clear that an individual's intake of naphthalene depends on a variety of conditions, including but not restricted to a person's urban, suburban, or rural location, proximity to hazardous waste sites, relation to smokers, fresh paint or lacquer in a house, use of moth repellants,

burning wood or stoves, weather conditions, activity (running on a treadmill as opposed to running outside), time spent in traffic, geographic location, and inhalation rate.

The presence of moth repellants and smoke, either from cigarettes or burning wood, contribute greatly to the amount of naphthalene in indoor air. The mass of naphthalene detected in the mainstream smoke of one commercial unfiltered cigarette brand was 3 μg, and a mass of 46 μg has been detected in sidestream smoke (U.S. EPA, 2003d). In addition, naphthalene levels of 67 ppb (350 μg m^{-3}) were measured from 36 mothballs in one woman's cupboard (U.S. EPA, 2003d); even so, this concentration is well below the regulatory agencies' standards according to Table 1.3. One study, in which nine people (eight adults and one child) were exposed to several hundred mothballs in their homes, reported nausea, vomiting, abdominal pain and anemia. A naphthalene concentration of 20 ppb was measured in one of the above homes, and after the mothballs were removed, the symptoms subsided (OEHHA, 2003). By comparing the regulatory standards for naphthalene exposure to the documented concentrations at which symptoms are present, it is clear that the effects of naphthalene exposure are felt long before any regulatory standards are exceeded. This fact alone should be a driving force for more stringent naphthalene regulations, especially since naphthalene is a main component in mothballs. Moth repellents are typically made up of 95-100% naphthalene or paradichlorobenzene, and concentrations are rarely high enough to effectively kill moths and their larvae. Clothes that have been stored with mothballs absorb naphthalene, which continues to volatilize for days, and this can cause toxic effects in people if a large amount is inhaled or if inhaled on a regular basis. However, one of the largest concerns with mothballs is that they look like candy and are often eaten by children (Goldberg, 1995).

1.7 Research Objectives

The specific objectives of this research are to:

(1) Measure the rate of direct volatilization of naphthalene at the phytoremediation site. In order to determine the rate of direct volatilization, a surface measurement device was developed to measure vapor fluxes from the subsurface. The surface

measurement includes a dynamic surface flux chamber that is described in more detail in Chapter 2.

(2) Identify the most influential factor affecting direct volatilization. Based on the flux results, the most influential factors that affect volatilization in the field were determined. Because field sites vary greatly, volatilization rates will also vary, depending on contaminant properties, soil properties, and environmental conditions. More specifically, the volatilizing trends depend on groundwater level, depth to source, source thickness, soil type, the presence of preferential pathways, soil moisture, rainfall, humidity, pressure, and temperature.

(3) Assess whether the trees at the site enhance naphthalene volatilization based on physical processes in the subsurface. These processes include lowering the groundwater table during periods of high transpiration rates and the seasonal up-and-down movement of the groundwater by the trees.

(4) Determine health risks associated with use of land above the contaminated soil and groundwater. A mathematical vapor intrusion and infiltration model was applied to quantify the human health risks associated with the accumulation of the gas vapors in an enclosed space, such as the basement of a house. The vapor intrusion model uses soil properties, specific source conditions, and building characteristics to determine an attenuation ratio, which is a dimensionless ratio of the gas vapor concentration in an enclosed space to the vapor concentration at the source. Large amounts of naphthalene vapors volatilizing from the subsurface and infiltrating into an enclosed space can become harmful when inhaled on a regular basis.

(5) Estimate biodegradation rates for naphthalene in the unsaturated zone from experimental column studies. The amount of directly volatilizing contaminants in the field is related to the biodegradation rates of naphthalene, which were determined by laboratory experiments. In the laboratory, soil columns were constructed using soil from the site to evaluate the behavior of naphthalene within the unsaturated zone under controlled conditions. These soil columns are described in greater detail in Chapter 3.

(6) Compare the mechanisms of direct volatilization and biodegradation of naphthalene in the unsaturated zone. Transport by diffusion in the unsaturated zone followed by biodegradation has significant remediation implications.

References

Agency for Toxic Substances and Disease Registry (ATSDR) (2003). Toxicological profile for naphthalene, 1-methylnaphthalene, 2-methylnaphthalene. Atlanta, GA, U.S. Department of Health and Human Services, Public Health Service.

Al-Yousfi, A. B., R. J. Chapin, et al. (2000). "Phytoremediation - the natural pump-and-treat and hydraulic barrier system." Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management **4**(2): 73-77.

"Are "inert" ingredients in pesticides really benign?" (1999) Journal of Pesticide Reform **19**(2).

Auer, L. H., N. D. Rosenberg, et al. (1996). "The effects of barometric pumping on contaminant transport." Journal of Contaminant Hydrology **24**: 145-166.

Bekku, Y., H. Koizumi, et al. (1997). "Examination of four methods for measuring soil respiration." Applicable Soil Ecology **5**: 247-254.

Burken, J. G. and J. L. Schnoor (1998). "Predictive Relationships for Uptake of Organic Contaminants by Hybrid Poplar Trees." Environmental Science and Technology **32**(21): 3379-3385.

Burken, J. G., C. Ross, et al. (2001). "Benzene toxicity and removal in laboratory phytoremediation studies." Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management **5**(3): 161-171.

Chaplin, B. P., G. N. Delin, et al. (2002). "Long-Term Evolution of Biodegradation and Volatilization Rates in a Crude Oil-Contaminated Aquifer." Bioremediation Journal **6**(3): 237-255.

Choi, J., F. D. Tillman, et al. (2002). "Relative Importance of Gas-Phase Diffusive and Advective Trichloroethene (TCE) Fluxes in the Unsaturated Zone under Natural Conditions." Environmental Science & Technology **36**(14): 3157-3164.

Gao, F., S. R. Yates, et al. (1997). "Design, Fabrication, and Application of a Dynamic Chamber for Measuring Gas Emissions from Soil." Environmental Science & Technology **31**(1): 148-153.

Gao, F. and S. R. Yates (1998a). "Laboratory study of closed and dynamic flux chambers: Experimental results and implications for field application." Journal of Geophysical Research **103**(D20): 26115-26125.

Gao, F. and S. R. Yates (1998b). "Simulation of enclosure-based methods for measuring gas emissions from soil to the atmosphere." Journal of Geophysical Research **103**(D20): 26127-26136.

Goldberg, J. (1995). Clothing Moths, Washington Toxics Coalition.

Heikkila, P. R., M. Hameila, et al. (1987). "Exposure to creosote in the impregnation and handling of impregnated wood." Scandinavian Journal of Work, Environment, and Health **13**: 431-437.

Hutchinson, G. L., G. P. Livingston, et al. (2000). "Chamber measurement of surface-atmosphere trace gas exchange: Numerical evaluation of dependence on soil, interfacial layer, and source/sink properties." Journal of Geophysical Research **105**(D7): 8865-8875.

Jellali, S., H. Benremita, et al. (2003). "A large-scale experiment on mass transfer of trichloroethylene from the unsaturated zone of a sandy aquifer to its interfaces." Journal of Contaminant Hydrology **60**: 31-53.

Kruger, E. L., T. A. Anderson, et al. (1996). Phytoremediation of Soil and Water Contaminants - Preface. 212th National Meeting of the American Chemical Society (ACS Symposium Series 664), Orlando, FL.

Ma, X. and J. G. Burken (2003). "TCE Diffusion to the Atmosphere in Phytoremediation Applications." Environmental Science and Technology **37**(11): 2534-2539.

Massmann, J. and D. F. Farrier (1992). "Effects of atmospheric pressures on gas transport in the vadose zone." Water Resources Research **28**: 777-791.

Narayanan, M., L. E. Erickson, et al. (1999). "Simple Plant-Based Design Strategies for Volatile Organic Pollutants." Environmental Progress **18**(4): 231-242.

National Institute for Occupational Safety and Health (NIOSH) (1997). Pocket Guide to Chemical Hazards. Cincinnati, OH, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention.

Office of Environmental Health Hazard Assessment (OEHHA) (2003). Chronic Toxicity Summary of Naphthalene.

OEHHA (2004). Long-term Health Effects of Exposure to Naphthalene: Background and status of Naphthalene as a Toxic Air Contaminant and Potential Carcinogen.

Orchard, B. J., W. J. Doucette, et al. (2000). "Uptake of trichloroethylene by hybrid poplar trees grown hydroponically in flow-through growth chambers." Environmental Toxicology and Chemistry **19**(4): 895-903.

Pasteris, G., D. Werner, et al. (2002). "Vapor Phase Transport and Biodegradation of Volatile Fuel Compounds in the Unsaturated Zone: A Large Scale Lysimeter Experiment." Environmental Science & Technology **36**(1): 30-39.

Pumpanen, J., P. Kolari, et al. (2004). "Comparison of different chamber techniques for measuring soil CO2 efflux." Agricultural and Forst Meteorology **123**: 159-176.

Ramaswami, A. and E. Rubin (2001). "Measuring phytoremediation parameters for volatile organic compounds: Focus on MTBE." Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management **5**(3): 123-129.

Reichman, R. and D. E. Rolston (2002). "Design and Performance of a Gas Flux Chamber." Journal of Environmental Quality **31**: 1774-1781.

Robinson, B., S. Green, et al. (2003). "Phytoremediation: using plans as biopumps to improve degraded environments." Australian Journal of Soil Research **41**(3): 599-612.

Schnoor, J. L. (2002). Phytoremediation of Soil and Groundwater. Iowa City, IA, Ground-Water Remediation Technologies Analysis Center, Technology Evaluation Report TE-02-1**:** 45.

Smartt, H. (2002). Effects of the Desorption and Dissolution of Polycyclic Aromatic Hydrocarbons on Phytoremediation at a Creosote-Contaminated Site. Civil and Environmental Engineering. Blacksburg, VA, Virginia Tech. Master's thesis.

Smith, J. A., A. K. Tisdale, et al. (1996). "Quantification of Natural Vapor Fluxes of Trichloroethene in the Unsaturated Zone at Picatinny Arsenal, New Jersey." Environmental Science & Technology **30**(7): 2243-2250.

Susarla, S., V. F. Medina, et al. (2002). "Phytoremediation: An ecological solution to organic chemical contamination." Ecological Engineering **18**: 647-658.

Thorstenson, D. C. and D. W. Pollock (1989). "Gas transport in unsaturated zones: multicomponent systems and the adequacy of Fick's laws." Water Resources Research **25**(3): 477-507.

Tillman Jr., F. D., J.-W. Choi, et al. (2003). "A comparison of direct measurement and model simulation of total flux of volatile organic compounds from the subsurface to the atmosphere under natural field conditions." Water Resources Research **39**(10): 1284-1295.

Tillman Jr., F. D. and J. A. Smith (2004). "Design and laboratory testing of a chamber device to measure total flux of volatile organic compounds from the unsaturated zone under natural conditions." Journal of Contaminant Hydrology **75**: 71-90.

U.S. Department of Health and Human Services (1993). Registry of Toxic Effects of Chemical Substances (RTECS, online database). Bethesda, MD, National Toxicology Information Program, National Library of Medicine.

U.S. Environmental Protection Agency (U.S. EPA) (2003a). Air Toxic Website for Naphthalene. Accessed 10/15/04 at 4:45pm.

U.S. EPA (2003b). Announcement of Regulatory Determinations for Priority Contaminants on the Drinking Water Contaminant Candidate List, EPA-815-F-03-007.

U.S. EPA (2003c). Contaminant Candidate List Regulatory Determination Support Document for Naphthalene, USEPA Office of Water Report, EPA-815-R-03-014.

U.S. EPA (2003d). Health Effects Support Document for Naphthalene, USEPA Office of Water Report, EPA-822-R-03-005.

U.S. EPA (2004). List of inert pesticide ingredients.

CHAPTER 2

Direct volatilization of naphthalene at a creosote-contaminated site with a phytoremediation system: A field study

Elizabeth C. Booth, Linsey C. Marr, Mark A. Widdowson
418 Durham Hall, Department of Civil and Environmental Engineering
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061

Abstract

A creosote-contaminated site in Oneida, Tennessee was implemented with a phytoremediation system for hydraulic control and enhancement of the natural attenuation processes within the subsurface. The importance of direct volatilization of naphthalene from the subsurface was studied and its influences were investigated. Transport of naphthalene from the subsurface into the atmosphere was measured with a flux chamber. A maximum flux of 23 $\mu g\ m^{-2}\ hr^{-1}$ was measured in August 2004 in the most contaminated area. Results suggest that numerous factors affect volatilization, the most important of which is the groundwater level, and that the presence of the trees enhances the influence of such factors on direct volatilization.

Key Words

Phytoremediation, direct volatilization, naphthalene, flux chamber

2.0 Introduction

Phytoremediation, which is the use of plants to remediate groundwater and soil, has been applied to sites contaminated with chlorinated hydrocarbons, aromatic hydrocarbons, herbicides, surfactants, heavy metals, and nutrients (Davis et al., 1998). The benefits of this remediation technique are undeniable because it is cost-effective and environmentally friendly, requires minimal maintenance, and reduces risks associated with moving and disposing of contaminated soil and groundwater. Rhizosphere bioremediation and plant uptake are the two main processes by which plants accelerate remediation; and recent research has found that phytovolatilization, a specific mechanism of plant uptake, is a significant pathway for contaminant removal and remediation

(Newman et al.,1997; Burken and Schnoor, 1998; Narayanan et al., 1999; Schnoor, 2002; Ma and Burken, 2003).

Semi-volatile and volatile contaminants can volatilize out of the ground and enter the atmosphere through a process known as "direct volatilization." Both advection, driven by changes in atmospheric pressure, and diffusion, driven by concentration gradients, contribute to the total direct volatilization (Smith et al., 1996; Choi et al., 2002). The relative importance of each mechanism depends largely on site-specific and atmospheric conditions (Choi et al., 2002; Tillman et al., 2003). In order to measure the amount of contaminants that volatilize through the subsurface, researchers have designed and tested flux chambers in the field and laboratory (Smith et al., 1996; Gao et al., 1997; Reichman and Rolston, 2002; Jellali et al., 2003; Tillman et al., 2003; Tillman and Smith, 2004).

The magnitude of flux through the subsurface depends on environmental conditions such as soil characteristics and meteorological changes. Massmann and Farrier (1992) and Auer et al. (1996) found that variations in atmospheric pressure due to irregular fluctuations in weather patterns, commonly referred to as barometric pumping, enhance the transport of vapors in the subsurface. Auer et al. (1996) determined that contaminants near the ground surface mix more rapidly with atmospheric air, causing contaminants to be incorporated into the environment more rapidly than by diffusion alone. Smith et al. (1996) studied the diffusive flux of trichloroethylene (TCE) in the subsurface and found that changes in atmospheric pressure and temperature as well as soil moisture content are major influences on contaminant flux from the subsurface. Choi et al. (2002) attributed their flux measurement irregularities to differences in atmospheric pressure changes, soil air-filled porosity, and soil moisture content.

Studies of the relationship between vapor phase transport of contaminants in the subsurface and moisture in the form of soil water content, humidity, or precipitation, have produced conflicting results. Field measurements have determined that moisture is inversely proportional to diffusive fluxes because diffusion coefficients decrease as moisture rises (Choi et al, 2002; Smith et al., 1996; Narayanan et al., 1999). Davis et al. (1998) determined that during dry periods, a greater percentage of soil voids are filled with contaminants in the gas phase. In sharp contrast, Valsaraj et al. (1999) and Poulsen

et al. (2000) both concluded that diffusive flux is directly proportional to moisture; as the moisture decreases, sorption to the soil increases, and the flux of contaminants from the subsurface is reduced. The work of Poulsen et al. (2002) was conducted to determine sorption as a function of water content such that the sorption parameters are determined independently from soil surface area and texture. Various soil types were used to estimate sorption parameters for their model. In addition, Valsaraj et al. (1999) used three different field sediment types in their study and found that air concentrations during humid or wet conditions following a dry period will be large for each soil type.

The influence of the groundwater level on subsurface contaminants has also been addressed. Water level fluctuations vertically redistribute dissolved contaminants in the unsaturated and saturated zones (Lee et al., 2001). Natural fluctuations in the water level cause contaminants to distribute over an area termed the "smear zone" where volatilization and diffusion through the unsaturated zone can occur (Lahvis et al., 1999). "Smear zones" can occur with dense non-aqueous phase liquids (DNAPLs) due to density heterogeneities in the compound mixture. Lower density compounds, such as petroleum products, float on the water table (Lahvis et al., 1999). Because biodegradation rate constants increase with distance above the water table, the vertical redistribution of contaminants enhances the potential for contaminant degradation (Lahvis et al., 1999).

A phytoremediation system with hybrid poplar trees was implemented at a creosote-contaminated site in Oneida, TN. The system was installed in 1997 to serve as a hydraulic barrier and enhance the transfer of the contaminated groundwater into the more microbial active vadose zone and rhizosphere where contaminant degradation is greater relative to areas not impacted by trees. Additional remediation mechanisms include plant uptake and direct volatilization of contaminants into the atmosphere. The relative importance of these two mechanisms for contaminant removal is unknown, and the presence of the phytoremediation system may actually enhance direct volatilization. The extended record of groundwater, soil, and meteorological measurements at the site facilitate this study of the factors affecting direct volatilization. The main objectives of this study are to (1) measure the rate of direct volatilization of naphthalene at the site, (2) identify the most influential factor affecting direct volatilization, and (3) assess whether the presence of the trees enhances direct volatilization. This study focuses on

naphthalene since it comprises the majority of the contamination and is the most volatile component of creosote.

2.1 Methods

2.1.1 Site Description and background

The study area is located in Oneida, Tennessee approximately 60 miles northwest of Knoxville, Tennessee. Beginning in the early 1950s, the tie yard was used by the Tennessee Railway Company to treat railroad ties with creosote, and treatment continued intermittently from 1960 to 1966 and from 1968 to 1973. The site originally had an above-ground storage tank for creosote, a pressurized wood treatment unit, and a spur track for transporting the treated railroad ties. Sources of groundwater and soil contamination include an above-ground storage tank and an unlined holding pond that contained the discharged creosote. In 1990, creosote contamination was discovered in a nearby creek by the U.S. Army Corp of Engineers during a watershed project.

