

Tree Coring to Assess Subsurface Volatile Organic Compound Contamination

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User's guide to tree coring for VOCs

Introduction (Advantages and Limitations)

➤ Methodology

- Tree core collection
- Analysis
- Quality control

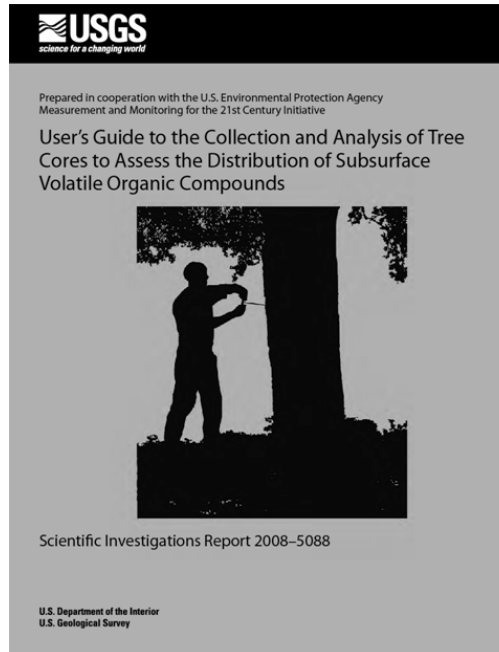
➤ Historical Perspectives and Technical Considerations

- Historical perspectives
- Technical rationale for method aspects.
- Factors influencing VOCs in tree cores

Appendix 1: Case Studies

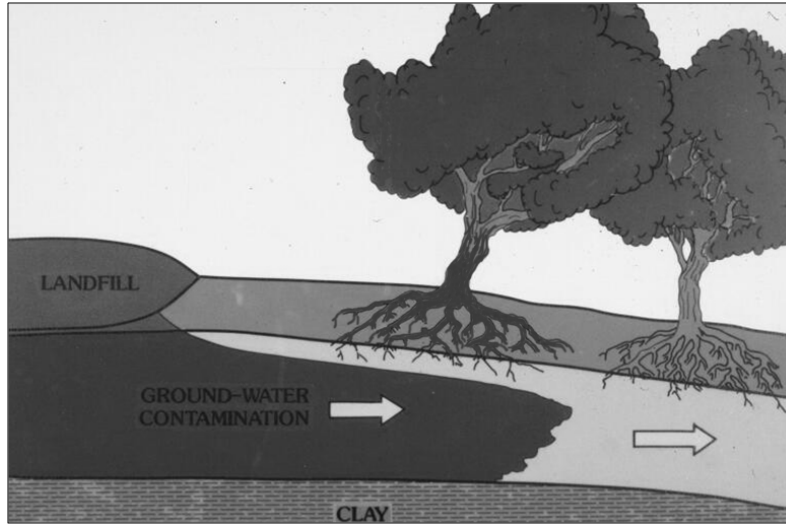
Appendix 2: Gas chromatography methodology

<http://pubs.water.usgs.gov/sir2008-5088>



Basic concept:

- Tree roots take up water, gasses, and associated contaminants from the subsurface.
- The contaminants move up the trunk.
- Tree coring provides a sample of the ground water beneath the tree.



Application

- Rapid and inexpensive reconnaissance tool for determining whether subsurface VOCs are present or for areally mapping subsurface VOCs.
- Useful for directing drilling efforts.
- Used at a variety of sites as tool in places where contamination is suspected but little or no subsurface information is available.

What types of VOCs are appropriate?

- Typically VOCs with a $\log K_{ow}$ of 0.5-3
- Previous investigations have found:
 - PCE, TCE, cDCE, VC
 - PCA, TCA, CT
 - Benzene, toluene, ethylbenzene, xylene isomers, MTBE

Advantages (1 of 3)

- Advantages:
 1. Can provide information in areas where access is limited (cultural influences, vegetation cover)
 2. Applicable to a wide variety of common ground-water VOC contaminants (chlorinated solvents and petroleum hydrocarbons)
 3. Presence of VOCs in tree cores is a strong indicator of subsurface VOCs.

Advantages (2 of 3)

4. Sometimes can be used to detect VOCs in soil gas.
5. Can detect VOCs at relatively low concentrations. Schumacher and others, (2004) detected PCE in tree cores where ground-water PCE was as low as 8 µg/L.
6. Rapid, simple method.
7. Can be field analyzed or analyzed later.
8. If analyzed later, the samples can be stored without refrigeration.

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References of tree coring related to soil gas: Struckhoff, 2003; Shumacher and others, 2004; Struckhoff and others, 2005; Vrobesky and others, 2006; 2008.

Advantages (3 of 3)

9. Inexpensive method. Borers cost a few hundred dollars and can be used indefinitely.
10. Minimum amt. of field equipment required. (Coring tool and bottles)
11. Sometimes tree-core parent/daughter VOC ratios can indicate areas of subsurface dechlorination.
12. Trees sample a large areal volume.

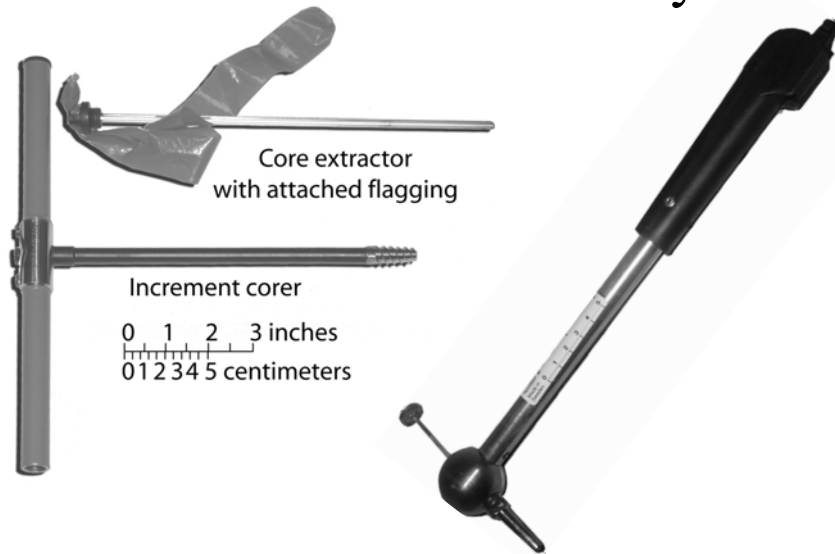
Limitations (1 of 2)

1. Absence of VOC detection in tree cores does not mean there are no VOCs in the subsurface.
2. Tree-core VOC concentrations provide only a generalized quantification of subsurface VOC concentrations.
3. Trees readily recover from coring, but care should be taken to avoid excess coring of an individual tree to reduce stress to the tree

Limitations (2 of 2)

4. Under some conditions, rainfall and winter dormancy can reduce VOC concentrations in tree cores.
5. A number of tree-related VOCs elute early on a typical short-column field gas chromatograph, potentially obscuring early eluting VOCs, such as vinyl chloride.

Methodology for Collection of Tree Cores for VOC analysis



➤ Mark the tree to facilitate returning to it.

- “engraved” aluminum tag, tree paint, wooden stake, flagging, etc., depending on esthetic issues and how long the tag needs to last.



➤ Take notes

- Location info: date, time, site, tree ID, etc.
- Tree info: species, stress indicators, diameter, etc.
- Core info: height of core, side of tree, unusual characteristics, etc.

Tree Coring



Collect cores from about the same height for the sake of comparison.

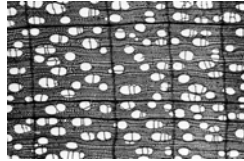
In general, a core near the ground can have higher VOC concs. than a core farther up the trunk, but for ease of collection, a simple approach is to use mean breast height (about 4.3 ft from the base).

How deep to core?

