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User's Guide to the Collection and Analysis of Tree Cores to Assess the Distribution of Subsurface Volatile Organic Compounds

Scientific Investigations Report 2008–5088

U.S. Department of the Interior
U.S. Geological Survey

Cover. **U.S. Geological Survey hydrologist using an increment borer to obtain a tree core** *(digitally modified photograph taken by Allison Vroblesky).*

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U.S. Geological Survey
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Conversion Factors and Datums

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square foot (ft^2)	0.09290	square meter (m^2)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
cubic inch (in^3)	16.39	cubic centimeter (cm^3)
cubic yard (yd^3)	0.7646	cubic meter (m^3)
	Flow rate	
foot per day (ft/d)	0.3048	meter per day (m/d)
foot per year (ft/yr)	0.3048	meter per year (m/yr)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
gallon per day (gal/d)	0.003785	cubic meter per day (m^3/d)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
	Hydraulic gradient	
foot per mile (ft/mi)	0.1894	meter per kilometer (m/km)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C=(°F-32)/1.8$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Abbreviations used in this report

BTEX	benzene, toluene, ethylbenzene, and xylene
*c*DCE	*cis*-1,2-dichloroethene
cm/yr	centimeter per year
DNAPL	dense non-aqueous phase liquid
ECD	electron-capture detector
GC	gas chromatograph
GC/MS	gas chromatograph/mass spectrometry
g/L	gram per liter
HSA	headspace analysis
kg	kilogram
K_{ow}	octanol-water partition coefficient
K_{wood}	equilibrium distribution of compounds between tree tissue and water
L/d	liter per day
$L/m^2/yr$	liter per square meter per year
mg/g	milligram per gram
mL	milliliter
mph	miles per hour
MTBE	methyl *tert*-butyl ether
OSWER	Office of Solid Waste and Emergency Response
OU	operable unit
PCA	1,1,2,2-tetrachloroethane
PCE	tetrachloroethene
PID	photoionization detection
ppbv	parts per billion by volume
ppmv	parts per million by volume
PRG	preliminary remediation goal
PT	purge-and-trap analysis
PVC	polyvinyl chloride
RCF	root concentration factor
SWMU	Solid Waste Management Unit
TCA	1,1,1-trichloroethane
TCE	trichloroethene
TMB	trimethylbenzene
TSCF	transpiration stream concentration factor
µg-h/kg	microgram in headspace per kilogram of wet core
µg/kg	microgram per kilogram
µg/L	microgram per liter
µL	microliter
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VC	vinyl chloride
VOA	volatile organic analysis
VOC	volatile organic compound

Common and scientific names of plants used in this report

Common name	Scientific name	Common name	Scientific name
Alder	*Alnus* sp.	Honeylocust	*Gleditsia* sp.
Apple, pear	*Prunus* sp.	Juniper	*Juniperus* sp.
Ash	*Fraxinus* sp.	Juniper, Ashe	*Juniperus* ashei
Aspen, cottonwood	*Populus* sp.	Larch	*Larix* sp.
Bald cypress	*Taxodium* sp.	Locust	*Robinia* sp.
Beech	*Fagus* sp.	Magnolia	*Magnolia* sp.
Birch	*Betula* sp.	Maple	*Acer* sp.
Blue beech	*Carpinus* sp.	Maple, box elder	*Acer negundo*
Buckeye	*Aesculus* sp.	Mulberry	*Morus* sp.
Cedar	*Thuja* sp.	Oak	*Quercus* sp.
Coffee tree	*Gymnocladus dioicus*	Oak, Texas live	*Quercus fusiformis*
Cottonwood, Eastern	*Populus deltoides*	Oak, White shin	*Quercus sinuata*
Cottonwood, Fremont	*Populus fremontii*	Osage orange	*Maclura pomifera*
Cottonwood, narrow leaf	*Populus angustifolia* James	Paulownia	*Paulownia* sp.
Dogwood	*Cornus* sp.	Pine	*Pinus* sp.
Douglas fir	*Pseudotsuga* sp.	Pine, loblolly	*Pinus taeda*
Elm, American	*Ulmus americana*	Poplar, hybrid	*Populus deltoides* x *Populus trichocarpa*
Elm, Cedar	*Ulmus crassifolia*	Redwood	*Sequoia* sp.
Elm, Chinese	*Ulmus parvifolia*	Rosewood	*Dalbergia sissoo*
Eucalyptus	*Eucalyptus* sp.	Russian olive	*Elaeagnus angustifolia*
False cypress	*Chamaecyparis* sp.	Sassafras	*Sassafras* sp.
Fig, laurel	*Ficus microcarpa*	Spruce	*Picea* sp.
Fir	*Abies* sp.	Sunflower	*Helianthus annuus*
Ginkgo	*Ginkgo* sp.	Sweetgum	*Liquidambar* sp.
Gum	*Nyssa* sp.	Sycamore	*Platanus* sp.
Hackberry, Southern	*Celtis laevigata*	Willow	*Salix* sp.
Hemlock	*Tsuga* sp.	Willow, Goodding's	*Salix gooddingii*
Holly	*Ilex* sp.		

User's Guide to the Collection and Analysis of Tree Cores to Assess the Distribution of Subsurface Volatile Organic Compounds

By Don A. Vroblesky

Abstract

Analysis of the volatile organic compound content of tree cores is an inexpensive, rapid, simple approach to examining the distribution of subsurface volatile organic compound contaminants. The method has been shown to detect several volatile petroleum hydrocarbons and chlorinated aliphatic compounds associated with vapor intrusion and ground-water contamination. Tree cores, which are approximately 3 inches long, are obtained by using an increment borer. The cores are placed in vials and sealed. After a period of equilibration, the cores can be analyzed by headspace analysis gas chromatography. Because the roots are exposed to volatile organic compound contamination in the unsaturated zone or shallow ground water, the volatile organic compound concentrations in the tree cores are an indication of the presence of subsurface volatile organic compound contamination. Thus, tree coring can be used to detect and map subsurface volatile organic compound contamination. For comparison of tree-core data at a particular site, it is important to maintain consistent methods for all aspects of tree-core collection, handling, and analysis. Factors affecting the volatile organic compound concentrations in tree cores include the type of volatile organic compound, the tree species, the rooting depth, ground-water chemistry, the depth to the contaminated horizon, concentration differences around the trunk related to variations in the distribution of subsurface volatile organic compounds, concentration differences with depth of coring related to volatilization loss through the bark and possibly other unknown factors, dilution by rain, seasonal influences, sorption, vapor-exchange rates, and within-tree volatile organic compound degradation.

Introduction

Tree roots absorb water and chemicals from the soil and transport them up the tree trunk. Thus, the chemical content of tree cores can be useful indicators of subsurface contamination (Vroblesky and Yanosky, 1990; Vroblesky and others, 1992, 1999; Yanosky and Vroblesky, 1992, 1995; Yanosky and others, 2001). A variety of volatile organic compounds (VOCs) from subsurface contamination are known to be taken up by plant roots into the trunks of trees. These compounds include benzene, toluene, ethylbenzene, xylene isomers, trimethyl benzene, methyl *tert*-butyl ether (MTBE), 1,1,2,2-tetrachloroethane, trichloroethene (TCE), tetrachloroethene (PCE), 1,1,1-trichloroethane (TCA), vinyl chloride (VC), and *cis*-1,2-dichloroethene (*c*DCE) (Burken, 2001; Burken and Schnoor, 1998; Hirsh and others, 2003; Landmeyer and others, 2000; Newman and others, 1997; Nietch and others, 1999; Trapp and others, 2007; Vroblesky and others, 1999, 2006). The presence of VOCs in tree trunks can allow a reconnaissance-level mapping of the ground-water plume by simple analysis of tree cores (Vroblesky and others, 1999, 2001, 2004). Determining the presence of subsurface VOCs is useful for evaluating the potential ingestion risks to human health from ground water and the potential for respiration risks from vapor intrusion into buildings.

The purpose of this report is to provide a guide to the use of tree coring as a tool to examine subsurface VOCs. To that end, the report is divided into two major parts. The first part of the report presents basic guidelines for a tree-coring investigation to examine subsurface VOCs. The second part of the report examines historical and technical issues related to tree coring as a tool to examine subsurface contamination. The technical considerations include rationale for various aspects of the methodology and a discussion of factors influencing VOC concentrations in tree cores. An understanding of the factors influencing VOC concentrations in tree cores is necessary to better plan field investigations and to understand the meaning of the results of the investigation. In addition, two appendixes are attached. Appendix 1 is a collection of case studies. Appendix 2 is a protocol by the U.S. Environmental Protection Agency (USEPA) for conducting air-sample analysis of VOCs using two different types of gas chromatographs. The analytical method reported in Appendix 2 has been tested only for selected VOCs (listed in Appendix 2). Additional testing would be required to determine the appropriateness of this method for the other VOCs discussed in the report.

Funding for this guide was provided by the USEPA's Office of Solid Waste and Emergency Response (OSWER) through its Measurement and Monitoring Technologies for the 21st Century Initiative *http://clu-in.org/programs/21M2/*. This initiative seeks to identify and disseminate information on promising measurement and monitoring technologies in response to waste management and cleanup needs. Methodologies described in this guide are also fully compatible with USEPA's Triad strategy to manage hazardous waste site decisionmaking uncertainty through systematic planning, dynamic work strategies, and real-time measurement technologies. More information on the Triad approach can be found at *http://www.triadcentral.org/*.

Tree coring to examine subsurface VOCs has several advantages and limitations over more invasive approaches to site investigations, such as well drilling. The advantages and limitations are listed below.

Advantages of Tree Coring as a Tool to Examine Subsurface Volatile Organic Compound Concentrations

1. Tree coring allows examination of unsaturated-zone and ground-water contamination in areas where cultural influences, vegetation cover, or concerns of landowners limit the ability to use more invasive reconnaissance approaches to site characterization using large mechanical equipment.

2. The method is applicable to a variety of VOCs commonly associated with vapor intrusion and ground-water contamination, including chlorinated solvents and petroleum hydrocarbons.

3. The presence of VOCs in tree cores is a strong indicator of subsurface VOC contamination. The relative concentrations of VOCs among tree cores from a particular site often can provide general information on the relative distribution of VOC concentrations in the subsurface.

4. Under some conditions, tree coring can be used to detect VOCs in soil gas (Struckhoff, 2003; Schumacher and others, 2004; Struckhoff and others, 2005b), providing a potentially useful tool for examining soil-vapor concentrations. Thus, tree coring for VOCs may be an effective approach for determining areas that have relatively high vapor-intrusion potential.

5. Tree coring can detect chlorinated solvents at relatively low concentrations. Schumacher and others (2004) determined that analysis of tree-core samples can be used to detect PCE contamination in soils at concentrations of several hundreds of micrograms per kilogram or less and PCE concentrations as low as 8 micrograms per liter (μg/L) in ground water in direct contact with the roots.

6. The method is rapid and uncomplicated. A tree core can be collected in less than 5 minutes. No decontamination of the core barrel is required, other than inspection to ensure that there is no particulate carryover, such as sections of tree core, remaining in the core barrel. The cores can be analyzed by the relatively simple gas chromatography.

7. The samples can be analyzed for preliminary results in the field after equilibrating for 5 minutes or longer or by heating to assist in directing the tree-coring effort, or can be transported back to a laboratory for later analysis.

8. If the samples are to be analyzed within a few days of collection, the cores can be stored without refrigeration.

9. The method is inexpensive. Increment borers can be purchased for a few hundred dollars and can be re-used for years with proper care. By contrast, well sampling is time consuming, and well sampling equipment can cost thousands of dollars. In the time it takes to sample a well, several tree cores can be collected.

10. A minimal amount of field equipment is required. A large number of tree cores can be collected rapidly with an increment borer and sample containers.

11. There is evidence that parts of the aquifer where there is preferential chlorinated-solvent dechlorination sometimes can be delineated by comparing parent/daughter ratios in tree cores (Vroblesky and others, 2004). Areas where the tree-core data indicate a low parent/daughter ratio, such as TCE/*c*DCE, relative to other areas of the site may be locations of enhanced subsurface dechlorination.

12. Because trees collect water from the subsurface over the lateral and vertical extent of their root system, trees provide information over a substantially larger volume than a well or soil sample. Tree coring targets contaminants in shallow horizons, such as the uppermost ground water, the capillary zone, and the unsaturated zone.

Limitations of Tree Coring as a Tool to Examine Subsurface Volatile Organic Compound Concentrations

1. Because there are a number of influences on tree-core VOC concentrations, the absence of VOCs in a tree core cannot be used to definitively show that VOC contamination is not present. It is possible that at the site in question, the tree roots do not extend to the contamination because the tree can obtain adequate water supplies from a source shallower than the contamination, or because the contamination is otherwise inaccessible to the tree.

2. The variety of influences on tree-core VOC concentrations renders it improbable that tree-core VOC

concentrations can be used in a quantitative way to deduce specific subsurface VOC concentrations. Instead, tree-core concentrations reflect the generalized distribution of high and low subsurface VOC concentrations.

3. While the proper collection of several cores from a single large tree typically does not result in lasting damage to the tree, care should be taken to avoid excess coring of individual trees to minimize stress to the tree.

4. Because incorporation of infiltrating rainwater into the transpiration stream can dilute in-tree VOC concentrations, higher tree-core VOC concentrations probably will be obtained if the cores are collected during a relatively dry period rather than immediately after a rain event. Cores collected during the dormant-growth season may contain lower VOC concentrations than cores collected during the summer, although multiple field studies found that the VOC content of tree cores still can be useful indicators of subsurface VOC contamination even during the dormant-growth season (Vroblesky and others, 1999, 2006; Richard Willey, U.S. Environmental Protection Agency, written commun., 2008).

5. When using headspace gas chromatographic analysis of tree cores on a typical field gas chromatograph (GC), a number of tree-related volatile compounds elute at about the same time as VC, potentially complicating identification of that compound.

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Several people outside of the U.S. Geological Survey (USGS) made important contributions to this publication. Richard Willey (USEPA) functioned as project manager and invested many hours in reviews, suggestions, and creative input. Manuscript reviewers from the USEPA included Scott Clifford, Charles Porfert, Anni Loughlin, Kathy Davies, Michael Adam, and Robert Alvey. Judy Canova from the South Carolina Department of Health and Environmental Control also provided review comments. Joel Burken of the University of Missouri-Rolla provided a colleague review of the manuscript. James Landmeyer provided a colleague review within the USGS. The suggestions and comments from these reviewers were invaluable and, in some cases, changed the direction of the manuscript.

Part 1. Methodology for Collection and Analysis of Tree Cores

Tree coring involves collecting a core from a tree and transferring the core to sample vials. The samples can be stored for a few days at room temperature prior to analysis. If longer storage is required, the samples should be refrigerated.

Tree-Core Collection

Tree cores are collected by using a tree-coring tool (fig. 1). The tree-coring tool consists of an increment borer and a core extractor. The core extractor is a component that easily can be misplaced in a forest because of its thin elongated shape. A practical approach is to tie a brightly colored plastic tape or cloth to the extractor (fig. 1).

1. **Choosing a tree-coring tool:** Increment borers are available in various lengths from 4 in. (inches) to 28 in., and in three diameters (0.169, 0.2, and 0.5 in.). Considering that most tree coring for VOCs involves coring to a depth of only about 3 in., increment borers from 8 to 10 in. long allow hands to be far enough from the tree so as not to scrape bark or come into contact with poison ivy vines yet not be so long as to become unwieldy. The smallest borer diameter is commonly used for general forestry applications, and the largest diameter is used when large amounts of wood are required for chemical analysis. Most of the investigations using increment borers to examine VOC concentrations in tree cores have used either 0.169- or 0.2-in. diameter borers. Increment borers also can be obtained in a two-thread or three-thread design. Three-thread designs typically advance farther per revolution than two-thread designs but can be more difficult to turn and to initially engage the wood than a two-thread design. Thus, two-thread designs are more suited to hardwoods, and three-thread designs are more suited to softwoods.

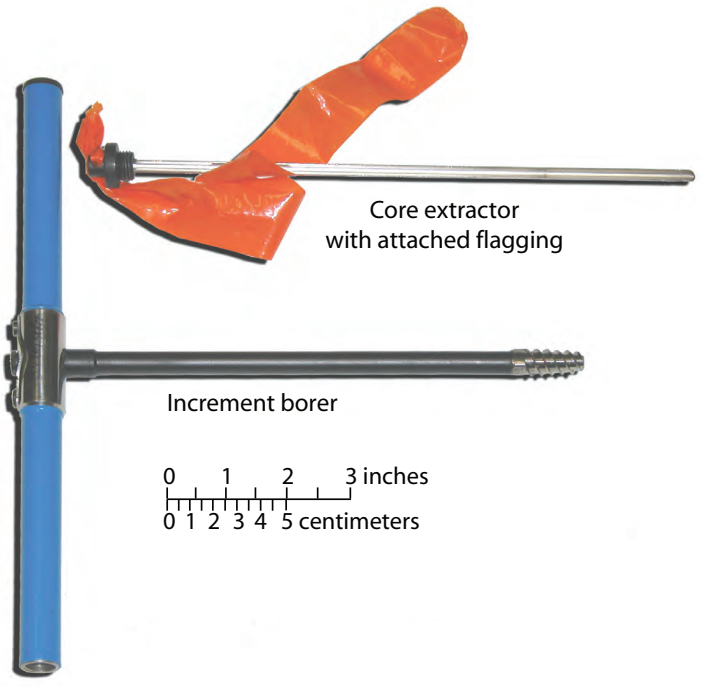

Figure 1. Typical tree-coring tool.

2. **Core-barrel sharpening:** Increment borers should be sharp enough to easily engage the wood. The borer needs sharpening when engaging the wood is difficult, when the borer cuts a rough core, when the edge feels dull to the touch, or when the extractor consistently fails to recover the core. It should not be assumed that a new borer is sharp; sharpening methods for increment borers can be found in Maeglin (1979) and Grissino-Mayer (2003).

3. **Core-barrel cleaning:** New increment borers should be cleaned prior to use in examining tree-core VOC concentrations because the new borers sometimes are coated with a thin layer of oil. In addition, researchers involved in tree coring for the use of dendrochronology often lubricate the interior of the core barrels. Such lubrication, however, is inappropriate for the use of tree cores to examine VOCs. Borers can be cleaned with soap and water. For increment borers with a diameter of 0.2 in., rifle-cleaning rods with an attached soft cloth are effective for cleaning inside the barrel. A clean cloth can be pushed through the core barrel, sealed in a vial, allowed to equilibrate with the headspace, and analyzed by headspace chromatography to verify that the cleaning removed potential interferences.

4. **Initiating coring:** The most difficult part about tree coring is initiating the coring. The boring should be started slowly and carefully to avoid sideways slippage of the bit against the tree trunk. One approach is to hold the borer shaft near the threaded bit with one hand while applying pressure toward the tree and turning the borer with the other hand. Folding chest plates and straps that wrap around the trunk also are commercially available as tools to assist in starting the bit into the tree. The coring should be approximately perpendicular to the tree trunk. Once the bit has begun drilling into the tree, both hands can be used to advance the borer. Increment borer drill chucks are available for use with a drill; however, standard 19-volt or less portable drills are not always powerful enough to collect a complete length of core.

5. **Core-collection location:** When conducting a tree-coring survey to examine the areal distribution of VOCs at a site, the cores should be collected from the trees at about the same height. A core collected near the ground usually provides higher VOC concentrations than a core collected higher up the trunk; however, for ease of core collection in typical applications, a simple approach is to use mean breast height, a commonly used forestry term meaning about 4.3 feet (ft) above land surface. In general, the core should be collected from the side of the tree suspected to be closest to the target contamination body. Dead or damaged parts of the tree should be avoided. Refer to the technical considerations section of this report for a more complete discussion of concentration variations with height above the ground and with azimuthal direction.

6. **Core length:** The length of the core should be consistent among the cored trees and should include the outermost growth ring. A core of the outermost 3 in. (not including the bark) is sufficient to identify the contaminants. A simple approach is to mark the core barrel at a distance from the bit equivalent to the length of a serum vial (approximately 3 in., not including the bark). By advancing the borer until the mark is at the inner edge of the bark, xylem cores of uniform length can be obtained that fit into the sampling vials. If necessary, the cores can be broken to make the vials easier to seal.

7. **Core removal:** The core is removed from the borer by means of an extractor (fig. 1). After the increment borer has been advanced into the tree to the desired depth, the extractor is fully inserted into the borer. The extractor should be inserted with the concave side of the extractor facing down. In typical forestry applications, the borer is then rotated one half turn counter clockwise to break the core, and the core is removed from the borer by pulling on the extractor. Often, this procedure will remove the entire core from the borer. In some cases, however, part of the core will remain in the borer because extractors sometimes lose their ability to adequately grip the core or because part of the core becomes wedged in the bit. Probable causes of a jammed core in the core barrel include a dull core-barrel bit and a dirty core barrel. To facilitate comparison of tree-core VOC concentrations, it is preferable to maintain uniform lengths of core samples and to seal the entire length of required core in sampling vials as soon as possible. Therefore, if the extractor begins to fail to recover the entire core from the barrel, an alternate approach should be used. The alternate approach is to insert the extractor fully into the borer once the depth of penetration has been reached, rapidly remove the borer from the tree, insert an unpainted golf tee into the end of the bit, and press it against the tree while removing the extractor and tree core. In most cases, this gently removes the entire core without damaging the cutting edge of the bit.

8. **Parts of the tree core to be included:** Because the bark is not involved in transpiration, inclusion of the bark in the sample is not necessary. If the bark is removed, however, care should be taken to avoid accidental removal of the outermost xylem growth ring in ring-porous trees (table 1; fig. 2) because the outermost ring is the dominant path for water transport through the trunk (Ellmore and Ewers, 1986). A more detailed discussion can be found in the section on technical rational for methodology. Inclusion of the inner part of the bark as part of the sample probably does not produce a substantial adverse effect on VOC headspace concentrations when the values are reported as parts per million by volume (ppmv) of headspace.

Table 1. Examples of nonporous, diffuse-porous, and ring-porous trees.

Nonporous	Diffuse porous	Ring porous
Bald cypress (*Taxodium* sp.)	Alder (*Alnus* sp.)	Ash (*Fraxinus* sp.)
Cedar (*Thuja* sp.)	Apple, pear (*Prunus* sp.)	Coffee tree (*Gymnocladus dioicus*)
Douglas fir (*Pseudotsuga* sp.)	Aspen, cottonwood (*Populus* sp.)	Honeylocust (*Gleditsia* sp.)
False cypress (*Chamaecyparis* sp.)	Beech (*Fagus* sp.)	Locust (*Robinia* sp.)
Fir (*Abies* sp.)	Birch (*Betula* sp.)	Mulberry (*Morus* sp.)
Ginkgo (*Ginkgo* sp.)	Blue beech (*Carpinus* sp.)	Oak (*Quercus* sp.)
Hemlock (*Tsuga* sp.)	Buckeye (*Aesculus* sp.)	Osage orange (*Maclura pomifera*)
Juniper (*Juniperus* sp.)	Dogwood (*Cornus* sp.)	Paulownia (*Paulownia* sp.)
Larch (*Larix* sp.)	Eucalyptus (*Eucalyptus* sp.)	Sassafras (*Sassafras* sp.)
Pine (*Pinus* sp.)	Gum (*Nyssa* sp.)	
Redwood (*Sequoia* sp.)	Holly (*Ilex* sp.)	
Spruce (*Picea* sp.)	Magnolia (*Magnolia* sp.)	
	Maple (*Acer* sp.)	
	Sweetgum (*Liquidambar* sp.)	
	Sycamore (*Platanus* sp.)	
	Willow (*Salix* sp.)	

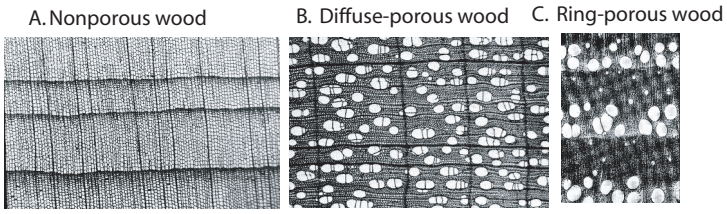

Figure 2. Comparison of nonporous, diffuse-porous, and ring-porous wood (reprinted with permission from Chaney, 2000).

9. **Timing of tree-core transfer to sample vials:** Tree cores should be sealed in vials immediately upon recovery from the tree. Volatilization loss begins immediately upon removal of the core from the tree. If the core is not sealed in a vial within several seconds of collection, it should be discarded, and a new core should be collected.

10. **Type of sample vial:** Either 20-milliliter (mL) glass serum vials or 40-mL volatile organic analysis (VOA) vials can been used for collecting tree cores for headspace analysis (figs. 3 and 4). Consistency should be maintained within an individual study area. The VOA vials have an advantage in that they do not require the use of a crimping tool; however, the crimp-top serum-vial cap provides a better seal than the VOA-vial cap because the VOA-vial seal is designed for use with water samples rather than air samples. In addition, for a given mass of TCE in a tree core, higher headspace TCE concentrations are found in the 20-mL vials as compared to the 40-mL vials because of dilution. Therefore, if the expected concentrations are relatively low, the vials are going to be stored for several days prior to analysis, or the vials will be heated, the 20-mL crimp-top serum vials offer a greater margin of confidence.

11. **Sample storage:** In general, TCE concentrations appear to be fairly stable for several days in sealed sampling vials containing tree cores; however, it is prudent to analyze the cores within a few days of collection. The samples should be stored in the dark because of the potential for photodegradation of the VOCs. If the tree-core samples will be analyzed within a few days of sample collection, the samples can be stored at room temperature prior to analysis to facilitate equilibration of the headspace in the vials with the VOCs in the enclosed tree core. If a longer period of time before analysis is anticipated, then refrigerating the cores will reduce the potential for vapor loss and decay. Refrigerated cores should be allowed to equilibrate for at least a few hours at room temperature or for a few minutes by heating prior to analysis.

12. **Map the location and mark the tree:** It is important to preserve a record of the location of cored trees so that the analytical results can accurately be related to the site. An

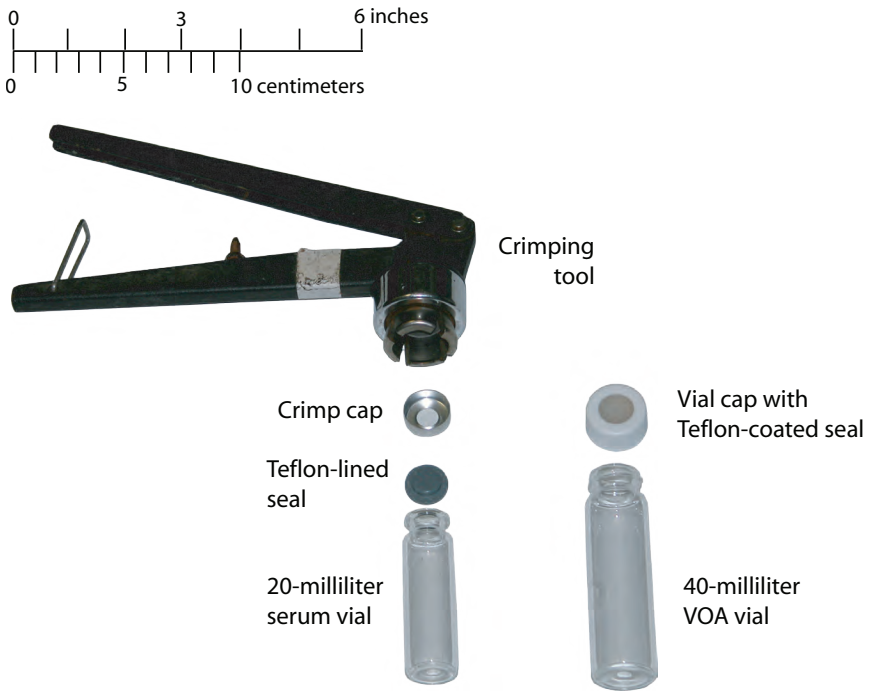

Figure 3. Crimping tool, 20-milliliter crimp-top serum vial, and 40-millilliter volatile organic analysis (VOA) vial used for collecting tree cores.