After discovery of the contamination, a consulting firm was contracted to implement a remediation plan and excavate the contaminated storage tank footings. Even though 1147 tons of contaminated soil and 1.3 tons of polycyclic aromatic hydrocarbons (PAHs) were removed, the total mass of creosote that leaked into the soil and groundwater is unknown. To control the movement of the contaminated groundwater and to aid in subsurface remediation, a phytoremediation system consisting of 1,120 poplar trees was installed between 1997 and 1998. This system, shown in Figure 2.1, includes an interceptor trench and oil-water separator that were installed to prevent further contamination of the nearby creek.

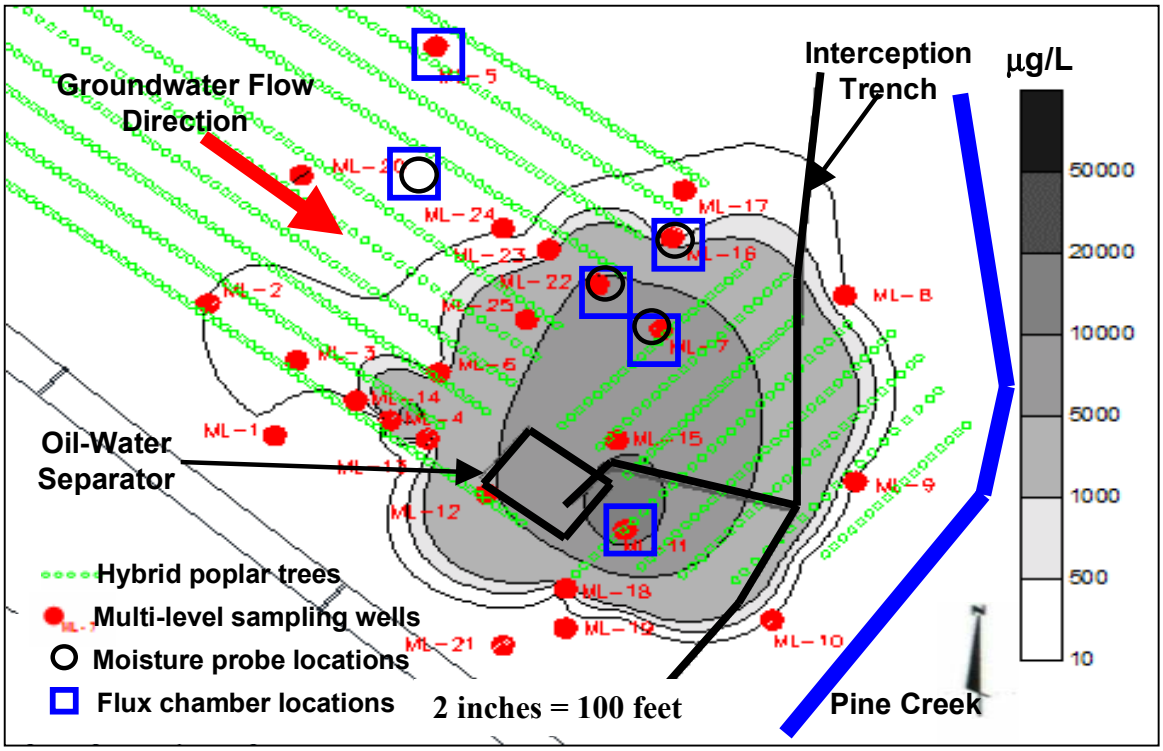

Figure 2.1 Deep (0-2.5 feet above bedrock) naphthalene groundwater concentrations (µg L^{-1}) in March 2004 with a high water table level and corresponding data collection locations.

Samples show that most of the contamination is present as a dense non-aqueous phase liquid (DNAPL) located about 8 to 12 feet below ground. The soil consists of three layers: a mixture of gravel and coal in the top few feet, then a layer of silty clay that is 5 to 6 feet thick, and silty sand in the lowest layer that is 4 to 5 feet thick and lies on top of shale bedrock. A series of groundwater monitoring wells and over twenty multi-level samplers (MLSs) were installed with ports located every foot above bedrock. In addition to monitoring wells, piezometers and pressure transducers were installed. A full weather station was set up at the site to monitor hourly changes in temperature, humidity, wind, and precipitation.

2.1.2 Chamber design and materials

A chamber was designed and built to measure the flux of gas vapors volatilizing from the ground surface. The chamber is designed to optimize the following considerations: (1) introduce clean, dehumidified air into the chamber, (2) minimize radiant heating of the chamber, (3) prevent unnatural diffusive and advective fluxes

through the subsurface, (4) maintain air flow over the enclosed soil surface similar to ambient conditions, (5) sustain a constant and uniform air flow over the soil surface to prevent concentration buildup and eliminate stagnant air zones in the chamber, (6) withstand harsh field conditions, and (7) reduce leak potential between the air inside the chamber and ambient air. Other important parameters that must be considered in the design of the flux chamber include its size and shape.

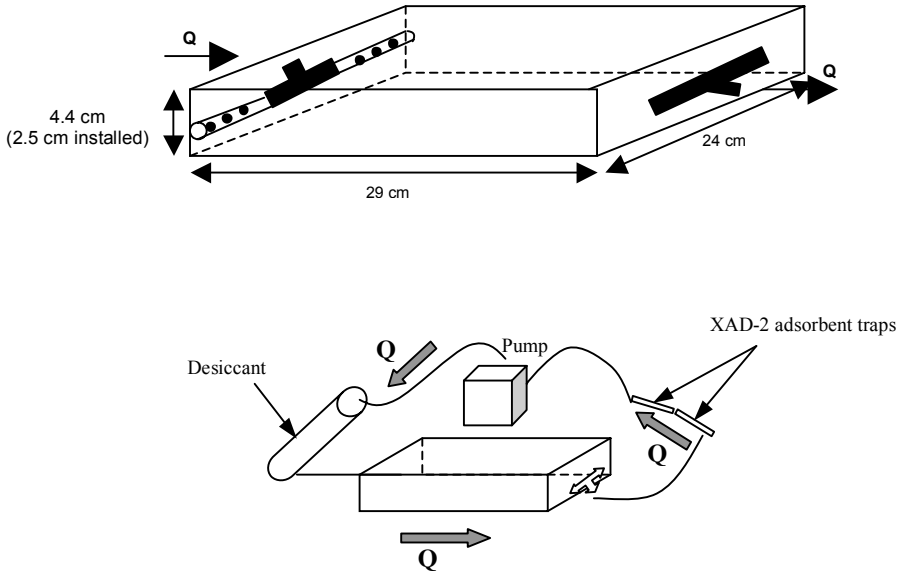

Figure 2.2 Schematic diagrams of the flux chamber.

A 22-gauge Type 304 stainless steel tray with dimensions 24 x 29 x 4.4-cm was used for the flux chamber body. When installed 1.9-cm deep into the ground, the chamber had an effective height of 2.5-cm. A 0.6-cm diameter hole was drilled 1.9-cm from the closed bottom of the tray (top when installed) to serve as the inlet. One tee-fitting was inserted into the inlet and two 0.6 cm diameter Teflon tubes, each 7.6-cm long, were fitted into the ends of the tee-fitting. To uniformly blow air down the length of the chamber, ten 0.3-cm holes were drilled into the Teflon tubing at equally spaced intervals. Caps were placed on the ends of the tubes to prevent air from leaking into the chamber through the open ends. Two 0.6-cm diameter holes, which serve as the outlets, were drilled 11.4-cm apart and 1.9-cm from the closed bottom of the tray on the opposite side of the inlet. Elbow fittings were inserted into the outlet holes and connected with

short pieces of Tygon tubing to a tee-fitting outside the chamber. The fittings combine the flow from the two outlets into one uniform flow.

A personal sampling pump (SKC PCXR8) was connected to the chamber to introduce clean air into the chamber and remove contaminated air at a constant flow rate of 2 L min^{-1}. As shown in Figure 2.2, air flowed from the pump through silicone tubing into a drying column that contained 0.57-kg of 8 mesh indicating Drierite (anhydrous $CaSO_4$) and then to the inlet of the chamber. The drying column was used to prevent water from condensing inside the tubing.

Air then entered the chamber, flowed along its length, and was pulled out of the chamber at the opposite end. Once the contaminated air was pulled out of the chamber, it passed through Tygon tubing into two XAD-2 sorbent tubes that were connected to the vacuum inlet of the pump. The second tube was intended to capture breakthrough from the first. Gas vapors present in the flow stream were trapped on the sorbent tubes, and clean air was returned back to the chamber.

The chosen flow rate represents a compromise between ambient conditions and experimental limitations. According to Reichman and Rolston (2002), a typical wind speed at 0.6 cm above the soil surface, which represents the height at which air enters and exits the chamber, is equivalent to 0.14 m s^{-1}, and this corresponds to a volumetric flow rate of 50 L min^{-1} in our 24 x 29 x 2.5-cm chamber. The recommended flow rate through the sorbent tubes is 1 L min^{-1} and the naphthalene extraction method NIOSH 5515 used for detecting PAHs recommends a flow rate of 2 L min^{-1}. In addition, the Drierite gas drying column used to dehumidify the air flowing into the chamber recommends a flow rate of 3.33 L min^{-1} for maximum efficiency. Therefore, a 2 L min^{-1} flow rate was selected to obtain high sorbent tube and Drierite efficiency and to minimize pressure variations in the chamber.

Flow rates for the incoming and outgoing sweep air are chosen to avoid inhibiting diffusive flow through the soil due to buildup of naphthalene at low flow rates and to prevent advective flow through the soil due to pressure variations at high flow rates. Concentrations in our chamber remained well below 0.006 μg L^{-1} except on one occasion when the chamber concentration was as high as 0.014 μg L^{-1}. In contrast, naphthalene concentrations in the void space of the unsaturated zone (0.85-m below the surface) were

found to be at least 0.3 μg L^{-1}. Ambient air blanks were run at the site to make sure chamber concentrations were similar to ambient concentrations, and we found that ambient naphthalene concentrations vary greatly due to the site's close proximity to a wood-preserving plant. In some cases, such as in October and May 2004, concentrations of naphthalene in the chamber were four to seven times greater than ambient concentrations. However, in April 2004, chamber concentrations were actually three times lower than ambient air concentrations. Generally we feel that the chamber was not significantly inhibiting or enhancing diffusion and advection through the soil.

2.1.3 Sampling and analysis method

The chamber was placed in areas of low, medium, and high contamination, as shown by Figure 2.1, as well as control sites outside the known area of soil and groundwater contamination. The selected sites coincide with the locations of measurements of groundwater level, groundwater concentration, soil moisture, soil gas, and tree flux. Field samples were obtained once a month, with the objective of observing seasonal changes.

Placement of the chamber required a flat area of ground to be selected with large rocks, sticks, and leaves that would obstruct the airflow within the chamber removed. To prevent soil disturbances, a square shovel was used to outline the flux chamber, creating a thin trench that the chamber sides fit into. The chamber was pushed 2-cm into the ground with a rubber mallet. Soil around the edges of the chamber was compressed to create a leak-proof seal that ensured no outside air was being drawn into the chamber. On the few occasions when the soil was extremely dry, the seal around the edges of the chamber was prepared with inert caulking to prevent leakage.

The tubing was then connected without any sorbent tubes and the pump was turned on for approximately five minutes to allow the system to reach steady state. Then, two new sorbent tubes were opened and inserted into the tubing. A plastic tub was propped up over the entire system to minimize the effects of radiant heating and rain while maintaining ambient conditions around the chamber. Sampling durations ranged from hours to weeks, and most samples were collected over a period of three days.

After sampling, the sorbent tubes were removed, capped, wrapped with aluminum foil, and stored at 4°C for no longer than 24 hours before extraction. Samples were

extracted with toluene following the NIOSH 5515 procedure and analyzed on a Hewlett-Packard 5890 gas chromatograph with flame ionization detection (FID) and a DB-5 capillary column. The injector, detector, and oven temperatures were set to 305°C, 310°C, and 80°C, respectively, with a temperature ramp of 10°C min^{-1}. Twenty-five percent of the samples consisted of field and lab blanks. The flux was determined by dividing the mass of naphthalene on the sorbent tubes by the soil surface area covered with the chamber and the sample duration.

2.2 Results and Discussion

2.2.1 Field experiment results

Naphthalene flux measurements were obtained once a month between October 2003 and October 2004. A total of 34 vertical flux measurements were made at the six locations as listed in Table 2.2 and displayed in Figure 2.1. The results show that higher and lower fluxes of naphthalene occur within areas of greater and lesser groundwater contamination, respectively, as expected. Areas of high contamination, especially around ML7 and ML11, consistently have higher fluxes than the other sampled locations. Figure 2.3 shows the time series of measured naphthalene fluxes at the site together with the 6.4% standard deviation that was determined from concurrent flux measurements in the most contaminated area. The highest naphthalene flux of 23 $\mu g\ m^{-2}\ hr^{-1}$ was measured in August at ML7, which is in the most contaminated area. ML22 is located in an area considered to have a medium level of contamination when the water table is high. When the water table is low, groundwater concentrations at ML22 increase significantly, causing the flux to also increase. The flux of naphthalene at locations ML16 and "Clean" are consistently lower than the other sampling positions because they are in areas of low and no contamination, respectively.

Table 2.1 Summary of field test location, date, and results.

Location	Date	Surface flux (μg m^{-2} hr^{-1})
ML 7	10-Oct-03	2.73
(high)	5-Mar-04	3.19
	23-Apr-04	3.46
	24-May-04	4.77
	14-Jun-04	2.74
	7-Jul-04	1.57
	9-Aug-04	23.45
	3-Sep-04	9.51
	8-Oct-04	4.40
	10-Oct-04	1.33
ML 11	5-Mar-04	2.42
(high)	23-Apr-04	4.87
	24-May-04	6.12
	14-Jun-04	1.71
	16-Jul-04	0.60
	9-Aug-04	16.87
	3-Sep-04	7.49
	10-Oct-04	1.15
ML 22	5-Mar-04	3.76
(medium)	23-Apr-04	1.85
	24-May-04	3.04
	14-Jun-04	3.51
	7-Jul-04	0.67
	9-Aug-04	16.02
	3-Sep-04	2.65
	10-Oct-04	1.19
ML 16	7-Jul-04	1.36
(low)	9-Aug-04	5.57
	3-Sep-04	3.10
	10-Oct-04	1.35
Clean	16-Jul-04	0.85
	9-Aug-04	1.68
	3-Sep-04	5.78
	10-Oct-04	1.39

When the water table is at its lowest and dry conditions persist, the difference in sampling locations is amplified, such as in August and September. Throughout most of the year when the water table is high, the flux is consistently between 1 and 6 μg m^{-2} hr^{-1} regardless of the level of groundwater contamination present. The large decrease in fluxes in July and October 2004 (except ML7 in October 2004) are explained by large rain events before and during sampling. In August 2004, large increases in fluxes were measured at ML16 and ML22 due to a large rain event during the last few hours of

sampling. Sampling at ML7 and ML11 was completed before the rain began, so the flux at these locations was not affected. The area associated with groundwater concentrations greater than 10 μg L^{-1} as shown in Figure 2.1 is approximately 950 m^2 (0.25 acres), and within this area, the average naphthalene flux from the soil is 15 μg m^{-2} hr^{-1} in the Summer and Fall months, five times higher than the average value of 3 μg m^{-2} hr^{-1} measured in the Winter and Spring months.

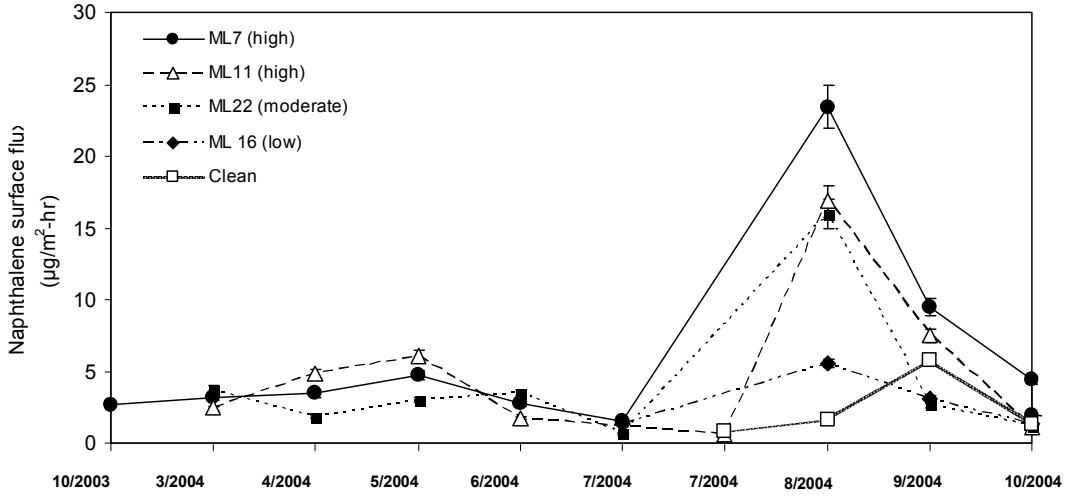

Figure 2.3 Naphthalene surface flux time series at various locations at the research site.

2.2.2 Meteorological influence

Of the many meteorological factors which may influence direct volatilization, we examined precipitation, soil moisture, humidity, pressure and temperature. Poulsen et al. (2000) and Valsaraj et al. (1999) determined that organic contaminants adsorb to sediments, and as the soil moisture content, air relative humidity, or precipitation increase, the water molecules displace the hydrophobic compounds from the sediments, causing the compounds to enter the soil air voids and be transported to the atmosphere. Fluctuations in barometric pressure due to changes in weather patterns can also influence the amount of contaminants that volatilize from the subsurface. It is believed that large changes in atmospheric pressure increase the subsurface movement of gas vapors, and this either causes vapors to be transported into the atmosphere more quickly or for air to infiltrate down into the subsurface (Massmann and Farrier, 1992; Auer et al., 1996). Temperature can also influence gas transport through the subsurface by altering the

volatility of the contaminant. High temperatures increase volatility and cause the contaminants to enter the gas phase more readily.

