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Vapor phase uptake of volatile organic contaminants by hybrid poplar trees

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Department:

VAPOR PHASE UPTAKE OF VOLATILE ORGANIC CONTAMINANTS BY HYBRID POPLAR TREES

by

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ABSTRACT

Phytoremediation, the use of plants to immobilize, degrade or remove contaminants from the environment, shows great promise as a remediation technique for many contaminated sites. Phytovolatilization in particular is of great interest for sites contaminated with chlorinated solvents and other volatile organic compounds (VOCs), many of which are recalcitrant to biodegradation. Hybrid poplar trees have been shown to uptake, translocate and volatilize numerous aqueous-phase VOCs, however vapor phase uptake of such compounds has only recently been observed and for only one contaminant, tetrachloroethylene (PCE). One semi-volatile and five volatile compounds were dosed to poplar trees in aqueous and vapor phase and studied for uptake in a laboratory setting. Uptake, translocation and subsequent volatilization were confirmed with collection of gas diffused from tree stems and headspace analysis of tree tissue samples. Uptake was then evaluated with regards to each contaminant's physical and chemical characteristics. For remediation of some contaminated sites, including sites where vapor intrusion is a primary concern, this improved understanding of plant uptake of VOCs may make phytoremediation a more viable alternative, with benefits including low start-up cost and maintenance, natural appeal and minimal disruption to the site.

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It is my opinion that the work I have done will have a positive impact on our efforts to make our environment a better place. When I think of a person whose life had only positive impacts on those around her in her time on earth, I think of my grandmother, Violet Jaggi. So finally, I would like to dedicate all of my effort, as well as whatever benefits come from this work, to her memory.

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1. INTRODUCTION

1.1. BACKGROUND

Phytoremediation, the use of plants to remove, immobilize or detoxify contaminants from polluted soil and groundwater, is a promising remediation technique due to its low implementation and maintenance costs, ecological benefits and natural aesthetic qualities. Because of its non-invasive nature and absence of mechanical pumps and other equipment, phytoremediation also allows for use of the site during remediation. However, not all sites and contaminants make good phytoremediation candidates. In order to determine when phytoremediation is a viable option, an understanding about the uptake and fate of contaminants, as well as the mechanisms at work in and around the plant, is necessary. These mechanisms determine the removal and/or degradation of contaminants by plants, as well as the mobility of those contaminants.

Subgroups of phytoremediation make use of these mechanisms to sequester, volatilize or degrade contaminants in groundwater and soil. Phytoextraction is the use of the plant to remove and store metals in its tissues, and phytostablization, which also deals mainly with metals, uses the plant to immobilize the contaminant in order to minimize its potential threat. Organic contaminants may be subject to one or a combination of three pathways: rhizodegradation, phytodegradation and phytovolatilization. Rhizodegradation utilizes the bacteria present in the root zone of the plant to break down the contaminant. Exudates produced by the roots of the plant create an ideal environment for bacteria to proliferate and degradation action is therefore enhanced (Kuiper et al. 2004). In the case of phytodegradation, the contaminant is broken down not by bacteria, but by the plant tissues themselves after uptake. The contaminant and its metabolites may then be stored in the plant, which is a concern. In order to determine conclusively that plant tissues were capable of mineralizing trichloroethylene (TCE), researchers at the University of Washington (Newman et al.1997) tested degradation capabilities of hybrid poplar tree cell cultures and observed metabolites such as trichloroethanol, trichloroacetic acid, and dichloracetic acid, and obtained similar results using both axenic tumor cells and whole plant experiments (Gordon et al. 1998).

Volatile organic contaminants (VOCs) often lend themselves to uptake and translocation through plant material, often followed by volatilization of the contaminant out of the tree, or phytovolatilization. Plant uptake of contaminants is continually being better understood and, with the help of new technology, is even directly observable in some cases. Wild et al. (2005) used a two-photon excitation microscopy technique to observe uptake and some degradation of phenanthrene and anthracene in wheat and maize root cells. After uptake, in the case of compounds which are highly volatile, the majority of the contaminant may leave the tree completely unchanged before any degradation takes place. Figure 1.1 shows the mechanisms at work in and around the tree while Table 1.1 defines the mechanisms.

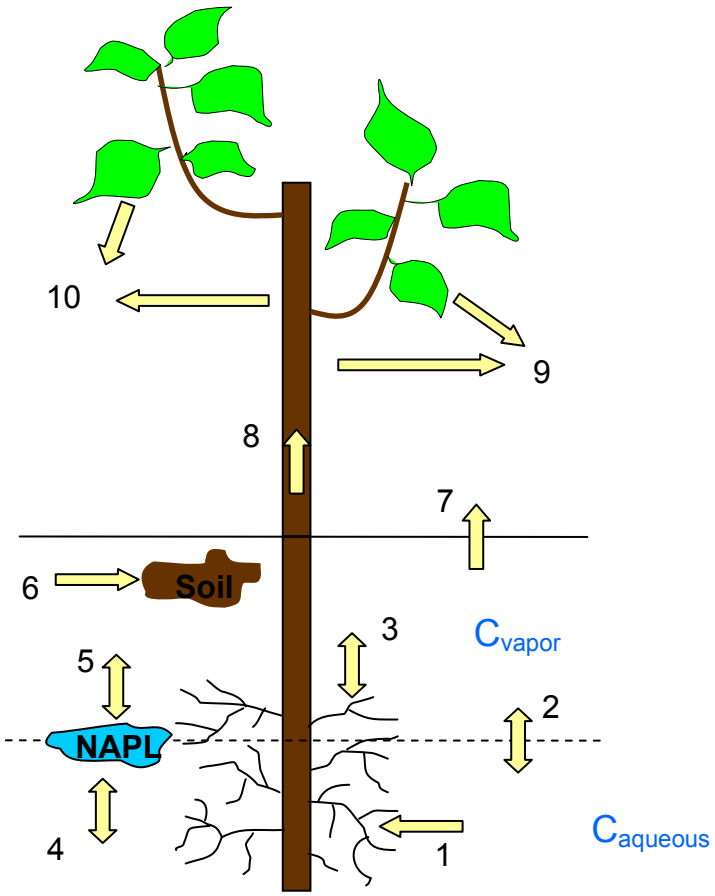

Figure 1.1 Mechanisms that determine movement of contaminants in and around trees.

Table 1.1 Mechanisms in and around hybrid poplar trees which determine contaminant movement.

	Mechanism	**Controlling Parameters**
1	Plant uptake, aqueous	K_{ow}
2	Partitioning to vapor	Henry's constant, fugacity
3	Plant uptake, vapor	K_{ow}, vapor pressure
4	Dissolution	$C_{aqueous}$
5	Volatilization from pure product	vapor pressure
6	Sorption to soil	K_{ow}, organic content of soil
7	Vapor loss to atmosphere	Henry's constant
8	Translocation	transpiration, K_{ow}, plant type
9	Transpiration	climate, plant type
10	Volatilization	Henry's constant, fugacity

As the atmosphere is a highly reactive environment, most compounds that diffuse out of a tree will break down in air in a fraction of the time that it would take them to break down in the groundwater. In this way, phytovolatilization utilizes the plant as a solar-driven pump to put the contaminant into the atmosphere where it becomes highly diluted and its half-life is greatly reduced, however each chemical can behave differently due to properties. The multiple, concurrent mechanisms illustrate why representative studies of field conditions are difficult to mimic in a lab setting, and why each tree must be treated not as a replicate of its counterparts, but as a complex individual.

New findings of contaminant transport and fate offer new applications and also uses for plume delineation. Recently, Struckhoff et al. (2005) determined that uptake of

vapor phase VOCs was not only possible, but was actively observed at a phytoremediation field site in New Haven, Missouri. Although this phenomenon was shown to happen with tetrachloroethylene (PCE), the mechanism was not well understood. Uptake of the PCE vapor at the New Haven site could be an artifact of the site geography, the contaminant, or any other number of factors. Because this was the first known direct observation of vapor phase uptake, it was not known if the same results could be observed with other chlorinated solvents or other classes of contaminants.

1.2. GOALS AND OBJECTIVES

The main goal of this research is to evaluate vapor phase uptake of numerous contaminants by hybrid poplar trees using lab-scale experiments. Uptake of a variety of vapor phase volatile and semi-volatile organic compounds will be evaluated based on their physical and chemical parameters and will also be compared to uptake of the same VOCs in aqueous phase. Specific objectives of this research are to:

- Evaluate if uptake, translocation and diffusion of chlorinated solvents and aromatic hydrocarbons in both aqueous and vapor phases occurs in hybrid poplar trees

- Demonstrate how the uptake and fate of contaminants is dependent on physical, chemical and bio-interactive characteristics

- Evaluate if phytovolatilization could be a useful remediation approach for sites with vapor intrusion or if more research is needed

Completion of these objectives will lead to a better understanding of VOC uptake and fate in plants. Furthermore, they may support the central hypothesis that vapor phase contaminants can be taken up and treated with phytoremediation.

2. REVIEW OF LITERATURE

2.1. OVERVIEW

Phytoremediation covers many types of contaminant removal, immobilization and degradation. Not all applications of phytoremediation require uptake of contaminants into the plant tissues. Rhizodegradation utilizes bacteria in the rhizosphere (root zone) to mineralize the contaminant. Phytostabilization is used to minimize contaminant transport and risk, utilizing the plant for hydraulic control, in which the action of pulling water towards the plant for purposes of transpiration captures the contaminant and keeps it from dispersing with the ground water. In the case of some phytoremediation subgroups such as phytovolatilization, phytodegradation and phytoextraction, however, uptake is essential. In order to determine when one of these mechanisms will be useful as a remediation technique, understanding plant uptake in depth is necessary. Plant uptake is a complex subject dependent on environmental conditions (soil moisture, organic content, temperature and pH), contaminant characteristics (solubility, vapor pressure, and octanol-water partitioning coefficient), and specific plant characteristics (rooting patterns and enzymes) (Susarla et al. 2002). Vapor phase uptake from the unsaturated zone has only recently been noted (Struckhoff et al., 2005).

2.2. UPTAKE

Aqueous contaminant uptake in plants has been studied for decades. Briggs et al. (1982) were the first to determine that uptake could be correlated with contaminant lipophilicity. Lipophilicity is the affinity of a molecule for an organic environment relative to an aqueous environment. This affinity is described numerically by the octanol-water partitioning coefficient, K_{ow}. A low K_{ow} value indicates a hydrophilic or "water-loving" contaminant, and a high value describes a lipophilic contaminant. Given the wide range of values, the logarithm of K_{ow} is used, the log K_{ow}. Using barley shoots, Briggs et al. (1983) determined that optimal uptake occurred at log K_{ow} = 4.5. The majority of moderately lipophilic contaminants reached a maximum constant concentration in the stems after only 24 or 48 hours and this equilibrium time increased with contaminant lipophilicity. Subsequently, soybean plants were evaluated for uptake

using a series of compounds with log K_{ow} values ranging from 0.93 to 5.28. A distribution of log K_{ow} versus transpiration stream concentration factor (TSCF) revealed a similar finding to that of Briggs et al. with maximum TSCF occurring around the mid-range of log K_{ow} 2.5 – 3.5 when using excised soybeans and a laboratory pressure cell (Hsu et al. 1990). Optimal TSCF in relation to log K_{ow} was also evaluated using a hydroponic reactor and poplar cuttings by Burken and Schnoor (1998). Uptake of 12 contaminants with log K_{ow} values ranging from 0.87 to 5.04 revealed that optimal uptake occurred with an approximate log K_{ow} of 2.50.

Specific contaminants have been investigated, including their fate after uptake. Atrazine, which has a log K_{ow} of 2.56, fits right into the ideal uptake range and has been shown experimentally to be taken up by plants (Burken and Schnoor 1996). After uptake by hybrid poplar trees, atrazine was shown to be metabolized in the roots, stems and leaves, and this degradation increased with longer exposure to tree tissues (Burken and Schnoor 1997).

Because of its moderate log K_{ow} value of 2.33 (Schwarzenbach et al. 1993), trichloroethylene (TCE) is readily taken up by plants. As with all chemicals which make their way into a plant, its fate after uptake is of serious concern. When TCE was fed to edible garden plants such as tomatoes, carrots and spinach, a portion of the contaminant was shown to be metabolized and the products stored in the plant as a bound residue. Transformed TCE bound to the plant tissue is typically considered less toxic than the original compound. The plants contained enzymes that are known to be capable of TCE degradation, such as cytochrome P450 and glutathione-S-transferase, which most likely carried out this process (Schnabel et al. 1997).

In some cases, uptake of a contaminant by a plant may not lead to a satisfying conclusion, as in the case of uptake of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), a highly persistent explosive. Poplar trees were shown to easily take up HMX without observable toxicity effects, even under saturated conditions. However, 70% of translocated HMX was found to be stored in the leaves unchanged. As leaves dried up

and fell off the tree, more than half of the HMX was leached back out of the leaves into water (Yoon et al. 2002). Uptake of HMX by poplar trees would therefore not serve as a useful remediation technology unless the trees were engineered to degrade the HMX or plant materials were subsequently destroyed. This re-illustrates the importance of understanding the fate of a contaminant after uptake.

Uptake of numerous organic contaminants has also been observed on a field scale. These are decidedly important observations if phytoremediation is to be used as a practical remediation solution. At a site in South Carolina, groundwater was found to be contaminated with the gasoline components benzene, toluene, ethylbenzene and xylenes (BTEX) and the fuel oxygenate methyl *tert*-butyl ether (MTBE). Tree cores obtained from mature trees growing over the contaminated plume were found to contain all of the compounds in their woody biomass, whereas no contaminants were detected in the cores of trees growing in areas known to be outside the plume (Landmeyer et al., 2000). A similar observation was made at the Savannah River Site, also in South Carolina. Headspace of cores from trees at the site were shown to contain TCE and *cis*-1,2-dichloroethene, both of which were present in groundwater at the site (Vroblesky, 1999). Tree coring was also used to further delineate contamination in the vadose zone in the work of Struckhoff et al. (2005).

In some cases, man-made field-scale experiments were used to make the jump from lab-scale. Hybrid poplar trees were shown to remove, and to some extent mineralize, TCE (Newman et al., 1999) and carbon tetrachloride (Wang et al., 2004) from simulated aquifers under controlled field studies, however the majority of the contaminants were not accounted for. Volatilization from these plants has also been noted to occur by Wang et al. (2004) and Burken and Newman (personal communication, 2007).

Even in situations where phytoremediation may not be the best candidate for remediation, plants and their uptake of contaminants can tell a great deal about a site, as in the case of an emerging technology called phytomapping. In the case of

phytomapping, concentrations of contaminants present in tree cores can approximately indicate the concentration of the contaminants in the groundwater. There are still many unknowns associated with phytomapping, but lab tests support its credibility. Ma and Burken (2003) found a linear correlation between the concentration of TCE in tree cores and the concentrations of aqueous TCE to which the roots were exposed. At Aberdeen Proving Ground in Maryland, phytomapping was used to delineate a TCE and 1,1,2,2-tetrachloroethane (TeCA) plume with great accuracy and with minimal disturbance to the site (Weishaar et al. 2006).

2.3. VOLATILIZATION AFTER UPTAKE

For VOCs, volatilization after uptake is a likely scenario. These contaminants tend to be somewhat resistant to degradation in the subsurface and often lend themselves to plant uptake given intermediate log K_{ow} values. Phytovolatilization depends on several mechanisms: successful uptake of the contaminant, translocation through the xylem and diffusion out of the plant material. Although some volatilization may occur through the stems and leaves of a plant, the major fate of VOCs which are phytovolatilized is diffusion from the xylem of the transpiration pathway (Ma and Burken, 2003). A fraction of the contaminant may also be degraded and translocated in the phloem or remain in the plant as bound residue (Collins et al., 2002). As previously discussed, uptake is greatly dependent on the log K_{ow} of the contaminant. The tendency of the contaminant to diffuse out of the plant can be quantified by vapor pressure and Henry's constant. Generally, contaminants with a vapor pressure higher than 0.01 atm or dimensionless Henry's constant higher than 0.1 will readily volatilize from plants (Burken and Schnoor, 1999).

In the work of Burken and Schnoor (1998) which showed uptake of 12 different contaminants, the experimental setup was a two chambered hydroponic system which collected all gas diffused from the cuttings. Semi-volatile and non-volatile chemicals were shown to be taken up by the tree, but were not present in the top part of the chamber due to their inability to volatilize. More volatile contaminants such as TCE, benzene, toluene and ethylbenzene were shown to volatilize from the plant after uptake. This same

setup was used by Ma et al. (2004) to confirm uptake and volatilization of MTBE by poplar trees.