Figure 4. Crimp-top serum vial containing tree core.

effort should be made to mark the approximate location of each cored tree on a site map. If necessary, the tree locations can be precisely mapped by surveying at a later date. The cored trees should be marked in some way to facilitate returning to the site to follow up on the investigation. A variety of tree-marking methods are available. The most long-term marking method involves "engraving" the tree identification number on an aluminum tag with a ball-point pen and nailing the tag to the tree. Depending on esthetic issues and how long the tree-tag needs to last, other means of marking the tree with an identification number include tree paint, marked wooden stakes driven into the ground adjacent to the tree, or colorful flagging with the identification number written on the flag tied around the tree.

13. **Tree-coring damage:** Although tree coring can impart local damage to tree trunks, most trees are capable of compartmentalizing the damage and healing within 2–3 years with no adverse effects. Trees that have a more difficult time recovering are generally those that are short-lived species or suppressed individuals. Sealing the core-hole does not appear to accelerate the repair and probably is not necessary. A more detailed discussion is available in the section of this report titled "Tree-Core Collection" in the "Technical Rationale fore Methodology" section.

14. **Supportive data to be collected:** A variety of data should be collected in conjunction with tree coring to assist in interpretation of the results. The data are summarized in table 2.

Table 2. Field data to be collected during tree-coring investigation.

Location information:
• Date/time. • Site location. • Unique tree identifier. • Location of tree in study area. • Note unusual geographic issues, such as if the tree is in an island in a parking lot where rainfall infiltration may be limited, on the edge of a cliff where depth to ground water may be large, on a stream bank where bank storage may constitute part of the tree's water supply, or other factors of potential interest. • Temperature and weather conditions at the time of collection and for approximately 3 days prior to the sampling, based on the nearest weather station.
Tree characteristics:
• Species. • Indications of tree stress (damaged bark, dead branches, etc.). • Whether or not there are leaves on the tree. • Tree diameter (can be measured with tree-diameter tape measure). • Note whether or not the tree is considered to represent background conditions.
Core-collection information:
• Height of tree core. • Side of the tree from which the core was collected. • Note whether duplicate samples were collected. • Note whether an air blank was collected at the tree. • Note any unusual core characteristics, such as a hollow or rotten interior of the tree.

Tree-Core Analysis

Analysis of the tree-core samples involves allowing an initial equilibration period for the VOCs in the tree core to partition into the sampling media, typically headspace air. The media is then analyzed by gas chromatography.

1. **Sample equilibration time:** Once the tree cores are sealed in the sample vials, the VOCs associated with the tree core begin to volatilize into the vial headspace. The volatilization is fast enough so that detectable quantities of TCE can accumulate within the vial within minutes. In a field test for this investigation where the ambient air temperature was about 27 °C, analysis of the samples about 5 to 6 minutes after capping the vials was adequate to detect subsurface VOC contamination. In some cases, however, VOC concentrations in the tree-core vials can increase substantially by allowing the cores to equilibrate at room temperature overnight. Variations in equilibration time can be caused by differences in ambient temperature, differences in heating of the core by friction during coring, and other unidentified factors. If an important part of the investigation is to compare concentrations among tree cores at a particular site, then allow enough equilibration time so that the VOC concentrations are less sensitive to factors related to core collection. Overnight equilibration at room temperature is a commonly used approach. Alternatively, heating the vials can transfer larger amounts of the VOCs into the headspace, resulting in an increased sensitivity. A simple block heater or water bath can be used in the field with a power inverter connected to a car battery to heat the cores in sealed vials at 60–70 ºC for a few minutes. An advantage of field analysis of tree cores is that it can be used to direct the field sampling effort.

2. **Sample analysis:** In general, the simplest analytical approach for tree cores in vials is to use headspace analysis (HSA) gas chromatography. The headspace can be analyzed by purge-and trap (PT) or by direct injection onto a GC column by syringe. The photoionization detectors (PID) and the electron-capture detector (ECD) are both useful gas chromatographic tools for tree-core analysis. A protocol for HSA of VOCs is included as Appendix 2 in this report. The protocol reported in Appendix 2 has not been tested for all analytes reported to have been detected in tree cores in this report. Analytes not listed in the Appendix should be tested to determine the applicability of the method. A variety of VOC-concentration reporting units have been used in tree-coring investigations, but because semiquantitative data are typically sufficient, a simple approach is to use a consistent sample-vial volume, collect a consistent core size, and report the results as the volume of the VOC per billion volumes of ambient air.

Quality Control and Assurance

Four types of quality control and assurance samples should be collected to maintain the integrity of the data. The sample types are duplicate samples, air-blank samples, background samples, and trip blanks.

1. **Duplicate samples:** Duplicate samples consist of two core samples collected in separate vials. The samples should be collected from the same tree with the second core collected approximately 1 in. below the first core. The cores should be of equal length. These samples provide information on the variability of VOC concentrations caused by collection and analysis. The number of duplicate samples collected should be about 10 percent of the total number of trees cored.

2. **Air-blank samples:** Air-blank samples are collected by rapidly waving an empty vial in the air in the vicinity of the target tree. The vial then is capped, transported, and analyzed in the same manner as the tree cores. This measurement provides information on the influence of air pollution on the sample quality. If TCE were present in analysis of a tree core, for example, but not in the air blank sample collected adjacent to the tree, then ambient air can be eliminated as the source of the detected TCE, demonstrating that the TCE is associated with the core. Ambient air samples should be collected at various locations across the study area and whenever there is a suspicion that airborne contaminants may provide interference, as is sometimes the case near active gasoline stations or dry-cleaning facilities. It also is possible that some level of VOC concentration may be present in the air by virtue of plant evapotranspiration. In general, the dilution factors and wind influences are large enough that VOC concentrations in excess of air standards for gas-phase contamination are unlikely to be caused by phytovolatilization; however, at least one investigation found that possible action-level exceedances might occur with highly toxic substances, such as VC and carbon tetrachloride, if they are present in ground water at levels above kilogram amounts in a single plume of a few hectares, and released by vigorously growing plants under hot, dry conditions (Narayanan and others, 2004).

3. **Background sample:** A background sample for a particular tree species consists of a core of that species collected from an uncontaminated area. Background samples are used because trees can contain natural VOCs, such as toluene, that can be detected during gas chromatographic analysis of the cores. The background sample ensures that target compounds detected in trees from a contaminated area are not a misinterpretation of naturally occurring volatile compounds that elute on a gas chromatograph at the same time as the target compounds. A background sample should be analyzed for each tree species.

4. **Trip blanks:** Trip blanks are air-filled vials sealed in a contaminant-free environment. The trip blanks are taken to the field and are kept with the tree-core samples once they are collected. The purpose of the trip blank is to determine whether exposure to target compounds during sample transportation could have resulted in false detections of contaminants.

Part 2. Historical Perspectives and Technical Considerations

Part 2 of this report provides an overview of historical perspectives related to the use of tree coring with an emphasis on application of the method to examining uptake of organic contaminants. In addition, this section of the report provides technical rationale for various aspects of the methodology and examines factors influencing VOC concentrations in tree cores.

Historical Perspectives

Tree cores have been widely used for dendrochronology and other environmental applications since the early part of the 20th century when an American astronomer, A.E. Douglass, related tree-core widths to climatic wet and dry periods (Douglass, 1919). Examination of plants as a mechanism to remediate subsurface organic contaminants dates back at least to the early 1960s (Castelfranco and others, 1961).

Early interest in the uptake of organic chemicals by plants had an emphasis on agrochemicals (Shone and Wood, 1972, 1974). These authors used the transpiration stream concentration factor (TSCF) to normalize the compound concentration in the transpiration stream with respect to root-zone bulk compound concentrations (Shone and Wood, 1974). Briggs and others (1982) showed that TSCFs of nonvolatile compounds were related to the properties of the chemical being taken up by the plant, particularly, the degree to which the compound was hydrophobic. Burken (1996) showed that the same general factors control plant uptake of VOCs. Thus, since the 1990s, it was clear that VOCs could be taken up into trees through the root system (Burken, 1996; Burken and Schnoor, 1998; Compton and others, 1998; Davis and others, 1998a; Newman and others, 1997; Vroblesky, 1998; Vroblesky and others, 1999).

The first application of tree-core chemistry to map VOCs in ground water was at the Savannah River Site in South Carolina (Vroblesky, 1998; Vroblesky and others, 1999). This investigation involved tracking a chlorinated solvent plume beneath a flooded cypress swamp. Headspace analysis of cores from 97 trees (6 species, predominantly bald cypress [*Taxodium distichum*]) growing over ground-water contamination in a forested flood plain of the Savannah River in South Carolina showed that *c*DCE and TCE concentrations in tree cores

reflected the configuration of the ground-water contamination plume, despite the fact that most of the trees were growing in a few feet of uncontaminated standing water from the Savannah River.

Landmeyer and others (2000) extended the application of tree cores from examining subsurface chlorinated solvents to examining subsurface petroleum hydrocarbons. They found MTBE and the conventional gasoline compounds benzene, toluene, ethylbenzene, and the isomers of xylenes and trimethylbenzene in cores from oak trees (*Quercus* sp.) growing above petroleum-hydrocarbon contaminated ground water. Additional evidence of MTBE uptake by trees was seen in other investigations by examining biomass of trees (Brown and others, 2001), transpiration gasses (Parfitt and others, 2000), and bioreactor experiments (Hong and others, 2001; Ramaswami and Rubin, 2001).

VOCs in tree cores have been used to delineate ground-water contamination plumes in a variety of locations. Field tests have been conducted in Colorado (Vroblesky and others, 2004), Florida (Doucette and others, 2003), Maryland (Burken, 2001; Weishaar and Burken, 2005), Missouri (Schumacher and others, 2004), South Carolina (Vroblesky and others, 2004), Texas (Vroblesky and others, 2004), and Utah (Doucette and others, 2003; Lewis and others, 2001). Trapp and others (2007) investigated tree coring as a tool for screening subsurface pollution in Europe and published a concise guide to field sampling. At least one study examined chloride concentrations in tree rings to estimate the onset of chlorinated hydrocarbon contamination (Yanosky and others, 2001). VOC analysis of tree cores has been used to detect subsurface VOC contamination and to direct subsequent drilling efforts in areas where there were little or no pre-existing characterization data (Schumacher and others, 2004; Vroblesky and Casey, 2004; Sorek and others, 2008).

VOC analysis of tree cores has been used to monitor ground-water plumes (Gopalakrishnan and others, 2005). Tree cores have been used to show that some of the trees at the leading edge of a ground-water TCE contamination plume began to take up TCE in increasing amounts over time as the plume approached (Vroblesky and others, 2004). The variety of applications and successful field tests indicate that tree coring can be a viable reconnaissance tool for examining subsurface VOCs.

In some cases, analysis of stems and branches has been shown to be a less intrusive approach to tracking subsurface VOCs than collection and analysis of tree cores (Vroblesky and others, 2004; Gopalakrishnan and others, 2007). In general, however, the VOC concentrations in stems appear to be lower than the VOC concentrations in tree cores, sometimes resulting in stem analyses that produce false negatives (Vroblesky and others, 2004). A recent modification of the tree-coring approach involves inserting activated carbon into the core hole, followed by recovery and analysis of the activated carbon (Sheehan and others, 2007). In most cases, simple HSA of tree cores is an adequate approach to locating and mapping subsurface VOCs; however, the activated-carbon approach has the potential to detect VOCs at lower levels than HSA in situations where such sensitivity is needed. In areas of high chlorinated VOC concentrations (greater than 1 part per million by volume [ppmv] in tree-core headspace vials) where relatively little sensitivity is needed, simple field colorimetric tubes have been used to detect the contaminants in tree cores (Vroblesky and others, 2007b).

Technical Rationale for Methodology

In this section of the report, technical rationale is provided for various aspects of the tree coring methodology. In particular, this section includes discussions of parts of the trunk to be sampled, maintenance of the core hole after core collection, times involved in core transfer to sample vials, VOC stability in the sample vials, equilibration times, quality-control issues, and alternative approaches to collection and analysis of tree cores for VOC analysis.

Tree-Core Collection

The depth of coring depends on the length of core desired. In most cases, it is not necessary to core deeply into the trunk to obtain VOC concentrations. This is primarily because most of the water flow during transpiration is in the outer part of the trunk. In ring-porous trees (table 1), over 90 percent of water transported through the xylem is in the outermost growth ring (Ellmore and Ewers, 1986). Thus, inclusion of the outermost growth ring is particularly important in ring-porous trees. In diffuse-porous and nonporous trees, multiple growth rings conduct water. The preferential conductance of water in the outer part of the tree does not necessarily mean that the highest VOC concentrations are always in the outermost part of the trunk. Often, the VOC concentrations decrease from the inner to outer parts of the trunk (xylem), possibly related to volatilization loss through the bark (Ma and Burken, 2003). The inner part, or heartwood, of some trees is known to provide a waste repository for excess concentrations of some constituents (Tout and others, 1977; Vroblesky and others, 1992), although this issue has not been investigated for VOCs. Because increased concentrations of VOCs sometimes can be found in the inner relative to the outer part of the trunk, there may be instances where coring more deeply into the trunk can result in higher detection potential of VOCs in the tree cores. Field investigations, however, indicate that a core of the outermost 3 in. (not including the bark) can be sufficient to identify subsurface VOC contamination (Vroblesky and others, 1999, 2004)

Research indicates that sealing the tree core hole probably is not needed and sometimes can be harmful. Although it is clear that open boreholes can allow decay and disease (Toole and Gammage, 1959; Hart and Wargo, 1965; Shigo, 1967) and that tree wounds from increment borers can be associated with long streaks of discolored and decayed wood (Shigo, 1983), plugging the core holes does little to reduce

discoloration or decay (Meyer and Hayward, 1936; Lorenz, 1944; Hepting and others, 1949). In some cases, the swelling of dowel plugs inserted in the core hole has caused splits in the trunk near the entry hole (Hepting and others, 1949). In addition, wounds treated with wound dressing often form large callus ribs that turn inward to form "ram's horns," and there are no data to show that wound dressings stop decay (Shigo, 1983). In general, healthy dominant and co-dominant trees respond well to tree coring both by creating a chemical barrier to inhibit microbial invasion and by compartmentalizing infected wood when microorganisms bypass the chemical barrier (Shigo, 1974). Conifer species appear to be particularly resilient to coring (Meyer and Hayward, 1936; Shigo, 1985). A summary of the effects of coring on differing species can be found in Grissino-Mayer (2003). Core-damage studies showed that more than half of the core holes healed within 2–3 years, with most of the poorly healing trees being short-lived species or suppressed individuals (Meyer and Hayward, 1936, Lorenz, 1944; Hepting and others, 1949; Toole and Gammage, 1959). Further, several studies reported no evidence of tree mortality after increment coring (Meyer and Hayward, 1936; Lorenz, 1944; Hepting and others, 1949; Toole and Gamage, 1959; Hart and Wargo, 1965; Eckstein and Dujesiefken, 1999; van Mantgem and Stephenson, 2004) and little effect on tree mortality when stem wedge sections were removed using a chainsaw (Heyerdahl and McKay, 2001). Therefore, a practical approach is to leave the borehole unsealed. The open hole allows the borehole to dry, and the water and sap flow from the hole may cleanse the wound and discourage infection (Neil Pederson, Eastern Kentucky University, written commun., 2007). Some researchers use antiseptic approaches to minimize introduction of microorganisms to the core hole by either dipping the increment borer in alcohol between trees (Neil Pederson, Eastern Kentucky University, written commun., 2007) or by squirting antiseptic soap into the core hole (Lee Newman, University of South Carolina, oral commun., 2007). The effectiveness of these antiseptic approaches, however, has not been determined. To reduce stress to the tree, excessive coring of the same tree should be avoided.

Tree-Core Transfer to Sample Vials and Storage

Tree cores should be transferred to sealed vials as rapidly as possible because volatilization loss from the tree cores is rapid. A field test allowing the cores to remain in open vials for several minutes prior to sealing showed that TCE concentrations decreased by about 40 percent over a period of 5 minutes (fig. 5).

Other approaches to collect tree cores for analysis also have been used. Schumacher and others (2004) collected replicate cores in vials containing 5 mL of organic-free water and stored them upside down to limit volatilization loss through the septa. Rather than preventing VOC loss, however, the added water reduced the amount of detectable PCE. Up to 55 percent less PCE was detected in the samples containing water than in replicate samples not containing water. The

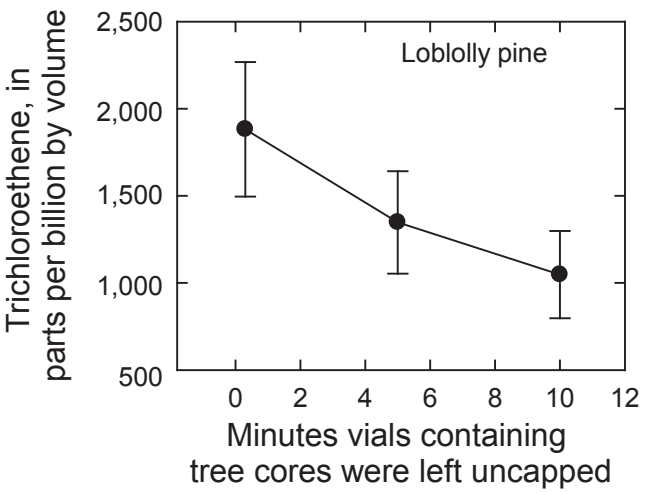

Figure 5. Loss of trichloroethene over time from uncapped 20-milliliter serum vials, Naval Weapons Station Charleston, South Carolina, 2006.

authors attributed the difference to a combination of PCE partitioning into the water phase and slightly longer time required to avoid spilling water from the vials while adding the core samples. Thereafter, the authors discontinued addition of water to the vials.

Methanol extraction also has been used for chemical analysis of tree cores (Landmeyer and others, 2000; Lewis and others, 2001). In the Landmeyer investigation, the cores were sealed in vials containing 5 mL of reagent-grade methanol. Methanol extraction used in combination with PT analysis can be an effective approach to confirm the identity of the detected compound by mass spectrometry.

An additional approach to collecting tree cores that has been reported is chilling the cores upon collection, transporting them back to the laboratory, freezing them until analysis, and then crushing the cores prior to analysis (Sorek and others, 2008). In the laboratory, the crushed cores were heated prior to analysis.

Changes in VOC concentrations can take place in the tree-core sampling vial over time. Sometimes these changes can be seen as changes in the amplitude of early-eluting chromatographic peaks typically not associated with groundwater contamination. To test the length of time that the tree cores for TCE analysis can be stored in sample vials prior to analysis, repeated sampling was done with a series of vials stored at room temperature, containing cores from a tree growing above contaminated ground water. Most vials showed no TCE volatilization loss from 24 hours to 19 days of storage (fig. 6). These data indicate that the vials can be stored for at least a few days prior to analysis. It should be cautioned, however, that it is prudent to analyze the samples within a few days of collection rather than waiting 19 days to avoid potential transformations or volatilization losses not evident in this investigation.

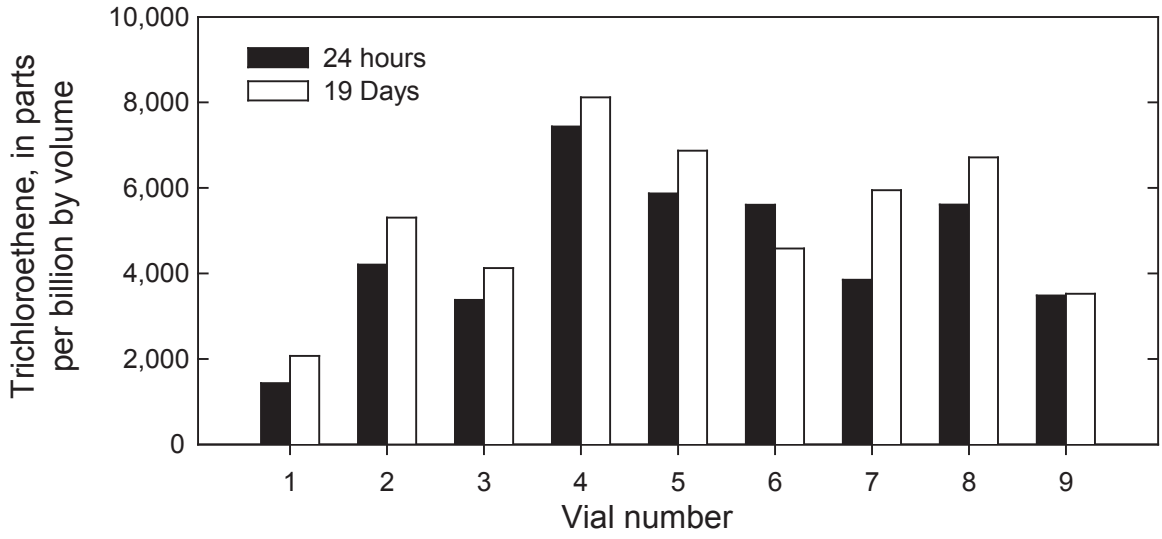

Figure 6. Headspace trichloroethene concentrations at 24 hours and 19 days of storage in sealed serum vials containing tree cores from a trichloroethene-contaminated site showing generally slight concentration increases in most cores and no evidence of volatilization loss over time.

Tree-Core Equilibration Time

VOCs begin to de-gas from tree cores immediately upon removal from the tree. In field investigations conducted for this user's guide, sufficient TCE concentrations to indicate the presence of subsurface contamination accumulated in crimp-capped serum vials containing tree cores within 5 minutes of collection. In tests where repeated vapor extractions were taken from the same tree-core vial over time, several vials showed that the TCE concentration in the vial headspace after 5 minutes of equilibration was approximately the same as allowing the vials to equilibrate overnight (fig. 7A, B, C, D). In other tree-core vials and on other sampling dates, however, TCE concentrations in the vial headspace increased by a factor of 2 or more after equilibrating overnight (fig. 7E). The factors controlling equilibration time probably include ambient air temperature, differences in heating of the core barrel by friction during coring, and other unidentified factors. The influences of these factors are not yet well understood. Thus, in general, it appears that analysis of tree cores within 5 minutes of core collection can be a useful indicator of subsurface TCE contamination. If the intent, however, is to compare VOC concentrations among several trees at the site, a prudent approach, until the factors that control equilibrium time are more thoroughly studied, is to treat all of the cores the same way and allow them to equilibrate approximately 24 hours or more (Landmeyer and others, 2000; Schumacher and others, 2004; Vroblesky and others, 2004). A comparison of cores allowed to equilibrate for 24 hours relative to 19 days shows that only slight concentration increases took place after 24 hours and there was no evidence of VOC loss (fig. 6).

An alternate field approach is to analyze the tree cores in the field after heating the cores in crimp-capped serum vials for about 5 to15 minutes. Field tests for development of this guide showed that field heating the cores produced TCE concentrations higher than in unheated cores or cores allowed to equilibrate at ambient temperature for 24 hours (fig. 7D). A similar relation was seen in field-heated cores with a reanalysis of the core after about 24 to 28 hours of equilibration at ambient temperature following heating (fig. 7F, G, H). Although it is possible that the lower TCE concentrations in the corresponding unheated sample the next day could represent volatilization loss during the previous heating, such loss probably is minor because similar TCE-concentration declines between the 5-minute time step and the unheated analysis the following day were seen whether the samples were heated for 40 minutes or for only 5 minutes (fig. 7G, H). Tests have not yet been done to determine the upper range of acceptable heating, but it is logical that some level of volatilization loss or thermal destruction could occur with excessive heating. Therefore, core heating should be maintained within the ranges cited above or should be tested.

In additional investigations of field heating conducted for this guide, duplicate cores were collected 0.75 in. apart from trees at Solid Waste Management Unit (SWMU) 17, Naval Weapons Station Charleston, South Carolina, in June 2006 and at the Durham Meadows Superfund Sites, Durham, Connecticut, in August 2006. At each site, one of the cores was heated for 5 minutes at 60–70 ºC and analyzed in the field within 10 minutes of collection. Comparison of VOC concentrations in vials containing tree cores shows that field heating the cores, in most cases, produced concentrations that were in the range of, or higher than, concentrations obtained after allowing the vials to equilibrate 24 to 30 hours at room temperature (fig. 8A). Although only two trees were tested for PCE, the limited data set implies that a similar correspondence applies to PCE (fig. 8B).

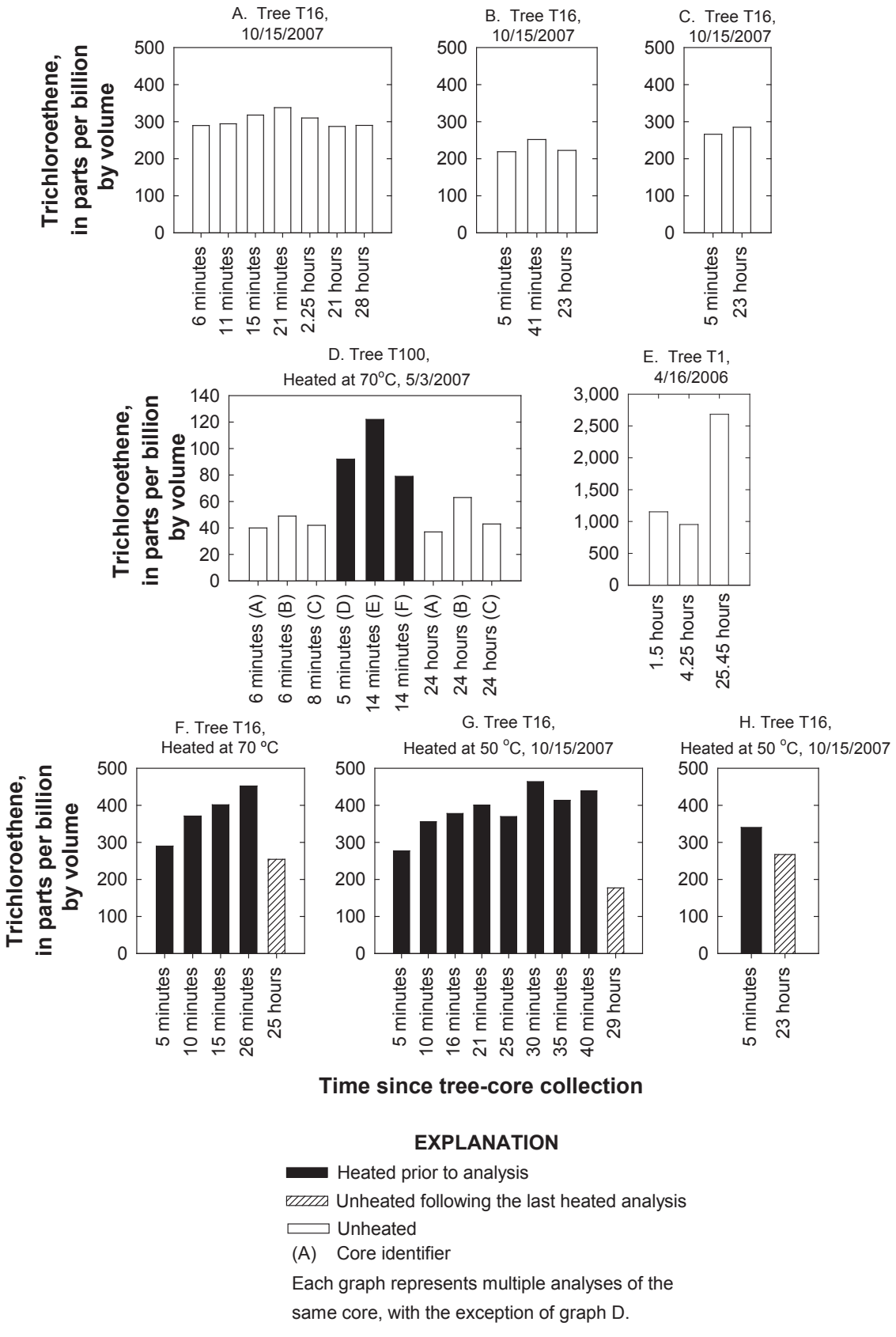

Figure 7. Trichloroethene concentrations over time in unheated and heated sealed serum vials containing loblolly pine tree cores from a trichloroethene-contaminated site showing little concentration change in cores from some trees after 5 to 6 minutes and an increase in sensitivity by field heating and analyzing the cores, Solid Waste Management Unit 17, Charleston, South Carolina.

