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# Chlorinated Ethenes from Groundwater in Tree Trunks

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The purpose of this investigation was to determine whether tree-core analysis could be used to delineate shallow groundwater contamination by chlorinated ethenes. Analysis of tree cores from bald cypress [*Taxodium distichum* (L.) Rich], tupelo (*Nyssa aquatica* L.), sweet gum (*Liquidambar stryaciflua* L.), oak (*Quercus* spp.), sycamore (*Platanus occidentalis* L.), and loblolly pine (*Pinus taeda* L.) growing over shallow groundwater contaminated with *cis*-1,2-dichloroethene (*c*DCE) and trichloroethene (TCE) showed that those compounds also were present in the trees. The cores were collected and analyzed by headspace gas chromatography. Bald cypress, tupelo, and loblolly pine contained the highest concentrations of TCE, with lesser amounts in nearby oak and sweet gum. The concentrations of *c*DCE and TCE in various trees appeared to reflect the configuration of the chlorinated-solvent groundwater contamination plume. Bald cypress cores collected along 18.6-m vertical transects of the same trunks showed that TCE concentrations decline by 30−70% with trunk height. The ability of the tested trees to take up *c*DCE and TCE make tree coring a potentially cost-effective and simple approach to optimizing well placement at this site.

## Introduction

The use of vegetation in studies of groundwater contamination has received increasing attention for a variety of reasons. Plants can remove contaminants from the subsurface by direct uptake and degradation (*1*−*6*), transpiration of volatile contaminants to the atmosphere (*6*−*8*), binding contaminants to plant tissue (*4*−*6*), and enchancing microbial growth and bioremediation in the rhizosphere (*9*−*13*). 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 trichloroethene (TCE) and *cis*-1,2-dichloroethene (*c*DCE), readily enter vegetation transpiration streams (*10*, *14*).

This investigation shows that TCE and *c*DCE are present in tree trunks growing above contaminated shallow groundwater. To our knowledge, this is the first investigation demonstrating that headspace analysis of tree cores can be an inexpensive and rapid method to delineate shallow TCE and *c*DCE groundwater contamination. In addition, this investigation presents data showing variations in concentrations of those compounds vertically upward along a tree trunk. Cores were collected from 97 mature trees growing above and in the vicinity of contaminated groundwater. Six different species of trees were examined. Cores from one tree were collected at various heights along the trunk.

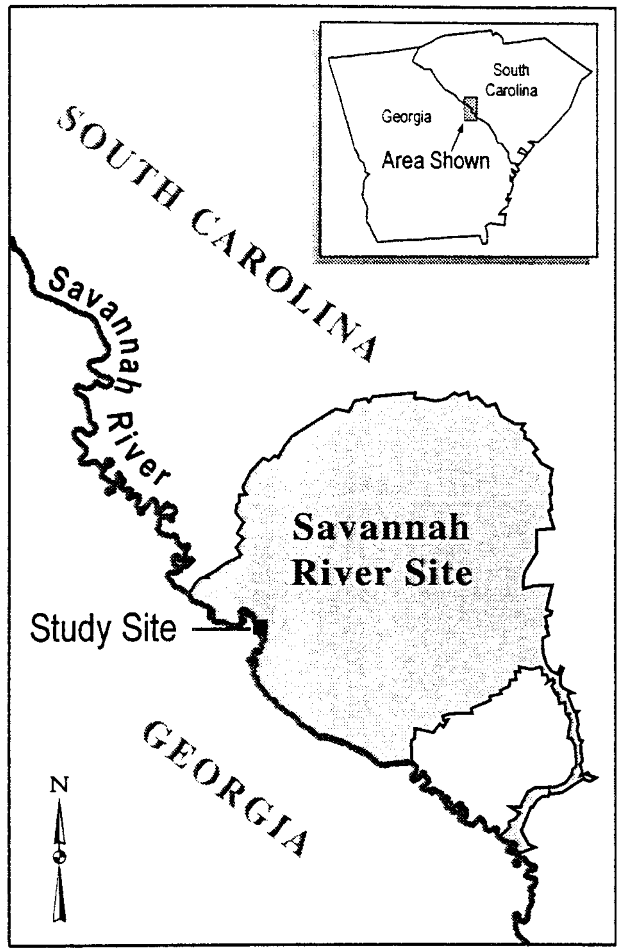


**FIGURE 1. Location of study area.**

**Study Area.** The study area is a forested flood plain of the Savannah River near the TNX Area, Savannah River site, SC (Figure 1). The flood plain consists of an upper and lower terrace, separated by an embankment ranging from about 1 to 2 m high. Northeast of the upper flood plain, land surface rises sharply to an upland terrace (the TNX Area) containing a former seepage basin. For a few days to a few months per year, the Savannah River inundates the lower flood plain (Figure 2). During most of the year, however, standing water is limited to low-lying areas of the upper and lower flood plains, indicated by marsh symbols in Figure 2.