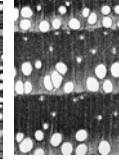
A. Nonporous wood



B. Diffuse-porous wood

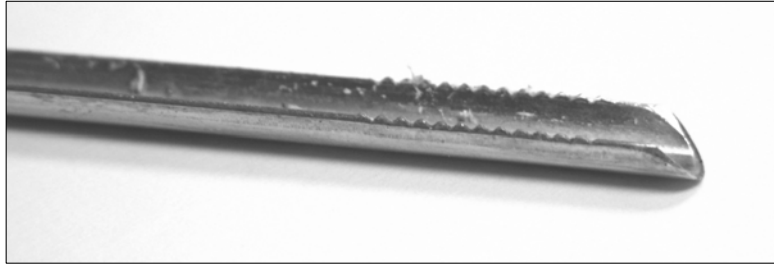


C. Ring-porous wood



- Water transport takes place in the outermost part of the trunk, so you don't have to core deep (not more than 2 to 3 inches).
- In ring-porous wood, such as oak, nearly all of the transpiration water moves through the outermost growth ring.
- In nonporous trees, such as pines, water transport is through several growth rings.
- In general, core length should be consistent across a particular study site and should be about the length of the sample jar being used.

Teeth on the core extractor

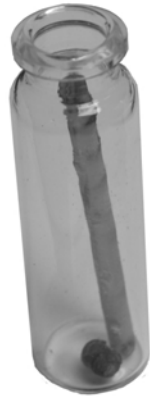


Core removal from core barrel:

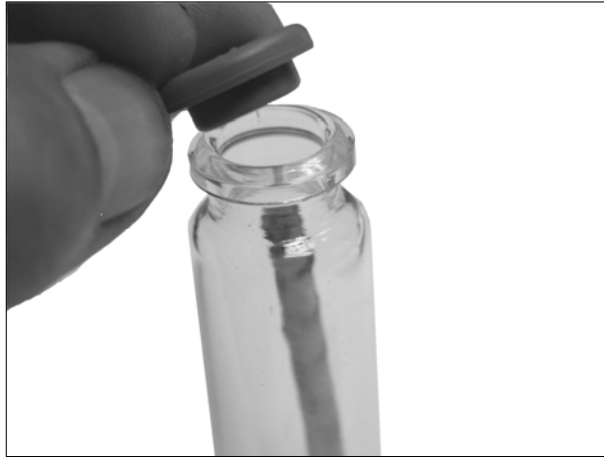
When you reach the coring depth, insert the extractor, turn the coring tool $\frac{1}{2}$ turn outward to break the core off, and pull it out.



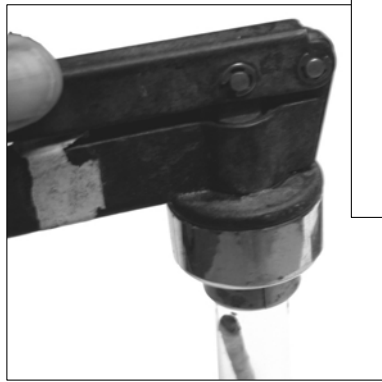
Transfer the tree core to a vial



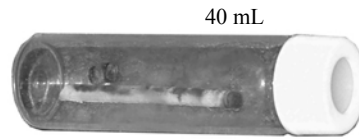
Cap the vial with Teflon-lined seal



Crimp cap on vial



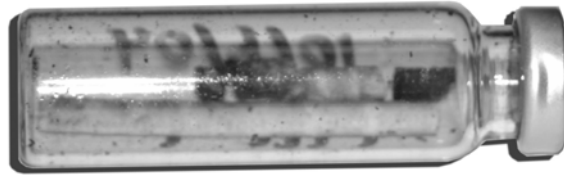
20 mL



40 mL

Or use standard VOA vial
(just remember that they are
made for water, not gases)

Tree core in vial



In general, the vials tend to begin fogging up within seconds of capping, indicating vapor transfer to the headspace.

Post-coring tree care

- Sealing the tree core hole probably is not needed and sometimes can be harmful.
- The open hole can allow decay and disease, but plugging the hole does little to reduce discoloration or decay.
- In general, healthy trees (particularly conifers) respond well to coring by self sealing and creating chemical barriers.
- So a practical approach is to leave the core hole unsealed.

Quality Control

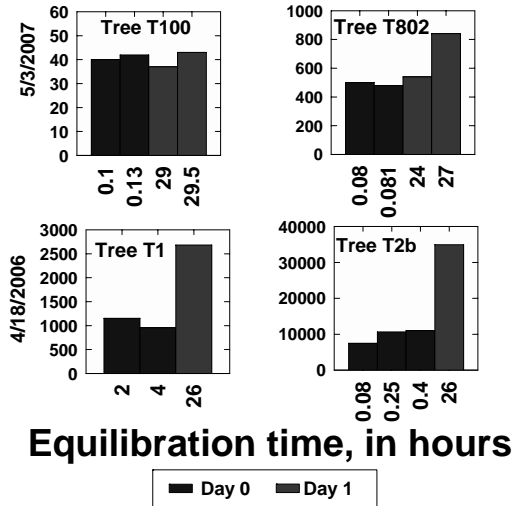
- Collect 10% duplicate samples (a second core slightly below the first core).
- Collect an air blank sample.
- Collect samples of background trees for each species to assure that the “contaminant” identification is not simply a natural VOC associated with the tree.

How long should the vials equilibrate before analysis?

Increasing equilibration time →

TCE in unheated cores over time

TCE, ppb/v

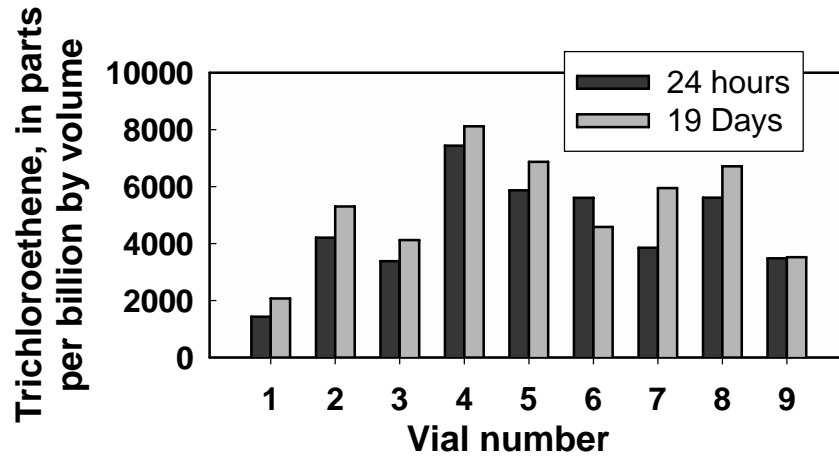


Vrobesky and others, 4th Int. Phytotechnologies Conference, Denver, CO., September 24-28, 2007.

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In some cases the tree VOC HSA concentration did not substantially change from 5 minutes after sampling to the next day. In other cases, the VOC concentration dramatically increased. The differences could be due to many factors, including the ambient temperature and how hot the core barrel became from friction during coring.

Comparison of tree-core equilibration after 1 day and 19 days



Vrobesky and others, 4th Int. Phytotechnologies Conference, Denver, CO., September 24-28, 2007.

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In a comparison test, TCE concentrations did not increase enough over 19 days to make it worth waiting more than 24 hours.