2.4. VADOSE ZONE REMEDIATION

Vadose zone contamination is of particular concern in areas where VOCs exist in their pure form. Due to their volatile nature, these contaminants will partition into the gas phase and become relatively mobile in the unsaturated soil. Currently, there are several remediation approaches available for these situations, but the use of phytoremediation is still very questionable.

Naturally occurring microbial degradation of a variety of contaminants in the vadose zone has been documented. Intrinsic aerobic degradation of aromatic hydrocarbon vapor was shown to take place in the vadose zone of contaminated sand at a site in Australia (Franzmann et al., 2002). In addition to mineralizing the VOCs, this microbial degradation hindered further movement of the contaminants through the vadose zone. Biodegradation of chlorinated solvents and pesticides as well as microbial colonization on solubilized metals has also been demonstrated in the vadose zone (Holden and Fierer, 2005).

Bioventing, an introduction of air flow which results in enhanced microbial degradation, is one promising solution for vadose zone remediation. Bioventing has also been shown to improve degradation of hydrocarbons. Shewfelt et al. (2005) found that degradation of gasoline components could be enhanced by bioventing with additional nitrogen, which was the limiting factor in naturally occurring hydrocarbon degradation. Like bioventing, soil vapor extraction introduces air flow through the vadose zone, but not in the interest of enhancing microbial processes, but exploiting the volatility of many organic compounds so that they may be removed from the subsurface and treated above ground (Suthersan, 1997). Such soil vapor extraction wells were used to successfully remediate carbon dioxide plumes by Zhang et al. (2004).

Limited research on phytoremediation specifically of the vadose zone suggests plants may actually create vadose zone contamination as vegetation pulls contaminated water from the water table up towards the unsaturated zone, but this is not necessarily a negative effect. High transpiration trees have been shown to hydraulically control MTBE plumes, thereby introducing MTBE contaminated water into the vadose zone near the trees where chances for aerobic biodegradation becomes significantly increased (Chard et al., 2001).

Vadose zone contamination becomes an even more urgent problem when considering the effects of vapor intrusion, in which contaminants exist near utilities or cables in vapor form, and therefore have a path of little resistance to buildings and foundations. In order to address this problem by means of a phytoremediation mechanism, an understanding of how plants and vapor phase contaminants will interact is important. Although this has been studied to some extent regarding microbial effects on the degradation of the contaminants in the rhizosphere, the idea of uptake of these vapor contaminants by plants has never been investigated in depth.

3. MATERIALS AND METHODS

3.1. REACTOR SETUP

Reactors were built using 1 L glass jars filled with alternating layers of gravel and potting soil. Layers from bottom to top were: 125 g of chert pea gravel, 320 g potting soil, 250 g chert pea gravel to act as a capillary barrier, landscaping cloth to be used as a silt barrier, and 320 g potting soil. Hybrid poplar cuttings (*P.deltoides* x *P.nigra*, clone DN34) approximately 30 cm long were planted in each jar, penetrating all layers of the reactor. Two Teflon tubes were also included in each reactor, one of which reached the bottom gravel layer and acted as a feed tube where the tree received water, and the second of which reached just above the capillary barrier and acted as a vapor tube. The jars were then sealed with Teflon-lined lids. The reactor set-up is shown below in Figure 3.1. The first time the reactors were watered, tap water was added through the feed tube until the water was just under the landscaping cloth layer. Each reactor was then covered with foil to discourage algal growth and weighed. This was recorded as the saturated weight of that particular reactor. Subsequent watering was carried out every two to three days on each reactor to return it to its saturated weight, thus creating a saturated zone and a vadose (unsaturated) zone inside each reactor. The capillary barrier was used to further define the two zones by preventing feed water from reaching above the second layer of gravel by capillary action. Although reactors were never allowed to dry out completely, this engineered water table was allowed to fluctuate slightly to simulate natural water table movement.

3.2. CONTAMINANT INTRODUCTION

Reactors were placed in a walk-in fume hood under a 250 Watt metal halide light bulb on 13-hour light cycles. Conditions in the fume hood were maintained at approximately 60% humidity and 22 – 25°C. After approximately 30 – 45 days when all trees showed significant growth of leaves and roots, the transpiration rate of each tree was determined by calculating the amount of water the tree used per day. Three trees with similar transpiration rates were put into three groups: A, B and C. Each group of

three was then randomly divided into groups 1, 2, and 3, each of which received different inputs during the experiment, as shown in Table 3.1 below.

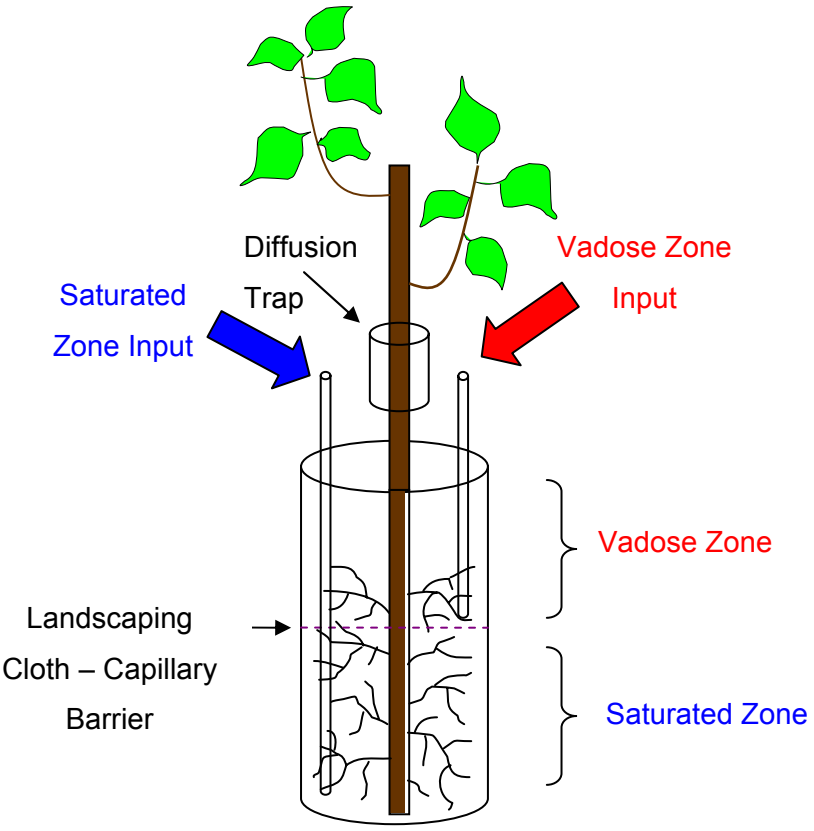

Figure 3.1 Reactor schematic with diffusion trap, in which volatilized contaminants were collected, and saturated and vadose zones which were used for delivery of aqueous and vapor phase contaminants, respectively.

Table 3.1 Saturated zone and vadose zone inputs to three treatment groups.

	Group 1	**Group 2**	**Group 3**
Vadose Zone Input	None	Continuous clean air exchange	Contaminated vapor
Saturated Zone Input	Contaminated water	Contaminated water	Clean water

Three reactors were included in each of these three groups including one reactor from each of the A, B and C groups. While care was taken to ensure that each reactor was as similar to its counterparts as possible, each tree is a biological individual, with varying transpiration and growth rates. The following table outlines the grouping of individual reactors (Table 3.2).

Table 3.2 Grouping of reactors in each treatment group.

	Group 1 (No Air Exchange)	**Group 2 (Clean Air Exchange)**	**Group 3 (Contaminated Air)**
Reactor #	1A	2A	3A
	1B	2B	3B
	1C	2C	3C

The three reactors in each group were prepared the same, and contaminants were introduced the same, however the variable growth and transpiration rates of the trees prohibit the three reactors in each group from serving as true replicates. Trichloroethylene (TCE), benzene, toluene, ethylbenzene, naphthalene and methyl *tert*-

butyl ether (MTBE) were dosed to all trees. Groups 1 and 2 received contaminated water at the concentrations shown below in Table 3.3.

Table 3.3 Aqueous concentrations dosed to reactors.

MTBE	10 mg/L
TCE	5 mg/L
Benzene	5 mg/L
Toluene	5 mg/L
Ethylbenzene	5 mg/L
Naphthalene	1 mg/L

Contaminants used in this experiment were chosen for a variety of reasons. Benzene, toluene, ethylbenzene and MTBE, all components of gasoline, often occur together in contaminated soil and groundwater from sources such as leaking underground storage tanks. As a highly soluble and non-reactive contaminant, MTBE plumes develop and move rapidly. TCE is not only of interest because it is a chlorinated solvent like PCE, but because of its recalcitrant nature under aerobic conditions and prevalence in the environment. According to the Agency for Toxic Substances and Disease Registry study of U.S. groundwater well contamination, TCE was the most commonly detected and highly concentrated VOC found (2006). Naphthalene, the only polycyclic aromatic hydrocarbon tested, was chosen because its physical and chemical characteristics are quite different from other contaminants in this study, evident by its hydrophobic nature and low solubility and vapor pressure. Naphthalene is also a current target for phytoremediation, and the fate is uncertain (Marr et al. 2006).

In order to have consistency in the experiment, trees in Group 3, which received their contaminants in vapor form, were given the same mass of contaminants as their counterpart in Group 1. For example, if reactor 1A received 0.2 mg of TCE in the form of 5 ppm feed water on a given day, reactor 3A would also receive 0.2 mg of TCE in vapor form on that day. Contaminated vapor was obtained by pulling a predetermined amount of headspace from bottles of saturated aqueous solutions of each contaminant. Trees were dosed every 2 or 3 days concurrent with watering over the course of 30 days. Clean water was delivered to trees in Group 3 with a 50 mL glass syringe to replace water used by transpiration. A second identical 50 mL syringe was used to deliver contaminated water to trees in groups 1 and 2. Contaminated vapor was delivered to trees in Group 3 using gastight syringes of various sizes. To avoid pushing the vapor back out of the reactors in Group 3, those trees were first watered, and then dosed with the vapor phase contaminants. After dosing, feed and vapor tubes were clamped shut, with the exception of vapor tubes on trees in Group 2, which were connected to the continuous clean air input. Air nozzles inside the fume hood were used as the source for the clean air exchange.

3.3. SAMPLE COLLECTION AND ANALYSIS

Samples of the gas diffused from each tree were collected from a diffusion trap onto a thermal desorber tube (Markes International, Pontyclun, England). The thermal desorber tubes were packed with Tenax, a polymer resin adsorbent made from 2,6-diphenylene-oxide. As Tenax is not an ideal sorbent for collecting MTBE, thermal desorber tubes packed with Carbograph, an activated carbon packing, were tested as well. Samples collected on the thermal desorber tube sorbent are desorbed and concentrated in an electronically controlled cold trap, which is then rapidly heated to desorb the entire sample into the capillary column of the gas chromatograph (GC). Because a large volume of air can be passed through the thermal desorber tubes, the concentration of small amounts of diffused contaminant over a long collection period creates an ideal method for detecting trace levels of organic vapor. In this experiment, thermal desorber tubes were switched out concurrently with dosing and analyzed by GC using the flame ionization detector (FID).

The diffusion trap setup, previously used by Ma and Burken (2003), was made with a 2.5 cm long glass tube which was placed around the cutting approximately 2.5 cm above the lid of the jar. The top and bottom of the glass tube were then sealed with Teflon and secured to the tree with Parafilm. An 18-gauge metal hypodermic needle was fastened to the thermal desorber tube using a lure lock connection and Teflon tape. The needle was then inserted through the Teflon at the bottom of the diffusion trap. On the back end of the thermal desorber tube, a piece of flexible tubing was attached and connected to a vacuum nozzle inside the fume hood at 3 mL per minute in order to prevent contaminants from building up inside the trap and thereby hindering diffusion out of the tree. A second 18-gauge hypodermic needle was inserted through the top Teflon seal of the trap to act as a vent. In order to prevent background contaminants from entering the trap, the vent needle was attached to a granular activated carbon (GAC) filter. The filter consisted of a 10 mL plastic syringe with the plunger removed, filled with 20-60 mesh GAC, and plugged with a small mass of glass wool. A detail of the diffusion trap is shown in Figure 3.2.

To ensure that the reactor design was adequate for the purposes of this study, approximately 5 mL samples of the clean water fed to trees in Group 3 were tested by GC approximately 4 to 6 hours after dosing the trees with contaminated vapor to check for cross-contamination from vapor contaminants into the saturated zone. This was done twice for each reactor in Group 3 throughout the course of the experiment.

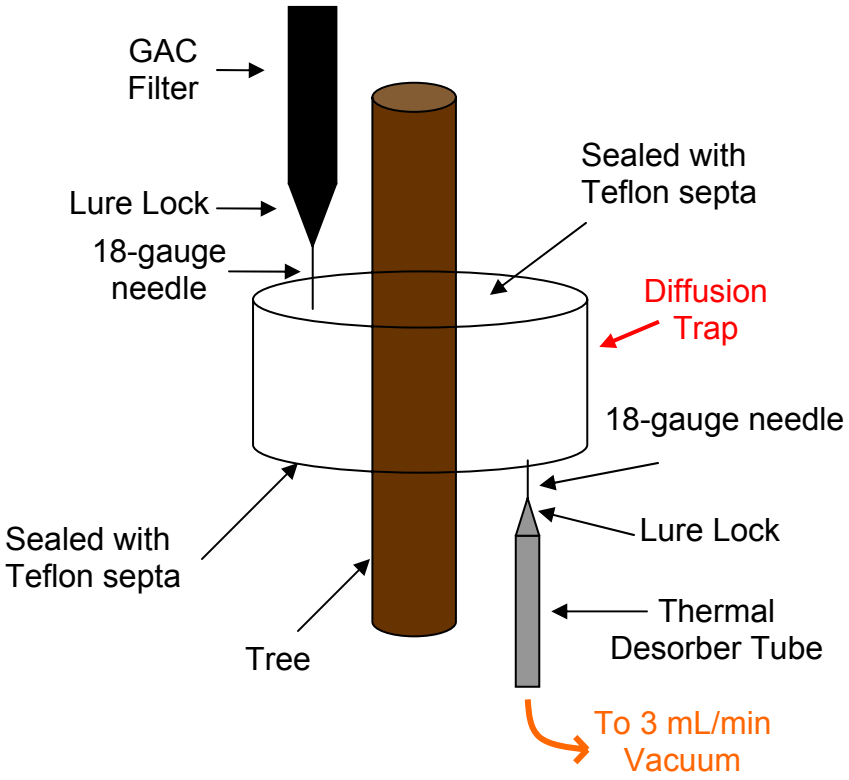

Figure 3.2 Detail of diffusion trap and thermal desorber tube setup. The glass trap was sealed with Teflon septa, vented with a GAC filter and the diffused gas sample was pulled through the thermal disrober tube with a vacuum.

3.4. TISSUE SAMPLE HEADSPACE CONCENTRATIONS

After dosing for approximately 1 month, reactors were dismantled and woody biomass from each tree was separated into six stem segments of approximately 5 cm each as shown in Figure 3.3. Each section of the tree was then placed in a clean 22 mL vial and capped immediately with a crimp top seal. The vials were allowed to equilibrate at room temperature for approximately 48 hours. Headspace from these samples was analyzed by GC using the FID. This method has been used previously by Vroblesky et al. (1999) and Ma and Burken (2002).

3.5. STANDARDS PREPARATION

Thermal desorber and headspace analysis contaminant concentrations were quantified by comparison to five-point standard curves. Thermal desorber standards were prepared by injecting all six contaminants at varying concentrations onto five clean, conditioned tubes. Vapor for MTBE, TCE, benzene, toluene and ethylbenzene was prepared in 250 mL glass bottles with mininert caps, each of which was filled halfway with 125 mL distilled water and enough of the respective contaminant to surpass saturation conditions, providing a small pool of NAPL phase contaminant to replenish the vapor phase contaminant in the headspace of the bottle. Naphthalene contaminated vapor was pulled directly from the headspace of a vial containing solid naphthalene crystals.