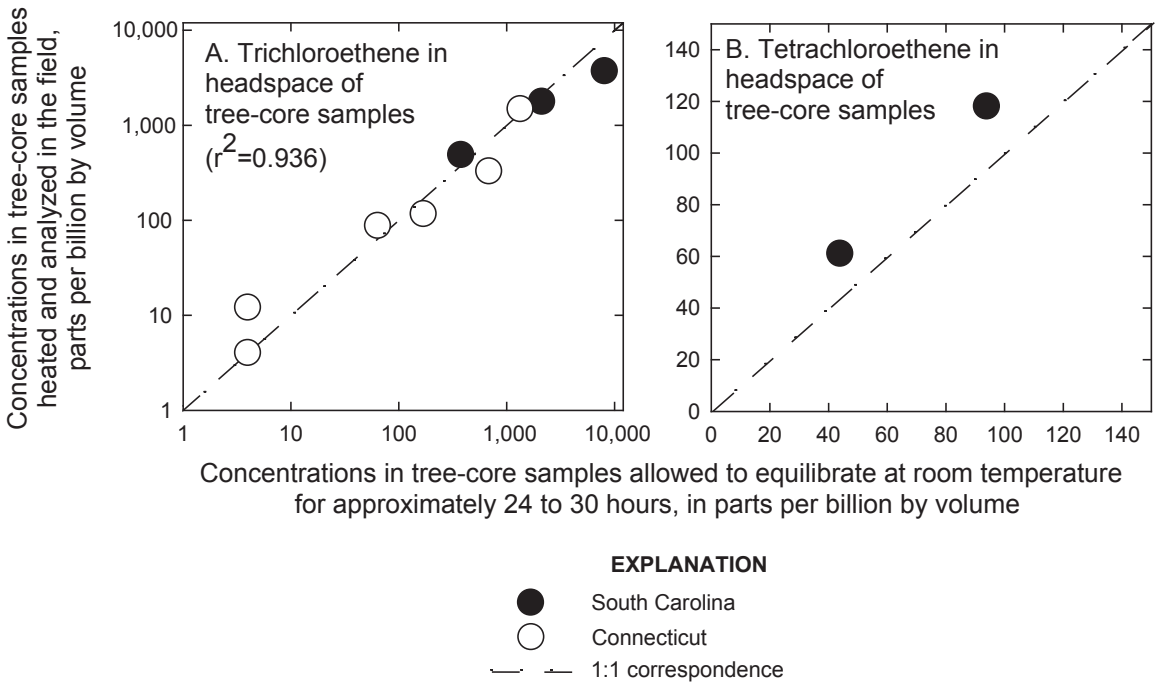

Figure 8. Field-heated and unheated (A) trichloroethene and (B) tetrachloroethene concentrations in 20-milliliter serum vials containing cores from trees growing over ground-water contamination showing that field heating the sample vials can produce VOC concentrations that are in the range of or higher than concentrations obtained by allowing the samples to equilibrate at room temperature overnight.

The data indicate that field heating and analysis of the tree cores can increase the sensitivity of VOC detection relative to unheated analyses in the field and can produce concentrations that are in the range of or higher than in tree cores allowed to equilibrate for a day. Because of the increased sensitivity by field heating and analysis, it is unlikely that this approach will fail to detect VOC contamination that otherwise would be detected by allowing the cores to equilibrate for a day. Thus, onsite analysis of tree cores can be used to direct the tree coring effort and optimize plume mapping.

Tree-Core Analysis

A variety of approaches have been used to analyze the VOC content of tree cores. In general, the simplest and preferred approach is to use HSA gas chromatography to analyze the cores (Vroblesky and others, 1999). HSA can be done either by direct injection or PT. Typical GC detectors used include the PID, which is sensitive to aromatic and unsaturated VOCs, and the ECD, which is sensitive to halogenated VOCs. A protocol for HSA of VOCs is included as Appendix 2 in this report (U.S. Environmental Protection Agency, 2003).

Analytical approaches other than HSA also have been used to analyze tree cores. Lewis (2001) compared HSA to methanol extraction coupled with PT to analyze TCE concentrations in tree cores. The methanol extraction measured approximately 2.7 times more TCE than the HSA approach in areas of medium to high ground-water TCE concentrations (greater than 800 μg/L). Tree cores were collected and placed into headspace vials with 10 mL of methanol or matrix modifying solution (an acidified sodium chloride solution). Comparisons were made between matrix modifying solutions of pH 2 and pH 10. Methanol-filled vials also were used because it was assumed that the methanol extraction would be more efficient than matrix modifying solution for removal of TCE from the tree core. No analytical difference was found between the pH 2 and pH 10 matrix modifying solutions; however, the study concluded that pH 2 matrix modifying solution was the most practical solvent for the analysis. The acidified matrix modifying solution enhances headspace sensitivity by raising the Henry's Law constant and reducing the potential for biological TCE degradation.

Doucette and others (2003) also used a methanol extract to analyze plant tissue. The vials containing plant tissue and methanol were agitated for 24 hours in a rotary tumbler. A syringe was used to extract 250 microliters (μL) of methanol from each vial, and the extract was diluted with 20 mL of deionized water. A PT gas chromatography approach was then used to analyze the samples for TCE. Variations of methanol-extraction approaches also were used by Landmeyer and others (2000) to analyze for fuel oxygenases, such as MTBE, that have a low vapor pressure. Lewis (2001) concluded

that although the methanol extraction produced higher TCE concentrations than the HSA, there are costs and analytical complications associated with the methanol extraction analyses that make HSA a preferable alternative.

Where increased sensitivity is needed relative to HSA, activated carbon has been inserted into a tree-core hole, followed by recovery and analysis of the activated carbon (Sheehan and others, 2007). This approach utilizes the tree-core hole rather than the tree core.

In a highly contaminated area where relatively little sensitivity is needed, field colorimetric gas-detector tubes (GasTec 133LL) have been used to rapidly and inexpensively detect VOCs in tree cores (Vroblesky and others, 2007b). This approach was used as part of the development of this field guide and utilized a simple modification of the Color Tec screening method (Kelso, 2005) to employ vials containing tree cores in air rather than the recommended vials containing water or sediment in water. The relative concentrations of total chlorinated VOCs obtained by the colorimetric method compared favorably to the quantitative analysis of total chlorinated VOCs obtained by gas chromatography at concentrations greater than 1 ppmv ($r^2 = 0.05$). Below total chlorinated VOC concentrations of 1 ppmv, the colorimetric method sometimes detected VOCs and sometimes did not. Below total chlorinated VOC concentrations of 0.7 ppmv, the colorimetric method failed to detect VOCs. The gas chromatographic method remained useful for detecting total chlorinated VOCs down to at least 10 ppbv.

Comparison of the colorimetric method to the gas chromatographic approach of field analyzing tree cores for chlorinated VOC content shows that both methods can provide effective detection of subsurface chlorinated VOCs at high concentrations (greater than 1 ppmv). At some sites, such as the Carswell Golf Course in Fort Worth, Texas, this level of detection is inadequate to detect the ground-water contamination (Vroblesky and others, 2004). At other sites, however, such as Solid Waste Management Unit 12 (tree-core TCE concentrations up to 10.19 ppmv) and Solid Waste Management Unit 17 (tree-core TCE concentrations up to 85 ppmv) at the Naval Weapons Station Charleston in South Carolina and at Air Force Plant PJKS in Colorado (tree-core TCE concentrations up to 2.191 ppmv) (Vroblesky and others, 2004), field analysis by using either gas chromatography or colorimetric method would be a viable means of locating the plume. Disadvantages of the colorimetric approach are that (1) it is substantially less sensitive than the field gas chromatograph and may miss parts or all of ground-water contamination plumes that are not reflected by relatively high tree-core VOC concentrations, and (2) the colorimetric approach is sensitive only to chlorinated VOCs with a larger influence of chlorinated alkenes relative to chlorinated alkanes. An advantage is that the colorimetric approach is simple to use, easily field portable, and inexpensive (less than about $10 per sample). At sites with sufficient concentrations of tree-core chlorinated VOCs, the colorimetric approach can be a viable, inexpensive reconnaissance tool without the need for a field GC.

Quality Control and Assurance

A field test conducted for this investigation in October 2005 to determine whether decontamination of core barrels was required between collecting cores from different trees showed that the decontamination was unnecessary for investigating TCE in tree cores. The test involved collecting a core from the trunk of a loblolly pine known from previous work to contain high concentrations of TCE. The core was immediately sealed in an empty 20-mL crimp-top vial. The core barrel was not cleaned following collection of the core. Within 6 minutes of collecting the core from the contaminated tree, a core was collected from a loblolly pine of similar diameter in a background area. This sequence was repeated two more times so that a total of three cores were collected from the contaminated tree and three from the uncontaminated tree. At no time during the coring was the core barrel cleaned. The cores were allowed to equilibrate with the headspace of the sample vials for approximately 24 hours at approximately 25 °C and then were analyzed by HSA using photoionization gas chromatography.

TCE concentrations in the contaminated tree ranged from 5,000 to greater than 10,000 ppbv (table 3). TCE was not detected in cores from the background tree at a detection limit of about 15 ppbv. Thus, the core barrel showed no evidence of TCE carryover from the contaminated to the uncontaminated cores. The data indicated that decontamination of the core barrel prior to sampling the background tree was unnecessary when investigating TCE. The probable reasons for the lack of carryover include the low sorption potential of VOCs to metal, the heat generated during the coring, and the volatility of the compounds. It should be cautioned, however, that the core barrel should be inspected to ensure that there is no particulate carryover, such as sections of tree core, remaining in the core

Table 3. Trichloroethene concentrations in tree cores collected within about 5 minutes of each other, using the same core barrel with no decontamination between cores, showing no carryover between core collections.

[ND, not detected at 15 parts per billion by volume; >, greater than]

Tree	Collection time, in hours: minutes	Trichloroethene, in parts per billion by volume
Background tree	13:55	ND
Contaminated tree	14:00	7,649
Background tree	14:04	ND
Contaminated tree	14:09	5,000
Background tree	14:14	ND
Contaminated tree	15:10	>10,000
Background tree	15:19	ND
Air sample near contaminated tree	15:10	ND
Air sample near background tree	15:19	ND

barrel that could adversely impact subsequent samples. In addition, TCE was the only compound examined during this test of potential carryover. Although the results technically apply only to TCE, they probably are applicable to other chlorinated solvents, based on their chemical similarity to TCE.

Factors Influencing Volatile Organic Compound Concentrations in Tree Cores

A variety of factors influence the ability of plants to be useful indictors of ground-water VOC contamination. These factors include the type of VOC, the tree species, the rooting depth, aqueous concentrations, the depth to the contaminated horizon, concentration differences around the trunk related to different sources of subsurface VOCs, concentration differences with depth of coring related to volatilization loss through the bark and possibly other unknown factors, dilution by rain, seasonal and climatic influences, sorption, and within-tree VOC degradation. The following sections discuss these factors in greater detail.

Types of Volatile Organic Compounds

Various VOCs are known to be taken up by plant roots into the trunks of trees and are, therefore, probable candidates for tree-coring investigations. VOCs that have been found in tree-coring investigations include benzene, toluene, ethylbenzene, xylene isomers, trimethylbenzene, MTBE, 1,1,-2-2-tetrachloroethane (PCA) (Hirsh and others, 2003), 1,1,1-trichloroethane, 1,1-dichloroethene, carbon tetrachloride (Sorek and others, 2008), VC (Trapp and others, 2007), TCE, PCE, and *c*DCE (Burken and Schnoor, 1998; Nietch and others, 1999; Vroblesky and others, 1999; Landmeyer and others, 2000; Burken, 2001; Davis and others, 2003). Sorek and others (2008) found that 1,1-dichloroethene appeared to be rarely detected in tree cores despite relatively high concentrations in the subsurface, possibly due to being lost by volatilization from the trunk and sampled tree cores.

Direct uptake of contaminants is controlled by a variety of factors, but in general, moderately hydrophobic organic compounds (octanol-water coefficient, log K_{ow} = 0.5–3), such as TCE and *c*DCE, readily enter the vegetation transpiration streams (Briggs and others, 1982, 1983; Schnoor and others, 1995). Hydrophobic chemicals (log K_{ow} greater than 3.5) are too strongly bound to roots and soil to be translocated within plants (Briggs and others, 1982; Schnoor and others, 1995). Early work considered very water soluble chemicals (log K_{ow} less than 0.5) to be neither sufficiently sorbed to roots nor passively transported through plant membranes (Briggs and others, 1982; Schnoor and others, 1995); however, a more recent investigation provides evidence that soluble, highly polar compounds (such as sulfolene with a log K_{ow} of -0.77) can be readily taken up by plant root systems (Dettenmaier and others, 2008). Thus, log K_{ow} (table 4) is an important factor influencing the ability of a compound to be translocated up the tree trunk.

Table 4. Chemical formula, Henry's Law constant, and log octanol-water partition coefficients for selected volatile organic compounds reported in tree-coring investigations.

[atm m^3/mol, atmosphere cubic meter per mole]

Compound	Formula	Henry's Law constant (atm m^3/mol)	log octanol-water coefficient
Tetrachloroethene	C_2Cl_4	$1.53x10^{-2}$	2.60
Trichloroethene	C_2HCl_3	$9.10x10^{-3}$	2.03
1,1-Dichloroethene	$C_2H_2Cl_2$	$1.8x10^{-2}$	1.84
cis-1,2-Dichloroethene	$C_2H_2Cl_2$	$3.37x10^{-3}$	1.86
Vinyl chloride	C_2H_3Cl	$1.22x10^{+00}$	0.60
1,1,1-Trichlorethane	$C_2H_3Cl_3$	$1.62x10^{-2}$	2.18
1,1-Dichloroethane	$C_2H_2Cl_2$	$5.42x10^{-3}$	1.79
Carbon tetrachloride	CCl_4	$2.40x10^{-2}$	2.78
Benzene	C_6H_6	$5.40x10^{-3}$	2.12
Toluene	C_7H_8	$6.70x10^{-3}$	2.65
Ethyl benzene	C_8H_{10}	$6.60x10^{-3}$	3.13
Xylene isomers	C_8H_{10}	$5.27x10^{-3}$ to $7.1x10^{-3}$	2.95 to 3.2
m-xylene	C_8H_{10}	$7.00x10^{-3}$	3.20
p-xylene	C_8H_{10}	$7.10x10^{-3}$	3.18
Methyl *tert*-butyl ether	$C_5H_{12}O$	$5.4x10^{-4}$	1.24

In general, the log K_{ow} correlates well with the root concentration factor (RCF) and the transpiration stream concentration factor (TSCF). The RCF describes the efficiency of solute movement from an external solution into the root system and is defined by Shone and Wood (1974) as:

RCF = (Concentration in roots) / (Concentration in external solution). (1)

The TSCF is defined by Shone and Wood (1974) as:

TSCF = (Concentration in the transpiration stream) / (Concentration in external solution). (2)

TSCF values have been measured for a number of compounds (Briggs and others, 1982; Burken and Schnoor, 1998; Davis and others, 1998b; Inoue and others, 1998). A TSCF of 1.0 indicates unrestricted passive uptake. A TSCF of less than 1.0 indicates some degree of exclusion by the plant, and a TSCF of greater than 1.0 indicates active uptake by the plant.

Various TSCF values for TCE have been reported. Davis and others (1996) reported a TSCF of 0.67 (at 1.5 grams per liter [g/L]) for TCE. Orchard and others (2000) found TSCF values of 0.02 to 0.22 with an average of 0.12 for TCE. Lockheed Martin (2000) used a TSCF value of 0.79 for TCE. The wide range of TSCF values probably reflects different experimental setups, such as hydroponic rather than soil growth or flowthrough chamber rather than static chambers, leaks, and other factors.

Doucette and others (2003) found that depending on the climate, 200 to 1,400 liters per square meter per year (L/m^2/yr) probably represents a reasonable range of annual transpiration values, and Wullschleger and others (1998) reported that 90 percent of the observations for maximum rates of daily water use were between 10 and 200 liters per day (L/d) for individual trees that averaged 70 ft in height. The authors concluded that reasonable values for yearly TCE plant uptake from a ground-water TCE concentration of 1 mg/L are 2.4–84 milligrams per square meter per year (mg/m^2/yr) (TSCF value of 0.12) to 525 mg/m^2/yr (TSCF value of 0.75) depending on the choice of TSCF values (Orchard and others, 2000).

The mass of TCE removed by plant uptake can be modeled by

$Mass = (TSCF)\,(C_{TCE})\,(T)\,(f)$ (Doucette and others, 2003), (3)

where $TSCF$ is assumed to be constant, C_{TCE} is the average ground-water concentration of TCE in milligrams per liter, T is the cumulative volume of water transpired per unit area per year in liters per square meter per year, and f is the fraction of the plant-water needs met by contaminated ground water. It should be cautioned, however, that TSCF does not include a vapor-transport term for uptake or loss and, thus, may provide misleading conclusions in situations where vapor transport is significant.

The f factor is difficult to measure at most phytoremediation sites described in the literature because ground-water use by plants tends to decrease as the availability of surface water increases (Nilsen and Orcutt, 1996). Doucette and others (2003) suggest that a range f from 0.1 to 0.5 is probably reasonable for climates with more than 16 in. of annual rain.

Although the equations based on log K_{ow} provide a generally useful predictive tool for examining uptake of organic compounds by plants, numerous exceptions exist (Burken and Schnoor, 1998). There are classes of compounds (such as nitroaromatics, phenols, and aromatic amines) that are more tightly bound to roots than predicted by the RCF because the sorption is related to biochemical bonding rather than to hydrophobic partitioning behavior. Binding to the roots for these compounds, such as aniline, nitrobenzene, catechol, and chlorobenzene, is irreversible (Dietz and Schnoor, 2001).

Subsurface Volatile Organic Compound Concentrations

Field investigations (Vroblesky and others, 1999, 2004; Schumacher and others, 2004) showed that the highest VOC concentrations in tree cores usually were found in trees growing above the highest ground-water or soil VOC concentrations, as indicated by samples from ground-water wells or soil-vapor surveys. Additional evidence for the correspondence between environmental VOC and tree-core VOC concentrations was shown in laboratory studies (Ma and Burken, 2002, 2003). Thus, it is clear that subsurface VOC concentrations can directly influence VOC concentrations in tree vascular tissues.

In one study, comparison of PCE concentrations in a number of tree-core samples and sediment samples 12 ft deep showed a linear relation for soil-PCE concentrations greater than 60 micrograms per kilogram (µg/kg) (Schumacher and others, 2004). Therefore, the PCE concentration in tree cores was found to be a good predictor of PCE concentrations in soil at 12 ft deep. In general, however, predictions of subsurface VOC concentrations based on tree-core results should be considered as a qualitative rather than quantitative relation and indicative of minimum concentrations.

In some cases, VOC concentrations in tree cores appear to correspond more closely to soil-gas VOC concentrations than to ground-water VOC concentrations (Schumacher and others, 2004). This finding raises the possibility that tree-core analysis may be useful as a rapid, inexpensive, relatively low-profile, non-intrusive reconnaissance tool to identify areas of potential vapor intrusion to be targeted by more definitive and cumbersome investigative approaches. In a limited study at the Nyanza Chemical Waste Dump Superfund Site, Massachusetts, tree cores were examined as a possible indicator of vapor intrusion (Vroblesky and others, 2006) (fig. 9). Trees N3, N5, and N8 contained TCE and were adjacent to buildings in which vapor intrusion by TCE had been identified.

In a separate study at the Durham Meadows Superfund Site, Connecticut (Vroblesky and others, 2008), TCA in tree trunks corresponded to TCA in soil gas, although the two studies were done 3 years apart (fig. 10). Thus, multiple studies

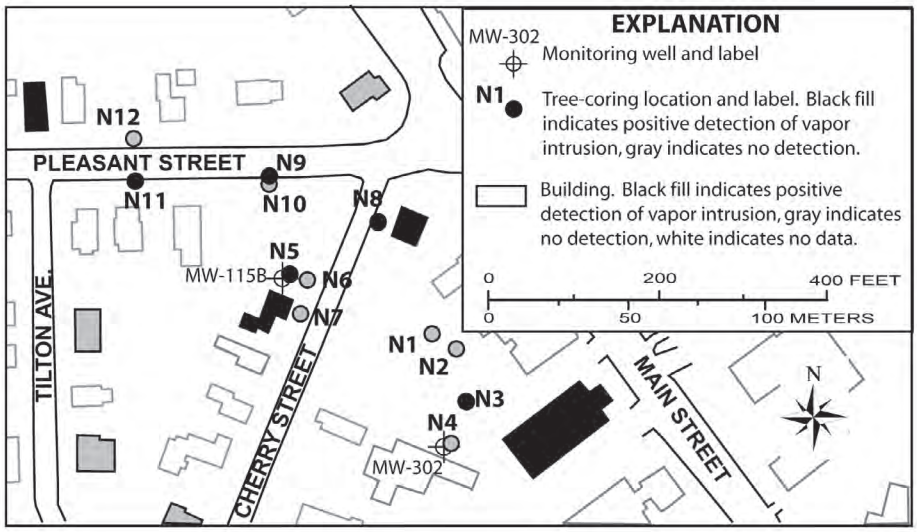

Figure 9. Trees cored at the Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts, August 2006 (modified from Vroblesky and others, 2006), showing proximity to wells and to buildings where vapor-intrusion investigations were conducted in 2004 (ICF Consulting, 2005).

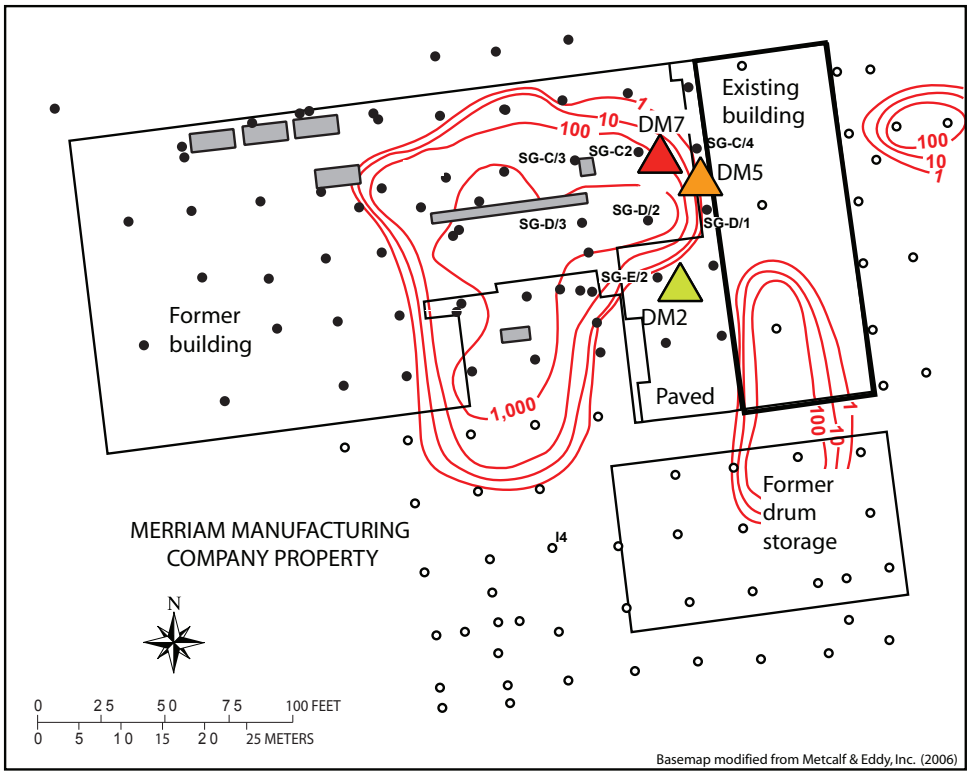

Figure 10. 1,1,1-Trichloroethane concentrations in tree cores in 2006 showing correspondence to the combined results of 2003 and 2006 soil-gas investigations at the Merriam Manufacturing Company property, Durham Meadows Superfund Site, Connecticut.

EXPLANATION

1 — 1,1,1-Trichlorethane in soil vapor, in parts per billion by volume , combination of soil gas surveys in 2003 and 2006 (Anni Loughlin, U.S. Environmental Protection Agency, written commun., February 2007)

DM2 — Tree containing less than 1.6 parts per billion by volume of 1,1,1-trichloroethane

DM5 — Tree containing 5.6 parts per billion by volume of 1,1,1-trichloroethane

DM7 — Tree containing 24 parts per billion by volume of 1,1,1-trichloroethane

Former areas of liquid storage in tanks and former paint booths

I4 — Soil-gas sampling point. Black indicates 2003 and open indicates 2006 sampling.

indicate that tree coring is a potential reconnaissance tool to identify areas of soil-gas and vapor-intrusion hazard.

Differences Among Tree Species

Plant utilization of ground water is partly dependent on plant species (Smith and others, 1991; Busch and others, 1992; Thorburn and Walker, 1994; Kolb and others, 1997). Studies also have shown that the degradation and bioavailability of contaminants in soil systems can vary with plant species (Shann and Boyle, 1994). In addition, comparisons of increment cores from trees of differing species growing near each other sometimes show VOC concentration differences that appear to be species-related. In a study in South Carolina (Vroblesky and others, 1999), oaks consistently contained less TCE than adjacent bald cypress or loblolly pines. In the same study, however, adjacent bald cypress and tupelo trees (*Nyssa* sp.) showed no significant differences in TCE concentrations from increment cores, indicating similar uptake of TCE. A possible contributing factor to the differences among some species is that conifers, such as bald cypress and loblolly pine, conduct water through more than the outermost growth ring, whereas in ring-porous trees (table 1), nearly all of the water is conducted through the outermost growth ring (Kozlowski and others, 1966; Ellmore and Ewers, 1986). Thus, the higher concentrations detected in conifers relative to the oaks may be because the cores, being of approximately equal length, incorporated more of the transpiration stream in conifers than in ring-porous trees. In another study, similar TCE concentrations were observed in increment cores in 1998 and 2000 from a willow (*Salix* sp.) and an eastern cottonwood (*Populus deltoides*) growing directly adjacent to each other (Vroblesky and others, 2004). Sorek and others (2008) found order of magnitude differences in TCE concentrations in a rosewood (*Dalbergia sissoo*) and laurel fig (*Ficus microcarpa*), despite comparatively small TCE concentration differences in the subsurface.

In one set of trees spaced within 30 ft of each other, Lewis (2001) found that the relative amount of TCE uptake among tested species appeared to follow the trend cottonwood (*Populus deltoides*) > Russian olive (*Elaeagnus angustifolia*) > poplar species (*Populus* sp.). There is some uncertainty with this conclusion, however, because of data limitations, such as the fact that only one of each species was compared, there were tree-diameter differences, and there were potential subsurface influences and spatial variations.

