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# UPTAKE, METABOLISM, AND PHYTOVOLATILIZATION OF TRICHLOROETHYLENE BY INDIGENOUS VEGETATION: IMPACT OF PRECIPITATION

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## SUMMARY OF PRACTICAL IMPLICATIONS

Field studies in Florida and Utah showed that indigenous vegetation contributed to the natural attenuation of trichloroethylene (TCE) in shallow groundwater plumes. However, despite similar exposure to TCE, plant uptake appeared greater at the Utah site where summer precipitation is minimal. Trichloroethylene was detected in all exposed plants at both sites, but plant concentrations were 10 to 100 times higher at the Utah site. Plant metabolites of TCE were also detected. Using a novel sampling technique, TCE was identified in transpiration samples collected at the Utah site, but not the Florida site. The lack of phytovolatilization and significantly lower TCE plant concentrations at the Florida site are most likely due to the smaller fraction of contaminated groundwater used by plants for transpiration because of the frequent precipitation. However, additional studies are necessary before definite conclusions can be drawn regarding the influence of climate on plant uptake. The impact of plants relative to other attenuation mechanisms was not directly evaluated at these sites and should be addressed in future studies.

## INTRODUCTION

### Impact of Vegetation on Trichloroethylene in Soil and Shallow Groundwater

Plants have profound effects on physical, chemical, and biological processes in soils and can significantly impact the fate of organic chemicals in soil. Understanding the fate of organic contaminants in plants and soils is critical in evaluating the effectiveness of phytoremediation, performing risk assessments, and quantifying the relative impact of plants on natural attenuation.

Increased microbial and chemical activity occurs on and around root surfaces and plants can take up, metabolize, and transpire organic chemicals. These activities are impacted by the extent of water that flows to the root surface *via* transpiration from plant leaves. If the water flow to the root is large enough, hydraulic control of contaminant plumes occurs. Plants can also come into direct contact with contaminants because of extensive root systems. In addition, root exudates may enhance cometabolic degradation in the rhizosphere. Laboratory studies using TCE have identified enhanced rhizosphere degradation, uptake and transpiration (phytovolatilization), and uptake and metabolism as potential plant mediated processes (Walton and Anderson 1990, Schroll *et al.* 1994, Anderson and Walton 1995, Narayanan *et al.* 1995, Gordon *et al.* 1997, Newman *et al.* 1997, Schnabel *et al.* 1997, Burken and Schnoor 1998, Orchard *et al.* 2000a, 2000b).

While the literature is generally consistent regarding the identification of phytoremediation processes, a consensus has not been reached about the magnitude of these processes and the effect on the overall fate of TCE. The lack of consensus is especially noticeable in describing the extent of plant uptake and phytovolatilization. For example, minimal root uptake and phytovolatilization of TCE have been reported in some studies (Schroll *et al.* 1994, Schnabel *et al.* 1997, Orchard *et al.* 2000a, 2000b) while extensive uptake and phytovolatilization have been described by others (Burken and Schnoor 1998).

Pilot data (Newman *et al.* 1997, Shang *et al.* this book) and field-scale data (Compton *et al.* 1998, Jones *et al.* 1998, Eberts *et al.* this book, Hirsh *et al.* this book) generally support the mechanistic observations reported in laboratory studies. However, most of these studies examined young trees that had been planted recently. Fewer studies have focused on the potential impact of mature vegetation growing within contaminated groundwater plumes. Yet this information is necessary to predict the long-term effectiveness of phytoremediation, determine the potential impact of vegetation on the overall natural attenuation process, and evaluate potential food-chain contamination.

The objective of this chapter is to compare the uptake, metabolism, and phytovolatilization of TCE by indigenous vegetation growing over contaminated groundwater at two sites that vary significantly in precipitation received. The two sites, located at Cape Canaveral Air Station (CCAS), Florida, and Hill Air Force Base (Hill AFB), Utah, were similar in ground-

water TCE concentration, depth from the ground surface to the water table, and in the relative duration of exposure to contaminants. These sites are, however, very different in climate, especially in the amount and frequency of precipitation. This difference in precipitation was used to examine the hypothesis that trees growing in semi-arid regions are more likely to obtain a greater fraction of water requirements from contaminated groundwater resulting in a higher uptake of TCE. Unique procedures for the collection and analysis of phytovolatilization and plant tissue samples were developed during these studies and will also be described.

### Organic Contaminant Uptake: Transpiration Stream Concentration Factor

Because of commercial interests, much of the plant uptake data and related theory for organic xenobiotic chemicals have been generated for pesticides. Much less information is available for other industrial organic chemicals. Plasma-membrane transporters mediating the uptake of sugar, amino acid, peptide, glutathione, and other biotic chemicals have been identified (*e.g.*, Delrot *et al.* 2001). However, the uptake of xenobiotic organic compounds by plants is believed to be a passive process (McFarlane 1995) related, at least in part, to the lipophilicity of the contaminant (Briggs *et al.* 1982) as described by the octanol-water partition coefficient ( $K_{ow}$ ).

The transpiration stream concentration factor ( $TSCF$ ) has been widely used to describe organic contaminant uptake by plants. The  $TSCF$  is a dimensionless ratio of the concentration in the xylem sap to bulk concentration in the root-zone solution (Russell and Shorrocks 1959)

$$TSCF = \frac{\text{Concentration in xylem sap}}{\text{Root-zone solution concentration}} \quad (18-1)$$

Because xylem sap concentrations are difficult to measure directly for intact plants,  $TSCF$  is often determined from measured shoot concentrations; the shoot-tissue concentration is normalized to the amount of water transpired during exposure to the chemical (*i.e.*, concentration in xylem sap is equal to milligrams of compound in shoots per liter of water transpired) assuming no phytovolatilization of the chemical. Almost all experimental  $TSCF$  values have been obtained in the laboratory where the root zone concentrations can be more easily measured and controlled. Accurate  $TSCF$  values are extremely difficult to determine in the field because of the inherent variability associated with root zone exposure (*i.e.*, soil and groundwater heterogeneity, variability in contaminant concentration, and groundwater *versus* surface water use).

A compound may be actively or passively taken up by plants or may be excluded. Active uptake ( $TSCF$  greater than 1) generally occurs with nutrient cations ( $\text{NH}_4^+$ ,  $\text{PO}_4^+$ , and  $\text{K}^+$ ) and requires the expenditure of metabolic

energy. With the possible exception of some hormone-like chemicals (2,4-dichlorophenoxyacetic acid or 2,4-D), there is no evidence of active uptake of anthropogenic chemicals (McFarlane 1995). Passive uptake ( $TSCF$  equal to 1) occurs when a chemical is taken up directly with water because of the gradient of water potential resulting from evapotranspiration (McFarlane 1995). A chemical is said to be excluded ( $TSCF$  less than 1) when uptake is not directly proportional (1:1) to water uptake, although the mechanism of uptake is still thought to be a passive process. It has been suggested that the passive uptake of organic contaminants may be driven by the concentration gradient formed as the solute accumulates on the outside of the root membrane (Marschner 1995). However, factors such as membrane permeability and xylem sap solubility of the contaminant may limit the extent or kinetics of passive uptake (Hsu *et al.* 1990). Sorption and rapid metabolism of contaminants within the tree would also act to reduce xylem concentrations and keep  $TSCF$  values from reaching 1.

One of the most widely cited studies involving the measurement and prediction of  $TSCF$  was performed by Briggs *et al.* (1982) who evaluated the uptake and translocation of two series of nonionic organic chemicals (*O*-methylcarbamoyloximes and substituted phenylureas) by 10-day-old intact barley (*Hordeum vulgare*) plants. All the chemicals having a value of the logarithm ( $\log$ ) of  $K_{ow}$  ranging from  $-0.57$  to  $4.6$  were found to have a  $TSCF$  less than 1 and it was concluded that the chemicals moved passively into the shoot with the transpiration water (Briggs *et al.* 1982). The bell-shaped data relating  $TSCF$  to the  $\log K_{ow}$  were fit using a Gaussian curve

$$TSCF = 0.784 \exp - \frac{(\log K_{ow} - 1.78)^2}{2.44} \quad (18-2)$$

suggested an optimal lipophilicity for maximum uptake and translocation at  $\log K_{ow} = 1.8$  ( $TSCF = 0.784$ ). The Gaussian fit inferred that compounds that were either highly polar ( $\log K_{ow}$  less than 0.5) or highly lipophilic ( $\log K_{ow}$  greater than 4.5) would not be significantly taken up by plants. The highly polar organic compounds were thought to be selectively rejected at the root lipid membranes, while the highly lipophilic molecules were bound to the roots and not translocated. Based on the curve, only organic chemicals of intermediate lipophilicity ( $\log K_{ow}$  between 0.5 and 4.5) are expected to pass to the xylem unhindered upon establishment of equilibrium with the root tissues. More recently, similar relationships between  $TSCF$  and  $\log K_{ow}$  have been reported by Hsu *et al.* (1990), Sicbaldi *et al.* (1997), and Burken and Schnoor (1998).

