

Prepared in cooperation with the U.S. Environmental Protection Agency

**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**

Scientific Investigations Report 2007–5212

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By Don A. Vroblesky, Richard E. Willey, Scott Clifford, and James J. Murphy

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Conversion Factors

Multiply	By	To obtain
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
foot per mile (ft/mi)	0.1894	meter per kilometer (m/km)

Abbreviations used in this report

111TCA	1,1,1-trichloroethane
°C	degree Celsius
µg/L	microgram per liter
mL	milliliter
ppb/v	parts per billion by volume
PCE	tetrachloroethene
TCE	trichloroethene
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	volatile organic compound

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

By Don A. Vroblesky¹, Richard E. Willey², Scott Clifford², and James J. Murphy²

Abstract

This study examined volatile organic compound concentrations in cores from trees and shrubs for use as indicators of vadose-zone contamination or potential vapor intrusion by volatile organic compounds into buildings at the Durham Meadows Superfund Site, Durham, Connecticut. The study used both (1) real-time tree- and shrub-core analysis, which involved field heating the core samples for 5 to 10 minutes prior to field analysis, and (2) delayed analysis, which involved allowing the gases in the cores to equilibrate with the headspace gas in the sample vials unheated for 1 to 2 days prior to analysis. General correspondence was found between the two approaches, indicating that preheating and field analysis of vegetation cores is a viable approach to real-time monitoring of subsurface volatile organic compounds. In most cases, volatile organic compounds in cores from trees and shrubs at the Merriam Manufacturing Company property showed a general correspondence to the distribution of volatile organic compounds detected in a soil-gas survey, despite the fact that most of the soil-gas survey data in close proximity to the relevant trees were collected about 3 years prior to the tree-core collection. Most of the trees cored at the Durham Meadows Superfund Site, outside of the Merriam Manufacturing Company property, contained no volatile organic compounds and were in areas where indoor air sampling and soil-gas sampling showed little or no volatile organic compound concentrations. An exception was tree DM11, which contained barely detectable concentrations of trichloroethene near a house where previous investigations found low concentrations of trichloroethene (0.13 to 1.2 parts per billion by volume) in indoor air and 7.7 micrograms per liter of trichloroethene in the ground water. The barely detectable concentration of trichloroethene in tree DM11 and the lack of volatile organic

compound detection in nearby tree DM10 (adjacent to the well having 7.7 micrograms of trichloroethene) may be attributable to the relatively large depth to water (17.6 feet), the relatively low soil-vapor trichloroethene concentration, and the large amount of rainfall during and preceding the tree-coring event. The data indicate that real-time and delayed analyses of tree cores are viable approaches to examining subsurface volatile organic compound soil-gas or vadose-zone contamination at the Durham Meadows Superfund Site and other similar sites. Thus, the methods may have application for determining the potential for vapor intrusion into buildings.

Introduction

Previous investigations have shown that analysis of tree cores may be used to detect subsurface volatile organic compounds (VOCs) (Vroblesky and others, 1999, 2004). Recent studies indicate that the method can also be used to detect VOCs in soil gas, even when the roots are not in contact with the contaminated ground water (Schumacher and others, 2004; Struckhoff, 2005a, 2005b), providing a potentially useful tool for examining soil-vapor concentrations. Typical tree-core sampling involves sealing a core in a vial, allowing the VOCs in the vial to equilibrate with the vial headspace for about 24 hours, and analyzing the sample by headspace gas chromatography (Vroblesky and others, 1999, 2004). If the tree-core samples could be analyzed onsite within a few minutes of collection, then the data could be used to direct the tree-coring effort and optimize plume mapping.

Purpose and Scope

The purpose of this report is to describe the results of a study to examine the use of real-time and delayed analysis of tree cores as indicators of potential vapor intrusion by VOCs at the Durham Meadows Superfund Site, Durham, Connecticut. The study was a cooperative effort between the

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U.S. Geological Survey (USGS) and the U.S. Environmental Protection Agency (USEPA). The study examined tree cores from 12 trees and 2 shrubs of various species and leaf samples from 1 shrub. Tree-core analyses were done both in the field, facilitated by using a block heater to speed the transfer of VOCs from the core to the headspace in the sample vial, and in the laboratory following the more widely used approach of allowing the cores to equilibrate 1 or 2 days prior to analysis. Laboratory analyses of the tree cores were done by the USGS both onsite and offsite, and by the USEPA at the USEPA laboratory in North Chelmsford, Massachusetts.

Site Description

The Durham Meadows Superfund Site is in the town of Durham, Connecticut, and includes an area of ground-water contamination generally centered on Main Street that encompasses industrial and residential properties, all of which are supplied with drinking water by individual bedrock wells (fig. 1). The site includes the Durham Manufacturing Company, a currently operating manufacturing facility located at 201 Main Street, and the Merriam Manufacturing Company property, a facility no longer in operation located at 281 Main Street. Both companies manufactured metal cabinets, boxes, and other items, and the companies' past disposal of wastewater in lagoons or sludge drying beds, spills at both facilities, and inadequate drum storage practices at the Merriam Manufacturing Company property, among other factors, contributed to the contamination at each facility and in the overall area of ground water surrounding both facilities (U.S. Environmental Protection Agency, 2005). Contamination from VOCs has been detected in soil and ground water on both industrial properties, as well as in residential drinking-water wells surrounding both facilities (Metcalf & Eddy, Inc., 2005). The contaminants included, but were not limited to, trichloroethene (TCE), tetrachloroethene (PCE), and 1,1,1-trichloroethane (111TCA). In the contaminated ground-water area, approximately 38 domestic-supply wells have been provided with drinking-water-treatment systems (U.S. Environmental Protection Agency, 2005). The subsurface consists primarily of overburden (till) overlying bedrock.

Methods

Vegetation cores were collected and analyzed from five trees (DM1 to DM5) and two shrubs (DM6 and DM7) on the Merriam Manufacturing Company property and seven trees elsewhere at the Durham Meadows Superfund Site (trees DM8 to DM14) (fig. 1). Leaves were collected from a shrub in front of a school (DM15).