Rooting Depth and Depth to the Contaminated Horizon

Rooting depth, or the proximity of the roots to the contaminated horizon, is a factor that potentially can influence VOC uptake in trees. To some extent, rooting depth is species-dependent. Trees of different species (Ehleringer and others, 1991) and even different size trees of the same species (Dawson and Pate, 1996) can obtain water from different sources. Some species, such as poplars, and willows, are genetically predisposed to develop roots extending to the water table or capillary fringe at depths ranging from 3 to 40 ft (Negri and others, 2003). In general, however, trees with the capability to root deeply will do so only if there is a hydrologic need to do so. In rainy climates where there is adequate water available for the plants from the soil zone, rooting depth will be limited. In some cases, where the depth to ground water increases, there is a corresponding increase in rooting depth and decrease in the ground-water contribution to the plant water use (Sepaskhah and Karimi-Goghari, 2005).

Few studies have rigorously examined rooting depth because of the difficulty in uncovering roots. Descriptions of rooting depths vary widely. A study in the United Kingdom of five willows and five poplar clones in differing soil types showed that although the rooting depths were more than 4 ft, 75 to 95 percent of the roots were in the top 14 in. (Keller and others, 2003). A study in central Texas used DNA sequencing of roots in caves 16 to 213 ft deep to examine the rooting depth of various species (Jackson and others, 1999). The tested species were southern hackberry (*Celtsi laevigata*), ash juniper (*Juniperus ashei*), white shin oak (*Quercus sinuata*), Texas live oak (*Quercus fusiformis*), American elm (*Ulmus americana*), and cedar elm (*Ulmus crassifolia*), and represent approximately three-fourths of the woody plants comprising the studied ecosystem. At least six tree species grew roots deeper than 16 ft, but only Texas live oak was found below 32 ft. The maximum rooting depth for that ecosystem was about 82 ft. The oxygen 18 (^{18}O) isotopic signature for stem water from a live oak confirmed water uptake from a depth of 59 ft.

The degree to which the roots are in intimate contact with the contaminated horizon appears to be an important control on the amount of contaminant uptake. A study was conducted in Colorado to examine eastern cottonwood trees that were about the same diameter (Vroblesky and others, 2004). Vroblesky and others (2004) found that a core from an eastern cottonwood where the depth to TCE-contaminated ground water (200 µg/L TCE) was about 24 ft contained 99 ppbv of TCE. In contrast, the TCE concentrations were substantially higher (2,191 and 552 ppbv) in cores from two eastern cottonwoods growing at the bottom of a creek erosional channel where the ground water was less than 3 ft deep, despite the presence of only 29 to 39 µg/L TCE in the ground water. The data strongly imply that the percentage of transpiration uptake composed of contaminated water was higher in trees in the drainage ditch where the roots were in more close contact with the contaminated ground water than in the upland trees where the depth to water was about 24 ft.

Tree coring has been used in field investigations to successfully detect subsurface VOCs in areas where the ground water was 20 to 25 ft deep (Schumacher and others, 2004; Vroblesky and others, 2004) and 59 to 65 ft deep (Sorek and others, 2008). In some studies, however, poor quantitation between tree VOCs and ground-water VOCs was attributed to

a relatively large depth to water (Cox, 2002; Schumacher and others, 2004). The probable causes for the poor correlation in areas of large depth to water include the lack of intimate contact between the contaminated ground water and the tree roots, the potential for tree roots to obtain soil water from shallower horizons when it is available (Mensforth and others, 1994; Thorburn and Walker, 1994; Dawson and Pate, 1996; Jolly and Walker, 1996), and the diffusion of VOCs out of the roots during upward transport (Struckhoff, 2003). The decrease in TCE concentration with increasing depth to water is consistent with predictions from ground-water modeling (Wise, 1997) and from observations that ground water can provide less of a contribution to plant-water use when it is deep or when shallower soil moisture is available (Zencich and others, 2002; Sepaskhah and Karimi-Goghari, 2005).

Perhaps a more meaningful conceptualization of rooting depth is the depth of hydraulic influence of the roots. An example is the engineered phytoremediation site using hybrid poplar (*Populus deltiodes x Populus trichocarpa*) at Aberdeen Proving Ground, Maryland, where the depth to the water table is 5 to 15 ft (Hirsh and others, 2003). A ground-water study at the site showed that water use by the poplar trees induced upward ground-water hydraulic gradients toward the roots, with the depth of hydraulic influence extending to 25 ft (Schneider and others, 2002). Thus, in some environments, trees can induce movement of water and the associated dissolved contaminants upward to the roots from areas beyond the physical extent of the roots.

It should also be noted that sites that have ground water at a depth that appears to be beyond the reach of the tree roots still may be viable candidates for use of tree coring as a tool to investigate subsurface VOCs. Studies have shown that soil gas can be an effective transport mechanism of VOCs to tree roots (Struckhoff, 2003; Schumacher and others, 2004; Struckhoff and others 2005a, b) and may explain some of the VOC detections in tree cores where a relatively large depth to water was reported. Sorek and others (2008) found chlorinated solvents in tree cores where the depth to the contaminated ground water was 59–65 ft, and where the same chlorinated solvents were present as soil gas in the vadose zone. In addition, hydraulic lift has the potential to transport contaminants from deeper to shallower parts of the soil where the water and solutes can be accessed by shallower rooted species. Hydraulic lift is a process by which differences in water potential allow trees to derive water from deep, wet roots and lose water through shallow dry roots. (Richards and Caldwell, 1987; Caldwell and others, 1998). Finally, tree roots tap the ground water indirectly by extending into the capillary fringe. Thus, in areas where the capillary fringe is large, tree roots can derive water from the ground water even when they appear to be too shallow to access it.

Subsurface Lithology

The subsurface lithology can have an influence on the ability of trees to be useful tools for examining VOCs in ground-water contamination. In general, tree roots extend to the depth necessary to maintain a water supply adequate for growth. If a confined contaminated aquifer is overlain by an unconfined uncontaminated aquifer, then it is unlikely that the trees will be useful indicators of the contamination because sufficient water can be obtained from a shallower source. If the confining layer is absent, however, then it is possible that the trees can sample the contaminated ground water, despite the fact that the contaminated ground water is overlain by a veneer of uncontaminated ground water. Field investigations found that roots from poplar trees induced upward hydraulic gradients toward the roots (Schneider and others, 2002; Hirsh and others, 2003).

The presence of a confining layer does not necessarily limit the use of tree coring as a tool for examining subsurface VOCs. A study in South Carolina examined the TCE concentrations in tree cores growing above a confined TCE-contaminated aquifer where a 9- to 10-ft-thick tight clay confining layer extended to land surface. In this case, the availability of shallow ground water for use by the trees was limited by presence of the clay. The roots of the trees in this area extended to the aquifer below the clay in order to maintain adequate water supply, as evidenced by the presence of live roots in multiple sediment cores below the clay (Vroblesky and others, 2007a). Despite the fact that the contaminated aquifer was confined beneath about 9 to 10 ft of tight clay, the distribution of trees containing TCE in tree cores closely matched the distribution of ground-water contamination (Vroblesky and others, 2004). The concept of tree roots seeking out sources of adequate water supply indicates that in fractured-rock environments where there is little saturated overburden, tree roots will preferentially sample the water-bearing fracture zones, potentially optimizing their use as indicators of shallow ground-water contamination in this hydraulically complex setting.

Concentration Differences Around the Tree Trunk

Studies have reported VOC concentration variations from cores collected on different sides of the same tree trunk (Vroblesky and others, 1999, 2004; Lewis, 2001; Schumacher and others, 2004; Sorek and others, 2008). Vroblesky and others (1999) found concentration differences ranging from 44 to 92 percent for TCE and from 6 to 90 percent for *c*DCE in cypress trees. The same trees, however, showed relatively good replication for cores collected 1 in. (approximately 25 millimeters (mm) apart (15.5 percent for TCE and 2.5 percent for *c*DCE), indicating that the coring approach did not contribute significant inconsistencies to the data. Schumacher and others (2004) found three- to five-fold differences in PCE concentrations around some tree trunks. Sorek and others (2008) found VOC concentration variations up to a factor of about 5 from differing sides of the same tree at the same height.

A variety of factors potentially can contribute to such directional variations, including injuries (Scholander and others, 1957), disease and insect damage (Kozlowski and

Pallardy, 1997), gas embolisms (Clark and Gibbs, 1957), and spiral transport up the trunk (Kozlowski and others, 1967; Schumacher and others, 2004). In some situations, however, directional differences in tree-core VOC concentrations are caused by variations in subsurface VOC concentrations taken up by root systems on differing sides of the tree (Vroblesky and others, 1999). A study of loblolly pines (*Pinus taeda*) showed that TCE concentrations in cores from a tree near the edge of a ground-water contamination plume were 61 to 68 percent lower on the sides of the tree facing away from the axis of contamination than on the sides of the tree facing toward the axis of contamination (Vroblesky and others, 2004). The data indicate that in some cases, the direction of the highest VOC concentration in a tree trunk may be an indicator of the direction toward the greatest subsurface VOC concentrations. Caution should be exercised with this approach, however, because of the potential for spiral transport up the trunk and other influences cited above (Kozlowski and others, 1967; Schumacher and others, 2004).

Volatilization Losses from the Tree Trunk

VOC concentration decreases up the trunk of a tree have been observed in some studies (Vroblesky and others, 1999; Schumacher and others, 2004). These changes may be caused by a variety of factors. In the first investigation using tree coring as a tool to examine ground-water VOC concentrations, a decrease in TCE concentration with height up a tree trunk was observed and hypothesized to be caused by volatilization loss through the bark (Vroblesky and others, 1999). Subsequently, laboratory and field investigations confirmed that volatilization loss through the bark can be a major mechanism for transfer of VOCs to the atmosphere (Davis and others, 1999; Burken, 2001; Ma and Burken, 2003), and upward decreases in concentration also were observed in an additional field investigation (Hirsh and others, 2003). One laboratory experiment utilized diffusion traps to capture VOCs leaking from stems and found that TCE leaked through the stems and in all cases, the amount of TCE in the uppermost traps was less than in the lowermost traps, indicating TCE loss up the trunk (Ma and Burken, 2003). VOC loss also can occur from the roots (Struckhoff, 2003). An additional effect of volatilization loss from the tree trunk is that VOC concentrations in the trunk sometimes decrease from the inner to the outer part of the trunk (Ma and Burken, 2003). Thus, in some cases, higher VOC concentrations may be obtained by coring deep into the tree rather than by collecting only the outermost rings.

The rate of diffusive loss from tree trunks may be influenced by the diameter of the trunk. Struckhoff (2003) found that a 0.5-in.-diameter poplar cutting planted in contaminated soil or water has a 24-percent concentration loss in 5 in. of height, whereas a 6.5-in.-diameter Chinese elm (*Ulmus parvifolia*) showed the same percent loss in 5 ft of height. The author concluded that the greater surface area to volume ratio in a smaller diameter section of tree will more quickly deplete the reservoir of PCE in the trunk. In support of this conclusion, Schumacher and others (2004) found that diffusion loss of PCE in small (0.5-in. diameter) trees occurred at a rate more than 10 times higher than in trees 6.5 in. in diameter.

Decreases in the VOC content of tree cores with increasing height up the trunk have not been observed at all sites (Vroblesky and others, 2004; Sorek and others, 2008). At a site in Texas, an upward increase in tree-core TCE concentrations was observed following a heavy rain (Vroblesky and others, 2004). The concentration increases up the tree appeared to represent a time series of water movement, with the lowest part of the trunk representing TCE-contaminated ground water diluted with infiltrating rainwater, and the upper parts of the tree representing pre-rain undiluted ground water. Thus, concentration changes up the trunk may be caused by a variety of factors. Consequently, a prudent approach when conducting a site survey to examine areal distribution of VOCs in tree cores is to collect all cores from the same height.

Rainfall Infiltration as a Dilution Mechanism

Plant utilization of ground water and uptake of groundwater contaminants depends partly on the reliability of rainfall. In areas where rainfall is unreliable, riparian trees may develop roots primarily in the capillary fringe and phreatic zone rather than throughout the soil profile (Ehleringer and Dawson, 1992), thus primarily utilizing ground water. Fremont cottonwood (*Populus fremontii*) and Goodding's willow (*Salix gooddingii*) growing along streams in western Arizona used ground water throughout the growing season regardless of the depth to water (Busch and others, 1992). Plants with roots disseminated in multiple soil zones may use various combinations of ground water, rainfall infiltrate, and stream water, sometimes responding opportunistically to rainfall events (Mensforth and others, 1994; Thorburn and Walker, 1994; Dawson and Pate, 1996; Jolly and Walker, 1996). Trees near a perennial stream in California used shallow soil water early in the growing season and then primarily used ground water in the later part of the season when the soil dried (Smith and others, 1991). Mature box elder (*Acer negundo*) trees used only ground water and did not seem to use perennial stream water or shallow soil water in northern Utah (Dawson and Ehleringer, 1991), but they did use soil water from precipitation at ephemeral and perennial stream reaches in Arizona (Kolb and others, 1997).

The potential for source water to trees to be affected by rainfall infiltration indicates that the VOC concentrations detected in cores from trees growing above contaminated ground water also may be affected by mixing with various water sources. For example, Doucette and others (2003) reported that TCE concentrations in plant tissue at Hill Air Force Base, Utah, where the climate is arid, were 10 to 100 times higher than at Cape Canaveral Air Station, Florida, where the climate is humid and rainy, despite similar TCE ground-water concentrations at both sites. The authors hypothesized that the TCE concentration difference in tree cores between the two sites was due to greater dilution effects

from rainfall at the Florida site than at the Utah site. It also is possible, however, that the difference could be due to the difference in sample-collection methods and analytical variability. Methanol extraction coupled with PT gas chromatography was used to analyze the Florida plant tissue, whereas HAS gas chromatography was used to analyze Utah plant tissue.

To determine the influence on VOC concentrations in tree cores of rainfall incorporation into transpiration stream, a field test was conducted using artificial irrigation of a mature cottonwood tree in Texas (Clinton and others, 2004; Vroblesky and others, 2004). The test involved measuring transpiration and tree-core TCE concentrations before and after irrigating the tree. The results showed rapid TCE concentration decreases and maximum transpiration value increases following the artificial irrigation. These data indicate that the uptake of irrigation water resulted in a rapid dilution of TCE concentrations in the trunk. Thus, VOC concentrations in tree cores collected after a rainfall may be less than before the rainfall. A possible exception to this may occur if the rainfall mobilizes contamination in the unsaturated zone.

Seasonal Influences

Clear seasonal trends in VOC concentration of tree cores has been observed in recent studies (Trapp and others, 2007; Sorek and others, 2008). Much higher TCE concentrations in the trees were recorded in the dry hot season than in the wet cold season. Other tree-coring investigations have shown concentration changes possibly related to seasonal influences. The TCE concentrations in bald cypress trees in South Carolina decreased from July to September to January (Vroblesky and others, 1999). Lewis (2001) reported that tree cores from cottonwoods and Russian olive trees contained significantly higher TCE in June 2000 and June 2001 than in the winter or even in May or late June to July of the same years. Thus, it appears that in some cases there are seasonal VOC concentration differences in trees with higher concentrations during the summer than the winter.

Controlled mesocosm experiments have shown that TCE flux to the atmosphere by transpiration of bald cypress seedlings is influenced diurnally and seasonally (Nietch and others, 1999). The flux decreased from day to night, probably because the stomata are closed at night (fig. 11). TCE flux also decreased from June to December as transpirative water use seasonally decreased (fig. 11). Interestingly, the study found that although the winter TCE flux was reduced relative to the summer flux, there was still significant TCE flux in the winter, implying that trees do not need to be conducting substantial amounts of water to remove TCE from the ground water.

Although seasonal variations in tree-core VOC concentrations sometimes are present, the seasonal variations do not appear to prevent the use of the tree coring as a tool to investigate subsurface VOC concentrations during winter months. The TCE concentrations in cores from a pine and an oak tree in Ashland, Massachusetts, were 17 ppbv in late August 2006 (Vroblesky and others, 2006), and approximately the same amount (14 and 18 ppbv, respectively) at the end of November 2006, after the leaves had fallen (Scott Clifford, U.S. Environmental Protection Agency, written commun., 2006). In addition, winter (February) tree cores provided the data that were successfully used in the first study to use tree cores as a tool to map subsurface VOCs (Vroblesky and others, 1999). Additional work is needed to fully understand the seasonal influences on tree-core sampling for VOCs.

Sorption

Organic compounds such as TCE have a tendency to sorb to plant tissue (Davis and others, 1998a). Newman and others (1997) found that a small percentage (3 to 4 percent) of TCE remained as an insoluble residue in poplar tree cells. Other

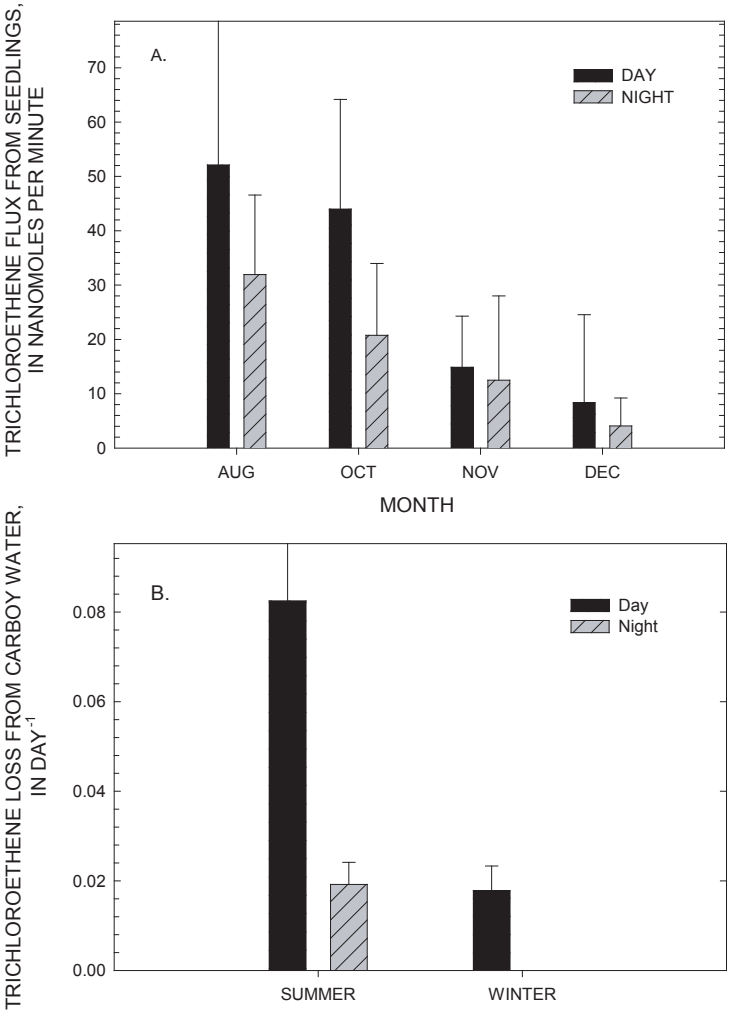

Figure 11. Trichloroethene removal from the rhizosphere of bald cypress seedlings as (A) nanomoles per minute through the aboveground part of the plant and (B) fractional trichloroethene loss from carboy water during the summer and winter (modified from Nietch and others, 1999).

investigations found that the predominant mass of VOCs in tree trunks may reside in the wood tissue (Ma and Burken, 2002, 2003; Struckhoff, 2003; Schumacher and others, 2004) with a greater amount of sorption in more lignified tissues, such as poplar trees, relative to young sunflower plants (*Helianthus annuus*) (Davis and others, 1998b). Thus, sorption of VOCs to the wood of the tree may be an important influence on tree-core VOC concentrations (Schumacher and others, 2004).

Sorption of VOCs onto wood is related to the compound Henry's Law constant and vapor pressure (Ma and Burken, 2002) and to the lipophilicity of the compounds, expressed as log K_{ow} (Trapp and others, 2001). In general, chlorinated hydrocarbons tend to be partly excluded or sorbed within plants, ethers are only slightly excluded or sorbed, and less polar gasoline constituents are more strongly excluded or sorbed than TCE (Burken, 1996; Makepeace and others, 1996; Davis and others, 1998a). The sorption of TCE is considerably stronger than that of TCA despite the greater log K_{ow} of TCA (Davis and others, 1998b). Chloroform and dichloromethane tend to be weakly sorbing compounds (Davis and others, 1998a).

Approaches to quantifying sorption of VOCs onto wood include examining the equilibrium distribution of VOCs between tree tissue and water (K_{wood}). Higher K_{wood} values indicate higher potential for sorption. Mackay and Gschwend (2000) measured sorption of benzene, toluene, and *o*-xylene to wood and found that the K_{wood} coefficients were between 6.6 and 28 milligrams per gram (mg/g) of dry wood to milligrams per milliliter of water, indicating a relatively high sorption capacity of wood. They also found that the sorption is linear and reversible.

Within-Tree Volatile Organic Compound Degradation

Phytodegradation, or the breakdown of organic contaminants within tree tissue, can take place inside the plant or within the rhizospere of the plant (Newman and Reynolds, 2004; Vroblesky and others, 2004). A study of willow and poplar trees used as a polishing step for mitigating a chlorinated solvent plume showed the presence in tree tissue of parent chlorinated ethenes and chloroacetic acids (oxidative transformation products), indicating the uptake and phytodegradation of the contaminants (Nzengung, 2005). Intermediate stable metabolites, apparently from the breakdown of chlorinated solvents, have been reported in various tree species growing above contaminated soils (Newman and others, 1997; Compton and others, 1998; Doucette and others, 1998; Gordon and others, 1998). The presence of intermediate degradation products and mass-balance considerations suggest that MTBE degradation may take place in mature trees (Rubin, 2007). Newman and others (1997) found that cells from poplar trees are capable of transforming and mineralizing TCE without the involvement of microbial metabolism. Vroblesky and others (2004) found that the tree-core TCE and *c*DCE distribution between the inner and outer parts of the trunk of a narrow-leaf cottonwood (*Populus angustifolia* James) tree core from Colorado was consistent with microbial dehalogenation of TCE within the apparently methanogenic conditions of the wetwood of the inner trunk. Wetwood conditions are caused by an infestation in the tree of methanogenic and other bacteria in the tree heartwood (Stankewich and others, 1971; Zeikus and Ward, 1974). Methanogenic conditions are associated with efficient dehalogenation of TCE to *c*DCE (Parsons and others, 1984, 1985; Kloepfer and others, 1985; Wilson and others, 1986). The data from a variety of investigations indicate that some level of VOC degradation can take place within the tree or rhizosphere. Phytodegradation that takes place in the rhizosphere, roots, or trunks of trees has the potential to reduce or alter the VOC concentrations detected in tree cores.

Summary

This manual provides a guide to the use of tree coring as a tool to examine subsurface VOCs. It examines some of the factors influencing the use of tree coring for that purpose and summarizes some case studies in which tree coring has been used to examine subsurface VOCs. Typical VOCs that have been detected in tree cores include benzene, toluene, ethylbenzene, xylene isomers, trimethyl benzene, MTBE, TCE, PCE, and *c*DCE. The method is inexpensive, portable, rapid, and uncomplicated. The presence of VOCs in tree cores is a strong indicator of subsurface VOC contamination; however, the lack of VOC detection does not necessarily mean that VOC contamination is not present.

Tree cores are obtained by use of a clean and sharp increment borer. The boring should be started slowly and carefully to avoid sideways slippage of the bit against the tree trunk. The core is removed from the borer by means of an extractor. The core should be transferred to a vial and sealed immediately upon recovery from the tree. The headspace in the vials should be given enough time to equilibrate with the VOCs in the tree core prior to analysis, typically about 24 hours for storage at room temperature to about 5 to 15 minutes for field-heated cores. Diffusion of TCE from the tree cores to the headspace in sample vials is fast enough, however, that analysis of unheated cores after 5 minutes can contain sufficient TCE to indicate the presence of TCE contamination. Core analysis can be performed using a variety of approaches, but HSA by gas chromatography often is the simplest approach. Quality control and assurance samples should be collected to ensure the integrity of the data.

A variety of factors influence the ability of plants to be useful indictors of ground-water VOC contamination. These factors include the type of VOC, the tree species, the rooting depth, aqueous concentrations, the depth to water, concentration differences around the trunk related to different sources of subsurface VOCs, concentration differences with

depth of coring related to volatilization loss through the bark and possibly other unknown factors, dilution by rain, seasonal influences, sorption, and within-tree VOC degradation.

References Cited

Azevedo, J.L., Maccheroni, Walter, Jr., Pereira, J.O., and de Araujo, W.L., 2000, Ednophytic microorganisms—A review on insect control and recent advances on tropical plants: Environmental Biotechnology, v. 3, no. 1, accessed January 12, 2006, at *http://www.ejbiotechnology.info/content/vol3/issue1/full/4/index.html*

Briggs, G.G., Bromilow, R.H., and Evans, A.A., 1982, Relationships between lipophicity and root uptake and translocation of non-ionized chemicals by barley: Pesticide Science, v. 13, p. 495–504.

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

Brown, K., Tyner, L., Grainger, D., and Perina, T., 2001, Impact of natural attenuation and phytoremediation on MTBE and fuel, *in* Magar, V., Gibbs, J.T., O'Reilly, K.T., Hyman, M.R., and Leeson, A., eds., Bioremediation of MTBE, alcohols, and ether, Sixth International In Situ and On-Site Bioremediation Symposium, June 4–7, 2001, San Diego, California: Columbus, Ohio, Battelle Press.

Burken, J.G., 1996, Uptake and fate of organic contaminants by poplar trees: Iowa City, Iowa, University of Iowa, Ph. D. dissertation, 215 p.

Burken, J.G., 2001, Uptake and volatilization of chlorinated solvents by poplars at field scale, *in* Leeson, A., Foote, E.A., Banks, M.K., and Magar, V.S., eds., Phytoremediation, wetlands and sediments: Columbus, Ohio, Batelle Press, p. 113–120.

Burken, J.G., and Schnoor, J.L., 1998, Predictive relationships for uptake of organic contaminants by hybrid poplar trees: Environmental Science and Technology, v. 32, p. 3379–3385.

Busch, D.E., Ingraham, N.L., and Smith, S.D., 1992, Water uptake in woody riparian phreatophytes of the southwestern United States—A stable isotope study: Ecological Applications, v. 2, p. 450–459.

Caldwell, M.M., Dawson, T.E., and Richards, J.H., 1998, Hydraulic lift—Consequences of water efflux for the roots of plants, Oecologia, v. 113, p. 151–161.

Castelfranco, P., Foy, C.L., and Deutsch, D.B., 1961, Non-enzymatic detoxification of 2-chloro-4,6-bis(ethylamino)-*s*-triazine (simazine) by extracts of *Zea Mays*: Weeds, v. 9, p. 580–591.

Chaney, W.R., 2000, Water and chemical movement beneath the bark: The Woodland Steward, Spring 2000, v. 9, no. 1, downloaded from *http://www.fnr.purdue.edu/inwood/past%20issues/WATERANDCHEMICAL.htm* (accessed on November 1, 2007).

Clark, J., and Gibbs, R.D., 1957, Studies in tree physiology, IV, Further investigations of seasonal changes in moisture content of certain Canadian forest trees: Canadian Journal of Botany, v. 35, p. 219–253.

Clinton, B.D., Vose, J.M., Vroblesky, D.A., and Harvey, G.J., 2004, Determination of the relative uptake of ground vs. surface water by *Populus deltoides* during phytoremediation: International Journal of Phytoremediation, v. 6, no. 3, p. 239–252.