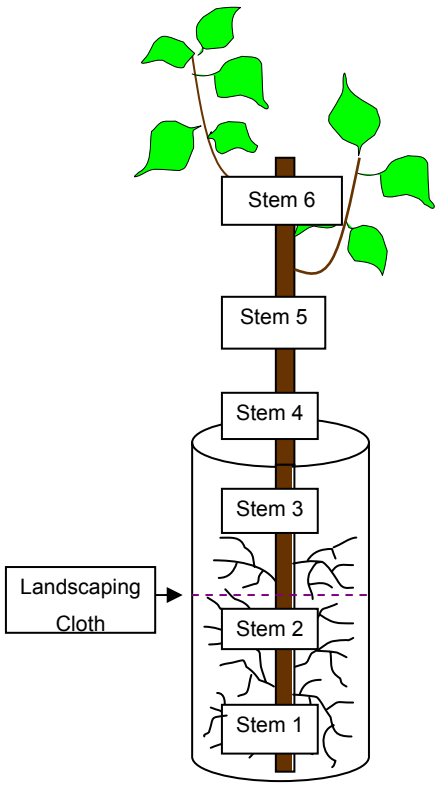

Figure 3.3 Nomenclature for tissue sample segments used for headspace concentration measurements.

Gastight syringes were used to pull a predetermined amount of headspace from the naphthalene crystals and the five bottles of saturated VOCs to obtain the five known masses of each contaminant which created the standard curve. A rubber pipette bulb was deflated and attached to the back end of the thermal desorber tube. The gastight syringe containing the contaminated vapor was inserted into the collecting end of the tube, and Teflon tape was wrapped around the opening of the tube to close the space between the syringe and the tube, minimizing the possibility of escape of the contaminant as it was injected. As the plunger of the syringe was pushed, the pipette bulb was inflated concurrently, pulling a slight vacuum through the tube to ensure that the maximum amount of contaminant would be captured on the Tenax. The tubes were immediately capped after the addition of each contaminant.

4. RESULTS AND DISCUSSION

4.1. EXPERIMENTAL SETUP

From the analysis of the diffusion traps and poplar tissues, hybrid poplar trees were shown to uptake and translocate each of the contaminants dosed in both aqueous and vapor phase as discussed below. Prior to this work, only PCE had been shown to be taken up by trees in vapor phase (Struckhoff et al. 2005). Collection of MTBE from the diffusion traps could not be confirmed because of problems with the collection method. Analysis of GC results indicates that MTBE was not retained on the Tenax packing of the thermal desorber tubes, and Carbograph packed tubes appeared to become saturated with water transpiring from the trees. Therefore, Tenax packed tubes were used despite their inability to retain MTBE. Aqueous uptake of MTBE by poplar trees has been previously confirmed by Ma et al. (2004) using activated carbon which captures MTBE more effectively than Tenax. Uptake and translocation of MTBE in this experiment was confirmed by tissue headspace concentrations, presented later in this section. Uptake of the other five contaminants tested was confirmed by collection from the diffusion traps and tissue samples. All five contaminants were present in every measurement taken from each of the three trees in the three groups: contaminated water and no air exchange (Group 1), contaminated water and clean air introduction (Group 2), and clean water and contaminated vapor input (Group 3).

Testing to ensure that the reactor design maintained adequate separation showed that contaminants were not present in the aqueous solution of the saturated zone at measurable levels. These samples from the saturated zone of reactors showed no presence of the contaminants introduced in the vapor phase. These tests indicate that the reactor design did maintain adequate separation of the vadose and saturated zones, and therefore cross-contamination from the vapor phase contaminants into the tree's water supply was minimal. Minimal contamination was anticipated. In order for vapor phase contaminants to reach the saturated zone, chemicals would have to diffuse downward faster than the tree transpires water. Vapor contaminants are unlikely to diffuse against the hydraulic gradient this rapidly.

As noted previously, due to variable water uptake, each tree is an individual and not identical replicates. Variability between the individuals was observed in the analytical data, including water transpiration rates and contaminant transpiration rates and concentrations. Therefore, quantifiable predictions about the amount of contaminant that will be taken up or diffused out of the tree cannot be made based solely on chemical and physical parameters of the contaminants, however, some general trends were observed in this experiment which can be better understood in relation to these parameters.

Briggs et al. (1982) were the first to make predictions for uptake based on a contaminants' log K_{ow} value. A log K_{ow} of 1.8 was determined to give an optimal transpiration stream concentration factor (TSCF) of approximately 0.8 when using barley and rye dosed with pesticides. TSCF, the concentration of the contaminant in the transpiration stream divided by the concentration in the bulk solution which is in contact with the roots, indicates how well the plant is taking up and translocating the contaminant. Burken and Schnoor continued this work with hydroponic lab-scale experiments using poplar trees which were tested for uptake of VOCs and indicated a slightly higher log K_{ow} of 2.50 for optimal uptake (1998). These mathematical relationships between the TSCF and log K_{ow} will be used for comparison to uptake demonstrated in this experiment, particularly the relationship developed by Burken and Schnoor, as this work included four of the six contaminants in this study. Table 4.1 shows the predicted TSCF values for each contaminant tested in this experiment using the log K_{ow} value shown in Table 4.2 and Burken's predictive relationship equation (1) followed by the relationship developed by Briggs (2). These predicted uptake values are for aqueous uptake only, with no consideration for vapor phase uptake. Additionally, these relationships do not account for the complications that arise from interactions with soil and microorganisms.

$$TSCF = 0.756 \exp\{-(\log K_{ow} - 2.50)^2 / 2.58\} \quad (1)$$

$$TSCF = 0.784 \exp\{-(\log K_{ow} - 1.78)^2 / 2.44\} \quad (2)$$

Table 4.1 Predicted TSCF values for each contaminant based on mathematical relationship to log K_{ow}.

Contaminant	**Predicted TSCF** Burken & Schnoor	**Predicted TSCF** Briggs
MTBE	0.338	0.634
TCE	0.754	0.663
Benzene	0.717	0.746
Toluene	0.745	0.558
Ethylbenzene	0.642	0.363
Naphthalene	0.568	0.282

Table 4.2 shows some physical and chemical characteristics of the contaminants used in this study. To reiterate, MTBE was dosed at 10 mg/L; benzene, toluene, ethylbenzene and TCE were dosed at 5mg/L; and naphthalene was dosed at 1 mg/L.

Table 4.2 Chemical and physical properties of contaminants tested.

Compound	Molecular Weight (g/mol)	Density (mg/mL)	Vapor Pressure (atm)	Solubility (mg/L)	Henry's K (unitless)	Log K_{ow} (unitless)
MTBE+	88.15	741	0.322	51,000	0.026	1.06
Benzene	78.1	876.5	0.126	1,789	0.228	2.13
Toluene	92.1	900	0.038	517.9	0.281	2.69
Ethylbenzene	106.2	900	0.013	168.3	0.330	3.15
TCE	131.4	1,456	0.098	1,100	0.38	2.42
Naphthalene*	128.2	997	0.00010	111.6	0.018	3.36

Schwarzenbach et al. (1993) except + from Chemfinder (2006). * - data is for solid.

4.2. VOLATILIZATION DATA

The cumulative mass of each contaminant collected was recorded for each reactor, and these values were averaged for the three individual reactors in each of the three treatment groups. These average cumulative mass values for each contaminant are presented numerically in Table 4.3 and graphically in Figure 4.1.

Table 4.3 Average cumulative mass of each contaminant collected from the diffusion traps of the three reactors in each treatment group. Average (Low, High).

	Cumulative Mass (ng)		
	Contaminated Water No Air	**Contaminated Water Clean Air**	**Clean Water Contaminated Vapor**
Benzene	4.4 (3.3, 5.9)	3.2 (2.1, 4.3)	3.6 (1.1, 6.2)
Toluene	7.9 (6.7, 9.4)	7.0 (3.9, 9.1)	10.0 (6.1, 16.7)
Ethylbenzene	4.6 (3.1, 5.5)	3.9 (1.9, 5.4)	3.2 (1.3, 6.2)
TCE	11.2 (4.4, 20.3)	14.3 (9.6, 21.6)	2.2 (1.5, 3.5)
Naphthalene	0.6 (0.5, 0.7)	0.3 (0.2, 0.5)	0.5 (0.4, 0.7)

All contaminants were taken up by trees from vapor phase and aqueous phase. This demonstrates without question that vapor phase benzene, toluene, ethylbenzene, TCE and naphthalene can be taken up, translocated and subsequently volatilized from trees.

Results for the four aromatic hydrocarbons tested (benzene, toluene, ethylbenzene and naphthalene) were similar regardless of the contaminants' delivery phase. In aqueous-phase introduction, less benzene, toluene and ethylbenzene was collected from the diffusion traps than TCE even though each was dosed at the same concentration.

Predicted TSCF values shown in Table 4.2 for benzene, toluene, ethylbenzene and TCE indicate that these four VOCs should have similar uptake, with ethylbenzene lowest.

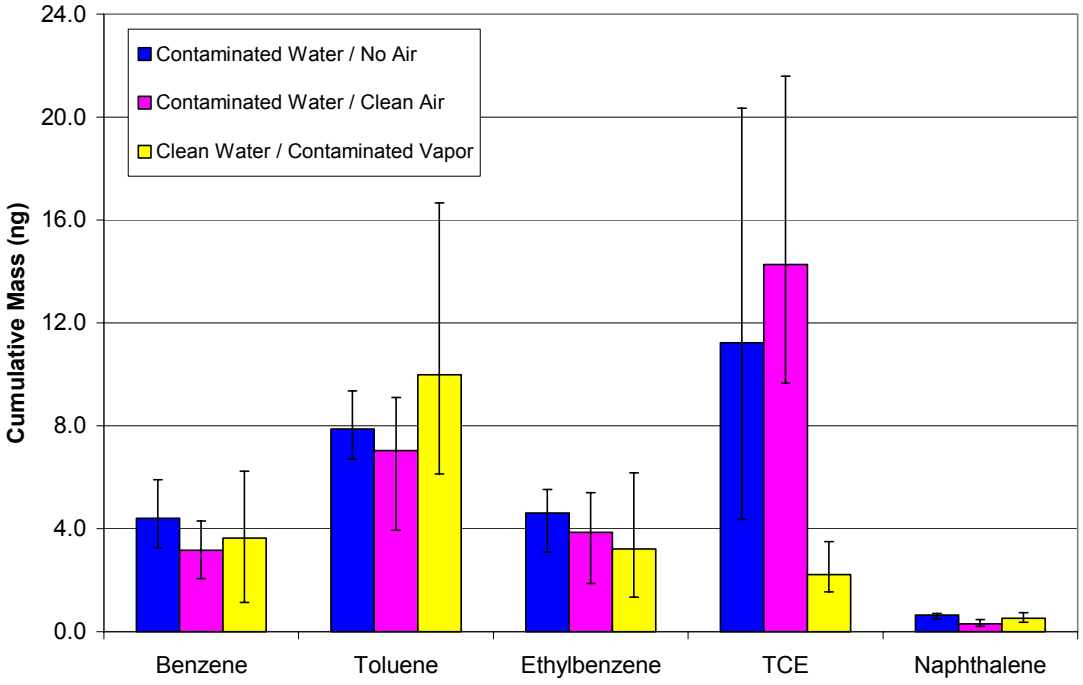

Figure 4.1 Average cumulative mass of each contaminant collected in the diffusion traps. Values are from the three trees in each group plotted as average; error bars represent high and low values.

Lower amounts of aromatic hydrocarbons collected compared to TCE may be explained partly by the addition of soil to this experiment in comparison to Burken and Schnoor's hydroponic reactor setup. Contaminants will sorb to soil depending on their log K_{ow} value and the fraction of organic content in the soil, and will also be subject to degradation by rhizosphere bacteria not present in a hydroponic setting. Considering bioavailability in a soil profile, benzene should be most readily taken up. Benzene,

toluene and ethylbenzene are also known to be amenable to aerobic degradation. Recent lab-scale experiments at UMR demonstrate that the fluctuation in the water table caused by the presence of a poplar tree improves aerobic conditions in the rhizosphere, encouraging benzene degraders and other bacteria to proliferate (Weishaar unpublished data). Benzene, ethylbenzene and to some extent, toluene, are known to be aerobically degradable, while TCE is not (Norris 1994). Lower amounts of these contaminants collected from the diffusion traps when compared with TCE most likely stem from decreased availability due to rapid degradation in the rhizosphere prior to uptake.

In the case of TCE, a significantly greater mass was collected from trees dosed with aqueous-phase TCE. The phase of TCE during delivery did impact its fate; uptake and/or diffusion of vapor phase TCE did not occur as quickly as with aqueous-phase. This trend may be explained by the high dimensionless Henry's constant of TCE. At 0.38, is the highest dimensionless Henry's constant of any contaminant tested here. As Henry's constant is essentially an air-water partitioning coefficient, this high number indicates that TCE is more likely to exist in vapor form than dissolved in water. For trees in Group 3, TCE was introduced in vapor phase, and likely to stay in this phase, as opposed to partitioning into the water in the transpiration stream. This tendency to not dissolve into water may have prevented a substantial fraction of the vaporous TCE from entering the transpiration stream of the tree and being translocated up to the diffusion traps.

Cumulatively, less benzene was collected from all aqueous-dosed reactors when compared with TCE and toluene. The log K_{ow} and Henry's constant for benzene seem favorable for phytovolatilization, and the predicted TSCF is comparable to that of TCE and toluene. However, previous studies, as well as ongoing research, suggest that benzene is subject to significant biodegradation in the rhizosphere. In this study, mass balance closure was not an objective and benzene degradation rapidly progresses to mineralization, so no measurement of degradation was possible via direct methods. Degradation is hypothesized to be the reason for the lower benzene mass collected because TCE and toluene are not as rapidly degraded as benzene. In fact, some studies

show that TCE and toluene only experience significant biodegradation with the addition of nutrients to the soil (Holden and Fierer, 2005). Recently in the Burken lab, enhanced degradation of BTEX compounds has been shown, and enumeration of BTEX degrading organisms revealed significantly higher BTEX degraders were present (Weishaar, 2007, personal communication). Overall, the cumulative amount of benzene collected does not appear dependent on its phase during dosing.

Results for ethylbenzene volatilization were similar to those of benzene volatilization. This may be due to the fact that, apart from a lower solubility, chemical characteristics for ethylbenzene are quite similar to those of benzene. Both were also most likely aerobically degraded in the rhizosphere, decreasing their availability to the trees. Slightly less ethylbenzene was collected when compared with toluene. With a log K_{ow} value of 3.15, ethylbenzene is increasingly farther from the optimal range of 1.8 – 2.50 and translocated less efficiently. Therefore, the higher lipophilicity may explain the difference in mass collection of the two contaminants. Ethylbenzene's relatively high dimensionless Henry's constant of 0.330 makes it a good candidate for vapor uptake, but its hydrophobicity makes it a likely candidate for binding in the root epidermis and other plant tissues along the translocation pathway, hindering translocation and subsequent volatilization.

The least amount of contaminant collected from all reactors was naphthalene, which is anticipated from its chemical properties. Several properties concurrently contribute to this result. Firstly, naphthalene, the only polycyclic aromatic hydrocarbon in this experiment, has the lowest solubility and predicted TSCF (Table 4.1) of any of the contaminants tested. Low solubility reduces the ability of the plant to take up the contaminant due to decreased availability. Furthermore, with a log K_{ow} of 3.36 and dimensionless Henry's constant of 0.018, naphthalene is the most lipophilic and least volatile contaminant tested here. These factors make it probable that substantial amounts of naphthalene would have become sorbed to the soil and bound to the root tissues. It is also the second heaviest contaminant in the study, further retarding diffusion into or out of the tree.

In order to normalize the data shown in Figure 4.1, the average cumulative masses for each contaminant were divided by that contaminant's average cumulative mass for Group 1 (Figure 4.2), because conditions for Group 1, dosed with contaminated water and no active air exchange, were the closest to naturally occurring environmental conditions. This presentation reiterates that the aromatic hydrocarbons tested produced lower cumulative masses under aerobic conditions, likely due to enhanced biodegradation in the rhizosphere. Higher mass of TCE, which is not amenable to aerobic biodegradation, was collected from trees with clean air exchange than those without. TCE is known to be subject to anaerobic degradation by reductive dechlorination (Kleopfer et al., 2005), which may explain the lower level of TCE mass collected from trees in Group 1, which received no air exchange.