Because the presence of VOCs in soil vapor at the Merriam Manufacturing Company property was widespread and well documented (U.S. Environmental Protection Agency, 2005), tree-core locations in that area were selected on the

basis of the availability of suitable trees. Outside of the Merriam Manufacturing Company property, a limited number of trees were chosen for this investigation based on (1) properties where a shallow ground-water monitoring well had been recently installed for contamination investigation and where the property owner granted access for tree-coring purposes, and either (2) information that vapor-intrusion or soil-gas concentrations showed the presence of subsurface VOCs near that location, or (3) the trees were within an area where VOC concentrations above about 1 percent of the solubility limit of the respective VOC was thought to be present in bedrock (Metcalf & Eddy, Inc., 2005; fig. 1). In some cases (trees DM8 and DM9), no ground-water data were available, and only trace detections of VOCs were found in soil gas and indoor air from the adjacent home (Kahn, 2005), but the trees were sampled because they were in an area suspected to contain VOCs, they were adjacent to a house with an active drinking-water-treatment system, and the property owner granted access for tree-coring purposes.

Vegetation cores were obtained on August 29, 2006, by use of a 0.169-inch (in.) diameter increment borer. Cores were collected from 14 trees of various species, which included two maples, two mulberries, two hemlocks, and one each of catalpa, poplar, Staghorn sumac, dogwood, sycamore, oak, and an unidentified shrub (table 1). In addition, leaf samples were collected from an unidentified shrub (DM15) in front of Strong School.

All cores were approximately 3 in. in length from trees with a diameter of 4 in. or greater. Cores from DM6 and

Table 1. Descriptions of trees and shrubs examined in this investigation.

Tree	Diameter of trunk, in inches	Species
DM1	40	Maple (<i>Acer</i> sp.)
DM2	4.75	Catalpa (<i>Catalpa</i> sp.)
DM3	not measured	Poplar (<i>Populus</i> sp.)
DM4	not measured	Mulberry (<i>Morus</i> sp.)
DM5	4	Mulberry (<i>Morus</i> sp.)
DM6	2.75	Staghorn sumac (<i>Rhus typhina</i>)
DM7	2.2	Unidentified shrub, possibly silverberry (<i>Elaeagnus commutata</i>)
DM8	not measured	Hemlock (<i>Tsuga canadensis</i>)
DM9	not measured	Hemlock (<i>Tsuga canadensis</i>)
DM10	9.9	Dogwood (<i>Cornus florida</i>)
DM11	18.6	Unidentified tree
DM12	42.2	Sycamore (<i>Platanus occidentalis</i>)
DM13	15.4	Maple (<i>Acer</i> sp.)
DM14	31.5	Oak (<i>Quercus</i> sp.)
DM15	0.3	Unidentified shrub