Our results indicate that precipitation has the greatest influence on the short-term flux of contaminants through the subsurface. Precipitation events either a few days before or during sampling create noticeable decreases in fluxes. Even low intensity rainstorms can greatly influence the flux, and we have observed that more than 0.2 inches of rain significantly affect the flux, such as in July and October 2004 (except ML7 in October 2004). The infiltrating rainwater, duration of rainfall, pressure fluctuations, and moist soil all work together to retain the volatilizing contaminants in the soil matrix.

Conversely, rainfall during the last few hours of sampling causes an increase in fluxes. In August 2004, 0.5 inches of rain fell during the last five hours of a three-day sample at locations ML16 and ML22, and we measured a dramatic increase in the flux. We attribute this increase to the rain event because rain is the biggest indicator of pressure drops, increases in humidity and soil moisture, and decreases in temperature, which we have correlated with higher fluxes. Sampling at the other locations was completed before the rain began, so those flux measurements were not affected. The infiltrating rain within the vicinity of the flux chamber probably displaced contaminants from the void space. They were then horizontally transported toward the dry area of soil covered by the chamber and vertically transported up through the soil and into the chamber, i.e. a "chimney" effect.

2.2.3 Groundwater table influence

We have found the groundwater table level to be the most important factor in controlling the flux. Figure 2.4 shows seasonal trends of naphthalene flux as a function of the water table elevation. In the Winter, water table elevations are at their highest and range between 1428 ft and 1431 ft. The water table decreases throughout the Spring and Summer as the trees transpire, and dissolved contaminant concentrations in the groundwater increase. As the water table continues to retreat, reaching its lowest levels in the Fall, residual contaminants likely remain within the unsaturated zone from when the water table was higher. During these times, the water table elevation remains consistently around 1425 ft. This vertical transport of contaminants causes contaminants to become trapped in the soil matrix in an area above the water table where volatilization

through the unsaturated zone can occur. When the contamination is exposed to air-filled void spaces under dry weather conditions, ideal conditions for large contaminant fluxes are created.

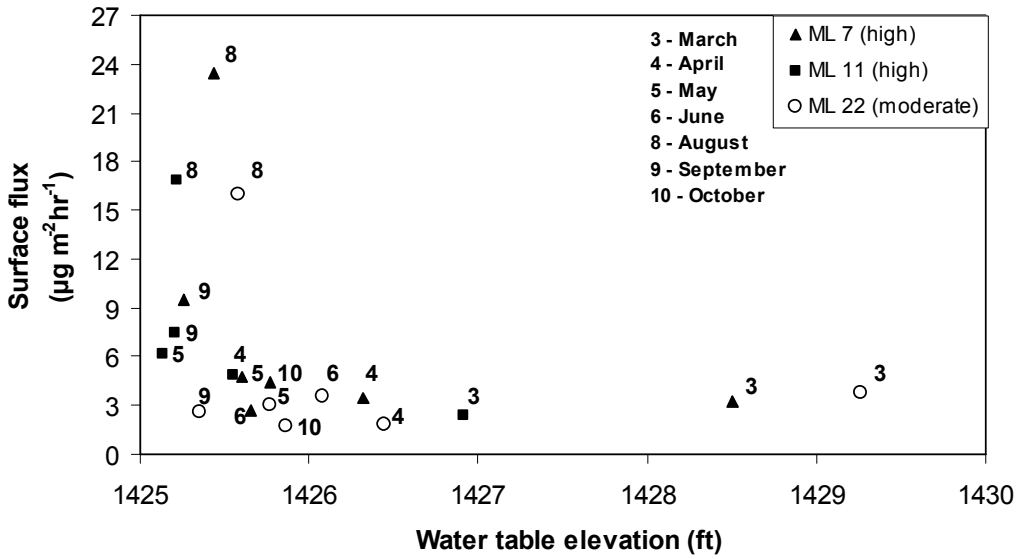

Figure 2.4 Surface flux as a function of water table elevation.

2.3 Impact of phytoremediation on direct volatilization

Our results indicate that the presence of the trees plays a major role in the flux of contaminants by drawing down the water table during periods of high transpiration rates, therefore causing groundwater concentrations to increase. Additionally, the up-and-down movement of the groundwater table generated by the trees' seasonal and diurnal transpiration rate variations exposes residual contaminants, thereby enhancing the flux. In general, the groundwater table's impact on the flux is enhanced by the trees.

Tree transpiration rates, which are related to the trees' utilization of groundwater sources, are influenced by meteorological factors such as solar radiation, temperature, wind velocity, and pressure gradients, as well as soil moisture content and plant characteristics (Viessman and Lewis, 1996; Serrano, 1997). In addition, transpiration rates are a function of precipitation, season, root depth, soil type, vegetation density, and type of plant (Serrano, 1997). It is evident from the seasonality of our data that the transpiration rates of the trees influence the groundwater table level, which in turn

influences the upper groundwater concentrations and the flux of contaminants through the subsurface.

Without trees at the site, the influence of groundwater fluctuations on contaminant fluxes would not be so apparent; transpiration appears to have a significant effect on direct volatilization. Two monitoring wells recorded groundwater elevation levels before the phytoremediation system was installed. In one well, the groundwater elevation remained constant around 1427.5 feet before any trees were planted, but once the trees began to grow, the effects of the trees on the groundwater elevation was evident as elevations fluctuated between 1425.76 and 1429.75 feet. In the other well, the groundwater elevation remained constant at 1424.7 feet before the trees were planted, and afterwards, it fluctuated between 1423.7 and 1425.6 feet. Both wells were located a distance of 150 to 200 feet away from the phytoremediation system, and even at this distance, the effect of the trees is apparent. Before the phytoremediation system was installed, the water table at the most contaminated areas did not drop below 1426 feet based on previous measurements, and from Figure 2.4, we can deduce that the flux would not exceed 5 $\mu g\ m^{-2}\ hr^{-1}$.

Naphthalene concentrations in the groundwater increase as the water level decreases at the study site. When the saturated thickness is high, such as in March or April, the level of naphthalene in the upper layers of the groundwater is relatively low. When the saturated thickness is depleted, such as in August and September, the concentration of naphthalene in the upper portion of the saturated thickness is high. Figure 2.5 shows groundwater concentrations and naphthalene surface fluxes both as a function of the groundwater table level. The concentration of naphthalene in groundwater is represented as the average concentration measured from the top two ports of the multi-level sampling devices. The figure shows that naphthalene surface fluxes are correlated with groundwater concentrations and elevations. The reduced number of data points compared to Figure 2.4 results from removing rain events that affected the surface flux and groundwater concentration values.

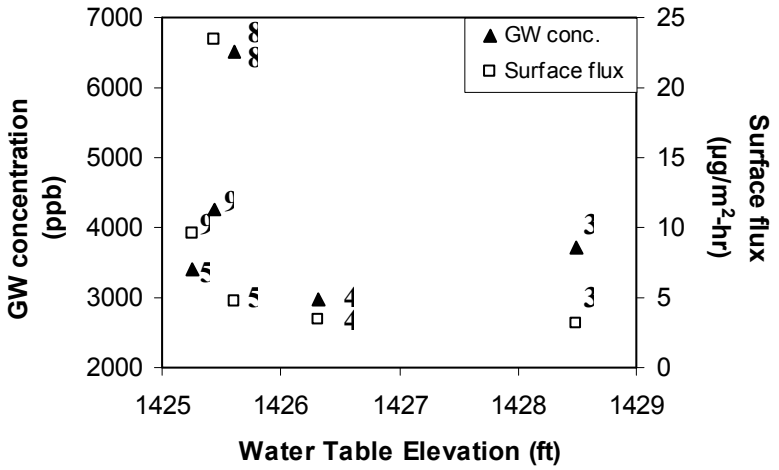

Figure 2.5 Top averaged groundwater concentrations and surface fluxes at ML7, the most contaminated area of the site, as a function of the water table elevation. The data labels represent the months the sample was taken: 3 = March, 4 = April, 5 = May, 8 = August, 9 = September.

A significant decrease in transpiration rates occurred between July and September because tree roots were probably unable to penetrate the deeper and thinned saturated zone. This increase in the unsaturated zone thickness and subsequent increase in groundwater naphthalene concentrations as the groundwater level lowered likely allowed residual contaminants to be exposed to air-filled void spaces and diffuse upward through the soil column. The up-and-down movement of the groundwater level has a significant impact on fluxes since residual contaminants become trapped in the unsaturated zone, and under the right conditions, volatilize upward.

Contaminant vapor transport through the soil indirectly enhances the natural attenuation processes in the subsurface. Schnoor (2002) states that PAH degradation depends on the presence of lower molecular weight compounds to trigger enzyme stimulation. Higher naphthalene concentrations in the unsaturated zone stimulate the microbes and cause biodegradation rates to go up (ATSDR, 2003). Lahvis et al. (1999) determined that biodegradation rates increase with distance above the water table and are highest in the unsaturated zone. With enhanced biodegradation rates, the rate at which contaminants are degraded is much higher, and this causes contaminants to be removed from the ground more efficiently. Additionally, higher biodegradation rates increase the concentration gradient, which in turn causes more volatilization due to diffusion.

Therefore, increases in contaminant fluxes through the Summer and Fall may enhance the bacterial degradation of naphthalene during the Winter months due to acclimatized microbes. This is one way in which volatilizing contaminants indirectly improves the effectiveness of biodegradation in the subsurface at phytoremediation sites.

2.4 Summary

We have illustrated an effective and efficient way to measure the flux by means of a flux chamber that can be used at other contaminated sites to determine human health risks associated with volatilizing contaminants. We have also found that several factors affect volatilization, the most important of which is the groundwater level, and that the presence of a phytoremediation system enhances this factor. Through field data presented in Appendix B, we have shown the significance of precipitation, soil moisture, pressure, temperature and humidity on contaminant flux.

Because we have observed a correlation between large fluxes and low groundwater levels caused by transpiring trees, human health risk at the site must be assessed. Long-term exposure to naphthalene in an enclosed space, such as a basement of a house, may significantly alter health even though the volatilization process enhances site remediation. Appendix C details the application of a vapor intrusion model to the site under conservative conditions. From the model, the concentration of naphthalene that infiltrates into a house remains below regulatory standards and levels at which health effects such as nausea and headaches have been reported. Therefore, the increase in naphthalene volatilization due to the trees at the site does not pose a human health risk and instead enhances site remediation by triggering enzyme stimulation throughout the soil column and acting as a separate transport mechanism that removes naphthalene from the contaminated groundwater and soil.

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References

Agency for Toxic Substances and Disease Registry (ATSDR) (2003). Toxicological profile for naphthalene, 1-methylnaphthalene, 2-methylnaphthalene. Atlanta, GA, U.S. Department of Health and Human Services, Public Health Service.

Auer, L. H., N. D. Rosenberg, et al. (1996). "The effects of barometric pumping on contaminant transport." Journal of Contaminant Hydrology **24**: 145-166.

Burken, J. G. and J. L. Schnoor (1998). "Predictive Relationships for Uptake of Organic Contaminants by Hybrid Poplar Trees." Environmental Science and Technology **32**(21): 3379-3385.

Choi, J., F. D. Tillman, et al. (2002). "Relative Importance of Gas-Phase Diffusive and Advective Trichloroethene (TCE) Fluxes in the Unsaturated Zone under Natural Conditions." Environmental Science & Technology **36**(14): 3157-3164.

Davis, L. C., M. K. Banks, et al. (1998). Plant Based Bioremediation. Bioremediation: Principles and Practice, Vol. 2, Biodegradation Technology Developments. S. K. Sikdar and R. L. Irvine. Lancaster, PA, Technomic.

Gao, F., S. R. Yates, et al. (1997). "Design, Fabrication, and Application of a Dynamic Chamber for Measuring Gas Emissions from Soil." Environmental Science & Technology **31**(1): 148-153.

Jellali, S., H. Benremita, et al. (2003). "A large-scale experiment on mass transfer of trichloroethylene from the unsaturated zone of a sandy aquifer to its interfaces." Journal of Contaminant Hydrology **60**: 31-53.

Lahvis, M. A., A. L. Baehr, et al. (1999). "Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions." Water Resources Research **35**(3): 753-765.

Lee, J.-Y., J.-Y. Cheon, et al. (2001). "Factors affecting the distribution of hydrocarbon contaminants and hydrogeochemical parameters in a shallow sand aquifer." Journal of Contaminant Hydrology **50**(1-2): 139-158.

Ma, X. and J. G. Burken (2003). "TCE Diffusion to the Atmosphere in Phytoremediation Applications." Environmental Science and Technology **37**(11): 2534-2539.

Massmann, J. and D. F. Farrier (1992). "Effects of atmospheric pressures on gas transport in the vadose zone." Water Resources Research **28**: 777-791.

Narayanan, M., L. E. Erickson, et al. (1999). "Simple Plant-Based Design Strategies for Volatile Organic Pollutants." Environmental Progress **18**(4): 231-242.

Newman, L. A., S. E. Strand, et al. (1997). "Uptake and biotransformation of trichloroethylene in hybrid poplars." Environmental Science and Technology **31**(4): 162-1067.

Poulsen, T. G., T. Yamaguchi, et al. (2000). "Predicting volatile organic vapor sorption from soil specific surface area and texture." Journal of Environmental Quality **29**: 1642-1649.

Reichman, R. and D. E. Rolston (2002). "Design and Performance of a Gas Flux Chamber." Journal of Environmental Quality **31**: 1774-1781.

Schnoor, J. L. (2002). Phytoremediation of Soil and Groundwater. Iowa City, IA, Ground-Water Remediation Technologies Analysis Center, Technology Evaluation Report TE-02-1**:** 45.

Serrano, S. E. (1997). Hydrology for Engineers, Geologists and Environmental Professionals: An Integrated Treatment of Surface, Subsurface, and Contaminant Hydrology. Lexington, Kentucky, HydroScience Inc.

Smith, J. A., A. K. Tisdale, et al. (1996). "Quantification of Natural Vapor Fluxes of Trichloroethene in the Unsaturated Zone at Picatinny Arsenal, New Jersey." Environmental Science & Technology **30**(7): 2243-2250.

Tillman Jr., F. D., J.-W. Choi, et al. (2003). "A comparison of direct measurement and model simulation of total flux of volatile organic compounds from the subsurface to the atmosphere under natural field conditions." Water Resources Research **39**(10): 1284-1295.

Tillman Jr., F. D. and J. A. Smith (2004). "Design and laboratory testing of a chamber device to measure total flux of volatile organic compounds from the unsaturated zone under natural conditions." Journal of Contaminant Hydrology **75**: 71-90.

Valsaraj, K. T., R. Ravikrishna, et al. (1999). "Air emissions from exposed contaminated sediments and dredged material." Environmental Science & Technology **33**(1): 142-149.

Viessman, W. and G. L. Lewis (1996). Introduction to Hydrology, 4th edition. New York, HarperCollins.

CHAPTER 3

Quantifying first-order aerobic biodegradation rates of naphthalene in unsaturated soil through a column study

Elizabeth C. Booth, Rikke G. Andersen, Linsey C. Marr, John T. Novak, Mark A. Widdowson

418 Durham Hall, Department of Civil and Environmental Engineering
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061

Abstract

The vapor-phase transport of naphthalene in the unsaturated zone was studied in a soil column experiment using site-specific uncontaminated and contaminated soil. This research was conducted to compare the transport of naphthalene through soil that had been exposed to naphthalene in the field and soil that has not been exposed to naphthalene, and determine first-order biodegradation rate coefficients for naphthalene. We hypothesize that the combined mechanisms of contaminant transfer to the vadose zone, followed by rapid biodegradation, may increase the rate of remediation in contrast to biodegradation that occurs only in the saturated zone under high groundwater conditions.

A total of seven soil columns, including blanks, were constructed and analyzed over 231 days. Vertical concentration profiles of naphthalene, carbon dioxide, and oxygen were obtained every 14 days to assess the transport of naphthalene in the unsaturated zone. Sorbed naphthalene concentrations, total organic carbon, and soil moisture contents were also used to compare bacterial activity in the columns. Biodegradation rates of naphthalene were determined by fitting a first-order model to our measured concentration profiles. Our research suggests that there are differences between the bacterial activity of the contaminated and uncontaminated soils, but that over time, these differences are reduced. Diffusion of contaminants into the unsaturated zone and subsequent biodegradation have significant remediation capabilities for contaminated groundwater and soil sites.

Key words

Naphthalene, column, biodegradation, phytoremediation, volatilization

3.0 Introduction

The remediation of subsurface contamination remains a challenging problem. Biodegradation and volatilization are the dominant mechanisms of contaminant removal at natural attenuation sites (Jin et al., 1994; Lahvis et al., 1999; Pasteris et al., 2002). For volatile groundwater and soil contaminants, volatilization is dominant in the early stages of plume evolution, while biodegradation dominates in the later stages (Chaplin et al., 2002). Phytoremediation, a technique that uses plants to immobilize and remove contaminants, is thought to enhance both biodegradation and volatilization.

Determining the biodegradation kinetics of compounds through soil is important for predicting the time scale for complete remediation and for developing strategies to accelerate remediation. The combined mechanisms of contaminant transfer to the vadose zone followed by rapid biodegradation may speed up remediation in contrast to biodegradation that occurs only in the saturated zone under high groundwater conditions. Most studies involving biodegradation kinetics are conducted with microcosm experiments. However, these types of experiments have limited application to biodegradation in the unsaturated zone because (1) microcosms are saturated with water, so the mass transfer of naphthalene and oxygen are different due to slower diffusion in water, (2) microcosms are considered batch reactors and there is a microbial acclimatization period before degradation occurs, and (3) microcosms do not have a continuous supply of contaminant but instead have a high concentration that is depleted over time.

In order to determine biodegradation kinetics under controlled settings, columns are often constructed in the laboratory to mimic natural conditions and provide researchers with valuable information regarding contaminant transport. Columns are an effective means to investigate the influence of subsurface conditions on contaminants, and unlike microcosms, mimic mass transfer rates found in the field, maintain a constant supply of contaminant source, and are analyzed under steady-state conditions (Jin et al., 1994; Baehr and Baker, 1995; Allen-King et al., 1996a,b; Moyer et al., 1996; Höhener et al., 2003).