Chlorinated solvents are present in the groundwater beneath parts of the upper flood plain. The dominant contaminants are TCE and *c*DCE. The probable source of the chlorinated solvents is leakage from a former seepage basin in the TNX Area (Figure 2). Groundwater flows through unconsolidated sands toward a drainage ditch that empties into the Savannah River. Depth to the water table beneath the flood plain ranges from the land surface to about 1.5 m. The groundwater flow rate in the flood plain is approximately 0.46 m/day (*15*).

Vegetation in the swamps of the flood plain primarily consists of bald cypress [*Taxodium distichum* (L.) Rich],

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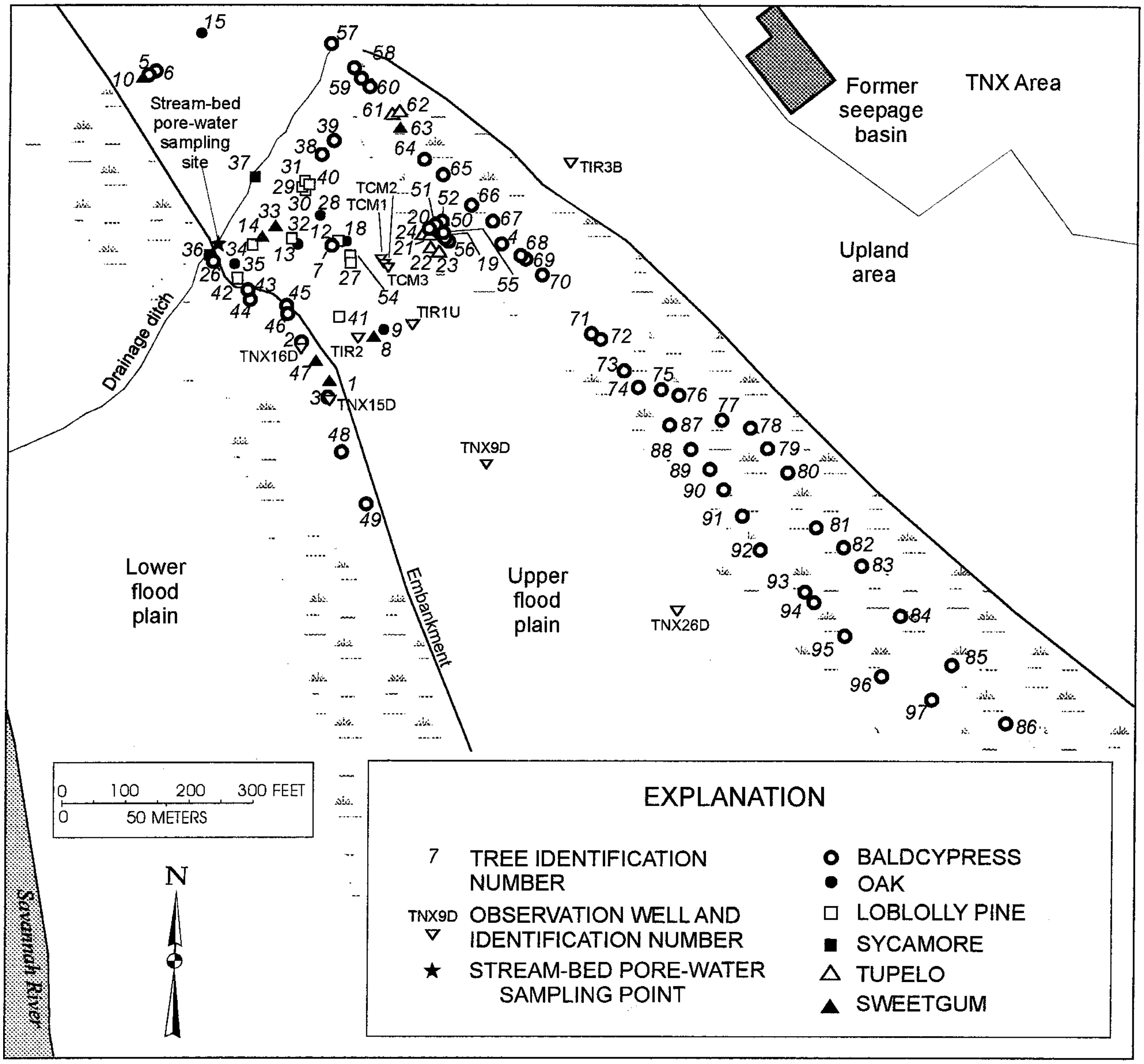


**FIGURE 2. Location and identification numbers of test trees and observation wells on the Savannah River flood plain, TNX Area, Savannah River site, SC.**

tupelo (*Nyssa aquatica* L.), and sweet gum (*Liquidambar stryaciflua* L.). In drier parts of the flood plain, oak (*Quercus* spp.), loblolly pine (*Pinus taeda* L.), and sweet gum are dominant with a relatively small population of bald cypress and sycamore (*Platanus occidentalis* L.).