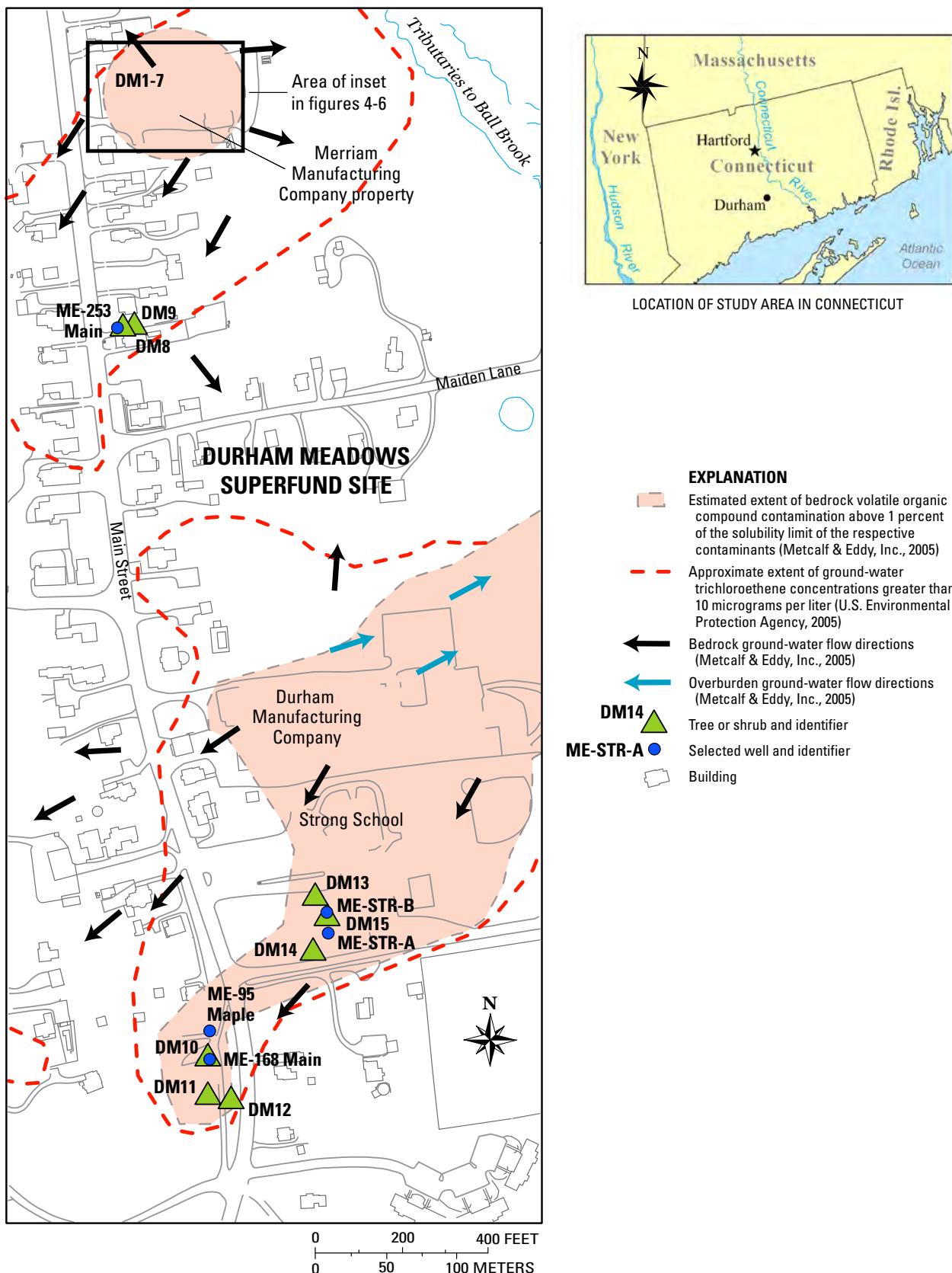


Figure 1. Locations of trees and shrubs outside of the Merriam Manufacturing Company property, selected wells near trees, estimated extent of volatile organic compound contamination, and approximate direction of ground-water flow, Durham Meadows Superfund Site, Durham, Connecticut (modified from Metcalf & Eddy, Inc., 2006).

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DM7 were approximately 2 in. long. The sample from DM15 consisted of leaves and stems. All vegetation core holes were sealed by inserting a wooden dowel rod. Each core was transferred to a 20-milliliter (mL) serum vial and sealed with a crimp cap within 30 seconds of collection. At most trees, cores were collected in duplicate, less than 1 in. apart and labeled as cores "A" and "B." The cores were either heated and analyzed soon after collection or were stored at approximately 25 degrees Celsius ($^{\circ}\text{C}$) until analyzed. At DM1, three collocated cores were collected less than an inch apart and labeled "A," "B," and "C." Air blanks collected and analyzed from near trees DM1 and DM4 did not contain VOCs.

All of the cores labeled with the suffix "A" were analyzed after preheating the core using a block heater (fig. 2) to speed the transfer of VOCs from the cores to the headspace in the vial, except for the cores labeled DM7A and DM10A. The "A" cores from vegetation sites DM1 to DM6 were heated to 60–70 $^{\circ}\text{C}$ for 5 to 10 minutes immediately prior to analysis and were analyzed hot, onsite within 1 hour of collection by the USGS. Core DM7A was stored overnight and analyzed the following day, first by analyzing the unheated core, then heating the core and reanalyzing the same sample. Core DM10A was analyzed the day after core collection without heating the core.

All of the cores labeled "B," except cores DM7B and DM10B, were stored at room temperature and analyzed unheated the day after collection by the USGS. Cores DM7B and DM10B were analyzed 2 days after collection by the USEPA, Region 1. In addition, cores DM2A and DM5A were reanalyzed by the USEPA, on September 1, 2006, 2 days after the initial analysis by the USGS. Thus, three of the five tree-core vials analyzed by the USEPA had been previously analyzed by piercing the septum of the cap with a syringe. Tree cores DM7B and DM10B were analyzed by the USEPA and did not have punctured septa from a previous analysis.

Sample analysis was accomplished by use of two approaches. Core samples were analyzed either on the day of collection or the day following collection by the USGS using photoionization detection on a Photovac 10SPlus gas



Figure 2. Block heater used to field heat the vegetation cores prior to field analysis.

chromatograph. Selected cores were analyzed by the USEPA using electron-capture detection on a Shimadzu 14A gas chromatograph. Minor differences in concentrations between USGS and USEPA data sets were expected because the samples were (1) equilibrated using different methods (heating versus nonheating), (2) analyzed using different methods (photoionization versus electron-capture), and (3) analyzed on different dates.

Results and Discussion

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 can be fast enough so that detectable quantities of TCE can accumulate within the vial within minutes, although the equilibration rate sometimes can be gradual enough that after about 26 hours, the headspace TCE concentrations can be more than double those in the vial after only a few hours (D.A. Vroblesky, unpub. data, 2007). Field heating the sealed cores increases the volatilization rate of VOCs from the tree cores into the headspace of the vial. During this investigation, VOC concentrations in vegetation cores analyzed in the field after 5 to 10 minutes of heating showed close agreement ($r^2 = 0.913$) with VOC concentrations in unheated cores allowed to equilibrate 24 to 30 hours prior to analysis (fig. 3; table 2). In some cases, heating the tree cores can increase the equilibrium headspace VOC concentrations relative to unheated cores. The head-space TCE concentration in tree-core vial DM7A was 30 parts per billion by volume (ppb/v) after heating and was only 7 ppb/v after the same vial

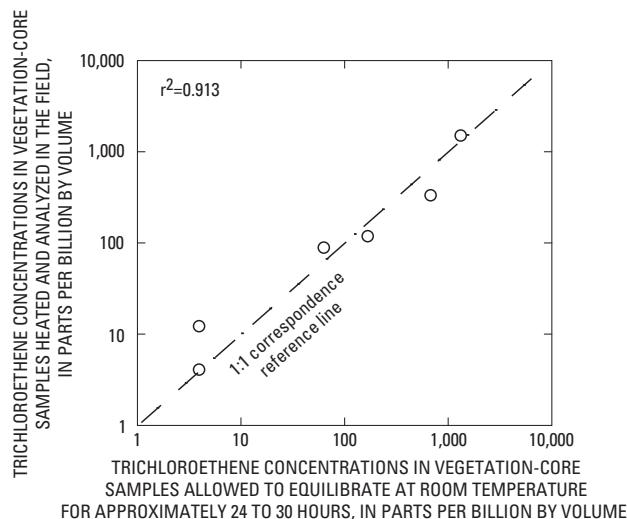


Figure 3. Comparison of trichloroethene concentrations in field-heated and analyzed vegetation cores to unheated vegetation cores analyzed the following day, Merriam Manufacturing Company property, Durham Meadows Superfund Site, Durham, Connecticut, August 29–30, 2006.

Table 2. Concentrations of volatile organic compounds detected in vegetation cores, Durham Meadows Superfund Site, Durham, Connecticut, 2006.

