12-2008

Volatilization of Trichloroethylene from Shallow Subsurface Environments: Trees and Soil

Rachel Melanie Winters
Utah State University

12-2008

Volatilization of Trichloroethylene from Shallow Subsurface Environments: Trees and Soil

Rachel Melanie Winters
Utah State University

VOLATILIZATION OF TRICHLOROETHYLENE FROM SHALLOW SUBSURFACE ENVIRONMENTS: TREES AND SOIL

by

Rachel M. Winters

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Civil and Environmental Engineering

Approved:

_____	_____
Dr. William Doucette Environmental Chemistry Major Professor	Dr. Bruce Bugbee Crop Physiology Committee Member
_____	_____
Dr. Ryan Dupont Environmental Engineering Committee Member	Dr. Byron Burnham Dean of Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah

2008

ABSTRACT

Volatilization of Trichloroethylene from Shallow Subsurface Environments:

Trees and Soil

by

Rachel M. Winters, Master of Science

Utah State University, 2008

Major Professor: Dr. William J. Doucette
Department: Civil and Environmental Engineering

Results from two previous studies conducted at Operable Unit 2 (OU2) of Hill Air Force Base, Utah indicate that the phytovolatilization (volatilization from leaves and trunk) of TCE by indigenous trees as well as soil surface flux may play a significant role in the removal of TCE from shallow groundwater plumes around the base. Previous studies investigated late summer and early autumn TCE leaf volatilization but no attempt was made to examine potential TCE volatilization seasonal variability and the volatilization of TCE directly from tree trunks. Whole tree transpiration rates were also not directly measured. To address those limitations and improve removal estimates, TCE removal via volatilization from leaves and tree trunks at OU2 was measured monthly during a growing season. Sap flow sensors were installed in several representative trees to directly measure transpiration rates.

Transpiration rates were estimated between 15 and 160 L/day by sap flow meter data collected in 2007 and 2008. With an average growing season of 150 days, estimated TCE loss to the atmosphere through leaf volatilization was 107 to 211 mg/tree/year. An

additional 4.1 mg/tree/year was estimated to volatilize directly from tree trunks. No definite seasonal trends in phytovolatilization were observed.

Soil surface flux over 12,200 m^2 equated to an overall loss of 390 g/year (180 days per year), with combined losses from all volatilization pathways of a maximum of 424 g/year, assuming an estimated 30 trees. This was one-sixth the removal of the interceptor trench installed in 1997, which is significant considering there was no additional cost for natural attenuation removal.

Tree cores, branches, groundwater, precipitation, and nearby canal samples were collected to analyze for stable isotopes of hydrogen and oxygen. Stable isotope results, low summer precipitation, and TCE core sample concentrations suggest that the trees are using shallow groundwater as their primary source of water. There was no indication of any significant yearly or seasonal variability in TCE leaf and trunk volatilization, groundwater concentrations, and groundwater use by trees.

(122 pages)

ACKNOWLEDGMENTS

I am sincerely indebted to several people for helping me through this long road. I am especially thankful for my advisor, Dr. Doucette, for his guidance, patience, encouragement, and willingness to help. I am also indebted to my committee members, Dr. Bruce Bugbee and Dr. Ryan Dupont, for the time, advice, and guidance.

I would also like to acknowledge the Select Engineering Services (SES), Hill Air Force Base, and the Utah Water Research Laboratory for funding this project. I am appreciative of Brandon Chard and Kyle Gorder for their help and encouragement.

There are so many people who have helped me while sampling and trudged through the sweltering heat. Their help and moral support have given me the drive to finish. Without these fine people it could not have been possible: Dr. Michael Peterson, Clint Rogers, Andy Hall, Erik Dettenmaier, Hailey Farrera, Hannah Spinner, Crystal Viator, Brittney Wilkes, Julie Chard, Dave Furmage, and Jared Ervin.

I am thankful for moral support from friends and roommates who listened to my constant worries and frustrations, enabling me to get through the rough patches. I am sincerely grateful for my family, Matt, Steph, and especially my parents, Tim and Karen Winters, for their love, time, and support that they have shown me throughout my educational experience. Without their prayers and constant support it would have been impossible.

Rachel M. Winters

CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Due to improper use and disposal trichloroethylene (TCE) has become one of the most frequently detected groundwater contaminants in the United States. The remediation of TCE contaminated groundwater is an important concern for many Air Force bases around the country because of its widespread use as a degreasing agent during aircraft cleaning and maintenance. The environmental fate of TCE is of great importance as it is a suspected carcinogen, recalcitrant in most aerobic groundwater environments, and is difficult to remediate particularly when it exists in the environment as a dense non-aqueous phase liquid (DNAPL) (EPA, 1999a). Current practices of TCE remediation include bioremediation (often using biostimulation and bioaugmentation), air stripping, chemical oxidation, soil venting, and in-well aeration. Although these techniques can be effective, they are often costly and time intensive.

The removal of TCE and similar chlorinated solvents by trees growing over contaminated plumes has been proposed as a cost-effective alternative remediation approach. Using plants as a means of *in situ* treatment of compounds within soil, sediments, and groundwater is known as phytoremediation (Dietz and Schnoor, 2001). Trees growing over shallow contaminated aquifers can take up TCE passively along with the water they use for transpiration. The potential pathways associated with the phytoremediation of TCE include: volatilization of the compound into the atmosphere from leaves and trunk (i.e., phytovolatilization), metabolism, and sequestration (sorption, deposition within vacuoles) within the plant. The use of phytoremediation to remediate TCE and other compounds within shallow aquifers has been investigated in laboratory (Newman et al., 1997; Burken and Schnoor, 1998; Orchard et al., 2000b; Ma and Burken

2002, 2003; Chard et al., 2006; Graber et al, 2007) and field scale studies (Newman et al., 1999; Vroblesky, Nietch, and Morris, 1999; Lewis, 2001; Burken and Xingmao, 2002; Ma and Burken, 2003; Vroblesky et al., 2004; Zaugg, 2004; Rogers, 2006; Doucette et al., 2007).

In addition to phytoremediation, several studies have shown a qualitative relationship between the concentration of plant tissues and the concentration in the groundwater (Vroblesky, Nietch, and Morris, 1999; Lewis, 2001; Ma and Burken, 2002; Vroblesky et al., 2004). If verified at a variety of sites, trees could be used as a less costly approach to delineating TCE groundwater plumes as compared to the traditional groundwater sampling methods. Trees could be used as preliminary monitoring tools to detect areas of contamination for monitoring well placement.

Phytoremediation can be an appealing alternative to more costly and invasive methods of remediation, but its effectiveness in removing contaminants has not been directly quantified in most field applications. One of the major difficulties in evaluating the effectiveness of phytoremediation is quantifying the removal of TCE and other volatile organics attributed to phytovolatilization. Phytovolatilization is defined by the EPA as the uptake and transpiration of a compound by a plant which is then released to the atmosphere through transpiration (EPA, 1999b). Loss of TCE by volatilization through trunks and branches has also been reported to be more important than volatilization through leaves in TCE at some sites (Burken and Xingmao, 2002). In addition, direct volatilization of TCE from the soil surface may also be important at sites where the groundwater is relatively shallow.

Data collected in this study helped to improve our understanding of the potential impact of trees on the removal of TCE from shallow groundwater through phytovolatilization. Estimated phytovolatilization removal of TCE was then compared to that removed directly by volatilization from the soil surface and to the TCE removed using a groundwater interceptor trench.

Project Background

Hill Air Force base (HAFB) is located approximately 30 miles north of Salt Lake City. It has been an active maintenance and repair facility for military aircraft since the early 1940s. Improper disposal of chlorinated solvents, primarily TCE, has led to contamination of several shallow groundwater aquifers. The base is divided into 12 Operable Units, each having been assessed for remediation options. Operable Unit 2 (OU2), a field site located in South Weber, Utah, on the northeast side of the base, has been selected for the main focus of this project. Figure 1 shows an aerial view of OU2 including an overlay of the dissolved TCE plume.

In 1997 a 50-foot interceptor trench was installed at the leading edge of the plume 22 to 35 feet below the ground surface to contain and prevent spreading of contamination at OU2. It was designed to collect groundwater with TCE concentrations above 5µg/L at a rate of 10 to 100 gallons per minute. The trench has been estimated to remove 2.5-9.0 kg TCE/year over the last 9 years. From 2007 to 2008 the trench removed approximately 2.5 kg. Although this approach has effectively removed a portion of the TCE in the groundwater, it was costly to install ($450,000) and yearly operation and maintenance costs are approximately $20,000. The results of two previous

studies at OU2 suggest that the removal of TCE by mature trees growing at OU2 may be similar in effectiveness and far less costly.

The first study performed in August and September 1999 (Doucette, 2000) was initiated in the Seep Area prior to tree removal in an effort to improve the Seep water collection system. The focus of the study was to determine if trees were taking up TCE from the groundwater by collecting phytovolatilization and plant tissue samples. Groundwater concentrations in the Seep ranged from 270 to 10,000 µg/L. The TCE leaf and stem concentrations ranged from 110 µg/kg to as high as 38,000 µg/kg in the tissue on a dry weight basis. TCE metabolites, trichloroethanol (TCEt) and trichloroacetic acid (TCAA), were found in the leaves at dry weight concentrations of non-detect (ND) to 750 µg/kg and ND to 440 µg/kg, respectively. Phytovolatilization samples collected from the leaves ranged from ND to 2,200 µg/L of water transpired. Soil surface flux samples collected within the Seep indicated that TCE was emitted at 28 to 750 µg-TCE/d-m^2.

Samples were also taken below the canal where TCE groundwater concentrations were lower, historically 100 to 1000 µg/L. No TCE was detected in the leaves but metabolite concentrations were 730 to 7,300 µg/kg, 40 to 990 µg/kg, and ND to 4,000 µg/kg for TCEt, TCAA, and DCAA, respectively. Transpiration stream concentrations ranged from 80 to 365 µg TCE/L. No TCE was detected in soil flux samples below the canal.

In Fall 2005, a similar sampling study (Rogers, 2006) was conducted primarily on trees below the canal (Figure 1) growing above groundwater with an average TCE concentration of 185 µg/L. Leaf tissue samples ranged from 1.0 to 465 µg TCE/kg on a fresh weight basis. Leaf phytovolatilization samples averaged 16 µg TCE/L of transpired

water. Based on an average of 152 L of water transpired per day per tree, the loss of TCE from phytovolatilization was estimated between 410,000 and 730,000 µg/tree/year (410 to 730 mg/yr). Stable isotope samples (O and H) were used to quantify water sources afforded inconclusive results, but due to climate conditions and tree TCE concentrations, it was determined the trees were likely using groundwater. No metabolites were found in any of the tree sampled. Soil surface flux sampling resulted in a flux of 6-256 µg-TCE/d-m^2.

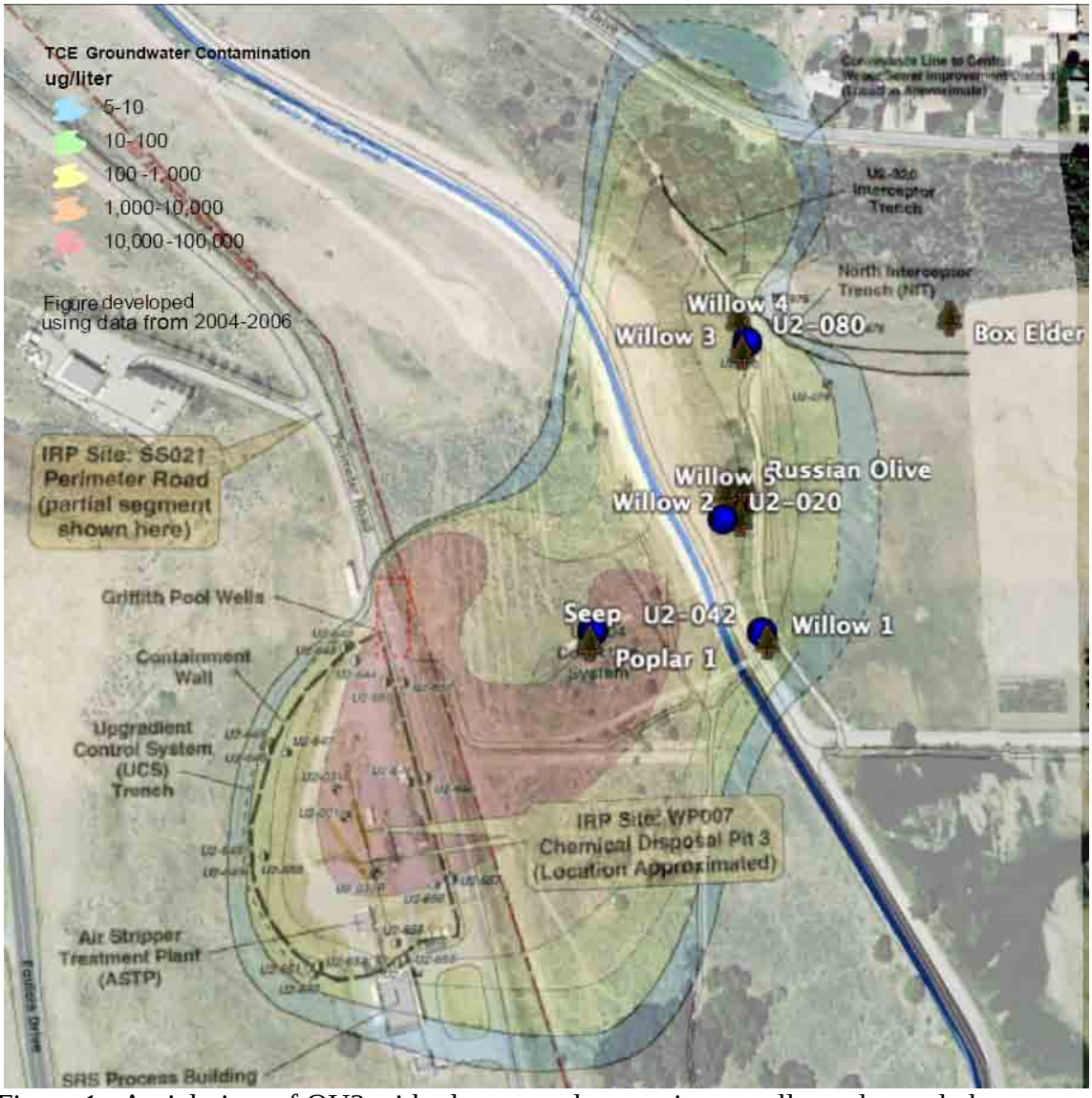

Figure 1. Aerial view of OU2 with plume overlay, pertinent wells, and sampled trees.

Comparing the two sampling events, the TCE concentrations in the trees and in phytovolatilization samples were up to three orders of magnitude greater in the Seep Area than below the canal. The differences between the two studies are likely due to the significantly higher groundwater concentrations in the Seep than below the canal.

Both studies showed that there are measurable amounts of TCE lost to the atmosphere via phytovolatilization and that trees at OU2 could potentially remove a significant amount of TCE from groundwater. Preliminary data indicated that the amount of TCE lost from soil surface flux could also be significant.

Even though the previous sampling efforts showed that there are significant natural attenuation pathways occurring at OU2, there were several limitations in using the data collected to predict yearly removals. In both instances only one time interval was assessed therefore seasonal variability could not be evaluated. The previous phytovolatilization sampling was focused primarily on losses from the leaves through transpiration, but according to Burken et al. (2002) diffusion from tree trunks could potentially be a significant loss and impact estimates of TCE volatilization.

The close proximity of the field site to the university enabled frequent sampling trips that could capture possible seasonal variations. Previous water transpiration estimates were based on weather data, consequently sap flow meters were installed to quantify water transpiration for several individual trees. To better estimate the TCE removed by trees at OU2, an apparatus was constructed that could sample the TCE diffusion directly from trunks at multiple heights along the trunk. Measuring trunk and leaf volatilization simultaneously provided additional data to scale TCE volatilization from a whole tree.

Thesis Objectives

The main objectives of this thesis research were to quantify the amount of TCE removed from shallow TCE contaminated aquifers within a section of Hill AFB OU2 through the following processes: phytovolatilization (TCE volatilization associated with water transpired), volatilization through trunk and stem, and volatilization directly from the soil surface, and compare the TCE removed by these processes to TCE removed via the interceptor trench installed at OU2 in 1997 to determine if natural attenuation/phytoremediation could be a viable remediation option at OU2 and similar sites. In order to complete the main objectives the following specific tasks were completed:

1. Using a flow through chamber system, measure the amount of TCE phytovolatilized from leaves as a function of water transpired from representative tree branches. Combine this information with measurements of whole tree transpiration made using a Dynamax sap flow system or estimated using the approach by Ferro et al. (2001) to scale the individual measurements to whole trees.
2. Measure the amount of TCE volatilized directly from tree trunk and soil surfaces using a recirculating flux chamber system. Appropriately scale these measurements to estimate the amount of TCE removed within the sampling area by these mechanisms.
3. Evaluate potential seasonal changes in the amount of groundwater used by the trees relative to precipitation using stable isotopes of oxygen and hydrogen. Determine how this impacts phytovolatilization.

4. Compare data collected in 2007 to previous limited sampling events in 1999 and 2005 to examine the variability of TCE concentrations in groundwater and phytovolatilization samples over time.

Modeling

A conceptual site model for OU2 is presented in Figure 2 for the tree-mediated natural attenuation processes that have been identified for TCE. In this conceptual model, TCE is taken up into deep-rooted trees along with contaminated groundwater. Since the site is located in a semi-arid climate with an average of 20 inches of annual precipitation, surface precipitation is likely not the main source of water used by trees. Stable isotopes of hydrogen and oxygen can be used to identify the fraction of groundwater used to supply the overall water needs of the trees. Once TCE has been taken up into the plant, the compound can be sorbed in the tissues, metabolized, or volatilized to the atmosphere through the trunk or leaves of the tree.

While the model is conceptually simple, scaling considerations present several challenges. Ideally, leaf volatilization is best scaled to the amount of water collected during sampling. However, in some cases it can be found that water is not collected even though TCE can be found. During mid-summer sampling events, lack of water can be attributed to extremely hot temperatures that cause the trees to stop transpiring in efforts to conserve water. Other potential reasons for lack of water collection are improper drying of silica traps or leaks within the sample collection system. Also, the sensitivity of gravimetric water measurements may be insufficient during low transpiration events when very small amount of water are transpired.

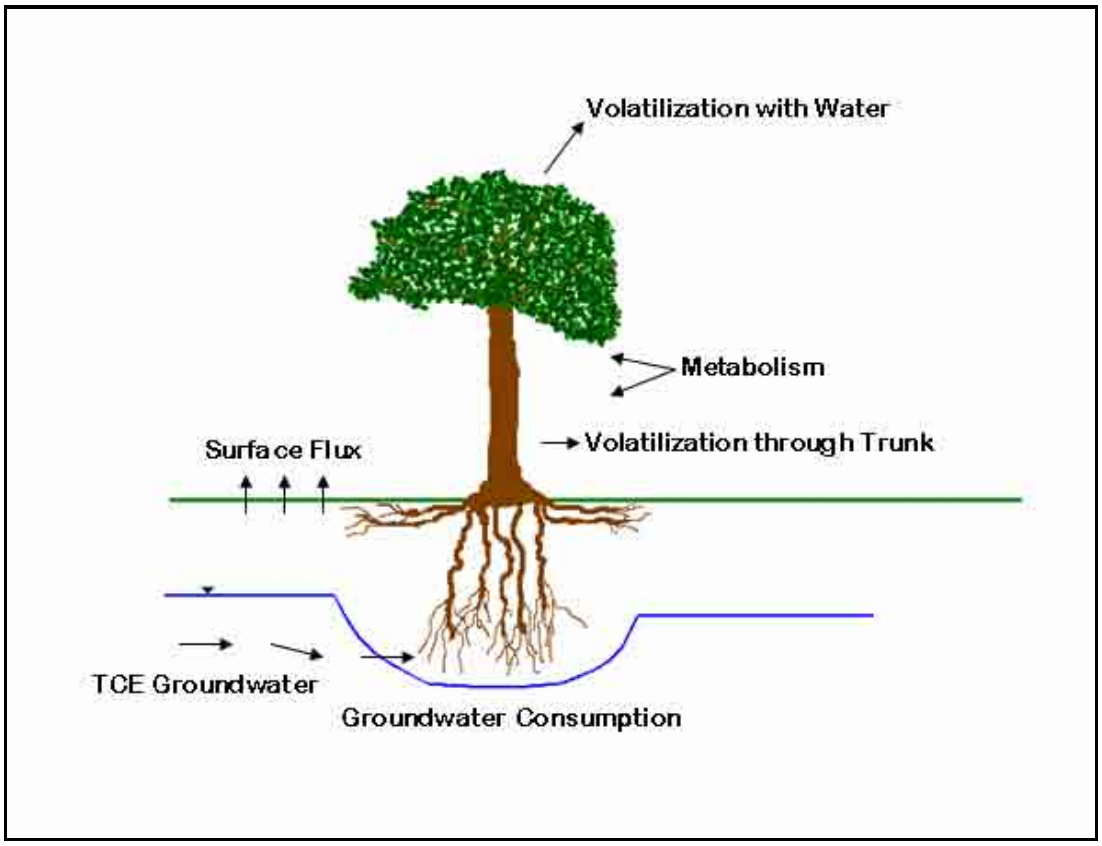

Figure 2. Conceptual model for the fate of TCE within trees and soil at OU2.

When the amount of water transpired during a sampling event is below detection limits, branches can be collected and brought back to the laboratory for leaf area measurement. Flux of TCE from the leaves can then be normalized to leaf area. However, this approach is more difficult to scale to tree and canopy levels. Trunk volatilization is also challenging to scale due to difficulties associated with collecting accurate trunk area measurements. Along with losses from tree volatilization, metabolism occurring within the plant can also be difficult to quantify. Accurately obtaining representative soil surface flux measurements can be difficult. Several different parameters such as atmospheric pressure, soil moisture, soil temperature, depth to groundwater, and groundwater concentration greatly affect the flux of TCE from the soil.

In order to accomplish the objectives stated in the previous section, several aspects of the conceptual model (Figure 2) were investigated in depth. A large portion of this project relied on the estimation of the amount of water transpired by trees at OU2 throughout the growing season. Mechanistically it was most appropriate to scale the amount of TCE phytovolatilized to the amount of water transpired during sample collection. However during some sampling events in 2006 and 2007 TCE was still emitted from the leaves and captured on most Tenax traps even when water was not collected.

Digital photographs of sampled trees were taken during the growing season and in the late fall after leaves had fallen from the tress. Adobe Photoshop Extended Creative Suite 3 was then used to digitally estimate the leaf area for each tree. It was then possible to scale the TCE losses to a whole tree via leaf area. Aerial photographs and manual counting of trees growing over contaminated area were used to scale over the entire OU2 canopy.

Estimating Annual Transpiration and TCE Uptake

Estimating the removal of TCE from trees requires water collection during phytovolatilization samples that can then be scaled to the water transpired over the entire year. One approach to estimating the amount of water transpired (Vt) within a given period of time (cm^3/month) is by using Equation 2 (Ferro et al., 2001).

$$Vt = PET * Kc * LAI * A \quad (2)$$

In this equation, PET is the potential evapotranspiration during the time period, expressed in cm/month. PET can be calculated using the Penman-Monteith equation, that is not displayed in this paper (Allen et al., 1998). Evapotranspiration is calculated as function

of radiation, soil heat flux, temperature, vapor pressure, and wind speed. The evapotranspiration for values that are specific to Hill Air Force Base can be found in Table A-1 of Appendix A for 2006 and 2007 (UET-Net, 2008). Kc is the dimensionless crop coefficient which is the rate of water used per leaf and is a percentage of the PET. Leaf area index (LAI) is described as the ratio of leaf area per unit of ground surface (ft^2 leaf area/ft^2 ground area). The variable A is the ground area covered by the selected tree leaf canopy in cm^2. The Kc value that was used is 0.5. It was experimentally determined in a study conducted by Ferro et al. (2001) in Ogden, Utah, using hybrid poplar trees. The LAI was also estimated to be 3 and was used for all calculations in this study.

The transpiration stream concentration factor (TSCF), or the concentration of TCE in the xylem sap divided by the TCE concentration of groundwater used by the trees, can be used along with the groundwater concentrations measured in the field (C_{TCE}), the amount of water transpired annually (Vt calculated using Equation 1), and the fraction of contaminated groundwater utilized for plant needs (*f*), to estimate the annual mass of TCE removed by a particular tree as shown in Equation 3 (Orchard et al., 2000b). Values of TSCF range from 0.02 to 0.75 (Burken and Schnoor, 1998; Orchard et al., 2000b)

$$\text{Annual mass of TCE taken up by a tree} = (TSCF)*(C_{TCE})*(Vt)*(f) \quad (3)$$

If the transpiration stream concentration (TSC) (the mass of TCE in per liter of transpired water) is directly measured in the field the annual TCE uptake by a tree can be expressed in the following equation (4):

$$\text{Annual mass of TCE taken up by a tree} = TSC*Vt \quad (4)$$

Sap flow velocity sensors provide another method approach to directly estimate transpiration rates. Thermal dissipation sap velocity sensors (TDP) (Dynamax, Houston, TX) were placed in six different trees at OU2 in August 2007. The TDP sensors were installed in the sapwood of trees where water was flowing. The sensors measured sap flow by using heat dissipation through the sapwood (Dynamax, 2007). The temperature probes sent a heat line source from the needle and the heat sensor to the surrounding sapwood area (Figure 3).

When sap was not flowing or was low, the temperature difference between the two sensors was high or at the maximum. When large amounts of sap flow, temperature differentials were smaller. The TDP sensors were connected to a CR1000 datalogger (Campbell Scientific, Logan, UT) which recorded the output and was stored until downloaded. A picture of the datalogger and solar panel for the sap flow meter is located in Figure 4.