## Methods

Cores were collected with an increment borer from 97 trees on the Savannah River flood plain in South Carolina during January, February, July, August, September, and October 1997 and January and February 1998 (Table 1). The trees included 64 bald cypress, 5 tupelos, 12 loblolly pines, 3 sycamores, 6 oaks, and 7 sweet gums (Figure 2). Part of the area contained groundwater contaminated with TCE and *c*DCE. Trees 11, 16, 17, and 53 were control oak, loblolly pine, sweet gum, and sycamore trees, respectively, collected from offsite areas not shown in Figure 2.

The cores used to delineate contamination in Figures 3 and 4were collected from the northeastern side of the respective tree. All cores used to examine areal distribution of contamination were collected from a height of approximately 1.5 m above ground, except for tree 7a (which was collected from 9 m on August 11, 1997, and from 3 m on October 1, 1997) and trees 20z and 21z (which were collected from about 1.8 m).

At selected trees, two cores were collected approximately 25 mm horizontally from each other to compare replication. The average concentration difference between replicate cores was 15.2% for TCE in six replicate pairs and 2.5% for *c*DCE in three replicate pairs. A bald cypress (tree 7) also was cored at various heights along its trunk. A bucket truck was used to access the tree, which grew adjacent to an unpaved road.

Upon collection, the cores (approximately 68 mm in length) immediately were removed from the coring tools and placed in 20-mL glass vials. At selected sites, ambient air samples also were collected by waving an empty 20-mL glass vial in the air for several seconds. Teflon-coated septum caps then were crimped onto the vials. The vials were heated at 40 °C for 12 h to vaporize volatile compounds in the cores. The vials then were cooled to room temperature, and a 100 $\mu$L sample of the headspace was collected into a gas syringe. Gas samples were analyzed by photoionization detection on a Photovac 10S Plus gas chromatograph. Concentrations are reported here as nanomoles of gas per liter of core water

TABLE 1. Concentrations of *cis*-1,2-Dichloroethene (*c*DCE) and Trichloroethene Vapor (TCE) (Expressed as nmol/L of Gas per Volume of Water) in Tree Cores from the TNX Flood Plain, Savannah River Site, SC[a]