[TCE, trichloroethene; ppb/v, parts per billion by volume; PCE, tetrachloroethene; 111TCA, 1,1,1-trichloroethane; <, less than; —, analysis not done; *, core C; **, unheated reanalysis of core A; ***, analysis of both the original and a duplicate core showed the same results]

Tree	Analysis by U.S. Geological Survey					Analysis by U.S. Environmental Protection Agency				
	Core A, unless otherwise noted (heated)		Core B, unless otherwise noted (unheated)			Core ID	Date of analysis	111TCA, in ppb/v	TCE, in ppb/v	PCE, in ppb/v
	Date of analysis	TCE, in ppb/v	Date of analysis	TCE, in ppb/v	PCE, in ppb/v					
DM1	8/29/2006	12	8/30/2006	4	<16	—	—	—	—	—
DM1	8/30/2006	7*	8/30/2006	5*	<16*	—	—	—	—	—
DM2	8/29/2006	4	8/30/2006	4	16	A	9/1/2006	<1.6	9.2	12
DM3	8/29/2006	1,472	8/30/2006	1,342	582	A	9/1/2006	97	1,730	255
DM4	8/29/2006	326	8/30/2006	687	308	—	—	—	—	—
DM5	8/29/2006	116	8/30/2006	170	41	A	9/1/2006	5.6	212	20
DM6	8/29/2006	87	8/30/2006	64	<16	—	—	—	—	—
DM7	8/30/2006	30	8/30/2006	7**	<16**	B	9/1/2006	24	6.4	<1.3
DM8***	—	—	8/30/2006	<3	<16	—	—	—	—	—
DM9	—	—	8/30/2006	<3	<16	—	—	—	—	—
DM10	8/29/2006	<3	8/30/2006	—	—	B	9/1/2006	<1.6	<1.8	<1.3
DM11	8/30/2006	<3	8/30/2006	3	<16	—	—	—	—	—
DM12	—	—	8/30/2006	<3	<16	—	—	—	—	—
DM13	—	—	8/30/2006	<3	<16	—	—	—	—	—
DM14	—	—	8/30/2006	<3	<16	—	—	—	—	—
DM15	—	—	8/30/2006	<3	<16	—	—	—	—	—

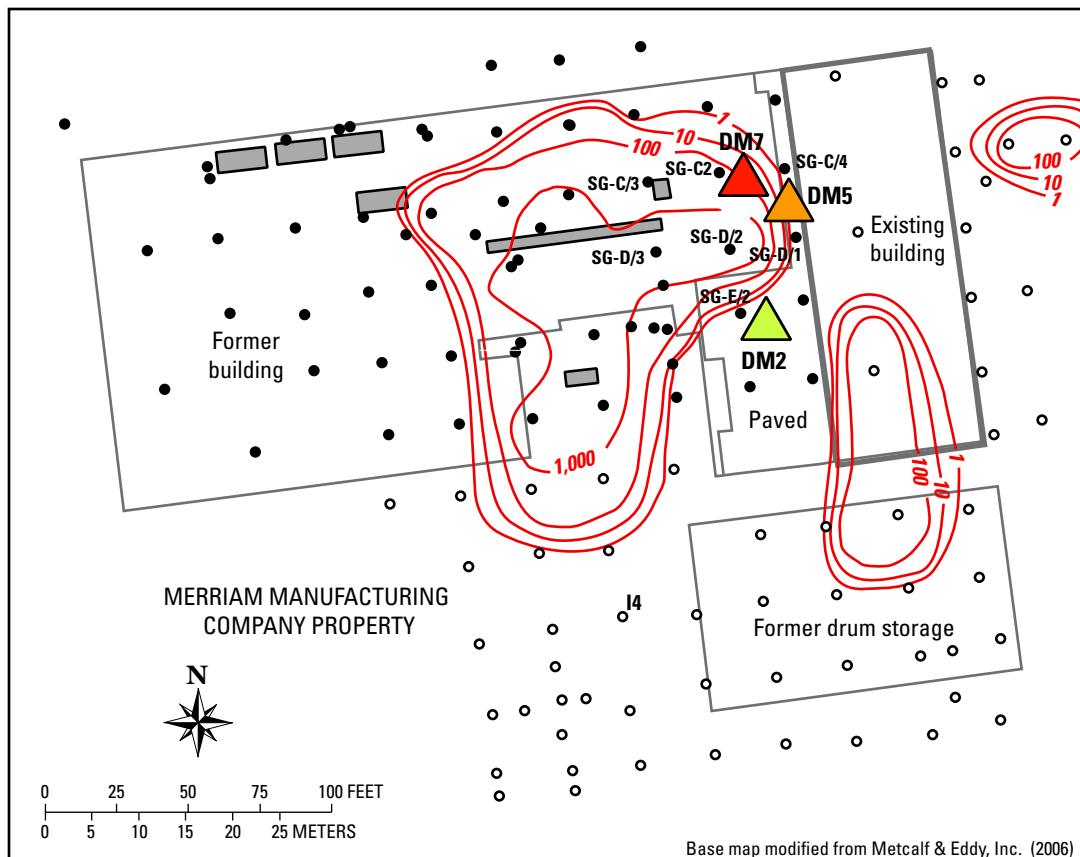
was allowed to cool to room temperature. A duplicate core (DM7B) allowed to equilibrate at room temperature overnight and analyzed 2 days later contained 6.4 ppb/v of TCE, which was a similar value to the room-temperature TCE concentration in tree-core vial DM7A. Thus, field analysis of preheated vegetation cores represents a viable approach to examining subsurface VOC concentrations. Field analysis of tree cores after heating has an advantage over allowing the cores to equilibrate at lower temperatures or for longer periods because the real-time data allow field personnel to more efficiently select trees to sample while mapping subsurface contamination. In some cases delayed analysis may be suitable, however, such as when field analytical equipment are not available, or when there are only a few trees available to sample so there is no need to use real-time data to direct the sampling effort.