Columns have been constructed to study the transport of vapor-phase contaminants and to determine aerobic biodegradation kinetics of contaminants in

unsaturated soils (Jin et al, 1994; Moyer et al, 1996; Pasteris et al, 2002; Höhener et al., 2003). Jin et al. (1994) found that 30 cm of soil cover was enough to stop volatilization losses of toluene due to biodegradation in the unsaturated zone, and that soil pre-exposed to the substrate has higher removal rates. Moyer et al. (1996) found that hydrocarbon concentrations were reduced by 45-92% over the first 0.6 m of an intact soil core, and total hydrocarbon concentrations were reduced by 75% due to aerobic biodegradation in the unsaturated zone. In a large-scale lysimeter experiment, Pasteris et al. (2002) found that aerobic biodegradation of fuel compounds removed three times more fuel mass than volatilization. Their first-order biodegradation rates ranged from $<0.05\ d^{-1}$ to $8.7\ d^{-1}$ for various fuel compounds. In a sequential study, Höhener et al. (2003) determined first-order aerobic biodegradation and Monod kinetic rates for 12 compounds and found that easily biodegradable compounds had strongly curved profiles with rate coefficients greater than $1\ d^{-1}$ and slowly biodegradable compounds had more linear profiles with rate coefficients less than $0.01\ d^{-1}$. While most of these studies include hydrocarbon contaminants and MTBE, studies investigating the behavior of naphthalene in unsaturated soil columns are few.

Naphthalene is known to be biodegradable under both anaerobic and aerobic conditions. Biodegradation is mostly accomplished under aerobic conditions and declines when soil conditions become anaerobic (ATSDR, 2003). In soil, the biodegradation of naphthalene occurs quickly if the soil is contaminated with other polycyclic aromatic hydrocarbons. In addition, the rate of biodegradation of naphthalene increases as naphthalene concentrations increase (U.S. EPA, 2003b). In water, naphthalene biodegrades significantly faster when adsorbed to sediments than when in the top layers of water. However, when in the top layers of turbulent water, volatilization is the main mechanism by which naphthalene is removed, and in slow flowing water, biodegradation dominates. Naphthalene has a short-life in most waters and soils because of its tendency to volatilize and biodegrade (ATSDR, 2003). It has a vapor pressure of 0.087 mm Hg at 25°C, solubility of 31.7 mg L^{-1} at 20°C, and Henry's constant of 4.6×10^{-4} (ATSDR, 2003). Researchers have found that naphthalene volatilization is significant at the soil surface but decreases as depth increases, and it has been determined that naphthalene travels rapidly through sandy soil (U.S. EPA, 2003a).

Direct volatilization at phytoremediation sites may be responsible for a significant portion of the overall remediation of soil and groundwater, and may indirectly increase the effectiveness of biodegradation. As volatilization rates increase, naphthalene concentrations throughout the soil column increase and may stimulate bacteria that also degrade other polycyclic aromatic hydrocarbons (PAHs). Schnoor (2002) states that PAH degradation depends on the presence of lower molecular weight aromatic compounds to trigger enzyme stimulation. Therefore, higher vapor-phase contaminant concentrations throughout the soil column can cause biodegradation rates to increase (ATSDR, 2003). Higher biodegradation rates also create greater concentration gradients, which increases the rate of transport by diffusion.

A phytoremediation system using hybrid poplar trees was implemented at a creosote-contaminated site in Oneida, Tennessee. The system was put into place in 1997 to act as a hydraulic barrier and to enhance the transfer of the contaminated groundwater into the more microbial active vadose zone and rhizosphere where contaminant biodegradation is increased. This research focuses on naphthalene since it comprises the majority of the creosote and is the most volatile.

The purpose of our research is to quantify the rate of biodegradation of naphthalene in the unsaturated zone at a creosote-contaminated site. To supplement field experiments and to determine aerobic biodegradation rate coefficients, we have developed a series of columns containing contaminated and uncontaminated soil from a phytoremediation site in Oneida, TN. Sterilized and bacterially active soil columns were constructed so the behavior of naphthalene under different contaminant exposure levels could be analyzed. We hypothesize that contaminated soil from the site has enhanced bacterial populations that degrade naphthalene more efficiently than uncontaminated soil from the site, and that there will be significant differences between the soil columns: sterilized versus live and uncontaminated versus contaminated; such that biodegradation rate coefficients can be calculated. Ultimately, these rates can be compared against measurements of volatilization to determine the most important mechanisms of contaminant remediation at the site.

3.1 Experimental Methods

3.1.1 Columns

In order to replicate the transport of naphthalene (NAP) vapors through the unsaturated zone, seven columns were constructed, as shown in Table 3.1.

Table 3.1 Descriptions of the columns

Column no.	Exposure type	Bacterial activity	Source
1	Contaminated soil	Sterile	NAP
2	Contaminated soil	Live	NAP
3	Uncontaminated soil	Sterile	NAP
4	Uncontaminated soil	Live	NAP
5	Contaminated soil	Live	No source
6	No soil	n.a.	NAP
7	No soil	n.a.	No Source

The column with the contaminated soil and no naphthalene source (5) was constructed to determine background concentrations of naphthalene present in the contaminated soil. The blank column with no soil and a naphthalene source (6) was constructed to monitor naphthalene losses through connections, fittings, and sorption to column material. The blank column with no soil and no naphthalene source (7) was constructed to determine if there were naphthalene sources from the column material itself.

At the end of April 2004, soil was collected from both contaminated and clean locations at the phytoremediation site, as shown in Figure 3.1. Figure 3.1 also shows shallow naphthalene groundwater concentrations at the time the soil was obtained. The soil was obtained directly above the groundwater table, corresponding to a depth of 0.9 to 1.5-m below ground surface at the contaminated location and a depth of 1.5 to 2.1-m at the clean location. Soil parameters such as moisture content, density, and porosity were determined from intact field samples. Because equipment was not available to obtain undisturbed soil samples at those depths, topsoil was used for the density and porosity measurements. The moisture content was 0.11 g g^{-1}, the bulk density was 1.6 g cm^{-3}, and the porosity was 37%.

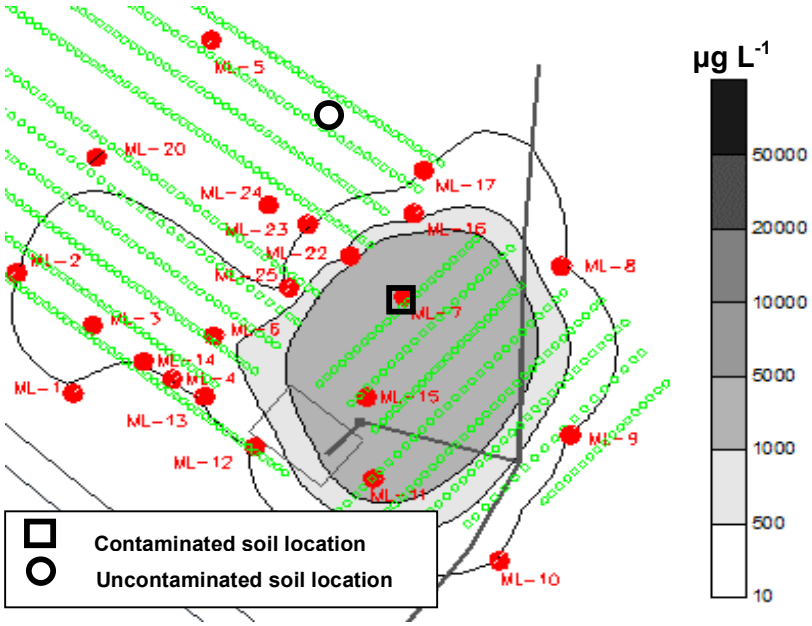

Figure 3.1 Shallow (2.5-6 feet above bedrock) naphthalene groundwater concentrations in March 2004.

After the soil parameters were determined, a portion of each soil type was placed in an autoclave for sterilization. This soil was autoclaved more than 15 times over a period of 40 days to eliminate organisms that might regerminate between cycles. The water content of the sterile soil was adjusted back to 0.11 g g^{-1} to account for any water lost during autoclaving, and the live soil was air dried and brought back up to a water content of 0.11 g g^{-1} with distilled water.

The column shown in Figure 3.2 is 71-cm in height and 5-cm in diameter and is constructed of PVC (polyvinyl chloride) pipe. A male coupling PVC socket fitting and threaded cap comprise the ends of each column. A piece of metal mesh on top of a metal strainer plate was placed in the bottom of each column to prevent soil from falling into the source cap.

Sampling ports 3-mm in diameter were drilled along the length of the column. A 0.05-m long piece of 3-mm outer-diameter stainless steel high pressure tubing was inserted 2.54-cm into each sampling port for the purpose of obtaining a vertical concentration profile of the soil air with a syringe. The steel tubing was then outfitted with brass compression fittings and GC septa. The column is equipped with seven sampling ports spaced 5-cm apart at the bottom and 10-cm apart at the top as displayed in Figure 3.2. The spacing of the sampling ports is smaller at the bottom of the column to

account for the expected fast biodegradation of naphthalene. For the two blank columns (6 and 7), only two sampling ports were installed, one at the bottom and middle of the column.

Five grams of naphthalene crystals (Fisher Scientific) were placed in aluminum bowls in the bottom of each column except for the blanks with no source (5 and 7). Teflon tape and PTFE paste sealer were then applied to the bottom and top socket fittings, and both caps were tightened and sealed with epoxy to prevent air from entering the columns. In addition, the interface between the steel tubing of the sampling ports and the column was glued with epoxy. This epoxy, a 1:1 mixture of a curing agent and resin that contains no naphthalene, was allowed to cure for two hours before application.

Lab air entered the column system, as illustrated in Figure 3.2, and flowed through a sorbent tube intended to capture background contaminants. The clean air then traveled through a water bath, which consisted of a 125 mL Erlenmeyer flask filled with 100 mL of distilled water, to prevent the soil from drying out and allow oxygenated air to enter the column. Air entered (and exited) the column headspace through a 3-mm diameter steel tube outfitted with a compression fitting and Teflon tubing, flowed over the surface of the soil in the top of the column, and mixed with the contaminant. The now contaminated air was pulled out of the column and into two XAD-2 sorbent tubes. The second sorbent tube served to capture any breakthrough from the first. Clean air leaving the sorbent tubes flowed through a valve and then into a vacuum pump. The pump pulled laboratory air through each column at a flow rate of 0.5 L min^{-1} that was checked and adjusted daily. This flow rate takes into account manufacturers' recommendations of the sorbent tube efficiency as well as the NIOSH 5515 extraction procedure recommendations. The columns were maintained in the dark at constant temperature (23.1°C) and humidity (38.4%) and monitored over a period of 231 days.

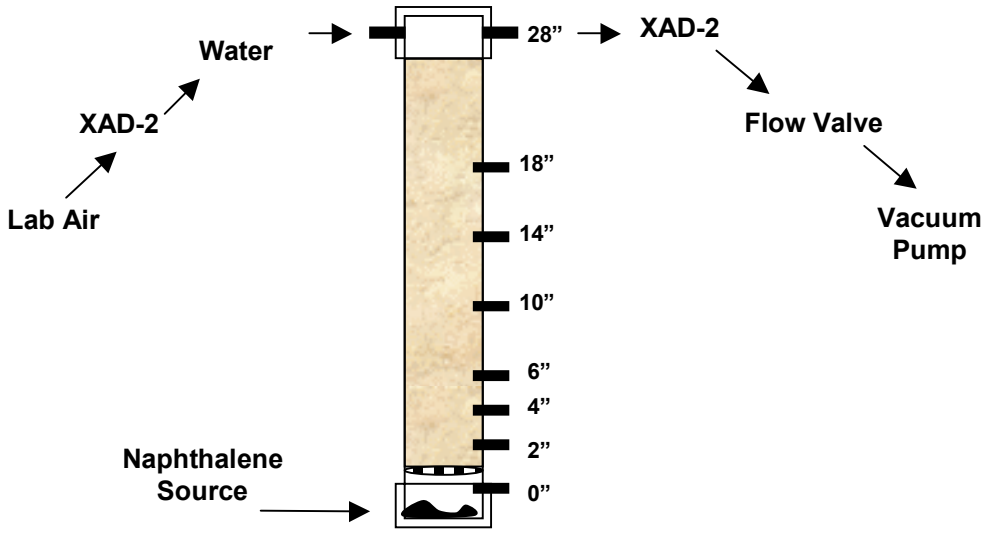

Figure 3.2 Column diagram showing sampling port locations and experimental setup.

3.1.2 Analytical methods

Vertical concentration profiles were obtained biweekly by using a gastight syringe to pull 100-200 µl samples of air from each column sampling port. Blank samples of the laboratory air were run to determine background concentrations as well as blank samples of clean air to determine contaminant carryover in the syringe. In order to acquire a representative sample, 20 µl of stagnant air were pulled out of the port and expelled before the actual sample was taken. The syringe was then reinserted into the port and slowly pumped to gently mix the soil gas and obtain a uniform sample. Samples were taken from each port until the standard deviation of at least two measurements fell below 20%. Samples were manually injected in a Hewlett-Packard 5890 gas chromatograph with flame ionization detection (GC-FID) and a DB-5 capillary column. The injector, detector, and oven temperatures were set to 250°C, 310°C, and 80°C, respectively, with a temperature ramp of 10°C min^{-1}. Liquid naphthalene standards were used for the calibration curve.

Sorbent tubes at the top of the column were intended for a mass balance, but saturation of the XAD-2 resin by contaminants in the laboratory air prevented a quantitative mass balance. Used sorbent tubes were capped, wrapped with aluminum foil, and stored at 4°C for no longer than 24 hours before extraction. Samples were

extracted following the NIOSH 5515 procedure with toluene and analyzed on an automated Hewlett-Packard 5890 GC-FID and a DB-5 capillary column.

Carbon dioxide and oxygen samples were obtained biweekly during the weeks when naphthalene was not sampled using the same sampling method as described above for the naphthalene profiles. Oxygen samples, 100-200 μL in volume, were analyzed on a GOW-MAC GC Series 580 instrument (Bridgewater, N.J.) with a Thermal Conductivity Detector (TCD) and Propaq Q packed column. Carbon dioxide samples, 100-200 μL in volume, were analyzed on a Shimadzu GC-14A (Kyoto, Japan) with a TCD detector and Propaq Q packed column.

3.2 Results and Discussion

3.2.1 Sterile and live columns

Vertical concentration profiles for the contaminated soil, one of which is sterile and one which is live, are shown in Figures 3.3 and 3.4. Because profiles are noisier on some days, those profiles which most clearly illustrate the differences between the sterile and live columns are shown, even though they were measured on different days. The shapes of the profiles did not differ substantially over time. The linear nature of the sterile profiles suggests that the sterile columns have reached steady-state, which occurred after day 49. Large differences between the sterile and live profiles signify that a substantial amount of biodegradation occurred in the live column within the first 5 centimeters of unsaturated soil, but that very little biodegradation occurs in the sterile column. The more linear profiles in the two sterile columns also suggest that diffusion is the dominant processes affecting naphthalene transport. By connecting the end points of the line to the sterile data, one can see that there is mass loss throughout the column. The mass loss is in agreement with the loss of naphthalene determined in Column 6, which is the column with a naphthalene source and no soil. Naphthalene may have been lost through the fittings and column material as well as through surviving bacteria in the soil.

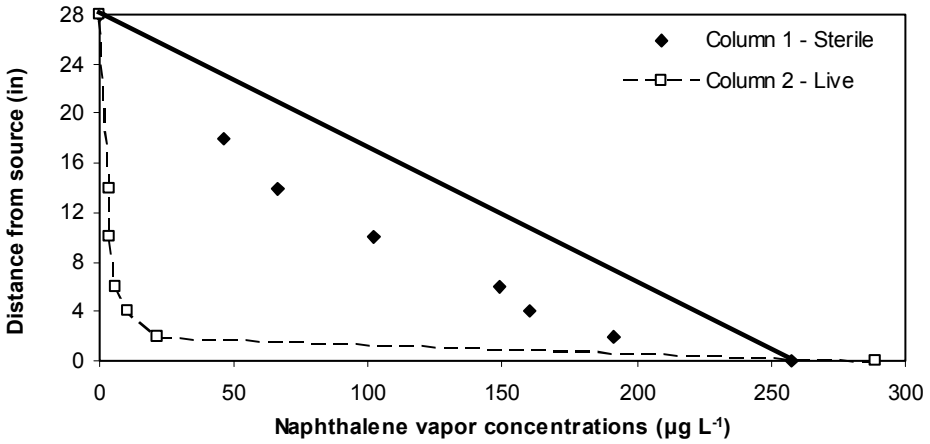

Figure 3.3 Naphthalene vapor concentration profiles in the contaminated soil columns (sterile and live) after 89 and 151 days, respectively.

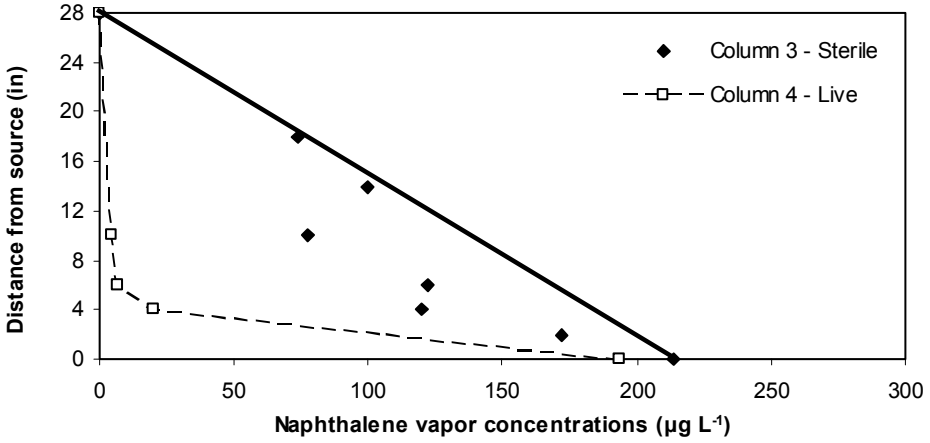

Figure 3.4 Naphthalene vapor concentration profiles in the uncontaminated soil columns (sterile and live) after 182 and 89 days, respectively.