Sample analysis approaches

- Headspace analysis (HSA)
 - Simple, cheap, probably sensitive enough for most shallow TCE ground-water plumes
- Methanol extraction:
 - Produces higher TCE concentrations than HSA, but costs more.
 - Extracts more than just the volatiles.
- Activated carbon (contact Joel Burken)
 - Very sensitive, but more expensive than HSA
 - Uses the corehole rather than the core.
- Field colorimetric gas-detector tubes
 - Very quick and easy, but useful only at high concentrations

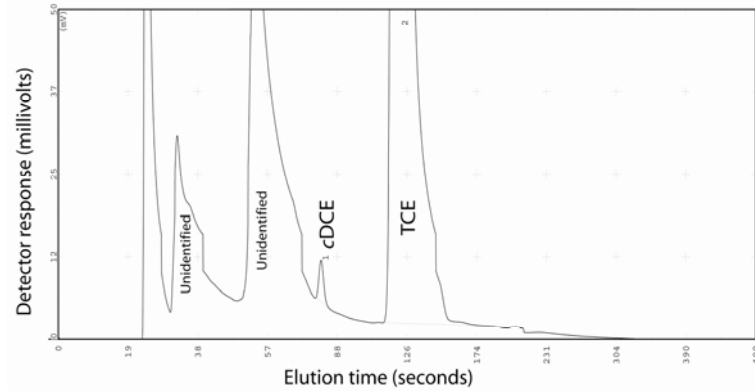
Headspace sampling of vial



Inject the headspace into a gas chromatograph



Typical chromatograph of tree core showing chlorinated solvents



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There typically are early eluting chromatographic peaks associated with natural volatile compounds in the tree.

Heaters that can be used in the field with a power inverter and a battery



Block heater



Water bath

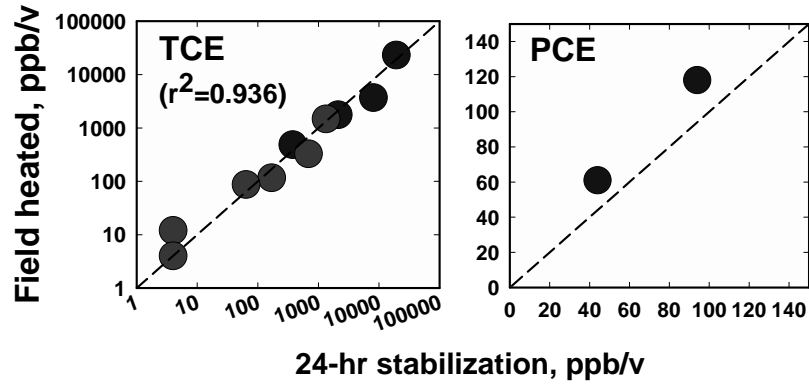
Vroblesky and
others, 4th Int.
Phytotechnologies
Conference, Denver, CO.,
September 24-28, 2007.

60-70 C for about 5 minutes

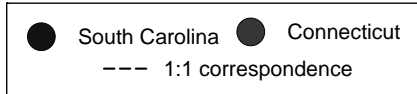
29

Equilibration time sometimes can be substantially shortened by heating the sample in the field.

Comparison of field heated and analyzed tree cores to unheated tree cores analyzed after 24 hours

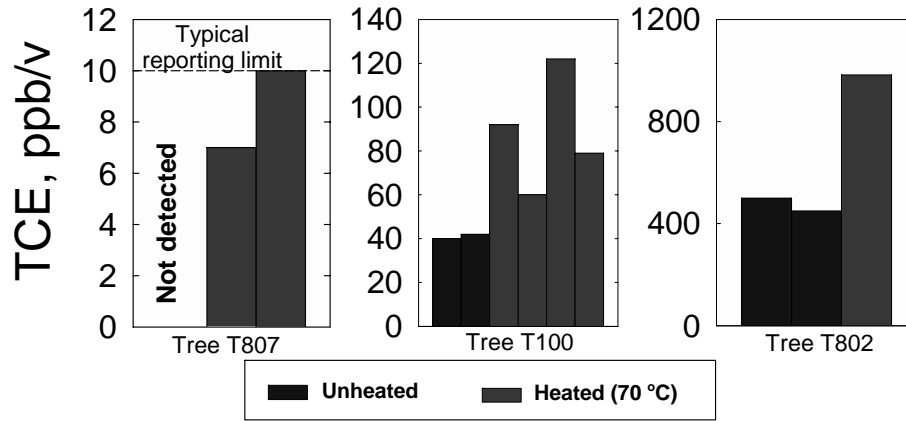


Vrobesky and others, 200, USGS SIR2007-5212.



Comparison of field heated to unheated tree cores 5 min. after collection

(NWS Charleston SWMU17)



Vroblecky and others, 4th Int. Phytotechnologies Conference, Denver, CO., September 24-28, 2007.

Field analysis

- Field analysis can be used to direct the tree coring effort and optimize plume mapping.
- Heating the cores can increase the potential for VOC detection.
- Don't heat them too much or you will volatilize tree constituents that complicate the chromatogram, potentially have vapor loss, and possibly stink up the place.

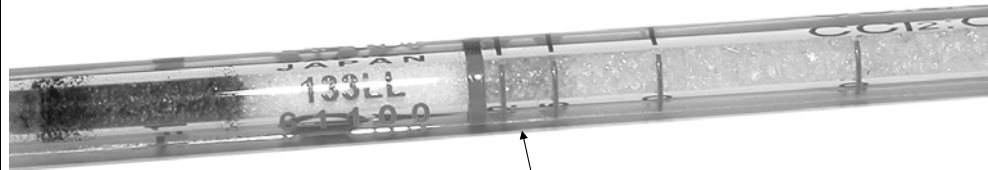
Colorimetric device



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For very high concentrations (>1 ppmv), a simple colorimetric approach can be used in the field to detect VOCs in tree cores.

Gastube from tree core



Chlorinated VOCs are present

Vrobesky and
others, 4th Int.
Phytotechnologies
Conference, Denver, CO.,
September 24-28, 2007.

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This is a colorimetric response from a tree core done within a few minutes of core collection showing that chlorinated VOCs are present.

Comparison to field GC

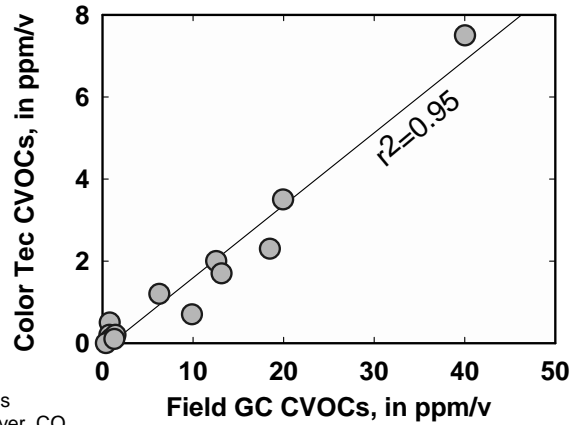


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We did a field comparison of our modified ColorTec method to what we would find using a typical field gas chromatograph.

Comparison of colorimetric to field GC tree-core analysis after heating

Difference in magnitude is because colorimetric is calibrated for water



Vroblesky and others, 4th Int. Phytotechnologies Conference, Denver, CO., September 24-28, 2007.

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We got a very linear correlation between the field GC results and the simple colorimetric method at high tree-core VOC concentrations (>1 ppmv). The scale on the Color Tec axis is simply a relative scale. At

Comparison of field GC to colorimetric approach

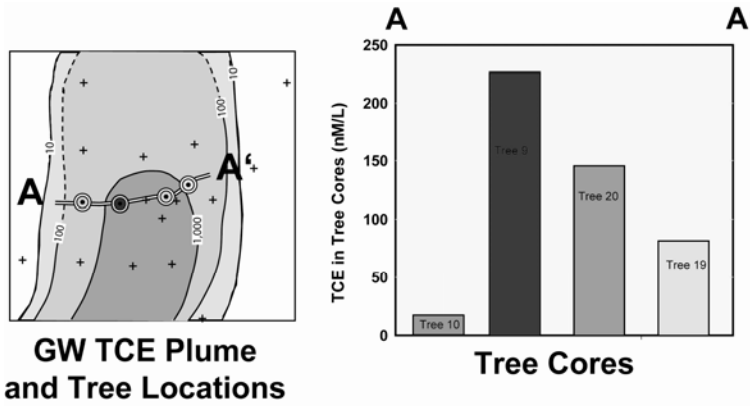
- Good detection and relative correlation to field GC at GC vapor concentrations >1 ppmv, although the gas tubes have a different reporting scale.
- In the range of 0.7-1 ppmv (field GC), the values are at the detection limit for the colorimetric.
- CVOC concentrations <0.7 ppmv (field GC) are not detectable with the colorimetric approach. Field GCs are sensitive down to about 0.01 ppmv for TCE.
- The colorimetric method is inexpensive and easy for field analysis where tree-core concentrations are high (>1 ppm/v). (~\$1500 for the reusable kit, about \$5.65/analysis)

Vroblesky and others, 4th Int. Phytotechnologies Conference, Denver, CO., September 24-28, 2007.