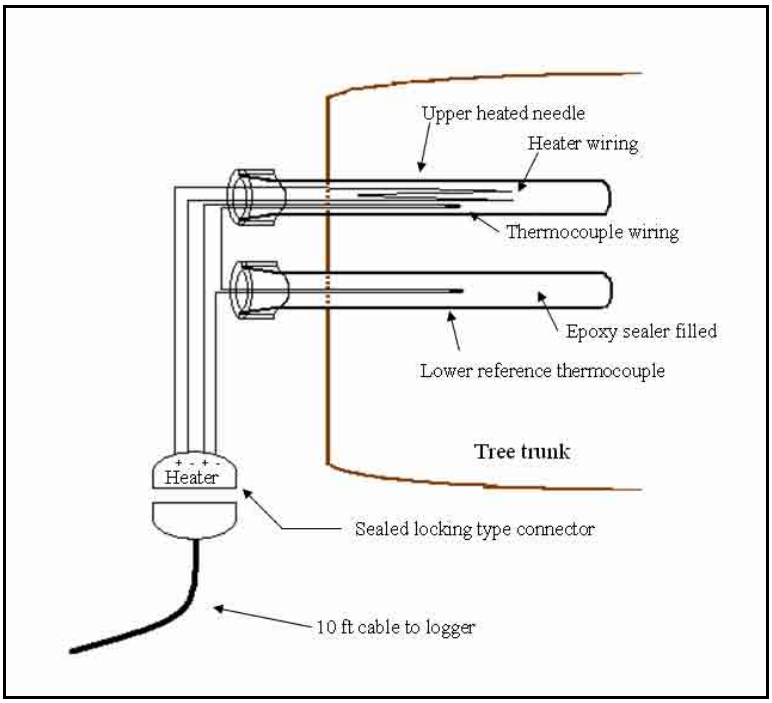

Figure 3. Schematic of sap flow velocity probe inserted into tree trunk.

Figure 4. Datalogger and solar panel for sap flow velocity meter below OU2 canal and above sampled trees.

Estimation of TCE Trunk Volatilization

An estimation of TCE lost from the trunk was made by multiplying the measured flux of TCE by the total area of the trunk. An attempt to scale TCE losses from the trunk via water transpired was also made by adding a silica trap to the trunk volatilization apparatus. However, no measurable water was collected during the 30 minute sample collection period.

It is possible that TCE can be transpired through the tree trunk with water, but insufficient gravimetric methods limited the ability to measure water collected. Methods used in this thesis allowed for much smaller amounts of TCE (picograms) to be measured than water (milligrams). To make a proper estimation of TCE losses from tree trunks, TCE was only scaled to trunk area. To measure the trunk area of the whole tree, digital

photos were taken in late fall after the leaves had fallen from the trees. Adobe Photoshop Extended Creative Suite 3 was then used to estimate the trunk area for scaling TCE losses for a whole tree.

Estimation of TCE Soil Surface Flux

Soil surface flux concentrations were measured during November 2007 and June 2008 to determine TCE losses solely by emission from the soil surface. A comparison between apparatus used in this study and the apparatus used in the Rogers (2006) study was done to determine if both apparatuses perform similarly. This was performed in lab using a TCE emitter that released a continuous amount of TCE over long periods of time. Making a comparison between the two apparatuses allowed for the use of the 2005 data as part of the estimated losses from soil surface flux.

Scaling TCE Phytovolatilization Losses to OU2

Information gained from scaling the TCE losses from the leaves by water or leaf area was combined with trunk losses which provided whole tree estimations of TCE losses. Aerial photographs and manual counting of trees were employed to produce an estimate of trees possibly contributing to phytovolatilization of TCE at OU2. The combined soil surface flux and canopy estimation was then compared to the interceptor trench TCE removal.

LITERATURE REVIEW

TCE Properties

Trichloroethylene (TCE) is a colorless, volatile organic solvent that has been used in a variety of industrial applications as a degreaser and paint remover. Due to widespread use and improper disposal, it has become one of the most prevalent groundwater contaminants in the United States.

A description of environmentally relevant chemical properties for TCE and a common anaerobic degradation product, DCE, are provided in Tables B-1 and Table B-2 of Appendix B. Like most chlorinated solvents, the density of TCE is greater than water. Improper dumping of the liquid phase has caused the formation of DNAP pools in bottom of groundwater aquifers. Remediation of TCE DNAPLs is difficult and expensive. The identification of TCE as a probable carcinogen (HSDB, 2006b) in addition to its widespread groundwater contamination have motivated its remediation efforts for TCE contaminated sites.

Remediation Approaches

Several remediation approaches have been used to remove or degrade TCE *in-situ* including air stripping, soil venting, in-well aeration, chemical oxidation, and bioremediation. Physical processes such as air sparging or air stripping, and soil vapor extraction (Soesilo and Wilson, 1997) can be used to remediate TCE. In these processes, air is pumped into the subsurface to force the chemical from the groundwater into the vapor phase. Vacuum pumps collect contaminated air and the chemical is removed from the air stream. Despite the effectiveness of these technologies, implementation and

operation and maintenance costs can be considerable. Oxidation of TCE is possible using chemicals such as potassium ferrate or hydrogen peroxide (Russel, Matthews, and Sewell, 1992). The chemical is injected into the subsurface and allowed to react. This method can be difficult to implement if the conditions of the aquifer are highly variable and the compound is not evenly distributed. Biodegradation utilizes indigenous microorganisms or cultured bacteria that can degrade these compounds (Conuet et al., 2000; Major et al., 2001). At many sites under anaerobic conditions, TCE can be reduced to cis- or trans-dichloroethene (DCE), vinyl chloride, and eventually to ethene. Unfortunately, if the degradation of TCE is incomplete, the intermediate breakdown products formed (DCE and vinyl chloride) are no less hazardous than TCE.

Phytoremediation, or the use of plants as a remediation tool, is an inexpensive and atheistically pleasing alternative to other mechanical, chemical, or biological remediation techniques. Plants can be used for *in situ* remediation of soils, sludges, sediments, and groundwater by removing, containing, or degrading the compounds of concern (EPA, 1999b). Phytoremediation has been effective in removing such compounds as: metals, pesticides, solvents, explosives and polycyclic aromatic hydrocarbons, and chemicals in landfill leachates. Processes utilized by the plant to remediate compounds include: sorption or precipitation in the root zone (metals); breakdown of the contaminant within the plant, roots, or rhizosphere (organics); or uptake and transpiration of the contaminant through the plant (volatiles).

Plant Uptake

Lab scale (Newman et al., 1997; Burken and Schnoor, 1998; Orchard et al., 2000b; Ma and Burken, 2003; Li et al., 2005; Doucette et al., 2007) and field studies

(Newman et al., 1997, 1999; Doucette et al., 2003, 2007; Clinton et al., 2004; Zaugg, 2004; Rogers, 2006) have been used to help identify the plant pathways and uptake mechanisms of organic chemicals such as TCE in various plant systems. Plant uptake of chlorinated solvents is thought to be a passive process when contaminated water is utilized for nutrient transport (McFarlane, 1995). Passive uptake of compounds is a function of plant and chemical properties. The octanol-water partition coefficient (log K_{ow}), or the concentration ratio obtained at equilibrium when a chemical is allowed to partition between a two phase mixture of octanol and water (Baum, 1998), has been used to estimate plant uptake. With a moderately hydrophobic log K_{ow} of 2.33 to 2.61, TCE has been shown in several laboratory and field studies to enter into the leaves, stems, and trunks of plants (Chappell and EPA, 1997; Newman et al., 1997, 1999; Burken and Schnoor, 1998; Vroblesky, Nietch and Morris, 1999; Orchard et al., 2000a, 2000b; Lewis 2001; Burken and Xingmao, 2002; Doucette et al., 2003; Ma and Burken, 2003; Vroblesky et al., 2004, Zaugg, 2004, Rogers 2006).

Once a compound is in the plant, the efficiency of transpiration stream movement of compounds from roots to the shoots can be defined by the TSCF (McFarlane, 1995). The TSCF is the concentration in the xylem sap divided by the concentration in the external solution. The published TSCF values vary significantly for TCE ranging from 0.02-0.75 (Burken and Schnoor, 1998; Orchard et al., 2000b).

Phytovolatilization Sampling

Various laboratory and field studies have been conducted in order to gain a better understanding of plant transpiration and TCE removal from contaminated groundwater (Newman et al., 1997, 1999; Doucette et al., 2003; Ma and Burken, 2004; Zaugg, 2004;

Rogers, 2006). Sample collection can include one of the following three types of methods: flow-through systems, static chamber systems, and open-path systems.

An investigative study performed in 1999 (Doucette, 2000) was initiated to determine the impact of plants on the natural attenuation of TCE at OU2. A flow through chamber was used to sample transpiration from leaves of trees growing over TCE and perchloroethylene (PCE) contaminated groundwater. Two areas at OU2 were investigated: the Seep Area and below the canal (Figure 1). The Seep Area has historically had groundwater concentrations that were 10 times higher than below the canal. Seep groundwater concentrations were as high as 5,860 µg/L and 32 µg/L for TCE and PCE, respectively. The TSCs ranged from ND to 2,200 µg TCE/L of transpired water. The PCE TSC was much lower than for TCE, but was only measured as high as 38 µg/L of water transpired. An estimate of 10 to 200 L/day of water transpired (Wullschleger, Meinzer, and Vertessy, 1998) was used to scale TCE losses to a whole tree. Research from this investigation indicated that phytovolatilization of chlorinated solvents could be a significant fate pathway at OU2.

A later study was performed in 2005 (Rogers, 2006) to compare phytoremediation occurring at OU2 to that of Vandenberg Air Force Base, California. Results from OU2 showed much lower TSC levels than in the previous 1999 study. Since the trees were removed in the Seep Area to improve drainage, only trees below the canal were sampled in this later study. The investigation showed an average TSC of 16 µg TCE/L of transpired water. Each tree was calculated to transpire 152 L/day of water per 180-day growing season, amounting to 0.41 to 0.73 g of TCE phytovolatilized per tree per year. In both investigations at OU2, sampling was performed at only one time and did not

address the seasonal variability of transpiration or other potential diffusive pathways that can contribute to phytovolatilization of chlorinated solvents. Both investigations supported the fact that TCE was taken into the plant by groundwater use. Neither considered the possibility of losses attributed to the trunk, or directly measured water use by trees. Both relied on the estimations from Wullschleger Meinzer, and Vertessu (1998) or the approach of Ferro et al. (2001). Wullschleger, Meinzer, and Vertessu complied whole-tree water 52 studies performed from 1970 to 1998 on maturetrees. Various techniques were used to measure transpiration rates. It was found that 90% of the observations were between 10 and 200 L/day water. The average tree height was 21 meters.

In a model proposed by Ma and Burken (2004), five factors that are thought to contribute to the transport of contaminants through trees are: advective transport upward in xylem, advective transport downward in phloem, sorption and desorption between transpiration stream and biomass, dispersion and diffusion, and metabolism. Possible diffusion from the tree trunks was later addressed in a study performed by Ma et al. (2003) using poplar whips. In this experiment, poplar whips were grown hydroponically and in soil that had been spiked with known amounts of TCE. Small glass diffusion traps were placed at two areas along the stem. Air flowed through the trap at 0.1 L/min. An activated carbon trap was positioned at the outlet of the diffusion trap to capture any TCE that had diffused from the whip. Once in the plant, TCE was shown to diffuse through the stems.

Currently little field work has been done to assess trunk volatilization in mature trees as a potential fate pathway. Hybrid poplars growing over TCE and PCE

contaminated groundwater were planted in 1996 at Aberdeen Proving Ground J-Field Site and were the object of a full scale trunk diffusion study (Burken and Xingmao, 2002). Tedlar bags were cut, wrapped around the tree trunks at an upper and lower height, and fastened to the trunk using adhesive tape. Activated carbon traps were placed at the valve/hose barb arrangement with a sampling pump set at 1 L/min to collect air. Two Teflon tubes were placed at the opposite side of the tree to allow air to enter the apparatus. Results from this study showed that chlorinated solvents did diffuse from these tree trunks with no significant difference from the upper and lower diffusion samplers, but in some cases slightly higher concentrations were detected in the upper samplers. There was no attempt to determine the rate at which TCE and PCE can flux from the tree trunks.

Soil Flux Sampling

Another potentially important fate pathway identified at OU2 is the volatilization of TCE from the soil surface (Rogers, 2006). Factors that can influence the flux of TCE from soil include: soil moisture content, soil temperature, changes in groundwater depth, vegetation, and possibly atmospheric pressure. The amount of moisture in the soil can decrease the amount of TCE in the soil air by inhibiting the diffusive flux (Smith, Tisdale, and Cho, 1996). Rainfall events cause water with a zero TCE concentration to infiltrate the soil forcing TCE to migrate from the soil vapor into the water phase (Smith, Tisdale, and Cho, 1996) which can reduce soil vapor flux concentrations.

Temperature is another factor that can greatly influence the amount of gases emitted from soils (Lindberg et al., 1995). As temperature increases, compounds tend to enter the vapor phase. Small increases in temperature can greatly affect the surface flux.

In a study performed testing the air/surface exchange of mercury vapors, the amount of mercury measured exponentially increased with increasing soil temperature (Lindberg et al., 1995).

Other factors that can influence surface flux are depth to groundwater and the presence of vegetation. Smith et al. (1990) studied a TCE groundwater contaminated site at Picatinny Arsenal in New Jersey. Soil gas sampling indicated that the TCE gas concentrations decreased as the distance above the water table increased. The deeper the groundwater table, the lower the flux. In a study performed by Marr et al. (2006), the thickness of the saturation zone and depth to groundwater had a significant effect on the naphthalene concentration at phytoremediation site in Oneida Tennessee. They also reported that the presence of trees in the phytoremediation system reduced the saturated zone thickness. This decrease in the saturated zone thickness in turn increased the naphthalene flux.

Soil surface flux was measured in the 1999 and 2005 investigations at OU2 (Doucette, 2000; Rogers, 2006). Flux measurements were as high as 750 μg-TCE/d-m^2 in the Seep Area during the 1999 sampling period. The 2005 investigation showed that TCE flux measurements were as high as 256 μg-TCE/d-m^2. These samples were collected near groundwater sampling wells and trees located below the canal where the groundwater TCE concentrations were lower. Since both of these investigations were conducted around the same time of year, no seasonal variability due to depth to groundwater or temperatures could be examined. Rogers (2006) estimated over a 180-day growing season, potential losses could be as high as 46 mg/m^2. The potential of the

soil surface flux as a significant fate pathway could be increased with the addition of tress.

Tree Core Relationships

Several factors can affect contaminate uptake by plants including: plant transpiration, groundwater accessibility, sources of water to the roots (surface versus groundwater), and chemical properties of the contaminant. Because trees have been shown to passively uptake contaminants from groundwater, they may be a useful tool for locating areas of contamination. Several studies (Vroblesky, Nietch, and Morris, 1999; Lewis, 2001; Vroblesky et al., 2004) have shown that tree coring in areas of contamination can be an effective method of detecting TCE contamination in groundwater. This method is less expensive and faster than soil core sampling for groundwater monitoring.

Although no quantitative relationship between groundwater contaminants and tree core concentrations has been reported, several qualitative relationships have been demonstrated (Vroblesky, Nietch, and Morris, 1999; Lewis, 2001; Vroblesky et al., 2004; Sorek et al., 2007). Trees growing over higher levels of groundwater contamination generally have higher concentrations in their trunk cores than those growing over groundwater at lower concentrations. This technique of using tree cores to locate contamination could then be used as a preliminary screening tool for establishing monitoring well placement.

In an effort to correlate groundwater concentrations to core concentrations, several approaches have been examined (Briggs et al., 1983; Gabarini and Lion, 1986).

Gabarini et al. (1986) reported relating the Log Kow of TCE and Toluene to the lignin normalized wood water sorption coefficients (K_{lignin}) by the following equation (5):

$$\text{Log } K_{lignin} = 0.95 \log Kow - 0.48 \quad (5)$$

From this equation, the tree core concentrations can be related to the groundwater concentrations using the log K_{ow} of TCE.

TCE Metabolism

Once the compound is in the plant and transpiration is occurring, other fate pathways such as metabolism can occur. When a plant passively uptakes TCE, metabolism can occur (Newman et al., 1997, 1999; Doucette et al., 2003). Newman et al. (1999) in a controlled field study using poplar trees, suggested that TCE can be taken up by the plant and then may be dechlorinated within the plant tissue (Newman et al., 1999). Three common metabolites of TCE are trichloroethanol (TCEt), trichloroacetic acid (TCAA), and dichloroacetic acid (DCAA) (Newman et al., 1997). In a study performed by Newman et. al (1997), tumor cells from hybrid poplar trees converted TCE to TCEt and DCAA, and TCAA. It is also hypothesized that microbes in the rhizosphere may be able to degrade TCE into its smaller constituents through this dechloriniation process (Walton and Anderson, 1990).

During the 1999 study at OU2 (Doucette, 2000), TCEt, TCAA, and DCAA were found in both the leaves of trees located in both the Seep and canal locations. Concentrations ranged from ND to 7,300 µg TCEt/kg tissue, ND to 990 µg TCAA/kg tissue, and ND to 4,000 µg DCAA/kg tissue. All concentrations were on a dry weight basis. The study performed in 2005 (Rogers, 2006) no metabolites were found in any of the samples collected. Extraction and analysis methods were essentially the same except

in that electron capture detector (ECD) was used in the 1999 study during analysis, whereas a mass spectrometer was used in the later studies.

Plant Water Stable Isotopes

Identifying water sources used by plants can help in determining a compound's fate in a planted environment. If water sources can be identified, tools are available to estimate the amount of water used. The change of the fractionation of some of these isotopes come from: (1) variations in water taken up by plants (groundwater, surface, precipitation) (2) leaf water enrichment during transpiration and the atmospheric conditions (i.e., humidity) (3) and variation of water in the cells producing organic matter (Flanagan, Ehleringer, and Pataki, 2005). Because precipitation can affect the fractionation of stable isotopes, it is important to investigate the precipitation stable isotope ratios along with other possible water sources. Fractionation of precipitation can vary greatly depending on the time of year due to selective condensation of stable isotopes (Flanagan and Ehleringer, 1991)

Since there are a few factors that can change the fractionation of stable isotopes, water has been used as a valuable tool to help identify water usage patterns in vegetation in laboratory and field studies (Flanagan and Ehleringer, 1991; Doucette et al., 2003; Clinton et al., 2004; Rogers, 2006). Clinton et al. (2004) studied the fractionation of two mature eastern cottonwoods, which included irrigation of hydrogen (D) and oxygen (^{18}O) enriched water to gain a better understanding of water use patterns. The cottonwoods growing over TCE and DCE contaminated groundwater at the Naval Air Station in Texas were irrigated with D and ^{18}O enriched irrigation water from a nearby reservoir. Stable isotope samples were collected before and after irrigation. Results were that the isotopic

signatures increased greatly indicating that the irrigation water was quickly taken up by the trees. Another significant result was that the TCE concentrations decreased by an average of 21% after irrigation, indicating that TCE free water will dilute TCE concentrations within the tree. Results indicated that there was preferential use of precipitation and surface water within trees. This can affect the efficiency of phytoremediation of contaminated groundwater in areas of high precipitation or access to other uncontaminated surface water sources.

To determine an isotopic ratio, the ratio is compared to a standard, which is commonly Vienna-Standard Mean Oceanic Water (VSMOW) (Flanagan, Ehleringer, and Pataki, 2005). The compositions are denoted by the deviation to the isotopic concentration of VSMOW as displayed in Equation 6,

$$\delta = \left(\frac{R_{Sample}}{R_{Standard}} - 1 \right) \times 1000 \tag{6}$$

where R is the ratio of the heavier isotope divided by the lighter isotope (Equation 7).

$$R = \frac{D}{H} \; or \; \frac{^{18}O}{^{16}O} \tag{7}$$

The samples are analyzed using mass spectroscopy. Plants that may have several different water source contributions require modeling to determine the amount contributed by each source.

MATERIALS AND METHODS

Phytovolatilization Sampling

Samples were collected to determine the potential flux of TCE from leaves to the atmosphere using the portable flow-through apparatus illustrated in Figure 5. Figure 6 shows a photograph of the leaf phytovolatilization apparatus sampling Willow 4 at OU2. The sampling approach used in this study was similar to that described by Doucette et al. (2003), Zaugg (2004), and Rogers (2006).

A glass chamber was used to enclose a 20 cm section of a branch on the tree of interest being careful to minimize contact of the leaves. The chamber was sealed on the open end with closed-cell foam and electrical tape to produce a flexible, yet tight seal around the stem and chamber. Compressed air (Airgas Certified Standard-SPEC grade) purged the chambers of TCE and water vapor for 15 minutes. This grade of compressed air, containing 315-385 ppm CO_2, was used to maintain natural stomatal response. The resulting slightly positive chamber pressure also minimized the potential introduction of any TCE from ambient air surrounding the chamber (i.e., TCE volatilizing directly from the soil surface or surrounding leaves). Any cylinders of air used for sampling were tested for TCE and CO_2 at the UWRL prior to field use. Cylinders with high levels of TCE or inadequate levels of CO_2 were returned and a new cylinder was tested before use.

All tubing and connections attached to the chamber were constructed of either stainless steel or Teflon to minimize sorption of TCE. Portable sampling pumps were used to subsample the air leaving the chamber. Sub-sampling at relatively high flow rates (6 to 10 L/min) was necessary to minimize humidity increases within the chamber and prevent the condensation of transpired water on the interior walls of the chamber.

Sample collection time intervals were between 20 to 40 minutes using subsampling flow rates of 100 to 150 mL/minute. Specific time intervals and flow rates were recorded for each sampling period.

Tenax TA® was used as the sorbent for the TCE traps because of its high sorption capacity for volatile chlorinated organics and low affinity for water. Silica gel traps were used to determine the amount of water transpired. The volume of gas sample (3 to 7 L) collected was calculated from the flow rate through the Tenax TA® trap and the sampling time. After sampling, Tenax TA® traps were sealed with stainless steel or brass caps, placed in bubble-pack envelopes, and taken to the UWRL at Utah State University for analysis. Chamber blanks and ambient air samples were collected. Prior to going to the field and between each sampling event, the interior of the glass chamber surfaces were rinsed with methanol.

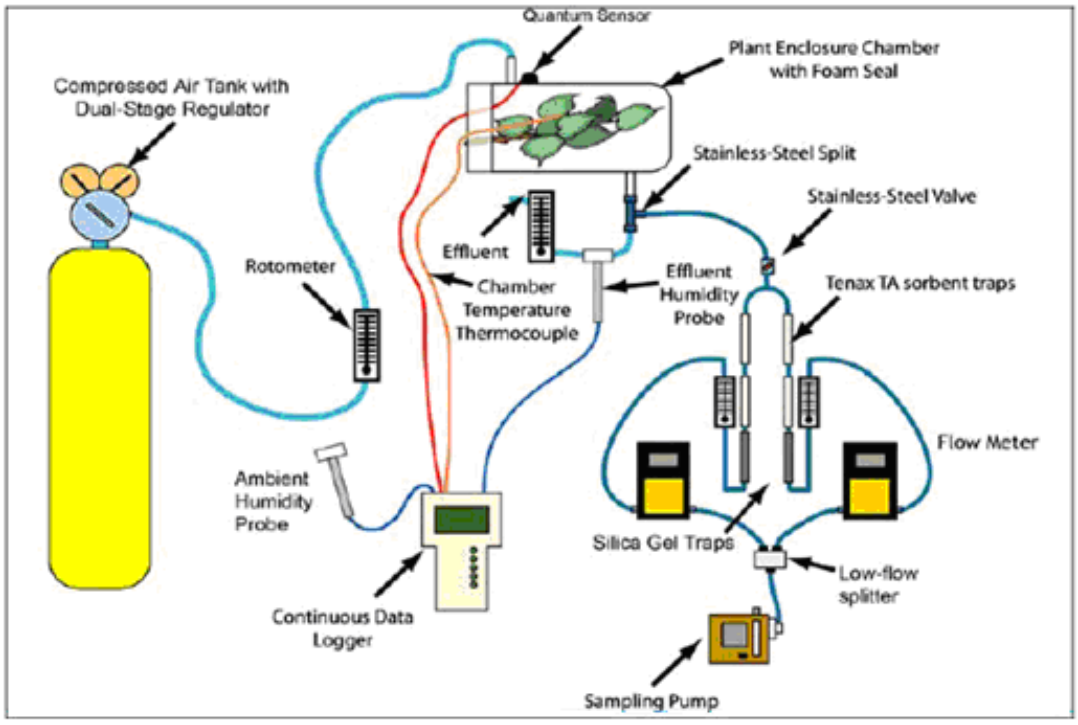

Figure 5. Phytovolatilization sampling apparatus used to measure leaf volatilization (Rogers, 2006).

Figure 6. Leaf volatilization sampling at Willow 4.

The amount of water transpired during phytovolatilization sampling was determined with a portable balance by measuring the mass of condensed water collected on the silica traps. Traps were weighed prior to and after connection to the sample effluent stream. The weight of the water collected and the volume of effluent passing through the trap was used to determine the ratio of TCE to water transpired.

Following transpiration gas collection, the leaves within each chamber were collected, transported to the Research Greenhouse at USU, and area measured with a leaf area meter (LICOR Instruments, Model 6000), which functions by interception of light by a solid surface. The meter was calibrated with standard disks of a known area. The accuracy of the measurement was plus or minus 5 percent. Leaf area was used in scaling

calculations when insufficient transpired water was collected and for relative comparisons with trunk and soil surface flux measurements.

Trees were selected for phytovolatilization sampling based on the results of trunk core samples. Only trees showing measurable levels of TCE in trunk cores were sampled for phytovolatilization. The branch used for phytovolatilization sampling was selected using four criteria: accessibly, health, adequate sunlight, and proximity to a coreable tree trunk.

Trunk Volatilization Sampling

Volatilization of TCE through trunk surfaces was sampled by using a recirculating enclosure consisting of a miniature pump (Gast, Benton Harbor, MI), a rectangular piece of Tedlar (cut from a sampling bag SKC, Eight Four, PA), Tenax sorbent traps, a manifold constructed from stainless steel, and appropriate Swagelok fittings (as shown in a the schematic in Figure 7). The manifold was constructed to mix the air under the Tedlar enclosure as well as prop the enclosure off the trunk to improve air mixing.