3.2.2 Contaminated and uncontaminated soil

Because the presence of naphthalene in the contaminated soil from the site promotes the growth of naphthalene degraders, we hypothesize that the contaminated soil will have higher biodegradation rates than the uncontaminated soil. This trend can be seen in Figure 3.5, where it is evident that more naphthalene is degraded in Column 2 than in Column 4. Because the source vapor concentrations fluctuated with each sampling period, which we attribute to small volume sampling errors and syringe

inaccuracies, concentrations throughout the column were normalized to the source concentration measured at the bottommost port. This normalization also allows us to directly compare the concentrations of each column on the same scale.

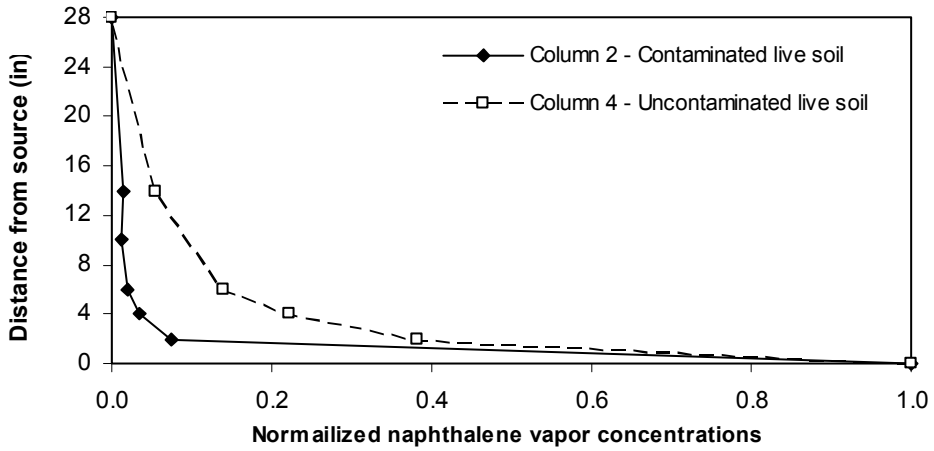

Figure 3.5 Comparison of bacterial activity in contaminated and uncontaminated soil columns on day 151. Normalized naphthalene vapor concentration profiles are shown.

Oxygen and carbon dioxide profiles further illustrate differences in bacterial populations. High carbon dioxide and low oxygen levels generally indicate increased bacterial activity, and this trend is evident in our columns. The two sterile columns maintained oxygen levels between 20 and 20.9% throughout the length of the column. The contaminated live column had oxygen levels ranging between 15 and 20.9%, with oxygen decreasing with depth. Oxygen levels near the source of the live columns were lowest in the contaminated soil column by about 3.5%, as shown in Figure 3.6. The uncontaminated live column had higher oxygen levels ranging between 18.5 and 20.9%, with oxygen also decreasing with depth.

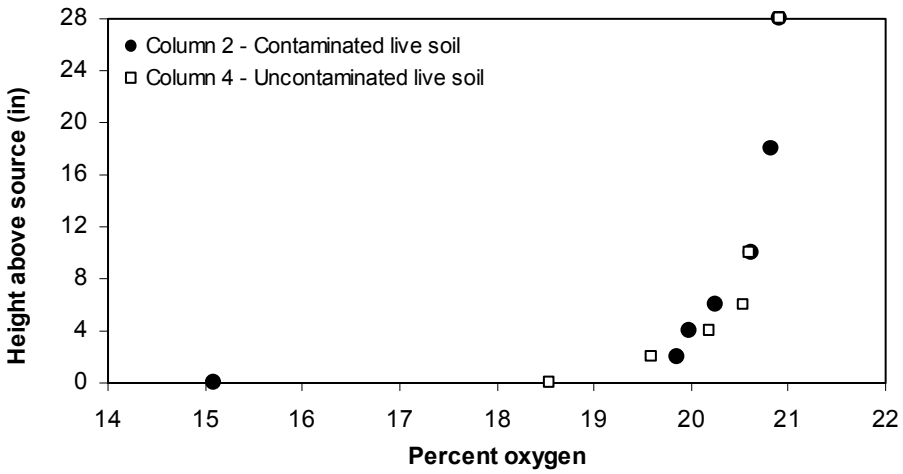

Figure 3.6 Live soil column oxygen profiles after 229 days.

Carbon dioxide is one of the best indicators of bacterial activity in soil, and both sterile columns had very low levels of carbon dioxide ranging between 0.135 and 0.046%. The carbon dioxide in the uncontaminated sterile soil column was more variable and overall lower than in the contaminated sterile soil column. The live columns had significant differences in carbon dioxide levels near the source. For instance, the live contaminated soil column had carbon dioxide levels ranging from 3.2 to 0.046%, while the live uncontaminated soil column had carbon dioxide levels ranging from 0.84 to 0.046% with both increasing with depth, as shown in Figure 3.7. As seen in Figure 3.5, a significant amount of naphthalene is degraded within the first few inches of soil, and this explains the high carbon dioxide levels near the source. We suspect the difference between the two live soil columns is that bacterial populations previously acclimatized to naphthalene are present in the contaminated soil.

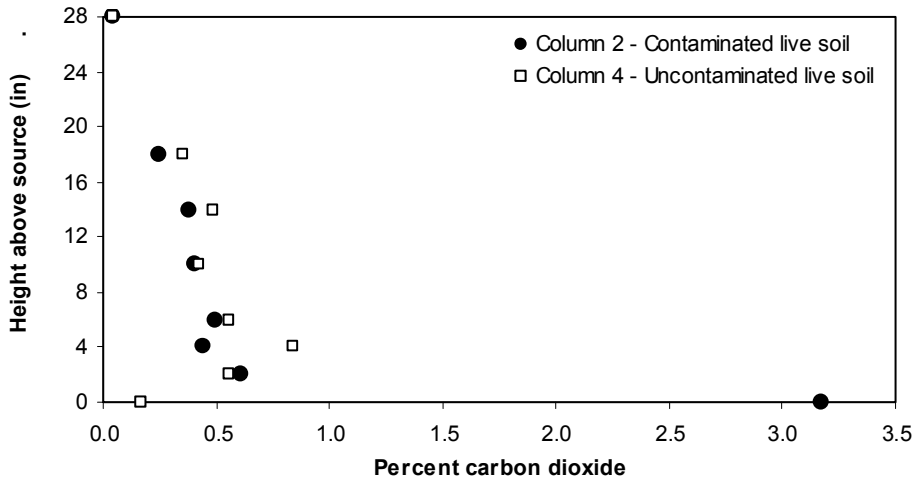

Figure 3.7 Live soil column carbon dioxide profiles after 229 days

In addition to oxygen and carbon dioxide column profiles, naphthalene soil concentrations were measured at the end of the 231-day experiment. Concentrations in the contaminated sterile column increased with depth and ranged between 10-120 μg g^{-1} dry soil. Concentrations in the uncontaminated sterile column varied greatly and ranged between 10-1200 μg g^{-1} dry soil. These large variations can be attributed to altered soil properties evident after sterilization, discussed below. On the other hand, both live columns maintained an averaged soil concentration of 12 μg g^{-1} dry soil throughout their length.

Total organic carbon samples were also analyzed at various depths. Both contaminated soil columns (live and sterile) had approximately 60% more organic carbon than the uncontaminated soil columns (live and sterile). In addition, the live contaminated soil column had 12% more organic carbon than the sterile contaminated column, and the live uncontaminated soil column had 20% more organic carbon than the sterile uncontaminated column. The contaminated soil blank column that contained no naphthalene had 50% more organic carbon than the uncontaminated soil columns (live and sterile) with naphthalene, which further illustrates the differences between the contaminated and uncontaminated soil.

3.2.3 Biodegradation rates

Höhener et al. (2002) outlined an analytical solution that describes first-order biodegradation at steady-state under the following assumptions: (1) diffusion is the dominant transport process, (2) sorption is linear and reversible, (3) volatilization obey Henry's law, (4) the biodegradation reactions obey first-order kinetics, (5) the soil diffusion coefficients in soil air are reduced by a tortuosity factor, and (6) diffusion in soil water is very slow as compared to diffusion in soil air and thus negligible.

$$C_a = C_{a,0} \; at \; z = 0 \tag{1}$$

$$C_a = 0 \; at \; z = L \tag{2}$$

$$C_a = C_{a,0} \frac{\sinh\left[\sqrt{\frac{\mu_c^1}{D}}(L-z)\right]}{\sinh\left[\sqrt{\frac{\mu_c^1}{D}}L\right]} \tag{3}$$

Where C_a [g m^{-3}] is the soil air concentration at distance z [m] from the source, $C_{a,o}$ [g m^{-3}] is the concentration in the source headspace, L [m] is the length of the soil column, D [m^2 day^{-1}] is the effective diffusion coefficient of a compound in soil air, and μ^1_c [day^{-1}] is a lumped first-order rate coefficient. This lumped first-order rate coefficient (μ^1_c) depends on factors such as the maximum specific substrate utilization rate (υ_{max}), the biomass in the aqueous phase (X), the half-saturation constant in the aqueous phase (K_s), and Henry's law constant (H). The effective diffusion coefficient in soil (D)

$$D = \theta_a \, \tau_a D_a \tag{4}$$

is reduced by a tortuosity factor (τ_a) given by Millington and Quirk (1961) below as

$$\tau_a = \frac{\theta_a^{2.33}}{\eta_{tot}^2} \tag{5}$$

such that θ_a (m^3 air m^{-3} total) is the volumetric soil air content, η_{tot} (m^3 voids m^{-3} total) is the total porosity, and D_a [m^2 day^{-1}] is the molecular diffusion coefficient of a compound in air.

Equation 3 was fitted with our concentration profiles to obtain a first-order biodegradation rate coefficient (μ^1_c) for the column experiment. The effective diffusion coefficient was calculated using known column soil moisture contents and total porosity

with a molecular diffusion coefficient (D_a) of 0.562 m^2 day^{-1} for naphthalene at 23°C as described by Cho et al. (1992). The volumetric soil air content (θ_a) depends on the soil moisture content and the bulk density. We chose to use a bulk density value of 1.6 g cm^{-3} and averaged soil moisture contents in each column measured at the end of the experiment. For both live columns (contaminated and uncontaminated soil), θ_a was 0.2 m^3 air m^{-3} total; for the contaminated sterile column, θ_a was 0.25 m^3 air m^{-3} total; and for the uncontaminated sterile column, θ_a was 0.31 m^3 air m^{-3} total.

Figure 3.8 shows the model fit with our data that yields a biodegradation rate coefficient of 13±1 day^{-1} for the contaminated live column. Figure 3.9 shows the model fit for the uncontaminated live column that yields a biodegradation rate coefficient of 12±1 day^{-1}. Both biodegradation rate coefficients displayed below were determined from vertical concentration profiles at day 207. The contaminated and uncontaminated live columns both had an average soil moisture content of 0.125 g g^{-1} after completion of the experiment, which was a 13.6% increase from the initial moisture content of 0.11 g g^{-1}.

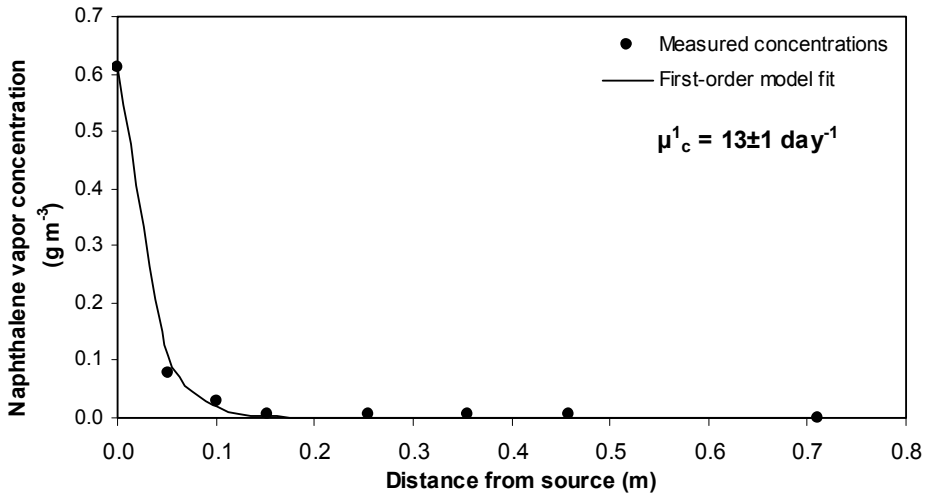

Figure 3.8 Naphthalene profiles for the contaminated live column along the column length after 207 days.

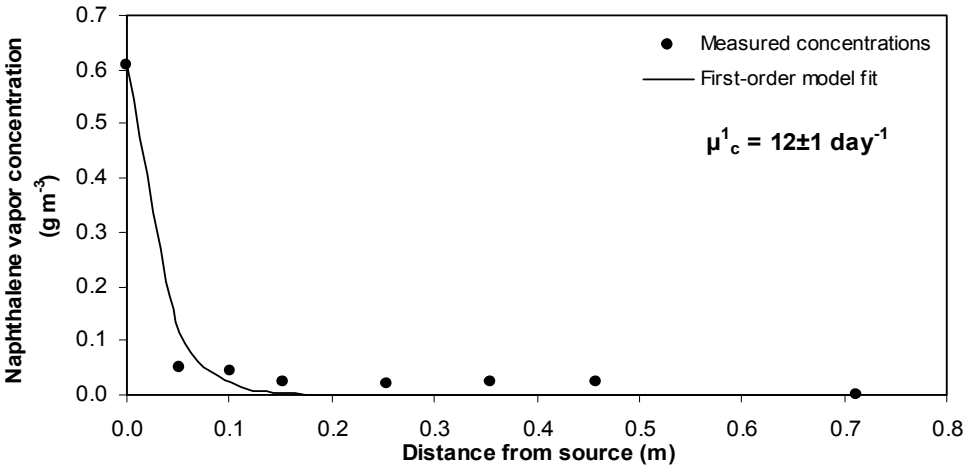

Figure 3.9 Naphthalene profiles for the uncontaminated live column along the column length after 207 days.

Figure 3.10 shows the first-order biodegradation coefficient model fit with our data from the contaminated sterile column at day 222. Figure 3.11 shows the first-order biodegradation coefficient model fit for the uncontaminated sterile column at day 182.

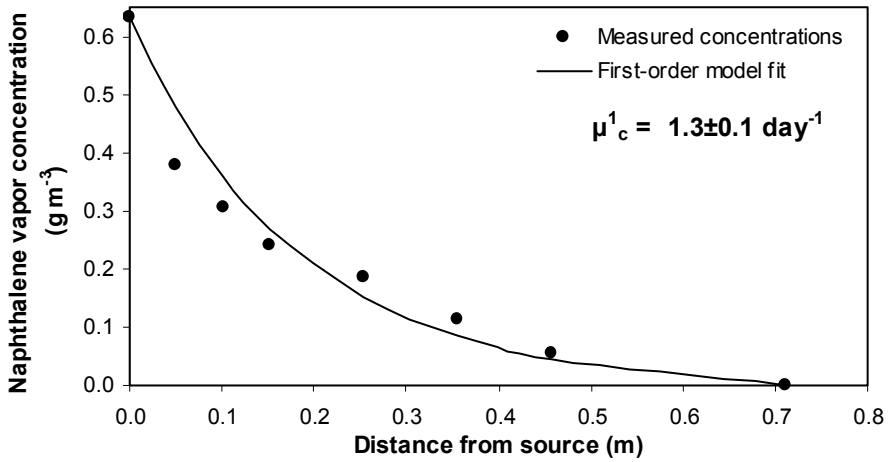

Figure 3.10 Naphthalene profiles for the contaminated sterile column along the column length at day 222.

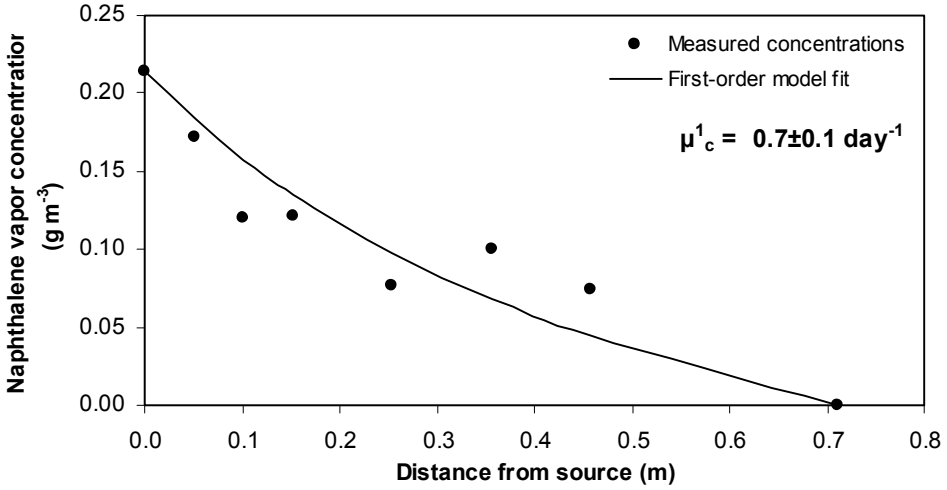

Figure 3.11 Naphthalene profiles for the uncontaminated sterile column along the column length at day 182.

The sterile columns exhibited very low biodegradation rates, on the order of 10 times lower than the live columns, signifying that bacteria were not present in large numbers and reinforcing the importance of contaminant transport by diffusion and/or advection rather than purely removal by biodegradation. Even though the moisture content in the sterile columns was originally adjusted to 0.11 g g^{-1} and water baths humidified the incoming air, the sterile columns lost considerable moisture. The sterile contaminated soil moisture content had decreased by 33% to 0.074 g g^{-1}, and the sterile uncontaminated soil moisture content decreased even more by 67% to 0.036 g g^{-1}. We hypothesize that autoclaving the soil changed soil properties and caused these decreases to occur.