Merriam Manufacturing Company Property, Durham Meadows Superfund Site

VOCs were found in cores from all of the trees and shrubs (DM1 to DM7) collected at the Merriam Manufacturing Company property (table 2). Soil-gas investigations at

the Merriam Manufacturing Company property showed the presence of subsurface VOCs in 2003 and 2006 (figs. 4–6) (Anni Loughlin, U.S. Environmental Protection Agency, written commun., February 2007). Most of the trees and shrubs available for coring at the Merriam Manufacturing Company property were near locations where the soil-gas data were collected approximately 3 years before the vegetation-core data (figs. 4–6). Therefore, a close correspondence between the 2006 tree- and shrub-core data and the 2003 soil-gas data would not be expected. In most cases, however, the tree- and shrub-core data showed an apparent correspondence to the soil-gas data.

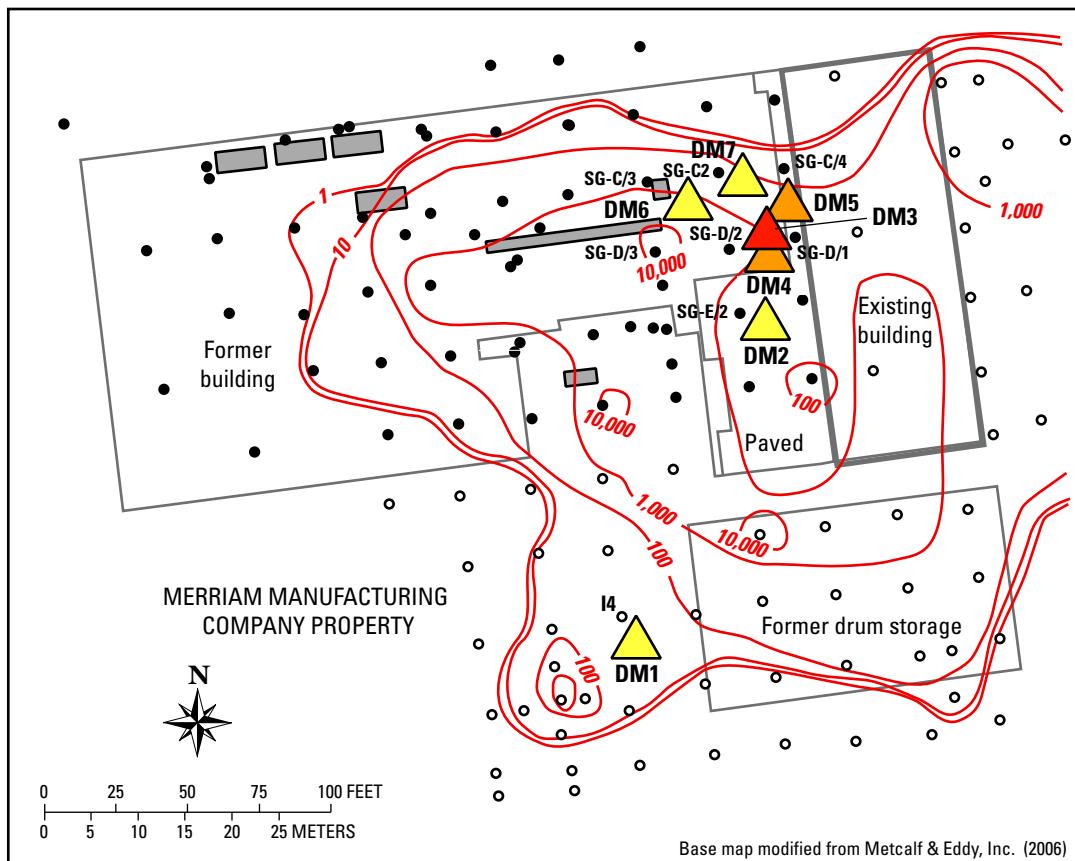
Vegetation cores from the three trees or shrubs that were analyzed for 111TCA in 2006 showed a close correspondence to the soil-gas 111TCA concentration distribution from 2003 (fig. 4). The 111TCA concentration in the core from shrub DM7 was higher than in the core from tree DM5, consistent with the 2003 soil-gas survey that showed higher 111TCA concentrations near shrub DM7 than near tree DM5 (fig. 4). Tree DM2 contained no 111TCA and was located in an area where the 2003 soil-gas survey did not detect 111TCA (fig. 4).



EXPLANATION

- Former areas of liquid storage in tanks and former paint booths
- 1 — 1,1,1-Trichloroethane 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)
- I4 ○ Soil-gas sampling point. Black indicates 2003 and open indicates 2006 sampling
- 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

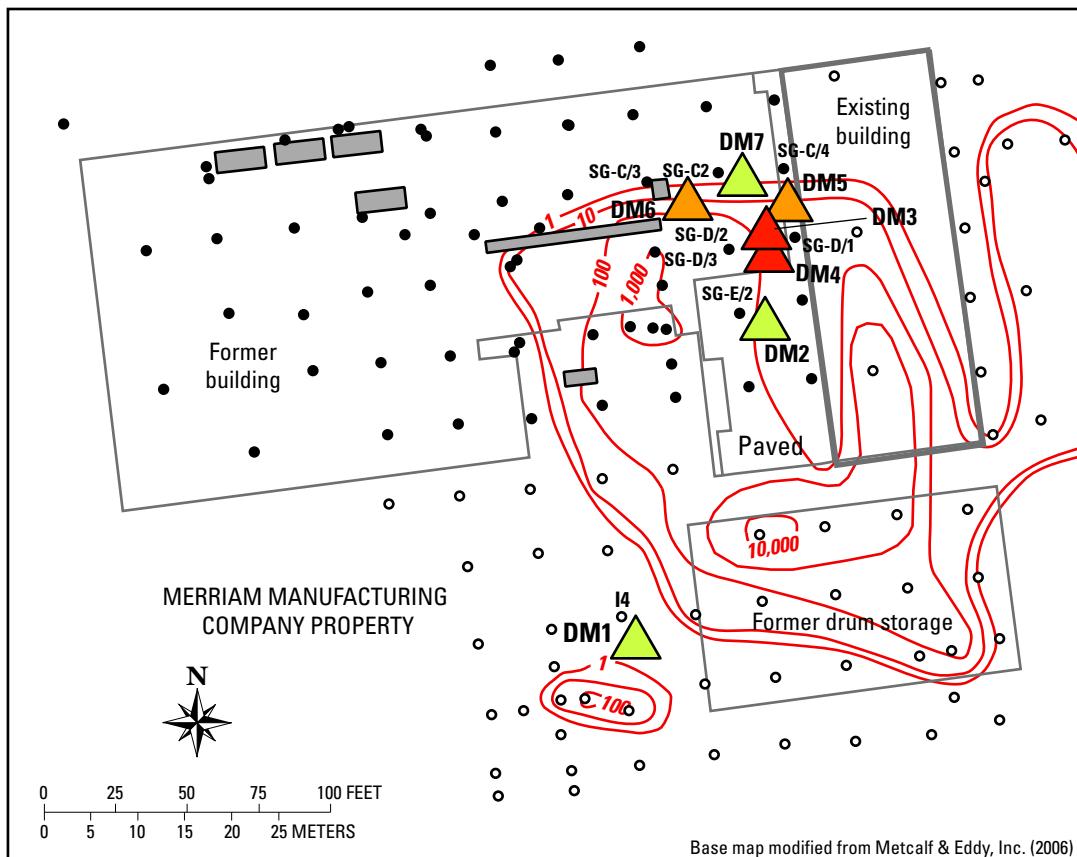
Figure 4. 1,1,1-Trichloroethane concentrations in vegetation cores in 2006, and in the combined results of 2003 and 2006 soil-gas investigations at the Merriam Manufacturing Company property, Durham Meadows Superfund Site, Durham, Connecticut.