The Tedlar enclosure was fastened to the tree using duct tape and silicone sealant (Figure 8). Special care was made to ensure there were no gaps between the bark and the Teldar enclosure. A metering value was used to adjust the flow rate though the system from 100 to 150 ml/min. The air moving through the enclosure was directed through a series of Tenax sorbent traps to remove any volatile organic compounds. The area of the trunk or branch under the Tedlar enclosure was measured after the system was removed from the tree.

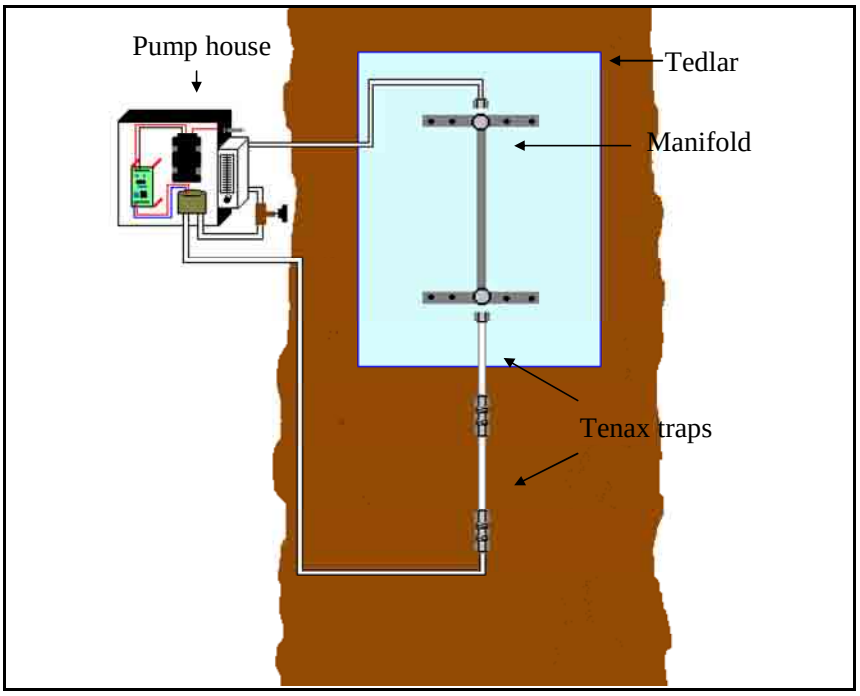

Figure 7. Trunk volatilization schematic.

Figure 8. Trunk volatilization collection at Poplar 3 (OU2).

Soil Flux Sampling

Soil flux samples were collected using a 1.4 L stainless steel chamber fitted with influent and effluent Swagelok fittings. Inside, the Swagelok fittings extended to two long stainless steel manifolds. Two Tenax tubes were placed in series on the effluent side of the chamber. The influent to the pump (SKC Personal Air Sampler Model 222, Eighty Four, PA) was connected to the second trap. Two 12V DC brushless fans (RadioShack) powered by batteries were placed under the apparatus to increase mixing. Uncontaminated sand was plied heavily around the edges of the apparatus to help minimize infiltration of uncontaminated air. The pump then circulated the air collected inside the chamber. This apparatus (Figure 9) was constructed similar to others used to sample TCE soil vapor flux (Tillman and Smith, 2004; Rogers, 2006). The apparatus was assumed to be a continuously stirred tank reactor (CSTR) and the recirculating design should eliminate or minimize the build up of pressure that can induce artificially high or low results. If the pressure in the system is too high, the built up pressure may not allow TCE to flux naturally from the soil. If the pressure is too low, the system may be pulling air from the soil, therefore increasing the natural flux.

Sample locations were selected based on proximity to wells, proximity to previously sampled trees, and in the open field near the interceptor trench. Samples were collected at a flow rate of 90 mL/min for 30 to 55 minutes, depending on previous estimates as to prevent overloading of the traps. Temperature under the chamber was monitored and the chamber was shaded from sunlight to prevent any significant temperature increases that would adversely impact VOC sampling flux.

Figure 9. Soil vapor flux sampling apparatus with re-circulating pump and Tenax traps.

Tenax Trap Analysis

Tenax traps were analyzed using a thermal desorption gas chromatography/mass spectrometry (GC/MS) procedure. Due to instrument problems two different thermal desorption units were used to analyze the Tenax traps.

The following method was used for samples collected up to May 2007. Trap samples were introduced into a Hewlett-Packard® 6890/5793 GC/MS equipped with a DB-624 capillary column (30 m x 0.25 mm ID x 1.4 µm film thickness) using a Tekmar 6000 AeroTrap Desorber equipped with cryo-focusing and moisture control-system. Desorber operating conditions were as follows: 1 minute trap sweep at 35°C; cryo-trap temperature = -165°C; Tenax trap desorb = 200°C for 10 minutes; cyro-trap desorb =

225°C for 1 minute. The moisture control system and the various traps were thermally cleaned between each sample.

Chromatographic conditions were as follows: DB-624, 30 m x 0.25 mm, 1.4 µm film thickness column (J&W Scientific, Folsom, CA); helium carrier gas at 0.7 mL/min (3.52 psi); temperature program 35ºC for 3 min to 170 ºC at 30ºC/min, then 170 to 200ºC at 50 ºC/min. with a 1 min. hold at the final temperature; split ratio was 15:1 and the GC inlet temperature was set at 250°C. The MS was operated in selected ion monitoring (SIM) mode. An external standard approach was used to quantify the mass of TCE and DCE collected in each trap. Standards were prepared by loading known amounts of TCE dissolved in methanol onto clean Tenax traps with a microsyringe.

The following method and instrument was used for samples collected after May 2007. Tenax trap samples during phytovolatilization and soil flux sampling were introduced into a Hewlett-Packard® 6890/5793 GC/MS equipped with a DB-624 capillary column (30 m x 0.25 mm ID x 1.4 µm film thickness) using a Perkin Elmer TurboMatrix ATD Automated Thermal Desorber. The desorber operating conditions were as follows: 5 minute trap purge; cryo-trap temperature = -30°C; Tenax tube desorb = 300°C for 10 minutes; cryo-trap temperature program -30°C initial temperature to 320°C at 40°C/s, transfer to GC/MS at 225°C. The moisture control system, traps, and tubes were thermally cleaned between each sample. The desorber operated at 9.4 psi causing a nominal flow rate of 1 mL/min.

Chromatographic conditions were as follows: DB-624, 30 m x 0.25 mm, 1.4 µm film thickness column (J&W Scientific, Folsom, CA); temperature program 35ºC for 2 min to 170 ºC at 30ºC/min, then 170 to 230ºC at 70 ºC/min. with a 1 min. hold at the final

temperature. The MS was operated in selected ion monitoring (SIM) mode. An external standard approach was used to quantify the mass of TCE and DCE collected in each trap. Standards were prepared by loading 1 µL of known amounts of TCE, dissolved in methanol onto clean Tenax traps with a microsyringe. Standard amounts range from 1.0 to 10,000 ng.

Plant Tissue Sampling for TCE and DCE

Twenty milliliter Headspace vials (Kimble Glass, Vineland, NJ) containing 10 mL of Matrix Modifying Solution (MMS) consisting of a saturated sodium chloride solution acidified to a pH of 2 with phosphoric acid (EPA SW-846, Method 5021 as Matrix Modifying Solution <http://www.epa.gov/epaoswer/hazwaste/test/pdfs/5021.pdf>) were pre-weighed. Using a 5.15mm increment borer (Forestry Suppliers, Inc., Jackson, MS), 1 to 3 grams of tree core tissue (fresh weight) were collected and placed immediately into the headspace vial with gloved hands. Figure 10 displays the incremental borer just before core removal from the trunk. Once the core was placed in the headspace vial, the vial was sealed with a Teflon coated butyl rubber septa and an aluminum crimp-top (National Scientific 20 mm open seal with Teflon/Butyl, National Scientific No. C4020-36A).

Antibiotic ointment was put inside the bore hole in the trunk to prevent infection of the tree. The hole was then sealed using silicone. The collected samples and quality control samples were transported back to the Utah Water Research Laboratory in an ice chest at 4^{o}C for analysis. The samples were re-weighed to determine the weight of the tissue analyzed.

Figure 10. Incremental borer used collect tree cores.

TCE Analysis of Plant Tissue and Groundwater Samples

To determine TCE and DCE concentrations within the collected plant tissues and groundwater, a headspace GC/MS method was used. Two milliliter headspace samples were introduced into a Hewlett-Packard® 6890 GC/5973 MS (running EnviroQuant, Chemstation G1701AA version D.03.00 data acquisition and analysis software) by using a Tekmar 7000HT Headspace Analyzer/Autosampler. The autosampler platen/sample temperature was set to 80 ºC. Samples were allowed to equilibrate for 10 minutes and the transfer line and sample loop temperatures were 180 ºC. Chromatographic conditions

were as follows: DB-624, 30 m x 0.25 mm, 1.4 µm film thickness column (J&W Scientific, Folsom, CA); helium carrier gas at 0.7 mL/min (3.52 psi); temperature program 35 ºC for 2 min to 170 ºC at 30 ºC/min, then 170 to 230 ºC at 70 ºC/min. with a 1 min. hold at the final temperature (total run time = 8.36 min.); split/splitless inlet vent flow 10.4 mL/min.; and split ratio of 2:1. The GC/MS was operated in SIM mode for TCE, c-DCE, t-DCE, and vinyl chloride.

The concentrations of TCE in the plant tissue and groundwater samples were then determined indirectly from TCE headspace concentrations. A minimum of five different external standards (minimum of five different concentrations), made by spiking known amounts of a commercial standard (Supelco, Bellefonte, PA) into MMS, were used to define the relationship between the headspace and MMS concentrations. The standards were made directly in headspace vials prior to calibration. Calibration verification standards and instrument blanks were place at the beginning and end of each run, as well as after every 10 samples to ensure the instrument was within calibration throughout the sample analysis period. Using an average fresh sample weight of 1.4 grams and GC/MS detection limit of 100 pg, the average detection limit for TCE in plant tissue was calculated to be 0.2 µg/kg.

Plant Tissue Collection for Metabolites

Large quantities (15 to 20 grams) of healthy leaves were collected from branches using gloved hands. The leaves were immediately placed in glass jars with Teflon-lined screw-top lids. The samples were then placed in a cooler and stored at 4^{o}C until return to the UWRL where they were frozen until analysis.

TCE Metabolite Analysis

Plant tissue was collected during sampling events and extracted using sodium hydroxide (NaOH) for haloacids followed by a methyl tert-butyl ether (MTBE) extraction. This extraction method was similar to the method reported by Newman et al. (1997). Approximately 5 grams of tissue was macerated and placed in a Teflon centrifuge tube with 7-10 mL of 0.25 M (NaOH). The tube was then shaken for 15 minutes and centrifuged at 9000 rpm for 10 minutes. The supernatant was carefully removed with a glass pipette and placed in a 50 mL clear plastic centrifuge tube. Addition of 0.25 M NaOH, shaking, and centrifugation was repeated a total of three times after which 4 mL of 50% sulfuric acid was added to reduce the pH below 0.5. Approximately 8 g of sodium chloride, along with 7 mL of MTBE was added to the centrifuge tube. This was then shaken for 15 minutes and then centrifuged at 2500 rpm for 5 minutes. The supernatant was again removed with a glass pipette and placed in a 25 mL volumetric flask. The addition of MTBE, shaking, and centrifugation was repeated a total of three times. The volumetric flask was then brought up to volume with MTBE.

The liquid extract was then passed through an anhydrous sodium sulfate packed pipette and transferred to two 2 mL GC vials (Fisher Scientific International, Inc., Hampton, NH). One GC vial was capped to be analyzed for TCEt, while the other vial required the addition of 0.2 mL of diazomethane, prepared using Dizald reagent (CAS # 80-11-5, Sigma-Aldrich, St. Louis, MS) and was allowed to rest for 30 minutes. The second vial was analyzed for TCAA and DCAA.

After the extractions were complete, a GC/MS was used to determine the concentrations of TCAA, DCAA, and TCEt. A 1 μL sample in MTBE was introduced

into an Agilent 6890 GC/5973 MS (running EnviroQuant, Chemstation G1701AA version D.03.00 data acquisition and analysis software) using an Agilent 7683 Series Injector. The analyses were performed in SIM mode (m/z 60, 95, and 130). Chromatographic conditions were as follows: column-DB-624, 30 m x 0.25 mm, 1.4 μm film thickness column (J&W 41 Scientific, Folsom, CA), helium carrier gas at 0.6 mL/min (3.52 psi), inlet temperature 200ºC, temperature program 35ºC for 2 minutes to 225ºC at 10ºC/min with a 2 minute hold at the final temperature (total run time = 23 min), set in splitless mode with purge flow of 20 mL/min for 2 minutes, MS quad temperature was 150ºC and MS source temperature was 230ºC.

Stable Isotope Sample Collection

One to 3 grams of tree core or stems were collected by either an incremental borer or garden clippers and placed directly into narrow test tubes. After the samples were collected, the test tube was capped with Teflon-lined septa and stored at 4^{o}C for analysis of $^{18}O/^{16}O$ and D/H.

Using a peristaltic pump and Teflon tubing, groundwater was pumped directly into 40 mL vials and sealed carefully with a Teflon-lined rubber septa to prevent a headspace. Aliquots of groundwater were then placed in 2 mL glass vials. The water was then sampled for $^{18}O/^{16}O$ and D/H analysis.

Stable Isotope Analysis

All samples collected for stable isotope analysis were sent to the University of Utah Stable Isotope Ratio Facility for Environmental Research (SIRFER) laboratory for analysis. Water for isotope analysis was extracted from stem tissue using a cryogenic

vacuum distillation technique (Ehleringer and Osmond, 1989). In this technique, frozen stem samples were placed in an evacuated chamber consisting of an ignition tube and water collection tube. The frozen stem samples in the ignition tube were then boiled and the resulting water was frozen using a liquid nitrogen trap placed on the water collection tube. On completion of the extraction, the resulting water samples were sealed in an airtight vial and stored until analyzed by MS. Oxygen isotope ratios were determined using a Finnigan Delta-S isotope mass spectrometer using CO_2 equilibration. Samples were also analyzed for hydrogen isotope ratios using a chromium reduction furnace to convert liquid water to hydrogen gas.

Digital Measurement of Leaf and Trunk Area

In order to determine the leaf and bark areas for each tree, digital photographs of the trees were taken at the end of the growing season. When the leaves were still on the trees, a 76.5 cm by 41 cm bright orange object was placed approximately half way through the tree to determine the canopy density coefficient of each tree. These digital photographs were used to determine the leaf area for scaling leaf volatilization by using Adobe Photoshop Extended Creative Suite 3. The yardstick used was measured for pixel length reference. Figure 11 displays an example of Willow 1 used for leaf area measurement. After the unwanted background or unnecessary trees were removed from the photograph (Figure 12), the number of pixels was calculated. The software then used the pixel length of the yard stick to calculate the area of leaves in the entire picture. The canopy density coefficient was multiplied by the total area which then accounted for half the tree. The area was then doubled to account for the back half.

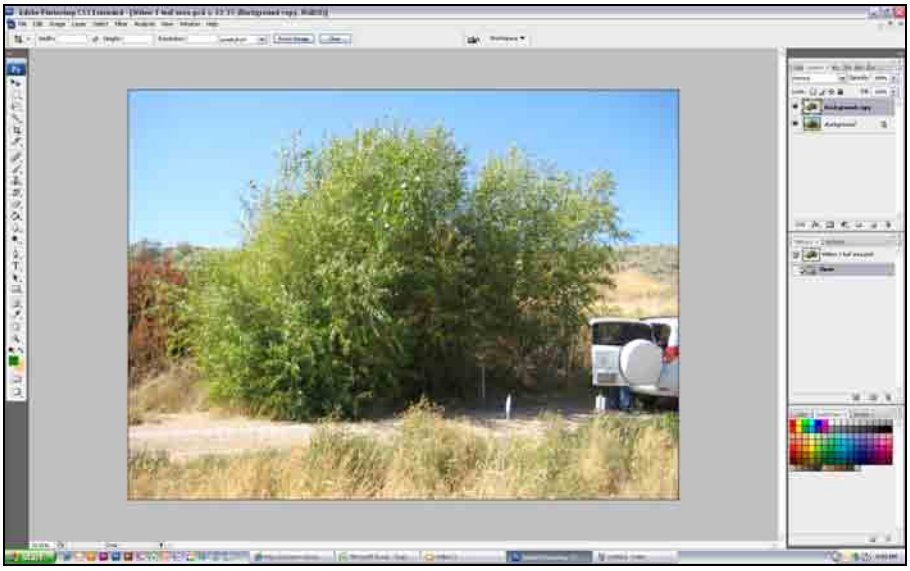

Figure 11. Photograph of Willow 1 used for leaf area measurement.

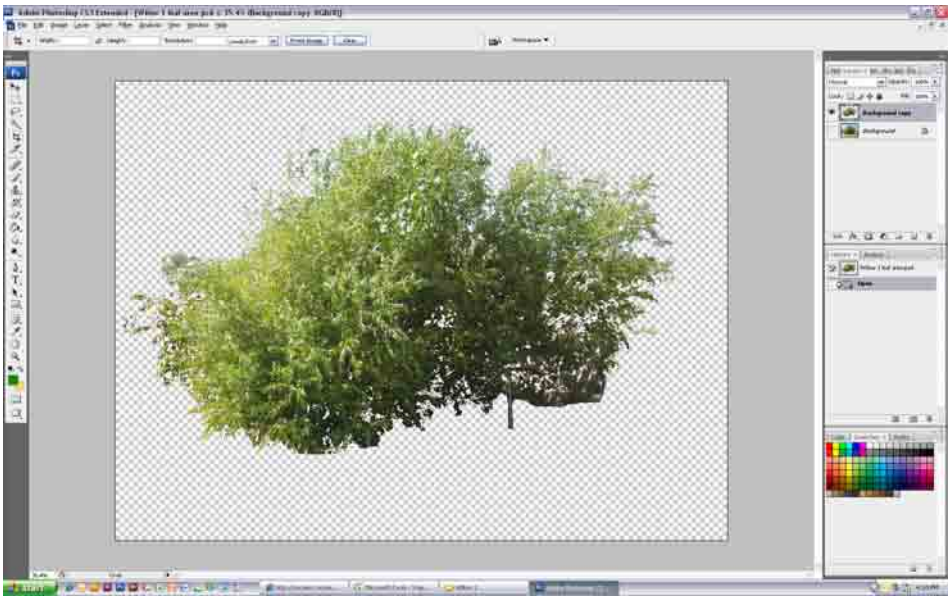

Figure 12. Background removed from Willow 1 for leaf area analysis.

Digital photographs were taken again in November 2007 when all leaves had fallen from the trees. The same process to measure leaf area was used to measure trunk area. An object of known length was placed in the picture as a pixel reference (Figure 13). The background and small branches were digitally removed from the photograph with the main trunk of the tree remaining (Figure 14).

In order to produce a three-dimensional trunk area from a two-dimensional estimate, it required the area to be multiplied by the number pi. This only accounted for the front half of the trunk, so the area was then doubled to produce an approximate trunk area for the entire tree.

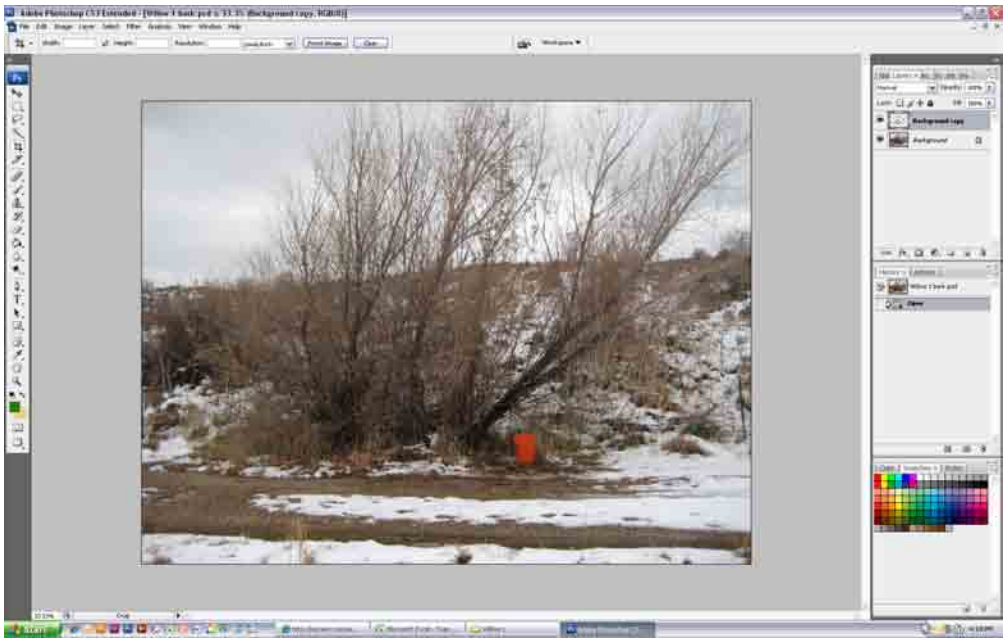

Figure 13. Photograph from Willow 1 used to measure bark area.

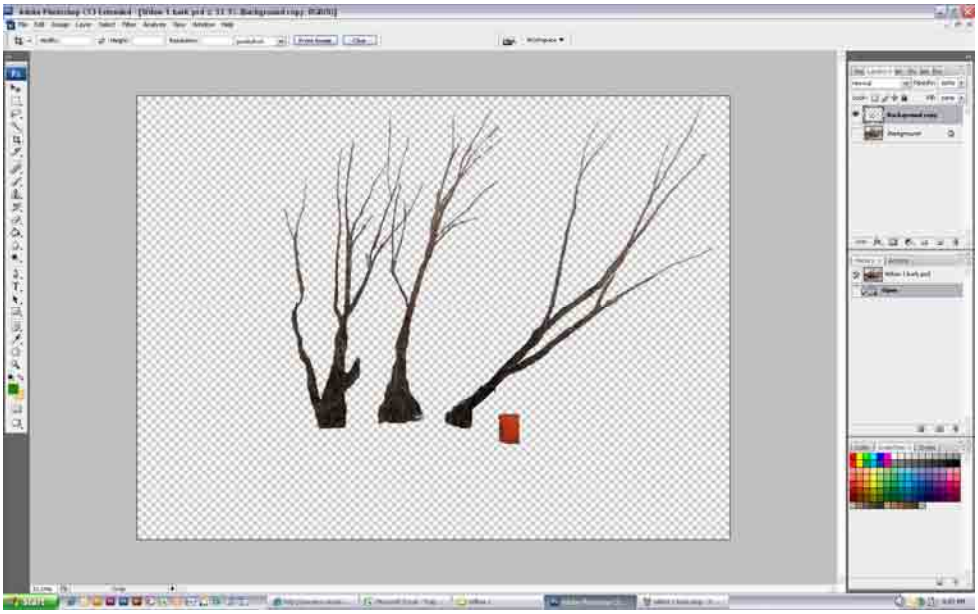

Figure 14. Image of Willow 1 with background digitally removed.

RESULTS AND DISCUSSION

OU2 Field Sampling Overview

Table 1 is a summary of all field samples collected in 2006, 2007, and 2008. Several trees were re-sampled in 2006 along the plume to ensure TCE was still present in previously sampled trees. Tree selection was based partially on previous volatilization sampling. Other factors such as accessibility to tree branches and location within the plume (Figure 1) helped to determine which trees were appropriate for sampling. Approximately 530 ft separated the sampled trees.

Table 1. Summary of field work performed

Date	Analysis Type						
	TC	GW	LV	TV	SSF	SI	M
2006							
7/21-7/28	X	X					
7/31	X	X					
8/18	X	X					
9/18	X		X	X		X	
9/30	X		X	X			X
10/18	X	X		X		X	
2007							
5/14-5/18	X	X	X	X	X	X	
6/26-6/27	X	X	X	X		X	X
9/12-9/21	X	X	X	X		X	X
11/5					X		
11/10	X	X					
12/5					X		
2008							
8/13					X		
8/15		X	X				

TC: Tree Cores; GW: Groundwater; LV: Leaf Volatilization;
TV: Trunk Volatilization; SSF: Soil Surface Flux;
SI: Stable Isotopes; M: Metabolites

Groundwater samples were collected near trees sampled for phytovolatilization and soil surface flux measurements. Samples were analyzed for TCE and stable isotopes of O and H. Groundwater samples were collected during each phytovolatilization sampling event to determine fluctuations in the TCE groundwater concentrations and stable isotope (H and O) composition. Tree core samples were also taken to determine TCE plant tissue concentrations. Precipitation samples for stable isotope analysis were collected at the UWRL. Leaf phytovolatilization and blank chamber samples were also collected from a mature willow tree at the UWRL to determine if there was any source of TCE and DCE contamination within the system as well as in the carrier gas. Tree cores collected from a Willow tree located at the UWRL were used as non-exposed control samples.

Groundwater Sampling

A summary of TCE concentrations in groundwater samples collected from monitoring wells is presented in Table 2. The complete set of measured groundwater concentrations of TCE, c-DCE, t-DCE, and vinyl chloride for all wells are presented in Tables C-1, C-2, and C-2 of Appendix C for the 2006, 2007, and 2008 seasons, respectively. Table 2 reports TCE concentrations from years 2005 through 2008.