Figure 3.12 shows the first-order biodegradation rate coefficients for the uncontaminated and contaminated live and sterile columns over time. By the end of the experiment, both the contaminated and uncontaminated live soil columns had reached approximately the same biodegradation rate of 13±1 and 12±1 day^{-1}, respectively. From this figure, it is evident that the contaminated soil column attained high degradation rates much faster than the uncontaminated soil column. By using the Millington and Quirk (1961) equation for diffusion through soil with an initial water content of 0.11 g g^{-1} for both live columns, we estimate that naphthalene takes 14.6 days to diffuse the length of the soil column. Based on this, it is evident that the large increases in biodegradation

rates occurred well after naphthalene had diffused through the column. Even if the microbes in both live columns were inhibited at the beginning of the experiment because of high naphthalene concentrations, the microbes in the contaminated soil were more apt to handle the naphthalene concentrations than the microbes in the uncontaminated soil.

Biodegradation rates in the contaminated live soil began to increase after day 60, reached a plateau, and began to decline around day 90 probably due to an overabundance of microbes that were not able to sustain their high biodegradation rates with the constant supply of naphthalene. Biodegradation rates in the uncontaminated live soil began to increase at day 150, a full 90 days after the contaminated live soil biodegradation rates increased. This result shows that microbes are degrading naphthalene more efficiently in the contaminated live soil column; their greater efficiency can be attributed to the greater acclimatization time of the microbes to naphthalene in the field.

Biodegradation rate coefficients for both the sterile columns were variable over time but remained below 1.8 day^{-1}. The biodegradation rates of the uncontaminated sterile soil stayed consistently below 1.2 day^{-1}, while the rates of the contaminated sterile soil were more variable. This variation can be attributed to sampling errors, as stated in section 3.1.2. From the figure, it is evident that the live soil had much higher biodegradation rates than the sterile soil.

In comparison, Höhener et al. (2003) determined biodegradation rates for twelve volatile hydrocarbon compounds and MTBE in unsaturated sand columns and found first-order biodegradation rates of toluene, *n*-octane, and *n*-decane to be 1.31, 5, and 13.5 day^{-1}, respectively, after 23 days. Jin et al. (1994) conducted unsaturated soil column experiments to determine biodegradation kinetics of toluene. By using a short column (20-cm), fresh soil that had not been pre-exposed to toluene, and a toluene source concentration of 140 mg L^{-1}, they estimated a degradation rate constant of 34.2 day^{-1}. With a longer column (40-cm), pre-exposed soil, and the same source concentration, degradation rates of toluene increased to 42.5 day^{-1}. Pasteris et al. (2002) used a large-scale lysimeter experiment to determine biodegradation kinetics of volatile fuel compounds. They found first-order biodegradation rates in the unsaturated zone to range from <0.05 day^{-1} for MTBE up to 8.7 day^{-1} for octane.

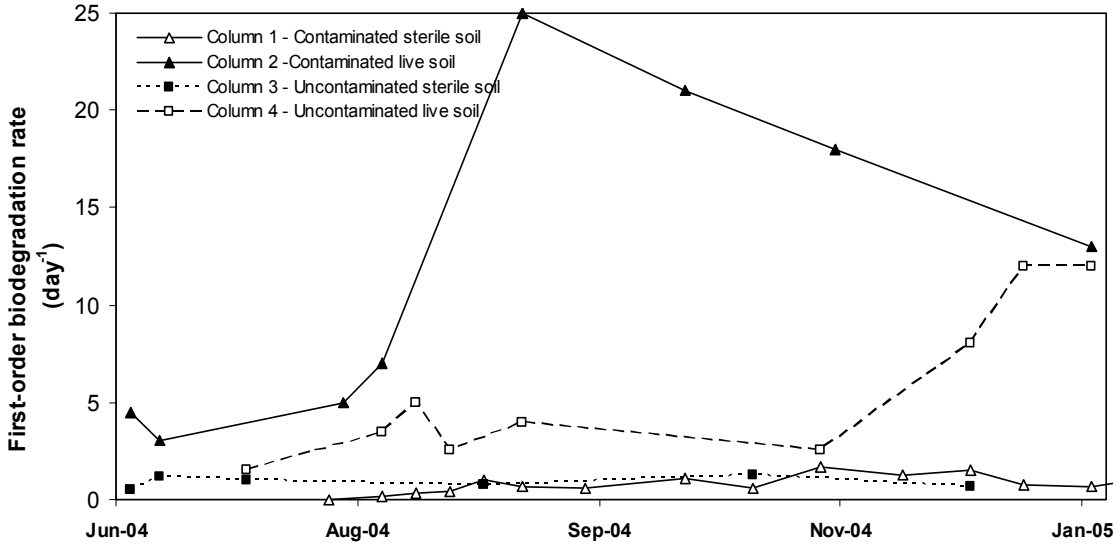

Figure 3.12 First-order biodegradation rates of the uncontaminated and contaminated live and sterile columns over time.

Properties of the sterilized soil may have changed after being autoclaved. These different properties could affect naphthalene sorption and movement through the column. Measured sorbed naphthalene concentrations throughout the length of the column show that naphthalene has a higher sorption to the soil in the sterile columns than the live columns. Sieve analysis revealed that the grain-size distributions in each column were the same, but it appears as though the autoclaving process may have changed the soil at the molecular level. In fact, it seems as though the autoclaved soil acted as a sponge for the humidified air that entered the top of the column and for the water that was added to obtain an initial moisture content of 0.11 g g^{-1} at the beginning of the experiment. Previous soil column studies were conducted at water contents ranging from 0.06 to 0.11 g g^{-1} (Jin et al., 1994; Höhener et al., 2003). Even at these low water contents, sufficient biodegradation occurred. The significance of the lower moisture contents does not appear to discourage bacterial activity based on the low moisture content levels used in other studies. More significant is the effect of moisture content on diffusion of naphthalene through the soil, which could skew the modeled biodegradation rates.

3.3 Summary

Based on the first-order rate expression $C = C_o exp(-\mu t)$ and a first-order rate (μ) of 13 day^{-1}, an initial naphthalene vapor concentration (C_o) of 0.612 g m^{-3} similar to the headspace concentration above pure naphthalene crystals will be 73% biodegraded within 2.4 hours. Over this same time, naphthalene can move 4.73-cm (1.86-in) by diffusion through soil with a moisture content of 0.125 g g^{-1}, density of 1.6 g cm^{-3}, and porosity of 37%. Therefore at contaminated sites, diffusion of contaminants through the vadose zone is essential for obtaining a high level of contaminant biodegradation. Especially because Lahvis et al. (1999) determined that biodegradation rates increase with distance above the water table and are highest in the unsaturated zone. This indicates that the combined mechanisms of naphthalene transfer from the saturated to the vadose zone followed by rapid biodegradation enhance remediation.

Through this study, we have shown that biodegradation plays an important role in decreasing vapor-phase naphthalene concentrations, as seen by the significant decrease in concentration between the source and the first few inches of soil. We have also shown that there are differences between the bacterial activity of the contaminated and uncontaminated soils, but over time, these differences are minimized. At contaminated sites, biodegradation rates in uncontaminated soil can be enhanced with a phytoremediation system.

A phytoremediation system not only enhances biodegradation by promoting bacterial activity in the rhizosphere but also enhances biodegradation elsewhere in the vadose zone by promoting movement of contaminants through the subsurface. In a previous study, we determined that a phytoremediation system enhances direct volatilization due to its influence on the groundwater table level, which, in turn, alters groundwater concentrations. The enhancement of contaminant transfer through the vadose zone by direct volatilization helps soils that have had no previous exposure to the contaminant become acclimatized to it much faster, which increases the effectiveness of bioremediation by building up an enriched microbial population (Jin et al., 1994). Allen-King (1996b) found that the activity and number of microorganisms was significantly increased with increased exposure to toluene in their unsaturated soil column experiments. The work presented here suggests that a phytoremediation system has the

potential to increase biodegradation rates in the unsaturated zone in the early stages of plume evolution.

Acknowledgements

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References

Agency for Toxic Substances and Disease Registry (ATSDR) (2003). Toxicological profile for naphthalene, 1-methylnaphthalene, 2-methylnaphthalene. Atlanta, GA, U.S. Department of Health and Human Services, Public Health Service.

Allen-King, R. M., R. W. Gillham, et al. (1996a). "Fate of dissolved toluene during steady infiltration through unsaturated soil: 1. Method emphasizing chloroform as a volatile, sorptive, and recalcitrant tracer." Journal of Environmental Quality **25**: 279-286.

Allen-King, R. M., R. W. Gillham, et al. (1996b). "Fate of dissolved toluene during steady infiltration through unsaturated soil: 2. Biotransformation under nutrient-limited conditions." Journal of Environmental Quality **25**(287-295).

Baehr, A. L. and R. J. Baker (1995). "Use of a reactive gas transport model to determine rates of hydrocarbon biodegradation in unsaturated porous media." Water Resources Research **31**(11): 2877-2882.

Cho, K., T. Irvine Jr., et al. (1992). "Measurement of the diffusion coefficient of naphthalene into air." International Journal of Heat and Mass Transfer **35**(4): 957-966.

Chaplin, B. P., G. N. Delin, et al. (2002). "Long-Term Evolution of Biodegradation and Volatilization Rates in a Crude Oil-Contaminated Aquifer." Bioremediation Journal **6**(3): 237-255.

Höhener, P., C. Duwig, et al. (2003). "Biodegradation of petroleum hydrocarbon vapors: laboratory studies on rates and kinetics in unsaturated alluvial sand." Journal of Contaminant Hydrology **66**: 93-115.

Jin, Y., T. Streck, et al. (1994). "Transport and biodegradation of toluene in unsaturated soil." Journal of Contaminant Hydrology **17**: 111-127.

Lahvis, M. A., A. L. Baehr, et al. (1999). "Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions." Water Resources Research **35**(3): 753-765.

Millington, R. J. and J. P. Quirk (1961). "Permeability of porous solids." Transactions of the Faraday Society **57**: 1200-1207.

Moyer, E. E., D. W. Ostendorf, et al. (1996). "Petroleum hydrocarbon bioventing kinetics determined in soil core, microcosm, and tubing cluster studies." Ground water monitoring and remediation (Winter): 141-153.

Pasteris, G., D. Werner, et al. (2002). "Vapor phase transport and biodegradation of volatile fuel compounds in the unsaturated zone: a large scale lysimeter experiment." Environmental Science & Technology **36**(1): 30-39.

Schnoor, J. L. (2002). Phytoremediation of Soil and Groundwater. Iowa City, IA, Ground-Water Remediation Technologies Analysis Center, Technology Evaluation Report TE-02-1**:** 45.

U.S. EPA (2003a). Contaminant Candidate List Regulatory Determination Support Document for Naphthalene, USEPA Office of Water Report, EPA-815-R-03-014.

U.S. EPA (2003b). Health Effects Support Document for Naphthalene, USEPA Office of Water Report, EPA-822-R-03-005.

APPENDIX A

Quality assurance and quality control procedures

This appendix describes the detailed quality assurance and quality control tests that were performed in development of the flux chamber.

A.1 Flux chamber variability

The flux chamber and sorbent tubes were tested in the laboratory to check chamber design efficiency, contamination carryover by the chamber, flow rate efficiencies, and sorbent tube breakthrough and saturation levels. This simple laboratory setup consisted of placing 0.5 grams of naphthalene crystals in the bottom of a 30 L cooler, leaving 3 L of headspace volume above the naphthalene, and filling the cooler with 20 L of uncontaminated commercial playground sand. The top of the cooler was sealed and the naphthalene was allowed to reach equilibrium for three days before any experiments were run. After the system reached equilibrium, the cooler was unsealed and the chamber was pushed into the top 2 cm of sand.

The standard deviation of naphthalene fluxes measured by three chambers in the laboratory was 6.7%, which is in good correlation with the standard deviation of 6.4% determined in the field. The experiment shows that this method is repeatable and that there are no major differences between the chambers that we use. Figure A1 compares the recovery of each chamber.

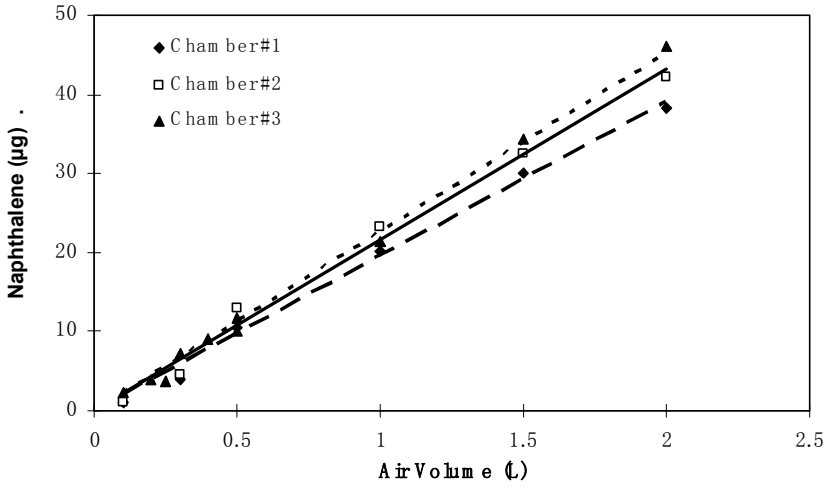

Figure A.1 Comparison of chambers used in the field.

A.2 Effect of drying tubes

Laboratory experiments were also conducted to test the effect that drying tubes have on naphthalene concentrations, as shown in Figure A2. Due to a drop in temperatures at night in the field, water condenses on the inside of the sorbent tubes and decreases their efficiency. In order to minimize such condensation, drying tubes (SKC226-44, 6x70 mm size, 1 section, 250 mg sorbent) were placed directly after the chamber and before the sorbent tubes. The mass of naphthalene captured on the sorbent tubes with the drying tubes was compared to the mass captured without drying tubes. Tests indicated that naphthalene vapors were trapped by the drying tubes and caused a 36.6% decrease in the mass, leading to an underestimation of the flux. Based on this data, the drying tubes were not used in the field measurements, but instead a drying column was used to dehumidify the clean air before it entered the chamber.

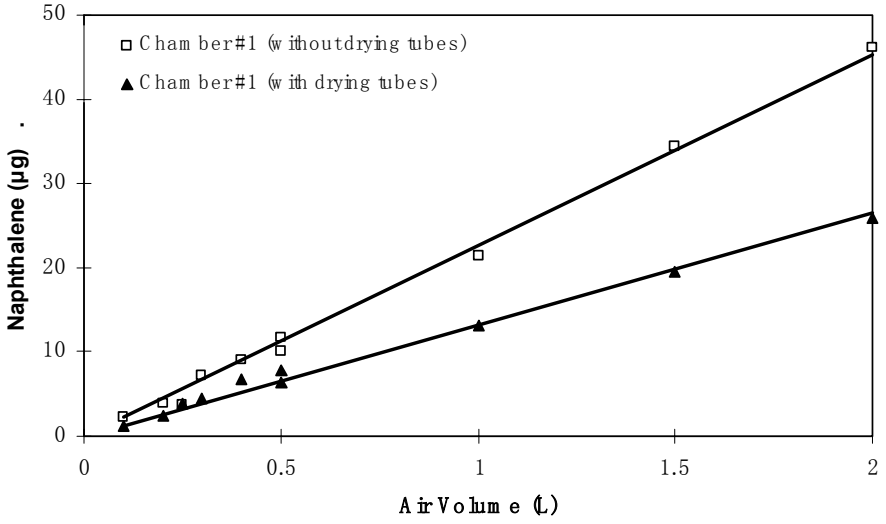

Figure A.2 Naphthalene mass captured on sorbent tubes with and without drying tubes.

A.3 Sorbent tube validation

XAD-2 sorbent tubes (SKC 226-30-04, 8x110 mm size, 2 sections, 50/100 mg sorbent) were tested in the laboratory by placing several grams of naphthalene crystals in a 5 L Teflon bag, letting the system equilibrate, and pulling the naphthalene vapors out of the bag and through two sorbent tubes in series using a personal sampling pump. The XAD-2 resin was designed to effectively trap polycyclic aromatic hydrocarbons as listed

by the air sampling company SKC. Because the sorbent tube distributing company recommends a flow rate of 1 L min^{-1} and the extraction method (NIOSH 5515) recommends a flow rate of 2 L min^{-1}, we chose to test flows ranging from 0.5 L min^{-1} to 2 L min^{-1} to determine the optimal air flow rate for trapping naphthalene. Based on the results, 1.5 L min^{-1} and 2 L min^{-1} yield the most naphthalene mass with a 0.18% difference between the two. Reducing the flow to 500 mL min^{-1} resulted in a 20% decrease in naphthalene mass recovered.

Breakthrough and saturation levels for naphthalene were also determined in laboratory tests using the same setup as described above. From the results, it appears that naphthalene breaks through the first sorbent tube at 600 μg. However, this can vary greatly based on how the sorbent tubes were manufactured, the flow rates used, the presence of preferential pathways in the resin, and the constituents in the air. For example, outdoor soil surface samples have shown that naphthalene can breakthrough the first sorbent tube at levels as low as 1 μg. For this reason, special care is taken to make sure multiple sorbent tubes are used to prevent any mass loss, and blanks are utilized to differentiate background contamination from the true samples. Other tests reveal that the resin in one single sorbent tube can hold as much as 14,000 μg of naphthalene regardless of how much breaks through. Just as with the above tests, this one was also conducted in controlled conditions and this amount may vary widely depending on how many resin sites are taken up by other contaminants.

APPENDIX B

Meteorological influences on naphthalene flux

This appendix describes detailed results of our investigation into the meteorological influences on naphthalene flux. Many of the results are inconclusive and are therefore not reported in Chapter 1 due to space considerations.

B.1 Precipitation influence

Precipitation events either a few days before or during sampling create noticeable decreases in fluxes measured. Even mild rainstorms can greatly influence the flux. Figure B.1 highlights the samples that were negatively affected by rain. We have observed that more than 0.2 inches of rain significantly affect the flux. The infiltrating rainwater, duration of rainfall, pressure fluctuations, moist soil, and raised groundwater level and all work together to suppress the volatilizing contaminants.