| tree | date | *c*DCE (nmol/L) | TCE (nmol/L) | species | tree | date | *c*DCE (nmol/L) | TCE (nmol/L) | species |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1/22/97 | nd | <50 (<50) | swe | 45 | 1/30/98 | 54 | 310 | cyp |
| 1 | 10/1/97 | 60 | <20 | swe | 46 | 1/30/98 | 15 | 536 | cyp |
| 2 | 1/22/97 | nd | 935 (735) | cyp | 47 | 1/30/98 | <10 | <50 | cyp |
| 2 | 1/22/97 | nd | 180 | cyp | 48 | 1/30/98 | <10 | <50 | cyp |
| 2 | 10/1/97 | 55 | 220 (180) | cyp | 49 | 1/30/98 | <10 | <50 | cyp |
| 2 | 1/30/98 | <10 | 376 | cyp | 50 | 1/30/98 | 12 | 415 | cyp |
| 3 | 1/22/97 | nd | 245 (380) | cyp | 51 | 1/30/98 | 18 | 221 | cyp |
| 3 | 2/13/97 | nd | 110 | cyp | 52 | 1/30/98 | 25 | 430 | cyp |
| 3 | 10/1/97 | 210 | 100 | cyp | 53 | 1/30/98 | <10 | <50 | cyp |
| 3 | 1/16/98 | <10 | 298 | cyp | 54 | 1/30/98 | <10 | 1324 | cyp |
| 3 | 1/30/98 | <10 | <50 | cyp | 55 | 1/14/98 | 99 | 966 | cyp |
| 4 | 1/22/97 | nd | 410 (445) | cyp | 56 | 1/14/98 | 124 | 242 | cyp |
| 5 | 2/13/97 | nd | <50 | cyp | 57 | 1/16/98 | <10 | <50 | cyp |
| 5 | 8/11/97 | <10 | <50 | cyp | 58 | 1/14/98 | <10 | <50 | cyp |
| 6 | 2/13/97 | nd | <50 | cyp | 59 | 1/14/98 | <10 | <50 | cyp |
| 7a | 8/11/97 | 61 (63) | 35 040 (35 150) | cyp | 60 | 1/14/98 | <10 | <50 | cyp |
| 7a | 10/1/97 | 175 (176) | 4370 (4350) | cyp | 60 | 1/30/98 | <10 | <50 | cyp |
| 7 | 7/23/97 | 225 (215) | 8590 (9360) | cyp | 61 | 1/14/98 | <10 | <50 | tup |
| 7 | 9/9/97 | nq | 3180 | cyp | 62 | 1/14/98 | <10 | <50 | tup |
| 7 | 1/30/98 | 24 (17) (35) | 2093 (2094) (2942) | cyp | 63 | 1/14/98 | <10 | 28 | cyp |
| 8 | 8/11/97 | <10 | 230 | swe | 64 | 1/14/98 | <10 | 96 | cyp |
| 9 | 8/11/97 | <10 | <50 | oak | 65 | 1/14/98 | <10 | 272 | cyp |
| 9 | 9/9/97 | <10 | <50 | oak | 66 | 1/14/98 | 29 | 167 | cyp |
| 9 | 1/30/98 | <10 | <50 | oak | 66 | 1/26/98 | 23 (25) | 244 (242) | cyp |
| 10 | 9/9/97 | <10 | <50 | swe | 66 | 2/17/98 | 55 (53) | 216 (212) | cyp |
| 11 | 9/9/97 | <10 | <50 | oak | 67 | 1/14/98 | 71 | 351 | cyp |
| 12 | 9/9/97 | 110 | 730 | lob | 68 | 1/14/98 | <10 | 46 | cyp |
| 12 | 1/30/98 | <10 | 1742 | lob | 69 | 1/14/98 | <10 (<10) | 310 (265) | cyp |
| 13 | 9/9/97 | 40 | <50 | oak | 70 | 1/14/98 | <10 (<10) | 49 (45) | cyp |
| 13 | 1/30/98 | <10 | <50 | oak | 71 | 1/14/98 | <10 | 249 | cyp |
| 14 | 9/9/97 | <10 | 60 | swe | 71 | 1/16/98 | <10 | 128 | cyp |
| 14 | 1/30/98 | <10 | <50 | swe | 72 | 1/14/98 | <10 | 219 | cyp |
| 15 | 9/9/97 | <10 | <50 | oak | 72 | 1/16/98 | <10 | 213 | cyp |