The Seep concentrations, located near Poplar 1, vary between 55 and 72 µg/L. Well U2-020, located near Poplar 3, Willow 2, and the Russian olive, fluctuates between 137 and 275 µg/L. Well U2-080, near Willow 3 and Willow 4, fluctuates between 90 and 164 µg/L. Well U2-042, adjacent to Willow 1, was the least sampled and also had the lowest concentration of the groundwater sampled of 27µg/L. Well U2-042 was the only well that dramatically increased from 2007 to 2008. All other well concentrations did not

Table 2. Groundwater summary for 2005 to 2007

Year		Wells			
		Seep	U2-020	U2-080	U2-042
2005					
	Mean TCE Conc. (µg/L)	71.6	191.5	163.5	NS
	95% Confidence Interval	2.0	6.5	34.5	
	Number of Samples	6	9	9	
2006					
	Mean TCE Conc. (µg/L)	79.6	136.8	90.1	NS
	95% Confidence Interval	22.7	12.1	5.8	
	Number of Samples	6	9	9	
2007					
	Mean TCE Conc. (µg/L)	54.8	275.2	107.8	27.4
	95% Confidence Interval	5.9	38.8	25.2	18.0
	Number of Samples	5	12	12	12
2008					
	Mean TCE Conc. (µg/L)	NS	170.9	258.6	155.8
	95% Confidence Interval		55.9	91.7	5.2
	Number of Samples		3	3	3

NS- Not sampled

significantly vary. Without any drastic remediation efforts, contaminant addition, or changes in TCE source, the groundwater concentrations should remain constant.

Leaf Phytovolatilization Sampling

Previous studies at OU2 in 1999 and 2005 have shown that trees at this site phytovolatilize TCE. Phytovolatilization samples were collected from two trees at OU2 in the fall of 2006 to determine if the trees were still photovolatilizing measureable amounts of TCE. Additional samples were taken in the spring, summer, and fall of 2007. The number of samples on each tree collected, average transpiration stream concentrations (µg/L), and leaf flux concentrations (pg/cm^2/min) are listed in Table 3 for each corresponding year. Replicate samples and samples with non-detectable amounts of water were not used in calculating the average values. Replicate samples were not used

after it was observed that sample replication on the same branch induced considerable stress on the plant.

A full summary of data collected during the 2006, 2007, and 2008 sampling events are located in Appendix C in Tables C-4, C-5, and C-6, respectively. The TSCs were calculated using the amount of TCE collected on the Tenax traps divided by the amount of water collected on the corresponding silica trap for each sampling train. It was then converted to µg/L assuming the relationship of 1kg of water equals 1 L of water. The flux of TCE from the leaves was calculated by dividing the amount of TCE collected on the trap by the sampling duration, the leaf area, and the split ratio. The split ratio was the ratio of the total flow in through system to flow through the Tenax and silica traps.

Using the TSC values in Table 3, the amount of TCE transpired can be scaled to a 150-day growing season. A Dynamax sap flow meter was installed in August 2007 to aid in estimating whole tree transpiration rates. Several problems arose when collecting data in 2007. The whole system was installed in August, late in the growing season, which limited the data collected. The battery for the system was grossly undersized so data points were collected mostly between 1 p.m. and 1 a.m. (while the solar panel was in the sun long enough to charge the battery). The battery was replaced in the early summer of 2008. Transpiration was measured from June 26 to August 15 in 2008. The amount of water transpired for each sensor was summed (g/hour) from June 26 to August 15 and divided by the number of days of sample collection. The transpiration rates for each sensor ranged from 15 L/day to 160 L/day (Table 4), with an overall average of 60 L/day of water transpired.

Table 3. Summary of leaf volatilization samples collected in 2006 and 2007

	2006			2007		
Tree	Times sampled	Average TSC (µg/L)	Average leaf flux (pg/cm^2/min)	Times sampled	Average TSC (µg/L)	Average leaf flux (pg/cm^2/min)
Poplar 3	1	NWC	6.2	3	3.1	1.3
Russian Olive	NS	NS	NS	5	1.1	0.8
Willow 1	1	NWC	33.2	5	30.0	3.3
Willow 3	NS	NS	NS	3	5.1	2.3
Willow 4	NS	NS	NS	3	2.4	0.9
Overall Average		0	19.7		11.9	1.9

Table 4. Sap flow sensor data for 2008

Tree	Sensor	Transp. (L/day)	Average Transp. (L/day)	Leaf Area (cm^2)	Trunk diameter at 1 m above ground (cm)
Poplar 3	TDP1	73.3			
Poplar 3	TDP2	158.9			
Poplar 3	TDP3	94.9	109.0	446,804	44
Russian Olive	TDP6	14.8			
Russian Olive	TDP7	16.1	15.4	298,319	93
Willow N of Russian Olive	TDP11	98.1			
Willow N of Russian Olive	TDP12	384.9*	98.1	Not Calc.	25
Willow 2	TDP4	30.0			
Willow 2	TDP5	62.0			
Willow 2	TDP15	74.1	55.4	327,189	30
Willow E of Poplar 3	TDP13	37.9			
Willow E of Poplar 3	TDP14	56.5	47.2	Not Calc.	28
Willow N of Poplar 3	TDP9	34.0			
Willow N of Poplar 3	TDP10	23.0	28.5	Not Calc.	18
Overall Average =		59.5			

*Value was not used because of suspected sensor damage.

The reason estimates varied may be due to the positioning within the plume and size of the tree. Poplar 3 was the tallest of the trees at the site, therefore in the sun most of the day, which can increase the amount of water transpired. All the willows ranged from 28 to 98 L/day. The smaller trees (Willow north or Poplar 3 and Willow east of Poplar 3), which were shaded by larger trees have lower transpiration rates as they did not receive direct sunlight during the majority of the day.

The Russian olive had the smallest transpiration rate of all the trees sampled. This may have been due to the uneven bark thickness on the tree, sizing of the probe, and the inability to properly reach the sapwood where the sap flows. This would have given an artificially low transpiration rate if the sapwood was not reached. Sensor 12 in the Willow north of the Russian olive was found outside the tree late in the 2007. The sensor was replaced, but there may have been significant damage to the sensor while outside of the tree, therefore the data from TDP 12 was not used.

The equation from Ferro et al. (2001) was also used to estimate transpiration rates of 227 L/day and 241 L/day for 2006 and 2007, respectively, which is higher than the sap flow meter measurements. This estimate is slightly higher than other estimates made by Roger (2006) (152 L/day) and Wullschleger, Meinzer, and Vertessy (1998) (10 to 200 L/day). Despite the efforts to directly measure transpired water, digital approximation of leaf area had to be used to scale volatilization when no water was collected during sampling.

No water was collected from the trees sampled in 2006; therefore the average emission rate of 2026 mg/tree/year was based on measured leaf flux and total leaf area. The results for this year may be skewed because Willow 1 and Poplar 3 were the only

trees sampled, and the TSC of Willow 1 had been consistently and significantly higher than any of the other trees sampled at OU2. The average TSC for all trees in 2007 was 11.9 µg/L. A summary of calculation made in Table 5 used a 150-day growing period with an average of 60 L/day transpiration rate and the calculated leaf area to estimate and compare the amount of TCE lost by leaf volatilization in 2006 and 2007. The amount of TCE lost due to water transpiration was 107 mg/tree/year, whereas losses based on leaf area were estimated to be 211 mg/tree/year.

A sampling event was performed in August 2008 to verify if the TSC were comparable to previous years (Table C-6 of Appendix C). A summary of the TSC, the leaf flux, and losses are in Table 6. Only three trees were sampled: Willow 1, Poplar 3, and Willow 4. These trees were chosen because they intersected the plume and were sampled in previous years. The average TSC was 18.9 µg/L and the average flux concentrations were 2.8 pg/cm^2/min, which are both slightly higher than the previous 2 years, but still fell into the same range as the previously sampled years.

Table 5. Summary of TCE losses from leaves in 2006 and 2007

		2006		2007	
Tree	Leaf Area (cm^2)	Losses based on TSC (mg/yr/tree)	Losses based on area (mg/yr/tree)	Losses based on TSC (mg/yr/tree)	Losses based on area (mg/yr/tree)
Poplar 3	446,804	0.00	595.0	38.5	151.7
Russian olive	298,319	NS	NS	13.6	10.8
Willow 1	492,524	0.00	3529.1	378.3	463.3
Willow 3	491,025	NS	NS	63.8	239.8
Willow 4	637,100	NS	NS	30.7	102.2
Overall Average		0	2062.1	107.2	210.9

NS: not sampled

Multiplying the low and high measured average TSC values of 2.4 to 46 µg/L from 2007 and 2008 (Tables 3 and 6) by the sap flow transpiration estimates (15 to 160 L/day) and a 150-day growing season, a range of values of TCE phytovolatilized from 5.4 mg to 1 g/yr per tree can be calculated. This also assumes that the trees use contaminated groundwater for all their water needs.

The phytovolatilization data indicated that there was no general trend attributed to seasonal change. Some trees were transpiring more TCE at the beginning of the growing season, while others displayed higher rates at the end. The Russian olive completely stopped volatilizing TCE towards in the last sampling event, possibly in response to extreme heat in the summer months. Another possible reason for lack of seasonal trends may be from consistency in groundwater concentrations. Constant groundwater concentrations would mean the TSC should be steady state, unless access to other water sources (precipitation or irrigation) is available.

Table 6. Summary of 2008 leaf phytovolatilization sampling measurements and results and corresponding losses

		2008				
Tree	Leaf Area (cm^2)	Times sampled	Avg. TSC (µg/L)	Losses based on TSC (mg/yr/tree)	Average leaf flux ($pg/cm^2/min$)	Losses based on area (mg/yr/tree)
Poplar 3	446,804	1	46.0	414.4	5.7	551.9
Russian olive	298,319	NS	NS	NS	NS	NS
Willow 1	492,524	1	33.8	304.2	1.9	200.3
Willow 3	491,025	NS	NS	NS	NS	NS
Willow 4	637,100	1	9.4	84.5	1.1	236.4
Overall Average			18.9	170.1	2.8	683.2

NS: not sampled

The sample concentrations have not changed significantly from 2005 to 2007, but have decreased significantly since the 1999 study. The groundwater TCE concentrations were reported to range from 100 to 1000 µg/L in 1999 with a TSC ranging from 80 to 363 µg/L. The highest concentration groundwater detected below the canal area since the 1999 study was 390 µg/L. The decrease in the groundwater TCE concentration may have led to the decrease in TCE TSC.

Trunk Volatilization Sampling

An apparatus was built and tested to measure possible volatilization of TCE from mature trees sampled for leaf volatilization. A large concern was the potential of volatile contaminants off-gassing from the materials used to fasten the apparatus to trees (duct tape and silicone). In order to assess this, the apparatus was placed on the TCE-free willow at the UWRL used for leaf volatilization control samples. After trial events, it was determined that no volatile contaminates were detected from the apparatus materials. The apparatus was then deemed suitable for trial field studies at TCE contaminated sites such as OU4 and OU2. Trial events were conducted in the fall of 2006 on the large cottonwood at OU4 used in previous studies at USU. This tree has had consistently high amounts of TCE present in both tree cores and the transpiration stream.

Large amounts of TCE were found to volatilize from the OU4 Cottonwood in flux samples collected for 30 minutes. In order to assess the affects of non-continuous bark cover, an experiment was performed with a cored trunk on the OU4 Cottonwood. First the trunk was sampled in the usual manner. Next, the apparatus was removed from the trunk and a core was bored and left unsealed. The apparatus was then replaced in the same location as previously sampled, and trunk volatilization was re-sampled. Flux

measurements with the core removed from the trunk were significantly higher than the flux samples taken with undisturbed bark.

Once the apparatus proved sufficient for TCE collection, two more systems were constructed to allow for simultaneous collection from three heights along the tree trunk. Samples were collected three times during 2007. The data were used to determine any spatial variation along the trunk as well as any seasonal variations within the data. The area of the apparatus combined with the digital measurement of the tree trunk allowed for whole-tree scaling.

A summary of the samples taken at OU2 during the 2006 and 2007 sampling events and the average trunk flux rates are in Table 7. A full summary of the 2006 trunk volatilization results are located in Table C-7 and the 2007 sampling results are in Table C-8 of Appendix C.

Table 7. Summary of trunk volatilization samples taken and flux results for 2006 and 2007

	2006		2007	
Tree	Times sampled	Average trunk flux ($pg/cm^2/min$)	Times sampled	Average trunk flux ($pg/cm^2/min$)
Willow 1	1	0.02	5	1.32
Willow 2	NS	NS	4	0.02
Willow 3	1	NS	4	0.04
Willow 4	NS	NS	3	0.03
Poplar 3	NS	0.02	4	0.06
Overall Average*		0.02		0.04

NS: not sampled

* Overall average not including Willow 1

The amount of TCE volatilizing from Willow 1 increased dramatically from 2006 to 2007. This may have been due to any number of factors including: non-continuous or damaged bark, TCE concentrations within the tree, increased dependency on groundwater use from lack of precipitation, plant stress due to heat during sampling event, or variability of water movement in the trees due to changing growing season from year to year. Sampling from cored and uncored trees has shown that trees with areas of compromised bark can have significantly higher volatilization rates than areas with uncompromised bark. It was believed that this value was not representative of the rest of the trees at OU2 and was not used in the calculations.

Assuming that the any seasonal fluctuations were negligible, the average flux rate over the 2006 and 2007 period was 0.04 ($pg/cm^2/min$) (not including Willow 1 2007 values). Using the flux rate and the corresponding digitally calculated trunk area, an average TCE loss and a 150-day growing season, the average flux was calculated to be 4.1 mg/tree/year (Table 8). Using the measured high of 1.32 $pg/cm^2/min$, the trunk area from Willow 1, and a 150-day growing season, it was calculated that a possible high 62 mg/tree/year could be lost from tree trunks.

Because the trees were already volatilizing TCE in the spring, it might be beneficial to hold sampling periods during the early spring and winter time to determine if the trees at OU2 volatilize TCE from their tree trunk all year around. More sampling periods over longer amounts of time would be necessary to determine any significant losses. This could provide a more complete estimate of TCE losses if found to volatilize year round.

Table 8. Estimated TCE losses from trunk volatilization and yearly losses in 2006 and 2007

		2006	2007
Tree	Trunk Area (cm^2)	Losses based on area (mg/yr/tree)	Losses based on area (mg/yr/tree)
Willow 1	218,292	1.04	62.2
Willow 2	274,583	NS	1.4
Willow 3	270,399	NS	2.5
Willow 4	277,132	NS	1.6
Poplar 3	600,470	1.95	9.6
Overall Average*		1.50	4.1

NS: not sampled

* Overall average not including Willow 1

Soil Flux Sampling

Previous surface soil flux sampling conducted in 2005 recorded a maximum flux of 256 $\mu g/m^2$/day (Rogers, 2006). Samples were taken at Willow 1, Well U2-020, and Well U2-080. The flow-through sampling apparatus used in the 2005 sampling required an external gas source, which was complicated and difficult to maneuver within a field setting. Efforts to reduce the sampling apparatus size and maximize portability resulted in a newly designed chamber. A re-circulation flow chamber eliminated the need for the external carrier gas required for the old system. The new design was modeled on previous sampling equipment designed for soil flux sampling at OU2.

To determine if the two approaches (flow through and re-circulation) provided similar results, both apparatuses were used to collect samples simultaneously in June 2008 at the OU2 site within a few feet of each other. Preliminary analyses indicated that

the soil surface flux was highly variable even over short distances (2-3 feet). It was then determined that an in-lab side-by-side comparison using a TCE permeation device (Metronics Dynacal, Poulsbo, WA) where the temperature and attachment surface could be controlled would provide a more accurate comparison. The TCE emitter was placed below the apparatus and the apparatus was then fastened to a glass surface using silicone. The flux was measured over a period of 330 minutes. Results displayed in Figure 15 indicated that the there was some variability associated with the sampling process. An analysis of variance (ANOVA) was used to determine if the sampling apparatus and the sampling time affected the flux. Results from the ANOVA indicated that there is no statistical difference between the apparatuses, but there was a time difference. There seemed to be a decreasing trend in flux over the time the flux was sampled.

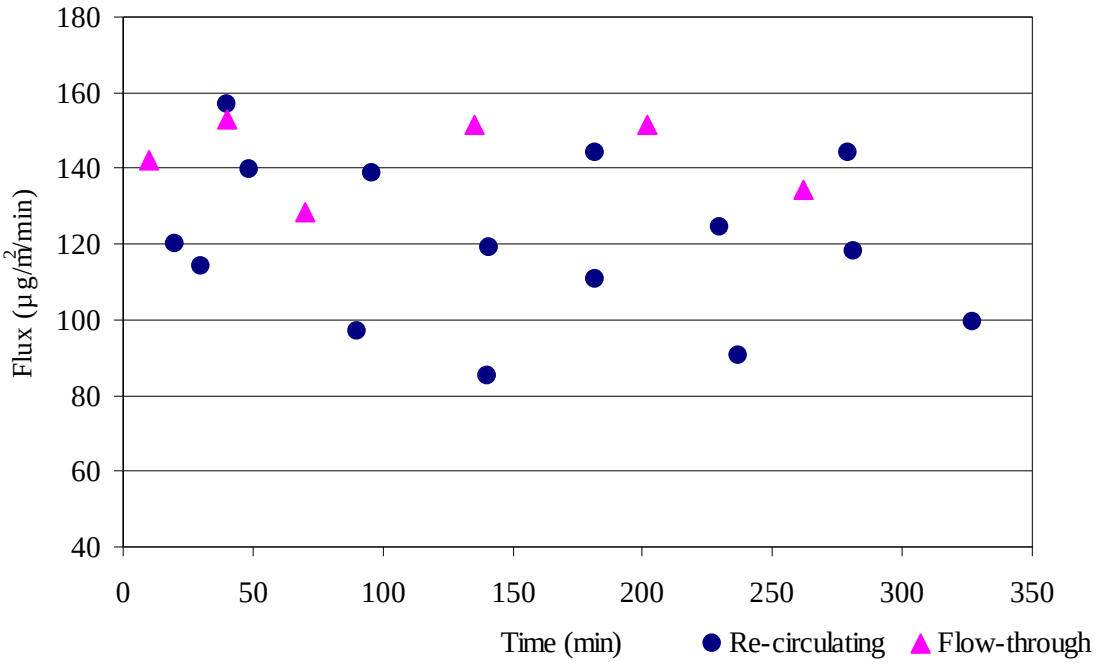

Figure 15. Comparison of soil flux apparatuses performed in-lab using TCE emitters.

Historical groundwater data and previous field sampling locations (2005 events) were used to establish an area over which TCE would be emitted from the soil. Table 9 displays the soil flux locations and concentration with nearby groundwater concentrations and depth. A full summary of the flux measurements is in Table C-9 of Appendix C. Figure 16 shows where in the plume the samples were taken.

Digital measurement of the plume area using Adobe Creative Suite 3 showed that there was approximately 28,115 m^2 of surface area where TCE may be emitted from the soil surface. This area included portions that were covered in trees and extended up to South Weber Drive on the north end of the plume. Sample collection in November 2007 indicated that TCE was still fluxing from the soil. This might be because the ground was not completely frosted or snowed covered. This meant that soil might be fluxing TCE up to, or more than 6 months out of the year (approximately 180 days).

Table 9. TCE soil surface flux and groundwater concentrations from 2008

Location	Date Analyzed	TCE Soil Surface Flux ($\mu g/m^2/day$)	Depth to GW (ft)	Nearby GW conc. ($\mu g/L$)
U2-046	8/14/2008	136.5	11.8	994*
Poplar 3	8/14/2008	495.1	13.2	171
U2-020	8/14/2008	1.0	13.2	171
U2-237	8/14/2008	27.0	5.9	9.9***
N of pump shed	8/14/2008	3.6	13.6	75*
Willow 3	8/14/2008	1.6	11.2	259
Willow 1	8/15/2008	71.8	5.9	156

*2006 data

***Provided by Hill Air Force Base

plume at OU2.

Since the flux measurements varied greatly over the plume, the Thiesson Polygon method was used to determine an area over which each flux measurement would correspond. It is based on the hypothesis that, for every point in the area, the best estimate of flux is the measurement physically closest to that point. This approach is implemented by drawing perpendicular bisectors to straight lines connecting each two measurement locations. This yields a set of closed areas known as Thiessen polygons as shown in Figure 17. A boundary addition of 10% was used around the perimeter of the polygons.

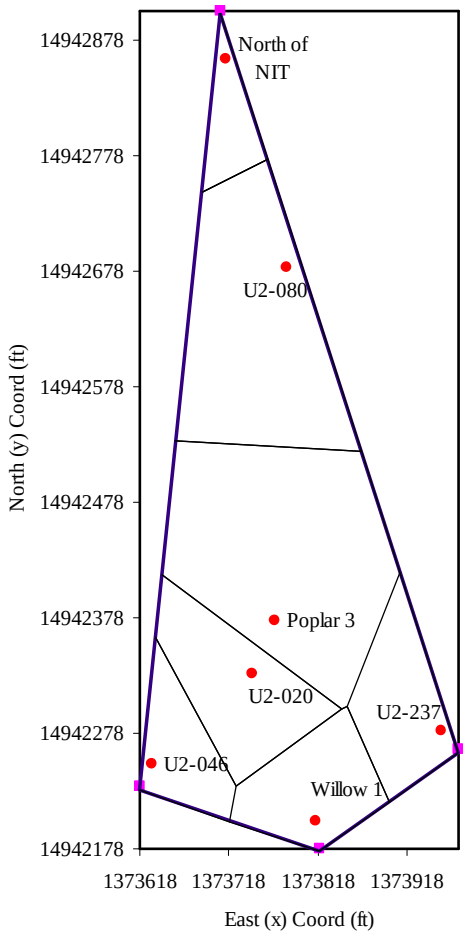

Figure 17. Polygons generated from the Thiesson Polygon method. Each polygon's area and corresponding flux measurement was used to calculate an overall loss for the area below the canal.

The area of each constructed polygon from the Thiesson polygon method was then calculated. Each sampling point, each point's geographic X and Y Universal Transverse Mercator (UTM) coordinates, and corresponding areas are in Table 10. Poplar 3 had the largest area, which also corresponds to the largest flux measurement. The total area over which the flux measurements were scaled was 12,200 m^2. This was less than half the area calculated by digital measurement of the plume. The boundary layer of 10% could be increased until the full 28,000 m^2 is accounted for.

Using the calculated areas from the Thiesson polygon method, the corresponding flux for each polygon, and a 180-day frost-free season, a total loss was calculated to be 391 g/year (Table 11). Because Poplar 3 had the largest area and the largest flux measurement, the total loss may be skewed higher than the actual flux.

Table 10. Summary of the soil surface flux points and the areas calculated from the Thiesson Polygon method

Sampling point	X-Coord. (feet)	Y-Coord. (feet)	Area (ft^2)	Area (m^2)
U2-046	1373631.934	14942251.1	8,757.2	813.6
Willow 1	1373815.661	14942201.9	12,842.2	1193.1
U2-237	1373956.737	14942280.7	12,640.2	1174.3
Poplar 3	1373769.729	14942375.8	42,037.6	3905.4
U2-020	1373743.482	14942329.9	16,430.1	1526.4
U2-080	1373782.852	14942680.9	33,237.5	3087.9
North of NIT	1373713.955	14942861.4	5,457.7	507.0
Totals			131,402.5	12,207.7

Table 11. Summary of soil surface flux, flux areas from Thiesson Polygon method, and yearly losses

Sampling point	Area (m^2)	Measured Flux ($\mu g/m^2/day$)	TCE Loss ($\mu g/day$)	TCE Loss (g/yr)
U2-046	813.6	136	110645.0	19.9
Willow 1	1193.1	72	85902.0	15.5
U2-237	1174.3	27	31706.5	5.7
Poplar 3	3905.4	495	1933182.3	348.0
U2-020	1526.4	1	1526.4	0.3
U2-080	3087.9	1.6	4940.6	0.9
North of NIT	507.0	3.6	1825.3	0.3
Totals	12207.7			390.6

*Based on a 180 day season

Two factors that have been previously correlated to flux of volatile organic compounds were depth to groundwater (Smith, Tisdale, and Cho, 1996) and groundwater concentrations (Kerfoot, 1987). Higher groundwater TCE concentrations generally mean higher TCE flux from the soil surface. Also, shallower groundwater generally means higher soil surface flux. In order to determine if these two factors have affected the soil surface flux at OU2, the fluxes were plotted against the depth to groundwater (Figure 18) and the groundwater concentration (Figure 19). Because the flux was so variable over the soil surface, it was difficult to determine if soil surface flux can be related to either groundwater depth or concentration. Neither graph indicated a strong relationship between either soil surface flux and groundwater TCE concentrations or soil surface flux and depth to groundwater. This correlation could be improved by additional measurements performed in open areas away from trees. A correlation between soil flux and proximity to trees would also be beneficial in estimating soil surface flux

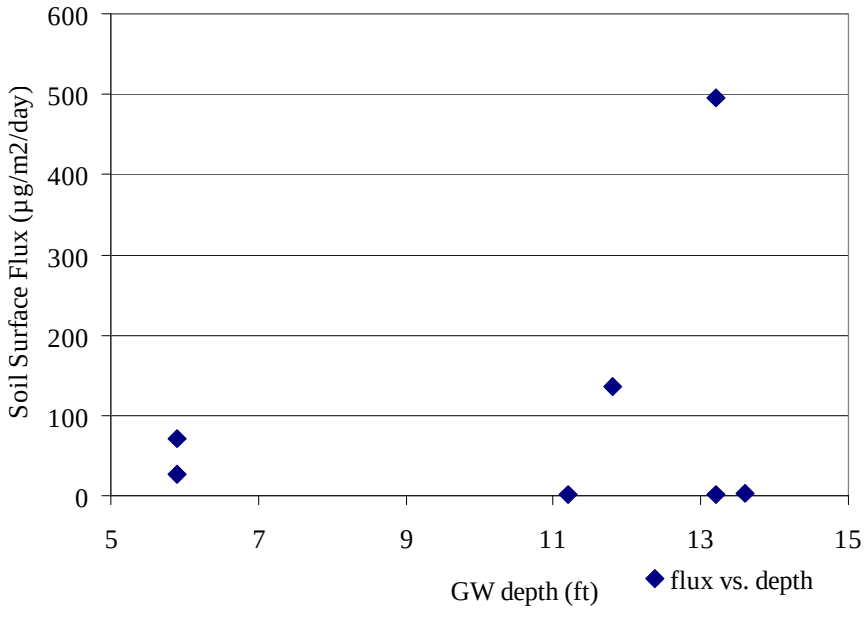

Figure 18. TCE soil surface flux versus groundwater depth from 2008.