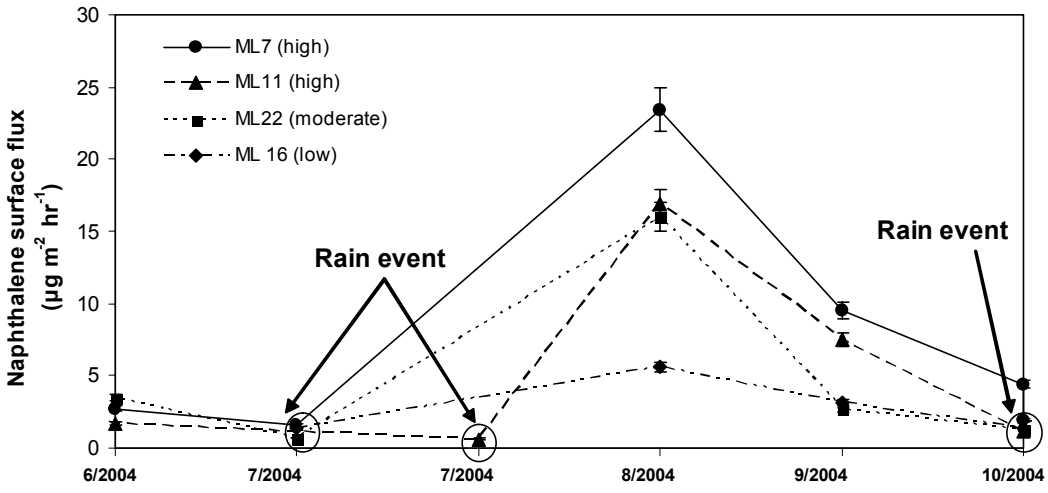

Figure B.1 The effect of precipitation on the flux measured. Samples that are circled are samples that were significantly decreased due to large rain events before and/or during sampling.

Conversely, rainfall during the last few hours of sampling causes an increase in the flux, as depicted by Figure B.2. In August 2004, 0.5 inches of rain fell during the last five hours of a three-day sample, which caused a dramatic increase in the flux measured. The fluxes at ML22 and ML16 are consistently below the fluxes at ML7 and ML11 except on this one occasion. This occurrence agrees with the theories of both Poulsen et

al. (2000) and Valsaraj et al. (1999) who state that organic contaminants adsorb to sediments and as the moisture content, air relative humidity, or precipitation increase, the water molecules displace the hydrophobic compounds from the sediments, causing the compounds to enter the soil air voids and be transported to the atmosphere. In addition, the chamber and protective plastic tub covers the underlying soil, preventing rain from infiltrating through the subsurface directly below the flux chamber. Massmann and Farrier (1992), who studied the effect of barometric pumping on vapor transport, found that pressure fluctuations, common to rain events, cause the horizontal movement of contaminants in the subsurface. Contaminants that are displaced from the sediments within the vicinity of the flux chamber may be horizontally transported toward the area of soil covered by the chamber and vertically transported up through the dry soil and into the chamber.

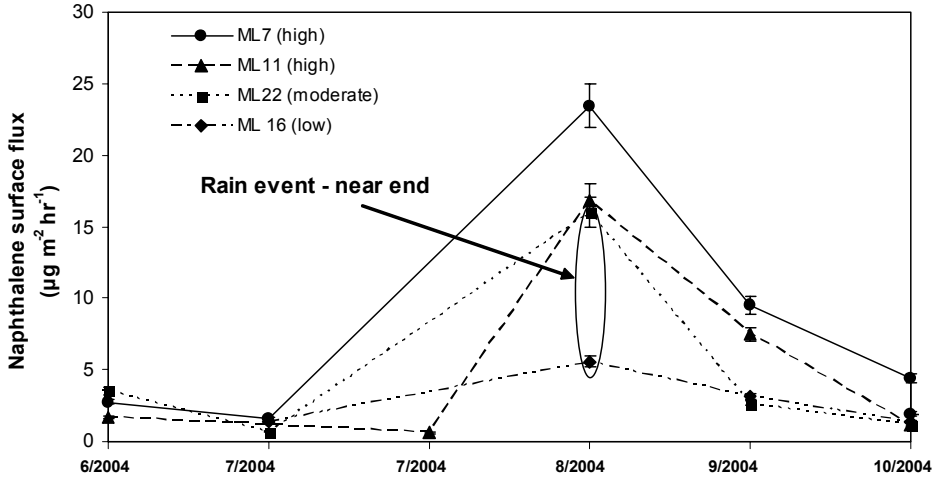

Figure B.2 The effect of precipitation on the flux measured. 0.5 inches of rain fell during the last five hours of a three day sample in August 2004 on ML22 and ML16, which caused a dramatic increase in the flux measured.

B.2 Pressure influence

Fluctuations in barometric pressure due to changes in weather patterns can also influence the amount of contaminants that volatilize from the subsurface. It is believed that large changes in atmospheric pressure increase the subsurface movement of gas vapors, and this either causes vapors to be transported into the atmosphere more quickly

or air to infiltrate down into the subsurface (Massmann and Farrier, 1992; Auer et al., 1996). The weather station at the site records barometric pressure data every half-hour. Figure B.3 shows the surface flux as a function of the maximum pressure change during each sampling event. Unfortunately, there are not enough useful data points to conclude that pressure fluctuations directly influence the flux. In addition to minimal data points, the lack of a well-defined relationship in the figure can be attributed to increased condensation at the time of high pressure being exactly balanced by the increased volatilization at low pressure (Auer et al., 1996). The relationship between pressure and flux is better illustrated by comparing the pressure change over time, as shown in Figures B.4 and B.5, instead of at a specific moment.

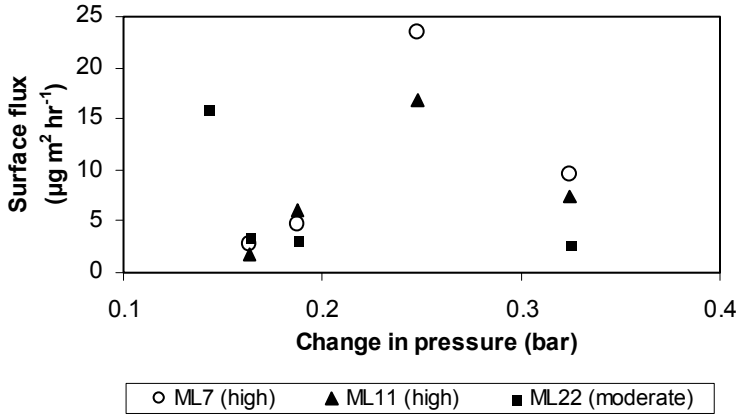

Figure B.3 The effect of the change in pressure during each sampling event on the flux measured.

As the pressure decreases, contaminated air in the subsurface moves upward toward the ground surface, and as the pressure increases, clean atmospheric air flows into the subsurface, and these two actions illustrate how barometric pumping can increase the speed at which contaminants are mixed with the atmosphere. It is commonly known that large pressure fluctuations occur before and after periods of rainfall. As stated above, the July flux measurements were severely decreased by rainfall before and during sampling, but the August flux measurements were actually increased by rainfall at the end of the sampling period. Rainfall and pressure are directly related, as shown by Figures B.4 and B.5. In the July figure (Figure B.4), one can see that in addition to the abundant rain there was a steady drop in pressure in the middle of the sample period and then an increase in pressure at the very end of the period. This drop in pressure was too slow to

create any noticeable changes in the flux. However, in the August figure (Figure B.5), one can see that there was a drop in pressure during the entire duration of the sample, and a sudden greater drop in pressure near the end of sampling that probably caused advection of contaminants from the subsurface. The sample in August also occurred right before a large rain event, and according to Poulsen et al. (2000) and Valsaraj et al. (1999), the increase in humidity may have influenced the flux as described above.

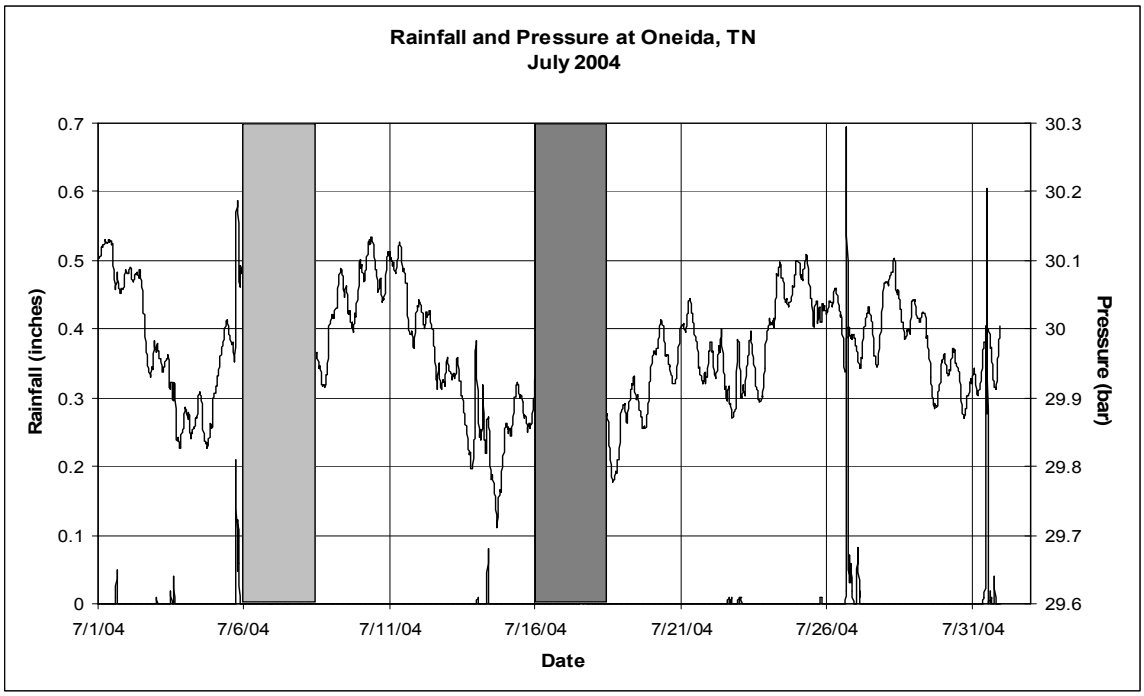

Figure B.4 The effect of pressure during each sampling event on the flux (continuous measurements in July 2004). The shaded areas are the two separate sampling periods. The spikes along the bottom represent the rainfall, and the continuous line represents the pressure. Both sampling dates show a steady decrease in pressure over the entire period and the first sample shows a significant amount of rain before sampling while the second sample shows a significant amount of rain during sampling.

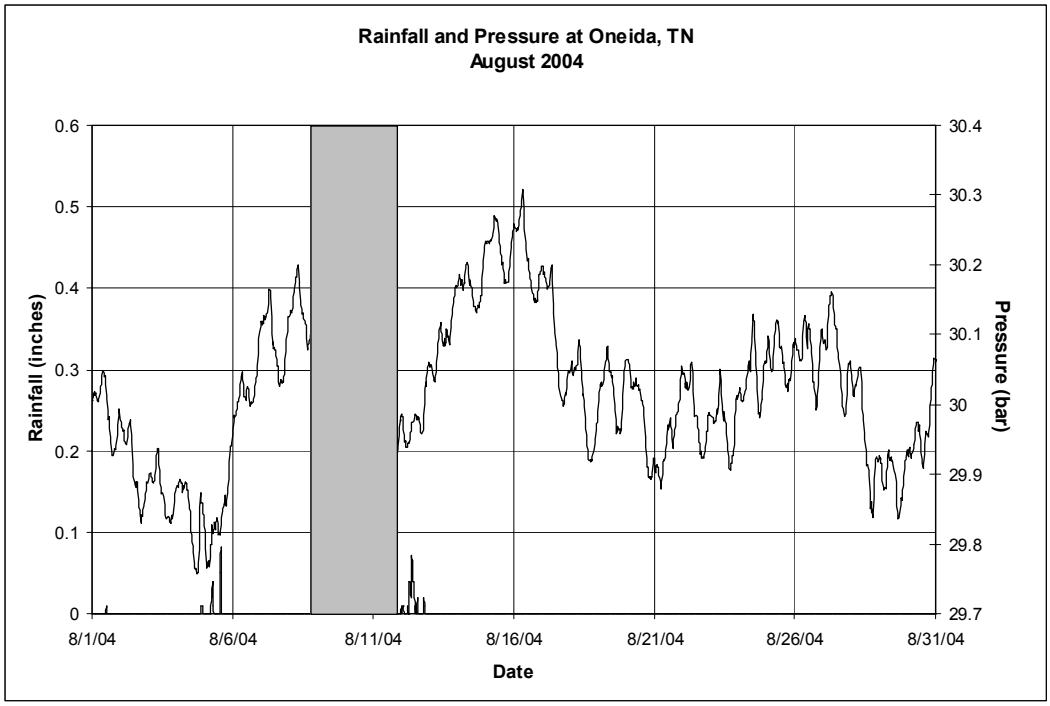

Figure B.5 The effect of pressure during each sampling event on the flux measured (continuous measurements in August 2004). The shaded area is the sampling period. The spikes along the bottom represent the rainfall, and the continuous line represents the pressure. There is a sudden decrease in the pressure at the very end of the sample period that is accompanied by rainfall. This caused a large increase in contaminant flux through the subsurface.

B.3 Soil moisture influence

Soil moisture contents by weight fell between 14 and 26%, increasing with depth and changing with soil type. Figure B.6 displays the correlation between flux and soil moisture content. Moisture content at the most shallow depth was used because its moisture fluctuates more due to the nature of the topmost soil, and it is hypothesized that the topmost layer will have a greater influence on volatilization to the atmosphere. From the graph one can see that as the moisture content decreases the flux increases. The results do contradict the theories of Poulsen et al. (2000) and Valsaraj et al. (1999), that an increase in moisture content creates an increase in flux. However, the results, which highlight the inversely proportional nature of soil moisture content and flux, agree with the theory of Davis et al. (1998). They found that during periods of dry conditions, especially in the summer, a greater percentage of soil voids are filled contaminants in the

gas phase. These contaminants are transported through the subsurface and into the atmosphere; hence the flux increases with a decrease in moisture.

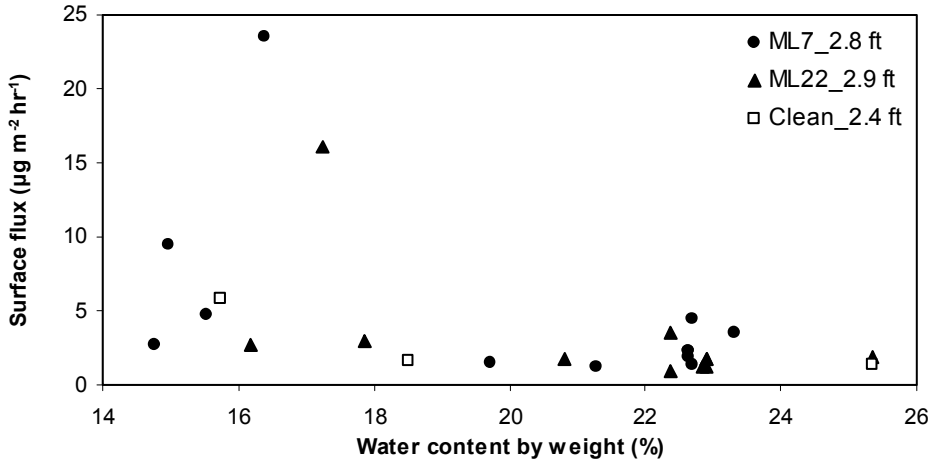

Figure B.6 Soil water content and surface flux. ML7 represents the most contaminated locations, ML22 represents the moderately contaminated locations, and "Clean" represents the areas of very little contamination. The distances are measured down from the ground surface.

B.4 Temperature and humidity influence

The influence of dry conditions can also be illustrated by examining the temperature and humidity. Volatility increases with temperature, however, we have recorded the highest fluxes at the beginning of Fall when the temperature begin to drop and dry conditions persist. Figures B.7 and B.8 show that low average temperatures and low minimum humidity correspond to higher flux values, respectively. These conditions occur at the end of Summer and beginning of Fall, when groundwater levels are lowest.

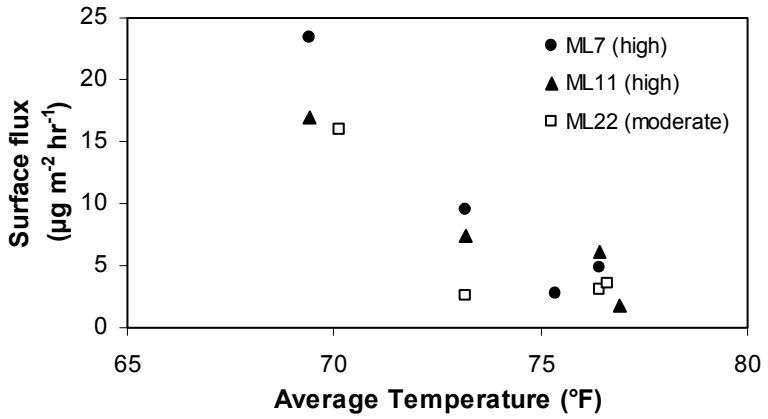

Figure B.7 The correlation between average atmospheric temperature and surface flux.

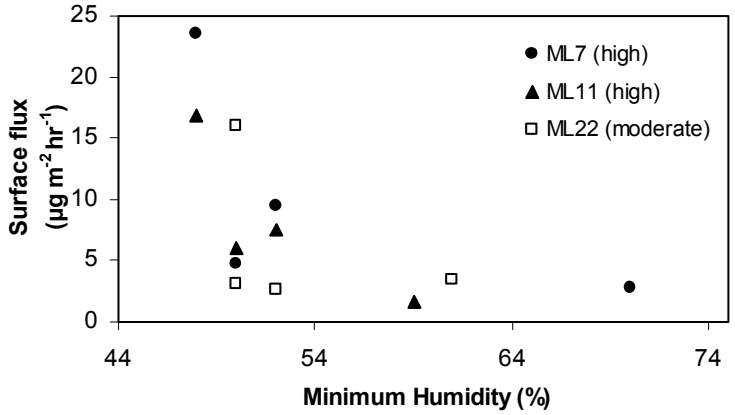

Figure B.8 The correlation between the minimum atmospheric humidity and surface flux.