EXPLANATION

- Former areas of liquid storage in tanks and former paint booths
- 1 — Trichloroethene 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)
- Soil-gas sampling point. Black indicates 2003 and open indicates 2006 sampling
- DM2** ▲ Tree or shrub containing 4 to 100 parts per billion by volume of trichloroethene
- DM5** ▲ Tree or shrub containing 101 to 300 parts per billion by volume of trichloroethene
- DM7** ▲ Tree or shrub containing greater than 300 parts per billion by volume of trichloroethene

Figure 5. Trichloroethene concentrations in vegetation cores in 2006, and in the combined results of 2003 and 2006 soil-gas investigations at the Merriam Manufacturing Company property, Durham Meadows Superfund Site, Durham, Connecticut.

**EXPLANATION**

- Former areas of liquid storage in tanks and former paint booths
- 1 —** Tetrachloroethene 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)
- I4 ○ Soil-gas sampling point. Black indicates 2003 and open indicates 2006 sampling
- DM2** ▲ Tree or shrub containing less than 20 parts per billion by volume of tetrachloroethene
- DM5** △ Tree or shrub containing 20 to 170 parts per billion by volume of tetrachloroethene
- DM7** ■ Tree or shrub containing greater than 500 parts per billion by volume of tetrachloroethene

Figure 6. Tetrachloroethene concentrations in vegetation cores in 2006, and in the combined results of 2003 and 2006 soil-gas investigations at the Merriam Manufacturing Company property, Durham Meadows Superfund Site, Durham, Connecticut.

TCE concentrations in tree and shrub cores from the Merriam Manufacturing Company property also showed a general relation to soil-gas TCE concentrations (fig. 5). Trees DM2, DM6, and DM7 contained less than 300 ppb/v of TCE (table 2). The closest corresponding soil-gas sampling points in 2003 to those trees also contained less than 300 ppb/v of TCE (table 3). The trees containing the highest TCE concentrations were trees DM3 (1,472 ppb/v) and DM4 (326 ppb/v; table 2). These trees are grouped together in the same part of the site, likely indicating that this is an area of relatively high

Table 3. Concentrations of volatile organic compounds in soil-gas samples in 2003 and 2006 near the vegetation analyzed in 2006 for this investigation, the Durham Meadows Superfund Site, Durham, Connecticut.

[TCE, trichloroethene; PCE, tetrachloroethene; 111TCA, 1,1,1-trichloroethane, ND, not detected]

Tree	Nearby soil-gas locations	Concentrations of volatile organic compounds in soil gas, in parts per billion by volume ^a			Date of soil-gas survey
		111TCA	TCE	PCE	
DM1	I4	ND	18	ND	2006
DM2	SG-E/2	ND	253	109	2003
DM3	SG-D/2	4,334	9,119	771	2003
DM3	SG-D/1	ND	422	12	2003
DM4	SG-D/2	4,334	9,119	771	2003
DM4	SG-D/1	ND	422	12	2003
DM5	SG-D/1	ND	422	12	2003
DM5	SG-C/4	1,010	208	ND	2003
DM6	SG-C/3	ND	ND	ND	2003
DM7	SG-C/2	248	82	ND	2003

^aAnni Loughlin, U.S. Environmental Protection Agency, written commun., February 2007.

subsurface TCE concentrations. A soil-gas location (SG-D/2) near trees DM3 and DM4 had more than 9,000 ppb/v of TCE in 2003 (table 3). A mid-range concentration of TCE was found in tree DM5 (116 ppb/v, USGS analysis; table 2). The closest 2003 soil-gas sampling points to tree DM5 also had mid-range TCE concentrations (208 to 422 ppb/v; table 3).

Although only one cored tree (DM1) was in the vicinity of data-collection points from the 2006 soil-gas data, the TCE concentration in the tree also was similar to the soil-gas data. Tree DM1 contained a relatively low concentration of TCE (4–12 ppb/v), and is in a location where the 2006 soil-gas survey found relatively low TCE (18 ppb/v at site I4, fig. 5, table 3).

The relation between PCE concentrations in vegetation cores and soil gas is less apparent than it is for 111TCA and TCE concentrations in vegetation cores and soil gas (fig. 6). Tree DM1 and shrub DM6 contained no detectable concentrations of PCE (table 2). Consistent with this lack of detection, PCE concentrations in soil gas near tree DM1 and shrub DM5 in 2003 and 2006 were low (12 ppb/v at SG-D/1) or not detected. Tree DM2 also did not contain detectable concentrations of PCE; however, the nearest soil-gas sample (SG-E/2) to tree DM2 contained 109 ppb/v of PCE in 2003 (table 3).