Selected factors
influencing VOC
concentrations in tree
cores

TCE concentrations in tree cores are partly a function of TCE concentrations in ground water

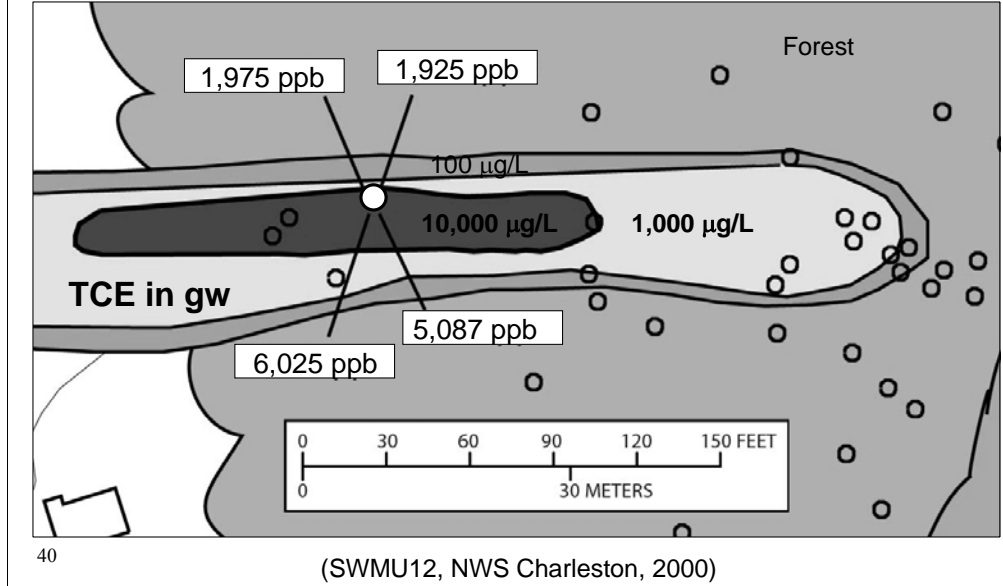
(Carswell Golf Course, TX)



Oak trees

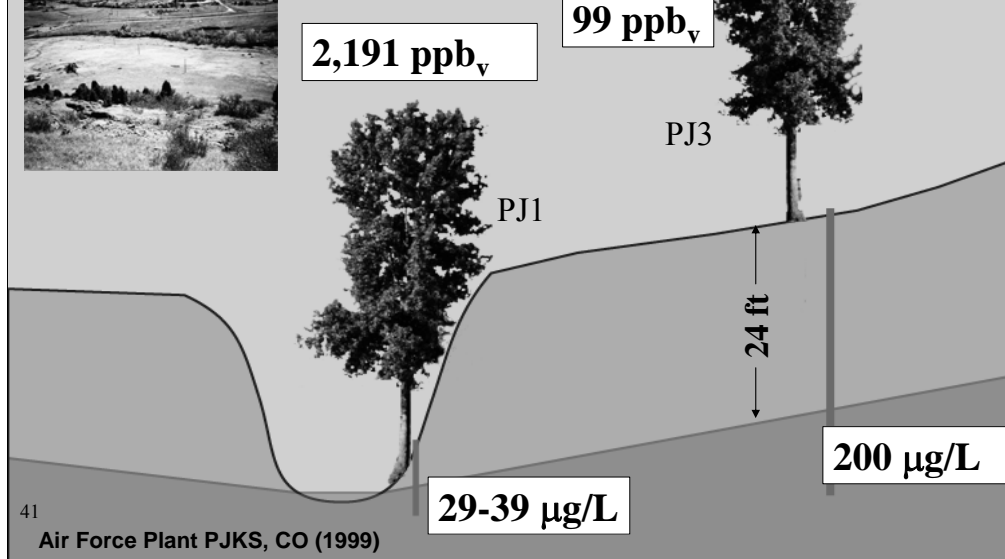
TCE concentrations around the trunk near the edge of a plume

Vroblesky and others, 2004, GWMR, v. 24, p. 124-138



Concentrations in this tree were substantially higher on the side facing the main body of contamination. This may not always be true because in some trees, upward movement of water spirals around the tree.

Differences in TCE concentrations relative to water-table depth



More intimate contact between the tree roots and the contaminated water can produce substantially higher tree-VOC concentrations than in a tree whose roots are more vertically distant from the contaminated water. This is partly because the tree in less intimate contact with the contaminated water probably has other sources of water (such as recharge capture).

Comparison of TCE in adjacent cottonwood and willow.



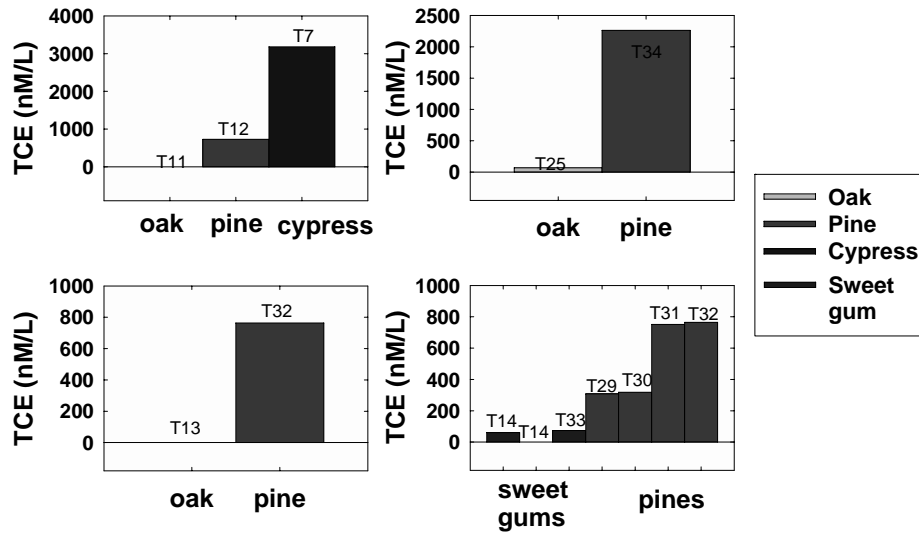
42

Vrobesky and others, 2004, GWMR, v. 24, p. 124-138

These trees are adjacent to each other and have similar TCE concentrations, despite being different species. However, they are both diffuse porous, so they probably move water in similar ways.

Species comparison: TCE in adjacent trees, SRS, 1998

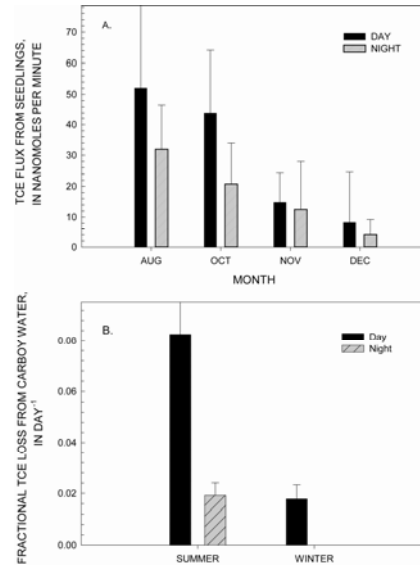
Vroblesky et al., 1999, ES&T, v. 33, p. 510-515.