Compton, H.R., Haroski, D.M., Hirsh, S.R., and Wrobel, J.G., 1998, Pilot-scale use of trees to address VOC contamination, *in* Wickramanayake, G.B., and Hinchee, R.E., eds., Bioremediation and Phytoremediation, First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 18–21, 1998, Monterey, California: Columbus, Ohio, Battelle Press, p. 245–249.

Cox, S.E., 2002, Preliminary assessment of using tree-tissue analysis and passive-diffusion samplers to evaluate trichloroethene contamination of ground water at Site SS–34N, McChord Air Force Base, Washington, 2001: U.S. Geological Survey Water-Resources Investigations Report 02–4274, 13 p.

Davis, L.C., Banks, M.K., Schwab, A.P., Muralidharan, N., Erickson, L.E., and Tracy, J.C., 1996, Plant based bioremediation, *in* Sikdar, S.K., and Irvine, R.L., eds., Bioremediation: Lancaster, Pennsylvania, Technomics Publishing Company.

Davis, L.C., Erickson, L.E., Narayanan, M., and Zhang, Q., 2003, Modeling and design of phytoremediation, *in* McCutheon, S.C., and Schnoor, J.L., eds., Phytoremediation—Transformation and control of contaminants: Hoboken, New Jersey, John Wiley and Sons, Inc., p. 663–694.

Davis, L.C., Lupher, D., Hu, J., and Erickson, L.E., 1999, Transport of trichloroethylene through living plant tissues, *in* Proceedings of the 1999 Conference on Hazardous Waste Research, St. Louis, Missouri, May 24–27, 1999, p. 203–209.

Davis, L.C., Vanderhoof, S., Dana, J., Selk, K., Smith, K., Goplen, B., and Erickson, L.E., 1998b, Chlorinated solvent movement through plants monitored by Fourier transform infrared (FT–IR) spectroscopy: Journal of Hazardous Substances Research, v. 1, no. 4, p. 1–26.

Davis, L.C., Vanderhoof, S., and Lupher, D., 1998a, Sorption of trichloroethylene (TCE) and other halogenated aliphatics on plant materials, *in* Erickson, L.E., and Rankin, M.M., eds., Proceedings of the 1998 Conference on Hazardous Waste Research, Kansas State University, Manhattan, Kansas, p. 319–325.

Dawson, T.E., and Ehleringer, J.R., 1991, Streamside trees that do not use stream water: Nature, v. 350, p. 335–337.

Dawson, T.E., and Pate, J.S., 1996, Seasonal water uptake and movement in root systems of phreatophytic plants of dimorphic root morphology—A stable isotope investigation: Oecologia, v. 107, p. 13–20.

Dettenmaier, E.M., Doucette, W.J., Bugbee, B., and Hall, A., 2008, Reexamining the relationship between plant uptake of organic chemicals and octanol water partition coefficients, *in* Platform Abstracts of the Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 19–22, 2008, Monterey, California: Columbus, Ohio, Battelle Press, session B6.

Dietz, A.C., and Schnoor, J.L., 2001, Advances in bioremediation: Environmental Health Perspectives, v. 109, supplement 1, p. 163–168.

Doucette, W.J., Bugbee, B., Hayhurst, S., Plaehn, W., Downey, D., Taffinder, A., and Edwards, R., 1998, Phytoremediation of dissolved-phase trichloroethylene using mature vegetation, *in* Wickramanayake, G.B., and Hinchee, R.E., eds., Bioremediation and Phytoremediation, First International Conference on Remediation and Recalcitrant Compounds, May 18–21, 1998, Monterey, California: Columbus, Ohio, Battelle Press, p. 251–256.

Doucette, W.J., Bugbee, G.B., Smith, S.C., Pajak, C.J., and Ginn, J.S., 2003, Uptake, metabolism, and phytovolatilization of trichloroethylene by indigenous vegetation—Impact of precipitation, *in* McCutcheon, S.C., and Schnoor, J.L., eds., Phytoremediation—Transformation and control of contaminants: Hoboken, New Jersey, John Wiley and Sons, Inc., p. 561–588.

Douglass, A.E., 1919, Climatic cycles and tree growth: Carnegie Institute of Washington Publication Number 289, v. 1, 127 p.

Eckstein, D., and Dujesiefken, D., 1999, Long-term effects in trees due to increment borings.: Dendrochronologia, v. 16–17, p. 205–211.

Ehleringer, J.R., and Dawson, T.E., 1992, Water uptake by plants—Perspectives from stable isotope composition: Plant, Cell, and Environment, v. 15, p. 1073–1082.

Ehleringer, J.R., Philips, S.L., Schuster, W.F.S., and Sandquist, D.R., 1991, Differential utilization of summer rains by desert plants: Oecologia, v. 88, p. 430–434.

Ellmore, G.S., and Ewers, F.W., 1986, Fluid flow in the outermost xylem increment of a ring-porous tree, *Ulmus americana*: American Journal of Botany, v. 73, no. 12, p. 1771–1774.

Gopalakrishnan, Gayathri, Negri, M.C., Minsker, B.S., and Werth, C.J., 2005, Monitoring soil and ground water plumes using trees in an existing phytoremediation system: Presented at the 3rd International Phytotechnologies Conference, April 19–22, 2005, sponsored by The U.S. Environmental Protection Agency and the Midwest Hazardous Substance Research Center, Atlanta, Georgia.

Gopalakrishnan, Gayathri, Negri, M.C., Minsker, B.S., and Werth, C.J., 2007, Monitoring subsurface contamination using tree branches: Ground Water Monitoring and Remediation, v. 27, no. 1, p. 65–74.

Gordon, M., Choe, N., Duffy, J., Ekuan, G., Heilman, P., Muiznieks, I., Ruszaj, M., Shurtleff, B., Strand, S., Wilmot, J., and Newman, L., 1998, Phytoremediation of trichloroethylene with hybrid poplars: Environmental Health Perspective, v. 106, no. 4, p. 1001–1004.

Grissino-Mayer, Henri, 2003, A manual and tutorial for the proper use of an increment borer: Tree-Ring Research, v. 59, no. 2, p. 63–79.

Hart, J.H., and Wargo, P.M., 1965, Increment borer wounds—penetration points for *Ceratocystis fagacearum*: Journal of Forestry, v. 63, no. 1, p. 38–39.

Hepting, G.H., Roth, E.R., and Sleeth, B., 1949, Discoloration and decay from increment borings: Journal of Forestry, v. 47, p. 366–370.

Heyerdahl, E.K., and McKay, S.J., 2001, Condition of live fire-scarred ponderosa pine trees six years after removing partial cross sections: Tree-Ring Research, v. 57, p. 131–139.

Hirsh, S.R., Compton, H.R., Matey, D.H., Wrobel, J.G., and Schneider, W.H., 2003, Five-year pilot study, Aberdeen Proving Ground, Maryland, *in* McCutheon, S.C., and Schnoor, J.L., eds., Phytoremediation—Transformation and control of contaminants: Hoboken, New Jersey, John Wiley and Sons, Inc., p. 635–659.

Hong, M.S., Rarmayan, W.F., Dortch, I.J., and Chiang, C.Y., 2001, Phytoremediation of MTBE from a groundwater plume: Environmental Science and Technology, v. 35, no. 6, p. 1231–1239.

ICF Consulting, 2005, Indoor air human health risk assessment, Nyanza Chemical Waste Dump Superfund Site Operable Unit II, Ashland, Massachusetts: Consultant's report to the U.S. Army Corps of Engineers, New England District, October 25, 2005 [variously paged].

Inoue, J., Chamberlain, K., and Vromilow, R.H., 1998, Physiochemical factors affecting the uptake by roots and translocation to shoots of amine bases in barley: Pesticide Science, v. 54, p. 8–21.

Jackson, R.B., Moore, L.A., Hoffmann, W.A., Pockman, W.T., and Linder, C.R., 1999, Ecosystem rooting depth determined with caves and DNA: Proceedings of the National Academy of Sciences of the United States of America, v. 96, p. 11387–11392.

Jolly, I.D., and Walker, G.R., 1996, Is the field water use of *Eucalyptus largiflorens* F. Meull affected by short-term flooding?: Australian Journal of Ecology, v. 21, p. 173–183.

Keller, C., Hammer, D., Kayser, A., Richneer, W., Brodbeck, M., and Sennhauser, M., 2003, Root development and heavy metal phytoextraction efficiency—Comparison of different plant species in the field: Plant Soil, v. 249, p. 67.

Kelso, P.W., 2005, An innovative field-based analytical method for low-level detection of chlorinated compounds in groundwater and soil samples (The Color-Tec Method); accessed June 13, 2008, at *http://www.clu-in.org/conf/tio/pasi/colortec_description.pdf*

Kloepfer, R.D., Easley, B.B., Haas, B.B., Jr., Deihl, T.G., Jackson, D.E., and Wurrey, C.J., 1985, Anaerobic degradation of trichloroethylene in soil: Environmental Science and Technology, v. 19, no. 3, p. 277–280.

Kolb, T.E., Hart, S.C., and Amundson, R., 1997, Boxelder water source and physiology at perennial and ephemeral stream sites in Arizona: Tree Physiology, v. 17, p. 151–160.

Kozlowski, T.T., Hughes, J.F., and Leyton, L., 1966, Patterns of water movement in dormant gymnosperm seedlings: Biorheology, v. 3, p. 77–85.

Kozlowski, T.T., Hughes, J.F., and Leyton, L., 1967, Dye movement in gynmosperms in relation to tracheid alignment: Forestry, v. 40, p. 209–227.

Kozlowski, T.T., and Pallardy, S.G., 1997, Physiology of woody plants (2d ed.): San Diego, California, Academic Press, 411 p.

Landmeyer, J.E., Bradley, P.M., and Vroblesky, D.A., 2000, MTBE in trees transpiring gasoline-contaminated ground water, presented at the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 22–25, 2000, Monterey, California: Columbus, Ohio, Battelle Press.

Lewis, Kerry, 2001, The relationship between tree-core and groundwater trichloroethylene concentrations for groundwater plume delineation: Logan, Utah, Utah State University, Department of Environmental Engineering, M.S. thesis, 188 p.

Lewis, K., Doucette, W., Bugbee, B., and Ginn, J., 2001, Relationship between trichloroethylene concentrations in tree cores and ground water for plume delineation, *in* Proceedings of the Society of Toxicology and Environmental Chemistry (SETAC) 22nd Annual Meeting Abstract Book, November 11–15, 2001, Baltimore, Maryland.

Lockheed Martin, 2000, J-Field phytoremediation project—Field events and activities through July 31, 2000, Aberdeen Proving Ground, Edgewood, Maryland, August 31, 2000: Consultant's report to the U.S. Environmental Protection Agency, 28 p.

Lorenz, R.C., 1944, Discoloration and decay resulting from increment borings in hardwoods: Journal of Forestry, v. 42, p. 37–43.

Ma, X., and Burken, J.G., 2002, VOCs fate and partitioning in vegetation—Use of tree cores in groundwater analysis: Environmental Science and Technology, v. 36, no. 21, p. 4663–4668.

Ma, X., and Burken, J.G., 2003, TCE diffusion to the atmosphere in phytoremediation applications: Environmental Science and Technology, v. 37, p. 2534–2539.

Mackay, A.A., and Gschwend, P.M., 2000, Sorption of monoaromatic hydrocarbons to wood: Environmental Science and Technology, v. 34, no. 5, p. 839–845.

Maeglin, R.R., 1979, Increment cores, how to collect, handle, and use them: Madison, Wisconsin, U.S. Department of Agriculture, Forest Service General Technical Report FPL 25, 18 p.

Makepeace, V.D., Davis, L.C., Dana, J., Selk, K., Smith, K., Hammaker, R.M., Fateley, W.G., and Erickson, L.E., 1996, Measuring contaminant flux through plants by fourier transform infrared (FT–IR) spectrometry, *in* Proceedings of the HSRC/WERC Joint Conference on the Environment, May 21–23, 1996, Albuquerque, New Mexico: Manhattan Kansas, Kansas State University, p. 577–582.

Mensforth, L.J., Thorburn, P.J., Tyerman, S.D., and Walker, G.R., 1994, Sources of water used by riparian *Eucalyptus camaldulensis* overlying highly saline ground water: Oecologia, v. 100, p. 21–28.

Metcalf & Eddy, Inc., 2006, Technical memorandum for site-wide shallow groundwater investigation, final, Durham Meadows Superfund Site, Durham, Connecticut: Consultant's report to the U.S. Environmental Protection Agency, November 2006 [variously paged].

Meyer, W.H., and Hayward S.B., 1936, Effect of increment coring on Douglas-fir: Journal of Forestry, v. 34, p. 867–869.

Narayanan, M.N., Erickson, L.E., and Davis, L.C., 2004, Simple plant-based design strategies for volatile organic pollutants: Environmental Progress, v. 18, no. 4, p. 231–242.

Negri, M.C., Gatliff, E.G., Quinn, J.J., and Hinchman, R.R., 2003, Root development and rooting at depths, *in* McCutheon, S.C., and Schnoor, J.L., eds., Phytoremediation—Transformation and control of contaminants: Hoboken, New Jersey, John Wiley and Sons, Inc., p. 233–262.

Newman, L.A., and Reynolds, C.M., 2004, Phytodegradation of organic compounds: Current Opinion in Biotechnology, v. 1, no. 3, p. 225–230.

Newman, L.A., Strand, S.E., Duffy, J., Choe, Nami, Ekuan, G., Ruszaj, M., Shurtleff, B.B., Wilmoth, J., Heilman, P., and Gordon, M.P., 1997, Uptake and biotransformation of trichloroethylene by hybrid poplars: Environmental Science and Technology, v. 31, no. 4, p. 1062–1067.

Nietch, C.T., Morris, J.T., and Vroblesky, D.A., 1999, Biophysical mechanisms of trichloroethene uptake and loss in bald cypress growing in shallow contaminated ground water: Environmental Science and Technology, v. 33, no. 17, p. 2899–2904.

Nilsen, E.T., and Orcutt, D.M., 1996, Physiology of plants under stress: New York, New York, John Wiley and Sons, 704 p.

Nzengung, V.A., 2005, Case studies of phytoremediation of petrochemicals and chlorinated solvents in soil and ground water, *in* Hatcher, K.J., ed., Proceedings of the 2005 Georgia Water Resources Conference, April 25–27, 2005, Athens, Georgia.

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

Parfitt, D.G., Arnold, C., and Kaltreider, M., 2000, Root uptake and transpiration of gasoline oxygenates by *Pinus radiata* [abst.]: Tenth Annual West Coast Conference on Contaminated Soils and Groundwater, March 20–23, 2000, San Diego, California.

Parsons, F., Lage, G.B., and Rice, R., 1985, Biotransformation of chlorinated organic solvents in static microcosms: Environmental Toxicology and Chemistry, v. 4, p. 739–742.

Parsons, F., Wood, P.R., and DeMarco, J., 1984, Transformation of tetrachloroethene and trichloroethene in microcosms and ground water: Journal of the American Water Works Association, v. 72, no. 2, p. 56–59.

Ramaswami, A., and Rubin, A., 2001, Measuring phytoremediation parameters for volatile organic compounds—Focus on MTBE: Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, July 2001, p. 123–129.

Richards, J.H., and Caldwell, M.M., 1987, Hydraulic lift—Substantial nocturnal water transport between soil layers by *Artemesia tridentate* roots: Oecologia, v. 73, p. 486–489.

Roy F. Weston, Inc., 2000, Electronic map of Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts, filename MAPPH.DWG, November 2005.

Rubin, E.G., 2007, Evidence for phytodegradation of MTBE from coupled bench-scale and intermediate-scale tests: Journal of Environmental Engineering, v. 133, no. 4, p. 389–396.

Schneider, W.H., Hirsh, S.R., Compton, H.R., Burgess, A.E., and Wrobel, J.G., 2002, Analysis of hydrologic data to evaluate phytoremediation system performance, *in* Gavaskar, A.R., and Chen, A.S.C., eds., Proceedings of the Conference on Remediation of Chlorinated and Recalcitrant Compounds—Third International Conference, March 20–23, 2002, Monterey, California: Columbus, Ohio, Battelle Press, 2B–26.

Schnoor, J.L., Licht, L.A., McCutcheon, S.C., Wolf, N.L., and Carreira, L.H., 1995, Phytoremediation of organic and nutrient contaminants: Environmental Science and Technology, v. 29, no. 7, p. 318A–323A.

Scholander, P.F, Ruud, B., and Leivestad, H., 1957, The rise of sap in a tropical liana: Plant Physiology, v. 32, p. 1–6.

Schumacher, J.G., Struckhoff, G.C., and Burken, J.G., 2004, Assessment of subsurface chlorinated solvent contamination using tree cores at the Front Street Site and a former dry cleaning facility at the Riverfront Superfund Site, New Haven, Missouri, 1999–2003: U.S. Geological Survey Scientific Investigations Report 2004–5049, 35 p.

Sepaskhah, A.R., and Karimi-Goghari, Sh., 2005, Shallow ground-water contribution to pistachio water use: Agricultural water Management, v. 72, p. 69–80.

Shann, J.R., and Boyle, J.J., 1994, Influence of plant species on in situ rhizosphere degradation, *in* Anderson, T.A., and Coats, J.R., eds., Bioremediation through rhizosphere technology: American Chemical Society, Washington DC, p. 71–81.

Sheehan, E.M., Burken, J.G., Karlson, U., Mayer, P., and Legind, C., 2007, Plant sampling for ground-water investigations [abst.]: Fourth International Phytotechnologies Conference, September 24–26, 2007, Denver, Colorado, p. 43.

Shigo, A.L., 1967, Successions of organisms in discoloration and decay of wood: International Review of Forestry Research: v. 2, p. 237–239.

Shigo, A.L., 1974, A tree hurts too: Broomall, Pennsylvania, Forest Service, Northeastern Forest Experiment Station, Report NE–INF–16–73, 28 p.

Shigo, A.L., 1983, Tree defects—A photo guide: Broomall, Pennsylvania, Forest Service, Northeastern Forest Experiment Station, General Technical Rep NE–82, 167 p.

Shigo, A.L., 1985, Compartmentalization of decay in trees: Scientific American, v. 252, no. 4, p. 96–103.

Shone, M.G.T., and Wood, A.V., 1972, Factors affecting absorption and translocation of simazine in barley: Journal of Exploratory Botany, v. 23, no. 74, p. 141–151.

Shone, M.G.T., and Wood, A.V., 1974, A comparison of the uptake and translocation of some organic herbicides and a systemic fungicide by barley: Journal of Experimental Botany, v. 25, p. 390–400.

Smith, S.D., Wellington, A.B., Nachlinger, J.A., and Fox, C.A., 1991, Functional responses of riparian vegetation to streamflow diversions in the eastern Sierra Nevada: Ecological Applications, v. 1, p. 89–97.

Sorek, A., Atzmon, N., Dahan, O., Gerstl, Z., Kushisin, L., Laor, Y., Mingelgrin, U., Nasser, A., Ronen, D., Tsechansky, L., Weisbrod, N., and Graber, E.R., 2008, Phytoscreening—The use of trees for discovering subsurface contamination by VOCs: Environmental Science and Technology, v. 42, p. 536–542.

Stankewich, J.P., Cosenza, G.J., and Shigo, A.L., 1971, *Clostridum quercicolum* sp. N., isolated from discolored tissues in living oak trees: Antonie van Leeuwenhoek Journal of Microbiology and Serology, v. 37, p. 299–302.

Struckhoff, G.C., 2003, Uptake of PCE vapor by plant—Impacts for phytoremediation: Rolla, Missouri, University of Missouri, Department of Environmental Engineering, unpublished M.S. thesis, 57 p.

Struckhoff, G.C., Burken, J., and Schumacher, J., 2005a, Vadose zone PCE—An important source and fate in planted systems: Presented at the 3rd International Phytotechnologies Conference, April 19–22, 2005, sponsored by The U.S. Environmental Protection Agency and the Midwest Hazardous Substance Research Center, Atlanta, Georgia.

Struckhoff, G.C., Burken, J., and Schumacher, J., 2005b, Vapor-phase exchange of perchloroethene between soil and plants: Environmental Science and Technology, v. 39, p. 1563–1568.

Thorburn, P.J., and Walker, G.R., 1994, Variations in stream water uptake by *Eucalyptus camaldulensis* with differing access to stream water: Oecologia, v. 100, no. 3, p. 293–301.

Toole, E.R., and Gammage, J.L., 1959, Damage from increment borings in bottomland hardwoods: Journal of Forestry, v. 57, no. 12, p. 909–911.

Tout, R.E., Gilboy, W.B., and Spyrou, N.M., 1977, Neutron activation studies of trace elements in tree rings: Journal of Radioanalytical Chemistry, v. 37, p. 715.

Trapp, Stefan, Larsen, Morten, Legind, C.N., Burken, Joel, Machackova, Jinna, and Karlson, U.G., 2007, A guide to vegetation sampling for screening of subsurface pollution; accessed April 9, 2008, at *www2.er.dtu.dk/Homepages/stt/GuidetoVegetationSampling.pdf*

Trapp, Stefan, Miglioranza, K.S.B., and Mosbak, Hans, 2001, Sorption of lipophilic organic compounds to wood and implications for their environmental fate: Environmental Science and Technology, v. 35, no. 8, p. 1561–1566.

U.S. Environmental Protection Agency, 2003, Method 5021A, Volatile organic compounds in various sample matrices using equilibrium headspace analysis; accessed December 2, 2005, at *http://www.epa.gov/epaoswer/hazwaste/test/pdfs/5021a_r1.pdf*

van Mantgem, P.J., and Stephenson, N.L., 2004, Does coring contribute to tree mortality?: Canadian Journal of Forestry Research, v. 34, p. 2394–2398.

Vroblesky, D.A., 1998, Chlorinated ethene uptake and loss in tree trunks: U.S. Geological Survey Department of Defense Environmental Conservation (DODEC) meeting, May 4–8, 1998, Tampa, Florida.

Vroblesky, D.A., and Casey, C.C., 2004, Tree coring as an optimization tool for monitoring-well placement, Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 24–27, 2004, Monterey, California: Columbus, Ohio, Battelle Press.

Vroblesky, D.A., Casey, C.C., Harvey, G., Morris, J.T., and Vose, J.M., 2001, TCE and DCE in tree trunks in diverse environments, Sixth International In Situ and On-Site Bioremediation Symposium, June 5, 2001, San Diego, California: Columbus, Ohio, Battelle Press.

Vroblesky, D.A., Casey, C.C., Petkewich, M.D., Lowery, M.A., Conlon, K.J., and Harrelson, L.G., 2007a, Investigation of ground-water contamination at Solid Waste Management Unit 12, Naval Weapons Station, Charleston, North Charleston, South Carolina: U.S. Geological Survey Scientific Investigations Report 2006–5311, 81 p.

Vroblesky, D.A., Clinton, B.D., Vose, J.M., Casey, C.C., Harvey, G.J., and Bradley, P.M., 2004, Groundwater chlorinated ethenes in tree trunks—Case studies, influence of recharge, and potential degradation mechanism: Ground Water Monitoring and Remediation, v. 24, no. 3, p. 124–138.

Vroblesky, D.A., Nietch, C.T., and Morris, J.T., 1999, Chlorinated ethenes from ground water in tree trunks: Environmental Science and Technology, v. 33, no. 3, p. 510–515.

Vroblesky, D.A., Willey, R.E., Clifford, Scott, and Jenkins, David, 2007b, Real-time mapping of ground-water VOC contamination with tree cores: Fourth International Phytotechnologies Conference, September 24–28, 2007, Denver, Colorado.

Vroblesky, D.A., Willey, R., Clifford, S., and Murphy, J., 2006, Data from tree-coring investigation near the Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts, August 30, 2006: U.S. Geological Survey Data Series 218, 5 p.

Vroblesky, D.A., Willey, R.E., Clifford, Scott, and Murphy, J.J., 2008, Real-time and delayed analysis of tree and shrub cores as indicators of subsurface volatile organic compound contamination, Durham Meadows Superfund Site, Durham, Connecticut, August 29, 2006: U.S. Geological Survey Scientific Investigations Report 2007–5212, 12 p.

Vroblesky, D.A., and Yanosky, T.M., 1990, Use of tree-ring chemistry to document historical ground-water contamination events: Ground Water, v. 28, no. 5, p. 677–684.

Vroblesky, D.A., Yanosky, T.M., and Siegel, F.R., 1992, Increased concentrations of potassium in heartwood of trees in response to ground-water contamination: Environmental Geology and Water Science, v. 19, no. 2, p. 71–74.

Weishaar, J., and Burken, J.G., 2005, Phyto-mapping to delineate a chlorinated VOC plume at Aberdeen Proving Ground, Maryland: Presented at the 3rd International Phytotechnologies Conference, April 19–22, 2005, sponsored by The U.S. Environmental Protection Agency and the Midwest Hazardous Substance Research Center, Atlanta, Georgia.

Wilson, B.H., Smith, G.B., and Rees, J.F., 1986, Biotransformations of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer material—A microcosm study: Environmental Science and Technology, v. 20, no. 10, p. 997–1002.

Wise, D.P., 1997, Modeling the uptake and transpiration of TCE using phreatophytic trees: Wright-Patterson Air Force Base, Ohio, Air Force Institute of Technology, M.S. thesis, 318 p.

Wullschleger, S., Meinzer, F., and Vertessy, R.A., 1998, A review of whole-plant water use studies in trees: Tree Physiology, v. 18, p. 499–512.

Yanosky, T.M., Hansen, B.P., and Schening, M.R., 2001, Use of tree rings to investigate the onset of contamination of a shallow aquifer by chlorinated hydrocarbons: Journal of Contaminant Hydrology, v. 50, p. 159–173.

Yanosky, T.M., and Vroblesky, D.A., 1992, Relation of nickel concentrations in tree rings to ground-water contamination: Water Resources Research, v. 28, no. 8, p. 2077–2083.

Yanosky, T.M., and Vroblesky, D.A., 1995, Element analysis of tree rings in ground-water contamination studies, *in* Lewis, T.E., ed., Tree rings as indicators of ecosystem health: Boca Raton, Florida, CRC Press, Inc., p. 177–208.

Zeikus, J.G., and Ward, J.C., 1974, Methane formation in living trees—A microbial origin: Science, v. 184, p. 1181–1183.

Zencich, S.J., Froend, R.H., Turner, J.V., and Gailitis, Vit, 2002, Influence of ground-water depth on the seasonal sources of water accessed by *Banksia* tree species on a shallow, sandy coastal aquifer: Oecologia, v. 131, no. 1, p. 8–10.

Appendix 1. Case Studies

This section contains four case studies investigating volatile organic compounds in ground water using tree cores. The case studies are of varying length and detail because of differences among the copyrights associated with the original publication sources. Case Study 1 was the first investigation demonstrating that tree-core analysis could be used to delineate shallow ground-water contamination by chlorinated ethenes. Case Studies 2 and 3 are previously unpublished investigations. Case Study 2 examines a site where data from tree coring provided a reconnaissance-level understanding of the plume distribution and allowed optimization of well placement. In Case Study 3, the search for a public-supply-well contaminant source encompassed much of the city of New Haven, Missouri, but tree coring allowed the investigation to be narrowed to a 1-acre area. Although much of the work involving tree coring has been directed toward chlorinated solvents, Case Study 4 shows that tree coring also can be used to detect subsurface petroleum hydrocarbons and methyl *tert*-butyl ether (MTBE).

Case Study 1: Chlorinated Ethenes from Ground Water in Tree Trunks

Summarized from: Vroblesky, D.A.,[1] Nietch, C.T.,[2] and Morris, J.T.,[2] 1999, Chlorinated ethenes from ground water in tree trunks: Environmental Science and Technology, v. 33, no. 3, p. 510–515.