Possible explanations for the PCE-concentration differences between tree DM2 and the nearest soil-gas sample (SG-E/2) may be that the comparison is inappropriate because (1) the heterogeneity of the soil-gas concentrations may be such that soil PCE concentrations differ between the tree and the soil-gas sample locations, (2) the 3 years that elapsed between the soil-gas survey and the tree coring may have allowed changes in the soil-gas PCE concentration, such as from dechlorination or volatilization, or (3) the substantial amount of rain preceding and during collection of the vegetation cores may have diluted the contaminated water and gas being taken up by the vegetation (Vroblesky and others, 2004). The cores were collected on a day of heavy rain and after multiple days of rain (3.57 in.), as measured in Meriden, New Haven County, Connecticut, approximately 10 miles from the Durham Meadows Superfund Site (National Climatic Data Center, 2007; table 4).

The general correspondence between soil-gas data and vegetation-core data implies that the VOCs detected in the trees and shrubs at the Merriam Manufacturing Company property were related to soil-gas, vadose-zone water, or residual vadose-zone contamination. The depth to overburden ground water at the Merriam Manufacturing Company property was deeper than the rooting depth of at least one VOC-containing tree at the site. The depth to overburden ground water was 15 to 20 feet (ft) in parts of the property and was deeper than the drilling-refusal depth of 20 to 24 ft in other parts of the property (Anni Loughlin, U.S. Environmental Protection Agency, written commun., February 2007). The maximum depth of root tolerance in 3-year-old

Table 4. Precipitation in New Haven County, Connecticut, from August 25 through August 29, 2006.

(National Climatic Data Center, 2007)

Date	Precipitation, in inches
8/25/2006	1.27
8/26/2006	0.07
8/27/2006	1.15
8/28/2006	0.17
8/29/2006	0.91

mulberry trees was reported to be between about 1 and 2 ft in well-drained soils (Peper, 1998). Although Bunger and Thomson (1938) found mulberry roots extending to about 7.9 ft deep, approximately 70 percent of the large roots were in the top 2 ft of soil. In 12- to 14-year-old mulberry trees growing in contaminated soil (polyaromatic hydrocarbons), root systems were found to extend to a depth of only about 3.6 to 3.9 ft, with 70 percent of the large roots in the top 2 ft of soil (Olson and Fletcher, 1999; Olson and others, 2001).

Potential sources of the apparently shallow VOCs detected by the mulberry trees include soil gas, residual VOCs sorbed onto shallow soil, or VOCs transferred from deeper horizons to shallower sediment by hydraulic lift through the roots of nearby deeper-rooted trees. 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). Hydraulic lift is a less probable mechanism for providing the VOCs detected by the shallow rooted species at the Durham Meadows Superfund Site because the large amount of rain preceding and during tree-core collection probably wet the shallow soil, reducing the potential for hydraulic lift. Moreover, water extracted by plants during the wet season typically comes from shallow layers where the root system is densest (Canadell and others, 1996). Because the tree coring was done following and during heavy rainfall events, it is likely that most of the water and VOCs taken up by the mulberry trees were derived from horizons shallower than the water table. Thus, at this site, tree-core data showing the presence of VOCs are indicative of shallow subsurface contamination.

Other Areas at the Durham Meadows Superfund Site

In the trees cored from areas at the Durham Meadows Superfund Site outside of the Merriam Manufacturing Company property, only one tree was found to contain VOCs. Tree DM11, an unidentified species, contained 3 ppb/v of TCE in core DM11B (table 2). The detection appears to be valid because a syringe blank analyzed immediately prior to analyzing tree core DM11B showed no detections of TCE concentration at 0.3 ppb/v.

In the house adjacent to tree DM11, the USEPA detected TCE at 0.29 ppb/v in the basement indoor air and 0.25 ppb/v in the first floor air (Kahn, 2005). PCE was detected at 0.13 ppb/v in the basement indoor air and 0.23 ppb/v on the first floor. TCE and PCE were found at low levels in the basement soil gas (1.2 ppb/v and 0.94 ppb/v, respectively), but not in soil-gas samples collected around the outside of the home.

Ground water from a monitoring well at the house upslope from tree DM11 showed the presence of 7.7 micrograms per liter ($\mu\text{g/L}$) of TCE from about 12.8 to 17.3 ft below land surface on August 11, 2006 (well ME-168 Main; Metcalf & Eddy, Inc., 2006), although a dogwood tree (DM10) directly

adjacent to the well contained no VOCs. The depth to ground water at the well was approximately 17.6 ft (Metcalf & Eddy, Inc., 2006). Slightly farther away at well ME-95 Maple (fig. 1), ground-water VOC concentrations were less than 1 $\mu\text{g/L}$ at a depth of 15.89 to 17 ft (Metcalf & Eddy, Inc., 2006). Thus, although relatively high VOC concentrations were found in water from the bedrock (fig. 1; Metcalf & Eddy, 2005), substantially lower VOC concentrations were found in water from the overburden. The lack of VOC detection in tree DM10 and barely detectable concentrations of TCE in tree DM11 probably is a combination of the relatively low soil-vapor TCE concentration, the relatively large depth to water, and the heavy amount of rainfall during and preceding the tree coring. The trace TCE detection in tree DM11 (and not tree DM10) may be because tree DM11 is in more intimate contact with the ground water by virtue of its larger size and lower elevation. The lack of VOC detections in the tree cores and shrub cutting (DM8–DM15) at the remaining sites in the Durham Meadows Superfund Site is consistent with the fact that indoor air sampling and soil-gas sampling at locations near those trees showed only low or no VOC concentrations.

In May 2005, the USEPA collected soil-gas and air-grab samples from a home adjacent to trees DM8 and DM9. Indoor air samples showed only trace concentrations (less than 2 ppb/v) of VOCs, making it unlikely that VOCs associated with contaminated ground water were entering the home (Kahn, 2005). No ground-water data are available from that site because well ME-253 Main, drilled in July 2006, did not encounter water to the depth of refusal at 13.7 ft (Metcalf & Eddy, Inc., 2006).