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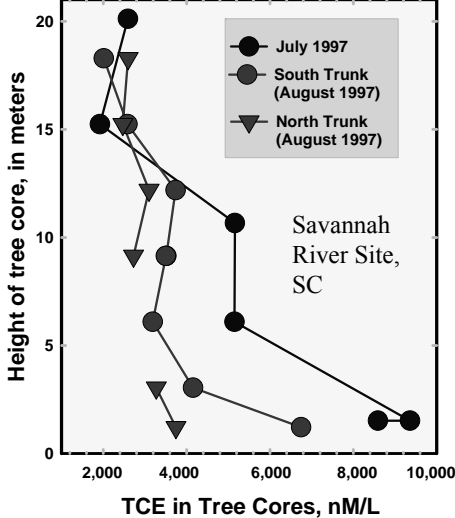
These graphs represent clusters of closely spaced trees of differing species. In general, pines and cypress contained more TCE than oaks and sweet gum.

Trees have higher VOC concentrations in the summer than in the winter



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Concentrations can vary with height up a tree trunk



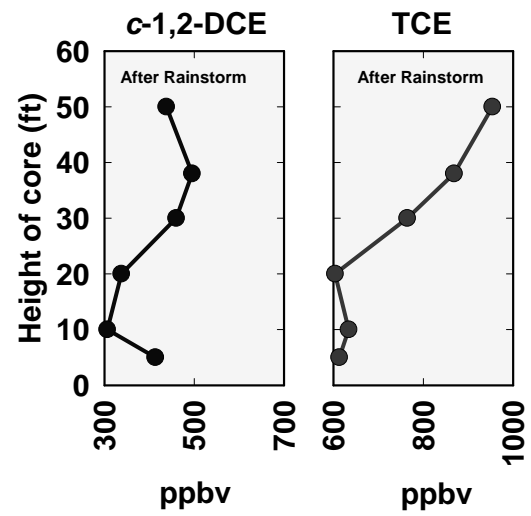
Vroblesky and others,
2004, GWMR, v. 24, p.
124-138

Eastern Cottonwood, Carswell Golf Course, Texas

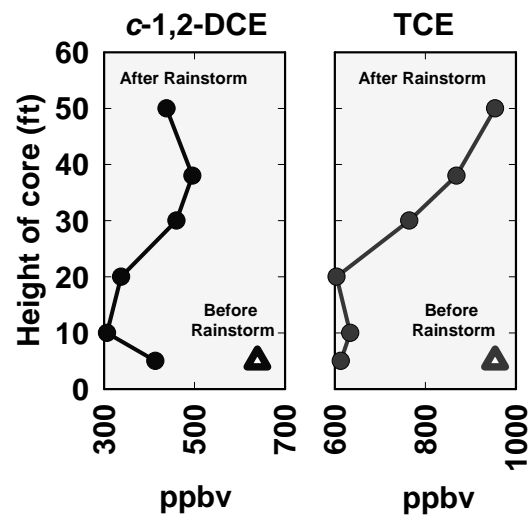


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VOCs up tree after rainstorm, Carswell, TX



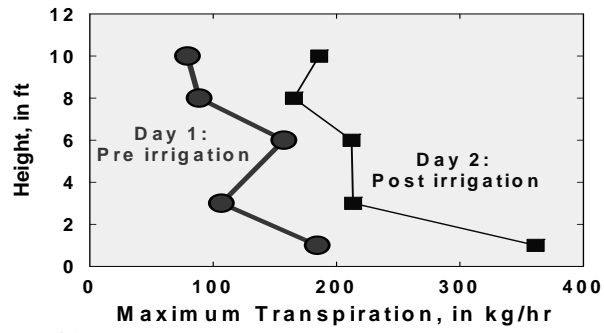
VOCs up tree before and after rainstorm, Carswell TX



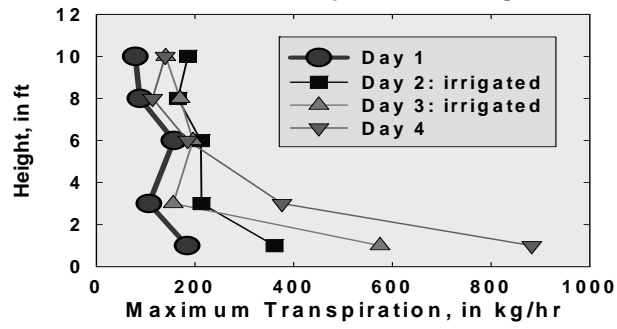


Cottonwood
instrumented for
irrigation test:
Carswell Golf
Course, TX

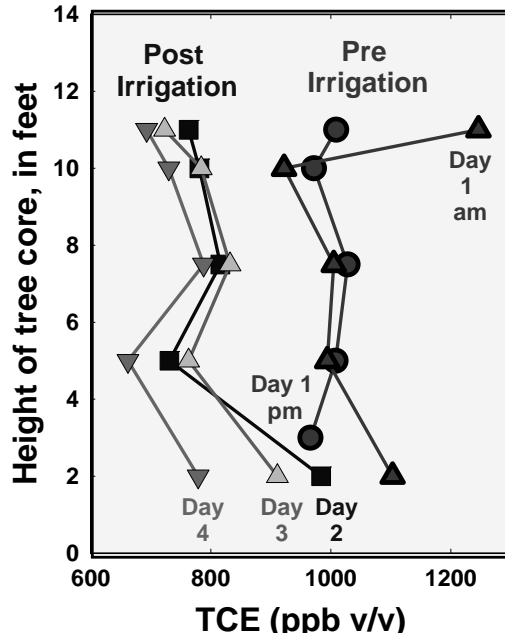
Maximum Transpiration During Artificial Irrigation of Cottonwood



Clinton and others, 2004, Int. J. Remed., v. 6, p. 239-252

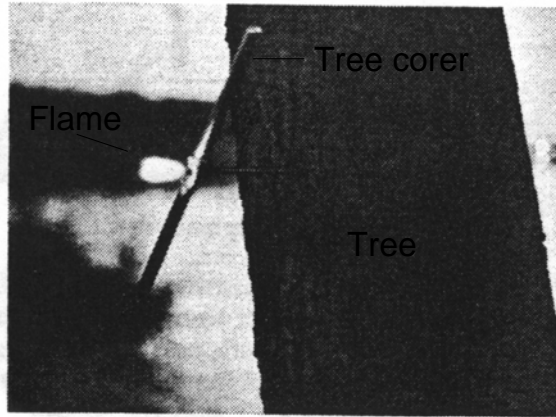


Avg. TCE in Tree Cores Before and After Artificial Irrigation



Vrobesky and others, 2004, GWMR, v. 24, p. 124-138

Photograph of a flame extruding
from a tree corer

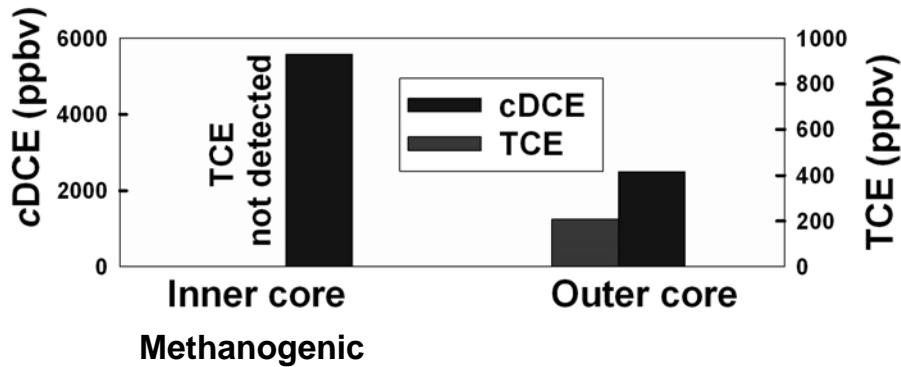


Methanogenic bacteria can infest the interior wood of visibly healthy trees in poorly drained soils, creating methanogenic conditions within the tree

Zeikus and Ward, 1974, Methane formation in living trees: A microbial origin: Science, v. 184, no. 4142

TCE and cDCE in the inner and outer tree core (AF Plant PJKS, Colorado)

TCE dehalogenation under
methanogenic conditions
TCE → cis-1,2-DCE



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Vroblesky and others, 2004, GWMR, v. 24, p. 124-138

This tree spit methane and water from the tree corer once the corer penetrated the inner part of the tree. Analysis of the cores showed that the inner core contained a substantial amount of methane relative to the outer core. The methanogenic conditions of the inner core were conducive to reductive dechlorination of TCE. The TCE and cDCE results from the inner core also implies inner-trunk dechlorination activity.