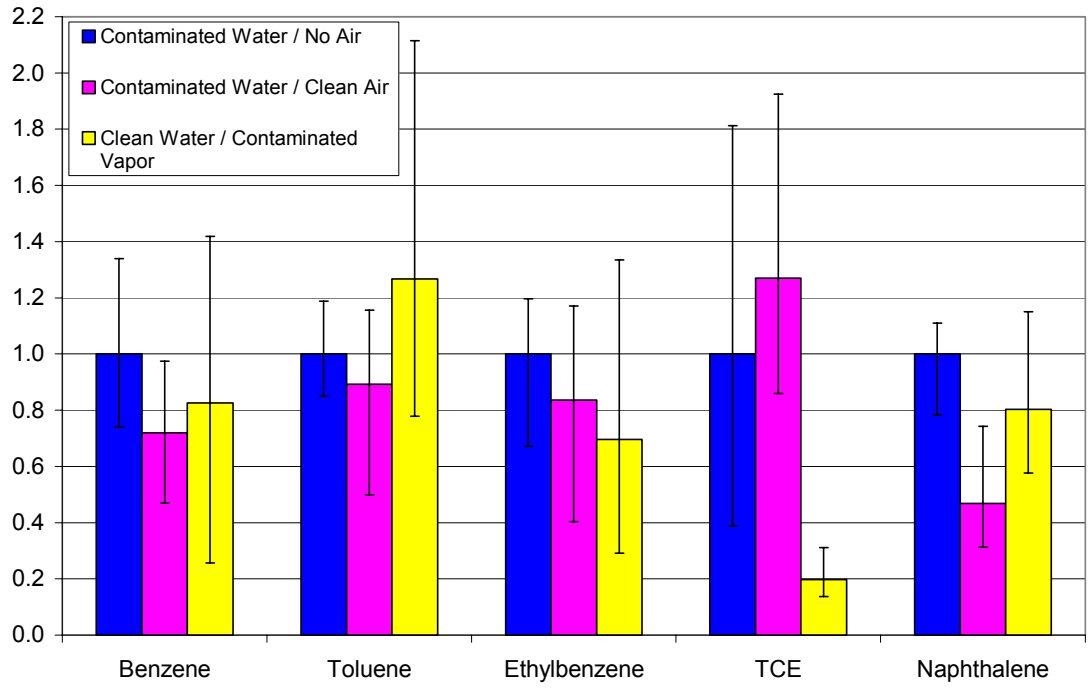

Figure 4.2 Average cumulative mass for each tree separated by contaminant and normalized to the average cumulative mass for trees in Group 1 (Contaminated water / No air exchange). Error bars represent high and low values also normalized to Group 1 values.

Qualitative trends from the mass of each contaminant collected are shown in Table 4.4, ranking from highest mass to lowest mass collected. MTBE is not represented in this table because it was not retained by the Tenax in the thermal desorber tubes.

Table 4.4 Relative rank of mass diffusion for each contaminant with comparison to the introduction phase.

	Contaminated Water No Air			**Contaminated Water Clean Air**			**Clean Water Contaminated Vapor**		
	1A	1B	1C	2A	2B	2C	3A	3B	3C
Highest Mass ↓	TCE	TCE	T	TCE	TCE	TCE	T	T	T
	T	T	TCE	T	T	T	B	B	E
	E	B	B	B	E	E	E	TCE	TCE
	B	E	E	E	B	B	TCE	E	B
Lowest Mass	N	N	N	N	N	N	N	N	N

Naphthalene consistently was the lowest mass collected from every reactor. In the reactors fed with contaminated vapor, toluene ranked the highest in mass of contaminant collected. In general, the highest amount collected from reactors fed with aqueous contaminants was TCE. Benzene and ethylbenzene maintained similar relative rank, regardless of in what phase the contaminant was fed.

4.3. TREE TISSUE HEADSPACE CONCENTRATION DATA

Although uptake of MTBE could not be determined from samples collected from the diffusion traps, headspace collected from the tissue samples did confirm that MTBE was taken up and translocated by poplar trees in both aqueous and vapor phases.

Previous research has shown aqueous MTBE to be taken up by hybrid poplar trees with volatilization to the atmosphere being a dominant removal mechanism (Rubin and Ramaswami 2001; Ma et al. 2004). This study presents the first confirmation that poplar trees will uptake, translocate and volatilize vapor phase MTBE from the vadose zone, Figure 4.3.

Headspace concentrations from tissue samples are shown only for MTBE. Concentrations of segments four through six for each tree were averaged into one representative concentration for a single tissue sample from each reactor as shown in Figure 4.3. Segments four through six were chosen because all were located above the cap of the reactor, ensuring that all were subject to similar conditions. Headspace concentrations for TCE were not substantially different from volatilization data so they are not shown. Benzene, toluene and ethylbenzene concentration data was not considered useful as substantial degradation was suspected during the equilibration time in the vial, and is therefore not shown.

Naphthalene was not detected in any headspace samples. As low diffusion rates over days of sampling resulted in low mass of naphthalene collected in the diffusion traps, and due to its lipophilic nature, diffusion of naphthalene from the tissue samples was not anticipated.

Although the predicted TSCF for MTBE is low due to its low log K_{ow} value of 1.06, several studies have shown MTBE to be readily taken up and subsequently volatilized (Ramaswami and Rubin 2001; Ma et al. 2004). Recent work has shown that MTBE is not subject to significant biodegradation in the rhizosphere of poplar trees (Ramaswami et al. 2003), leaving more contaminant available for uptake. MTBE is known to be recalcitrant under anaerobic conditions (Suflita and Mormile 1993) and was shown to move through poplar trees unaltered (Ramaswami and Rubin 2001). Lower concentrations in the headspace of tissue samples from trees in Groups 2 and 3 therefore are not attributed to rhizosphere degradation or phytodegradation. As volatilization was shown to be an important removal mechanism with concentrations of MTBE in the tree

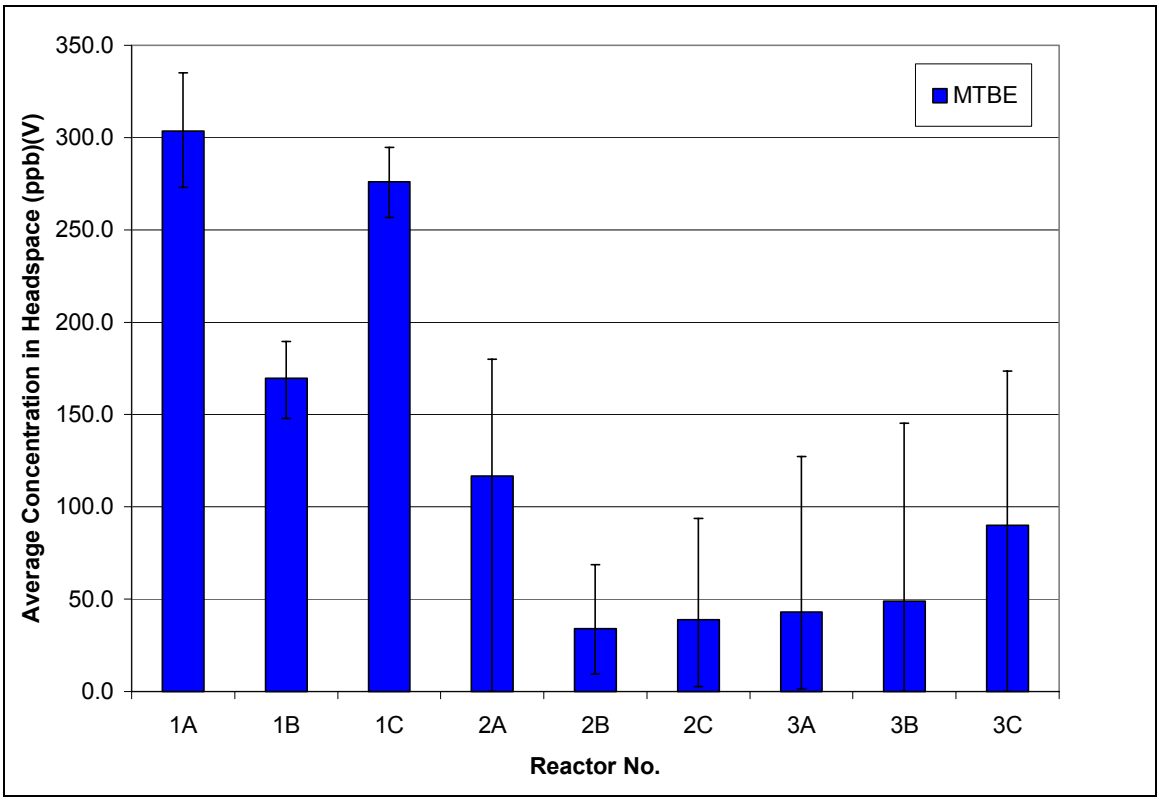

Figure 4.3 Average tissue headspace concentrations of MTBE in stem segments 4 – 6 (all stem pieces above cap of the reactor) from each tree.

tissues decreasing with height (Ma et al. 2004), diffusion out of the tree is also likely to occur in the unsaturated zone after aqueous uptake from the saturated zone. Air exchange in the vadose zone of trees in Group 2 would constitute an enhanced environment for such diffusion, creating a concentration gradient which would encourage diffusion out of the tree tissues. The absence of this air exchange in Group 1 would lead to less diffusion of MTBE out of the tree in the vadose zone, hence a higher concentration of contaminant left in the transpiration stream and above-septa tree tissues. Diffusion out of the tree must not have occurred as quickly as aqueous uptake occurred, or levels of MTBE in the samples of Group 2 would have been below detection because all contaminant would have already volatilized out. In order for vapor phase MTBE to be taken up by trees in Group 3, this slow diffusion process must occur into the tree as well,

crossing the cell membranes to reach the transpiration stream. This led to the low concentrations collected from tissue samples in Group 3, and explains why concentrations collected from Groups 2 and 3 were more similar to each other than they were to Group 1; aqueous-phase MTBE was readily taken up in Group 2, a large portion of which was subsequently volatilized back into the unsaturated zone, while levels of MTBE in Group 3 trees were never high because the uptake relied on diffusion, which appears to be slower than aqueous uptake.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSIONS

Uptake, translocation and volatilization of one semi-volatile and five volatile organic compounds occurred in hybrid poplar trees. These processes were confirmed by contaminant mass collected from diffusion traps attached to the stems and by headspace concentrations from stem samples at the completion of the experiment. Uptake from the vadose zone was noted for the first time for these contaminants.

Some general trends were observed based on the physical and chemical properties of the contaminants tested. Similar amounts of benzene and ethylbenzene were collected, both of which are aromatic hydrocarbons which are subject to significant biodegradation in the rhizosphere. A slightly higher amount of toluene was collected than the other aromatic hydrocarbons, as predicted by its higher TSCF value and optimal log K_{ow}. Due to naphthalene's high lipophilicity and low solubility, the lowest amount of any contaminant collected was naphthalene. For all of the above contaminants, phase during delivery did not seem to affect the amount collected. This was not true, however, for TCE, for which a significantly larger amount was collected from reactors dosed with aqueous phase contaminant than from vapor phase. Overall, the greatest amount of contaminant collected from all trees dosed with aqueous contaminants was TCE, which is believed to be due to the recalcitrant nature of TCE which increased its availability to the tree. Uptake of MTBE in both aqueous and vapor phase were confirmed by headspace concentrations of woody tissue, however, vapor phase uptake appears to be a slow diffusion process.

5.2. RECOMMENDATIONS

This research lays the groundwork for establishing vapor phase uptake of chlorinated solvents and aromatic hydrocarbons by plants as a possible alternative for vapor intrusion remediation. Now that vapor phase uptake of multiple contaminants by trees has been shown, the next steps can be taken to further understand the mechanism.

Because such a small amount of contaminant was collected in the diffusion traps, performing a mass balance on some of the vapor phase contaminants would provide an interesting insight into the true fate of the entire volume of the contaminant fed to the tree. Determining what fraction of the vapor contaminant is taken up by the tree and what fraction is lost to the atmosphere through the ground, sorbed to soil, degraded in the rhizosphere, etc. would provide more basis for whether or not phytoremediation could truly be a viable remediation alternative.

Additionally, because real field sites would have so many changing parameters, uptake of vapor contaminants could vary with changing conditions. Studying the nature of the uptake of contaminated vapor with a variety of soil porosities, plant types or rainfall amounts, for example, could yield valuable insight into the translation of this work into a field-scale environment.

APPENDIX A.