While the empirical relationships for uptake and translocation presented by Briggs *et al.* (1982) and others are useful for initial estimates, numerous examples involve significant over or under prediction of plant uptake. For example, McFarlane *et al.* (1987) found  $TSCF$  values lower than predicted for three chemicals having similar  $\log K_{ow}$  values, while significant uptake

and translocation of a water miscible compound (1,4-dioxane) has been reported (Aitchison *et al.* 2000). In addition, for a given compound and  $\log K_{ow}$ , several different *TSCF* values can often be found in the literature. Indeed, Briggs *et al.* (1982) suggest that it is a “gross oversimplification” to conclude that plant uptake and translocation are influenced only by reversible partitioning of the compound into the nonaqueous phases of the root.

### Estimating the Uptake of Trichloroethylene by Plants on a Field Scale

The significance of plant uptake in the removal of TCE from contaminated groundwater is still unclear, especially considering the wide range of *TSCF* values (0.02 to 0.75) that have been reported in the literature for TCE (*e.g.*, Burken and Schnoor 1998, Orchard *et al.* 2000b). The following simplified illustration highlights the critical variables involved in estimating TCE uptake by plants on a field scale.

Annual TCE uptake from a shallow aquifer per unit area per year can be estimated as follows

$$\text{Mass of TCE removed by plant uptake} = (TSCF)(C_{TCE})(T)(f) \quad (18-3)$$

where *TSCF* is assumed to be constant,  $C_{TCE}$  is the average groundwater concentration of TCE (milligrams per liter), *T* is the cumulative volume of water transpired per unit area per year (liters per square meter per year), and *f* is the fraction of the plant water needs met by contaminated groundwater. This expression assumes that  $C_{TCE}$  is constant. A more realistic calculation would incorporate the change in  $C_{TCE}$  over time as a function of the physical, chemical, or biological processes that may be occurring and possible changes in *TSCF* with exposure concentration.

Transpiration rates in the field vary widely depending on the soil-water availability and evaporative demand. Potential transpiration rates, calculated from pan evaporation rates, are widely used to schedule irrigation of crops. The potential transpiration rate can be 10 liters per square meter per day on hot days in well-watered soils in dry climates, but the cumulative annual transpiration rate is more useful in long-term phytoremediation calculations. The potential annual transpiration rate can be as high as 1800 liters per square meter per year in hot desert climates such as Arizona, and as low as 200 liters per square meter per year in cool, moist environments like Alaska (Camp *et al.* 1996, Allen *et al.* 1998). However, even well-watered crops can fail to attain the potential transpiration rate in the summer because of partial stomatal closure during periods of high evaporative demand. The difference between the actual and potential transpiration rates is larger in hot, desert environments. During winter months, deciduous trees drop leaves and evergreen trees have low transpiration rates as the result of shorter days, lower light levels, and colder temperatures. When forced to use groundwater, phreatophytic plants typically do not achieve the high transpiration rates that

occur with vegetation that uses surface water (Camp *et al.* 1996, Allen *et al.* 1998). Thus, the actual annual transpiration rate is usually below the potential rate. Depending on the climate, 200 to 1400 liters per square meter per year probably represents a reasonable range of values for annual transpiration (also see McCutcheon and Schnoor this book). In a recent review of 52 water-use studies since 1970, Wullschleger *et al.* (1998) found that 90 percent of the observations for maximum rates of daily water use were between 10 and 200 liters per day for individual trees that averaged 21 meters (70 feet) in height.

The fraction of groundwater used by plant roots is difficult to measure and is poorly characterized. As expected, groundwater use tends to decrease as the availability of surface water increases (Nilsen and Orcutt 1996). Additional studies using stable isotope techniques (Nilsen and Orcutt 1996) are necessary to determine a reasonable range of values for this parameter. Until such data are available, a range of groundwater use fractions from 0.1 to 0.5 is probably realistic for climates with more than 40 centimeters (16 inches) of precipitation per year.

Using a groundwater concentration of 1 milligram of TCE per liter, an average *TSCF* value of 0.12 (Orchard *et al.* 2000b), and the high and low estimates for transpiration rate and fraction of groundwater used, yearly plant uptake values ranging from 2.4 to 84 milligrams of TCE per square meter per year can be calculated using Equation 18-3. As additional information regarding transpiration rates and the fraction of groundwater used by plants becomes available, the estimated range can be narrowed. Using the *TSCF* value of 0.75 reported by Burken and Schnoor (1998) would increase the upper range value to 525 milligrams of TCE per square meter per year.

Calculations of this type should be used to determine if plant uptake might be a significant removal mechanism at a particular site. These calculations also show that contaminant uptake is likely more important in climates where rainfall is low during summer months, requiring plants to obtain a higher percentage of moisture from the water table.

### Scope and Objectives of Project

Field studies were conducted at CCAS and Hill AFB to determine if indigenous vegetation was involved in the uptake, volatilization, and metabolism of TCE from shallow contaminated groundwater plumes. Historical depth to groundwater (1.5 to 2.3 meters or 5 to 8 feet below ground surface) and groundwater TCE concentrations (1 to 10 milligrams of TCE per liter) were similar at the two sites but the amounts (CCAS: 127 centimeters per year or 50 inches per year and Hill AFB: 48 centimeters per year or 19 inches per year) and frequency of precipitation were very different. This difference between the two sites enabled us to qualitatively test the hypothesis that trees growing in semi-arid regions are more likely to obtain a greater fraction of water from contaminated aquifers resulting in higher tissue concentrations of TCE. A secondary objective was the development of a novel field sampling

technique for the determination of phytovolatilization and development of analytical methods for determining plant-tissue concentrations of TCE and TCE metabolites [2,2,2-trichloroethanol (TCET) 2,2,2-trichloroacetic acid (TCAA), and 2,2-dichloroacetic acid (DCAA)].

To better understand the potential exposure to and the fate and transport of TCE in the plants and soil, groundwater and soil samples were collected and analyzed for TCE and the potential metabolites. Surface flux measurements from the soil also were collected to quantify the amount of TCE volatilizing directly from the groundwater and soil surface within the system.

## SITE DESCRIPTIONS

### Cape Canaveral Air Station, Florida

Bounded by the Atlantic Ocean on the east and the Banana River on the west, CCAS is located on a barrier island in Brevard County, Florida. The main complex occupies about 6500 hectares (25 square miles) of assembly and launch facilities for missiles and space vehicles. The southern boundary is a manmade shipping channel, and the John F. Kennedy Space Center adjoins CCAS to the north.

The climate at CCAS is semi-tropical, with rainfall (127 centimeters or 50 inches) evenly spread throughout the year (Mallander 1990). This is equal to 1270 liters per square meters per year. Evapotranspiration has been previously estimated at approximately 75 percent of the annual rainfall or 950 liters per square meters per year (Mallander 1990).

The site of interest is the Ordnance Support Facility denoted CCAS Site 1381. From 1968 to 1977, the facility housed acid and solvent dip tanks for cleaning metal components. The chlorinated solvent plume at CCAS Site 1381 is thought to be a result of accidental spills and poor handling practices of the drummed solvents.

The CCAS Site 1381 has a shallow surficial aquifer with measured depths to groundwater between 1.0 and 1.5 meters (3.5 and 4.8 feet) above mean sea level (U.S. National Geodetic Vertical Datum), and approximately 1.5 meters (5 feet) below ground surface. Historical sampling events identified a region of TCE-contaminated groundwater (1 to 10 milligrams per liter) near the southwestern corner of the facility. Low concentrations of vinyl chloride and *cis*-1,2-dichloroethene have also been reported.