| 16 | 9/9/97 | <10 | <50 | lob | 73 | 1/14/98 | <10 | 71 | cyp |
| 17 | 9/9/97 | <10 | <50 | swe | 73 | 1/16/98 | <10 | 63 | cyp |
| 18 | 9/9/97 | 70 | <50 | oak | 74 | 1/14/98 | <10 | 78 | cyp |
| 18 | 1/16/98 | 90 | <50 | oak | 74 | 1/16/98 | <10 | 31 | cyp |
| 18 | 1/30/98 | <10 | <50 | oak | 74 | 2/17/98 | <10 | 25 | cyp |
| 19 | 1/14/98 | 47 | 780 | cyp | 75 | 1/16/98 | <10 | <50 | cyp |
| 20z | 1/14/98 | 18 | 119 | cyp | 76 | 1/16/98 | <10 | 44 | cyp |
| 20z | 1/30/98 | 23 | 174 | cyp | 77 | 1/16/98 | <10 | 87 | cyp |
| 20 | 1/30/98 | 16 (<10) | 283 (248) | cyp | 78 | 1/16/98 | <10 | 409 | cyp |
| 21z | 1/14/98 | 66 | 1021 | tup | 78 | 1/26/98 | <10 (<10) | 418 (454) | cyp |
| 21z | 1/30/98 | 42 | 1149 | tup | 78 | 2/17/98 | <10 (<10) | 196 (245) | cyp |
| 21 | 1/30/98 | 56 (49) | 1469 (1583) | tup | 79 | 1/16/98 | <10 | 200 | cyp |
| 23 | 1/14/98 | 74 | 426 | tup | 79 | 1/26/98 | <10 | 120 | cyp |
| 24 | 1/14/98 | 23 | 1033 | tup | 80 | 1/16/98 | <10 | 118 | cyp |
| 26 | 1/26/98 | 19 | 362 | cyp | 80 | 1/26/98 | <10 | 123 | cyp |
| 26 | 1/30/98 | 26 | 457 | cyp | 81 | 1/16/98 | <10 | <50 | cyp |
| 27 | 1/30/98 | <10 | 1241 | lob | 81 | 1/26/98 | <10 | <50 | cyp |
| 28 | 1/30/98 | <10 | <50 | oak | 82 | 1/16/98 | <10 | <50 | cyp |
| 29 | 1/30/98 | <10 | 308 | lob | 82 | 1/26/98 | <10 | 33 | cyp |
| 30 | 1/30/98 | <10 | 318 | lob | 83 | 1/26/98 | <10 | <50 | cyp |
| 31 | 1/30/98 | <10 | 751 | lob | 84 | 1/26/98 | <10 | <50 | cyp |
| 32 | 1/30/98 | <10 | 764 | lob | 85 | 1/26/98 | <10 | <50 | cyp |
| 33 | 1/30/98 | <10 | 74 | swe | 86 | 1/26/98 | <10 | <50 | cyp |
| 34 | 1/30/98 | <10 | 2263 | lob | 87 | 2/17/98 | <10 | 46 | cyp |
| 35 | 1/30/98 | <10 | 69 | oak | 88 | 2/17/98 | <10 | 43 | cyp |
| 36 | 1/30/98 | <10 | <50 | syc | 89 | 2/17/98 | <10 | 160 | cyp |
| 37 | 1/30/98 | <10 | 130 | syc | 90 | 2/17/98 | <10 | 148 | cyp |
| 38 | 1/30/98 | <10 | 106 | cyp | 91 | 2/17/98 | <10 | 270 | cyp |
| 39 | 1/30/98 | <10 | 116 | cyp | 92 | 2/17/98 | <10 | 48 | cyp |
| 40 | 1/30/98 | <10 | 118 | lob | 93 | 2/17/98 | <10 | <50 | cyp |
| 41 | 1/30/98 | <10 | 1131 | lob | 94 | 2/17/98 | <10 (<10) | <50 (<50) | cyp |
| 42 | 1/30/98 | <10 | 479 | lob | 95 | 2/17/98 | <10 | <50 | cyp |
| 43 | 1/30/98 | 32 | 296 | cyp | 96 | 2/17/98 | <10 | <50 | cyp |
| 43 | 2/17/98 | 33 | 153 | cyp | 97 | 2/17/98 | <10 | <50 | cyp |
| 44 | 1/30/98 | 11 | 824 | cyp | 98 | 2/17/98 | <10 | <50 | cyp |
| 44 | 2/17/98 | <10 (<10) | 270 (229) | cyp | 99 | 2/17/98 | <10 | <50 | cyp |