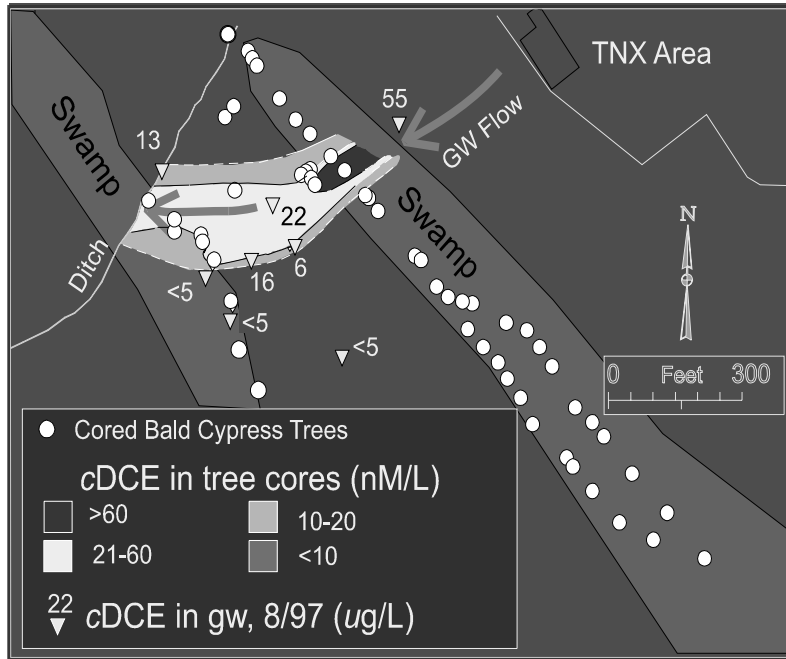
Chlorinated solvent degradation by trees

- Newman and others (1977) found that cells from poplar trees were capable of transforming and mineralizing TCE without microbes.
- Additional evidence for VOC degradation by trees includes the presence of oxidative transformation products in tree tissue (several researchers)

Field Examples

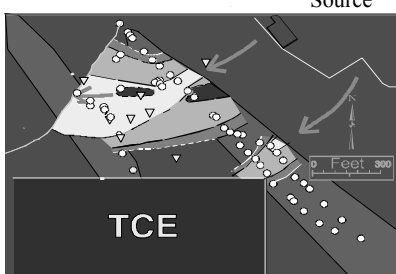
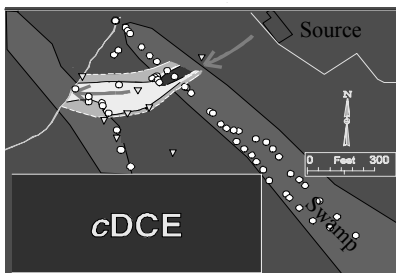
Ground-water TCE and cDCE plume under a swamp,
Savannah River Site, SC

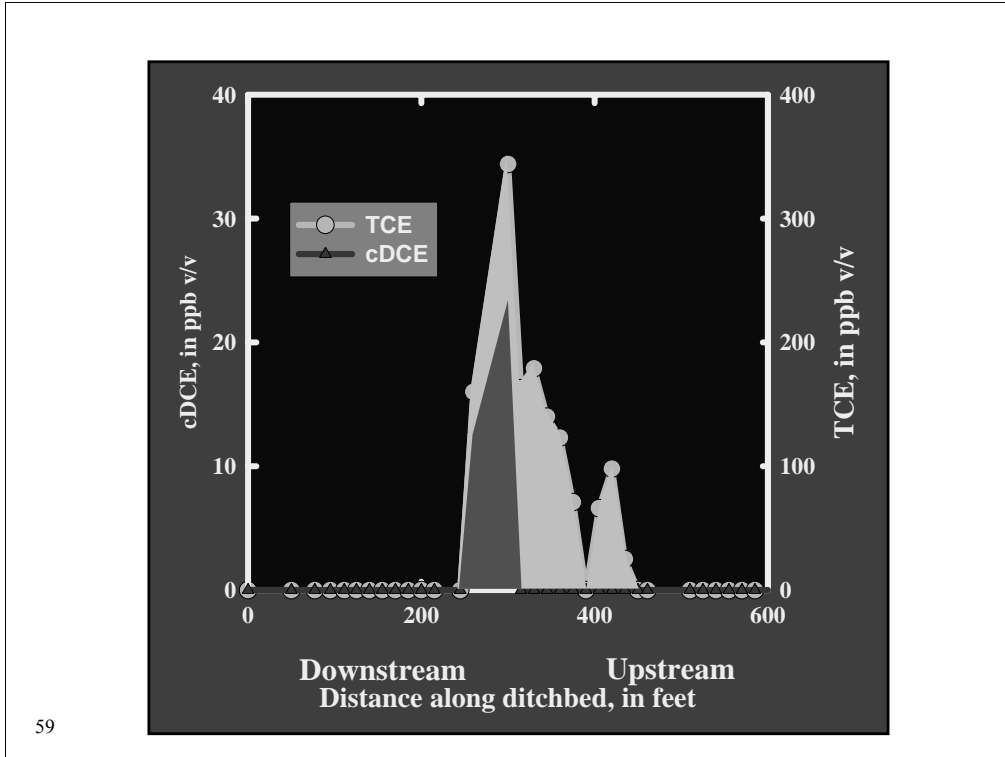




cDCE and TCE in Tree Cores, SRS, Jan/Feb 1998

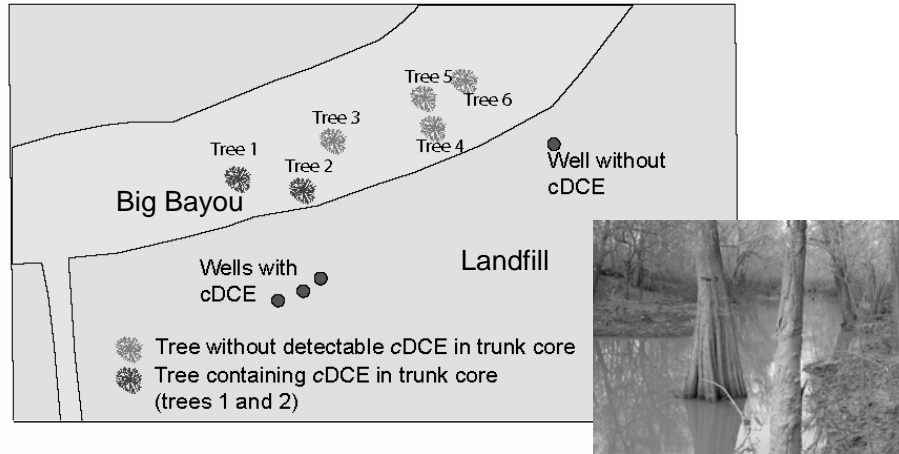
Vroblesky and others,
1999, ES&T, v. 33, p.
510-515





Results of passive vapor samplers beneath sediment in the ditch confirmed the plume extent defined by the tree cores.

cis-1,2-Dichloroethene in Tree Cores, England AFB,
LA, 3/11/03



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This is another site showing that trees in a swamp were capable of seeing chlorinated solvents beneath the swamp, even though the standing water was relatively uncontaminated.