This was the first investigation showing that tree-core analysis could be used to delineate shallow ground-water contamination by chlorinated ethenes. Headspace analysis of cores from 97 trees (6 species, predominantly bald cypress) growing over ground-water contamination in a forested flood plain of the Savannah River near the TNX Area, Savannah River Site, South Carolina (figs. 1.1 and 1.2), showed that *cis*-1,2-dichloroethene (*c*DCE) (fig. 1.2) and trichloroethene (TCE) (fig. 1.3) concentrations in tree cores reflected the configuration of the ground-water contamination plume. The distribution of bald cypress containing TCE was more widespread than the distribution of bald cypress containing *c*DCE and was found in trees farther south than the flow path from the source area at the former seepage basin, indicating the presence of a second plume of TCE in the aquifer (fig. 1.3).

Concentration variations around the tree trunks and a TCE concentration decline of 30 to 70 percent with increasing tree height up to 56 ft were observed. All tested tree species were capable of taking up TCE. Some tree species, such as tupelo and bald cypress, appeared to exhibit similar TCE or *c*DCE uptake potential. Oaks, however, appeared to contain less TCE than adjacent bald cypress or loblolly pines. Sweetgum also appeared to contain less TCE than loblolly pines.

Reference

Vroblesky, D.A., Nietch, C.T., and Morris, J.T., 1999, Chlorinated ethenes from ground water in tree trunks: Environmental Science and Technology, v. 33, no. 3, p. 510–515.

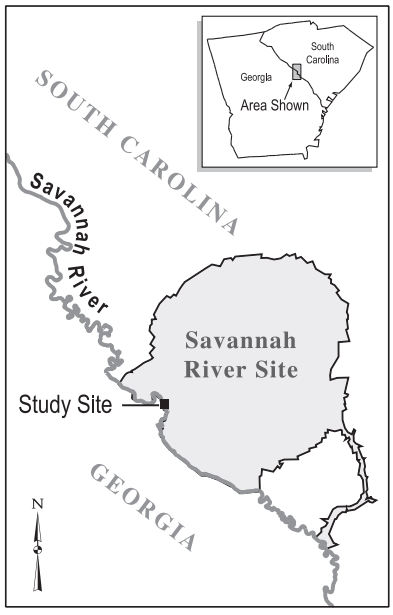

Figure 1.1. Location of study area [reprinted with permission from Vroblesky and others (1999), copyright (1999) American Chemical Society].

[1]U.S. Geological Survey, Columbia, South Carolina.

[2]University of South Carolina, Columbia, South Carolina.

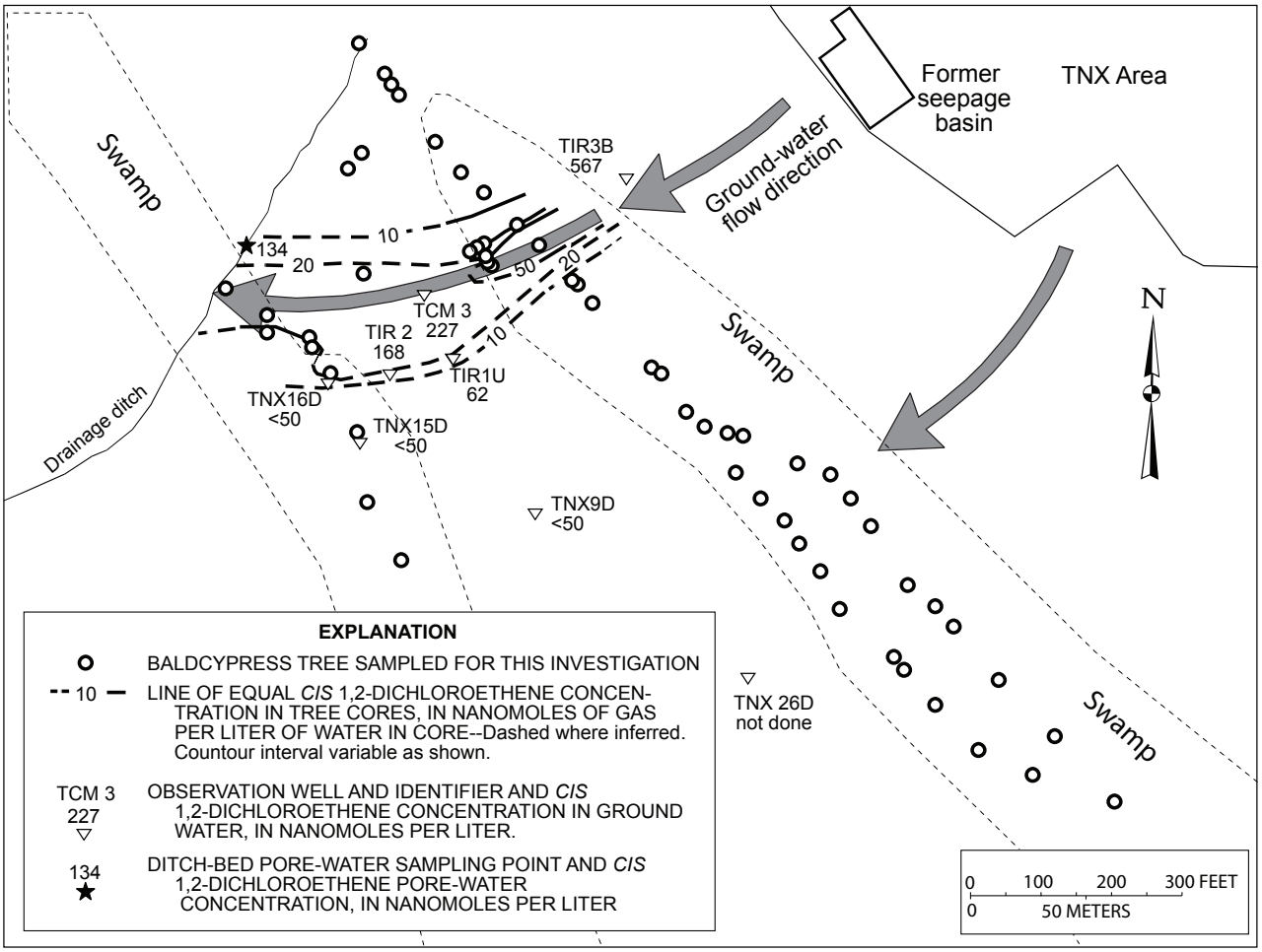

Figure 1.2. *cis*-1,2-Dichloroethene concentrations in bald cypress trunks in January and February 1998 and in ground water during August 1997 and ground-water flow, TNX flood plain, Savannah River Site, SC [modified and reprinted with permission from Vroblesky and others (1999), copyright (1999) American Chemical Society].

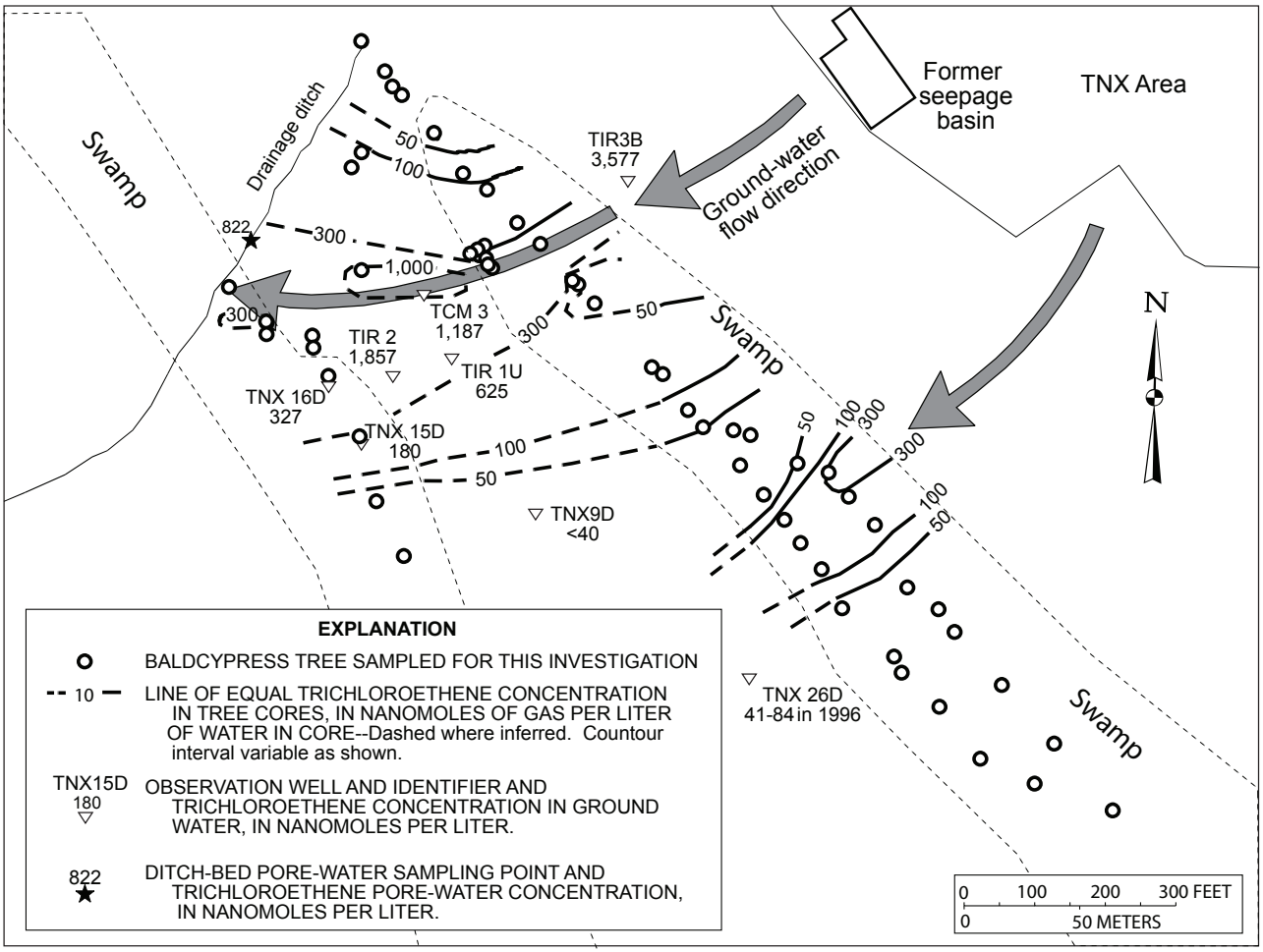

Figure 1.3. Trichloroethene concentrations in bald cypress trunks in January and February 1998 and in ground water during August 1997 and ground-water flow, TNX flood plain, Savannah River Site, SC [modified and reprinted with permission from Vroblesky and others (1999), copyright (1999) American Chemical Society].

Case Study 2: Tree Coring as a Guide to Well Placement, Solid Waste Management Unit 17, Naval Weapons Station Charleston, South Carolina, 2002

By Don A. Vroblesky[1] and Clifton C. Casey[2]

Abstract

Several tree cores were collected from Solid Waste Management Unit (SWMU) 17, Naval Weapons Station Charleston, South Carolina, as part of an effort to characterize the site and to direct monitoring-well placement. Analysis of the tree cores showed the presence of two distinct ground-water plumes. One of the plumes was composed predominantly of tetrachloroethene and the other was composed predominantly of trichloroethene. The data allowed optimization of well placement, and the subsequent well-sample analysis confirmed the tree-core data.

Introduction

Solid Waste Management Unit (SWMU) 17 at the Naval Weapons Station Charleston, South Carolina, is a flat-lying forested area in which the dominant tree species is loblolly pine. Well sampling at the site in 2001 showed 61–190 micrograms per liter (µg/L) of tetrachloroethene (PCE) and very low concentrations (less than 9 µg/L) of trichloroethene (TCE) in the shallow ground water (Tetra Tech NUS, Inc., 2004). Sampling of temporary wells in 2002, however, showed that other parts of the site contained 31,000 µg/L of TCE (Tetra Tech NUS, Inc., 2004) (fig. 2.1). The data indicated a need for additional monitoring wells to map the ground-water contamination. Initial investigations by the contractor, however, indicated that tidal changes caused substantial variations in ground-water-flow direction, complicating the planning of future monitoring-well placement (Tetra Tech NUS, Inc., 2004). Naval Facilities Engineering Command Southeast requested that the U.S. Geological Survey (USGS) conduct a tree-core survey as a reconnaissance tool to direct well placement. As part of the investigation, the USGS and Naval Facilities Engineering Command Southeast cored and analyzed 61 tree cores from the site in September 2002 (fig. 2.2). The cored trees consisted of 28 loblolly pines, 12 Chinese tallow (*Sapium sebiferum* L.), 6 sweet gum, 1 oak, and 12 trees of unknown species.

Tree cores were collected by use of an increment borer. The cores were sealed in crimp-cap 20-milliliter serum vials immediately upon recovery and analyzed by headspace analysis gas chromatography the day after sample collection. Comparison of duplicate cores showed a TCE concentration difference of less than 5 percent in a tree containing greater than 8,000 parts per billion by volume (ppbv) of TCE. Most of the tree cores were collected during a single day (September 11, 2002) and analyzed the following day. The remaining tree cores were collected 2 days later to expand on results from the first survey.

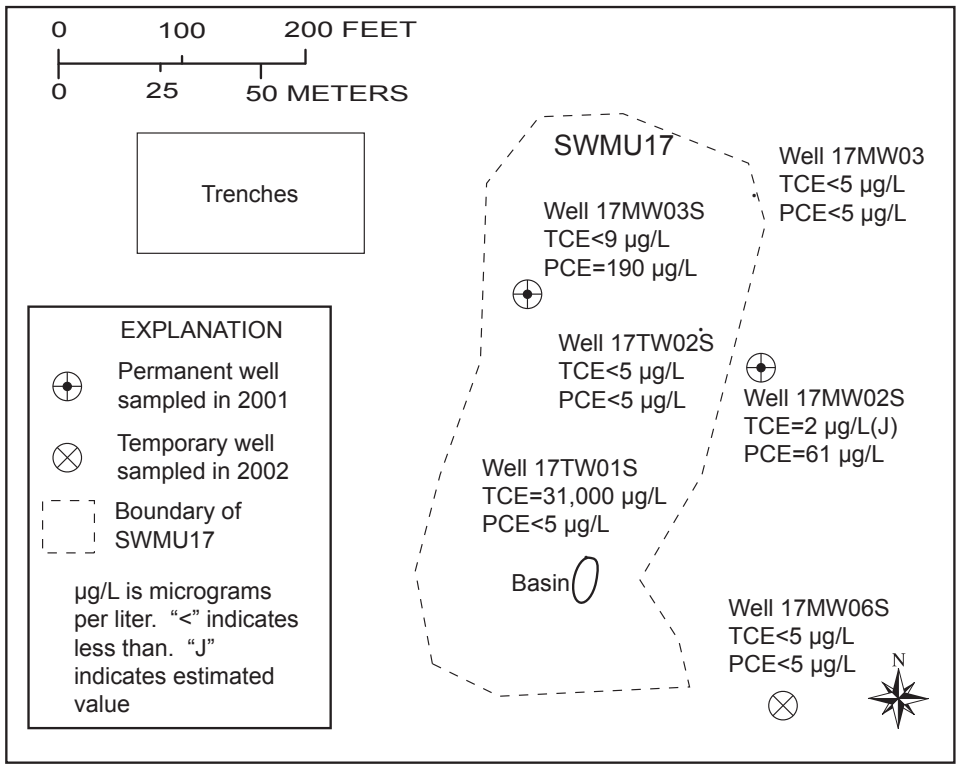

Figure 2.1. Locations of monitoring wells and concentrations of ground-water trichloroethene (TCE) and tetrachloroethene (PCE), Solid Waste Management Unit (SWMU) 17, Naval Weapons Station Charleston, South Carolina.

[1]U.S. Geological Survey, Columbia, South Carolina.

[2]Naval Facilities Engineering Command Southeast, North Charleston, South Carolina.

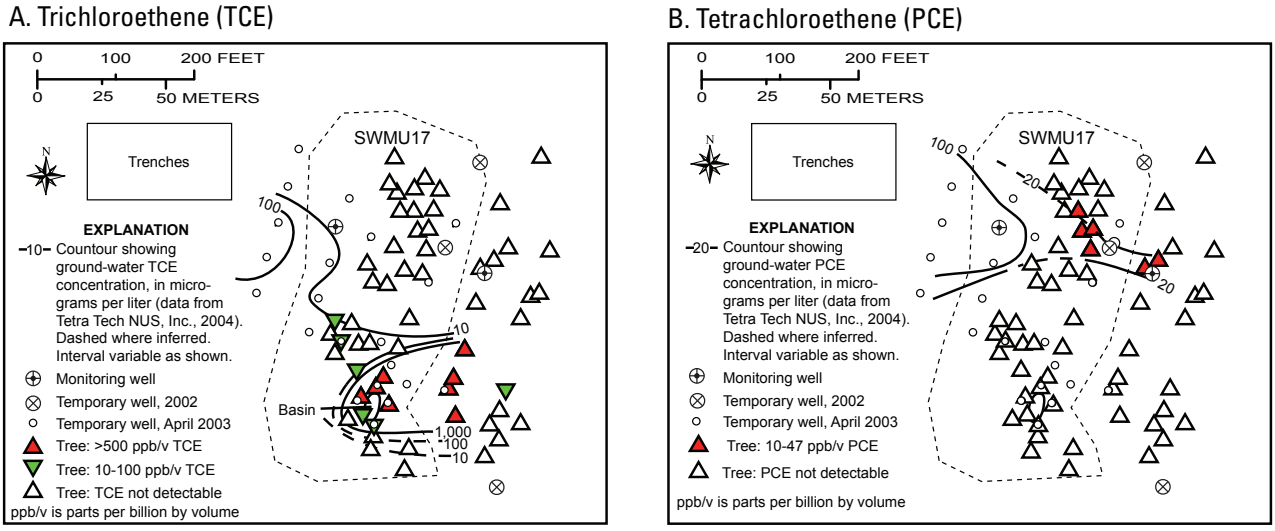

Figure 2.2. (A) Trichloroethene (TCE) and (B) tetrachloroethene (PCE) concentrations in tree cores in 2002 and ground water in 2002–2003 at Solid Waste Management Unit (SWMU) 17, Naval Weapons Station Charleston, South Carolina.

Analysis of the tree cores showed the presence of two distinct areas of ground-water contamination. In the southern part of SWMU17, trees contained TCE with no detectable PCE concentrations. The highest TCE concentrations found in the tree cores (860 to 85,160 ppbv) were from trees near a shallow drainage basin (fig. 2.2A). In the northern part of SWMU17, trees contained 10 to 47 ppbv of PCE, but no detectable TCE (fig. 2.2). Trees between the north and south sides of SWMU17 contained no detectable TCE or PCE.

Using the tree-coring results as a placement guide, the consultant installed and sampled 21 temporary wells in April 2003 (fig. 2.2). Analysis of ground water from the temporary wells, combined with historical data from earlier wells, confirmed the presence of the two distinct contamination plumes identified by the tree coring. As indicated by the tree coring, the southern plume consisted primarily of TCE, with the highest concentrations near the shallow drainage basin (9,000–95,000 µg/L) (Tetra Tech NUS, Inc., 2004). PCE concentrations were less than 6 µg/L. In the northern part of SWMU17 near the sampled trees, PCE concentrations in the ground water were 29 µg/L in the 2003 temporary well and 61 to 190 µg/L in previously tested wells, with TCE concentrations less than 10 µg/L (Tetra Tech NUS, Inc., 2004).

The distribution of volatile organic compounds (VOCs) in trees at the site strongly indicated that the shallow basin in the southern part of SWMU17 (fig. 2.1) was a source area for TCE ground-water contamination. Subsequent drilling and sampling of temporary wells confirmed that finding (fig. 2.2A). The lack of VOC detections in trees in the central part of SWMU17 strongly implied that the PCE contamination in the northern part of SWMU17 was unrelated to the TCE plume near the shallow basin. Again, subsequent drilling and sampling of temporary wells confirmed that finding and provided additional evidence indicating that the northern PCE plume appeared to be coming from the direction of some trenches across the road northwest of SWMU17 (fig. 2.2B). Thus, tree coring provided a simple, rapid, inexpensive reconnaissance tool and guide to optimize monitoring-well placement.

Reference Cited

Tetra Tech NUS, Inc., 2004, RCRA Facility Investigation documentation and data summary 2000–2003, for Old Southside Landfill—SWMU 16 and Old Southside Missile and Waste Oil Disposal Area—SWMU 17, Naval Weapons Station Charleston, Charleston, South Carolina: Consultant's report submitted to Southern Division Naval Facilities Engineering Command, January 2004 [variously paged].

Case Study 3: Operable Unit 4, Riverfront Superfund Site, Franklin County, Missouri

By John Schumacher[1]

Abstract

Tree coring for volatile organic compounds was used at a site in New Haven, Missouri, as a reconnaissance tool to locate the source area for tetrachloroethene-contaminated ground water that caused the abandonment of two public-supply wells. The ability to rapidly and inexpensively collect tree cores from a broad area throughout the town allowed the tree coring to eliminate some suspected source areas, such as transport through sanitary sewer lines, and eventually to narrow the search down to a 1-acre area. Subsequent drilling confirmed that the site identified by tree coring was a previously undetected, shallow source of tetrachloroethene and was a likely source of the tetrachloroethene-contaminated ground water.

Introduction

Ground-water contamination by tetrachloroethene (PCE) detected in two 800-feet (ft)-deep public-supply wells (wells W1 and W2) in 1986 in New Haven, Missouri, resulted in closure of those wells. The contaminated area is referred to as the Riverfront site, and consists of six operable units (OUs). The tree cores indicated that the probable contaminant source was OU4. Unlike the other OUs, however, there was no known PCE use or disposal at OU4, and the area was designated as an OU primarily because it was upgradient from contaminated city wells W1 and W2. The investigation was conducted in a series of iterations, beginning at the known PCE contamination in city wells W1 and W2 and moving upgradient to the south.

Phase I, 2001 Tree-Core Reconnaissance Sampling

In 2001, a reconnaissance sampling of water from streams (grab samples) and cores from 86 trees in OU4 and the surrounding area identified 2 stream reaches contaminated with PCE and 9 trees in the central part of OU4 containing PCE concentrations ranging from 0.58 to 117 micrograms in headspace per kilogram (µg-h/kg) of wet core (fig. 3.1). The largest PCE concentrations detected in trees were in trees JS106 (117 µg-/h/kg), a 30-inch (in.)-diameter hedge apple (*Maclura pomifera*) tree growing along an old fence row, and JS112 (99.1 µg-h/kg), a 36-in.-diameter cottonwood tree about 80 ft southwest of tree JS106. A large number of trees upslope from the contaminated stream reach in the east-central part of OU4 were cored based on a rumor that drums of waste may have been buried in that area; however, none of the trees cored along this stream contained detectable concentrations of PCE and a surface geophysical survey detected no buried metallic objects.

In 2001, trace concentrations of PCE (0.24 to 1.3 micrograms per liter (µg/L) in sanitary sewer lines that drained suspected source areas south of OU4 (U.S. Environmental Protection Agency, 2003a) raised concerns that OU2 was the source area and that the contamination was transmitted through the sanitary sewer and streams. Tree-core evidence, however, did not support this hypothesis. Although PCE was detected at concentrations between 5.0 and 14 µg-h/kg in three trees (JS100, JS104, and JS114) in proximity to the sanitary sewer main crossing OU4, most trees cored along the sewer main had no detectable PCE concentrations. More importantly, trees JS106 and JS112, which had the highest PCE concentrations, were several hundred feet from the sanitary sewer main. The 2001 stream and tree-core reconnaissance sampling had indicated that the PCE source in OU4 was local and shallow. By 2003, the source for the PCE plume in the bedrock aquifer was thought to reside within an 80-acre "suspect area" in the central part of OU4 (fig. 3.1) In mid-2003, PCE concentrations as large as 2,300 µg/L were detected at 138 ft deep in monitoring well cluster BW-10 that was installed downgradient (north) from this suspect area (fig. 3.1).

Phase 2, 2003 Tree-Core Sampling

To refine the size of the 80-acre suspect area, during the fall of 2003, an additional 62 trees were cored within the suspect area, including several trees around the former corporate guest house (fig. 3.1). PCE was detected above the 0.5 µg-h/kg detection threshold used for this study in only 5 of the 62 trees cored. Although 2 of the 16 trees cored at the former corporate guest house contained low (0.51 to 3.9 µg-h/kg) PCE concentrations, the largest PCE concentrations detected (21.2 to 100 µg/kg) were in 3 trees more than a block south of the former corporate guest house. Two of these trees [JS324 (PCE of 100 µg-h/kg) and tree JS340 (PCE of 74.9 µg-h/kg)] were within 90 ft of two trees that previously showed PCE contamination (trees JS106 and JS112) (fig. 3.2). Tree JS324 was a small (1.5-in. diameter) mulberry tree growing along the same old fence row as tree JS106, and tree JS340 was a 14-in.-diameter ash tree growing about 4 ft east of tree JS112. Based on the small size of tree JS324, the high

[1]U.S. Geological Survey, Rolla, Missouri.

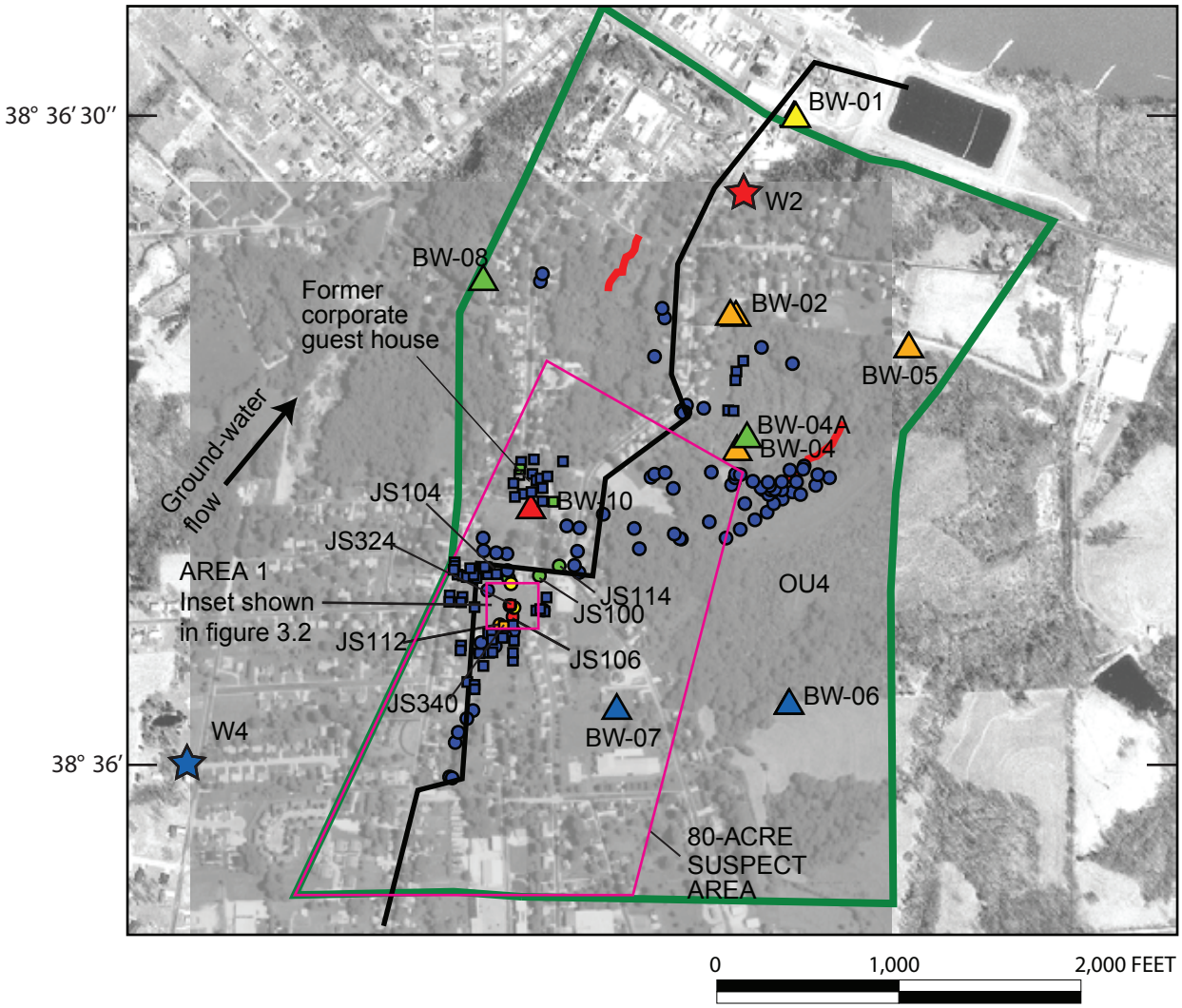

Figure 3.1. Location of tree-core samples and monitoring wells and tetrachloroethene (PCE) concentrations in Operable Unit 4, Riverfront Superfund Site, Franklin County, Missouri, as of 2003 (modified from U.S. Environmental Protection Agency, 2003a).