DIFFUSION TRAP DATA FOR EACH CONTAMINANT

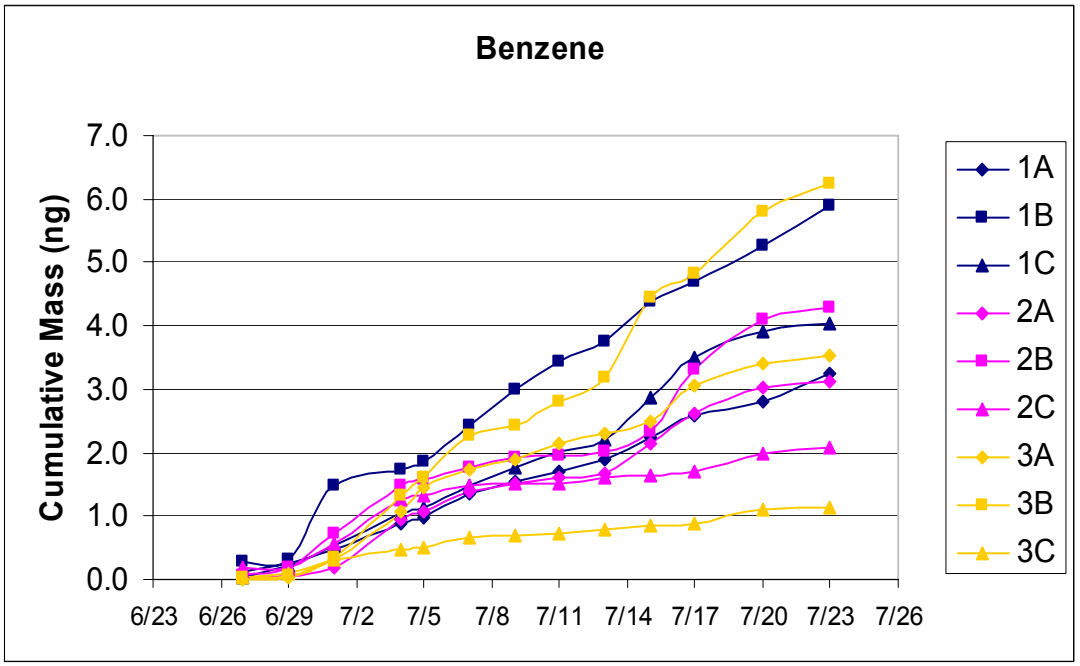

Figure A.1 Mass of benzene diffused per day from each reactor

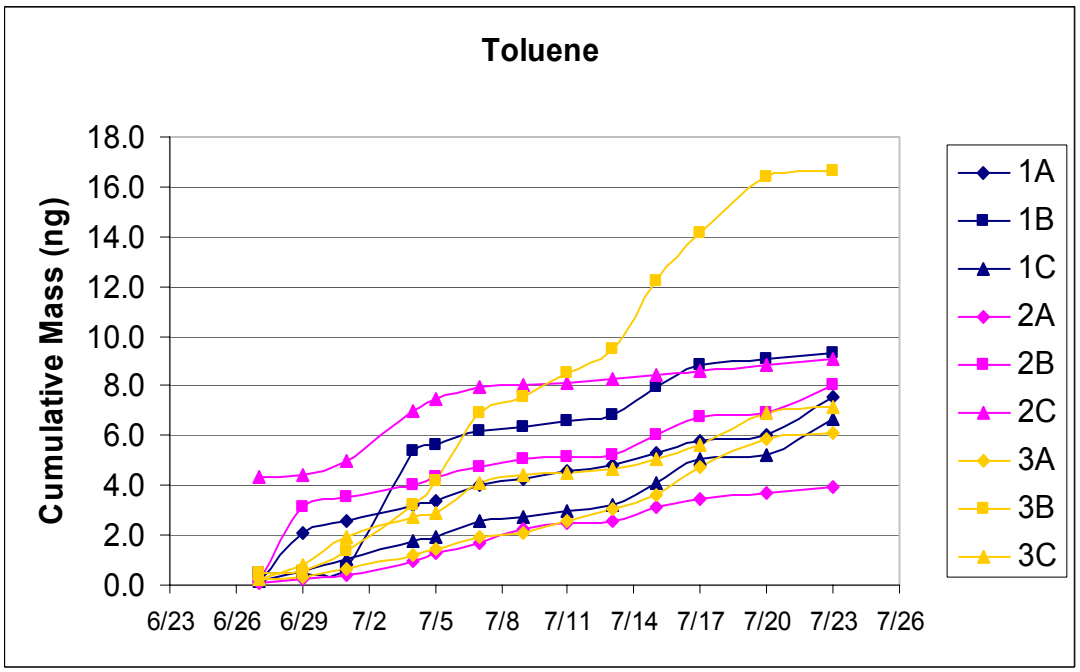

Figure A.2 Mass of toluene diffused per day from each reactor

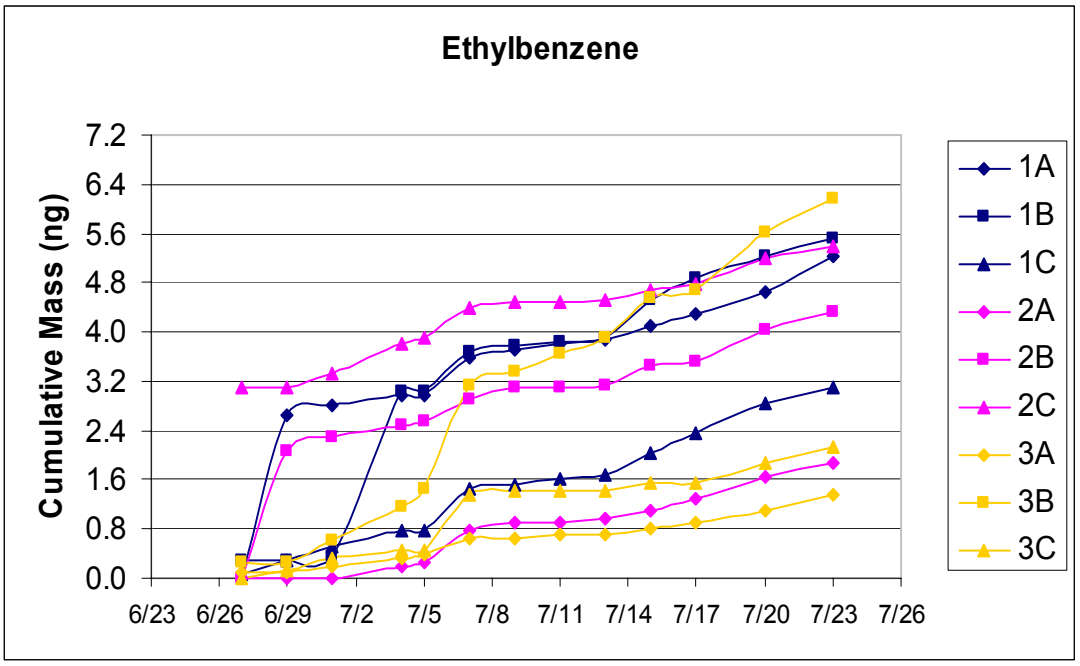

Figure A.3 Mass of ethylbenzene diffused per day from each reactor

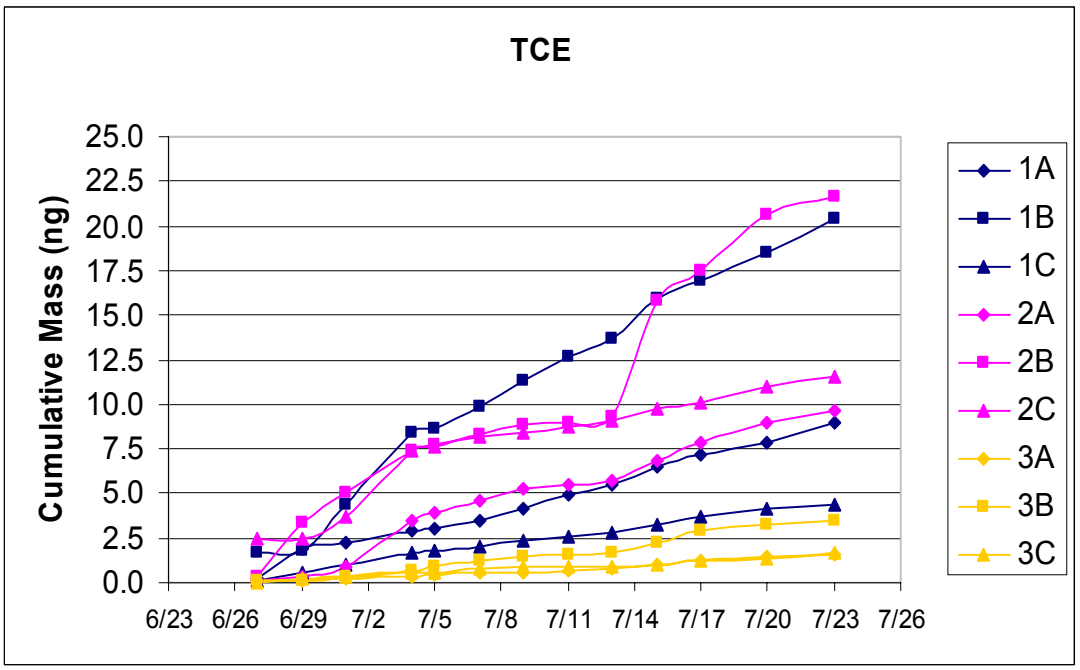

Figure A.4 Mass of TCE diffused per day from each reactor

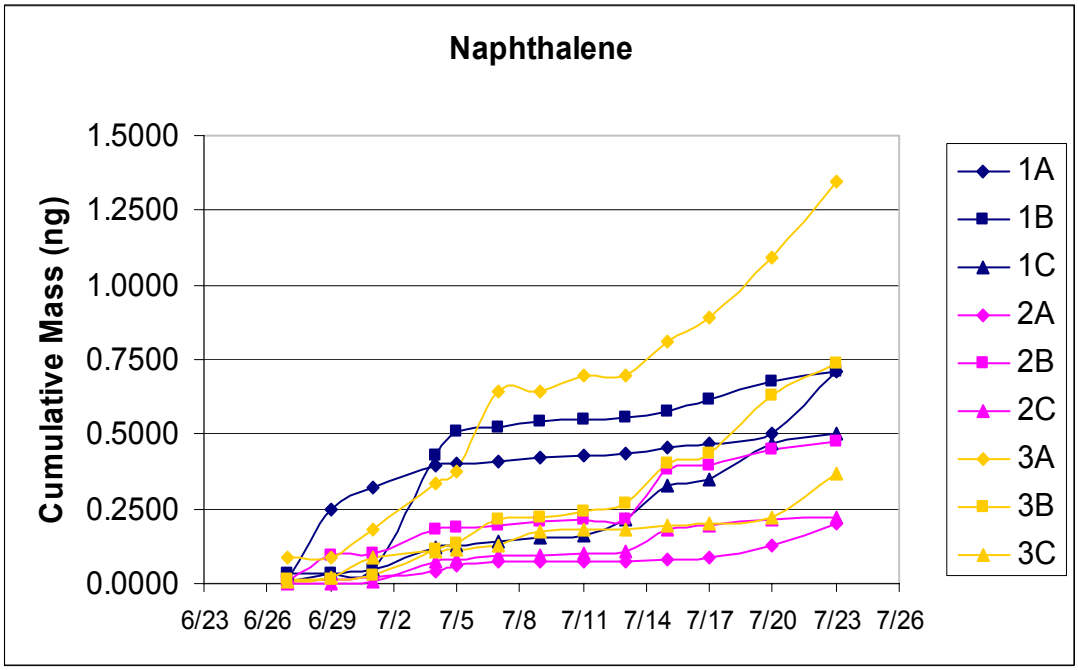

Figure A.5 Mass of naphthalene diffused per day from each reactor

APPENDIX B.