### Hill Air Force Base, Utah

Hill AFB is located in northern Utah about 40 kilometers (25 miles) north of Salt Lake City and about 8 kilometers (5 miles) south of Ogden. The Great Salt Lake is approximately 19 kilometers (12 miles) to the west of Hill AFB and the Wasatch Mountain Range is about 6.5 kilometers (4 miles) to the

east. The surface elevation ranges from approximately 1400 to 1500 meters (4600 to 5000 feet) above National Geodetic Vertical Datum of 1929. The climate in the vicinity of Hill AFB is temperate and semi-arid. The frost-free growing season is from May through September. The average annual precipitation recorded during the period 1978 to 1990 at a gage located 1 kilometers (0.5 mile) northeast of the base was 50.3 centimeters (19.8 inches). The majority of precipitation falls from October through May. May is usually the wettest month, and June and July are the driest months. Potential average annual evaporation is approximately 114 centimeters (45 inches) of water per year.

The specific site of interest at Hill AFB is designated as Operable Unit 2 (OU2). The disposal of chlorinated degreasing solvents, mainly TCE, in trenches between of 1967 and 1975 has resulted in the contamination of a shallow aquifer (not used as a drinking water source) at this site. Historically, groundwater concentrations of TCE within the plume have ranged from 0.4 to 10 milligrams per liter. Several other chlorinated solvents (1,1,1-trichloroethane, perchloroethylene, and *cis*-1,2-dichloroethylene) have also been found in groundwater samples collected at the site, at much lower concentrations than TCE.

## SAMPLE COLLECTION AND ANALYSIS

### Sampling Design

#### *Cape Canaveral Air Station*

The initial field sampling at CCAS was performed during the second week of June 1997. Follow-up plant tissue sampling occurred near the end of July and beginning of August 1997. Re-sampling of the transpiration gas and surface flux occurred at this site on September 24 and 25, 1997. Tissue and transpiration gas samples were collected from three plant species, identified within the current extent of dissolved-phase TCE contamination. These species included a live oak (*Quercus virginiana*), a castor bean (*Ricinus communis*), and a saw palmetto (*Serenoa repens*). The live oak (*Quercus virginiana*) was the largest and was expected to have the highest transpiration rate and deepest rooting depth of the three species sampled. The saw palmetto (*Serenoa repens*) is a shrub that is common to the region. The castor bean (*Ricinus communis*), is considered a "nuisance" plant growing at the site.

A second live oak (*Quercus virginiana*) was sampled east of the known extent of dissolved-phase TCE and was to originally serve as a "control." However, results from the initial sampling indicated that this tree may have been previously exposed to TCE and, therefore, not be an appropriate control. Therefore, leaf tissue was collected and analyzed from an off-base live oak (*Quercus virginiana*) (Orlando, Florida, 60 kilometers or 40 miles from the site) as a true control for these analyses.

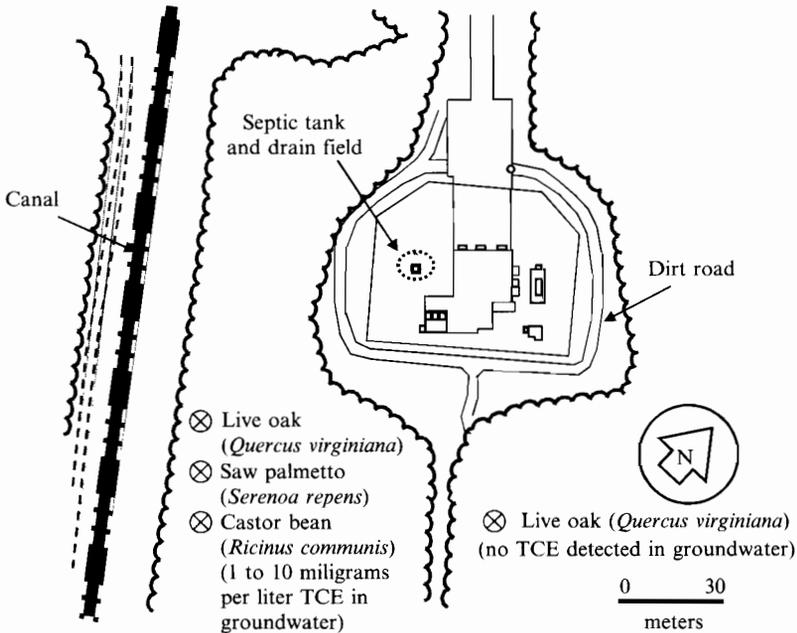
In addition, after completion of the field sampling in June 1997 and analysis of transpiration gas and surface flux samples, results indicated that the

carrier gas (compressed air of breathing quality) used during the initial sampling contained measurable levels of TCE (approximately 4.6 micrograms per cubic meter). Subsequently, sampling used carrier gas with lower levels of TCE (approximately 0.33 microgram per cubic meter).

Groundwater, soil, surface flux, and soil gas samples were also collected at several locations at the site. Soil cores used to determine root density were also collected near each of the sampled plants. The general sampling locations are illustrated in Figure 18-1.

**Hill Air Force Base**

Sampling took place during a 2-week period in late August and early September 1999 just prior to the trees at the seep location being removed as part of an effort to improve the efficiency of an existing seep water collection system. The removal of the trees enabled us to collect stem cores at 1-meter intervals along the entire length of the trees to document the vertical distribution of TCE within the trees at the seep location. In addition, the concentration of TCE in the trees removed from the seep area was monitored periodically over several months to examine the stability of TCE in the wood. Because of the short time (about 2 weeks) between the project initiation and the tree removal, the sampling effort focused on collection and analysis of plant tissue



**Figure 18-1** Plant sampling locations at Cape Canaveral Air Station Ordnance Support Facility 1381.

and transpiration gas samples from three species of trees located in three different places at OU2.

Trees from three areas (two within the historically defined groundwater TCE plume and one outside) located down gradient (east) of the source area were sampled. The seep location was situated on a steep hillside; the seasonal seeps are active mainly during the spring and after significant precipitation events. The canal location was at the bottom of the hillside just east of the Weber canal that supplies irrigation water to nearby agricultural interests.

Plant tissue and transpiration samples were collected from three species of trees, poplar (*Populus* spp.), Russian olive (*Elaeagnus angustifolia*), and willow (*Salix* spp.), at three different locations (nine total trees), two within the TCE-contaminated groundwater plume (seep and canal locations) and one outside (control location). The sample locations are illustrated in Figure 18-2. The age of the trees sampled in the seep location ranged from about 15 [willow

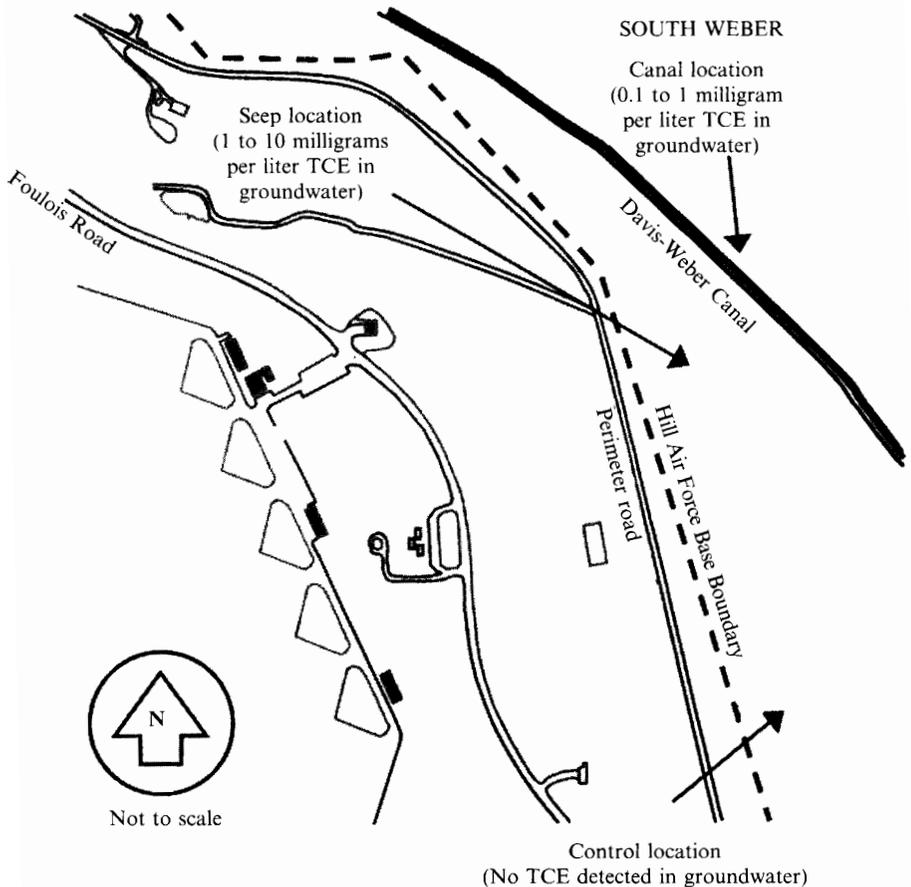


Figure 18-2 Plant sampling locations at Hill Air Force Base, Utah, Operable Unit 2.