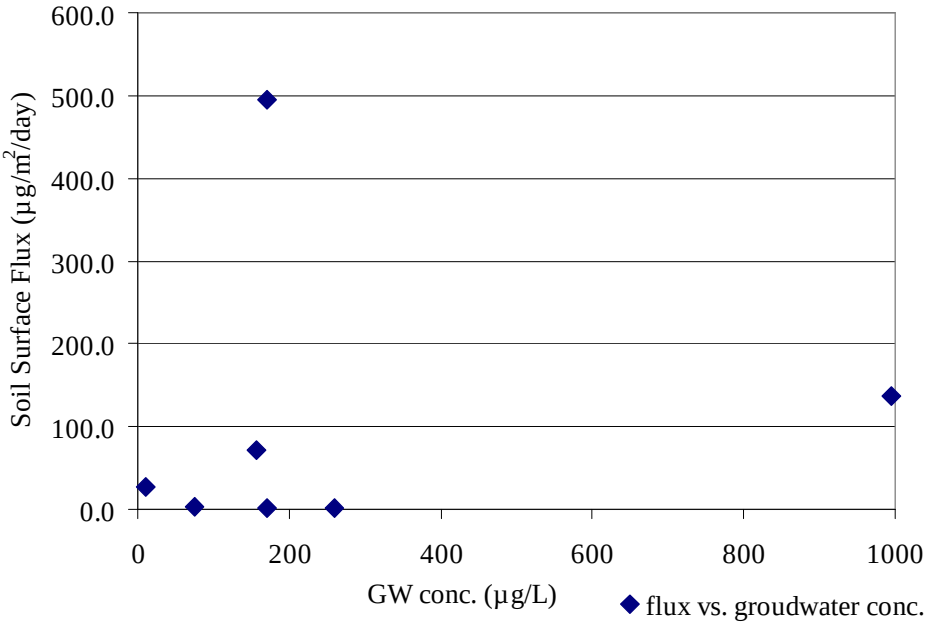

Figure 19. TCE soil surface flux versus groundwater concentrations from 2008.

Overall Volatilization Losses

Using the TSC values of 2.4 to 46 µg/L, the sap flow transpiration estimates (15 to 160 L/day), and a 150-day growing season, a range of values of TCE phytovolatilized from 5.4 mg to 1 g/yr per tree was calculated. Trunk losses are estimated to be 4.1 mg/tree/year, with a possible high of 62 mg/tree/year from Willow 1. Approximately 30 trees are growing over the plume area indicated in the Thiesson polygon area calculation. When combing these estimates and using the approximate number of trees in the plume the entire losses from the trees was 0.3 to 35 g/year.

From the data collected in this event and past sampling events it was evident that the soil surface may be a larger fate pathway than the trees. It was estimated that 390 g/year is lost to the atmosphere just from surface flux. Combined losses of the trees with

the soil losses ranged from 390 to 424 g/yr. Calculations for these losses can be found in Appendix D. If a tree planting project were instituted with the addition of 1000 tree, the losses from tree would increase from 0.3 to 35 g/yr to 9 to 1,160 g/year, potentially increasing the natural attenuation losses to over a kilogram of TCE removed per year. Increasing the amount of trees in the area could also help to increase the amount of TCE from soil surface flux , therefore removing even more TCE.

For the 2007-2008 contract year, 2.5 kg of TCE was removed by the interceptor trench. In comparing the losses via natural attenuation to the interceptor trench, natural attenuation processes removed one-sixth less TCE than the interceptor trench at no additional cost. This was significant in that there was no extra cost for these natural attenuation processes.

Although the methods of sampling leaf and trunk volatilization were effective, they were time intensive and required specialized equipment. To avoid this, simpler methods of sampling such as tree coring may be used if the relationship between core and leaf and trunk volatilization could be established. Appendix E addresses the possible relationship between tree cores and volatilization and metabolism at OU2. Appendix F displays the data associated with the samples collected in Appendix E.

Stable Isotope Results

Several tree cores, branches, and groundwater samples were collected for stable isotope analysis from OU2: once a year in 2005 and 2006, and three times during 2007. The data collected were used to compare the H and O stable isotope ratios with samples collected from precipitation events, the nearby canal at OU2, and nearby groundwater sources. Potential water sources were assessed, as well as the seasonal variations in

isotopic ratios. Table 12 shows the averages and standard deviation of the groundwater, canal water, tree cores, and precipitation samples collected during 2005 to 2007. All stable isotope collected in 2006 and 2007 results are listed in Table C-10 of Appendix C. Only a few samples were collected in 2006. In some instances, tree stems or braches were collected instead of cores to reduce stress on the tree from multiple coring events.

The average δD and $\delta^{18}O$ groundwater ratios in 2005, 2006, and 2007 remained constant from year to year. The fluctuation of the ratios may have been due to infiltration from precipitation events that have higher δD and $\delta^{18}O$ ratios.

Precipitation was only sampled twice within the 3 years and varies significantly. The 2005 samples were -2.5 and 3.5 for δD and $\delta^{18}O$, respectively, where as the 2007 samples were -99.9 and -13.9. The δD precipitation ratios can vary depending on the time of year, which may account for wide ranges of ratios (Flanagan and Ehleringer, 1991).

Table 12. Stable isotope samples from 2005 to 2007

Year	Sample Type	Average Delta D	Delta D St. Dev	Average Delta ^{18}O	Delta ^{18}O St. Dev
2005					
	Groundwater	-123.3	2.2	-16.3	0.3
	Cores/Stem	-129.5	1.5	-15.2	0.3
	Precipitation	-2.5	0.7	3.5	0.3
	Canal	-126.8	4.4	-16.7	0.8
2006					
	Groundwater	-125.0	NA	-15.7	NA
	Cores/Stem	-131.0	2.6	-15.0	0.3
	Precipitation	NS	NS	NS	NS
	Canal	NS	NS	NS	NS
2007					
	Groundwater	-117.3	3.1	-15.0	0.1
	Cores/Stem	-123.1	5.4	-13.8	2.4
	Precipitation	-99.9	2.8	-13.9	0.4
	Canal	NS	NS	NS	NS

NA: Only one sample was collected and a standard deviation could not be calculated.
NS: Not sampled.

At Coral Pink Sand Site in Southern Utah, precipitation δD values in February 1989 were -153. Later that year in July the ratio had increased to -10. Despite this large fluctuation in precipitation ratios, the ratios are still higher than the groundwater ratios indicating if infiltration of precipitation had occurred it would increase the stable isotope fractionation. The cement lined canal was tested along with the groundwater and precipitation samples as a possible water sources. The ratios of δD and $\delta^{18}O$ were -126.8 and -16.7, respectively. These values were close to the groundwater fractions measured in 2005.

The average core and stem ratios were slightly lower than the groundwater ratios, indicating that there may not have been significant amounts of precipitation previous to collection that could increase the stable isotope ratios. Figures 20 and 21 divides the δD and $\delta^{18}O$ ratios into seasonal sampling events.

The core ratios are approximately the same as the groundwater ratios. The δD ratios appear to decrease slightly over the growing season, whereas the δ18O remain relatively constant. Generally during transpiration evaporative enrichment of the stable isotopes occurs in the leaves and stems when the lighter isotopes of water evaporate faster than the heavier isotopes (Dongmann et al., 1974), therefore increasing the stable isotope ratios. Since there is a general decreasing trend in the δD and the δ18O it is unlikely that evaporative enrichment is happening in the stems and trunk.

Since OU2 is located in semi-arid climate with minimal amounts of precipitation water is scarce. The canal at OU2 is concrete lined, which minimizes infiltration. Using these factors, it is assumed that groundwater is the primary source of water for trees. It is

important to note that although there was surface water available in May of 2007 from spring runoff, the trees were still volatilizing TCE from both leaves and trunk.

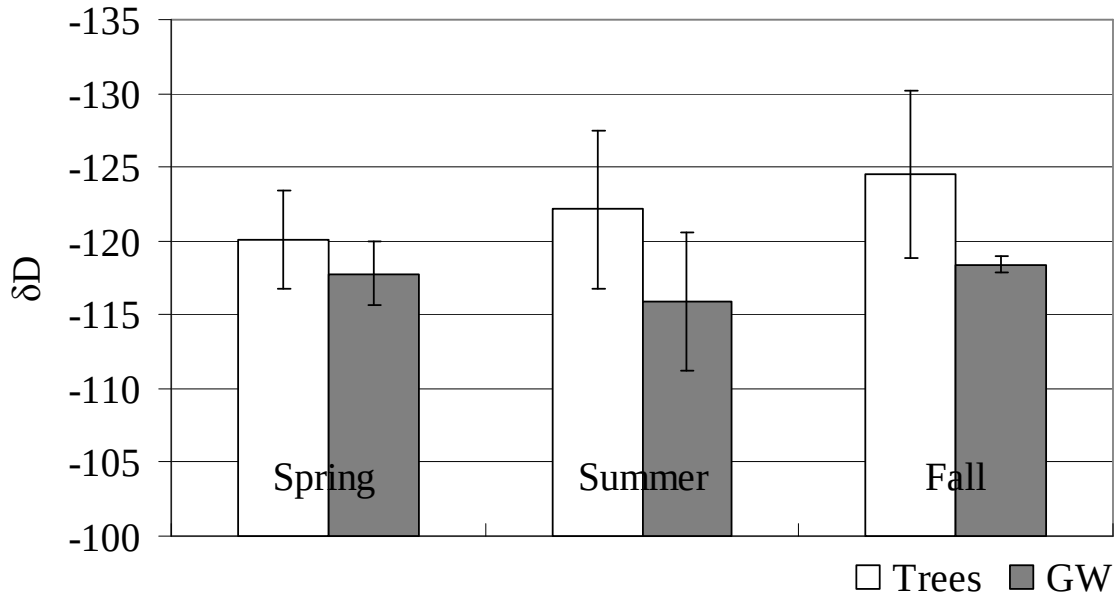

Figure 20. Delta D changes throughout the 2007 growing season.

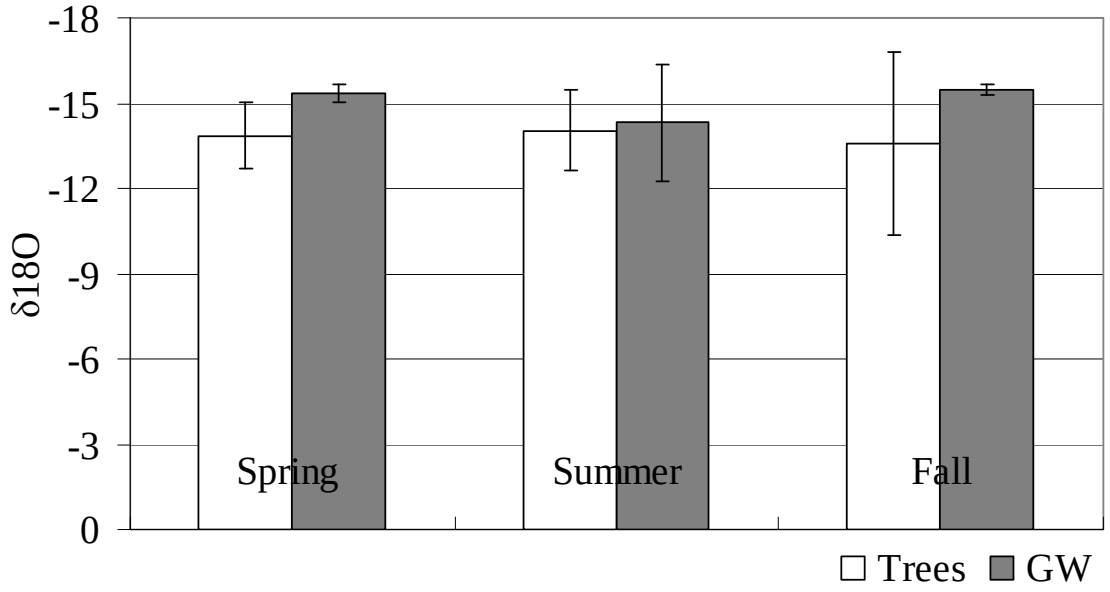

Figure 21. Delta 18O changes throughout the 2007 growing season.

Discussion

Experimental results verified the 2005 estimates performed at OU2, indicating that leaf phytovolatilization remained constant through the years. This was contingent upon the steady state of accessible groundwater concentrations and continual use of groundwater. Trunk volatilization had been observed at other sites in the United States. This research suggests that trunk volatilization was happening at OU2, but was not nearly as significant as losses from leaf volatilization.

Soil surface flux was estimated to be a much larger fate pathway than trees. Combining the tree losses and soil surface flux losses only amounted to a maximum of 424 g/year, which was estimated lower than the observed removal in the interceptor trench. Increasing the number of sample measurements may lead to a better correlation between flux and depth to groundwater and flux and groundwater TCE concentration. Observations have been made that the presence of trees increases the amount of soil surface flux (Marr et al., 2006). Increasing the amount of trees may help increase the removal of TCE via from natural attenuation processes that would in turn decrease the dependence on the interceptor trench for removal.

Since the TSC and tree core concentrations of Willow 1 were significantly higher than other trees, the groundwater collected from the well adjacent to the tree may not be representative of the groundwater concentrations utilized.

System and Sampling Improvements

During leaf volatilization sampling, water was not collected in several samples. A better method of sample collection would reduce the sampling trains from two to one and

divert the excess flow to a silica trap. The excess flow could capture larger amount of water than the two sampling trains. A better method of sample duplication of leaf volatilization samples that limited the stress on the branch would helpful to verify data. Too much stress on the branch was observed in two consecutive half-hour sampling periods.

Although there was a groundwater monitoring well adjacent to Willow 1, there are concerns that there may be an unmonitored high source TCE groundwater that caused the TSC and trunk volatilization results to be much greater than the other trees. A push probe for groundwater collection may help in determining this possibility.

Better estimation of some of the parameters (LAI, Kc, and area covered by the canopy) in the Ferro et al. (2001) approach to volatilization estimation would help to refine and corroborate tree water transpiration.

SUMMARY AND CONCLUSIONS

Phytovolatilization processes have been investigated since 1999 at OU2 on Hill AFB, UT. The TCS ranged from 2.4 to 46 µg/L, with an overall TSC from 2007 of 11.9 µg/L. Assessments of average TCE losses from leaf volatilization based on leaf area and transpiration ranged from 107 to 211 mg/tree/year (2007 estimates). Total losses ranged from 5.4 mg/tree/year to 1 g/tree/year. Volatilization losses from the trunk are much less significant at only 4.1 mg/tree/yr. All estimations were made using a measured sap flow measurement of 15 to 160 L/day and an average of 60 L/day transpiration rate or the area of the individual tree (depending on water collection), and an average growing season of 150 days. It appeared that the volatilization and TSCs remain constant over time.

Soil surface flux ranged from 1 to 495 µg/m^2/day from samples collected in 2008. Using the Thiesson polygon method, an area of 12,200 m^2 and a 180 day frost-free season was used to calculate a TCE loss of 390 g/year loss. The combined soil and tree losses, it amounts to a 390 to 424 g/yr TCE loss. This was six times lower than the removal provided by the interceptor trench (based on 2007 estimates), but was a significant amount of removal for natural attenuation processes.

No significant seasonal verifiability was observed in any groundwater, stable isotope, or leaf and trunk volatilization samples. Groundwater concentrations remained relatively constant within the last three years of analysis.

These refined estimates of TCE could be improved upon by further approximating the parameters in the Ferro et al. (2001) approach. A better method of water collection during leaf phytovolatilization sampling could improve the TSC estimation. A better method of replication during leaf volatilization should be considered. A study performed

at a more uniform site (phytoplanting) could help answer other questions not answered by this study.

ENGINEERING SIGNIFICANCE

Phytovolatilization of TCE from the leaves and trunk of tree can be measured and scaled to whole trees and tree canopies. In addition to phytovolatilization, metabolism within the tree can be added to the overall impact of indigenous trees on contaminated groundwater systems. Soil surface flux measurements over contaminated plumes can be used to estimate the TCE surface flux over an entire groundwater plume. The tree estimation combined with the soil flux estimation can give a clearer picture of natural attenuation occurring at a site. The overall impact of natural attenuation can be weighed against more invasive and expensive measures to provide insight into the best remediation tactic.

Results from this study indicated that the addition of trees could greatly impact the removal of TCE over a shallow TCE contaminated aquifer. The addition of trees could also improve TCE losses due to soil surface flux, only increasing the effectiveness of phytoremediation as a remediation tactic.

Future studies of more uniform sites or controlled sites such as phytoplantings, may eliminate some of the variables encountered in this study and better answer questions outlined in this thesis.

(Lewis, 2001)

REFERENCES

Allen, R. G., L. S. Pereira, D. Raes, and M. Smith. 1998. Crop evapotranspiration-guidelines for computing crop water requirements. Food and Agriculture Organization of the United Nations, Rome.

Baum, E. J. 1998. Chemical property estimation: Theory and application. CRC Press Boca Raton, Florida. 386.

Briggs, G. G., R. H. Bromilow, A. A. Evans, and M. Williams. 1983. Relationship between lipophilicity and the distribution of non-ionized chemicals in barely shoots following uptake by the roots. Pesticide Science 14: 492-500.

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., and M. Xingmao. 2002. Chlorinated solvents phytoremediation: Uptake and diffusion. Remediation of chlorinated and recalcitrant compounds. Battelle Press, Monterey, California. 24-31

Chappell, J., and EPA. 1997. Phytoremediation of TCE using Populus. from http://purl.access.gpo.gov/GPO/LPS29737

Chard, B. K., W. J. Doucette, J. K. Chard, B. Bugbee, and K. Gorder. 2006. Trichloroethylene uptake by apple and peach tress and transfer to fruit. Environmental Science and Technology 40: 4788-4793.

Choiu, C. T., L. J. Peters, and V. H. Freed. 1979. A physical concept of soil-water equilibria for nonionic organic compounds. Science 206: 831-832.

Clinton, B. D., J. M. Vose, D. A. Vroblesky, and G. J. Harvey. 2004. Determination of the relative uptake of ground vs. surface water by Populus deltoides during phytoremediation. International Journal of Phytoremediation 6(3): 239-252.

Conuet, T. S., C. Sandefur, W. M. Eliason, S. E. Johnson, and C. Serna. 2000. Aerobic and anaerobic bioremediation of cis-1,2-dichloroethene and vinyl chloride. Bioremediation and phytoremediation of chlorinated and recalcitrant compounds. G. B. Wickramanayake, A. R. Gavaskar, B. C. Alleman and V. S. Magar. Monterey, Battelle Press.

Dietz, A. C., and J. L. Schnoor. 2001. Advances in phytoremediation. Environmental Health Perspectives 109(Supplement 1): 163-168.

Dongmann, G., H. W. Nurnberg, H. Forstel, and K. Wagner. 1974. The enrichment of $H_2{}^{18}O$ in the leaves of transpiring plants. Radiation and Biophysics 11: 41-52.

Doucette, W. J. 2000. Impact of plants on the natural attenuation of chlorinated solvents. Utah State University. Logan, Utah

Doucette, W. J., B. G. Bugbee, S. C. Smith, C. J. Pajak, and J. S. Ginn. 2003. Uptake, metabolism, and phytovolatilization of trichloroethylene by indigenous vegetation: Impact of precipitation, p. 561-588. In Phytoremediation: Transformation and Control of Contaminants. S. C. McCutcheon and J. L. Schnoor. John Wiley & Sons, Inc.

Doucette, W. J., J. K. Chard, H. Fabrizius, C. Crouch, M. R. Petersen, T. E. Carlsen, B. K. Chard, and K. Gorder. 2007. Trichloroethylene uptake into fruits and vegetables: three-year field monitoring study. Environmental Science and Technology 41: 2505-2509.

Dynamax. 2007. FLGS-TDP XM1000 sap velocity logger user manual, Houston TX.

Ehleringer, J. R., and C. B. Osmond. 1989. Stable Isotopes, p. In Plant Physiological Ecology: Field Methods and Instumentation. Chapman & Hall, London.

EPA. 1999a. Use of monitored natural attenuation at superfund, RCRA, corrective action, and underground storage tank sites. E. P. Agency. Office of Solid Waste and Emergency Response.

EPA. 1999b. Phytoremediation Resource Guide. Washington, D.C.

Ferro, A., J. Chard, R. Kjelgren, B. Chard, D. Turner, and T. Montague. 2001. Groundwater capture using hybrid poplar trees: Evaluation of a system in Ogden, Utah. Journal of Phytoremediation 3(1): 87-104.

Flanagan, L. B., and J. R. Ehleringer. 1991. Stable isotope composition of stem and leaf water; applications to the study of plant water use. Functional Biology 5: 270-277.

Flanagan, L. B., J. R. Ehleringer, and D. E. Pataki. 2005. Stable isotopes and biosphere-atmosphere interactions. Elsevier Academic Press, London. 318.

Gabarini, D. R., and L. W. Lion. 1986. Influence of nature of soil organics on the sorption of toluene and trichloroethylene. Environmental Science and Technology 20: 1263-1296.

Gosset, J. M. 1987. Measurement of Henry' Law Constants for C1 and C2 chlorinated hydrocarbons. Environmental Science and Technology 21(2): 202-8.

Graber, E. R., A. Sorek, L. Tsechansky, and N. Atzmon. 2007. Competitive uptake of trichloroethene and 1,1,1-trichloroethane by eucalyptus camaldulensis seedlings and wood. Environmental Science and Technology 41: 6704-6710.

Hansch, C., and A. Leo. 1995. Exploring QSAR, p. In Fundamentals and applications in chemistry and biology. American Chemical Society, Washington, D.C.

Horvath, A. L., F. W. Getzen, and Z. Maczynska. 1999. IUPAC-NIST solubility data series 67. Halogenated ethanes and ethenes with water. Journal of Physical and Chemical Reference Data 28(2): 449.

HSDB. 2006a. Perchloroethylene. Hazardous Substances Data Bank, from http://toxnet.nlm.nih.gov/

HSDB. 2006b. Trichloroethylene. Hazaardous Substances Data Bank, from http://toxnet.nlm.nih.gov/

HSDB. 2006c. cis-1,2-Dichlorotheylene. Hazardous Substances Data Bank

from http://toxnet.nlm.nih.gov/

HSDB. 2006d. trans-1,2-Dichloroethylene. Hazardous Subsstances Data Bank, from http://toxnet.nlm.nih.gov/

IARC. 1979. Monographs on the evaluation of the carcinogenic risk of chemicals to man. I. A. f. R. o. Cancer. World Health Organization. 20: 492.

Karlik, J. F., and A. M. Winer. 1999. Comparison of calculated and measured leaf masses of urban trees. Ecological Applications 9(4): 1168-1176.

Kerfoot, H. B. 1987. Soil-gas measurement for detection of groundwater contamination by volatile organic compounds. Environmental Science and Technology 21(10): 1022-1024.

Leighton, D. T., and J. M. Calo. 1981. Distribution coefficients of chlorinated hydrocarbons in dilute air-water systems for groundwater contamination applications. Journal of Chemical Engineering and Data 26(4): 382-85.

Lewis, K. L. 2001. The relationship between tree-core and groudwater TCE concentrations for groundwater plume delineation. MS thesis. Utah State University. Logan, Utah. 200.

Li, H., G. Y. Sheng, C. T. Chiou, and O. Y. Xu. 2005. Relation of organic contaminant equilibrium sorption and kinetic uptake in plants. Environmental Science and Technology 39(13): 4864-4870.

Lide, D. R., (Ed). 1998. CRC Handbook of chemistry and physics. CRC Press Boca Raton, Florida. 584.

Lindberg, S. E., K. H. Kim, T. P. Meyers, and J. G. Owens. 1995. Micrometeorological gradient approach for quantifying air/surface exchange of mercury vapor: tests over contaminated soils. Environmental Science and Technology 29: 126-135.

Lyman, W. J. 1982. Handbook of chemical property estimation methods. McGraw-Hill, New York. 481.

Ma, X. M., and J. Burken. 2004. Modeling of TCE diffusion to the atmosphere and distribution in plant stems. Environmental Science and Technology 38(17): 4580-4586.

Ma, X. M., and J. G. Burken. 2003. TCE diffusion to the atmosphere in phytoremediation applications. Environmental Science and Technology 37(11): 2534-2539.

Ma, X. M., and J. G. Burken. 2002. VOCs fate and partitioning in vegetation: use of tree cores in groundwater analysis. Environmental Science and Technology 36(21): 4663-4668.

Major, D. W., M. L. McMaster, E.E.Cox, B. J. Lee, E. E. Gentry, E. Hendrickson, E. Edwards, and S. Dworatzek. 2001. Successful field demonstration of bioaugmentation to degrade PCE and TCE to ethene. Bioaugmentation, Biobarriers, and Biochemistry: Proceedings of the Sixth International In Situ and On-Site Bioremediation Symposium. San Diego Battelle Press.

Marr, L. C., E. C. Booth, R. G. Andersen, M. A. Widdowson, and J. T. Novak. 2006. Direct volatilization of naphthalene to the atmosphere at a phytoremediation site. Environmental Science and Technology 40: 5560-5566.

McFarlane, J. C. 1995. Anatomy and physiology of plant conductive systems, p. 254. In Plant contamination modeling and simulation of organic chemical processes Lewis Publishers, Boca Raton, Florida.

Newman, L. A., S. E. Strand, N. Choe, J. Duffy, G. Ekuan, M. Ruszaj, B. B. Shurtleff, J. Wilmoth, P. Heilman, and M. P. Gordon. 1997. Uptake and biotransformation of trichloroethylene by hybrid poplars. Environmental Science and Technology 31(4): 1062-1067.