DIFFUSION TRAP DATA FOR EACH REACTOR

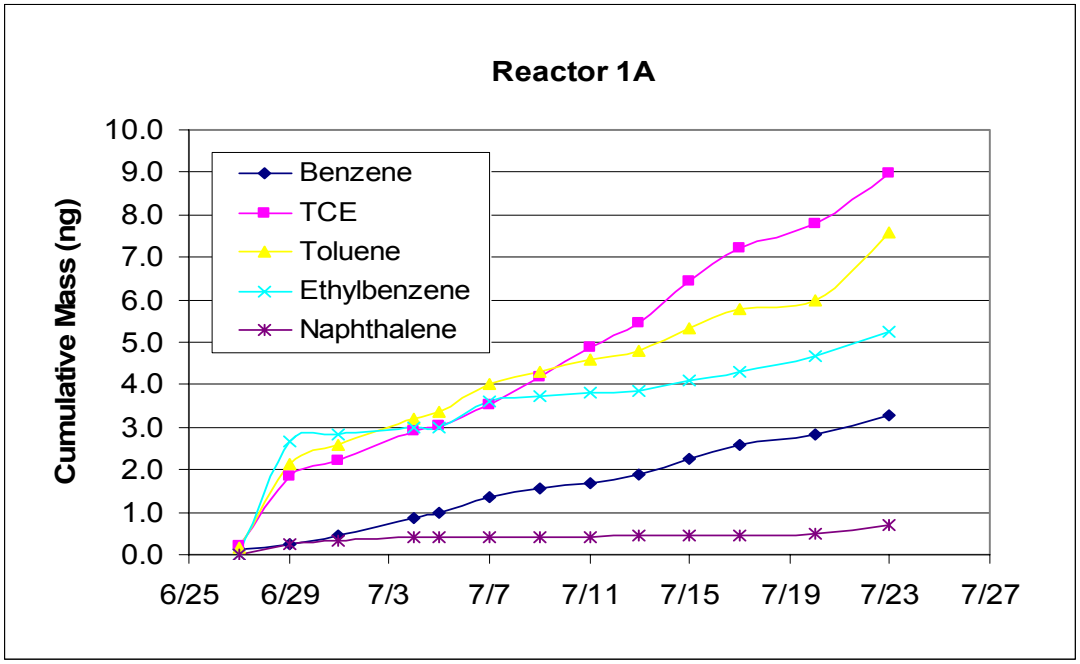

Figure B.1 Mass of each contaminant diffused per day from reactor 1A

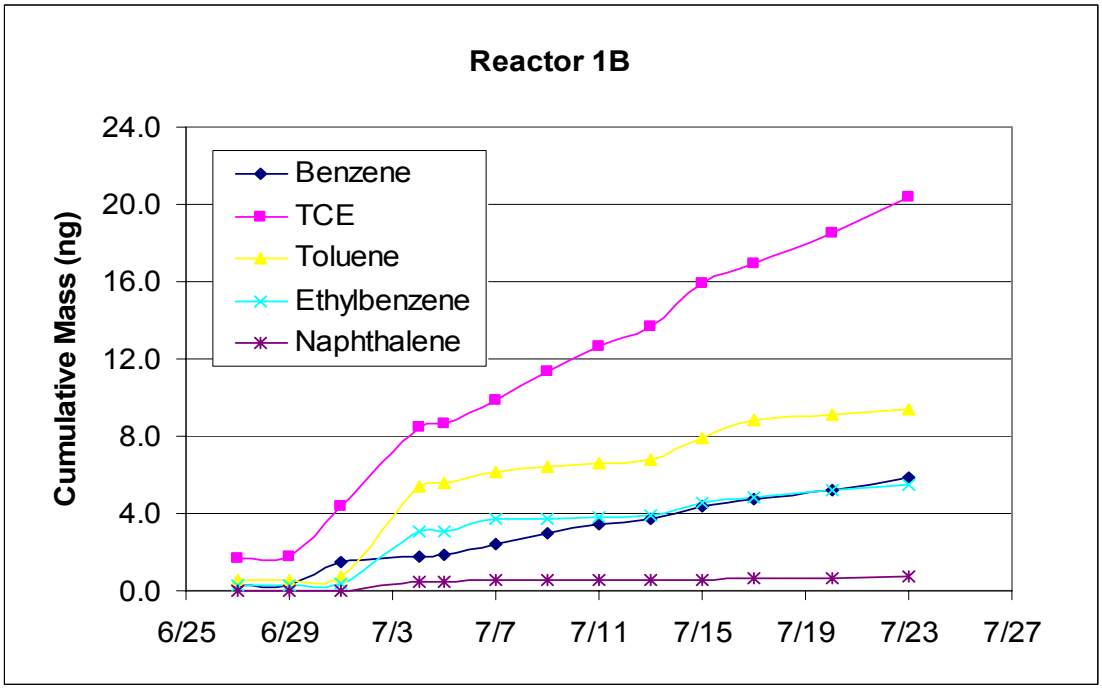

Figure B.2 Mass of each contaminant diffused per day from reactor 1B

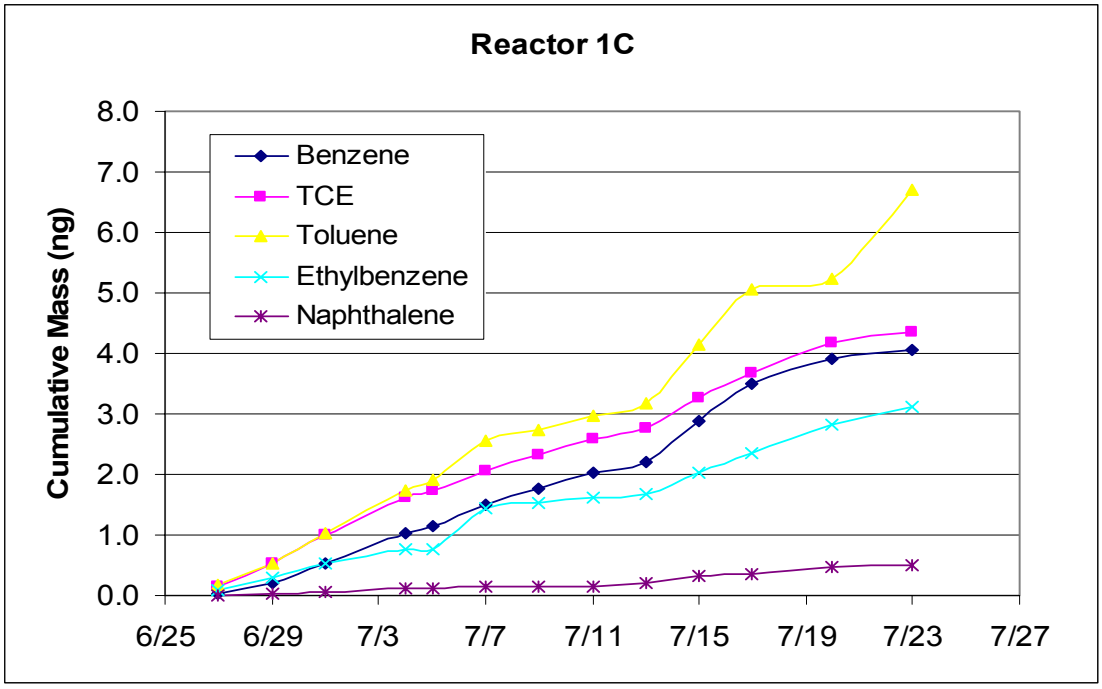

Figure B.3 Mass of each contaminant diffused per day from reactor 1C

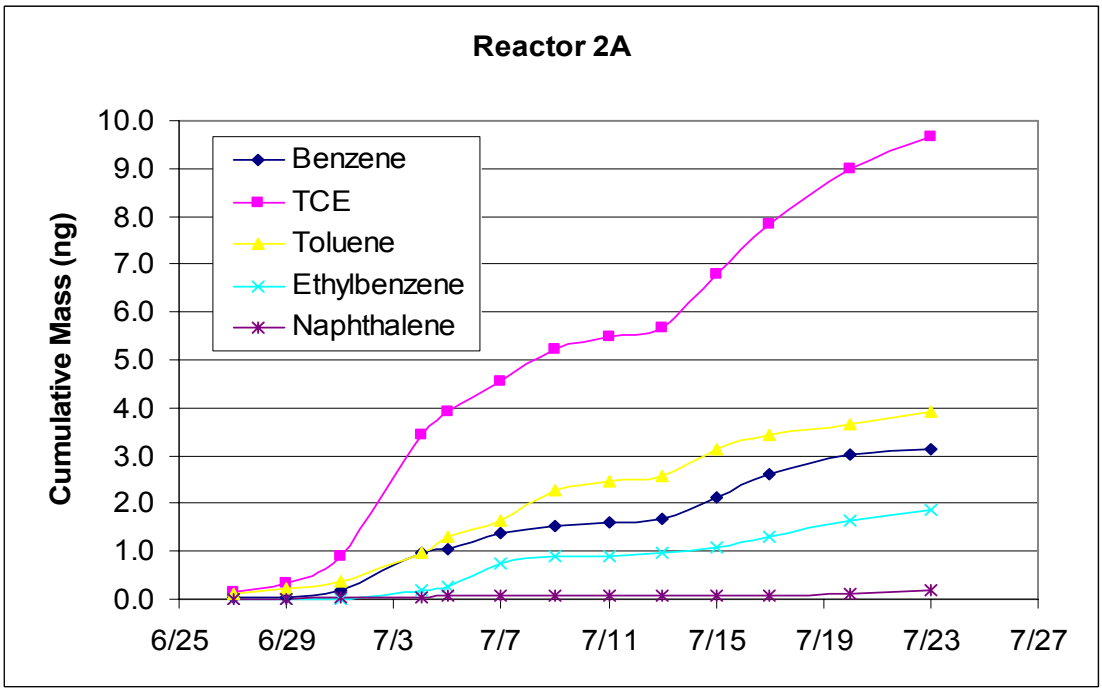

Figure B.4 Mass of each contaminant diffused per day from reactor 2A

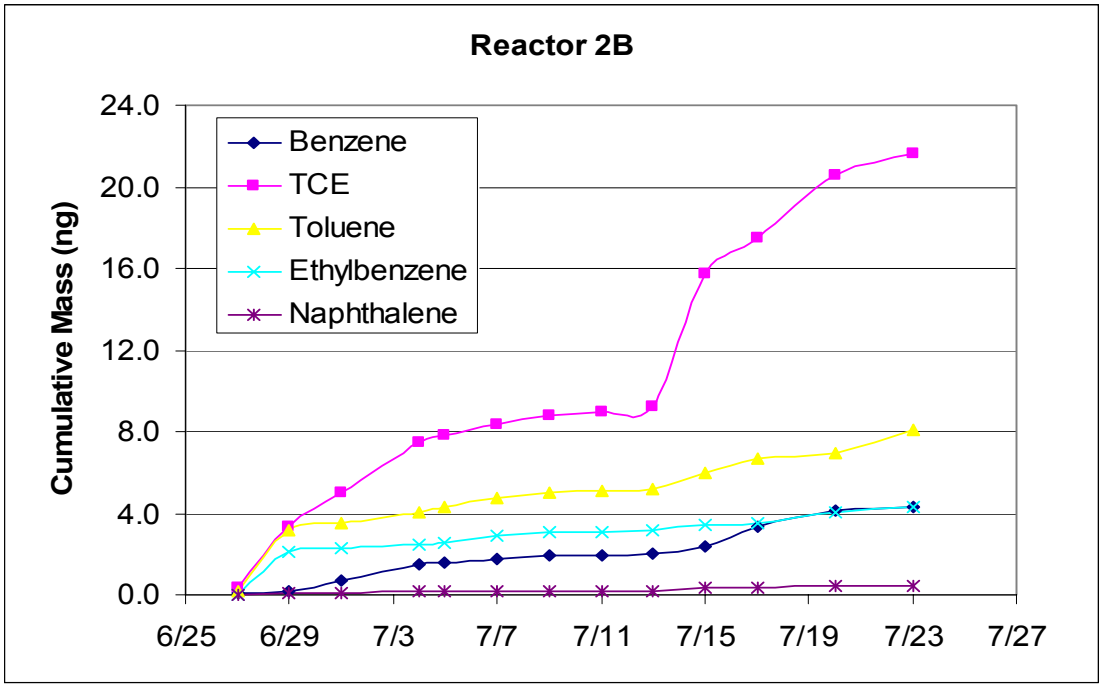

Figure B.5 Mass of each contaminant diffused per day from reactor 2B

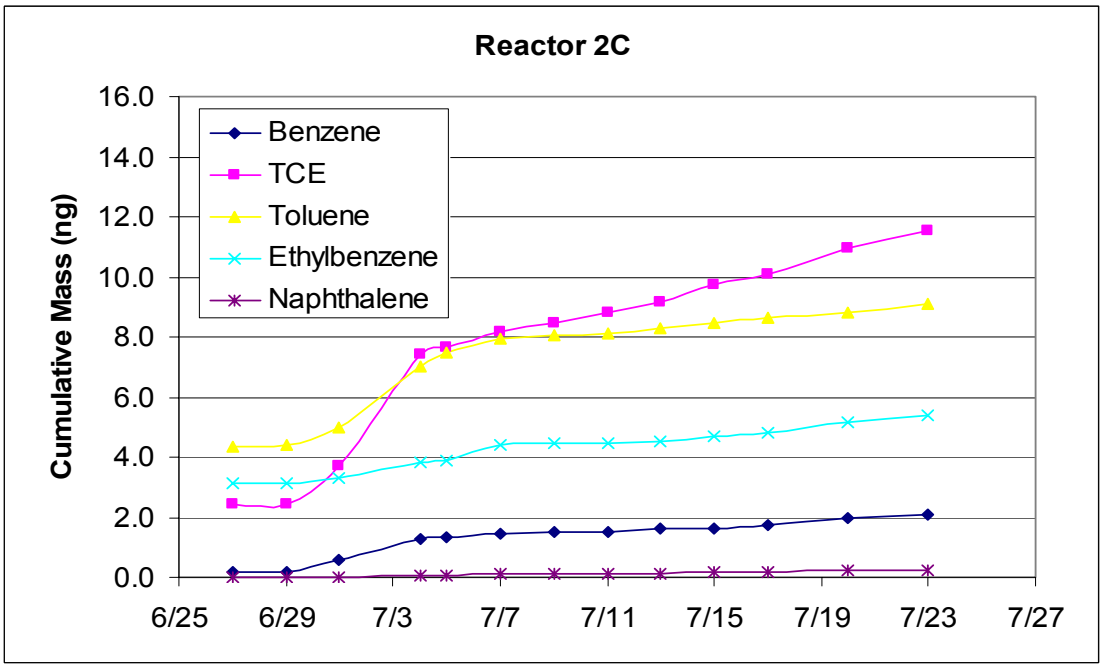

Figure B.6 Mass of each contaminant diffused per day from reactor 2C

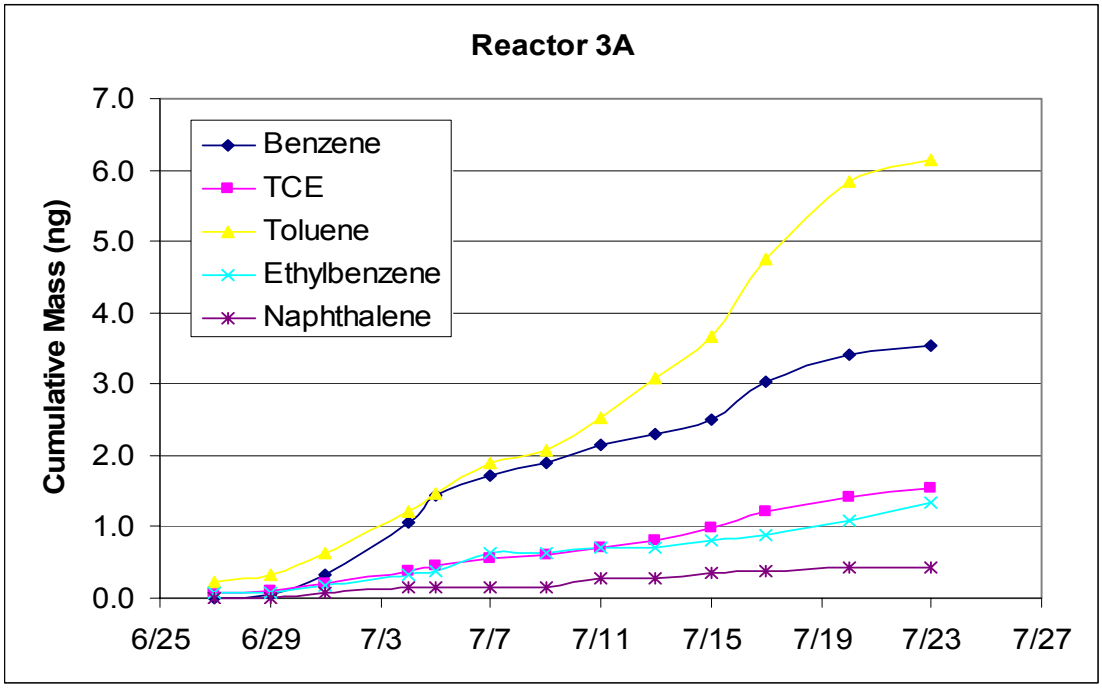

Figure B.7 Mass of each contaminant diffused from reactor 3A

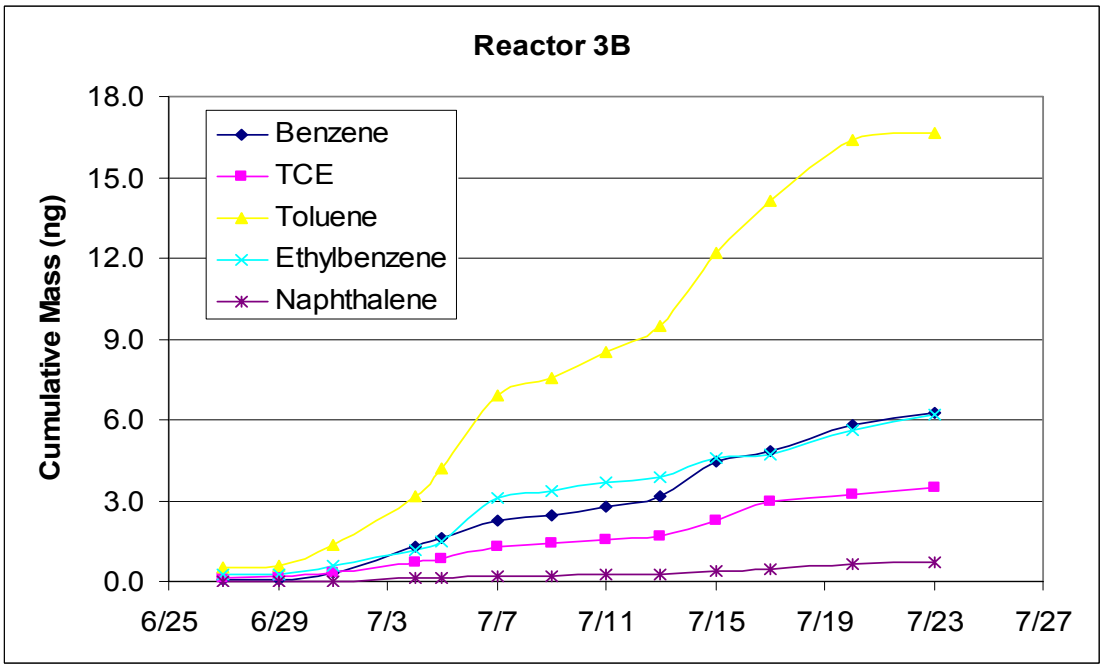

Figure B.8 Mass of each contaminant diffused from reactor 3B

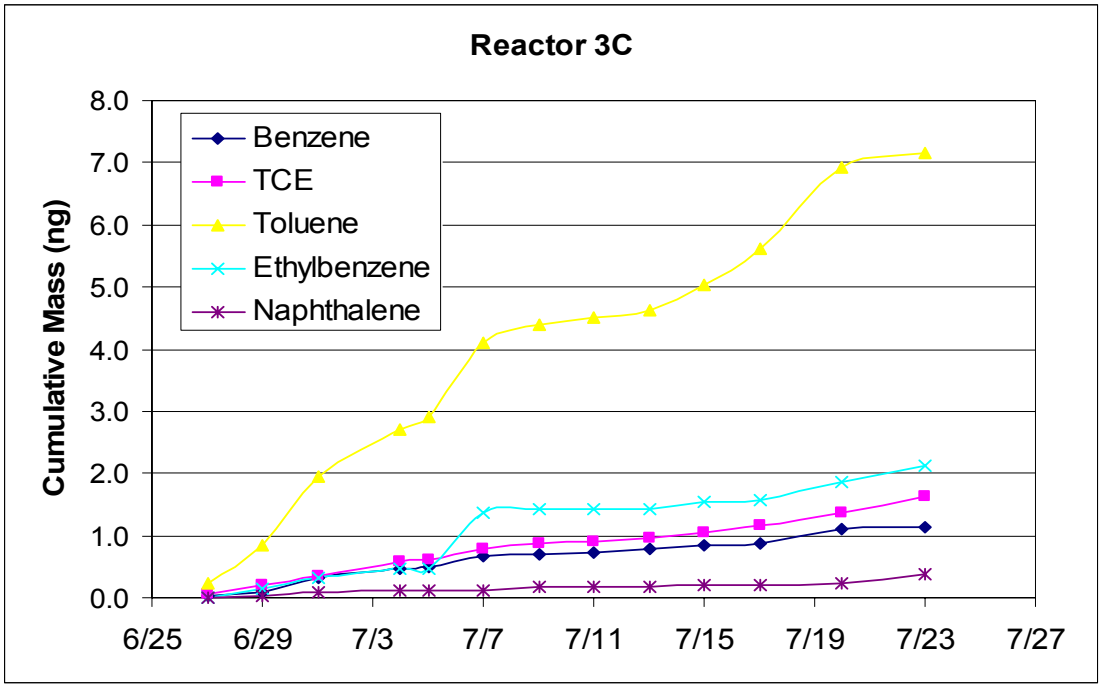

Figure B.9 Mass of each contaminant diffused per day from reactor 3C

APPENDIX C.

TRANSPIRATION DATA

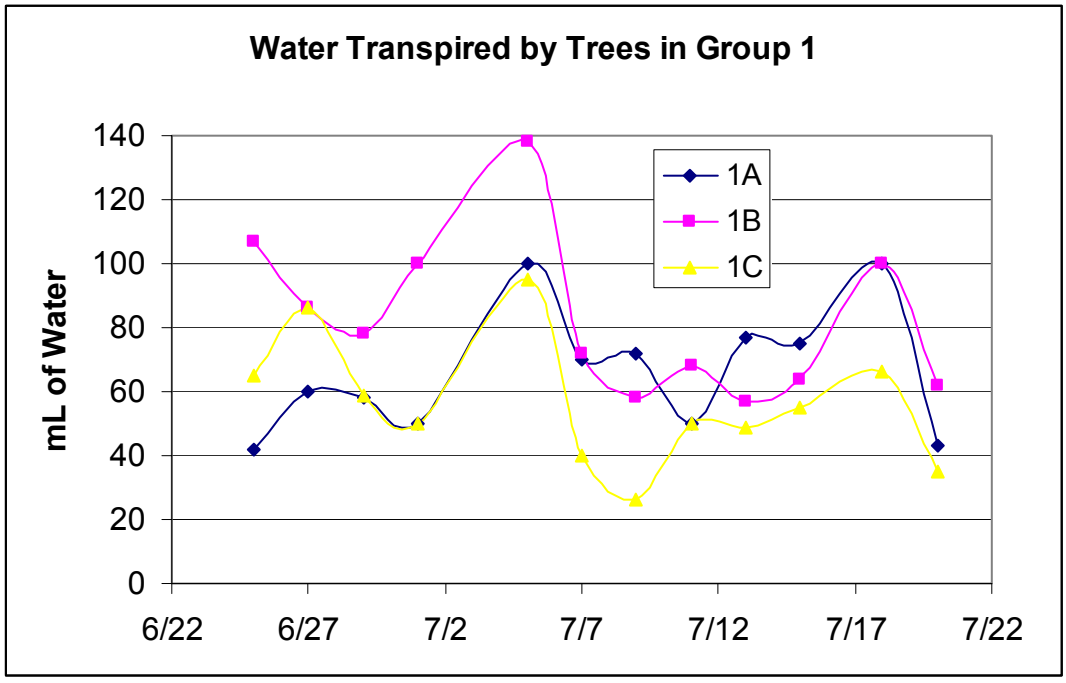

Figure C.1 Volume of water transpired from each reactor in Group 1 on days when sampling and dosing was conducted.