(*Salix* spp.)] to 30 [poplars (*Populus* spp.)] years based on ring counts. The heights of these trees ranged from 13.4 meters [(44 feet, poplar (*Populus* spp.)] [to 3 meters [(10 feet, willow (*Salix* spp.)]. The two locations within the plume were chosen mainly because of the depth to groundwater, groundwater TCE concentrations, and availability of mature trees. In the first location within the plume, the trees were growing in an area of seasonal groundwater seeps and at the time of sampling, the depth to groundwater was about 2.3 meters (7.5 feet, seep location). Sampling in the previous years had indicated that TCE concentrations in groundwater at this site ranged from 1 to 10 milligrams per liter. The second location within the plume was about 30 meters (100 feet) downgradient from the first location, just below a concrete-lined irrigation canal (canal location). Historically, groundwater TCE concentrations below the canal location have been about a factor of 10 lower than at the seep location. Some leakage of irrigation water from the canal into the shallow aquifer has been documented and contributes to the seasonal variability in groundwater TCE concentrations at the canal location. The control location was about 100 meters (330 feet) south of the seep location in an area where no TCE has been detected in the groundwater.

### Plant Sample Collection

Because of the differences in physical-chemical properties, separate collection and extraction procedures were used for the volatile TCE and the three semi-volatile chlorinated metabolites (TCET, TCAA, and DCAA). In addition, slightly different sample collection and analysis procedures for TCE were used at the CCAS and Hill AFB sites. At CCAS, methanol extracts of the plant tissue were analyzed for TCE using purge and trap gas chromatography with an electron-capture detector. However, because of problems associated with excessive foaming during purging (mainly leaves and roots), a headspace gas chromatography method was subsequently used to determine TCE in plant tissue collected from Hill AFB.

### Trichloroethylene Samples at Cape Canaveral Air Station

Leaf samples (2 to 5 grams fresh mass) were removed from the branches by gloved hand and placed directly in pre-weighed 40 milliliter glass vials equipped with Teflon<sup>®</sup>-lined rubber septa. After the plant tissue samples were added to the vials, the vials were weighed again to determine the amount of plant tissue collected and then filled with purge-and-trap-grade methanol, to minimize volatilization losses during transport and to serve as the extraction solvent. The vials were again weighed to determine the amount of methanol added, capped, and shipped at  $4 \pm 2^\circ\text{C}$  for analysis. Stem tissue samples were collected from the live oaks (*Quercus* spp.) by drilling a 6-millimeter (0.25-inch) hole directly into the stem, and directing the shaving into the pre-weighed vials using a funnel. For the plants that were not woody [(saw palmetto (*Serenoa repens*) and castor bean (*Ricinus communis*)], stem tissue was cut into small

sections with stainless steel pruning shears and placed directly into the pre-weighed vials as described for the leaf samples. Roots samples were collected in a similar manner after digging a small pit at the base of each plant.

### ***Trichloroethylene Samples at Hill Air Force Base***

Leaf samples were collected in the same manner as previously described for the CCAS site, except that the pre-weighed vials contained 20 milliliters of a saturated sodium chloride solution acidified to pH 2 with phosphoric acid. This was done to facilitate the gas chromatographic analysis of the headspace following the procedure outlined in the U.S. Environmental Protection Agency SW-846 Method 5021 ([http://www.epa.gov/epaoswer/hazwaste/test/5\\_series.htm](http://www.epa.gov/epaoswer/hazwaste/test/5_series.htm)) for soils. After samples were added, the vials were weighed again to determine the amount of plant tissue collected. The vials were capped and put on ice until analysis. Stem core samples, taken using a 12-millimeter (0.5-inch) increment borer (Forestry Suppliers, Inc.), were also placed directly into vials containing the acidified sodium chloride solution. Stem core samples were used at Hill AFB instead of drill shavings after it was determined through side-by-side sample collection and analysis that the core samples consistently yielded higher results by a factor of two (Lewis 2002). Root samples were to be collected only from trees in the seep location after being pulled from the ground as part of the “seep collection system improvement” process. However, only large woody roots, close to the tree trunks, were available for sampling because the fine roots were lost during the tree-removal process. Because these roots were not representative of the entire root structure, these samples were not analyzed.

### **Metabolite Samples**

Samples of plant tissue (10 to 30 grams fresh mass) were collected for extraction and analysis of TCET, TCAA, and DCAA. Tissue samples were placed directly in pre-weighed wide-mouth glass vials equipped with Teflon<sup>®</sup>-lined lids. After the plant-tissue samples were added, the vials were reweighed, capped, and shipped at  $4 \pm 2$  °C for analysis.

### **Plant Tissue Extraction and Analysis Methods**

#### ***Trichloroethylene at Cape Canaveral Air Station: Purge and Trap***

Plant samples from CCAS were analyzed for TCE using a purge-and-trap gas chromatographic method adapted from U.S. Environmental Protection Agency SW-846 Methods 5030 and 8010B (1996). Upon arrival at the laboratory, the vials containing the plant samples and methanol were agitated for 24 hours in a rotary tumbler. A 250-microliter aliquot of the methanol extract was removed from the sealed vial with a syringe, introduced into a purge vessel, and diluted with 20 milliliters of deionized water. The water-methanol

mixture was then purged with nitrogen for 12 minutes at 50 milliliters per minute and the TCE was concentrated on a Tenax trap. After a 20-second dry purge with nitrogen, the trap was thermally desorbed using a Dynatherm<sup>®</sup> desorber interfaced with a Shimadzu<sup>®</sup> GC14A gas chromatograph equipped with a 75 meter by 0.45 millimeter DB-VRX (2.5 micrometer film thickness) capillary column (J&W Scientific, Folsom, California) and electron capture detector. Column flow was 8 milliliters per minute of nitrogen and the column oven temperature was 50 °C isothermal. At these conditions, the retention time for TCE was 8.8 minutes. The column was periodically baked out at 240 °C between samples, if baseline drift was observed. The electron capture detector and injection port temperatures were set at 300 and 210 °C, respectively.

#### ***Trichloroethylene at Hill Air Force Base: Headspace***

A headspace gas chromatographic method was used to determine TCE concentrations in the plant-tissue samples collected at Hill AFB. The headspace vials containing the plant tissue and modifier mixture were agitated for 24 hours in a rotary tumbler at 20 °C prior to analysis. This was followed by 12 hours of equilibration in a 40 °C water bath. A 10-microliter aliquot of the headspace was removed through the septa with a syringe and manually injected into a Shimadzu<sup>®</sup> GC14 gas chromatograph equipped with an electron capture detector and a 75 meter by 0.45 millimeter DB-VRX (2.5-micrometer film thickness) capillary column (J&W Scientific, Folsom, California). Column flow was 8 milliliters per minute of nitrogen and the column temperature was 90 °C isothermal. The detector and injection port temperatures were 300 and 210 °C, respectively.