Newman, L. A., X. Want, I. A. Muiznidks, G. Ekuan, M. Ruszaj, R. Cortellucci, D. Domroes, G. Karscig, T. Newman, R. S. Crampton, R. A. Hashmonay, M. G. Yost, P. E. Heilman, J. Duffy, M. P. Gordon, and S. E. Strand. 1999. Remediation of trichloroethylene in an artificial aquifer with trees: A controlled field study. Environmental Science and Technology 33(13): 2257-2265.

Orchard, B. J., W. J. Doucette, J. K. Chard, and B. Bugbee. 2000a. A novel laboratory system for determining fate of volatile organic compounds in planted systems. Environmental Toxicology and Chemistry 19(4): 888-894.

Orchard, B. J., W. J. Doucette, J. K. Chard, and B. Bugbee. 2000b. Uptake of trichloroethylene by hybrid poplar trees grown hydroponically in flow-through plant growth chambers. Environmental Toxicology and Chemistry 19(4): 895-903.

Riddick, J. A., W. B. Bunger, and T. K. Sakano. 1985. Techniques of chemistry fourth edition, Volume II. Organic Solvents. John Wiley, New York, NY.

Rogers, J. C. 2006. Phytovolatilization of trichloroethylene from mature trees: A comparison of two field studies. MS thesis. Utah State University. Logan, Utah. 129.

Russel, H. H., J. E. Matthews, and G. W. Sewell. 1992. TCE removal from contaminated soil and ground water. EPA.

Smith, J. A., C. T. Chiou, J. A. Kammer, and D. E. Kile. 1990. Effect of soil moisture on the sorption of trichloroethene vapor to vadose-zone soil at Picatinny Arsenal, New Jersey. Environmental Science and Technology 24: 676-683.

Smith, J. A., A. K. Tisdale, and H. J. Cho. 1996. Quantification of natural vapor fluxes of trichloroethene in the unsaturated zone at Picatinny Arsenal, New Jersey. Environmental Science and Technology 30: 2243-2250.

Soesilo, J. A., and S. R. Wilson. 1997. Site remediation planning and management. Lewis Publishers, Boca Raton, Fl. 409.

Sorek, A., N. Atzmon, O. Dahan, Z. Gerstl, L. Kushisin, Y. Laor, U. Mingelgrin, A. Nasser, D. Ronen, L. Tsechansky, N. Weisbrod, and E. R. Graber. 2007. "Phytoscreening": The use of trees for discovering subsurface contamination by VOCs. Environmental Science and Technology 42: 536-542.

Tillman, 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.

UET-Net. 2008. Hill Air Force Base Station. Division of Water Resources, Utah, from http://www.conservewater.utah.gov/et/etsite/summary.htm

Vroblesky, D. A., B. D. Clinton, J. M. Vose, C. C. Casey, G. J. Harvey, and P. M. Bradley. 2004. Ground water chlorinated ethenes in tree trunks: case studies, influence of recharge and potential degradation mechanism. Ground Water Monitoring & Remediation 24(3): 124-138.

Vroblesky, D. A., C. T. Nietch, and J. T. Morris. 1999. Chlorinated ethenes from groundwater in tree trunks. Environmental Science and Technology 33(3): 510-515.

Walton, B. T., and T. A. Anderson. 1990. Microbial degradation of trichloroethylene in the rhizosphere: potential application of biological remediation of waste sites. Applied and Environmental Microbiology 56(4): 1012-1016.

Wullschleger, S. D., F. C. Meinzer, and R. A. Vertessy. 1998. A review of whole-plant water use studies in tress. Tree physiology 18: 499-512.

Zaugg, N. W. 2004. The impact of mature trees on the fate of trichloroethylene at Hill Air Force Base, Operable Unit 4. MS thesis. Utah State University. Logan. 154.

APPENDICES

Appendix A – Evapotranspiration values for OU2

Table A-1. Summary of OU2 transpiration

	Eto (in) 2006	Eto (in) 2007	kc	LAI	Area (in^2)	Vt (in/month) 2006	Vt (in/month) 2007	Vt (L/month) 2006	Vt (L/month) 2007
Jan	0.95	0.76	0.5	3	46100	1.425	1.14		
Feb	1.47	1.28	0.5	3	46100	2.205	1.92		
Mar	2.38	2.93	0.5	3	46100	3.57	4.395		
Apr	4.03	4.31	0.5	3	46100	6.045	6.465	4567	4884
May	5.76	5.85	0.5	3	46100	8.64	8.775	6527	6629
Jun	6.86	7.28	0.5	3	46100	10.29	10.92	7774	8249
Jul	7.22	7.37	0.5	3	46100	10.83	11.055	8181	8351
Aug	6.23	6.54	0.5	3	46100	9.345	9.81	7060	7411
Sept	3.82	4.39	0.5	3	46100	5.73	6.585	4329	4975
Oct	2.16	2.48	0.5	3	46100	3.24	3.72	2448	2810
Nov	1.21	1.37	0.5	3	46100	1.815	2.055		
Dec	0.78	0.58	0.5	3	46100	1.17	0.87		
Total	42.87	45.14	Estimated Yealy Transpiration (L/year) =					40885	43310
			Estimated Monthly Transpiration (L/day) =					227	241

Eto - Evapotranspiration, Vt - Transpiration

Eto data for Clearfield, UT (UET-Net, 2008)

Crop Coefficient (kc) = 0.5 (Ferro et al. 2001)

Leaf Area Index (LAI) = 3 (Ferro et al. 2001)

Area of ground covered by tree canopy (A) = 46100 in^2 (canopy of 10 ft radius)

Appendix B – Chemical Properties of PCE, TCE and DCE

Table B-1. Chemical properties of PCE and TCE

Property	PCE		TCE	
	Value	Reference	Value	References
Chemical Formula	C_2-Cl_4	(HSDB, 2006a)	C_2-H-Cl_3	(HSDB, 2006b)
CAS #	127-18-4	(HSDB, 2006a)	79-01-6	(HSDB, 2006b)
Molecular Weight	165.83	(Lide, 1998)	131.39	(Lide, 1998)
Melting Point (^{o}C)	-22.3	(Lide, 1998)	-84.7	(Lide, 1998)
Boiling Point (^{o}C)	121.3	(Lide, 1998)	87.2	(Lide, 1998)
Vapor Pressure (mmHg @ 25^{o}C)	18.5	(Riddick, Bunger, and Sakano, 1985)	69.0	(Gosset, 1987)
Henry's Law Coefficient (25 ^{o}C, atm-m^3/mol)	0.0177	(Gossett, 1987)	0.00985	(Leighton and Calo, 1981)
Solubility (mg/L)	150	(IARC, 1979)	1,280	(Horvath, Getzen, and Maczynska, 1999)
Log K_{oc}	2.32	(Choiu, Peters, and Freed, 1979)	2.02	Estimated by equation 4-5 (Lyman, 1982)
Log K_{ow}	3.40	(Hansch and Leo, 1995)	2.61	(Hansch, C *et al.*, 1995)

Table B-2. Chemical properties of c-DCE and t-DCE

Property	c-DCE		t-DCE	
	Value	References	Value	References
Chemical Formula	C_2-H_2-Cl_2	(HSDB, 2006c)	C_2-H_2-Cl_2	(HSDB, 2006d)
CAS #	156-59-2	(HSDB, 2006c)	156-60-5	(HSDB, 2006d)
Molecular Weight	96.94	(Lide, 1998)	96.94	(Lide, 1998)
Melting Point (^{o}C)	-80	(Lide, 1998)	-49.8	(Lide, 1998)
Boiling Point (^{o}C)	60.1	(Lide, 1998)	48.7	(Lide, 1998)
Vapor Pressure (mmHg @ 25^{o}C)	200	(Riddick, Bunger, and Sakano, 1985)	331	(Gossett, 1987)
Henry's Law Coefficient (25 ^{o}C, atm-m^3/mol)	0.00408	(Gosset, 1987)	0.00928 @ 24^{o}C	(Gossett, 1987)
Solubility (mg/L)	6410	(Horvath, Getzen, and Maczynska, 1999)	4520	(Horvath, Getzen, and Maczynska, 1999)
Log K_{oc}	1.7	Estimated by equation 4-5 (Lyman, 1982)	1.54	Estimated by equation 4-5 (Lyman, 1982)
Log K_{ow}	1.86	(Hansch and Leo, 1995)	2.06	(Hansch and Leo, 1995)

Appendix C – OU2 Data

Table C- 1. Groundwater data TCE, DCE and VC concentrations at from OU2 and OU4 in 2006

Sample Name	Sample Location	Date Collected	TCE (µg/L)	c-DCE (µg/L)	t-DCE (µg/L)	VC (µg/L)	Depth to GW (ft)
Seep**	OU2	7/26/2006	128.8	949.2*	2.2	N.D	3.8
Seep***	OU2	7/26/2006	77.8	472.8*	1.4	N.D	3.8
Seep**	OU2	7/26/2006	95.6	565.6	1.4	N.D	3.8
U2-046***	OU2	7/26/2006	969.2*	109.2	ND	N.D	19.3
U2-046**	OU2	7/26/2006	725*	159.6	ND	N.D	19.3
U2-046**	OU2	7/26/2006	741.6*	109.8	ND	N.D	19.3
U2-020**	OU2	7/26/2006	146.5	3.6^	ND	N.D	15.5
U2-020**	OU2	7/26/2006	116.6	3.2^	ND	N.D	15.5
U2-020***	OU2	7/26/2006	150.4	3.4^	ND	ND	15.5
U2-080**	OU2	7/27/2006	78.6	18.8^	ND	ND	9.5
U2-080	OU2	7/27/2006	75.4	18.4^	ND	ND	9.5
U2-080	OU2	7/27/2006	85.8	15.8^	ND	ND	9.5
U2-081	OU2	7/31/2006	701.2*	52.8^	4.6	ND	11.0
U2-081	OU2	7/31/2006	736.6*	56.0^	5	ND	11.0
U2-081	OU2	7/31/2006	720.6*	54.8^	4.8	ND	11.0
U2-238	OU2	7/31/2006	9	5.2	ND	ND	11.5
U2-238	OU2	7/31/2006	8.2	5.0	ND	ND	11.5
U2-238	OU2	7/31/2006	7.6	4.6	ND	ND	11.5
Seep	OU2	8/18/2006	55.3	551.8*	1.88	ND	4.1
Seep	OU2	8/18/2006	60.3	665.5*	2.24	ND	4.1
Seep	OU2	8/18/2006	59.8	681.5*	2.26	ND	4.1
U2-046	OU2	8/18/2006	951.3	93.4	ND	ND	17.4
U2-046	OU2	8/18/2006	1010.2*	95.8	ND	ND	17.4
U2-046	OU2	8/18/2006	1020.7*	96.2	0.3	ND	17.4
U2-020	OU2	8/18/2006	129.7	2.8	ND	ND	14.1
U2-020	OU2	8/18/2006	101.0	2.8	ND	ND	14.1
U2-020	OU2	8/18/2006	134.8	2.7	ND	ND	.14.1
U2-080	OU2	8/18/2006	91.3	13.5	0.14	ND	15.6
U2-080	OU2	8/18/2006	90.6	13.7	0.14	ND	15.6
U2-080	OU2	8/18/2006	92.9	13.9	0.14	ND	19.2
U4-003	OU4	8/24/2006	0.7	1.3	ND	ND	19.2
U4-003	OU4	8/24/2006	0.8	1.4	ND	ND	19.2

Table C-1. Continued

U4-070	OU4	8/24/2006	85.4	4.5	ND	ND	14.5
U4-070	OU4	8/24/2006	80.1	4.5	0.12	ND	14.5
U4-070	OU4	8/24/2006	82.6	4.6	0.1	ND	14.5
U2-086	OU2	9/30/2006	7.9	0.5	ND	ND	3.9
U2-086	OU2	9/30/2006	8	0.5	ND	ND	3.9
U2-086	OU2	9/30/2006	7.53	0.5	ND	ND	3.9
U2-080	OU2	9/30/2006	96.4	12.7	0.14	ND	9.5
U2-080	OU2	9/30/2006	103.1	12.4	0.13	ND	9.5
U2-080	OU2	9/30/2006	97.2	12.7	0.14	ND	9.5
U2-020	OU2	9/30/2006	154.4	2.6	ND	ND	14.7
U2-020	OU2	9/30/2006	141.6	2.6	ND	ND	14.7
U2-020	OU2	9/30/2006	156.6	2.6	ND	ND	14.7
*The concentration was higher than the highest calibration standard.							
^Two of the three masses were the correct ratio, the third was correct but misshaped.							
**The headspace vial was punctured by the G.C. twice, but only injected once.							
***The sample were punctured twice and injected twice.							
ND: Non-Detect. Concentration was below instrument detection limits.							

Table C- 2. Groundwater data TCE, DCE and VC concentrations at from OU2 in 2007

Sample Name	Sample Location	Date collected	TCE (µg/L)	c-DCE (µg/L)	t-DCE (µg/L)	VC (µg/L)	Depth to GW (ft)
Canal	OU2	5/18/2007	ND	ND	ND	ND	surface
Canal	OU2	5/18/2007	ND	ND	ND	ND	surface
Canal	OU2	5/18/2007	ND	ND	ND	ND	surface
seep	OU2	6/27/2007	23.2	278	ND	ND	6.5
seep	OU2	6/27/2007	66.2	834	2.4	ND	6.5
seep	OU2	6/27/2007	55.8	810.6	2.8	ND	6.5
seep	OU2	5/18/2007	49.6	839.2	2.8	ND	6.0
seep	OU2	5/18/2007	51.4	842.4	4	ND	6.0
seep	OU2	5/18/2007	51.2	862	2.8	ND	6.0
U2-020	OU2	5/18/2007	258.8	4.34	ND	ND	10.5
U2-020	OU2	5/18/2007	257.2	4.24	ND	ND	10.5
U2-020	OU2	5/18/2007	234.1	4.1	ND	ND	10.5
U2-020	OU2	6/27/2007	388.2	ND	ND	ND	10.5
U2-020	OU2	6/27/2007	384.8	ND	ND	ND	10.5
U2-020	OU2	6/27/2007	389.6	ND	ND	ND	10.5
U2-020	OU2	9/21/2007	234.4	4.7	ND	ND	14.6
U2-020	OU2	9/21/2007	237.5	4.8	ND	ND	14.6
U2-020	OU2	9/21/2007	237.2	4.9	ND	ND	14.6
U2-020	OU2	11/5/2007	230.4	5.2	ND	ND	16.5
U2-020	OU2	11/5/2007	226.3	5.2	ND	ND	16.5
U2-020	OU2	11/5/2007	223.8	5.2	ND	ND	16.5
U2-042	OU2	5/18/2007	6.9	ND	ND	ND	6.1
U2-042	OU2	5/18/2007	5.9	ND	ND	ND	6.1
U2-042	OU2	5/18/2007	5.7	ND	ND	ND	6.1
U2-042	OU2	6/26/2007	81.9	0.2	ND	ND	6.5
U2-042	OU2	6/26/2007	78.1	0.2	ND	ND	6.5
U2-042	OU2	6/26/2007	80.1	0.2	ND	ND	6.5
U2-042	OU2	9/21/2007	12.6	ND	ND	ND	7.5
U2-042	OU2	9/21/2007	11.8	ND	ND	ND	7.5
U2-042	OU2	9/21/2007	12.2	ND	ND	ND	7.5
U2-042	OU2	11/5/2007	11.2	ND	ND	ND	11.6
U2-042	OU2	11/5/2007	11.6	ND	ND	ND	11.6

Table C-2. Continued

U2-042	OU2	11/5/2007	10.7	ND	ND	ND	11.6
U2-080	OU2	5/18/2007	95.0	12.0	0.2	ND	7.0
U2-080	OU2	5/18/2007	95.0	11.6	0.2	ND	7.0
U2-080	OU2	5/18/2007	94.0	12.1	0.2	ND	7.0
U2-080	OU2	6/27/2007	170.0	11.2	0.2	ND	10.5
U2-080	OU2	6/27/2007	188.8	12.7	0.2	ND	10.5
U2-080	OU2	6/27/2007	182.4	11.9	0.2	ND	10.5
U2-080	OU2	9/21/2007	74.7	7.9	ND	ND	7.1
U2-080	OU2	9/21/2007	75.2	8	ND	ND	7.1
U2-080	OU2	9/21/2007	76.1	8.2	ND	ND	7.1
U2-080	OU2	11/5/2007	75.5	6.3	ND	ND	8.6
U2-080	OU2	11/5/2007	82.1	6.8	ND	ND	8.6
U2-080	OU2	11/5/2007	85.0	7.1	ND	ND	8.6
U2-086	OU2	5/18/2007	17.7	1.9	ND	ND	6.1
U2-086	OU2	5/18/2007	16.1	1.7	ND	ND	6.1
U2-086	OU2	5/18/2007	16.8	1.7	ND	ND	6.1
ND: Non-detect							

Table C- 3. Groundwater data TCE, DCE and VC concentrations at from OU2 in 2008

Sample Name	Sample Location	Date Collected	TCE (µg/L)	c-DCE (µg/L)	t-DCE (µg/L)	VC (µg/L)	Depth to GW (ft)
U2-020	OU2	8/18/2008	227.9	ND	ND	ND	13.2
U2-020	OU2	8/18/2008	144.6	ND	ND	ND	13.2
U2-020	OU2	8/18/2008	140.3	ND	ND	ND	13.2
U2-042	OU2	8/18/2008	151.07	17.12	ND	ND	5.9
U2-042	OU2	8/18/2008	160.32	17.79	ND	ND	5.9
U2-042	OU2	8/18/2008	155.99	17.63	ND	ND	5.9
U2-080	OU2	8/18/2008	308.82	4.46	ND	ND	11.2
U2-080	OU2	8/18/2008	165.16	5.06	ND	ND	11.2
U2-080	OU2	8/18/2008	301.92	4.22	ND	ND	11.2

Table C-4. Leaf phytovolatlizatino sampling results from 2006

Tree Description	Trap	Date Collected	Mass TCE (pg)	Water collected (g)	Split ratio	TCE in Air (pg/L)	TCE per L of H_2O transpired (ug/L)	Sampling Time (min)	Leaf Area (cm^2)	Mass of TCE per leaf area ($pg/cm^2/min$)
Willow 1	right/front	9/18/2006	4647.8	ND	0.016	25.8	ND	30	291.4	32.6
Willow 1	right/back	9/18/2006								
Willow 1	left/front	9/18/2006	4924.0	ND	0.017	27.4	ND	30		33.8
Willow 1	left/back	9/18/2006								
Poplar 3	right/back	9/18/2006	2856.9	ND	0.016	15.9	ND	30	941.9	6.3
Poplar 3	right/front	9/18/2006								
Poplar 3	left/front	9/18/2006	2804.3	ND	0.016	15.6	ND	30		6.1
Poplar 3	left/back	9/18/2006								
gas blank	left/front	9/22/2006	ND	ND	0.016	ND	ND	30	NA	NA
gas blank	left/back	9/22/2006								
gas blank	right/front	9/22/2006	361.6	ND	0.006	2.0	ND	30	NA	NA
gas blank	right/back	9/22/2006								
ND - No measureable amount of water collected.										
NA: Not applicable because sample was a chamber blank.										

Table C-5. Leaf phytovolatilization sampling results from 2007

Tree Description	Trap	Date Collected	Total TCE (pg)	Water collected (g)	Split Ratio	TCE in Air (pg/L)	TCE per L of H2O transpired (µg/L)	Run duration (minutes)	area (cm^2)	TCE flux ($pg/cm^2/min$)
Poplar 3	left/front	5/15/2007	443.2	0.1	0.017	144.8	4.4	30	448	1.9
Poplar 3	left/back	5/15/2007								
Poplar 3	right/front	5/15/2007	700.1	0.1	0.016	238.1	7.0	30	448	3.2
Poplar 3	right/back	5/15/2007								
Poplar 3	left/front	6/26/2007	138.0	0.21	0.016	46.9	0.7	30	671	0.4
poplar 3	right/front	6/26/2007	32.9	0.25	0.017	10.6	0.1	30	671	0.1
Poplar 3	left/front	9/18/2007	1505.1	0.05	0.017	481.0	30.1	30	735.6	3.9
Poplar 3	left/back	9/18/2007								
Poplar 3	right/front	9/18/2007	2238.0	ND	0.010	1243.3	ND	30	735.6	10.1
Russian Olive	left/front	5/15/2007	1028.2	ND	0.017	342.7	ND	30	227	9.1
Russian Olive	left/back	5/15/2007								
Russian Olive	right/front	5/15/2007	495.2	ND	0.017	165.1	ND	30	227	4.4
Russian Olive	right/back	5/15/2007								
Russian Olive	left/front	5/15/2007	714.0	ND	0.017	228.9	ND	30	227	6.0
Russian Olive	left/back	5/15/2007								
Russian Olive	right/front	5/15/2007	ND	ND	0.162	ND	ND	30	227	ND
Russian Olive	left/front	6/26/2007	83.0	0.1	0.017	27.6	0.8	30	435	0.4
Russian Olive	right/front	6/26/2007	133.6	0.1	0.016	45.3	1.3	30	435	0.6
Russian Olive	left/front	6/26/2007	89.1	0.06	0.017	29.7	1.5	30	435	0.4
Russian Olive	right/front	6/26/2007	49.8	0	0.017	16.2	ND	30	435	0.2

Table C-5. Continued

Russian Olive	left/front	9/18/2007	ND	0.02	0.166	ND	ND	30	228.9	ND
Russian Olive	left/back	9/18/2007								
Russian Olive	right/front	9/18/2007	ND	ND	0.017	ND	ND	30	228.9	ND
Russian Olive	right/back	9/18/2007								
Willow 1	left/front	5/14/2007	ND	0.1	0.165	ND	ND	30	221	ND
Willow 1	left/back	5/14/2007								
Willow 1	right/front	5/14/2007	87.1	0.1	0.016	29.9	0.9	30	221	0.8
Willow 1	right/back	5/14/2007								
Willow 1	left/front	6/26/2007	656.5	0.04	0.017	212.4	16.4	30	229.7	5.5
Willow 1	right/front	6/26/2007	856.1	0.03	0.017	288.2	28.5	30	229.7	7.5
Willow 1	left/front	6/26/2007	468.9	0.03	0.017	152.8	15.6	30	197.8	4.6
Willow 1	right/front	6/26/2007	471.5	0.03	0.016	162.5	15.7	30	197.8	4.9
Willow 1	left/front	9/18/2007	170.6	0.03	0.018	54.1	5.7	30	150	2.2
Willow 1	left/back	9/18/2007								
Willow 1	right/front	9/18/2007	1036.7	0.01	0.016	350.9	103.7	30	150	14.0
Willow 1	right/back	9/18/2007								
Willow 1	left/front	9/18/2007	218.9	0.03	0.017	70.6	7.3	30	150	2.8
Willow 1	right/front	9/18/2007	185.3	0.01	0.017	61.0	18.5	50	150	1.5
Willow 3	left/front	5/16/2007	404.9	0.04	0.017	136.3	10.1	30	157	5.2
Willow 3	left/back	5/16/2007								
Willow 3	right/front	5/16/2007	ND	0.01	0.017	ND	ND	30	157	ND
Willow 3	left/front	5/16/2007	ND	0.01	0.112	ND	ND	30	157	ND
Willow 3	right/front	5/16/2007	403.1	0.09	0.017	134.4	4.5	30	157	5.1
Willow 3	right/back	5/16/2007								

Table C-5. Continued

Willow 3	left/front	6/27/2007	15.1	0.05	0.026	4.9	0.3	30	205	0.1
Willow 3	right/front	6/27/2007	ND	ND	0.026	ND	ND	30	205	ND
Willow 4	left/front	5/16/2007	508.0	0.08	0.017	167.7	6.3	30	235	4.3
Willow 4	left/back	5/16/2007								
Willow 4	right/front	5/16/2007	ND	0.06	0.008	ND	ND	30	235	ND
Willow 4	right/back	5/16/2007								
Willow 4	left/front	6/27/2007	ND	0.03	0.026	ND	ND	30	363	ND
Willow 4	right/front	6/27/2007	169.6	0.05	0.025	56.0	3.4	30	363	0.6
Willow 4	left/front	6/27/2007	135.2	0.04	0.024	46.9	3.4	30	363	0.5
Willow 4	right/front	6/27/2007	137.0	ND	0.024	48.0	ND	30	363	0.5
ND-Below method detection limit of 100 pg										

Table C-6. Leaf Volatilization sampling results from 2008

Tree Description	Trap	Date Collected	Total TCE (pg)	Water collected (g)	Split Ratio	TCE in Air (pg/L)	TCE per L of H2O transpired (µg/L)	Run duration (min)	Leaf area (cm^2)	TCE flux ($pg/cm^2/min$)
Willow 1	left/front	8/15/2008	704.4	0.08	0.021	231.79	8.80	30	635	1.73
Willow 1	left/back	8/15/2008								
Willow 1	right/front	8/15/2008	1810.2	0.14	0.044	291.78	12.93			2.18
Willow 1	right/back	8/15/2008								
Willow 1 dup	left/front	8/15/2008	725.85	0.07	0.022	231.09	10.37	30	635	1.73
Willow 1dup	left/back	8/15/2008								
Willow 1dup	right/front	8/15/2008	1479.18	0.18	0.041	251.95	8.22			1.88
Willow 1dup	right/back	8/15/2008								
Willow 4	left/front	8/15/2008	508.82	0.04	0.020	167.60	12.72	30	490	1.71
Willow 4	left/back	8/15/2008								
Willow 4	right/front	8/15/2008	908.95	0.15	0.036	169.17	6.06			1.73
Willow 4	right/back	8/15/2008								
Poplar 3	left/front	8/15/2008	2762.68	0.04	0.021	928.13	69.07	30	810	5.44
Poplar 3	left/back	8/15/2008								
Poplar 3	right/front	8/15/2008	4606.29	0.2	0.032	1022.26	23.03			5.99
Poplar 3	right/back	8/15/2008								