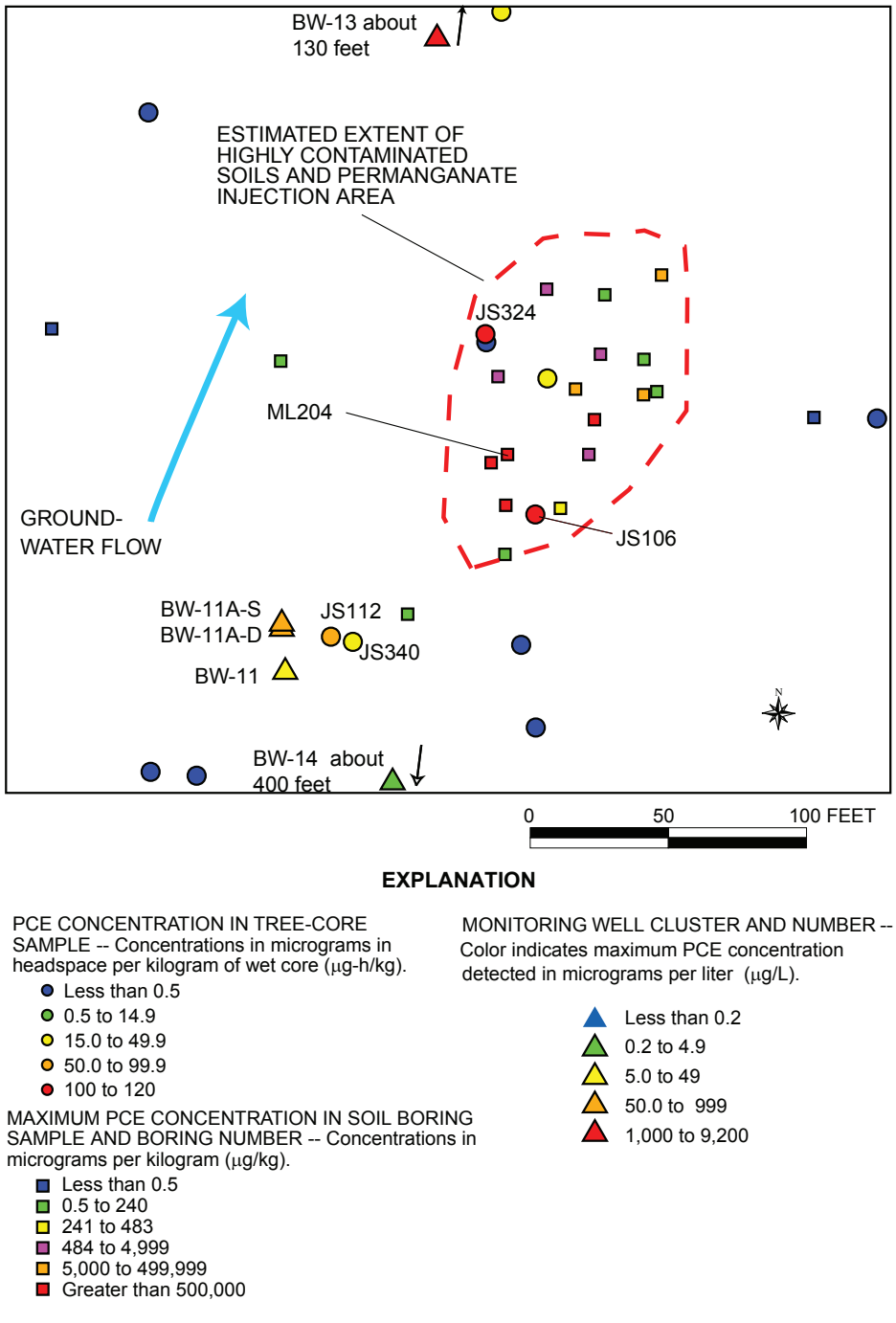

Figure 3.2. Locations of soil borings and tree-core samples in area 1 and tetrachloroethene (PCE) concentrations (modified from U.S. Environmental Protection Agency, 2003a).

PCE concentration in this tree was interpreted to indicate that the tree was growing in PCE-contaminated soil or shallow ground water. The PCE concentration of 74.9 µg-h/kg in tree JS340 was comparable to the concentration previously detected in the 2001 core sample from adjacent tree JS112 of 99.1 µg-h/kg, confirming results of the 2001 reconnaissance.

Using data from the 2001 and 2003 tree-core samples that contained PCE concentrations higher than 15 µg-h/kg, a probable PCE source area (referred to as area 1) of about 1 acre was delineated (fig. 3.1). The average PCE concentration detected in tree-core samples from area 1 was 75 µg-h/kg.

Based on delineation of area 1 by the tree-core sampling and the high PCE concentrations detected in well cluster BW-10, a nest of three monitoring wells (BW-11 cluster) was installed during 2004 adjacent to tree JS112 (fig. 3.2). Perched water containing several hundred micrograms per liter of PCE was encountered less than 15 ft deep during drilling at this location, confirming the presence of shallow PCE contamination initially detected by tree-core sampling. Data from the completed BW-11 cluster indicated PCE concentrations of 210 to 350 µg/L in perched water within the overburden (11.5 to 15.5 ft deep), PCE concentrations of 190 to 440 µg/L in the shallow bedrock (18 to 30 ft deep), and lower PCE concentrations (33 to 36 µg/L) deeper in the bedrock (94 to 130 ft deep). The measured PCE concentrations of 210 to 240 µg/L in perched water in well cluster BW-11 compared favorably to concentrations of about 400 µg/L predicted using the OU1 tree core and ground-water relation. The deeper monitoring interval at cluster BW-11 is of similar altitude to the deep interval at cluster BW-10 that contained much higher PCE concentrations (320 to 2,300 µg/L). A comparison of water-level measurements in the two clusters indicated that ground-water flow is northward from BW-11 toward BW-10. The substantially lower PCE concentrations in the deeper bedrock at cluster BW-11 as compared to those in cluster BW-10 and the presence of PCE in perched water within the overburden indicated that cluster BW-11 was slightly south and upgradient of a PCE source area.

Soil Sampling and Confirmation of Tree-Core Results

During 2004 and 2005, a total of 41 soil borings were done within area 1 (20 borings), at the former corporate guest house (11 borings), and along the sanitary sewer main (10 borings). These borings were installed to provide definitive evidence of the extent and magnitude of subsurface contamination within area 1, to confirm the absence of PCE contamination at the former corporate guest house, and to determine if widespread PCE contamination was present in soils near the sanitary sewer main. A total of 236 soil samples were collected and analyzed by a portable gas chromatograph (GC) for volatile organic compounds (VOCs) (234 samples) or fixed laboratory (23 samples). Continuous soil cores were obtained at each boring location and were typically subsampled every 2 ft of depth for portable GC analysis.

None of the soil borings at the former corporate guest house contained detectable concentrations of PCE or other target VOCs, confirming the tree-core data, which indicated an absence of shallow subsurface contamination at this facility. Four of 10 soil boring locations along the sanitary sewer line contained low (less than 240 micrograms per kilogram (μg/kg) concentrations of PCE. All concentrations detected in soils were less than one-half the U.S. Environmental Protection Agency (USEPA) Region 9 residential soil preliminary remediation goal (PRG) of 484 μg/kg. PCE detections in boreholes along the sewer line generally were found at depths greater than 12 ft.

Substantial PCE concentrations were detected in area 1 soil borings. PCE was detected in 18 of the 20 borings with a maximum concentration of 1,200,000 μg/kg in a laboratory soil sample collected from 13.5 ft deep in boring ML204 near the center of area 1 (fig. 3.2). Several thin (0.5-in.-thick) bands of black oily substance suspected to be PCE-rich DNAPL (dense non-aqueous phase liquid) were present at depths between 10 and 12 ft in this boring. On the basis of the soil boring data, the footprint of the PCE-contaminated soils inside area 1 was estimated to be less than about 5,000 square feet (ft^2) (Rob Blake, Black and Veatch Special Projects Corporation, oral commun., 2006). Generally, PCE concentrations in area 1 soil borings increased with increasing depth, with the largest extent of contamination in the 12- to 16-ft-deep interval. Contamination extended through the soil into the top of the weathered bedrock estimated at 11 to 18 ft below the surface. Using the soil boring data, the USEPA estimated the total volume of contaminated soil/residuum in area 1 is about 2,500 cubic yards (yd^3) containing an estimated 760 kilograms (kg) of PCE or about 125 gallons of pure PCE product.

To provide additional evidence that area 1 was the likely source of the bedrock PCE plume in the northern part of the city, in 2005, the USEPA installed two additional shallow (less than 145 ft deep) monitoring well clusters near area 1. One well cluster was installed upgradient (BW-14) and a second well cluster (BW-13) was installed about 600 ft downgradient from area 1 and about one-half the distance between area 1 and existing well cluster BW-10 (fig. 3.1). PCE concentrations in upgradient well cluster BW-14 were less than 2 μg/L, whereas PCE concentrations in the BW-13 cluster were 9,000 μg/L. Currently (2007), the USEPA is completing a removal action to address the contaminated soils in area 1 using in situ chemical oxidation (permanganate oxidation) and continuing with completion of the OU4 Remedial Investigation/Feasibility Study.

Selected References

Imes, J.L., and Emmett, L.F., 1994, Geohydrology of the Ozark Plateaus aquifer system in parts of Missouri, Arkansas, Oklahoma, and Kansas: U.S. Geological Survey Professional Paper 1414–D, 127 p.

Schumacher, J.G., Struckhoff, G.C., and Burken, J.G., 2004, Assessment of subsurface chlorinated solvent contamination using tree cores at the Front Street site and a former dry cleaning facility at the Riverfront Superfund site, New Haven, Missouri, 1999–2003: U.S. Geological Survey Scientific Investigations Report 2004–5049, 35 p.

U.S. Department of Commerce, 2002, Climatological Data, accessed March 2002 at *http://lwf.ncdc.noaa.gov/oa/ncdc.html.*

U.S. Environmental Protection Agency, 2001, Expanded site investigation/remedial investigation results for the Riverfront Superfund site, New Haven, Missouri: U.S. Environmental Protection Agency Region 7, Contract DW1495212801–2, 56 p.

U.S. Environmental Protection Agency, 2003a, Focused remedial investigation of operable units OU1 and OU3, Riverfront Superfund site, Franklin County, Missouri: U.S. Environmental Protection Agency Region 7, Contract DW1495217301–2, 128 p. plus appendixes.

U.S. Environmental Protection Agency, 2003b, Record of decision, Operable Unit 1, Front Street site, Franklin County, Missouri: U.S. Environmental Protection Agency Region 7, MOD981720246, 107 p. including appendixes.

U.S. Environmental Protection Agency, 2003c, Record of decision, Operable Unit 3, Old city dump site, Franklin County, Missouri: U.S. Environmental Protection Agency Region 7, MOD981720246, 53 p. including appendixes.

U.S. Environmental Protection Agency, 2006, Record of decision, Operable Unit 5, Old hat factory, Franklin County, Missouri: U.S. Environmental Protection Agency Region 7, MOD981720246, 53 p. including appendixes.

Case Study 4: MTBE and BTEX in Trees above Gasoline-Contaminated Ground Water

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Abstract

The fuel oxygenate compound methyl *tert*-butyl ether (MTBE) and the conventional gasoline compounds benzene, toluene, ethylbenzene, and the isomers of xylene and trimethylbenzene were detected and identified using purge-and-trap gas chromatography/mass spectrometry methods in core material of mature live oak trees (*Quercus virginiana*) located above a gasoline-contaminated shallow aquifer. Conversely, these gasoline compounds were not detected in core material of oaks located outside of the gasoline plume. This detection of gasoline compounds in trees at a contaminated field site is important, particularly for the more soluble and less biodegradable compounds MTBE and benzene, because it provides unequivocal field evidence that trees can act as sinks to remove contaminants from ground-water systems.

Introduction

Results of laboratory-scale studies have suggested that herbaceous and woody plants have the potential to take up a variety of dissolved petroleum-derived compounds during transpiration. For example, it has been recognized for some time that pesticide uptake can occur in a wide variety of non-woody plants, including barley (Schone and Wood, 1972; Donaldson et al., 1973; Briggs et al., 1982), bean (Lichtner, 1983), corn (Darmstadt et al., 1983; Leroux and Gredt, 1977; Upadhyaya and Nooden, 1980), peanuts (Hawxby et al., 1972), and soybeans (Moody et al., 1970; McFarlane et al., 1987; McCrady et al., 1987). For woody plants, Burken and Schnoor (1997) demonstrated the uptake and metabolism of the widely used herbicide atrazine by poplar trees (*Populus deltoides*). Additionally, a preliminary report (Newman et al., 1999) indicated that poplar (*Populus* spp.) and eucalyptus (*Eucalyptus* spp.) could take up the fuel oxygenate compound methyl *tert*-butyl ether (MTBE) under laboratory conditions. More recently, Burken and Schnoor (1998) reported the uptake, translocation, and volatilization of the common ground-water contaminants benzene, toluene, ethylbenzene, and xylene (BTEX) by poplar cuttings in short-term hydroponic experiments in the lab. Their results confirm that the relative ease of compound uptake is related to the logarithm of the octanol-water partition coefficient (log K_{ow}), as stated initially by Briggs et al. (1982). Essentially, compounds having a log K_{ow} between 0.5 and 3.0 are preferentially taken up by roots. Because the log K_{ow} of the ground-water contaminants MTBE, benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene are within this range (1.20, 2.13, 2.65, 3.13, 2.95, 3.20, and 3.18, respectively), their uptake during laboratory transpiration studies is not surprising.

However, the uptake of these gasoline compounds by mature trees has not been documented under field conditions. For example, in the study cited above (Burken and Schnoor, 1998) that indicated uptake of MTBE by poplar (*Populus* spp.) and eucalyptus (*Eucalyptus* spp.) cuttings under laboratory conditions, no MTBE uptake was measured in mature trees at an MTBE-contaminated site. This current study was undertaken, therefore, to determine if the soluble fuel compounds MTBE, benzene, toluene, ethylbenzene, and *o*-, *m*-, and *p*-xylenes shown to be taken up under laboratory conditions are present in mature live oaks growing above gasoline-contaminated ground water.

Study Site. The study site is a gasoline station (fig. 4.1) near Beaufort, South Carolina (SC). Fuel-oxygenated gasoline from a leaking underground storage tank was detected in the shallow, water-table aquifer in late 1991 (Landmeyer et al., 1996). The water-table aquifer is comprised of well-sorted sand. The water-table aquifer is underlain by a regional clay-rich confining unit at around 45 feet (ft) (13.7 m). There is less than 0.01% natural sedimentary organic matter in the sandy aquifer. The depth to water is about 13 ft (3.9 m) near the release area and from 9 to 2 ft (2.7 to 0.6 m) near a drainage ditch approximately 700 ft (215 m) downgradient (fig. 4.1) of the release area. Recharge to the water-table aquifer is by rainwater infiltration, with precipitation approaching 60 inches per year (in/yr) (132 cm/yr).

The study site is characterized by a dense stand of mature (>40 years old) live oak trees (*Quercus virginiana*) (fig. 4.1). Live oaks derive their common name from their ability to maintain leaves throughout winter, even though they are deciduous. As a result, live oaks transpire water continually throughout the year and, therefore, are an excellent genus to study transpiration-related processes. The trees at the site have well-developed and extensive networks of horizontal and vertical roots, as evidenced by conspicuous root material at

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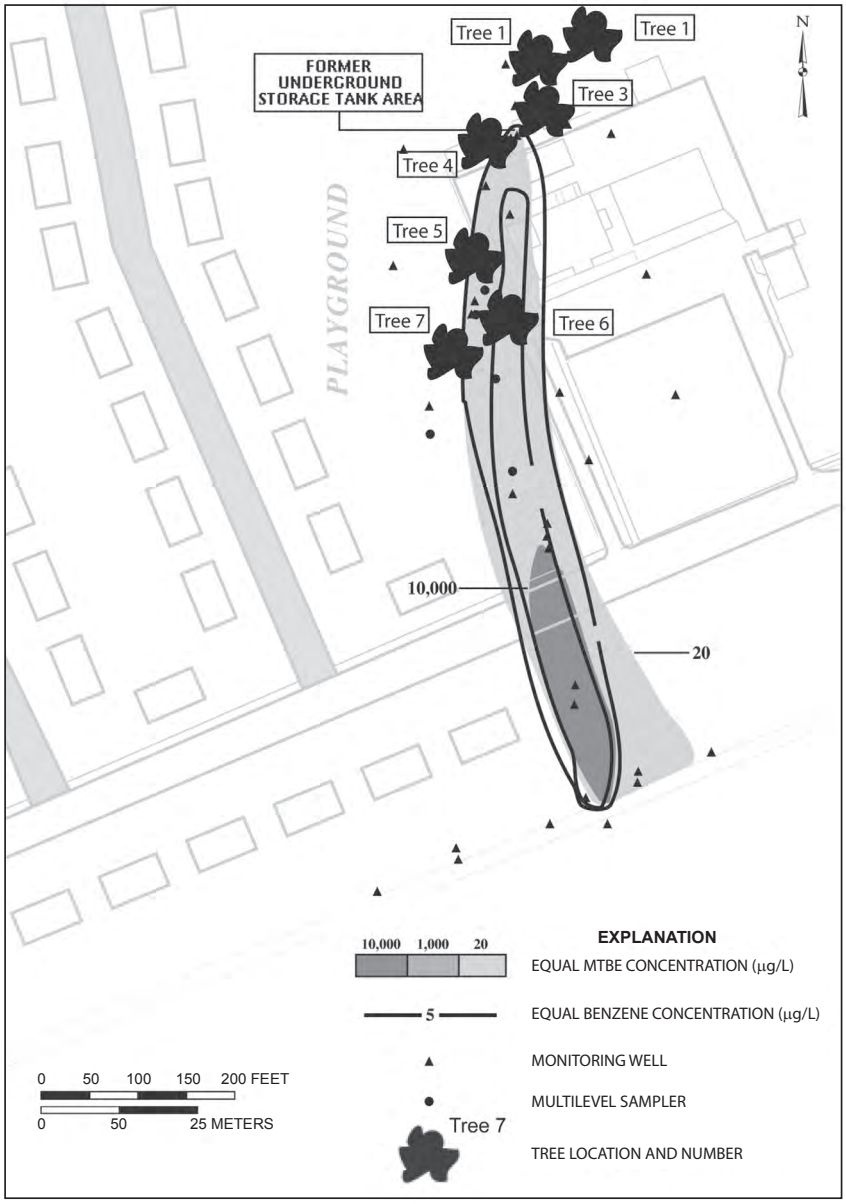

Figure 4.1. Study site near Beaufort, South Carolina, indicating location and reference number of tree samples, monitoring wells mentioned in text, and isoconcentration contours of methyl *tert*-butyl ether (MTBE) and benzene in ground water (collected January 1998).

land surface some distance from tree trunks and the presence of observable root material at the water table in boreholes completed near trees.

Methods

Ground-Water Geochemistry. The distribution of gasoline compounds as well as geochemical parameters that indicate the redox zonations at the site have been documented over seven sampling events between 1993 and 1998 (Landmeyer et al., 1996; Landmeyer et al., 1998). However, only the gasoline compound distribution will be discussed here. Conventional polyvinyl chloride (PVC) monitoring wells (2-inch [4.4 cm] diameter, screened across or below the water table with 12.5 ft [3.8 m] screens) and multi-level sampling wells (1-inch [2.2 cm] diameter, with variably spaced screened intervals) were analyzed for MTBE and BTEX at each sampling event. Before sampling, each well was purged until stable measurements of water temperature (in degrees Celsius) and pH (in standard units) were obtained. MTBE and BTEX samples were collected in 40-mL glass vials using a peristaltic pump at a low flow rate, preserved with 3 drops of concentrated hydrochloric acid, and capped using Teflon-lined septa. BTEX compounds were quantified using purge-and-trap gas chromatography with flame-ionization detection. MTBE was quantified using direct-aqueous injection gas chromatography with mass spectrometry (GC/MS) detection by the Oregon Graduate Institute (Church et al., 1997).

Tree-Core Sample Collection and Analysis. Cores of tree tissue were obtained from trees located in uncontaminated areas upgradient of the ground-water source area and plume, and from trees growing in the area delineated by dissolved-phase ground-water contamination (fig. 4.1) using an increment borer in mid-June 1999. Tree coring methods have been used previously to determine the presence of chlorinated solvents (Vroblesky et al., 1999) and metals (Forget and Zayed, 1995) in tree rings. Cores were collected at a height of 1 ft (0.3 m) above ground on the northeast side of each tree. Replicate cores about 2 inches apart were taken at each tree sampled. The average core collected was about 2.0 inches by 1/4 inch (volume of 0.09 in^3) (4 cm by 0.5 cm; volume of 0.72 cm^3), and consisted of the most recent growth rings, which contain the water-conducting xylem in ring-porous trees such as oaks. Each core was immediately placed into a 40-mL glass vial and capped with a Teflon stopper. At the time of sampling, the air temperature was about 85 degrees Fahrenheit (°F), skies were sunny, winds were from the west at 5 miles per hour (mph) and low relative humidity (<60%). Because the site is an active gas station, air samples for gasoline compound detection were also collected in 40-mL glass vials, after waving an open vial for a few seconds near the contaminated area downgradient of the fuel release.

In the laboratory, the volatile organic compounds in the tree core were separated and identified using a purge-and-trap

GC/MS method similar to U.S. EPA method 8260. Prior to purging of each sample, 5 mL of pesticide-grade methanol was added to each 40-mL vial containing core material, and brought to a final volume of 25 mL using organic-free reagent water. Each vial was then purged with helium, the volatile compounds trapped in a tube containing sorbent material, and manually injected onto a 30 m, 0.25 mm inside diameter capillary column coated with Rtx 502.2 (RESTEK) at a 1.4 μm film thickness. Identification of target gasoline compounds was confirmed by comparing sample mass spectra to the mass spectra of reference material from the National Institute of Standards and Technology under identical run conditions. Three internal standards (fluorobenzene, 2-bromo-1-chloropropane, and 1,4-dichlorobutane) and three surrogate standards (1,4-difluorobenzene, d8-toluene, 4-bromofluorobenzene) were used. Surrogate recoveries ranged between 93 and 100%. Target compound concentrations are reported as concentrations in micrograms per liter in the headspace of vials containing core material.

Results and Discussion

MTBE and BTEX Detection in Tree Cores. MTBE, benzene, toluene, ethylbenzene, and the xylene isomers were not detected in the headspace samples of core material collected from oaks growing hydrologically upgradient of the release area (table 4.1, Trees 1 and 2; fig. 4.1). Trees 1 and 2 are located about 146 ft (46 m) and 136 ft (45 m) north of well 5, respectively (fig. 4.1). Well 5 is located about 75 ft (35 m) upgradient of the release area, screened across the water table, and MTBE and BTEX concentrations there have remained below detection limits since monitoring activities began at the site in 1993 (Landmeyer et al., 1998).

However, MTBE, benzene, toluene, ethylbenzene, and the xylene isomers were detected in the headspace of core samples taken from trees growing above the former source area (table 4.1, Trees 3 and 4; fig. 4.1) and the delineated plume of ground-water contamination (table 4.1, Trees 5 and 6; fig. 4.1). Headspace samples of core material from Tree 3 had detections for toluene at 5.4 μg/L, and Tree 4 had no toluene but *m*-, *p*-xylene (5 μg/L total), and *o*-xylene (6.3 μg/L) were detected. These detections in Trees 3 and 4 are related to the residual contamination in the former source area due to incomplete removal of contaminated sediments in 1993 (Landmeyer et al., 1998). This incomplete removal of source-area material has also caused a "wake" of dissolved-phase contamination to continue to be observed between the source area and downgradient wells in the direction of ground-water flow, even 6 years after source removal activities (fig. 4.1).

Headspace samples of core material from live oaks sampled in the area delineated by gasoline compounds downgradient of the former source area contained chromatographic peaks confirmed by MS to be MTBE, benzene, toluene, ethylbenzene, and the xylene and trimethylbenzene (TMB) isomers (table 4.1, Trees 5 and 6; fig. 4.1). For example, headspace samples of core material from Tree 6, located about 11 ft (4 m) east of well 8 (fig. 4.1), had 54.0 μg/L MTBE, 4.8 μg/L benzene, 10.1 μg/L toluene, 8.5 μg/L ethylbenzene, 10.8 μg/L *m*- and *p*-xylene, 7.4 μg/L *o*-xylene, 6.1 μg/L 1,3,5-TMB, and 5.4 μg/L 1,2,4-TMB. The concentration of MTBE in Tree 6 was the highest detected in all trees cored. Tree 5 adjacent to Tree 6 had the highest detection of toluene (26.2 μg/L). In August 1998, samples of ground water from well 8, which is screened across the water table in the area where root penetration has been observed, had 5,800 μg/L MTBE, 508 μg/L benzene, 674 μg/L toluene, 149 μg/L ethylbenzene, and 580 μg/L total xylenes. This detection of MTBE and benzene in transpiration-stream water of a mature tree at a contaminated field site is the first known field-scale confirmation of laboratory-scale experimental data. Headspace samples of air collected from this area did not contain peak responses representative of MTBE, benzene, toluene, ethylbenzene, or the isomers of xylene or TMB (data not shown).

No compound detections for MTBE and BTEX were seen in headspace samples of core material from Tree 7 (table 4.1), even though this tree is located downgradient of the release area. This lack of compound detection can be explained by the location of Tree 7 being (1) at the edge of the delineated plume boundary (fig. 4.1), which probably results in the majority of transpiration

Table 4.1. Concentrations (in micrograms per liter) of the gasoline compounds MTBE, benzene, toluene, ethylbenzene, and the isomers of xylene and trimethylbenzene (TMB) in the headspace of vials containing tree cores collected at a field site near Beaufort, South Carolina, June 1999.