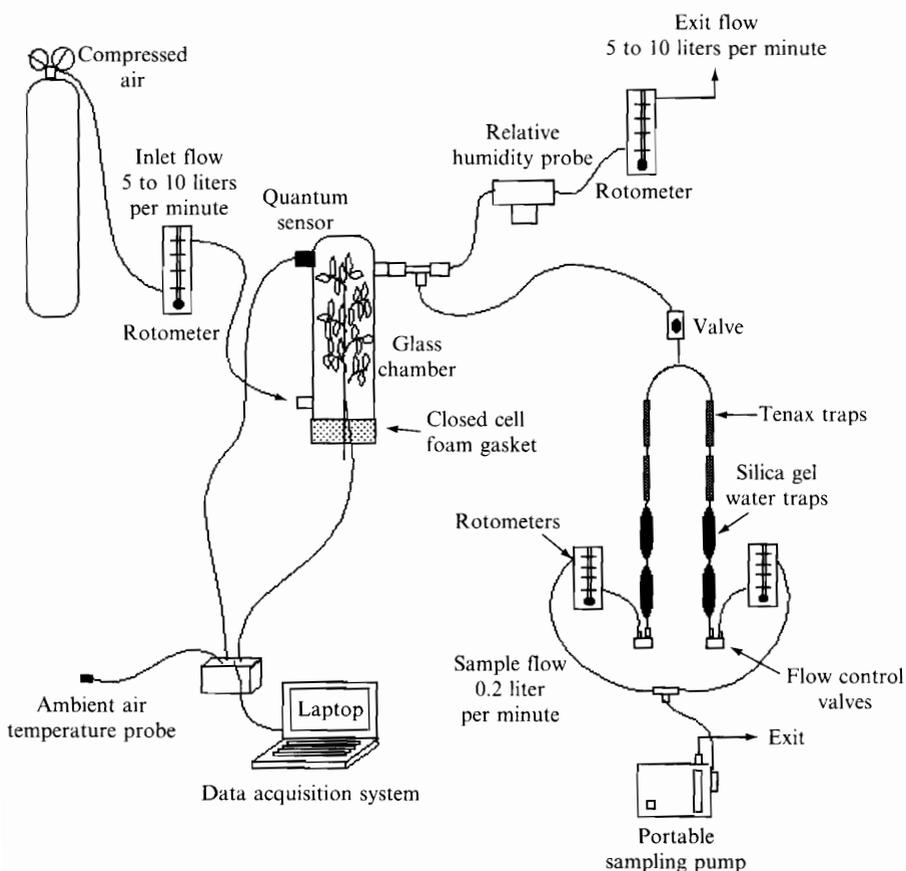
#### ***Trichloroethylene Metabolites***

Leaf-tissue samples were flash frozen in liquid nitrogen and macerated in a mortar. The "woody" tissues (stems and roots) were macerated using a coffee grinder. Approximately 5 grams of "processed" tissue were weighed into 60 milliliter Teflon<sup>®</sup> centrifuge tubes and combined with 15 milliliters of a 0.25 normal sodium hydroxide solution. The centrifuge tubes were shaken for 10 minutes on a reciprocating shaker and then centrifuged for 10 minutes at 9750 revolutions per minute. The supernatant was transferred from the Teflon<sup>®</sup> centrifuge tube to a glass centrifuge tube. This extraction procedure was performed a total of three times, each time combining the supernatant into the same glass centrifuge tube. The combined aqueous extracts were acidified to pH 1 with 50 percent sulfuric acid and, subsequently, extracted three additional times with 7 milliliters of methyl *tertiary*-butyl ether by shaking for 5 minutes followed by centrifugation for 5 minutes at 500 revolutions per minute. The supernatants from the triplicate methyl *tertiary*-butyl ether extractions were combined and brought to exactly 25 milliliters. The extract was dried over 2 grams of anhydrous sodium sulfate. A 2-milliliter

aliquot of the dried extract was derivatized with diazomethane and analyzed by gas chromatography with electron capture detection using the same instrument and operational conditions as previously described for TCE. With these conditions, the retention times were 4 minutes for TCEt, 5.2 minutes for TCAA, and 4.4 minutes for DCAA. The column was periodically baked out at 240 °C between samples, if baseline drift was observed.

### Plant-Transpiration Samples

Gas samples were collected to determine the potential flux of TCE from leaves to the atmosphere using the portable flow-through sampling apparatus illustrated in Figure 18-3. A glass chamber was placed over a representative section of each tree and sealed on the open end with closed-cell foam, latex silicon sealant, and electrical tape to produce a flexible yet tight seal around the stem and chamber. The chambers were fixed in the same location during



**Figure 18-3** Schematic of chamber system used to collect TCE in transpiration gases.

replicate sample collection. Compressed breathing air containing 300 to 400 parts per million by volume of carbon dioxide (to maintain natural stomatal response) was used to purge the chambers of TCE and water vapor. The resulting slightly positive chamber pressure minimized the potential introduction of any TCE that might be in the ambient air surrounding the chamber (*i.e.*, TCE volatilizing directly from the soil surface). Using cylinders of compressed air also served to minimize external power requirements. However, because of the difficulties encountered in obtaining commercial cylinders of compressed air that were free of TCE during the sampling at CCAS, we filled our own small containers (20 liters at 120 pounds per square inch or 0.83 megapascal) using a laboratory compressor when sampling at Hill AFB. Each cylinder could then be easily checked for TCE contamination prior to use in the field and refilled if necessary.

All tubing and connections attached to the chamber were constructed of stainless steel to minimize sorption of TCE. Typically, samples were collected at 15- to 30-minute intervals at 100 to 200 milliliters per minute using portable sampling pumps. Portable sampling pumps were used to subsample the air leaving the chamber. Subsampling was necessary because relatively high flow rates (6 to 10 milliliters per minute) were used to minimize humidity increases within the chamber and to prevent the condensation of transpired water on the interior walls of the chamber. Tenax was used as the sorbent for the TCE traps because of 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 collected (calculated from the flow rate through the Tenax trap and the sampling time), based on preliminary modeling and reported breakthrough volumes, ranged from 3 to 6 liters. After sampling, Tenax traps were sealed with stainless steel caps, placed in bubble-pack envelopes, and shipped to the laboratory at Utah State University for analysis. Samples were shipped at ambient temperature to prevent moisture from condensing in the traps.

A minimum of three replicate samples were collected from each of the three plant species within the plume area at both sites. Samples were also collected from the control plants outside the plume area. Chamber blanks and ambient air samples were collected at each sample location.

The sampling manifold was designed to simultaneously collect duplicate trap samples (with breakthrough traps) during each sampling period. Samples were analyzed by gas chromatography with electron capture or mass spectrometry detection. The electron capture detection was about 10 to 50 times more sensitive than mass spectrometry, but more susceptible to misidentification and quantification of coeluting chromatographic peaks that could not be separated.

For gas chromatography with electron capture detection analysis, trap samples were introduced into a Shimadzu<sup>®</sup> GC14 gas chromatograph equipped with electron capture detector and capillary column (J&W Scientific DBVRX, 2.5 micrometer film thickness, 0.45 millimeter inside diameter by 75

meter length) using an Environchem<sup>®</sup> Model 710 thermal desorber. For gas chromatography with mass spectrometer analysis, a Tekmar<sup>®</sup> 6000 thermal desorber was used to desorb Tenax traps directly to a Hewlett-Packard<sup>®</sup> 6890 gas chromatograph, equipped with a 5973 mass spectrometer and capillary column (Hewlett-Packard<sup>®</sup> HP-624, 30 meter length by 0.25 millimeter inside diameter by 1.4 micrometer film thickness). An external standard approach was used to quantify the mass of TCE collected in each trap.

Water transpiration rates were determined with a portable balance by measuring the mass of condensed water that collected in the silica traps. Traps were weighed prior to and after being connected to the sample effluent stream. The weight of the water collected and the volume of effluent passing through the trap were used to calculate the transpiration rate. Transpiration measurements were used to determine the ratio of TCE to water transpired. This ratio, coupled with seasonal evapotranspiration rates, can be used to estimate the impact of vegetation on the flux of TCE to the atmosphere. Transpiration rates also indicate whether normal metabolic function is occurring.

Prior to going to the field, and between each sampling event, the interior chamber surfaces were rinsed with methanol. To evaluate potential sorption onto the chamber, several chamber rinses were analyzed for TCE.