Table C-7. Trunk volatilization results from 2006

Tree Description	height (cm)	Diameter (cm)	cored/non-cored	front/back	Date Collected	Total TCE Mass	Run duration (minutes)	area (cm^2)	TCE flux ($pg/cm^2/min$)
OU4 Cottonwood	57	105	cored	front	10/18/2006	54674.37	20	1575	1.736
OU4 Cottonwood	57	105	cored	back	10/18/2006				
OU4 Cottonwood	140	95	cored	front	10/18/2006	52480.86	20	1575	1.666
OU4 Cottonwood	140	95	cored	back	10/18/2006				
OU4 Cottonwood	216	99	cored	front	10/18/2006	73210.98	20	1575	2.324
OU4 Cottonwood	216	99	cored	back	10/18/2006				
OU4 Cottonwood	52	105	non-cored	front	10/18/2006	56760.91	20	1575	1.802
OU4 Cottonwood	52	105	non-cored	back	10/18/2006				
OU4 Cottonwood	140	95	non-cored	front	10/18/2006	42316.21	20	1575	1.343
OU4 Cottonwood	140	95	non-cored	back	10/18/2006				
OU4 Cottonwood	216	99	non-cored	front	10/18/2006	31701.26	20	1575	1.006
OU4 Cottonwood	216	99	non-cored	back	10/18/2006				
Poplar 3	163	73	cored	front	10/18/2006	2050.3	30	1575	0.043
Poplar 3	163	73	cored	back	10/18/2006				
Poplar 3	40	48	non-cored	front	9/18/2006	ND	30	675	0.000
Poplar 3	40	48	non-cored	back	9/18/2006				
Poplar 3	160	41	non-cored	front	9/18/2006	518.53	30	675	0.026
Poplar 3	160	41	non-cored	back	9/18/2006				
Poplar 3	337	38	non-cored	front	9/18/2006	394.98	30	675	0.020
Poplar 3	337	38	non-cored	back	9/18/2006				

Table C-7. Continued

Willow 1	150	11	cored	front	10/18/2006	5201.49	30	800	0.217
Willow 1	150	11	cored	back	10/18/2006				
Willow 1	70	14	non-cored	front	9/18/2006	940.46	30	900	0.035
Willow 1	70	14	non-cored	back	9/18/2006				
Willow 1	170	11	non-cored	front	9/18/2006	697.78	30	900	0.026
Willow 1	170	11	non-cored	back	9/18/2006				
Willow 1	225	8	non-cored	front	9/18/2006	149.17	30	900	0.006
Willow 1	225	8	non-cored	back	9/18/2006				
ND-Below method detection limit of 100 pg									

Table C-8. Trunk volatilization results from 2007

Tree Description	height (cm)	diameter (cm)	cored/non-cored	front/back	Date Collected	Total TCE Mass (pg)	Run duration (minutes)	area (cm2)	TCE flux (pg/cm2-min)
Poplar 3	55	48	non-cored	front	5/15/2007	1759.6	30	1850	0.032
Poplar 3	55	48	non-cored	back	5/15/2007				
Poplar 3	175	45	non-cored	front	5/15/2007	ND	30	1850	ND
Poplar 3	175	45	non-cored	back	5/15/2007				
Poplar 3	260	40	non-cored	front	5/15/2007	507.0	30	1850	0.009
Poplar 3	260	40	non-cored	back	5/15/2007				
Poplar 3	120	45	non-cored	front	6/26/2007	691.5	30	1850	0.012
Poplar 3	120	45	non-cored	front	6/26/2007	3110.4	30	1850	0.056
Poplar 3	170	45	non-cored	front	6/26/2007	2116.0	30	1850	0.038
Poplar 3	170	45	non-cored	front	6/26/2007	4993.3	30	1850	0.090
Poplar 3	220	45	non-cored	front	6/26/2007	9712.9	30	1850	0.175
Poplar 3	220	45	non-cored	back	6/26/2007				
Poplar 3	220	45	non-cored	front	6/26/2007	7046.5	30	1850	0.127
Poplar 3	60	48	non-cored	front	9/14/2007	12325.1	30	1850	0.222
Poplar 3	60	48	non-cored	back	9/14/2007				
Poplar 3	190	45	non-cored	front	9/14/2007	6578.4	30	1850	0.119
Poplar 3	190	45	non-cored	back	9/14/2007				
Poplar 3	320	38	non-cored	front	9/14/2007	273.1	27	1850	0.005
Poplar 3	320	38	non-cored	back	9/14/2007				
Willow 1	80	17	non-cored	front	5/16/2007	9086.4	30	798	0.380
Willow 1	80	17	non-cored	back	5/16/2007				

Table C-8. Continued

Willow 1	145	13	non-cored	front	5/16/2007	ND	30	686	ND
Willow 1	145	13	non-cored	back	5/16/2007				
Willow 1	250	9	non-cored	front	5/16/2007	2714.9	30	423	0.214
Willow 1	80	17	non-cored	back	5/17/2007	14690.2	30	798	0.614
Willow 1	80	17	non-cored	front	5/17/2007				
Willow 1	145	13	non-cored	back	5/17/2007	428.1	30	686	0.021
Willow 1	145	13	non-cored	front	5/17/2007				
Willow 1	250	9	non-cored	back	5/17/2007	452.0	30	423	0.036
Willow 1	250	9	non-cored	front	5/17/2007				
Willow 1	120	15	non-cored	front	6/26/2007	45349.9	30	611	2.474
Willow 1	120	15	non-cored	front	6/26/2007	18643.8	30	611	1.017
Willow 1	166	12	non-cored	front	6/26/2007	1131.3	30	611	0.062
Willow 1	166	12	non-cored	front	6/26/2007	7557.3	30	611	0.412
Willow 1	228	14	non-cored	front	6/26/2007	8984.5	30	611	0.490
Willow 1	228	14	non-cored	back	6/26/2007				
Willow 1	228	14	non-cored	front	6/26/2007	16993.1	30	611	0.927
Willow 1	60	18	non-cored	front	9/12/2007	6513.7	30	1034	0.210
Willow 1	60	18	non-cored	back	9/12/2007		30		
Willow 1	155	14	non-cored	front	9/12/2007	77770.5	30	705	3.677
Willow 1	155	14	non-cored	back	9/12/2007		30		
Willow 1	252	9	non-cored	front	9/12/2007	143325.6	30	517	9.241
Willow 1	252	9	non-cored	back	9/12/2007		30		
Willow 2	52	35	non-cored	front	5/17/2007	ND	30	1850	ND
Willow 2	169	30	non-cored	front	5/17/2007	ND	30	1850	ND

Table C-8. Continued

Willow 2	338	25	non-cored	front	5/17/2007	ND	30	1850	ND
Willow 2	88	21	non-cored	front	6/26/2007	1069.3	30	1850	0.019
Willow 2	150	21	non-cored	front	6/26/2007	438.9	30	1850	0.008
Willow 2	233	21	non-cored	front	6/26/2007	7512.5	30	1850	0.135
Willow 2	85	30	non-cored	front	9/14/2007	ND	30	1850	ND
Willow 2	85	30	non-cored	back	9/14/2007				
Willow 2	85	30	non-cored	front	9/14/2007	330.9	40	1850	0.004
Willow 2	85	30	non-cored	back	9/14/2007				
Willow 2	215	28	non-cored	front	9/14/2007	904.8	30	1850	0.016
Willow 2	215	28	non-cored	back	9/14/2007				
Willow 2	215	28	non-cored	front	9/14/2007	938.3	40	1850	0.013
Willow 2	215	28	non-cored	back	9/14/2007				
Willow 2	280	30	non-cored	front	9/14/2007	2740.3	30	1850	0.049
Willow 2	280	27	non-cored	back	9/14/2007				
Willow 2	280	27	non-cored	front	9/14/2007	2758.9	40	1850	0.037
Willow 2	280	27	non-cored	back	9/14/2007				
Willow 3	82	22	non-cored	front	5/16/2007	ND	30	1850	ND
Willow 3	82	22	non-cored	back	5/16/2007				
Willow 3	82	22	non-cored	back	5/16/2007	ND	30	1850	ND
Willow 3	145	22	non-cored	front	5/16/2007	ND	30	1850	ND
Willow 3	145	22	non-cored	back	5/16/2007				
Willow 3	145	22	non-cored	front	5/16/2007	ND	30	1850	ND
Willow 3	145	22	non-cored	back	5/16/2007				
Willow 3	237	18	non-cored	front	5/16/2007	ND	30	1150	ND
Willow 3	237	18	non-cored	back	5/16/2007				
Willow 3	237	18	non-cored	front	5/16/2007	409.7	30	1150	0.012

Table C-8. Continued

Willow 3	44	22	non-cored	front	6/27/2007	229.7	30	1850	0.004
Willow 3	98	22	non-cored	front	6/27/2007	350.1	30	1850	0.006
Willow 3	137	26	non-cored	front	6/27/2007	141.7	30	1850	0.003
Willow 3	50	22	non-cored	front	9/12/2007	20927.7	35	1850	0.323
Willow 3	120	24	non-cored	front	9/12/2007	10744.3	35	1850	0.166
Willow 3	120	24	non-cored	back	9/12/2007				
Willow 3	230	19	non-cored	front	9/12/2007	ND	35	180	ND
Willow 3	230	19	non-cored	back	9/12/2007				
Willow 4	40	18	non-cored	front	5/16/2007	ND	30	1850	ND
Willow 4	91	19	non-cored	front	5/16/2007				
Willow 4	30	28	non-cored	front	6/27/2007	4484.1	30	1850	0.081
Willow 4	137	34	non-cored	front	6/27/2007	1734.0	30	1850	0.031
Willow 4	30	30	non-cored	front	9/12/2007	256.0	30	1850	0.005
Willow 4	30	30	non-cored	back	9/12/2007				
Willow 4	120	30	non-cored	front	9/12/2007	2275.7	30	1850	0.041
Willow 4	120	30	non-cored	back	9/12/2007				
ND: Non-Detect. The sample conceration was below instrument detection limits.									

Table C-9. Soil surface flux values from 2008

Location	Apparatus	With/ without fans	trap front/back	Date collected	Mass TCE Corrected (pg)	Sampling Time (min)	Chamber flow (L/min)	Total Chamber Flow (L)	Trap Set Flow (L/min)	Trap Set Flow Volume (L)	TCE in Air (pg/L)	TCE Soil Surface Flux ($\mu g/m^2/day$)
U2-046	new	W/O	front	5/15/2008	844.5	5	0.02	0.02	0.02	0.1	8444.7	7.7
U2-046	new	W/O	front	5/15/2008	541.9	5	0.02	0.02	0.02	0.1	5419.4	5.0
Poplar 4	new	W/O	front	5/15/2008	378.9	10	0.02	0.02	0.02	0.2	1894.4	1.7
Sap flow	new	W/O	front	5/15/2008	411.4	10	0.02	0.02	0.02	0.2	2057.1	1.9
N of pump shed	new	W/O	front	5/15/2008	0.0	15	0.02	0.02	0.02	0.3	0.0	0.0
Willow 1	new	W/O	front	5/15/2008	0.0	10	0.02	0.02	0.02	0.2	0.0	0.0
Poplar 3	new	W/O	front	5/15/2008	255.8	15	0.02	0.02	0.02	0.3	852.5	0.8
U2-080	new	W/O	front	5/15/2008	0.0	15	0.02	0.02	0.02	0.3	0.0	0.0
Willow 1	old	W/O	front	5/15/2008	439.6	10	2	20	0.109	1.09	403.3	9.2
Willow 1	old	W/O	back	5/15/2008								
U2-080	old	W/O	front	5/15/2008	1071.1	15	2	30	0.115	1.725	620.9	14.2
U2-080	old	W/O	back	5/15/2008								
Poplar 3	new	W/O	front	6/20/2008	19435.7	30	0.09	2.7	0.09	2.7	7198.4	29.7
Poplar 3	new	W/O	back	6/20/2008								
Poplar 3	old	W/O	front	6/20/2008	4986.4	30	2	60	0.126	3.78	1319.2	30.2
Poplar 3	old	W/O	back	6/20/2008								
U2-237	old	W/O	front	6/20/2008	798.9	30	2	60	0.115	3.45	231.6	5.3
U2-237	old	W/O	back	6/20/2008								
U2-237	new	W/O	front	6/20/2008	19487.7	30	0.09	2.7	0.09	2.7	7217.7	29.8
U2-237	new	W/O	back	6/20/2008								

Table C-9. Continued

Sap flow	old	W/O	front	6/20/2008	802.9	30	2	60	0.1	3	267.6	6.1
Sap flow	old	W/O	back	6/20/2008								
Sap flow	old	W/O	front	6/20/2008	6491.7	30	2	60	0.1	3	2163.9	49.6
Sap flow	old	W/O	back	6/20/2008								
Sap flow	new	W/O	front	6/20/2008	0.0	30	0.09	2.7	0.09	2.7	0.0	0.0
Sap flow	new	W/O	back	6/20/2008								
Sap flow	new	W/O	front	6/20/2008	0.0	30	0.09	2.7	0.09	2.7	0.0	0.0
Sap flow	new	W/O	back	6/20/2008								
U2-046	new	W	front	8/14/2008	89340.7	30	0.09	2.7	0.09	2.7	33089.1	136.5
U2-046	new	W	back	8/14/2008								
Poplar 3	new	W	front	8/14/2008	324010.2	30	0.09	2.7	0.126	3.78	85717.0	495.1
Poplar 3	new	W	back	8/14/2008								
U2-020	new	W	front	8/14/2008	660.3	30	0.09	2.7	0.115	3.45	191.4	1.0
U2-020	new	W	back	8/14/2008								
Willow 1	new	W	front	8/14/2008	7673.5	30	0.09	2.7	0.09	2.7	2842.0	11.7
Willow 1	new	W	back	8/14/2008								
U2-237	new	W	front	8/14/2008	17699.7	30	0.09	2.7	0.1	3	5899.9	27.0
U2-237	new	W	back	8/14/2008								
N of pump shed	new	W	front	8/14/2008	4281.5	55	0.09	4.95	0.09	4.95	865.0	3.6
N of pump shed	new	W	back	8/14/2008								
Willow 1	new	W	front	8/14/2008	7299.4	30	0.09	2.7	0.09	2.7	2703.5	11.2
Willow 1	new	W	back	8/14/2008								
Willow 3	new	W	front	8/14/2008	1018.6	30	0.09	2.7	0.09	2.7	377.2	1.6
Willow 3	new	W	back	8/14/2008								
Willow 1	new	W	front	8/15/2008	47023.6	30	0.09	2.7	0.126	3.78	12440.1	71.8
Willow 1	new	W	back	8/15/2008								

Table C-10. Stable isotope samples collected in 2006 and 2007

Tree Description	Location	Sample Type	Date Collected	delta D	Std dev delta D	delta 18O	Std dev delta 18O
Box Elder	OU2	stem	5/16/2007	-93.73	2.66	-4.57	0.45
Canal	OU2	groundwater	5/18/2007	-112.54	1.17	-13.57	0.17
Poplar 1	OU2	stem	5/14/2007	-117.47	1.10	-13.32	0.07
Poplar 1	OU2	stem	6/27/2007	-125.60	0.39	-14.24	NA
Poplar 1	OU2	stem	9/21/2007	-130.08	0.00	-15.37	0.06
Poplar 3	OU2	core	9/18/2006	-127.00	-14.70	-14.70	0.13
Poplar 3	OU2	core	9/18/2006	-133.00	-14.80	-14.80	0.11
Poplar 3	OU2	core	5/14/2007	-122.01	0.14	-14.27	0.04
Poplar 3	OU2	stem	5/14/2007	-113.92	1.64	-13.25	0.10
Poplar 3	OU2	stem	6/26/2007	-128.71	4.72	-15.31	0.38
Poplar 3	OU2	core	9/21/2007	-129.16	0.31	-15.47	0.03
Russian Olive	OU2	core	5/14/2007	-126.30	0.76	-14.47	0.02
Russian Olive	OU2	stem	5/14/2007	-119.13	2.45	-12.98	0.05
Russian Olive	OU2	stem	6/26/2007	-123.90	1.30	-14.17	0.14
Russian Olive	OU2	core	9/21/2007	-133.24	0.02	-13.99	0.03
Seep	OU2	groundwater	5/18/2007	-117.41	NA	-14.93	0.01
Seep	OU2	groundwater	6/26/2007	-108.98	1.14	-11.26	0.16
U2-020	OU2	groundwater	9/18/2006	-125.00	-15.70	-15.70	0.26
U2-020	OU2	groundwater	5/18/2007	-117.33	0.16	-15.47	0.02
U2-020	OU2	groundwater	6/26/2007	-117.85	1.16	-15.48	0.09
U2-020	OU2	groundwater	9/21/2007	-119.13	0.87	-15.59	0.05
U2-042	OU2	groundwater	5/18/2007	-115.21	0.41	-15.17	0.07
U2-042	OU2	groundwater	6/26/2007	-118.88	0.22	-15.42	0.14
U2-042	OU2	groundwater	9/21/2007	-117.55	0.60	-15.29	0.03
U2-080	OU2	groundwater	5/18/2007	-117.76	1.57	-15.48	0.28
U2-080	OU2	groundwater	6/26/2007	-117.97	2.28	-15.09	0.26
U2-080	OU2	groundwater	9/21/2007	-118.59	0.21	-15.54	0.06
U2-086	OU2	groundwater	5/18/2007	-121.25	0.07	-15.78	0.00
Willow 1	OU2	core	9/18/2006	-131.00	-14.90	-14.90	0.02
Willow 1	OU2	core	9/18/2006	-132.00	-15.10	-15.10	0.50
Willow 1	OU2	stem	5/14/2007	-118.11	NA	-15.07	NA
Willow 1	OU2	stem	6/26/2007	-121.11	1.34	-14.68	0.35
Willow 1	OU2	stem	9/21/2007	-130.77	0.40	-15.61	0.24
Willow 2	OU2	core	5/14/2007	-121.13	1.80	-11.35	0.23
Willow 2	OU2	stem	5/14/2007	-120.88	0.01	-14.97	0.09
Willow 2	OU2	stem	6/26/2007	-113.34	0.97	-11.26	0.01
Willow 2	OU2	core	9/21/2007	-128.40	0.17	-15.49	0.01
Willow 3	OU2	core	10/18/2006	-134.00	-15.10	-15.10	0.11
Willow 3	OU2	stem	5/16/2007	-120.56	1.10	-14.55	0.21
Willow 3	OU2	stem	6/27/2007	-120.05	0.55	-14.06	0.12
Willow 3	OU2	core	9/21/2007	-127.65	0.97	-15.24	0.08
Willow 4	OU2	core	10/18/2006	-129.00	-15.40	-15.40	0.00
Willow 4	OU2	stem	5/16/2007	-119.06	2.23	-13.74	0.19
Willow 4	OU2	stem	6/27/2007	-125.62	1.66	-14.73	0.12
Willow 4	OU2	core	9/21/2007	-117.42	0.72	-3.99	0.09
Precip-1	UWRL	Precipitation	11/2/2007	-97.89	0.94	-13.54	0.04
Precip-2	UWRL	Precipitation	11/2/2007	-101.89	1.17	-14.17	0.24

NA: Not enough water was collected from the sample to run more than one replicat and no standard deviation could be calculated.

Appendix D – Calculations for Entire OU2 TCE Removal

Leaf Volatilization

Average

Scaled to Transpiration = Average TSC (µg/L) * Transpiration (L/day/tree) * Growing Season (days)

=11.9 (µg/L) * 60 (L/day/tree) * 150 (days/year) = 107 (mg/tree/year) = 0.11 (g/tree/yr)

Scaled to Area* = Average flux (pg/cm^2/min) * Leaf area of tree (cm^2) * Growing season * (days)

= 0 to 33.8 (pg/cm^2/min) * 289,319 to 637,100 (cm^2) *150 (days) = 211 (mg/tree/yr) = 0.21 (g/tree/yr)

Minimum (based on TSC of 2.4 µg/L and 15 L/day transpiration rate)

= Average TSC (µg/L) * Transpiration (L/day/tree) * Growing Season (days)

=2.4 (µg/L) * 15 L/day/tree * 150 day/year = 5.4 mg/tree/yr = 0.005 g/tree/yr

Maximum (based on TSC of 46 µg/L and 160 L/day transpiration rate)

= TSC (µg/L) * Transpiration (L/day/tree) * Growing Season (days)

= 46 (µg/L) * 160 (L/day/tree) * 150 (days) = 1104 (mg/tree/yr) = 1.1 (g/tree/yr)

Trunk Volatilization (not including Willow 1)

Average

Scaled to Area^ = Average flux (pg/cm^2/min/tree) * Trunk area of tree (cm^2) * Growing season (days)

= 0 to 0.06 (pg/cm^2/min/tree) * 270,399to 600,470 (cm^2) * 150 days = 4.1 (mg/tree/yr) = 0.004 (g/tree/yr)

Maximum (based on Willow 1 flux of 1.32 pg/cm^2/min and trunk area)

= flux (pg/cm^2/min/tree) * Trunk area of tree (cm^2) * Growing season (days)

= 1.32 (pg/cm^2/min/tree) * 218,292 cm^2 * 150 days = 62 mg/yr/tree = 0.06 g/yr/tree

Soil Flux

Using the Thiesson Polygon method for calculating area and each corresponding soil flux measurement (see Table 11) the losses over 12,207 m^2 is 390 g/yr based on a 180 day season.

Total TCE Removed by Volatilization at OU2

Minimum

= Soil + Leaf Volatilization (based on transpiration) * 30 trees + Trunk Volatilization (based on tree average of 107 mg/tree/yr) * 30 trees

= 390 (g/yr) + 0.005 (g/yr) * 30 trees + 0.004 (g/yr) * 30 trees = 390 (g/yr)

Maximum

= Soil + Leaf Volatilization (based on area) * 30 trees + Trunk Volatilization (based on Willow 1) * 30 trees

= 390 + 1.1 (g/tree/yr) * 30 + 0.06 (g/tree/yr) * 30 = 424 (g/yr)

^The average flux for each tree was multiplied by the corresponding area for that tree. An overall average was then taken to scale to the entire canopy.

Appendix E – Tree Core Sampling and Metabolite Results and Conclusions

Tree Core Sampling

Tree core samples were collected at OU2 in the summer and fall of 2006, the spring, summer, and fall of 2007, and in the fall of 2008. The samples were taken from several trees that had also been studied during the 2005 sampling event. All tree cores taken at OU2 during 2006 are in Table F-1, the 2007 samples are located in Table F-2, and 2008 results are in Table F-3 of Appendix C.

Since OU2 has been heavily monitored, frequent sampling could be used to determine if tree core concentrations remain constant from year to year. Table E-1 displays the average tree core concentrations and their 95% confidence intervals. Only the trees that had been sampled all 3 years are reported in this table.

All trees core concentrations remain relatively constant throughout the years, with the exception of Willow 1 and Poplar 3, which vary significantly. In order to limit stress on the trees from multiple events, samples were taken at different heights and directions along the trunk. Rogers (2006) and Lewis (2001) each reported differences in TCE concentrations due to height while coring at OU2 and nearby OU4.

Rogers (2006) reported decreasing trends in 2 of the 3 trees sampled for core concentrations with height with concentrations varying between 36 µg/kg to 55 µg/kg for Willow 4 and 52 µg/kg to 73 µg/kg for Poplar 3. Lewis (2001) reported radial differences in the TCE concentrations varied up to 2 times around the tree trunk and found no consistent trends with height. These variations in sampling location may also contribute to the large confidence intervals in the tree core concentrations.

Table E-1. Yearly average TCE core concentration from 2005 to 2008

	Tree Core Concentrations (µg/kg)*							
	2005		2006		2007		2008	
Tree	Average	95% CI	Average	95% CI	Average	95% CI	Average	95% CI
Willow 1	659.1	380.4	203.3	43.9	153.3	70.0	223	3.4
Willow 2	105.4	57.2	155.9	138.5	72.1	31.6	175.8	0.5
Willow 3	56.9	4.4	42.4	14.4	34.4	6.8	94.1	11.49
Willow 4	41.6	10.9	55.2	6.0	25.1	8.8	81.6	25.6
Poplar 1	156.1	49.9	279.4	18.8	264.4	114.2	212.8	27.2
Poplar 3	78.1	26.8	51.1	8.5	39.9	13.1	233.5	66.9

* Based on a wet weight concentration
CI: Confidence Interval

Table E-2 summarizes the seasonal averages with the 95% confidence intervals. The only tree that showed an increasing trend through the season is Willow 4. Willows 1, 2, and 3, and Poplar 3 concentrations peaked in the summer months. Poplar 1 and the Russian olive have higher concentrations in the spring, decrease during the summer and then increase again in the fall. No general seasonal trends have been observed in the coring analysis. Figure E-1 is a plot of tree core concentrations versus the nearby groundwater concentrations. Willow 1 and Poplar 1 were not included in this plot because of their abnormally higher concentrations, but are displayed in Figure E-2. Both Willow 1 and Poplar 1 are similar in that they are both young trees that are much smaller than the other trees sampled at OU2.

Groundwater samples were collected within a few days of tree core collection. A comparison of groundwater TCE and tree core TCE concentrations were used to investigate a potential relationship. Table E-2 also shows a summary of the core samples with their corresponding groundwater concentrations. In an arid environment where the water source is mostly the contaminated groundwater, the trees cores should remain the

same concentration. The observed may change in the early spring when precipitation and snow melt may become the primary source of water.

In conjunction with TCE analysis, the tree cores and groundwater were analyzed for c-DCE and t-DCE. The samples collected showed an uneven distribution of c-DCE concentrations at OU2. In general, the trees that are growing over parts of the plume with higher TCE groundwater concentrations had higher TCE core concentrations than the ones growing over parts of the plume with lower TCE groundwater concentrations. The two exceptions are Willow 1 and Poplar 1, which are smaller, younger trees than the other trees sampled.

According to the relationship from Garbarini and Lion (1986), lignin normalized wood water sorption could be used to relate the trees cores to the groundwater concentration using Equation 5. Using a Log Kow value of 2.33 for TCE, the Log K_{lignin} value should be 1.73.