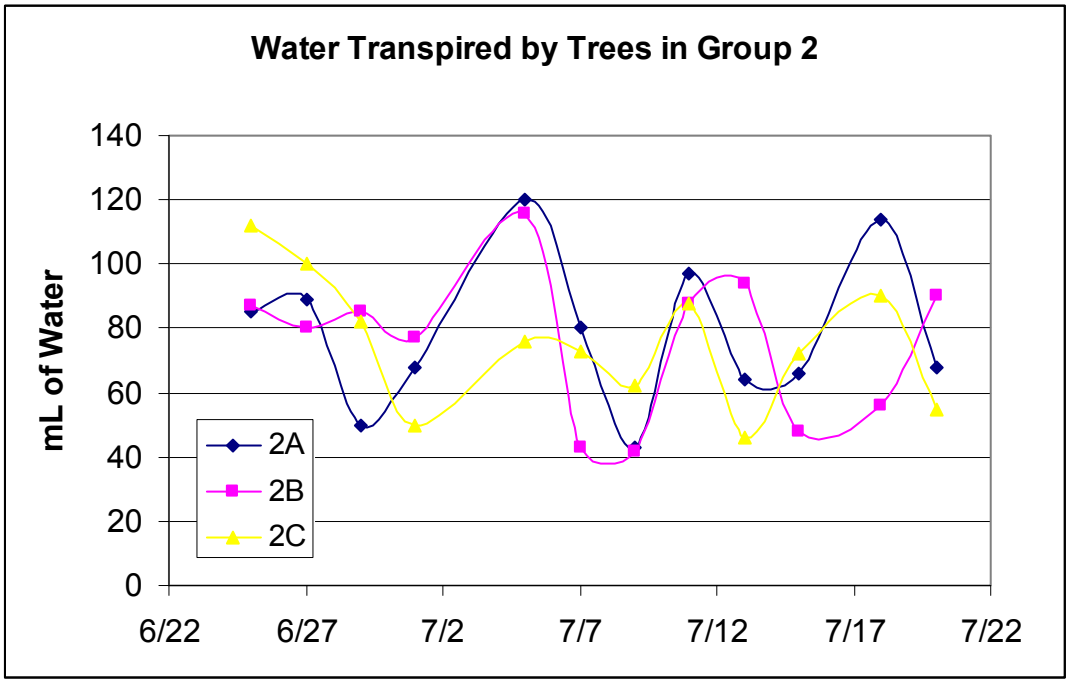

Figure C.2 Volume of water transpired from each reactor in Group 2 on days when sampling and dosing was conducted.

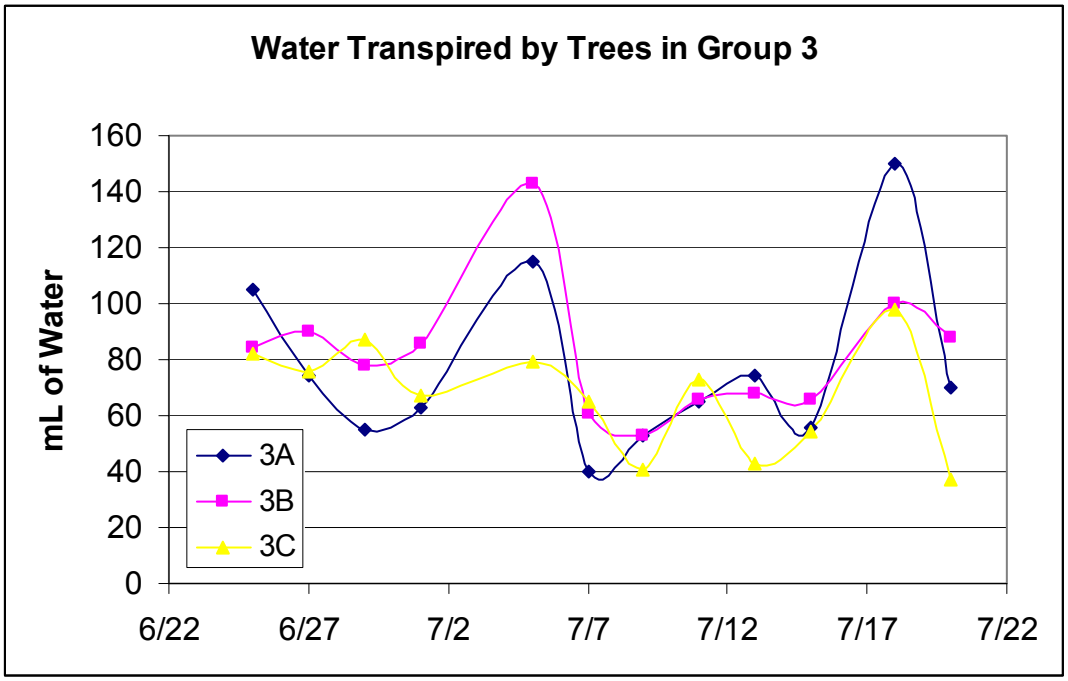

Figure C.3 Volume of water transpired from each reactor in Group 3 on days when sampling and dosing was conducted.

Table C.1 Overall average transpiration rate from each tree at the end of the experiment.

Reactor	Average Transpiration Rates (mL/day)
1A	29.5
1B	36.7
1C	25.0
2A	35.0
2B	33.6
2C	33.6
3A	34.1
3B	36.4
3C	29.7

APPENDIX D.

MASS OF CONTAMINANTS DOSED

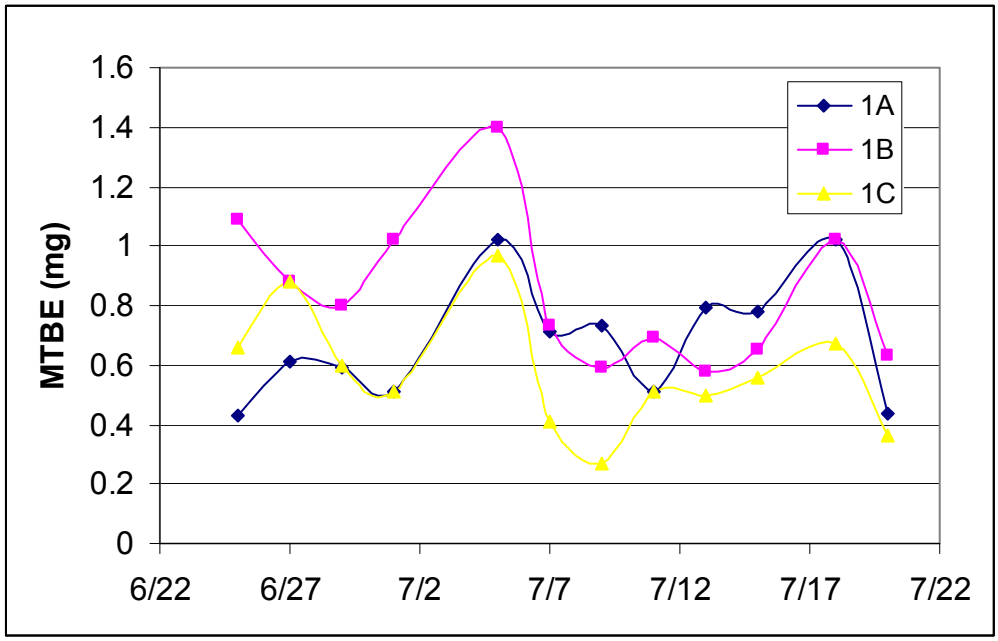

Figure D.1 Mass of MTBE in mg dosed to each tree in groups 1 and 3 during each dosing. Reactors 3A, 3B and 3C received the same mass of contaminant as reactors 1A, 1B and 1C respectively.

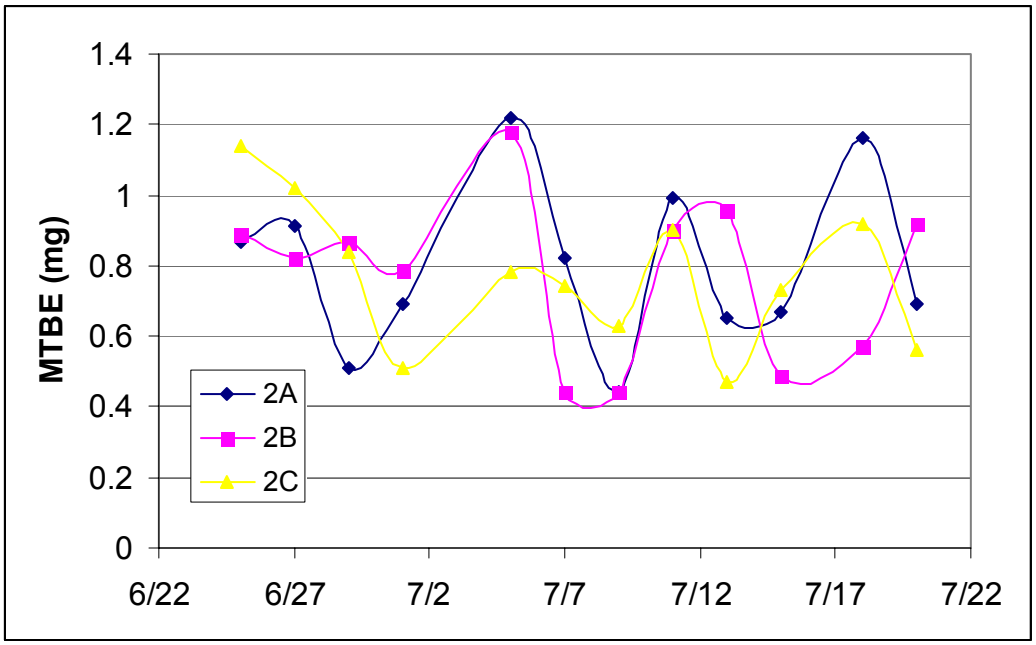

Figure D.2 Mass of MTBE in mg dosed to each tree in group 2 during each dosing.

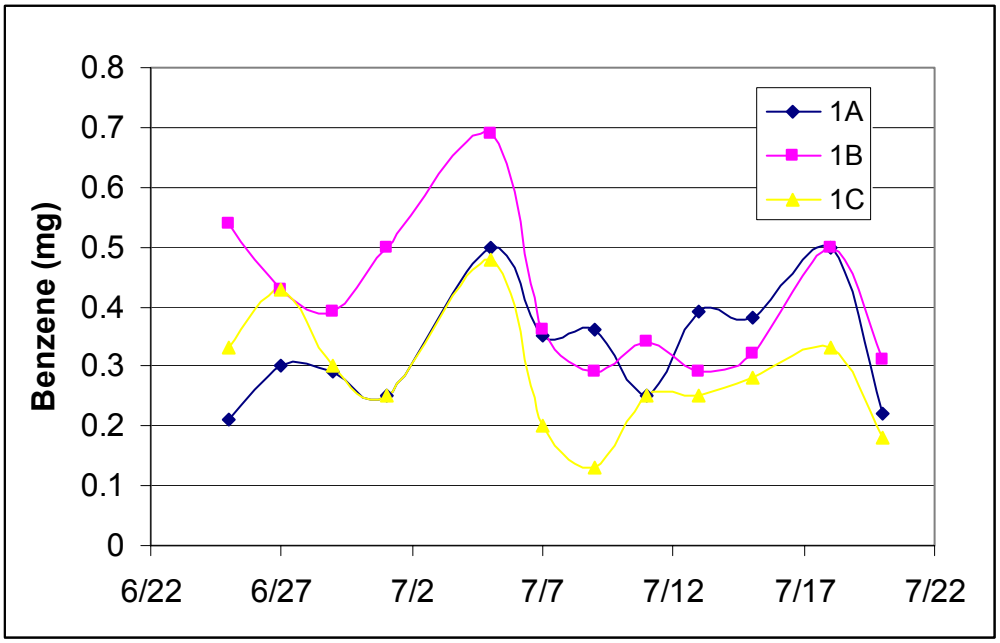

Figure D.3 Mass of benzene in mg dosed to each tree in groups 1 and 3 during each dosing. Reactors 3A, 3B and 3C received the same mass of contaminant as reactors 1A, 1B and 1C respectively.

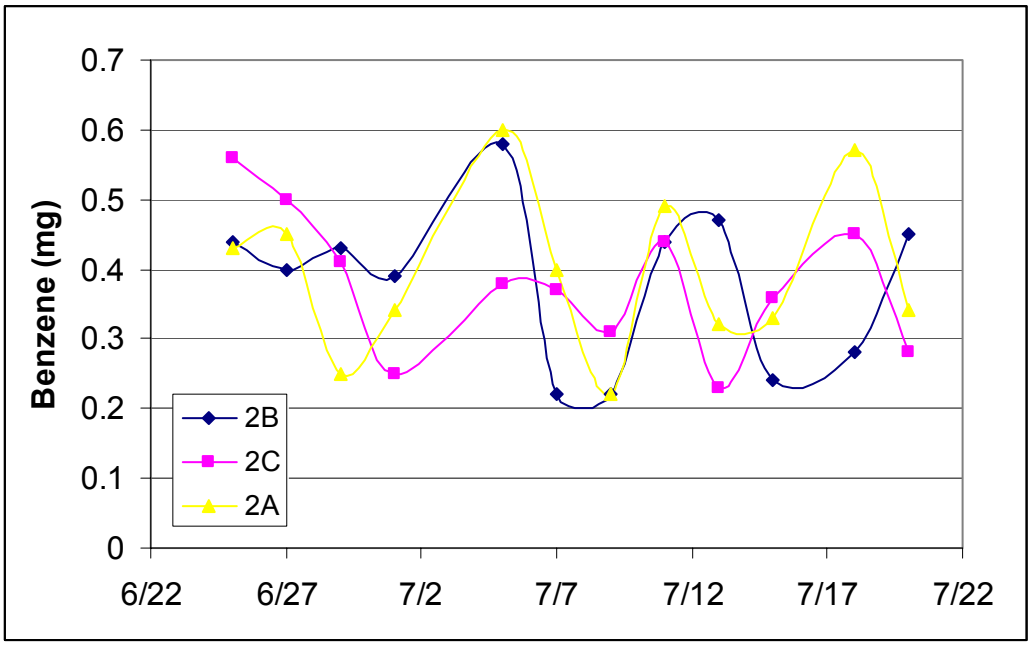

Figure D.4 Mass of benzene in mg dosed to each tree in group 2 during each dosing.

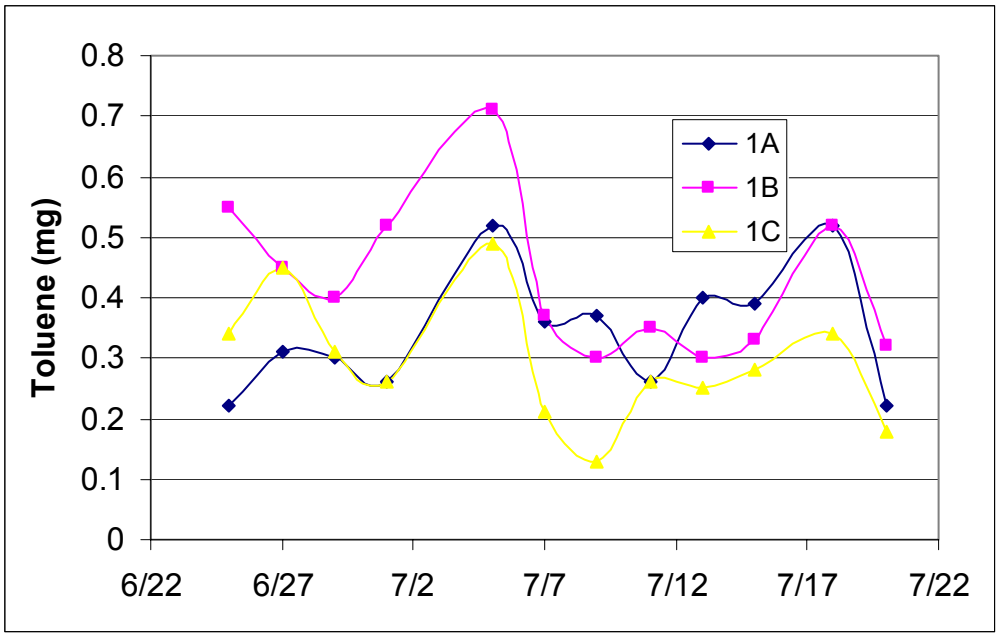

Figure D.5 Mass of toluene in mg dosed to each tree in groups 1 and 3 during each dosing. Reactors 3A, 3B and 3C received the same mass of contaminant as reactors 1A, 1B and 1C respectively.