Additionally, no detections of VOCs (less than 3 ppb/v) were found in cores of trees (DM13 and DM14) and clippings from a shrub (DM15) at the Strong School (fig. 1). Although 5.7 parts per million of VOCs were detected in July 2006 by photoionization screening of cuttings during well drilling at well ME-STR-B, no ground-water data are available because wells ME-STR-A and ME-STR-B (fig. 1) did not encounter water to the depth of refusal at 12.6 to 12 ft, respectively (Metcalf & Eddy, Inc., 2006). In 2005, only trace concentrations of TCE were found in soil vapor and indoor air at the site. The USEPA detected 0.92 ppb/v in the crawl space, 0.3 ppb/v in soil gas along the east wall of the school, and 0.4 ppb/v in soil gas along the west wall of the school (Kahn, 2005). The absence of VOCs in the analyzed tree and shrub samples may be due to the low concentrations of VOCs in the shallow subsurface, the relatively large depth to water, or the suppression of soil-gas concentrations by rainfall infiltration.

Summary

The U.S. Geological Survey and the U.S. Environmental Protection Agency participated in a joint effort to examine VOC concentrations in vegetation cores and shrub cuttings for use as indicators of potential vapor intrusion by VOCs at

the Durham Meadows Superfund Site, Durham, Connecticut. Cores were collected and analyzed from five trees (DM1 to DM5) and two shrubs (DM6 and DM7) at the Merriam Manufacturing Company property, a part of the Durham Meadows Superfund Site, and from seven trees elsewhere at the Durham Meadows Superfund Site (trees DM8 to DM14). Leaves were collected from an unidentified species of shrub in front of a school (DM15). The vegetation samples were obtained on August 29, 2006. Tree species included two maples, two mulberries, two hemlocks, and one each of catalpa, poplar, dogwood, sycamore, oak, and an unidentified tree. Shrubs included a staghorn sumac and two unidentified species.

The study used both (1) real-time vegetation-core analysis, which involved field heating the core samples for 5 to 10 minutes prior to field analysis, and (2) delayed analysis, which involved allowing the gases in the cores to equilibrate with the headspace gas in the sample vials for 1 to 2 days at room temperature prior to analysis. A general correspondence was found between the two approaches, indicating that field analysis of vegetation cores is a viable approach to real-time monitoring of subsurface volatile organic compounds. VOCs were found in cores from all of the trees and shrubs (DM1–DM7) collected at the Merriam Manufacturing Company property. In most cases, the vegetation-core data showed a general relation to the soil-gas data for 111TCA, TCE, and PCE, despite the fact that most of the soil-gas data collected in close proximity to the tree cores were collected about 3 years prior to the tree-core data. Cores from tree DM2 did not contain detectable PCE in 2006, however, although the nearest soil-gas sample (SG-E/2) to tree DM2 contained 109 parts per billion by volume of PCE in 2003. In the case of tree DM2, possible explanations for the difference between the tree-core and soil-gas PCE concentrations include (1) the heterogeneity of the soil-gas concentrations may be such that soil PCE concentrations differ between the tree and the soil-gas sample locations, (2) the 3 years that elapsed between the soil-gas survey and the tree coring may have allowed changes in the soil-gas PCE concentration, such as from dechlorination or volatilization, or (3) the substantial amount of rain preceding and during collection of the tree cores may have diluted the contaminated water and gas being taken up by the tree.

It is more likely that the VOCs detected in the trees and shrubs at the Merriam Manufacturing Company property were related to soil-gas or vadose-zone contamination rather than to direct uptake of ground water because (1) there was a general correspondence between the VOCs from vegetation samples and the VOCs from a soil-gas survey, (2) the depth to the water table at the Merriam Manufacturing Company property was greater than the probable depth of mulberry tree roots, and (3) the large amount of rain preceding and during the sampling probably reduced the potential, if any, for hydraulic lift by nearby deeper rooted species. Thus, at this site, vegetation-core data showing the presence of VOCs are indicative of shallow subsurface contamination. Because source areas sometimes are characterized by residual shallow soil contamination, the data from this investigation indicate

that tree coring may be a useful tool for locating contaminant source areas.

In the trees cored from three areas at the Durham Meadows Superfund Site outside of the Merriam Manufacturing Company property, VOCs were either not detected or barely detected. Although a previous investigation showed the presence of substantial VOC concentrations in ground water from bedrock in the areas where tree cores were collected, the VOC concentrations in ground water from the overburden in these areas appear to be substantially lower than those in the bedrock.

The only detected VOC in tree cores outside the Merriam Manufacturing Company property was TCE in tree DM11, and the concentration was barely above detection limits. An investigation showed low concentrations of TCE (0.13 to 1.2 ppb/v) in indoor air at the adjacent house, and 7.7 µg/L of TCE in the ground water. A dogwood tree (DM10) near the well containing 7.7 µg/L of TCE contained no detected VOCs. The lack of VOC detection in tree DM10 and barely detectable concentration of TCE in tree DM11 probably is a combination of the relatively large depth to water (17.6 ft), the relatively low soil-vapor TCE concentration, and the heavy amount of rainfall during and preceding the tree coring. The trace TCE detection in tree DM11 (and not tree DM10) may be because tree DM11 is in more intimate contact with the ground water by virtue of its larger size and lower elevation. The lack of VOC detections in the tree cores or bush cuttings at the remaining two sites in the Durham Meadows Superfund Site is consistent with the fact that indoor air sampling and soil-gas sampling at locations near those trees showed only low or no VOC concentrations.

The data from this investigation indicate that real-time and delayed analysis of vegetation cores are viable approaches to examining subsurface VOC soil-gas or vadose-zone contamination at the Durham Meadows Superfund Site. Thus, the methods may have application for determining the potential for vapor intrusion into buildings. The presence of VOCs in tree cores indicates the presence of subsurface VOCs and can be used as reconnaissance-level data to direct decisions regarding areas where more focused investigations may be warranted.

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