Table E-2. Summary of seasonal tree core concentrations in 2007

	Spring 5/15/2007		Summer 6/26/2007		Fall 9/18/2007	
Tree	GW Conc. (µg/L)	Core Conc. (µg/kg)*	GW Conc. (µg/L)	Core Conc. (µg/kg)*	GW Conc. (µg/L)	Core Conc. (µg/kg)*
Willow 1	6.2+0.7	135.6+9.6	80.0+2.2	307.1+56.0	12.2+0.5	110.4+39.4
Willow 2	250+15.7	19.0+5.3	387.5+2.8	107.2+77.4	236.4+2.3	92.46+26.3
Willow 3	94.7+0.6	25.5+10.6	180.4+10.9	36.7+17.1	75.3+1.0	29.97+1.4
Willow 4	94.7+0.6	19.4+1.8	180.4+10.9	21.1+6.0	75.3+1.0	44.29+13.4
Poplar 1	54.8+0.7	400.9	61.0+10.2	256.9+325.9	NS	279.8+88.4
Poplar 3	250+15.7	14.3+12.0	387.5+2.8	49.7+9.5	236.4+2.3	47.2+22.2

*Wet weight concentration

NS: Not sampled

Errors are equal to 95% confidence intervals.

When calculating the Log K_{lignin} from tree core concentration and groundwater concentrations collected from the field, the values ranged from -1.48 to 2.07. The high Log K_{lignin} of 2.07 is reasonable taking into account experimental errors involved with this measurement approach. The values lower than the calculated 1.73 may be due to losses due to volatilization from the tree trunk or metabolism within the tree. If younger trees such as Willow 1 and Poplar 1 are taking up equivalent amount of groundwater as larger, mature trees, but have much smaller mass, TCE may be at a maximum sorption capacity within the plant tissue. This would cause TCE tree core concentrations to be much higher than larger trees with significantly more mass.

While comparing the flux from leaf phytovolatilization to the tree core concentrations, it appeared there might be a relationship between tree core concentrations and leaf volatilization flux (FigureE-3). If this relationship can be investigated more fully, it might be possible to estimate phytovolatilization losses based on tree core concentrations, eliminating the use for in depth phytovolatization sampling.

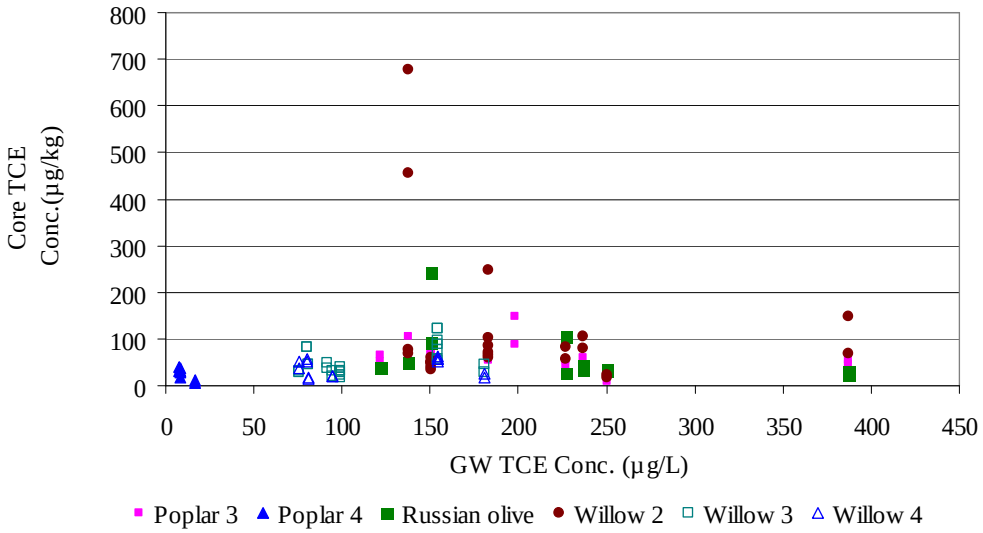

Figure E-1. Tree core concentration versus nearby groundwater concentration from 2005 to 2007.

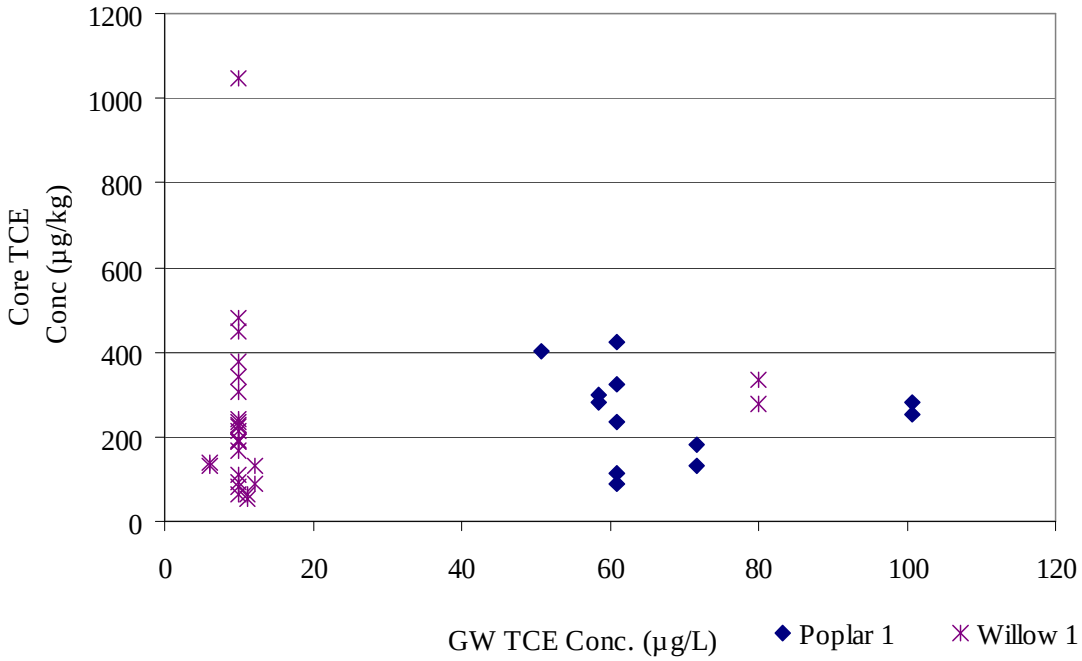

Figure E-2. TCE tree core versus TCE groundwater concentrations of Willow 1 and Poplar 1 from 2005 to 2007.

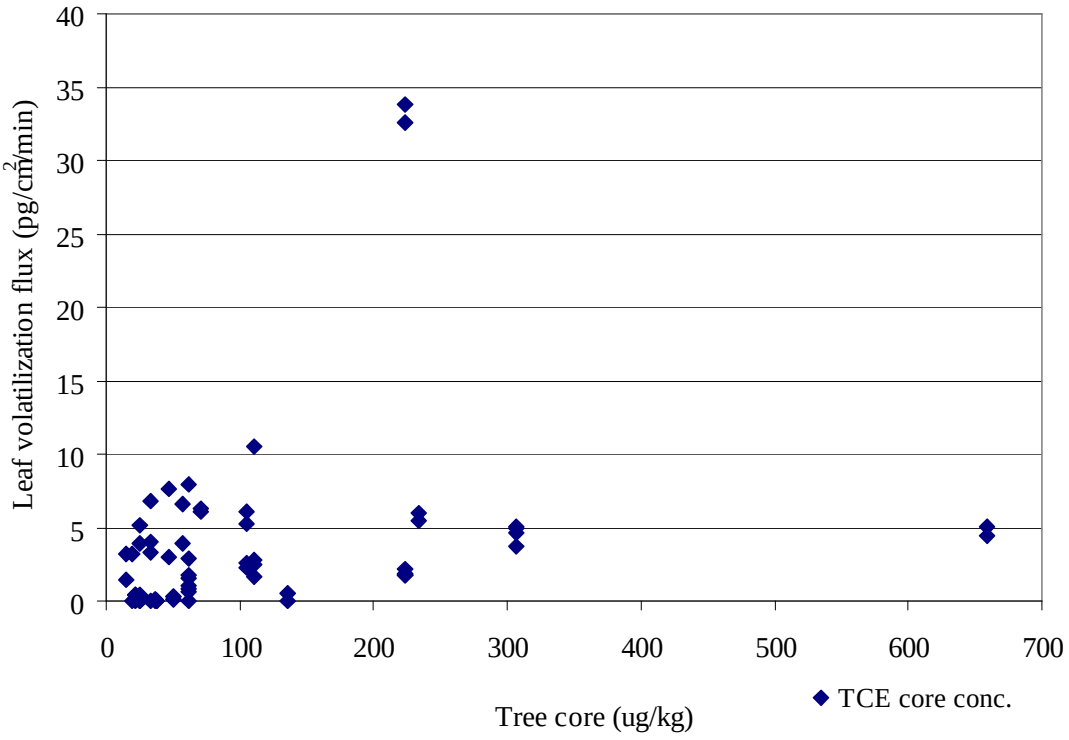

Figure E-3. TCE leaf volatilization flux versus TCE tree core concentrations.

Metabolite Sample Results

Several metabolite samples were collected at OU2 and OU8 between 2006 and 2007. Samples were extracted using the methods used in the 1999 and 2005 study. Samples were spiked with TCEt, DCAA, and TCAA. Recoveries of spikes were 80%. TCE metabolites were also not found in any of the leaf and stem samples collected in the 2005 study. In the 1999 study, metabolites ranged from ND to 7.3 mg/kg below the canal area where the 2005-2007 samples were collected. Reasons for this discrepancy may be due to the detector used on the GC or the extraction method. During the 1999 study an Electron Capture Detector (ECD) was used as the detector, whereas in the later study mass spectroscopy was used. The extraction method used in the 2005 to 2007 study may have been insufficient in extracting metabolites in all areas of the plant tissue

Using the Log K_{lignin} value of 1.73 and comparing it to the calculated range of -1.48 to 2.07, the discrepancy between the calculated and measured K_{lignin} value may be a result of metabolism of TCE within the plant. Although three different common metabolites were investigated, there may be other metabolic bi-products that were not analyzed. This could reduce the TCE core concentrations from expected values.

In order to determine if metabolism would be a significant fate pathway at OU2, the 1999 values were used to determine a loss attributed to metabolism. Using a leaf mass per area of crown projection of a of 290 g/m^2 of 8.7 meter *Populus euramerica* tree (Karlik and Winer, 1999), 7.3 mg/kg of leaves of metabolism, and a crown radius of 5 m, losses equated to 160 mg loss per tree per growing season. Since most of the observed tree concentrations and groundwater concentrations in the 2005 to 2008 studies were much lower than the 1999 study (µg/kg and µg/L instead of mg/kg and mg/L), it is likely

that metabolism is not a significant pathway at OU2, although a potentially significant fate pathway if identified at sites at higher concentrations.

Summary and Conclusions

No definitive correlation was made between groundwater, tree cores, trunk volatilization, and leaf volatilization. Fluctuations in tree core analysis could be due to height and radial differences in sampling. A possible correlation between tree core and phytovolatilization should be further investigated to simplify methods of estimating TCE losses. No seasonal trends were observed in tree core concentrations.

No metabolites were found in any of the samples collected from 2005 to 2007. Metabolism of TCE within the trees may not be an important part in the OU2 conceptual model. Further analysis and different procedures for extraction and analysis may help to find metabolites bound in different areas of the plant that couldn't be accessed with the extraction method used in this study.

Appendix F- Tree Core Data from 2006 to 2008

Table F-1 OU2 tree core TCE, DCE, and VC concentrations in 2006

Sample Name	Date Collected	TCE (ug/kg)	cis-DCE (ug/kg)	trans-DCE (ug/kg)	VC (ug/kg)	Sample Height (cm)	Sampling Direction	Diameter (cm)
Apple 1	7/31/2006	ND	ND	ND	ND	82	N	NA
Apple 1	7/31/2006	ND	ND	ND	ND	82	N	NA
Box Elder	7/31/2006	ND	ND	ND	ND	135	E	NA
Box Elder	7/31/2006	ND	ND	ND	ND	135	E	NA
Maple	7/31/2006	14.11	0.89	ND	ND	100	W	NA
Maple	7/31/2006	18.93	1.22	ND	ND	100	W	NA
Poplar 1	7/26/2006	281.598	28.11	ND	ND	69	N	NA
Poplar 1	7/26/2006	253.301	32.36	ND	ND	69	N	NA
Poplar 1	8/18/2006	299.51	50.15	ND	ND	17	E	NA
Poplar 1	8/18/2006	283.02	39.03	ND	ND	17	E	NA
Poplar 2	7/26/2006	ND	ND	ND	ND	82	E	NA
Poplar 2	7/26/2006	ND	ND	ND	ND	82	E	NA
Poplar 3	7/26/2006	106.28	64.66	ND	ND	122	W	NA
Poplar 3	7/26/2006	64.85	36.39	ND	ND	122	W	NA
Poplar 3	8/18/2006	51.32	78.69	ND	ND	122	S	NA
Poplar 3	8/18/2006	65.17	99.77	ND	ND	122	S	NA
Poplar 3	9/30/2006	48.06	45.57	0.29	ND	254	W	38
Poplar 3	9/30/2006	64.79	48.53	0.34	ND	254	W	38
Poplar 3	10/20/2006	49.96	41.56	0.33	ND	163	NA	73
Poplar 3	9/18/2006	66.6	49.9	0.3	ND	337	W	35
Poplar 3	9/18/2006	93.8	69.6	0.4	ND	337	W	35
Poplar 3	9/18/2006	73.3	34.5	0.2	ND	160	W	41
Poplar 3	9/18/2006	78.9	29.5	0.2	ND	160	W	41
Poplar 3	9/18/2006	55.5	18.3	0.1	ND	40	W	48
Poplar 3	9/18/2006	57.6	22.5	0.1	ND	40	W	48
Poplar 4	7/31/2006	31.90	13.56	0.42	ND	135	N	NA
Poplar 4	7/31/2006	36.29	16.55	0.57	ND	135	N	NA
Poplar 4	9/30/2006	40.59	13.09	0.47	ND	36.5	N	20
Poplar 4	9/30/2006	30.74	9.80	0.47	ND	36.5	N	20
Russian olive	7/27/2006	49.72	12.45	ND	ND	115	W	NA
Russian olive	7/27/2006	49.03	11.33	ND	ND	115	W	NA
Russian olive	8/18/2006	39.71	19.56	ND	ND	130	S	NA
Russian olive	8/18/2006	36.60	23.47	ND	ND	130	S	NA
Russian olive	9/30/2006	92.45	14.91	ND	ND	122	E	40
Russian olive	9/30/2006	241.02	15.52	ND	ND	122	E	40
ND: Sample concentrations were below instrument detection limit								
NA: Parameter was not recorded								

Table F-1. Continued

Sample Name	Date Collected	TCE (ug/kg)	cis-DCE (ug/kg)	trans-DCE (ug/kg)	VC (ug/kg)	Sample Height (cm)	Sampling Direction	Diameter (cm)
Willow 1	7/21/2006	62.63	17.12	0.51	ND	100	N	NA
Willow 1	7/21/2006	82.29	23.24	0.66	ND	100	N	NA
Willow 1	7/27/2006	375.98	94.17	0.16	ND	94	E	NA
Willow 1	8/18/2006	189.31	76.77	ND	ND	122	E	NA
Willow 1	8/18/2006	229.19	223.54	0.15	ND	122	E	NA
Willow 1	9/30/2006	93.94	80.59	ND	ND	115	E	14
Willow 1	9/30/2006	110.46	88.10	0.167	ND	115	E	14
Willow 1	9/30/2006	187.34	167.04	0.29	ND	102	E	14
Willow 1	10/20/2006	242.94	158.71	0.32	ND	150	E	11
Willow 1	9/18/2006	306.8	199.0	0.3	ND	310	E	8
Willow 1	9/18/2006	234.9	144.6	0.3	ND	310	E	8
Willow 1	9/18/2006	192.6	121.6	0.3	ND	170	E	11
Willow 1	9/18/2006	222.7	140.3	0.3	ND	170	E	11
Willow 1	9/18/2006	213.0	133.9	0.3	ND	70	E	14
Willow 1	9/18/2006	167.4	101.3	0.2	ND	70	E	14
Willow 1	7/27/2006	341.21	80.55	0.06	ND	94	E	NA
Willow 2	7/21/2006	456.64	100.81	0.21	ND	100	W	NA
Willow 2	7/21/2006	678.57	132.88	ND	ND	100	W	NA
Willow 2	7/26/2006	67.42	33.47	0.35	ND	125	W	NA
Willow 2	7/26/2006	75.94	71.27	0.55	ND	125	W	NA
Willow 2	9/30/2006	47.67	34.76	ND	ND	280	W	25
Willow 2	9/30/2006	58.68	52.62	0.33	ND	280	W	25
Willow 2	9/30/2006	40.51	36.70	0.19	ND	138	W	27
Willow 2	9/30/2006	33.44	32.70	ND	ND	138	W	27
Willow 2	9/30/2006	52.09	47.13	ND	ND	25	W	33
Willow 2	9/30/2006	48.07	45.40	ND	ND	25	W	33
Willow 3	7/31/2006	83.12	96.07	3.37	ND	84	W	NA
Willow 3	7/31/2006	83.10	91.48	2.37	ND	84	W	NA
Willow 3	8/18/2006	49.59	13.90	0.15	ND	105	NE	NA
Willow 3	8/18/2006	36.78	10.31	0.11	ND	105	NE	NA
Willow 3	9/30/2006	27.13	12.82	ND	ND	252	N	13
Willow 3	9/30/2006	30.97	17.03	ND	ND	252	N	NA
Willow 3	9/30/2006	22.78	8.72	0.12	ND	136	N	22
Willow 3	9/30/2006	18.32	12.29	ND	ND	136	N	22
Willow 3	9/30/2006	41.16	15.87	ND	ND	19	N	95
Willow 3	9/30/2006	31.24	12.22	0.09	ND	19	N	95
Willow 4	7/31/2006	52.12	16.09	0.63	ND	81	E	NA
Willow 4	7/31/2006	58.22	16.41	0.87	ND	81	E	NA
Willow 5	7/31/2006	46.20	3.66	0.29	ND	143	South	NA
Willow 5	7/31/2006	79.19	3.76	0.30	ND	143	South	NA

ND: Sample concentrations were below instrument detection limit

NA: Parameter was not recorded

Table F-2. OU2 Tree core TCE, DCE, and VC concentration in 2007

Sample Name	Date Collected	TCE (ug/kg)	cis-DCE (ug/kg)	trans-DCE (ug/kg)	VC (ug/kg)	Sample Height (cm)	Sampling Direction	Diameter (cm)
Apple	5/14/2007	ND	ND	ND	ND	85	North	20
Apple	5/14/2007	ND	ND	ND	ND	85	North	20
Box elder	5/14/2007	ND	ND	ND	ND	135	East	38
Box elder	5/14/2007	ND	ND	ND	ND	135	East	38
Box elder	11/5/2007	ND	ND	ND	ND	89	East	35
Poplar 1	5/14/2007	400.9	23.2	ND	ND	60	West	14
Poplar 1	6/27/2007	423.2	35.8	ND	ND	73	North	16
Poplar 1	6/27/2007	88.7	29.4	ND	ND	73	North	16
Poplar 1	9/21/2007	324.9	143.5	ND	ND	20	West	17
Poplar 1	9/21/2007	234.7	94.3	ND	ND	20	West	17
Poplar 1	11/5/2007	113.9	28.4	ND	ND	60	West	14
Poplar 3	5/14/2007	20.4	11.5	ND	ND	126	South	43
Poplar 3	5/14/2007	8.2	13.8	ND	ND	113	South	43
Poplar 3	6/26/2007	54.5	72.3	ND	ND	143	West	44
Poplar 3	6/26/2007	44.9	56.7	ND	ND	143	West	44
Poplar 3	9/21/2007	35.9	31.7	0.12	ND	66	West	49
Poplar 3	9/21/2007	58.5	73.7	0.22	ND	66	West	49
Poplar 3	11/5/2007	53.2	24.7	ND	ND	70	South	48
Poplar 3	11/5/2007	43.9	26.2	ND	ND	70	South	48
Poplar 4	5/18/2007	6.2	2.3	ND	ND	110	North	18
Poplar 4	5/18/2007	11.3	3.5	ND	ND	113	North	18
Russian Olive	5/14/2007	34.8	18.3	ND	ND	90	South	92
Russian Olive	5/14/2007	30.8	16.6	ND	ND	90	South	92
Russian Olive	6/26/2007	22.1	10.9	ND	ND	130	South	88
Russian Olive	6/26/2007	28.0	10.1	ND	ND	130	South	88
Russian Olive	9/21/2007	33.0	9.3	ND	ND	41	South	82
Russian Olive	9/21/2007	43.1	8.5	ND	ND	41	South	82
Russian Olive	11/5/2007	24.7	14.1	ND	ND	70	East	88
Russian Olive	11/5/2007	104.3	21.4	ND	ND	70	East	88
Willow 1	5/14/2007	140.5	84.1	0.55	ND	130	East	15
Willow 1	5/14/2007	130.7	61.1	0.43	ND	140	East	15
Willow 1	6/26/2007	278.5	105.3	ND	ND	NR	East	NA
Willow 1	6/26/2007	335.6	125.0	ND	ND	NR	East	NA
Willow 1	9/21/2007	130.5	124.0	ND	ND	142	East	14
Willow 1	9/21/2007	90.2	71.0	ND	ND	142	East	14
Willow 1	11/5/2007	54.9	53.3	ND	ND	47	East	9
Willow 1	11/5/2007	65.5	47.5	ND	ND	47	East	9
Willow 2	5/14/2007	16.3	10.9	ND	ND	134	South	27
Willow 2	5/14/2007	21.6	17.6	ND	ND	134	South	27
Willow 2	6/26/2007	146.7	56.7	ND	ND	182	South	27
Willow 2	6/26/2007	67.7	31.8	ND	ND	182	South	27
Willow 2	9/21/2007	105.9	44.4	ND	ND	102	South	30
Willow 2	9/21/2007	79.0	36.1	ND	ND	102	South	30
Willow 2	11/5/2007	82.5	34.4	ND	ND	90	South	29
Willow 2	11/5/2007	57.2	30.9	ND	ND	90	South	29

Table F-2. Continued

Willow 3	5/14/2007	20.0	7.7	ND	ND	71	North	24
Willow 3	5/14/2007	30.9	11.7	ND	ND	75	North	30
Willow 3	6/27/2007	45.5	23.6	ND	ND	94	West	29
Willow 3	6/27/2007	28.0	12.2	ND	ND	94	West	29
Willow 3	9/21/2007	29.3	10.3	ND	ND	140	North	23
Willow 3	9/21/2007	30.7	10.2	ND	ND	142	North	23
Willow 3	11/5/2007	46.9	14.8	ND	ND	70	West	29
Willow 3	11/5/2007	44.3	14.4	ND	ND	70	West	29
Willow 4	5/16/2007	20.3	7.3	ND	ND	110	Southeast	29
Willow 4	5/16/2007	18.5	9.6	ND	ND	110	Southeast	29
Willow 4	6/27/2007	18.1	11.9	ND	ND	41	Southwest	28
Willow 4	6/27/2007	24.2	15.2	ND	ND	41	Southwest	28
Willow 4	9/21/2007	51.1	20.3	ND	ND	76	West	29
Willow 4	9/21/2007	37.5	18.0	ND	ND	71	West	29
Willow 4	11/5/2007	17.7	14.6	ND	ND	60	West	29
Willow 4	11/5/2007	13.7	13.8	ND	ND	60	West	29
Willow E of Poplar 3	9/21/2007	90.8	44.0	ND	ND	79	West	28
Willow E of Poplar 3	9/21/2007	108.3	49.0	ND	ND	79	West	28
Willow S of RO	9/21/2007	36.7	69.8	ND	ND	150	South	18
Willow S of RO	9/21/2007	39.5	73.3	ND	ND	150	South	18
Willow S of RO	11/5/2007	76.9	73.0	ND	ND	60	South	18
Willow S of RO	11/5/2007	56.0	81.1	ND	ND	60	South	18
New maple	11/5/2007	ND	ND	ND	ND	70	East	25
Unknown S of Willow 1	11/5/2007	ND	ND	ND	ND	100	North	NA
NA: Apsect was not recorded								
ND: Non-detect. Sample concentration was below instrument detection limits.								

Table F-3. OU2 tree core TCE, DCE, and VC concentration in 2008

Sample Name	Sample Date	TCE (µg/kg) Wet Wt.	c-DCE (µg/kg) Wet Wt.	t-DCE (µg/kg) Wet Wt.	V.C. (µg/kg) Wet Wt.	Sample Height (cm)	Sample Direction	Diameter (cm)
Poplar 3	8/27/2008	267.7	75.3	ND	ND	30	S	NA
Poplar 3	8/27/2008	199.4	57.0	ND	ND	30	S	NA
Willow 2	8/27/2008	175.5	51.0	ND	ND	30	S	NA
Willow 2	8/27/2008	176.0	46.2	ND	ND	30	S	NA
Willow S of RO	8/27/2008	156.1	130.2	ND	ND	90	NW	NA
Willow S of RO	8/27/2008	117.3	89.1	ND	ND	90	NW	NA
Russian Olive	8/27/2008	52.4	7.0	ND	ND	60	W	NA
Russian Olive	8/27/2008	67.3	11.3	ND	ND	60	W	NA
Poplar 1	8/27/2008	226.6	70.3	ND	ND	30	W	NA
Poplar 1	8/27/2008	198.9	66.0	ND	ND	30	W	NA
Willow 1	8/27/2008	221.3	106.0	ND	ND	90	W	NA
Willow 1	8/27/2008	224.8	103.1	ND	ND	90	W	NA
Willow 4	8/27/2008	68.6	18.3	ND	ND	60	W	NA
Willow 4	8/27/2008	94.7	14.4	ND	ND	60	W	NA
Willow 3	8/27/2008	88.2	27.3	ND	ND	30	N	NA
Willow 3	8/27/2008	100.0	28.0	ND	ND	30	N	NA
NR: Not Recorded								
NR: Not Recorded								