The effect of temperature and humidity on surface fluxes are overwhelmed by the influence of the groundwater level. It is evident that many variables influence the flux, such as precipitation, pressure fluctuations, soil moisture, and atmospheric temperature and humidity. However, consideration of each of these variables and their mechanisms of action illustrates that the groundwater table level plays the most important role in controlling direct volatilization.

References

Auer, L. H., N. D. Rosenberg, et al. (1996). "The effects of barometric pumping on contaminant transport." Journal of Contaminant Hydrology **24**: 145-166.

Davis, L. C., M. K. Banks, et al. (1998). Plant Based Bioremediation. Bioremediation: Principles and Practice, Vol. 2, Biodegradation Technology Developments. S. K. Sikdar and R. L. Irvine. Lancaster, PA, Technomic.

Massmann, J. and D. F. Farrier (1992). "Effectsof atmospheric pressures on gas transport in the vadose zone." Water Resources Research **28**: 777-791.

Poulsen, T. G., T. Yamaguchi, et al. (2000). "Predicting volatile organic vapor sorption from soil specific surface area and texture." Journal of Environmental Quality **29**: 1642-1649.

Valsaraj, K. T., R. Ravikrishna, et al. (1999). "Air emissions from exposed contaminated sediments and dredged material." Environmental Science & Technology **33**(1): 142-149.

APPENDIX C

Potential for vapor intrusion at a phytoremediation site

Abstract

A vapor intrusion model was applied to the creosote-contaminated site to quantify the health risks associated with developing the site. Model input includes measurements of naphthalene flux at the surface and soil gas concentrations at depth, soil properties and assumed building foundation properties. Attenuation coefficients and indoor naphthalene vapor concentrations were calculated with the conservative assumptions of no biodegradation within the subsurface and no source depletion. Resulting indoor naphthalene concentrations range from 0.002 to 0.004 ppb, which is well below any regulatory standards and any levels at which health effects have been recorded.

C.1 Introduction

Volatile organic compounds (VOCs) in the subsurface are capable of migrating to the atmosphere by diffusion and advection. These contaminants are also capable of entering buildings located above the contamination by way of cracks in the foundation. Depressurization of a building and ventilation have the potential to draw the volatile compounds into the house where they may accumulate and cause adverse health effects. We have measured naphthalene directly volatilizing from the subsurface of a creosote-contaminated phytoremediation site, and this chapter presents our findings on whether naphthalene infiltrating into a theoretical house at the site presents a health risk to the occupants.

A mathematical model developed by Johnson and Ettinger (1991) (henceforth referred to as the J&E model) is utilized in this paper to predict vapor concentrations within a residential building at a site impacted by creosote contamination. This model calculates an attenuation coefficient: the vapor concentration of naphthalene in a building relative to the vapor concentration at the source. Contaminant vapor concentrations at the soil surface and near the source, as well as soil, chemical, and building properties are inputs to the model. The result is a dimensionless attenuation coefficient that is used by regulatory agencies to determine indoor exposure levels. The original model represents a

conservative case because Johnson and Ettinger (1991) did not include source depletion, biodegradation, or varying geographic strata, which would reduce indoor concentrations. Johnson et al. (1999) modified the original J&E model to account for first-order biodegradation and different soil layers, and Johnson et al. (2001) added oxygen-limited first-order biodegradation.

C.2 Methods

The J&E model determines an attenuation coefficient (α) by relating the estimated indoor vapor concentration C_{indoor} [mg m^{-3}] to the source zone vapor concentration C_{source} [mg m^{-3}]:

$$\alpha = \frac{\left[\frac{D_T^{eff} A_B}{Q_B L_T}\right] \exp\left(\frac{Q_{soil} L_{crack}}{D_{crack}^{eff} \eta A_B}\right)}{\exp\left(\frac{Q_{soil} L_{crack}}{D_{crack}^{eff} \eta A_B}\right) + \left[\frac{D_T^{eff} A_B}{Q_B L_T}\right] + \left[\frac{D_T^{eff} A_B}{Q_{soil} L_T}\right]\left(\exp\left(\frac{Q_{soil} L_{crack}}{D_{crack}^{eff} \eta A_B}\right) - 1\right)} \quad \text{(C1)}$$

such that $\alpha = C_{indoor} / C_{source}$ is the vapor attenuation coefficient, D_T^{eff} is the effective overall vapor-phase diffusion coefficient between the source and foundation [m^2 d^{-1}], D_{crack}^{eff} is the effective overall vapor-phase diffusion coefficient through the walls and foundation cracks [m^2 d^{-1}], A_B is the surface area of enclosed space in contact with soil [m^2], Q_B is the enclosed space air exchange rate [m^3 d^{-1}], Q_{soil} is the soil gas flow rate into enclosed space due to underpressurization [m^3 d^{-1}], L_T is the source to foundation separation [m], L_{crack} is the thickness of the enclosed space walls and foundation [m], and η is the fraction of enclosed space surface area open for vapor intrusion [m^2 m^{-2}].

To determine the effective vapor-phase porous media diffusion coefficient (D^{eff}) without including the effects of biodegradation, the Millington-Quirk formula is used (Johnson et al., 1999):

$$D^{eff} = D^{air} \frac{\theta_v^{3.33}}{\theta_T^2} + \left(\frac{D^{H_2O}}{H_i}\right) \frac{\theta_m^{3.33}}{\theta_T^2} \quad \text{(C2)}$$

where D^{eff} is the overall effective porous media vapor-phase diffusion coefficient [m^2 d^{-1}], D^{air} is the molecular diffusion coefficient in air [m^2 d^{-1}], D^{H_2O} is the molecular diffusion coefficient in water [m^2 d^{-1}], θ_v is the volumetric vapor content [m^3-vapor m^{-3}-oil], θ_m is the volumetric moisture content [m^3-H_2O m^{-3}-soil], θ_T is the total porosity [m^3-voids m^{-3}-soil], and H_i is the dimensionless Henry's constant. For varying layers, Equation C3 is used to determine the overall effective diffusion coefficient.

$$\frac{D_T^{eff}}{L_T} = \frac{1}{\sum_{i=1}^{n}\left(\frac{L_i}{D_i^{eff}}\right)} \tag{C3}$$

Table C.1 shows our site-specific values used to determine the overall effective diffusion coefficient within the most contaminated area. Based on soil transects obtained at the site, the soil layer type and depth are known as well as the volumetric moisture content at different depths. Porosity measurements of the top soil were taken the site, but since they do not represent the subsurface soil, assumptions using recognized relationships as noted in Table C.1 were used. These relationships relate volumetric moisture content, volumetric vapor content, and total porosity in different soil types while assuming that the total porosity ranges from 0.35 to 0.45 (Johnson et al., 1999). Table C.1 is a conservative case in which the biodegradation of naphthalene is assumed zero.

The resulting total effective diffusive coefficient represents the diffusion of naphthalene at 25°C through known layered strata at the site without biodegradation. The selected parameters represent an overestimation of indoor naphthalene concentrations because if this worst-case scenario is well below regulatory standards, there is no reason to account for biodegradation and diminishing sources, since such processes will further reduce indoor concentrations. However, if health effects have been documented at levels below this maximum, further analysis should be conducted.

Table C.1 Parameters used to determine the overall effective diffusion coefficient in layered strata without biodegradation

Soil Type	Depth [ft BGS]	Thickness (L_i) [m]	θ_m [m^3-H_2O m^{-3}-soil][a]	θ_T [m^3-voids m^{-3}-soil][a,b]	θ_V [m^3-vapor m^{-3}-soil][c]	D_i^{eff} [m^2 d^{-1}][d]	L_i/D_i^{eff} [m d^{-1}]
Clay	0-3	0.9	0.23	0.37	0.14	0.0061	147
Sand	3-7	1.2	0.25	0.37	0.12	0.0038	317
Dt^{eff}/L_T = 0.002 m day^{-1}							

[a] Using measured values at the site.
[b] Assuming that θ_T ranges between 0.35 and 0.45 (Johnson et al., 1999).
[c] $\theta_V = \theta_T - \theta_m$
[d] For D^{air} = 0.066 cm^2 s^{-1} (0.570 m^2 day^{-1}) at 25°C using equation developed by Cho et al. (1992) which states $D^{air} = 8.17708\times10^{-7}*T^{1.983}$ with temperature (T) in Kelvin (K) and the diffusion coefficient in cm^2 s^{-1} for a temperature range of 14.5°C ≤ T ≤ 53.96°C. $D^{H2O} = 6.6\times10^{-6}$ cm^2 s^{-1} (5.7×10^{-5} m^2 day^{-1}) following the relationship in Johnson et al. (1999), which is that molecular diffusion coefficients in water are roughly 1/10000 of molecular diffusion coefficients in air. H_i = 0.02 (dimensionless) at 25°C (Davis, 1997).

Hers et al. (2003) conducted a sensitivity analysis on the J&E model using a series of field data at contaminated groundwater sites and found that the model is most sensitive to moisture content and soil gas advection rates (Q_{soil}) into the building. When D_T^{eff} / L_T is high (≥0.001 m day^{-1}), contaminant vapor transport is controlled by advection; these values are associated with shallow and/or dry soils. When D_T^{eff} / L_T is relatively small (≤0.001 m day^{-1}) the attenuation coefficient is not sensitive to Q_{soil} and diffusion is the dominant transport process. Low D_T^{eff} / L_T values are associated with deep and/or wet soils, and moisture content becomes the controlling factor. For moderate values of D_T^{eff} / L_T, ranging from 0.001 to 0.002 m day^{-1}, the attenuation coefficient is sensitive to both Q_{soil} and moisture content. D_T^{eff} / L_T under our site specific conditions with two different soil layers as described in Table C.2 is 0.002 m day^{-1}, which represents moderate values and combines the effects of diffusion and advection. In this case, the model is insensitive to building properties, and transport depends largely on soil properties. Table C.2 lists predicted foundation and building parameters for the site based on values used in Hers et al. (2002) and Johnson et al. (1999). Due to the proximity of the groundwater table, house foundations have to be slab-on-grade as opposed to poured concrete basements, and corresponding building properties with this type of foundation were obtained from Hers et al. (2002).

Table C.2 Assumed parameters for slab-on-grade foundation and diffusion dominated soil. These parameters represent general field conditions used by risk-screening models to determine the vapor attenuation coefficient.

Parameters	Assumed values
A_B	50 m^2
Q_B	1200 m^3 day^{-1} [a]
Q_{soil}	1.5 m^3 day^{-1} (1 L min^{-1})
L_{crack}	0.15 m
D_{crack}	0.1 m^2 day^{-1}
H	0.0001 m^2 m^{-2}

[a] Corresponds to 12 exchanges per day in 100 m^3 enclosed space

Using the values in Table C.2 and D_T^{eff} / L_T calculated from Table C.1, the resulting attenuation coefficient (α) is 7.8×10^{-5}. The relationship between the attenuation coefficient and D_T^{eff} / L_T under the previously defined parameters is displayed in Figure C.1. Under worst-case scenarios, such that when there is only one sandy-soil layer and no biodegradation, D_T^{eff} / L_T becomes 0.003 m day^{-1} under our specific site conditions and the attenuation coefficient (α) becomes 1.14×10^{-4}. This result produces a marginal increase in indoor concentrations which are negligible in terms of health risks.

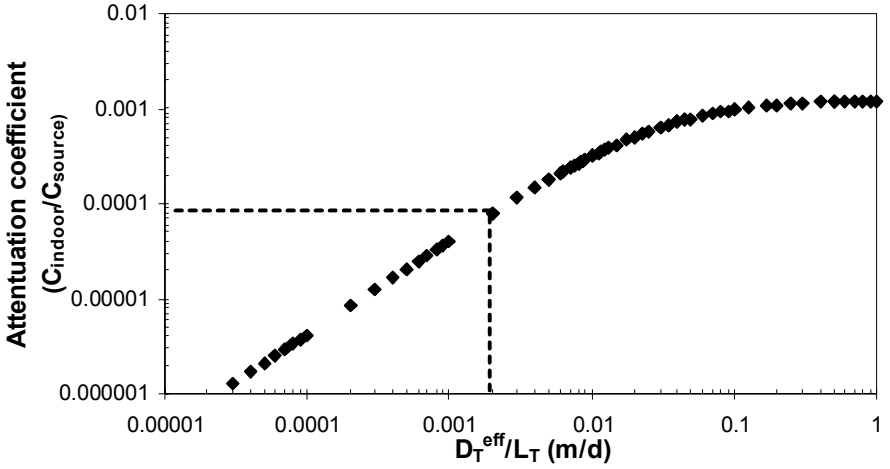

Figure C.1 Attenuation coefficients as a function of overall effective vapor-phase diffusion through the subsurface and distance from source. Parameters for this graph are given in Tables C.1 and C.2.

According to Johnson et al. (1999), C_{source} may be estimated using vapor concentrations near the source zone or near the ground surface. Johnson et al. (1999)

found that using concentrations near the surface may not well represent concentrations under a building due to surface barriers. In addition, vapor concentrations near the surface may not represent steady-state conditions as well as vapor concentrations directly above the source because vapor concentrations near the surface are subject to advective flow. Instead, they suggest that vapor concentrations close to the source be used as these are not affected by surface conditions. Therefore, soil gas concentrations measured at a depth of 2.1 m (6.8 ft) in the most contaminated area are used. An average Summer and Fall naphthalene gas concentration of 300 μg m^{-3} was obtained 0.067 m (0.22 ft) above the water table. By using the above calculated attenuation coefficient of 7.8×10^{-5} and a soil gas concentration of 300 μg m^{-3}, which represents the concentration of naphthalene directly above the source, an indoor naphthalene concentration of 0.0234 μg m^{-3} is calculated.

According to our field data, vapor concentrations near the source fluctuate with changing groundwater levels. Because of this fluctuation, we decided to compare indoor vapor concentrations predicted using soil gas measurements both at depth and near the surface. The upper asymptote of $\alpha = 1.2\times10^{-3}$ in Figure C.1 represents the circumstance where the source is close to the building, only attenuation due to mixing with indoor air is present, and soil diffusion resistance is insignificant. In other words, gas concentrations measured at the soil surface are assumed to be directly transported into the building under advective forces. In this case, the relationship between the soil gas and indoor concentration can be generalized as:

$$C_{indoor} = \frac{C_{soil\,gas}}{833} \qquad \text{(C4)}$$

where $C_{soilgas}$ is the concentration in the soil gas immediately adjacent to the basement wall or foundation. Since no building is present at our site, $C_{soilgas}$ represents the concentration of naphthalene at the surface of the soil measured by the flux chamber.

The average naphthalene concentration fluxing through the soil to the atmosphere in the Summer and Fall in the most contaminated area was 10 μg m^{-3}. By using this soil gas concentration in Equation C4, the resulting average indoor concentration is 0.012 μg m^{-3}. A comparison of the indoor vapor concentrations determined with soil gas

measurements at depth and at the surface reveals close agreement. In this case, average indoor concentrations range from 0.012 to 0.0234 μg m^{-3} (0.0023 to 0.0044 ppb), which is well below any regulatory standards or levels at which health effects have been reported.

The National Institute of Occupational Safety and Health recommended exposure limit (NIOSH REL) and the Occupational Safety and Health Administration permissible exposure limit (OSHA PEL) for naphthalene are both 50 mg m^{-3} (10 ppm). The Immediately Dangerous to Life or Health (IDLH) is 1,310 mg m^{-3} (250 ppm) (NIOSH, 1997). At our site, theoretical indoor naphthalene concentrations are well below the NIOSH REL and OSHA PEL by a factor of $2\text{-}4\times10^{6}$. Therefore, it is evident that infiltrating naphthalene vapors at our site will not negatively impact human health.

C.3 Conclusions

Because vapor intrusion models have gained recognition among regulatory compliance agencies as useful tools for assessing the risk associated with developing a previously contaminated site, we applied the Johnson and Ettinger model to determine conservative indoor naphthalene concentrations. This model was comprised of measured field data and assumed building and foundation properties. The resulting indoor naphthalene concentrations, estimated using conservative assumptions, are well below any regulatory standards and well below any concentrations at which health effects, such as nausea and headaches, have been observed.

References

Cho, K., T. Irvine Jr., et al. (1992). "Measurement of the diffusion coefficient of naphthalene into air." International Journal of Heat and Mass Transfer **35**(4): 957-966.

Davis, E. L. (1997). How heat can enhance in-situ soil and aquifer remediation: Important chemical properties and guidance on choosing the appropriate technique, EPA Ground Water Issue EPA/540/S-97/502**:** 18pages.

Hers, I., R. Zapf-Gilje, et al. (2002). "Comparison, validation, and use of models for predicting indoor air quality from soil and groundwater contamination." Soil and Sediment Contamination **11**(4): 491-527.

Hers, I., R. Zapf-Gilje, et al. (2003). "Evaluation of the Johnson and Ettinger model for prediction of indoor air quality." Ground Water Monitoring & Remediation **23**(2): 119-133.

Johnson, P. C. and R. A. Ettinger (1991). "Heuristic model for predicting the intrusion rate of contaminant vapors into buildings." Environmental Science & Technology **25**(8): 1445-1452.

Johnson, P. C., M. W. Kemblowski, et al. (1999). "Assessing the significance of subsurface contaminant vapor migration to enclosed spaces: site-specific alternatives to generic estimates." Journal of Soil Contamination **8**(3): 389-421.

Johnson, P. C., V. A. Hermes, et al. (2001). "An oxygen-limited hydrocarbon vapor migration attenuation screening model." Submitted to Environmental Science and Technology.

National Institute for Occupational Safety and Health (NIOSH) (1997). Pocket Guide to Chemical Hazards. Cincinnati, OH, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention.

VITA

Elizabeth Claire Booth was born on June 4, 1981 in Chattanooga, Tennessee. She graduated from Notre Dame High School in Chattanooga, TN in 1999 and moved to Auburn, Alabama to attend Auburn University. She obtained her Bachelor of Science degree in Civil Engineering from Auburn University in 2003. Following her undergraduate work, she enrolled in the Environmental and Water Resources graduate program at Virginia Polytechnic Institute and State University. Her requirements for a Master of Science degree in Environmental Engineering were fulfilled in 2005.