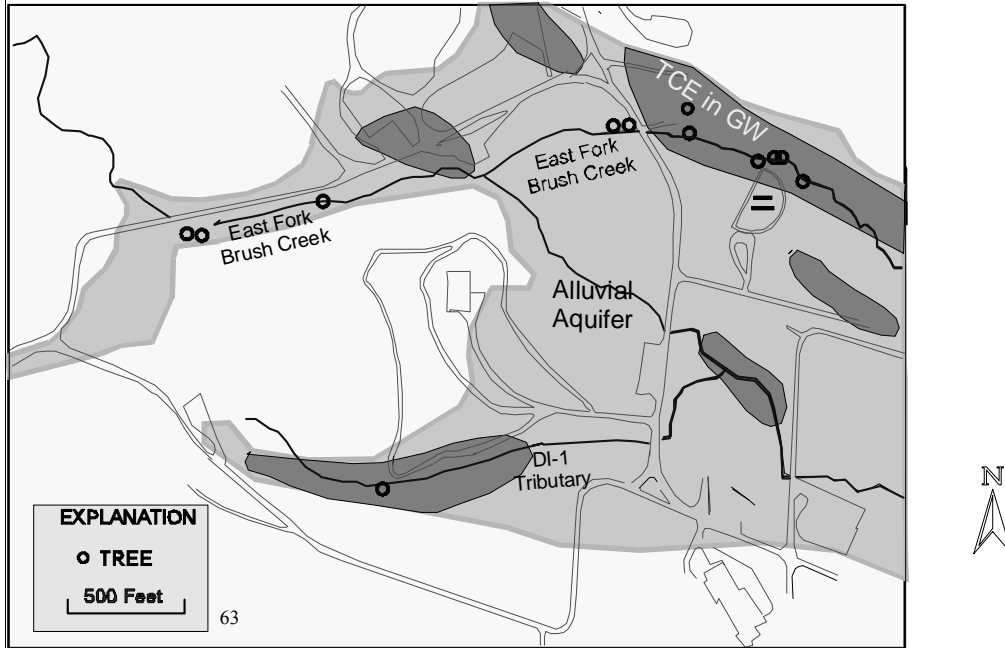
Air Force Plant PJKS, Colorado



Air Force Plant PJKS, Colorado



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SWMU12, NWS Charleston, SC



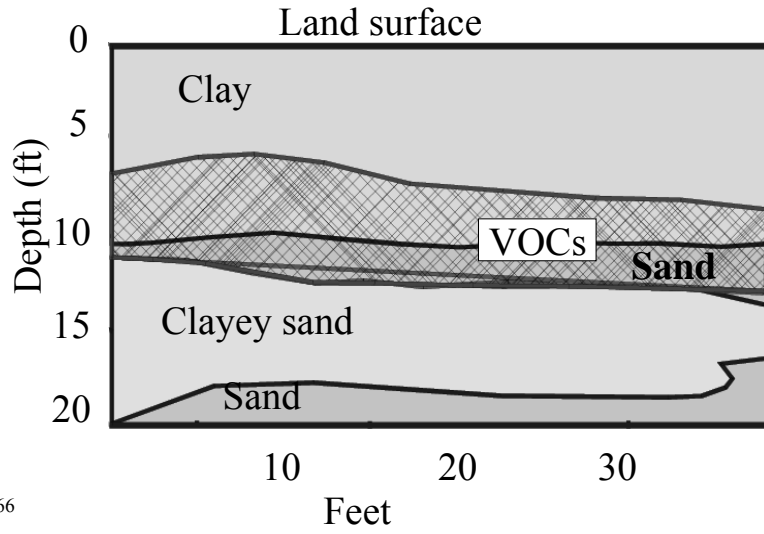
64

1 ft of tight soil overlying about 10 ft of plastic clay (shown below). Well 12MW-29S, SWMU12



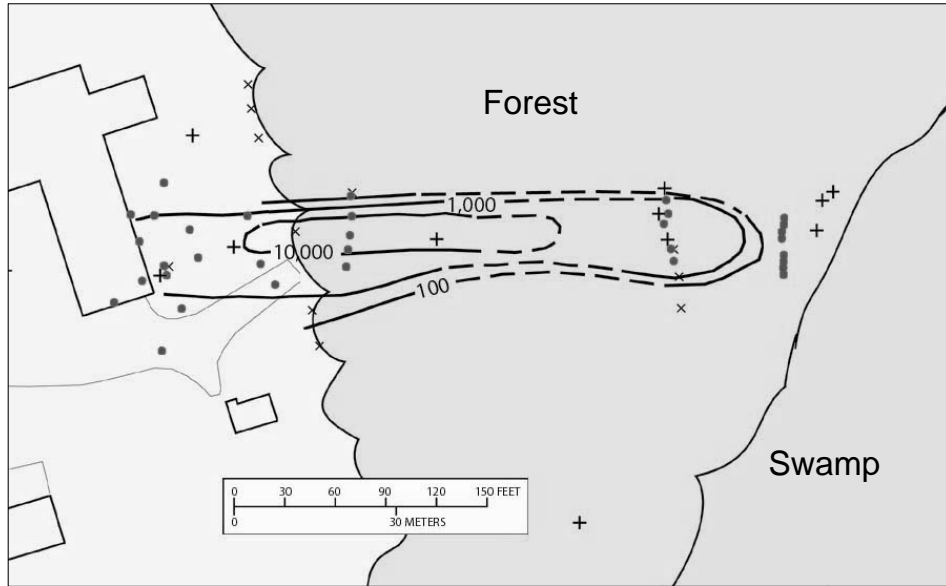
NWS Charleston, SC.

About 6 to 10 ft of tight clay above the aquifer



66

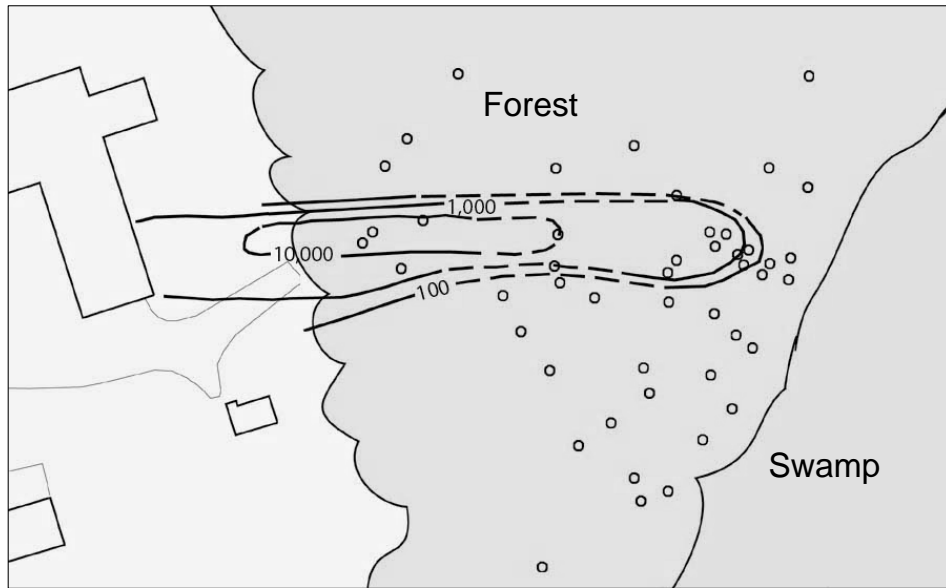
TCE in ground water ($\mu\text{g/L}$), SWMU12, NWS Charleston



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Vroblesky and others, 2004, GWMR, v. 24, p. 124-138