[Non detection is represented by nd, not analyzed by na]

Compound	Upgradient of Former Source Area		Former Source Area		Dissolved-Phase Plume		Vertical Flow Area	
	Tree 1	Tree 2	Tree 3	Tree 4	Tree 5	Tree 6	Well 7	Tree 7
MTBE	nd	nd	nd	nd	9.4	54	5,800	nd
Benzene	nd	nd	nd	nd	7.2	4.8	508	nd
Toluene	nd	nd	5.4	nd	26.2	10	674	nd
Ethylbenzene	nd	nd	nd	nd	nd	8.5	149	nd
m,p-Xylene	nd	nd	nd	5	10.1	10.8	580	nd
o-Xylene	nd	nd	nd	6.3	5.6	7.4		nd
1,3,5-TMB	nd	nd	nd	nd	7.8	6.1	na	nd
1,2,4-TMB	nd	nd	6	19.6	5.3	5.4	na	nd

water being derived from uncontaminated ground water, and (2) in an area where dissolved-phase contamination originally near the water-table surface is pushed deeper into the aquifer by vertical recharge of percolating rainwater (Landmeyer et al., 1998). This vertical displacement of the dissolved-phase plume deeper into the aquifer away from root interaction is why no trees were cored downgradient of Tree 7.

As stated above, the trimethylbenzene isomers 1,3,5-TMB and 1,2,4-TMB were also identified in the cored material in Trees 3, 4, 5, and 6 located above the original source area and delineated dissolved-phase plume (table 4.1). The TMB isomers are common components of gasoline, and because their solubility and sorption characteristics are similar to benzene and toluene, these relatively nonbiodegradable isomers are routinely used as conservative tracers to estimate biodegradation rates of aromatic hydrocarbons from field data (Weidemeier et al., 1997). The detection of the TMB isomers in transpiration stream water follows from a log K_{ow} of 3.78 for 1,2,4-TMB. The fact that trees can remove TMB isomers from contaminated ground water needs to be considered if TMB isomers are to be used as conservative tracers in ground-water studies of contaminant transport.

The chlorinated compounds chloroform and methyl chloride were detected in tree cores collected in uncontaminated and contaminated areas. Chloroform concentrations in the headspace of vials containing tree cores ranged from 18.7 to 89.1 µg/L, and methyl chloride concentrations ranged from 20.1 to 63.3 µg/L (data not shown). Chloroform and methyl chloride have log K_{ow}'s that would suggest uptake by trees (1.90 and 0.90, respectively). Their detection in tree cores suggests that the most likely source is chlorinated irrigation water. A nationwide survey of 1,501 shallow ground-water samples conducted by the U.S. Geological Survey indicated that chloroform was the most commonly detected volatile organic compound in shallow wells (Squillace et al., 1996).

The detection of the common ground-water contaminants MTBE, BTEX, and the TMB isomers in mature trees that grow above a shallow aquifer characterized by a fuel spill is important because it extends laboratory-scale observations to real field sites. These results suggest the possible use of trees to remove soluble gasoline-related compounds such as MTBE and benzene from contaminated ground-water systems. The transpiration process of trees requires large volumes of water (up to 53 gal/day for 5-year old trees [Newman et al., 1997]) to balance transpiration losses. Although trees most commonly use recent rainfall to meet short-term water demands, ground water can provide water during times of low precipitation to meet longer-term needs. Because tree-root systems often contact the water-table surface, the potential exists for sources of contaminants containing non-aqueous phase liquids, such as petroleum hydrocarbon compounds and chlorinated solvents dissolved in ground water to come into contact with tree roots, particularly in discharge zones where ground-water flowlines converge to bring even the denser chlorinated compounds to the surface. Results from our study suggest that trees exhibit the potential to uptake synthetic organic compounds dissolved in ground water, particularly those gasoline-related compounds that are accidentally released into the environment. It is not yet clear whether uptake of soluble ground-water contaminants by trees may serve to remove substantial amounts of hydrocarbons from contaminated ground-water systems. However, these results show that contaminant uptake occurs in measurable quantities, and suggest that this phenomenon may have important environmental applications.

References

Briggs, G.G., R.H. Bromilow, and A.A. Evans. 1982. *Pesticide Science*. 13, 495–504.

Burken, J.G., and J.L. Schnoor. 1997. *Environmental Science & Technology*. 31, 1399–1406.

Burken, J.G., and J.L. Schnoor. 1998. "Predictive relationships for uptake of organic contaminants by hybrid poplar trees." *Environmental Science & Technology*. 32, 3379–3385.

Church, C.D., L.M. Isabelle, J.F. Pankow, D.L. Rose, and P.G. Tratnyek. 1997. "Method for determination of methyl tert-butyl ether and its degradation products in water." *Environmental Science & Technology*. 31, 3723–3726.

Darmstadt, G.L., N.E. Balke, and L.E. Schrader. 1983. *Pesticide Biochem. Physiology.* 19, 172–183.

Donaldson, T.W., D.E. Bayer, and O.A. Leonard. 1973. *Plant Physiology.* 52, 638–645.

Forget, E., and J. Zayed. 1995. "Tree-ring analysis for monitoring pollution by metals," *in* Lewis, T.E., eds., *Tree rings as indicators of ecosystem health*: CRC Press, 157–176.

Hawxby, K., E. Basler, and P.W. Santelmann. 1972. *Weed Science.* 20, 285–289.

Landmeyer, J.E., F.H. Chapelle, and P.M. Bradley. 1996. "Assessment of intrinsic bioremediation of gasoline contamination in the shallow aquifer, Laurel Bay Exchange, Marine Corps Air Station, Beaufort, South Carolina." *U.S. Geological Survey Water-Resources Investigations Report 96-4026*, 50 p.

Landmeyer, J.E., F.H. Chapelle, P.M. Bradley, J.F. Pankow, C.D. Church, and P.G. Tratnyek. 1998. "Fate of MTBE relative to benzene in a gasoline-contaminated aquifer (1993–1998)." *Ground Water Mon. & Remed.* 18, 93–102.

Landmeyer, J.E., D.A. Vroblesky, and P.M. Bradley. 2000. MTBE and BTEX in trees above gasoline-contaminated ground water, *in* Wickramanayake, G.B., and others, eds., Case studies in the remediation of chlorinated and recalcitrant compounds, Proceedings of the 2nd International Conference on Remediation of Clorinated and Recalcitrant Compounds, Monterey, California, May 22–25, 2000, v. C2–7, p. 17–24.

Leroux, P., and M. Gredt. 1977. *Neth. Journal Plant Pathol.* 83, 51–61.

Lichtner, F.T. 1983. *Plant Physiology. 71*, 307–312.

McCrady, J.K., C. McFarlane, and F.T. Lindstrom. 1987. *J. Experimental Botany.* 38, 1875–1890.

McFarlane, J.C., T. Pfleeger, and J. Fletcher. 1987. *J. Environ. Quality*. 16, 372–376.

Moody, K., C.A. Kust, and D.P. Buchholtz. 1970. *Weed Science.* 18, 642–647.

Newman, L., S. Strand, J. Duffy, N. Choe, G. Ekuan, M. Ruszaj, B. Shurtleff, J. Wilmoth, P. Heilman, and M. Gordon. 1997. *Environmental Science & Technology*. 31, 1062–1067.

Newman, L.A., M.P. Gordon, P. Heilman, D.L. Cannon, E. Lory, K. Miller, J. Osgood, and S.E. Strand. 1999. "Phytoremediation of MTBE at a California naval site." *Soil & Groundwater Cleanup*. 42–45.

Schone, M.G.T., and A.V. Wood. 1972. *Weed Research*. 12, 337–347.

Squillace, P.J., J.S. Zogorski, W.G. Wilber, and C.V. Price. 1996. *Environ. Sci. & Tech*. 30, 1721–1730.

Upadhyaya, M.K., and L.D. Nooden. 1980. *Plant Physiology.* 66, 1048–1052.

Vroblesky, D.A., C.T. Nietch, and J.T. Morris. 1999. "Chlorinated ethenes from groundwater in tree trunks." *Environ. Science & Technol*. 33, 510–515.

Weidemeier, T.H., M.A. Swanson, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1997. *Intrinsic Bioremediation*: Battelle Press, 3(1), 31–51.

Appendix 2

AIR SAMPLE ANALYSIS
FOR
VOLATILE ORGANIC COMPOUNDS

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This reprint contains minor formatting modifications by the U.S. Environmental Protection Agency from document EIA-FLDGRAB4.WPD

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1.0 **Scope and Application**:

1.1 The procedure contained herein is applicable to all EPA Region I chemists performing screening for volatile organic compounds for air grab samples.

1.2 Reporting Levels:

Reporting levels can vary depending upon instrument performance and settings, as well as data quality objectives. Typical achievable reporting levels using a photoionization detector (PID) and an electron capture detector (ECD) are given below.

Analyte	Reporting limit in parts per billion by volume (ppb/v)
1,1- Dichloroethene:	10
trans-1,2- Dichloroethene:	10
cis-1,2-Dichloroethene:	15
Benzene:	10
Trichloroethene:	10
Toluene:	40
Tetrachloroethene:	2
Ethylbenzene:	50
Chlorobenzene:	50
m/p-xylenes:	50
o-xylene:	80
1,1,1- Trichloroethane:	6

1.3 This method may be used when the quality assurance objectives are either QA1 or QA2 as defined in Interim Final Guidance for the Quality Assurance/Quality Control Guidance for Removal Activities, April 1990. Briefly, QA1 is a screening objective to afford a quick preliminary assessment of site contamination. QA2 is a verification objective used to verify analytical (field or lab) results. A minimum of 10% of samples screened must be analyzed by a full protocol method for qualitative and quantitative confirmation.

2.0 **Summary of Method:**

2.1 Field screening using the portable gas chromatograph is used for tentative identification and quantitation of volatile organic compounds in air samples. This screening technique can provide quick and reliable results to assist in important on-site decision making.

2.2 An aliquot of the air sample is injected into a calibrated gas chromatography (GC) equipped with a photoionization detector (PID) and electron capture detector (ECD). The compounds are separated on a megabore capillary or packed column. Retention times are used for compound identification and peak heights are used for quantitation of the identified compounds.

2.3 This method can be used to provide analytical data in a timely manner for guidance of ongoing work in the field.

2.4 Based on the project=s data quality objectives (DQOs), the operator can modify some conditions. For example, the injection volumes can be changed depending on the levels found at the site.

3.0 **Definitions**:

3.1 FIELD DUPLICATES (FD1 and FD2): Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.2 Headspace: Air above water standard in sample vial.

3.3 Laboratory Duplicate (LD1 and LD2): Two injections from the same sample. The analyses of LD1 and LD2 give a measure of the precision associated with the laboratory procedure.

3.4 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.5 STOCK STANDARD SOLUTION -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.6 WORKING STANDARD SOLUTION -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.7 SECONDARY STANDARD - A standard from another vender or a different lot number that is used to check the primary standard used for quantitation.

4.0 **Health and Safety Warnings:**

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in these analyses. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs flush with large volumes of water.

4.2 Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

4.3 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

5.0 Cautions:

5.1 The stock standard and secondary stock standard are replaced every three months.

5.2 The working and secondary standards are good for 7 days provided these standards are stored on ice with no headspace.

6.0 Interferences:

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials must routinely be demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

6.2 Matrix interferences may be caused by contaminants that coelute with the target compounds. The extent of matrix interferences will vary considerably from source to source. A different column or detector may eliminate this interference.

6.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, a VOC free water blank should be analyzed following an unusually concentrated sample to assure that the syringe is clean.

7.0 Personnel Qualifications:

7.1 The analyst should have at least a four year degree in a physical science.

7.2 The analyst should be trained at least one week and have a working knowledge of this method and quality control before initiating the procedure.

7.3 All personnel shall be responsible for complying with all quality assurance/quality control requirements that pertain to their organizational/technical function.

8.0 **Equipment and Supplies:**

8.1 Photovac 10A10 portable gas chromatography equipped with a PID and a 4 ft, 1/8 in, SE-30 packed column.

8.2 Shimadzu 14A portable gas chromatography equipped with a PID, ECD, and a 30 m, 0.53 mm megabore DBPS 624 capillary column, or equivalent.

8.3 Syringes: Hamilton, steel barrel, 250 µL to 500 µL.

8.4 Vial: 40 mL VOA vials with Teflon lined septum caps.

8.5 Air Standard**:**

8.5.1 Standard Preparation and Use: Standard should be prepared in water at a l0 µg/L concentration, and labeled. Standards should be made up fresh weekly from a methanol stock solution (Supelco or equivalent vender), and stored with no head space on ice until ready for use. Standard preparation should be recorded in the **Field Standard Log** notebook. After preparation, the standard is placed into a 40 mL VOA vial, filling the vial to the top leaving no head space. The standard is then put into a cooler on an ice bath for storage until it is ready to use. When the standard is ready to use in connection with air sampling and analysis, l0 mL of liquid from the 10 µg/L standard VOA vial are withdrawn to give a head space above the liquid standard. The standard is then placed into an ice bath. It is important to realize that the concentration of the volatile organic compounds in the head space was calibrated at approximately 0 - l^{o}C. Therefore, it is **mandatory** that the working standard be stored in a cooler in an ice bath, septa side down.

8.5.2 The head space above a l0 µg/L aqueous standard at approximately 0 - 1°C **(Standard must be in an ice bath)** is used for an air standard. Through in-house experimentation, we have determined the vapor concentration* of various volatile organic compounds in the head space of a l0 µg/L aqueous standard at approximately 0 - l°C to be as follows:

1,1- Dichloroethene:	554 ppb/v
trans 1,2- Dichloroethene:	202 ppb/v
cis 1,2- Dichloroethene:	90 ppb/v
Benzene:	l51 ppb/v
Trichloroethene:	l42 ppb/v
Toluene:	l59 ppb/v
Tetrachloroethene:	201 ppb/v
Ethylbenzene:	l45 ppb/v
Chlorobenzene:	70 ppb/v
m/p-xylenes:	l36 ppb/v
o-xylene:	112 ppb/v
1,1,1- Trichloroethane:	330 ppb/v

9.0 **Instrument Preparation:**

The Photovac l0Al0 GC and the Shimadzu GC 14A should always have carrier gas flowing through their columns. The Photovac uses zero air and the Shimadzu uses zero nitrogen as carrier gas.

9.1 The following steps are taken before analysis of samples on the Photovac:

- Check detector. Insure that the detector source is on by observing the "source off" lamp (red) on the face of the instrument. When the source is on, the "source off" lamp should not be illuminated. Another method of checking the detector is to remove the detector housing with an allen wrench. With the detector on, you will observe a purple glow inside the Teflon detector chamber.

- Check carrier gas flow. The gas flow is checked using a flow meter hooked up to the detector out vent port. Flow can be adjusted to the desired rate by using the vernier knobs on the left side of the instrument face or by adjusting the delivery pressure on the carrier gas cylinder regulator. A desirable flow is from 200 - 600 cc/min, depending upon application.

- Check injection port septum. It is a good idea to put in a new septum before analyzing a large number of samples.

- Check to be sure that signal cable is connected from Photovac output to strip chart recorder input.

- Set strip chart recorder input to l00 MV full scale and chart speed to 60 cm/hr. for Photovac l0Al0. (Recorder input for Photovac l0S50 should be set to l V full scale).

- Adjust needle on Photovac output meter using the offset dial so when instruments attenuation is changed, the needle does not deflect. Setting the output somewhere between 4-l0 Mv DC will usually achieve this.

- Set recorder zero to 5% of chart full scale and establish an acceptable base line.

9.2 The following steps are taken before analysis of samples on the Shimadzu GC 14A using isothermal conditions.

- Check injection port septum. It is a good idea to put in a new septum before analyzing a large number of samples. The system must be cool before changing

the septum.

- Check PID detector Temperature. It should be set to 150^0C from the external PID power source. It can take up to 3 hrs. to warm up the detector from cold. Insure that the detector lamp is on by quickly observing the lamp (purple) on the left side of the instrument.

- Turn on the instrument and the instrument heaters on the face of the instrument. On the control keyboard, hit the START button and set the default temperature conditions.
    - Injector 125^0C
    - ECD detector 190^0C
    - Oven 60^0C

    - After a 30 -60 minute warm-up, monitor actual temperatures using the control keyboard.

- Check zero nitrogen carrier gas flow. The gas flow is checked using a flow meter hooked up to the detector out vent port. Flow can be adjusted to the desired rate by using the vernier knobs on the gas control unit on top of the instrument. A desirable flow is from 20 - 60 cc/min, depending upon application.

- Check to be sure that signal cables are connected from PID and ECD outputs to strip chart recorder inputs.

- Set strip chart recorder input to 5 MV full scale for the PID and 50 MV full scale for the ECD, and chart speeds to 60 cm/hr.

- Set recorder zero to 5% of chart full scale and establish acceptable base lines.

10.0 **Sample Analysis:**

Air analysis generally consists of taking a 200 µL volume grab sample of air using a 250 µL steel barrel syringe with a 2 inch, 25 gauge needle, and injecting it into the GC injection port.

At the sample collection location, flush the syringe barrel three times using the plunger. After flushing, pull the plunger up to the 200 µL point on the barrel and place a spare GC septa on the tip of the needle to seal in the sample. Get the

sample to the GC as soon as possible for analysis. Put the syringe needle into the GC injection port, and push the needle through the septum until the barrel comes up against the injection port and immediately push the plunger with a quick action. Turn on the strip chart recorder and note on the chart:

l. start of run
2. sample number
3. sample volume
4. attenuation or gain
5. any other relevant comments

The order in which analyses of a group of samples is performed is as follows:

l. Standard - Inject a 200 µL sample of your 10 µg/L standard, at 0 - 1 ^{0}C head space into the GC. Keep standard peaks at approximately 50% scale or more, if possible, by adjusting the attenuation or gain.

2. Repeat 10 µg/L standard to check for reproducibility. Standard chromatograms should have compound peak heights within **± 15%** of each other and identical retention times.

3. Inject the secondary standard for confirmation. The acceptance criteria is **± 20%** of the true value.

4. Blank - Inject a 200 µl sample of clean air into the gas chromatograph with the attenuation set at the same level or lower than what your samples will be run on. Blank clean air is taken from the head space above VOA free water in a 40 ml VOA vial.

5. Samples - Inject 200 µl sample volumes into the GC at the same attenuation or lower, than the standard was run. If contaminant levels on the chromatograms are off-scale on the recorder, adjust the attenuation or gain to decrease instrument response. If the chromatographic peaks are still off-scale rerun the samples using a smaller injection volume.

6. Repeat 10 µg/L standard every 10 samples and at the end of the sample batch to check the calibration and reproducibility. Standard chromatograms should have compound peak heights within **± 20%** of each other and identical retention times.

11.0 **Identification and Quantitation:**

Identifications of compounds present in a sample are made by matching retention times of peaks in the sample chromatogram to the retention times of standard peaks. After a compound is identified, quantitation is done by a peak height comparison.

Example: If the l0 µg/L aqueous standard head space had a benzene peak height of 32 units from a 200 µL injection with instrument attenuation at 2, an identified benzene peak l2 units high from an 200 µL sample injection with instrument attenuation at 2 would represent a sample concentration of 57 ppb benzene.

$$\frac{\text{32 units}}{\text{151 ppb/v *}} = \frac{\text{12 units}}{\text{X ppb/v}}$$

X = 57 ppb/v Benzene

* See Air Standard Section 8.5.2

12.0 **Data and Records Management:**

12.1 All work performed for the analyses of samples should be entered into the field screening logbook. The analyses data should be presented to the project manager on site. This is followed up by an Internal Correspondence Report that is reviewed by the Advanced Analytical Chemistry Expert from the Chemistry Section of the EIA Laboratory. Chromatograms generated should be saved and filed in the project folder. The samples analyzed should also be logged into the laboratory information management system.

12.2 Chromatograms:

12.2.1 Site name, analyst name, and date at the start of the chromatogram strip chart.

12.2.2 Every chromatogram/every sample/standard

Sample number or standard
Sample volume injected

Instrument gain or attenuation setting

13.0 **Quality Control:**

13.1 A blank and a one point standard is used for instrument=s calibration. Initially run 10 µg/L standard to determine retention times and response factors of instrument. Repeat a second 10 µg/L standard to check the reproducibility. **Acceptance criteria: within ± 15% difference from the first standard.**

13.2 Blanks are analyzed at the initial calibration and periodically to be sure of no carry over from previous injections. Technical judgment is used to determine frequency. **Acceptance criteria: No target compound peaks greater than one-half the reporting level.**

13.3 A second source standard containing some compounds of interest is analyzed daily to verify calibration standard. **Acceptance criteria: within ± 20% agreement of true value.**

13.4 A standard is run at least every 10 samples and at the end of the sample batch to update the instrument=s calibration due to changes from temperature fluctuations with respect to retention times and response factors. **Acceptance criteria: ± 20%D agreement with the previous calibration.**

13.5 Analyze upwind samples to determine background concentrations during outdoor ambient air sample events and report results.

13.6 Run field and laboratory duplicates when possible (i.e., soil gas analysis and passive vapor sample analysis). **The acceptance criterion is agreement within ± 20% RPD between the two values.**

13.7 When possible (i.e., soil gas, ambient air), GC/MS confirmation of 10% of the field samples analyzed should be performed. This is done, dependent upon the project data quality objective. Summa canisters are used for collecting confirmation samples for GC/MS confirmation.

14.0 **References:**

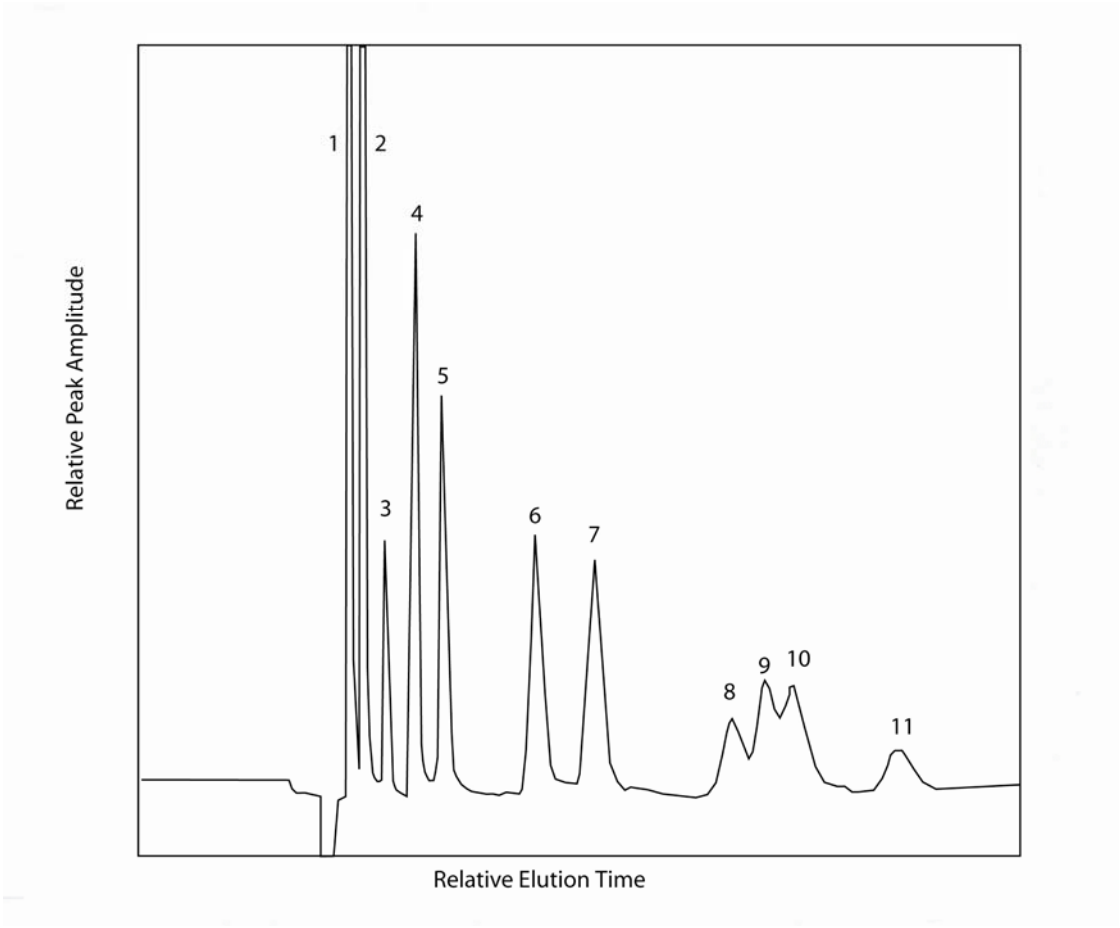
14.1 Interim Final Guidance for the Quality Assurance/Quality Control Guidance for Removal Activities, April 1990.

Quality Control Table			
QC Item	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Initial Calibration	Daily, before samples	< 15%D from the first std [1]	Inject another std, check system
Blank	Daily, every batch	< 1/2 RL [1]	Repeat blank injection, prepare a new blank, check system, increase RLs depending on the DQOs
Second Source Std	Daily, every batch	< 20%D, from the true value [1]	Inject another std, repeat initial calibration, check system
Continue Calibration	Every 10 samples and at the end	< 20%D, from the previous std [1]	Inject another std, repeat initial calibration, check system
Upwind Samples	Option, if the situation warranted	None. Report results [1]	
Field Duplicate	Option, depends on DQOs	< 20% RPD [1]	Repeat injection, run another duplicate
Lab. Duplicate	Option, depends on DQOs	< 20% RPD [1]	Repeat injection, run another duplicate

[1]= Acceptance criteria defined based on technical judgment

Figure 1
Volatile Organic Screening Method
Target Compound Chromatogram (PID)

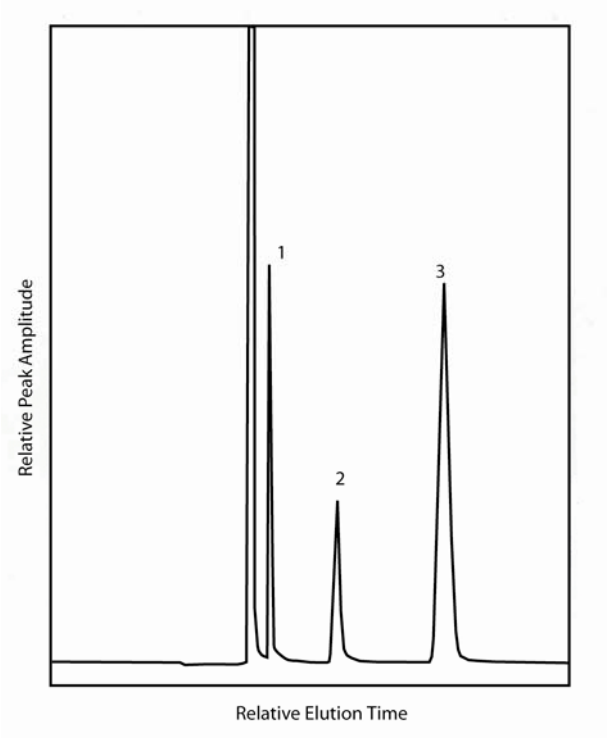
1. 1,1-Dichloroethene
2. t-1,2-Dichloroethene
3. c-1,2-Dichloroethene
4. Benzene
5. Trichloroethene
6. Toluene
7. Tetrachloroethene
8. Chlorobenzene
9. Ethyl Benzene
10. m/p-Xylenes
11. o-Xylene



Instrument: Shimadzu gas chromatography 14A
Detector: Photoionization Detector (PID)
Column: DBPS 624, 30 m, 0.53 micron
Temperature: 60°C
Carrier Gas: Zero grade nitrogen
Flow rate: 30-60 cc/min
Chart speed: 1 cm/min

Figure 2
Volatile Organic Screening Method
Target Compound Chromatogram (ECD)

1. 1,1-Dichloroethene
2. Trichloroethene
3. Tetrachloroethene



Instrument:	Shimadzu gas chromatography 14A
Detector:	Electron Capture Detector (ECD)
Column:	DBPS 624, 30 m, 0.53 micron
Temperature:	60^{o}C
Carrier Gas:	Zero grade nitrogen
Flow rate:	30-60 cc/min
Chart speed:	1 cm/min

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