### Additional Samples

At CCAS, soil cores were obtained near each plant species to determine the root length and area density within the unsaturated soil column. This was not done at Hill AFB due to logistical problems. Groundwater samples were collected and analyzed for TCE and the metabolites previously mentioned. Surface flux measurements were also collected near each plant to quantify the amount of TCE volatilizing directly from the groundwater and soil surface.

## RESULTS AND DISCUSSION

Direct pathways are uptake and metabolism, uptake and phytovolatilization, and uptake and accumulation. Trees may also impact the fate of TCE indirectly through enhanced rhizosphere degradation and by changing the subsurface environment through the removal of groundwater *via* transpiration. The sampling approach followed in this study was specifically designed to determine only if the direct pathways were occurring to a measurable extent.

### Exposure of Vegetation to Trichloroethylene

High annual precipitation (127 centimeters per year or 50 inches per year, Mallander 1990) and shallow root distributions (70 percent in the top 60

centimeters or 2 feet, 90 percent in the top 120 centimeters or 4 feet) at the CCAS site (Doucette *et al.* 1998, Hayhurst 1998) suggest that groundwater use by existing vegetation is much less than that obtained by precipitation. This would reduce the exposure of the vegetation to TCE at this site. However, at Hill AFB, minimal precipitation during the growing season, lack of surface irrigation, and shallow groundwater (approximately 2.3 meters or 7.5 feet below ground surface) suggest that trees obtain a substantial portion of water needs from the contaminated groundwater. The expected high use of groundwater at Hill AFB should increase TCE uptake relative to CCAS. Root distribution was not examined at the Hill AFB OU2 site because cores could not be collected prior to tree removal. The fraction of groundwater used by mature trees is difficult to directly measure in a field setting, and measurement was not attempted at these sites. Stable isotope measurements (Dawson 1996) could be used to obtain this information if similar studies are performed in the future.

Roots may also be exposed to vapor phase TCE. While this pathway was not directly evaluated, measurable levels of TCE found in soil gas and surface flux samples suggest that this exposure route could be important and should be evaluated in future studies.

### Groundwater Concentrations of Trichloroethylene

During the first sampling event at CCAS, groundwater-monitoring points were installed near each of the three test plants within the plume and near the live oak located east of the known extent of the TCE plume. Groundwater samples were collected for the analysis of TCE, DCAA, TCAA, and TCET. Samples for TCE were analyzed using a purge-and-trap gas chromatography with mass spectrometry method as outlined in SW-846 Method 8260A (U.S. EPA 1996). For TCE metabolites, groundwater samples were acidified to a pH less than 1, extracted with methyl *tertiary*-butyl ether, derivatized with diazomethane and analyzed by gas chromatography with electron capture detection. Results from the groundwater sampling showed that the TCE concentrations varied spatially throughout the test area. The lowest concentration of TCE in groundwater was found near the live oak (*Quercus virginiana*) at an average of  $0.5 \pm 0.09$  milligrams per liter (plus or minus one standard deviation) while the highest concentrations were found near the saw palmetto (*Serenoa repens*) ( $65 \pm 26$  milligrams per liter). By-products of reductive dechlorination, such as 1,1-dichloroethene (less than 1.1 to 1200 micrograms per liter), *cis*-1,2-dichloroethene (65 to 4800 micrograms per liter), *trans*-1,2-dichloroethene (less than 1.65 to 110 micrograms per liter), and vinyl chloride (less than 2 to 456 micrograms per liter), were also identified in the groundwater. Trichloroacetic acid (6 micrograms per liter) and TCET (2 micrograms per liter) were also found at two separate monitoring points. However, TCET was not found in the duplicate samples. Thus, the possibility

of microbial degradation of TCE to the target metabolites in the groundwater is unlikely, but cannot be ruled out.

At Hill AFB, groundwater samples were collected from six different multiple level monitoring wells at the seep location, 3 weeks prior to the tree sampling. The samples were analyzed by purge-and-trap gas chromatography with an electron capture detector. Trichloroethylene concentrations ranged from 0.3 to 5.9 milligrams per liter within the seep location. No groundwater samples from wells at the canal or control locations were collected during the time that the trees were being sampled. However, historical groundwater data for OU2 indicate the following range of groundwater concentrations of TCE: seep location (1 to 10 milligrams per liter), canal location (0.1 to 1 milligram per liter), and control location (no detectable TCE).

### **Surface Emission Flux at Cape Canaveral Air Station and Hill Air Force Base**

During the first sampling event at CCAS in June, 1997, measurable levels of TCE were found in all surface flux samples collected. However, as previously described, analysis of blanks and controls indicated that the source of TCE was the compressed breathing air used as the sweep gas for the flux measurements. Thus, no significant flux of TCE from the soil surface relative to blanks was observed. A second sampling event was carried out using the cleaner source of compressed air but again no statistical difference between samples and blanks was observed.

Because of the TCE contamination found in compressed breathing air during the CCAS sampling, pre-purified nitrogen was used as the sweep gas for the surface emission flux samples at the Hill AFB OU2 site. At the seep location, volatilization of TCE from the soil surface ranged from 28 to 750 milligrams per square meter per day while fluxes from undetectable to 9 milligrams per square meter per day were measured at the control location. As expected, the surface flux of TCE at the seep location decreased with increasing depth from surface to groundwater. The low levels of TCE found in several of the samples located at the control locations could indicate the presence of TCE contaminated groundwater outside the currently defined area of the plume, or analytical artifacts associated with inadequate Tenax-trap cleaning.

An additional factor to consider when evaluating the surface flux data is that the long-term surface emissions of TCE near plants could lead to the uptake or sorption of TCE vapor by leaves. While it is expected that this transfer would be small, the TCE tissue analysis cannot differentiate between uptake of atmospheric vapor *versus* translocation from the subsurface. However, ambient air samples collected during the sampling events showed no measurable concentrations of TCE.

TABLE 18-1 Maximum Concentrations (Milligrams per Kilogram of Dry Weight) of Trichloroethylene and Associated Metabolites in Plant Tissue Samples Collected at Cape Canaveral Air Station June and September 1997

Species	Tissue (month)	TCE <sup>a</sup>	TCEt <sup>a</sup>	TCAA <sup>a</sup>	DCAA <sup>a</sup>
Castor bean ( <i>Ricinus communis</i> )	Root (June)	0.012 (1/3)	<MDL <sup>b</sup> (0/2)	<MDL (0/2)	<MDL (0/2)
	Stem (June)	<MDL (0/3)	<MDL (0/2)	0.207 (2/2)	<MDL (0/2)
	Stem (September)	NA <sup>c</sup>	0.054 (1/1)	<MDL (0/1)	2.57 (1/1)
Saw palmetto ( <i>Serenoa repens</i> )	Leaf (June)	<MDL (0/3)	0.262 (2/2)	1.11 (2/2)	<MDL(0/2)
	Leaf (September)	NA	0.069 (1/2)	0.14 (2/2)	3.63 (2/2)
	Root (June)	0.048 (2/2)	<MDL (0/2)	0.131 (2/2)	<MDL (0/2)
	Stem (June)	0.002 (1/3)	<MDL (0/2)	0.394 (2/2)	<MDL (0/2)
	Stem (September)	NA	0.026 (1/1)	<MDL (0/1)	<MDL (0/1)
Live oak ( <i>Quercus virginiana</i> ): plume	Leaf (June)	<MDL (0/3)	0.086 (1/2)	0.125 (2/2)	<MDL (0/2)
	Leaf (September)	NA	<MDL (0/1)	<MDL (0/2)	0.48 (2/2)
	Root (June)	<MDL (0/2)	<MDL (0/2)	0.086 (2/2)	0.275 (2/2)
	Stem (June)	0.002 (2/3)	<MDL (0/2)	0.036 (1/2)	<MDL (0/2)
	Stem (September)	NA	0.058 (1/1)	<MDL (0/1)	0.602 (1/1)
	Leaf (June)	<MDL (0/3)	0.273 (4/6)	0.189 (3/3)	0.723 (1/3)
Live oak ( <i>Quercus virginiana</i> ): outside plume	Leaf (September)	NA	0.092 (1/1)	<MDL (0/1)	1.76 (1/1)
	Root (June)	<MDL (0/3)	<MDL (0/2)	0.063 (1/2)	<MDL (0/2)
	Stem (June)	<MDL (0/3)	<MDL(0/3)	0.038 (2/3)	<MDL (0/3)
	Stem (September)	NA	0.098 (1/1)	<MDL (0/1)	0.602 (1/1)
Live oak ( <i>Quercus virginiana</i> ): control, Orlando, Florida	Leaf (June)	<MDL (0/3)	0.295 (3/5)	0.132 (3/3)	<MDL (0/3)
	Leaf (September)	NA	<MDL (0/1)	0.399 (1/1)	1.17 (1/1)
	Leaf (September)	<MDL (0/1)	<MDL (0/1)	<MDL (0/1)	<MDL (0/1)

<sup>a</sup>Maximum concentration detected in dried tissue (number of samples greater than MDL<sup>b</sup> per total number of samples).