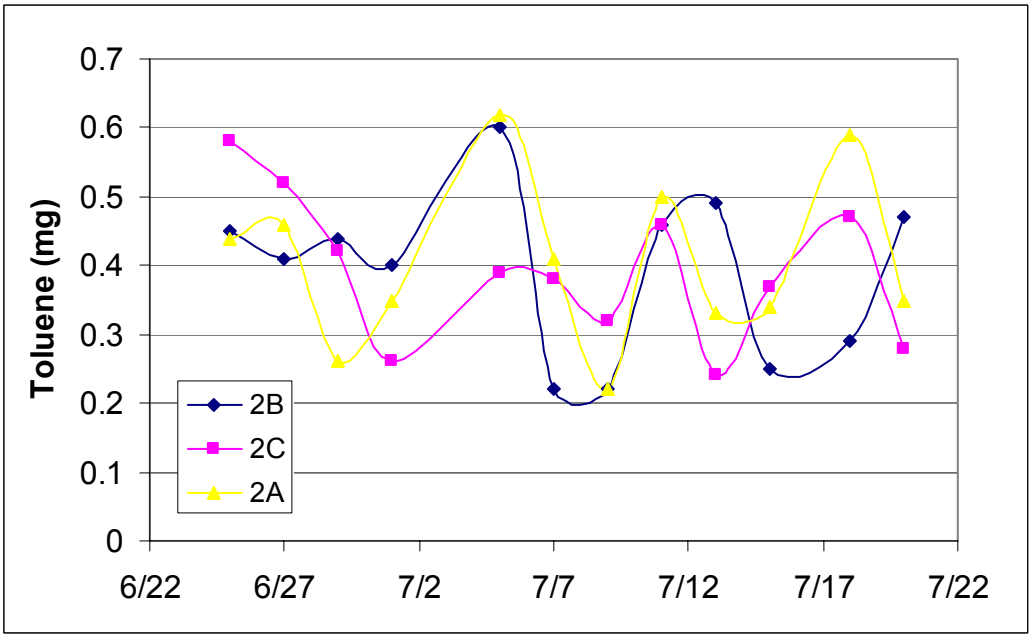

Figure D.6 Mass of toluene in mg dosed to each tree in group 2 during each dosing.

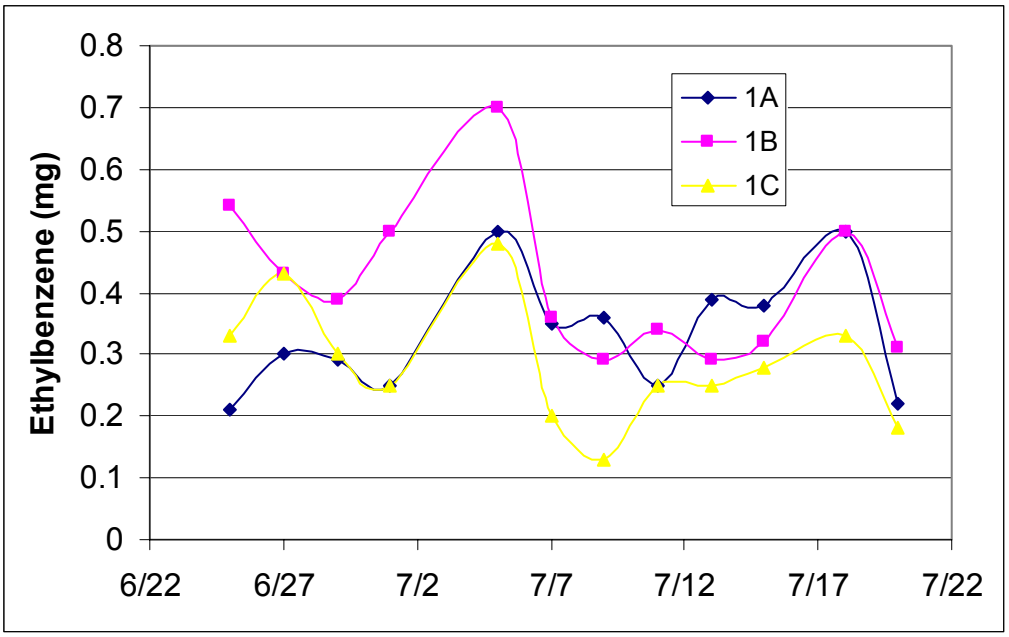

Figure D.7 Mass of ethylbenzene in mg dosed to each tree in groups 1 and 3 during each dosing. Reactors 3A, 3B and 3C received the same mass of contaminant as reactors 1A, 1B and 1C respectively.

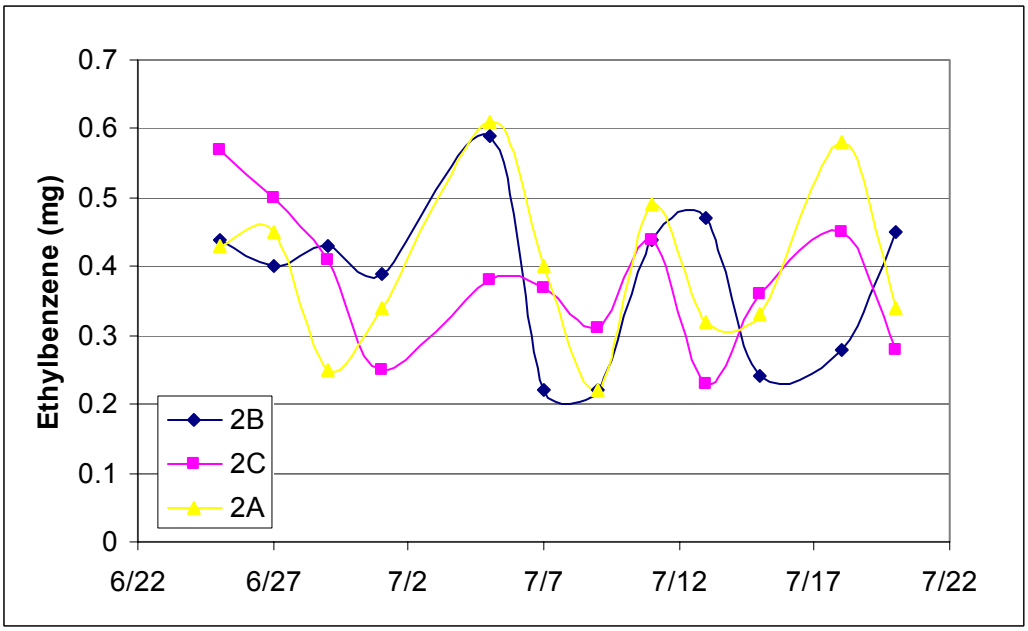

Figure D.8 Mass of ethylbenzene in mg dosed to each tree in group 2 during each dosing.

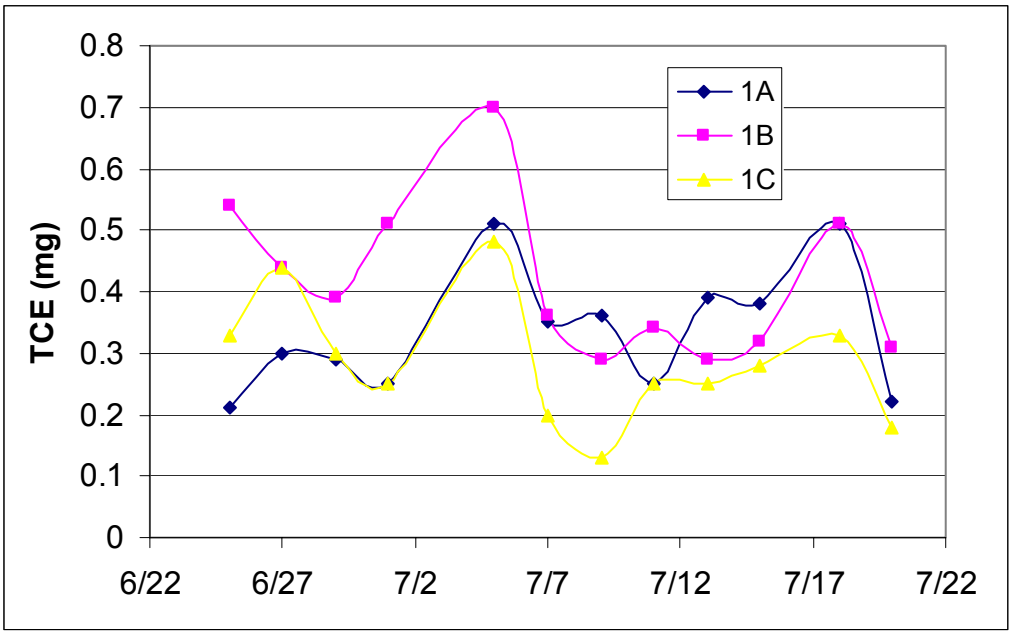

Figure D.9 Mass of TCE in mg dosed to each tree in groups 1 and 3 during each dosing. Reactors 3A, 3B and 3C received the same mass of contaminant as reactors 1A, 1B and 1C respectively.

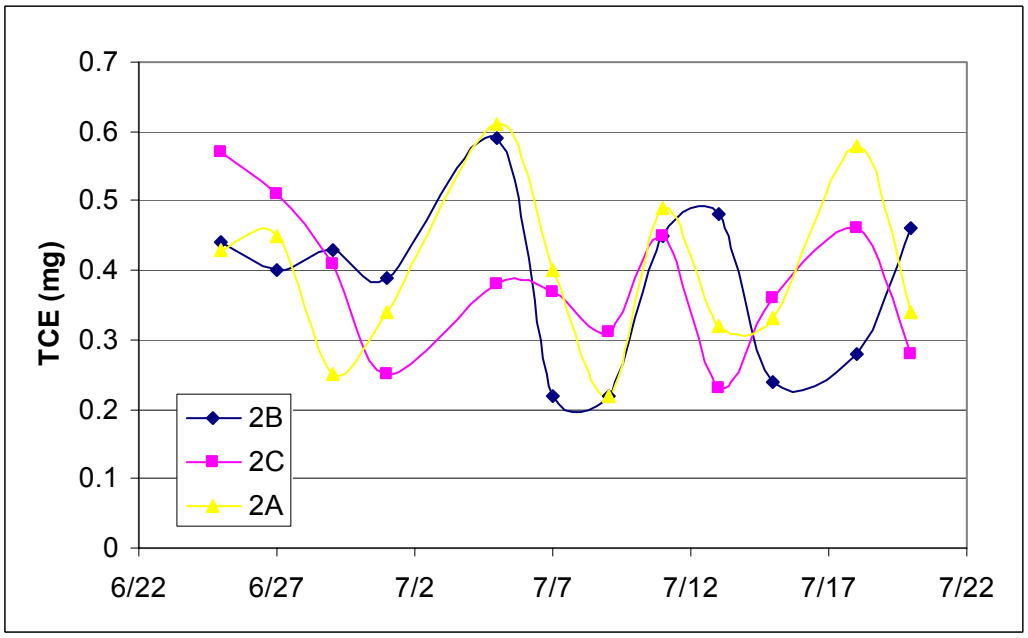

Figure D.10 Mass of TCE in mg dosed to each tree in group 2 during each dosing.

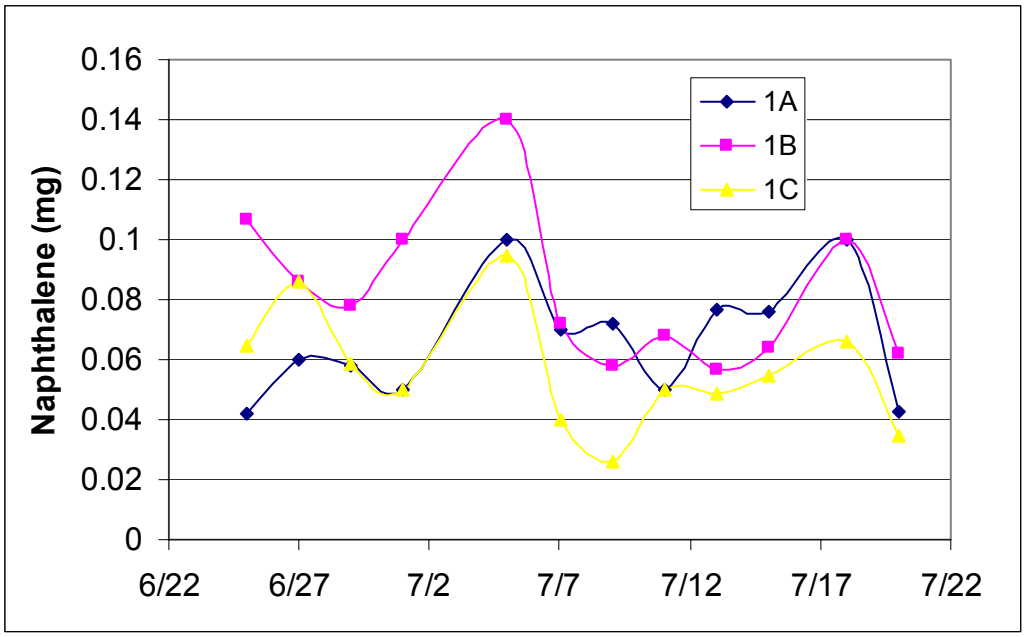

Figure D.11 Mass of naphthalene in mg dosed to each tree in groups 1 and 3 during each dosing. Reactors 3A, 3B and 3C received the same mass of contaminant as reactors 1A, 1B and 1C respectively.

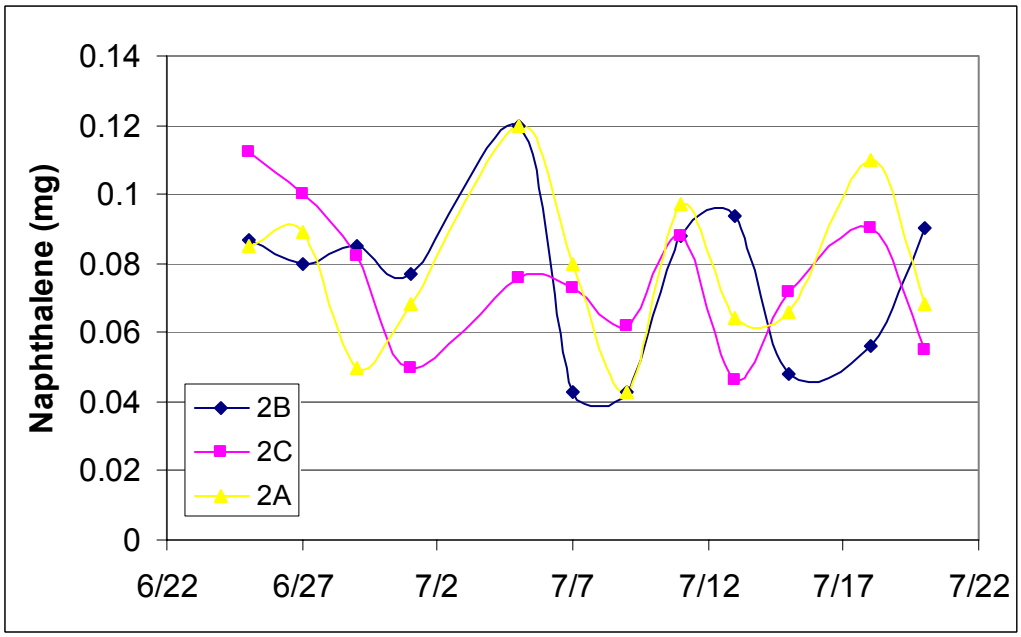

Figure D.12 Mass of naphthalene in mg dosed to each tree in group 2 during each dosing.

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VITA

Sally Rebecca Breite was born on October 23, 1979 in Florissant, Missouri. She attended Hazelwood Central High School, from which she graduated in the top 5% of her class in 1998. After graduation, she attended the University of Missouri – St. Louis and was the recipient of the UM – St. Louis Physics Department Alumni Scholarship and an active member of the Society of Physics Students, for which she served as Vice President. In her time at UM – St. Louis she also worked for two years as an undergraduate research student in the Center for Neurodynamics performing experimental biophysics research. She obtained her B.S. in Physics in May of 2003.

After deciding to redirect her career from physics to engineering, she went on to attend the University of Missouri – Rolla to pursue a Masters of Science degree in Environmental Engineering. She was a member of the Water Environment Federation and the Society of Women Engineers. She received her M.S. in Environmental Engineering in May of 2007.