[a] nd indicates analysis not done; nq indicates compound not quantified due to peak interferences; ( ) indicates concentration in replicate core sample collected 25 mm laterally from original core sample; cyp indicates bald cypress; lob indicates loblolly pine; tup indicates tupelo; swe indicates sweet gum; syc indicates sycamore.

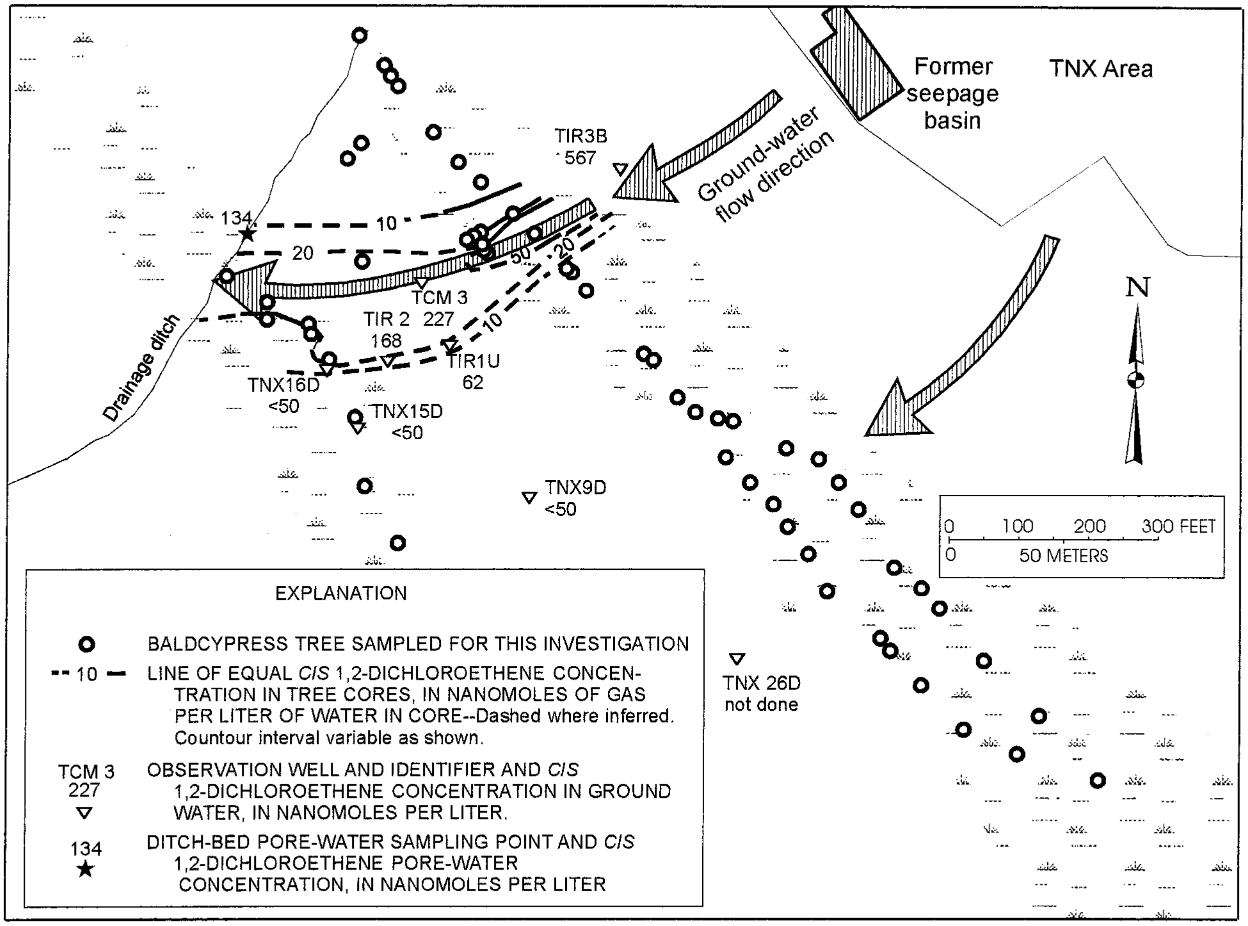


**FIGURE 3.** ***cis*-1,2-Dichloroethene concentrations in bald cypress trunks in January and February 1998 and in groundwater during August 1997 and groundwater flow directions (*15*), TNX flood plain, Savannah River Site, SC.**

(nmol/L). Statistical tests were done on concentrations based on core-water volume, and the core dry weight verified that the sample normalization procedure did not significantly affect the results.

Groundwater was purged and sampled from wells using a positive-displacement submersible pump. Casing water was purged until specific conductance stabilized. Groundwater was sampled from beneath the drainage ditch by pushing a 6.35-cm i.d. stainless steel sampling point into the streambed so that the screened interval (7.8 mm) was approximately 0.6 m below the stream base. Interstitial water was pumped from the piezometer using a peristaltic pump. Water was pumped at a slow rate, and a minimum amount of water (20 mL) was removed prior to collecting a water sample for volatile organic carbons (VOCs) to avoid dilution effects from mixing with streamwater. Water samples were collected in 40-mL glass bottles, capped with Teflon-lined bottle caps, and analyzed using U.S. Environmental Protection Agency Method 8240 (*16*).

Statistics were performed using the SAS software package (SAS Institute Inc., Cary, NC). Analysis of variance tests (PROC GLM) were used to evaluate differences in TCE and *c*DCE concentrations among tree species and between sites (control vs contaminated). Linear regression analysis was used to test for changes in TCE and *c*DCE with height above ground.

## Results and Discussion

Groundwater in the vicinity of several test trees contained TCE and lesser amounts of *c*DCE (Table 1). These compounds were not detected in air samples adjacent to the trees, indicating that the compounds were derived from below land surface. In May 1997, water samples from wells TIR 3B and TCM 3 contained 3577 and 1187 nmol/L of TCE, respectively (William Pidcoe, Westinghouse Savannah River Company, written communication, July 1997). Well TCM 3 also contained 246 nmol/L of *c*DCE. Numerical simulations (*15*) suggest that the path of contaminated groundwater flow from the former seepage lagoon is toward a reach of the drainage ditch near the embankment separating the upper and lower flood plains (Figure 3). Groundwater beneath the ditch, collected from a drive-point well screen (Figure 2) in the probable contaminant-discharge zone, contained 134 nmol/L of *c*DCE and 822 nmol/L of TCE in August 1997, providing supporting evidence for the hypothesized path of contaminant transport.

*cis*-1,2-Dichloroethene was present in cores from several bald cypress trees growing in the area of *c*DCE-contaminated groundwater. The area where *c*DCE was found in bald cypress trees was along a path coincident with the groundwater flow path from the former seepage basin (Figure 3) and coincided with areas where *c*DCE was found in groundwater. The data strongly suggest that the *c*DCE in tree trunks is derived from the contaminated groundwater originating from the former seepage basin.

TCE also was found in bald cypress trunks growing in the area of TCE-contaminated groundwater downgradient from the former seepage basin (Figure 4). The distribution of bald cypress containing TCE was more widespread than the distribution of bald cypress containing *c*DCE. Moreover, TCE also was found in tree 78 and the neighboring trees farther south than the flow path from the former seepage basin (Figure 4). These data suggest a second plume of TCE in the aquifer. Although no data was collected from well TNX 26D during 1997−1998, 41−84 nmol/L of TCE was found in