<sup>b</sup>MDL, Method detection limit for TCE = 0.0005 milligram per kilogram, TCEt = 0.02 milligram per kilogram, TCAA = 0.03 milligram per kilogram, and DCAA = 0.15 milligram per kilogram.

<sup>c</sup>Abbreviation used—NA: not available; (sample was either not collected or could not be analyzed).

## Trichloroethylene and Metabolite Concentrations in Plant Tissue

### *Cape Canaveral Air Station*

The results of the analysis of the plant tissue samples collected at CCAS in June and September 1997 are summarized in Table 18-1. Trichloroethylene, TCEt, TCAA, or DCAA were identified in all plant tissue types (root, stem, and leaf) and in all three species, including the on-site live oak (*Quercus virginiana*) believed to be outside the plume area. The highest concentrations of TCE (0.098 milligram per kilogram dry weight) were found in the trunk of the live oak (*Quercus virginiana*) that seemed to be outside the plume, while the highest concentrations of the metabolites (DCAA at 0.363 milligram per kilogram dry weight) were found in the leaf samples collected in September.

Detection of TCE and TCE metabolites in the live oak (*Quercus virginiana*) thought to be outside the plume area suggests exposure to TCE or an analytical problem. To further examine this finding, leaf samples were collected on July 21, 1997, from the two previously sampled on-site live oaks (*Quercus virginiana*) and a third live oak (*Quercus virginiana*) located off-site in Orlando, Florida. The off-site control showed no measurable levels of either TCE or the associated metabolites, while measurable levels of TCAA were found in most tissues of both of the on-site live oaks (*Quercus virginiana*) (0.036 to 0.399 milligram per kilogram dry weight). As previously suggested, accumulation of TCAA in the leaf tissue may be the result of previous exposure to TCE-contaminated groundwater, as live oak (*Quercus virginiana*) trees typically retain leaves for two growing seasons. No information is available regarding the stability of TCAA in leaf tissue, but some contaminants are stored in the vacuoles of the leaf. Another potential pathway that could account for the appearance of TCAA in the leaves is through the uptake and transformation of vapor phase TCE (Nzengung and Jeffers 2001) fluxing from the soil. However, as previously mentioned, ambient air samples collected at the site showed no detectable TCE and this pathway is unlikely to be important in most field situations.

### *Hill Air Force Base*

At the Hill AFB OU2 site, the TCE concentrations ranged from 0.15 to 8.1 milligrams per kilogram on a dry weight basis in tissues from trees growing above the contaminant plume (Table 18-2). No TCE or metabolites were found in tissues from trees growing in the control location. Concentrations in the stems were an order of magnitude greater than that found in the leaves, and the poplar (*Populus* spp.) and willow (*Salix* spp.) trees had two to four times greater TCE concentration than the Russian olive (*Elaeagnaceae angustifolia*). Stem TCE concentrations correlated with the concentration of TCE in the groundwater below (*i.e.*, the higher the groundwater concentration the higher the stem core concentration).

**TABLE 18-2 Average TCE and Metabolite Concentrations in Leaf and Stem Tissue of Poplar (*Populus* spp.), Russian Olive (*Elaeagnaceae angustifolia*), and Willow (*Salix* spp.) Collected at Hill Air Force Base Operating Unit 2 Seep and Control Locations, September 1999**

Location	Tree species	Tissue	Milligrams per kilogram of dry weight			
			TCE <sup>a</sup>	TCET <sup>a</sup>	TCAA <sup>a</sup>	DCAA <sup>a</sup>
Seep	Poplar ( <i>Populus</i> spp.)	Leaves	0.364 ± 0.12	0.741 ± 0.35	0.0180 ± 0.011	MDL <sup>b</sup>
		Stem	8.14 ± 5.8	MDL	MDL	MDL
Control	Poplar ( <i>Populus</i> spp.)	Leaves	MDL	MDL	MDL	MDL
		Stem	MDL	MDL	MDL	MDL
Seep	Russian olive ( <i>Elaeagnaceae angustifolia</i> )	Leaves	0.151 ± 0.05	MDL	0.390 ± 0.15	MDL
		Stem	1.94 ± 1.1	MDL	MDL	MDL
Control	Russian olive ( <i>Elaeagnaceae angustifolia</i> )	Leaves	MDL	MDL	MDL	MDL
		Stem	MDL	MDL	MDL	MDL
Seep	Willow ( <i>Salix</i> spp.)	Leaves	0.339 ± 0.33	MDL	MDL	MDL
		Stem	5.11 ± 3.4	MDL	MDL	MDL
Control	Willow ( <i>Salix</i> spp.)	Leaves	MDL	MDL	MDL	MDL
		Stem	MDL	MDL	MDL	MDL

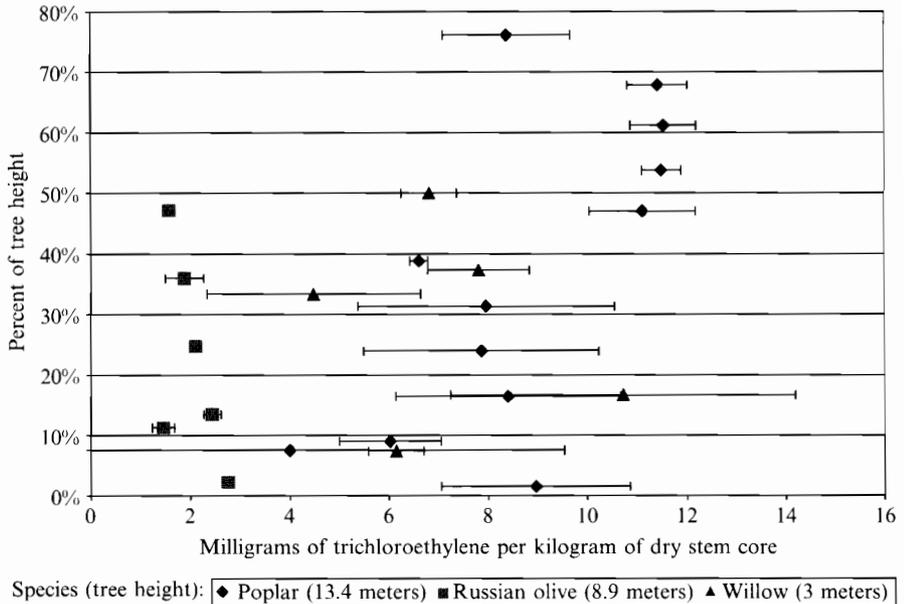
<sup>a</sup>Average ± standard deviation of at least three replicate samples.

<sup>b</sup>MDL: method detection limits for TCE = 0.02 milligram per kilogram, TCET = 0.05 milligram per kilogram, TCAA = 0.01 milligram per kilogram, and DCAA = 0.1 milligram per kilogram.

Metabolite concentrations in leaves ranged from below method-detection limits to 0.74 milligram per kilogram on a dry weight basis. No obvious trends were observed with regard to species or tissue type. The most prevalent metabolite was TCET whereas DCAA was least prevalent. It is interesting to note, however, that metabolite concentrations found in the leaves collected from the seep and canal locations at Hill AFB were similar to those observed at CCAS (Doucette *et al.* 1998, Hayhurst 1998). This is despite the plant tissue concentration of TCE being significantly higher at Hill AFB. The reason for this is unclear.