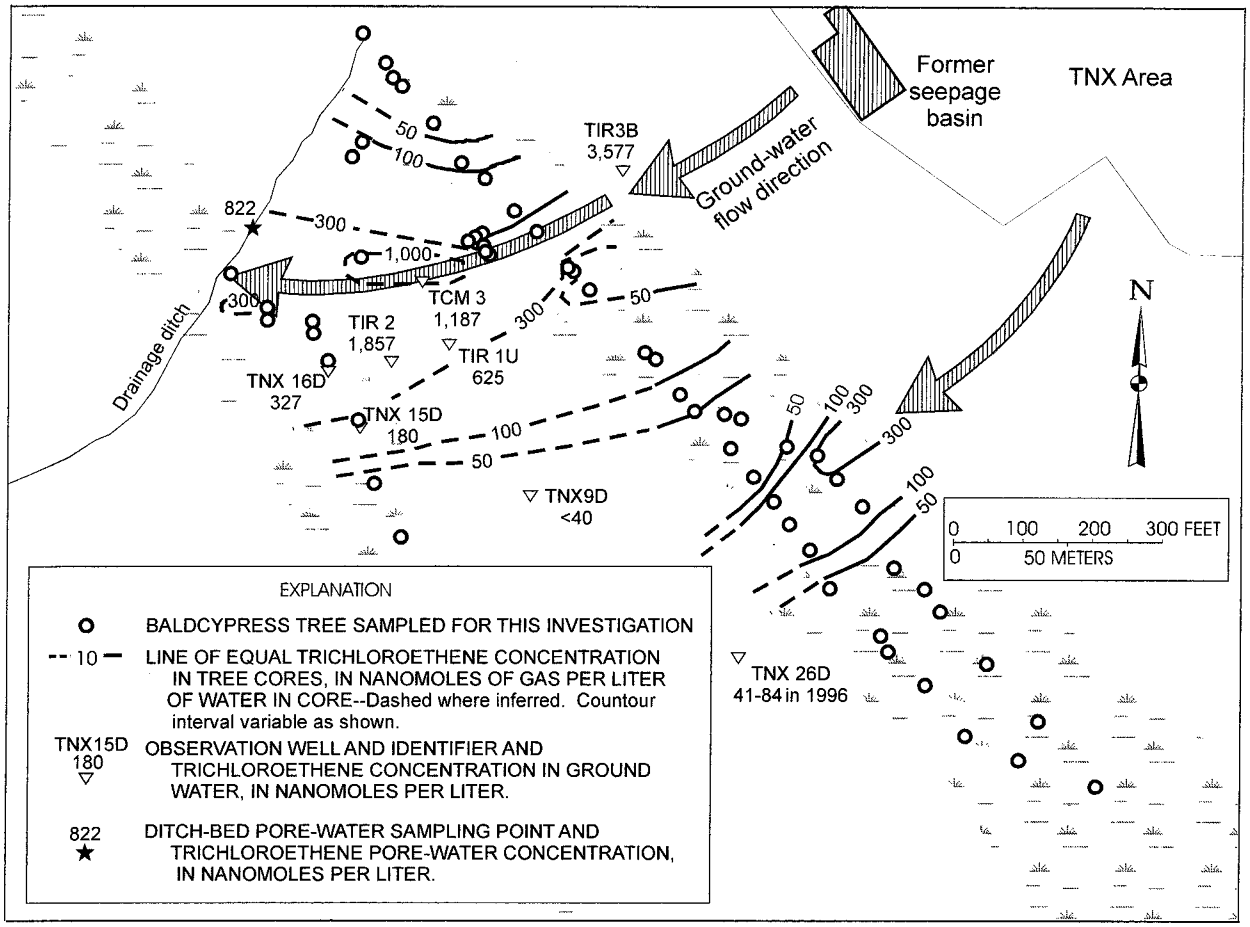


**FIGURE 4. Trichloroethene concentrations in bald cypress trunks in January and February 1998, in groundwater during May 1997 and 1996 (well TNX-26D only), and at the ditch-bed pore-water sampling point during August 1997 and groundwater flow directions (*15*), TNX flood plain, Savannah River Site, SC.**

groundwater at the well during 1996 (William Pidcoe, Westinghouse Savannah River Company, written communication, July 1998), supporting the hypothesis that the spatial distribution of TCE among bald cypress sampled across the area reflects the distribution of TCE in the shallow aquifer.

Examination of cores collected at various trunk heights of a bald cypress (tree 7) growing in an area of groundwater contaminated with TCE showed that concentrations of TCE decreased significantly with increasing trunk height ($p = 0.001$) (Figure 5) although *c*DCE concentrations did not ($p = 0.4$) (data not shown). Tree 7 branched into two trunks at a height of 2.1 m above ground. The two trunks are designated as southern and northern. TCE concentrations along the southern trunk of tree 7 during July and August decreased by about 70% and 53%, respectively, from near the ground to a height of about 17−18.6 m (Figure 4). The northern trunk of tree 7 showed an approximate 30% decrease in TCE concentrations over the same vertical distance in August 1997 (Figure 5).

The specific mechanism causing decreasing concentrations of TCE with increasing height in tree 7 (Figure 5) is not known. One possibility is that there is a loss mechanism for TCE along the transport pathway up the tree. Such a loss mechanism could be VOC volatilization followed by diffusion through the tree bark. The fact that water vapor is known to escape through the bark of trees, chiefly through lenticels (*17*), is consistent with the loss of TCE through the tree bark. The Henry's law constant is slightly larger for TCE (0.007 $m^3$ atm/mol) than for *c*DCE (0.0032 $m^3$ atm/mol), indicating that TCE has a slightly larger tendency to volatilize that *c*DCE