### Distribution of Trichloroethylene in Tree Stems at Hill Air Force Base Operable Unit 2

Vroblesky *et al.* (1999) reported that stem core concentrations of TCE decreased with increasing height for a single, bald cypress (*Taxodium distichum* L. Rich) tree sampled at the Department of Energy Savannah River Site in South Carolina. Those authors speculated that the decreasing concentration with increasing height might be due to the volatilization of TCE through the bark, transformation within the tree, or sorption to the plant tissues. At the OU2 seep location, the Russian olive (*Elaeagnaceae angustifolia*) appeared to follow a similar, but less pronounced trend, whereas the poplar (*Populus* spp.)



**Figure 18-4** Vertical distribution of trichloroethylene in three tree species [poplar (*Populus* spp.), Russian Olive (*Elaeagnaceae angustifolia*), and willow (*Salix* spp.)] at the seep location.

and willow (*Salix* spp.) trees showed no significant reduction in TCE concentration with an increase in height (Figure 18-4). In an ongoing project at another Hill AFB site, we monitored tree core concentrations of TCE in several cottonwood (*Populus deltoides*) and poplar (*Populus* spp.) trees, every month for a year. Concentrations measured in the winter months were relatively constant and only slightly less than those measured in the fall, suggesting that volatilization of TCE through the bark of a mature tree is probably not a significant loss mechanism at the Hill AFB site (Lewis 2002). The observation of uniform concentrations of TCE vertically within the trees at Hill AFB may indicate that rates of TCE uptake, sorption, and transformation have reached steady state.

### Results of Transpiration Gas Sampling

At CCAS, no statistical difference between transpiration gas samples and apparatus blanks was found during both the June and September sampling events. However, at the Hill AFB OU2 site, significant differences between samples and apparatus blanks were observed for the seep and canal locations. Trichloroethylene was also found in some of the transpiration samples collected from the control trees, but at levels that were not significantly different from the apparatus blanks, and 10 to 100 times less than samples at the seep and

**TABLE 18-3 Summary of Transpiration Data Collected from Three Tree Species at Hill Air Force Base, Operable Unit 2**

	Poplar ( <i>Populus</i> spp.)			Russian olive ( <i>Elaeagnaceae angustifolia</i> )			Willow ( <i>Salix</i> spp.)		
	Seep	Canal	Control	Seep	Canal	Control	Seep	Canal	Control
	Number of samples	6	1	4	10	2	3	5	1
TCE trapped (nanograms)	105	54.8	MDL <sup>a</sup>	24.0	16.0	8.00	68.7	12.5	4.71
Total flow (liters per minute)	3.0	3.8	3.2	4.0	3.3	4.7	3.0	6.0	4.0
Subsample flow (liters per minute)	0.133	0.130	0.145	0.148	0.130	0.130	0.142	0.130	0.130
Sampling time (minute)	21	30	19	18	30	15	19	30	15
Water measured (grams)	0.057	0.150	0.110	0.086	0.205	0.100	0.110	0.080	0.047
TSC (milligrams of TCE per liter of transpired water) <sup>b</sup>	2.20	0.365	MDL	0.346	0.0803	0.0779	0.793	0.156	0.133

<sup>a</sup>MDL: method detection limit (1 nanogram of TCE on a trap).

<sup>b</sup>Water condensation in chamber during sampling may have caused transpiration stream concentrations (TSC) to be overestimated by a factor of 5.

canal locations. Table 18-3 summarizes the results of transpiration sampling at Hill AFB OU2, including the mass of TCE and water collected in each sampling, sampling rates, and transpiration stream concentrations (TSCs) for TCE. The TSC is the ratio of mass of TCE collected on the Tenax trap to the mass (or volume, 1 kilogram is 1 liter) of water collected on the desiccant. The TSCs are used for extrapolation of the mass flux of TCE *via* transpiration.

### Trichloroethylene Transpired

The TSC values in Table 18-3 indicate the concentration of TCE transpired by the leaves in the sampling chambers at the seep and canal locations. The TSC values can be multiplied by a transpiration rate for the whole tree to predict the amount of TCE being phytovolatilized by each tree. This assumes that the TSCs are representative of all the leaves on the tree and are independent of the transpiration rate and the concentration of TCE in the groundwater.

One important consideration in obtaining accurate TSC values using a flow-through chamber is to maintain sufficient airflow through the chamber to prevent condensation of the transpired water. If water condenses in the chamber, the water flux will decrease, but the TCE flux will not be impacted, at least initially. Thus, water condensing in the chamber during the phytovolatilization measurements could result in TSC values that overestimate the ratio of TCE to water. It is important to note that some water vapor condensed in the chambers during these measurements even at flow rates of 3 to 6 liters per minute through the chamber. Subsequent field experiments performed at another Hill AFB site, show that water condensation could result in an overestimate of the TSC by as much as a factor of five (Zaugg *et al.* 2001). This potential overestimation should be considered when trying to estimate whole-tree TCE efflux from the data in Table 18-3. To prevent condensation in current measurements, we have shifted to smaller chambers and slightly higher flow rates.

### Scaling Transpiration and Trichloroethylene Efflux from Chambers to Entire Trees: Hill Air Force Base Example

The efflux of volatile compounds from whole trees is best extrapolated spatially and temporally from the ratio of TCE to water efflux as measured in the small chambers. This scaling requires the following:

1. The ratio of TCE to transpired water is the same in all leaves of the tree
2. The TCE is uniformly distributed within the root-zone
3. An estimate of the total transpiration rate of the tree

With access to ample water, and no competition from other trees, the daily transpiration rate of the largest trees in the seep location could be as high as 200 liters per day (Wullschlegel *et al.* 1998). Using the highest measured TSC

(2.2 milligrams per liter) from Table 18-3, each large tree would be capable of transpiring 440 milligrams of TCE per day. Over a 120-day growing season, each tree would transpire 53 grams of TCE. A more realistic estimate of transpiration for a typical tree in this location is about 40 liters per day. Similarly, because of the condensation problem associated with the chamber sampling, the highest TSC value in Table 18-3 is probably high by a factor of nearly five. Thus, using more realistic estimates of TSC (0.44 milligram per liter) and transpiration rate (40 liters per day), the phytovolatilization removal rate would be about 2 milligrams of TCE each year per tree. Principles of scaling are discussed in more detail at ([www.usu.edu/cpl](http://www.usu.edu/cpl)).

Another removal mechanism for TCE is through leaf drop in the fall. However, the amount associated with leaf drop appears to be much less than removed by phytovolatilization. If the total TCE and TCE metabolite contaminant concentration in the leaf tissue is 1 to 2 milligrams per kilogram of dry tissue weight, and if the leaf production rate is 0.2 milligram per kilogram of dry tissue weight per year, the TCE removal rate would be 0.2 to 0.4 milligrams per square meter of ground area per year. Even using the low estimate for phytovolatilization (2 grams per tree per year), this is only 10 to 20 percent of the amount removed in phytovolatilization.

## CONCLUSIONS

1. The identification of TCE, TCeT, TCAA, and DCAA in plants growing on TCE-contaminated groundwater at both sites establishes that the plant uptake and metabolism of TCE occurred in all the species sampled.
2. The concentrations of TCE in plant tissue were 10 to 100 times higher at Hill AFB than at CCAS, even though the groundwater concentrations below the vegetation were similar. We attributed the higher plant tissue TCE concentrations at Hill AFB to the higher fraction of contaminated groundwater used by the vegetation. This suggests that plants will have a greater impact on TCE attenuation at sites with lower rainfall during the growing season.
3. Trichloroethylene was found in transpiration gas samples collected from several trees located at the Hill AFB OU2 seep and canal locations, but no phytovolatilization was observed from any plants at the CCAS site. Estimates of TCE phytovolatilization by whole trees at Hill AFB range from 2 to 53 grams per tree per year.
4. The uniform vertical distribution of TCE in the trees, the presence of TCE in the transpiration gas, and the rough correlation with transpired water show that TCE is translocated through the trees. This suggests that uptake, sorption, and transformation within the tree are at steady state at this site. A steady state condition may be a requirement for significant phytovolatilization.

5. The significance of indigenous plants relative to other TCE-attenuation mechanisms was not specifically evaluated in this study. Additional studies addressing this issue are in progress.

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