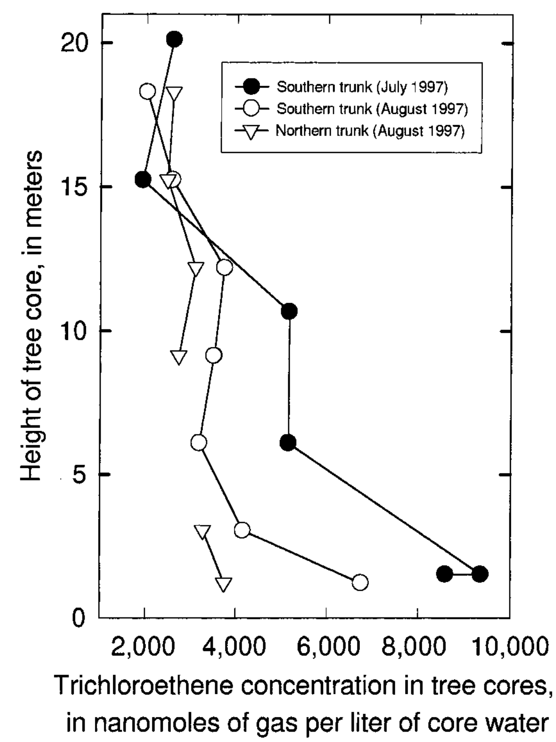


**FIGURE 5. Trichloroethene concentration in cores along the trunk of tree 7 (bald cypress). Cores from the northern trunk were not collected in July 1997.**

(*18*). Additional possible explanations include TCE degradation or sorption within the trunk, the potential for spiral transport of fluids up the trunk (*19*), or temporal changes in groundwater contaminant concentrations.

Although all of the cores collected for this analysis were from the northeastern part of each tree, selected trees were cored at various locations around the trunk to examine directional variability. Core data from different sides of individual trees showed concentration differences ranging from 44 to 92% for TCE and from 6 to 90% for *c*DCE. The relatively good replication in cores collected 25 mm apart (15.5% for TCE and 2.5% for *c*DCE) indicates that the coring approach did not contribute significant inconsistencies to the data. The source of the directional variation is not known but may be related to a variety of factors, such as injuries (*20*), disease and insect damage (*21*), gas embolisms (*22*), and variations in TCE concentration taken up by root systems on differing sides of the tree.

All species of trees examined from areas of groundwater contamination showed evidence of TCE or *c*DCE in the trunks. Some species appeared to exhibit similar uptake potential. Examination of a cluster of bald cypress and tupelo (trees 19−24, 50−52, and 55) showed no significant differences in concentrations between the species. In January 1998, the TCE concentration in bald cypress 7 was approximately 2000−3000 nmol/L, and high concentrations of TCE also were found in nearby loblolly pines 12, 27, and 54 (1742, 1241, and 1324 nmol/L, respectively). Bald cypress 43 also contained similar TCE concentrations (296 nmol/L) as adjacent loblolly pine 42 (479 nmol/L).

Oaks, however, appeared to contain less TCE than adjacent bald cypress or loblolly pines. In September 1997, oak 11 contained <50 nmol/L of TCE while a nearby loblolly pine (tree 12) contained 730 nmol/L of TCE and a nearby bald cypress tree (tree 7) contained 3180 nmol/L of TCE (Table 1). Similarly, in January 1997, a different oak (tree 35) contained only 69 nmol/L of TCE, whereas loblolly pines on either side of tree 35 contained 2263 (tree 34) and 479 (tree 42) nmol/L. Likewise, oak 13 contained less than 50 nmol/L of TCE while an adjacent loblolly (tree 32) contained 764 nmol/L of TCE. The consistency of the data implies that these findings are function of tree-species differences rather than an artifact of variability due to sampling a particular side of each tree.

Sweet gum also appeared to contain less TCE than loblolly pines. Sweet gums 14 and 33 contained <50 and 74 nmol/L of TCE, respectively, in January 1998, while loblolly pines on various sides of the sweet gums contained 765 (tree 32), 2263 (tree 34), 308 (tree 29), 318 (tree 30), and 751 nmol/L (tree 31) (Table 1).

Previous investigations also have noted concentration differences among species. Selected chlorinated compounds have been found to be degraded faster in the rhizosphere soil of monocot species than dicot species (*23*). Loblolly pines have been found to take up more TCE than grasses and legumes (*11*). In this investigation, the concentration differences also may partly be a function of the water-conduction differences between species. Conifers (such as bald cypress and loblolly pine) conduct water through more than the outermost ring, whereas in ring-porous trees (such as oak) nearly all of the water is conducted through the outermost growth ring (*24*, *25*). 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 the ring-porous trees.

The extensive areas of swamp and periodic flooding impart difficulties in installing and maintaining effective groundwater sampling wells at this site. The large number of trees available, however, and the ability of those trees to take up *c*DCE and TCE, even in areas of standing water, make tree coring a potentially cost-effective and simple approach to optimizing well siting in this type of environment.

## Acknowledgments

The use of trade names does not imply endorsement by the U.S. Geological Survey.

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