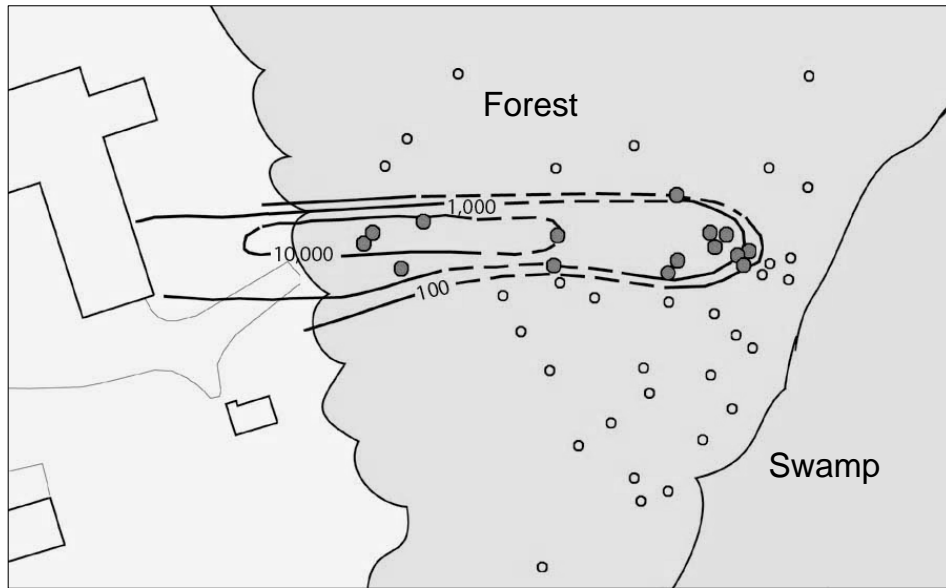
TCE in ground water ($\mu\text{g/L}$), and cored trees SWMU12



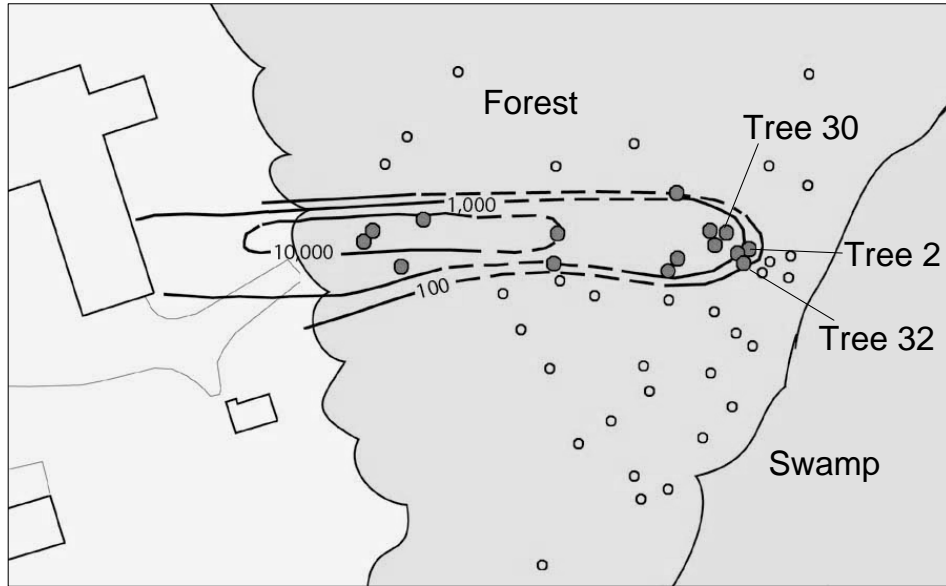
68

Vroblesky and others, 2004, GWMR, v. 24, p. 124-138

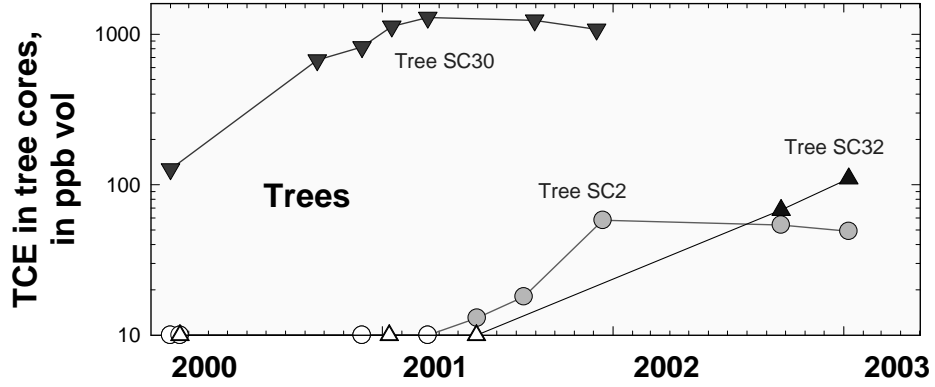
TCE in ground water ($\mu\text{g/L}$), and trees containing TCE



Locations of selected trees, SWMU12, Charleston SC



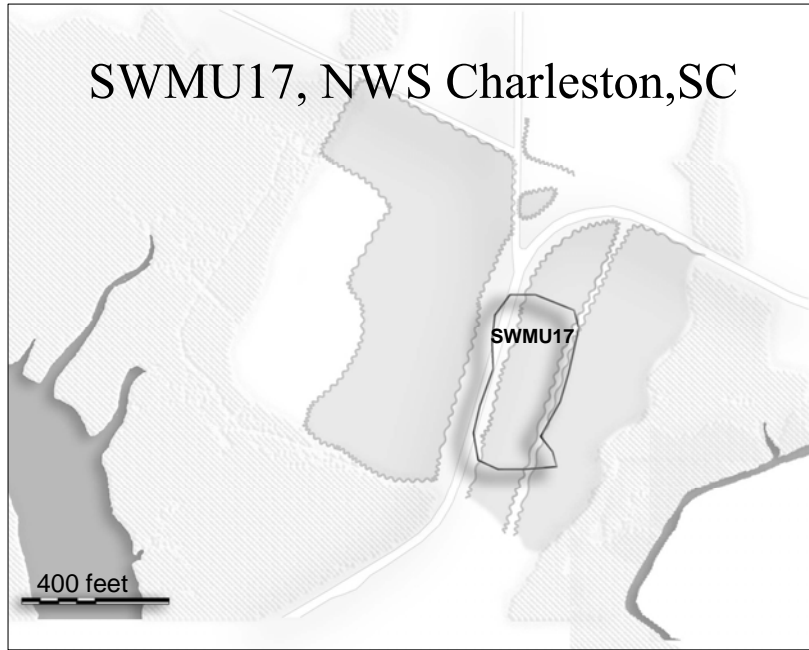
Changes in TCE over time in trees,
SWMU12, Charleston SC



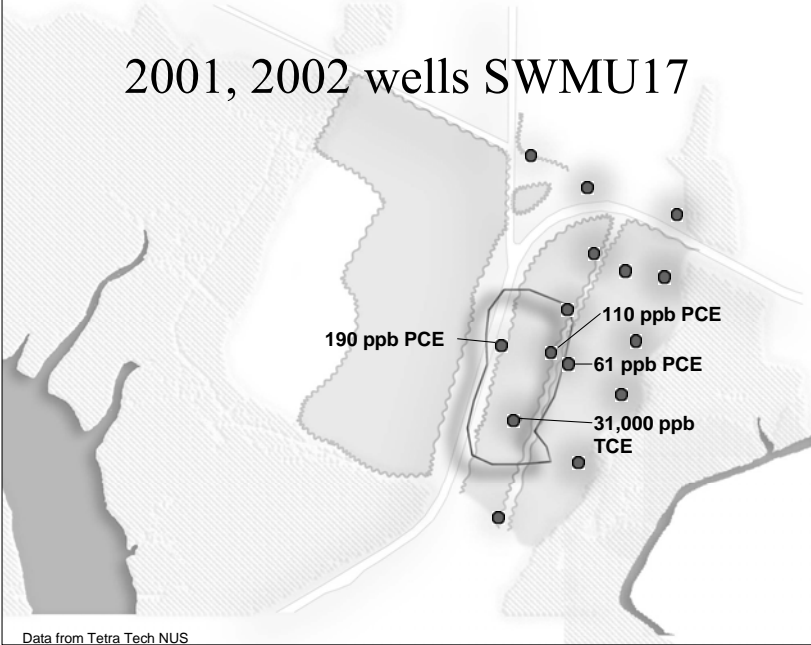
SWMU17, NWS Charleston



SWMU17, NWS Charleston, SC

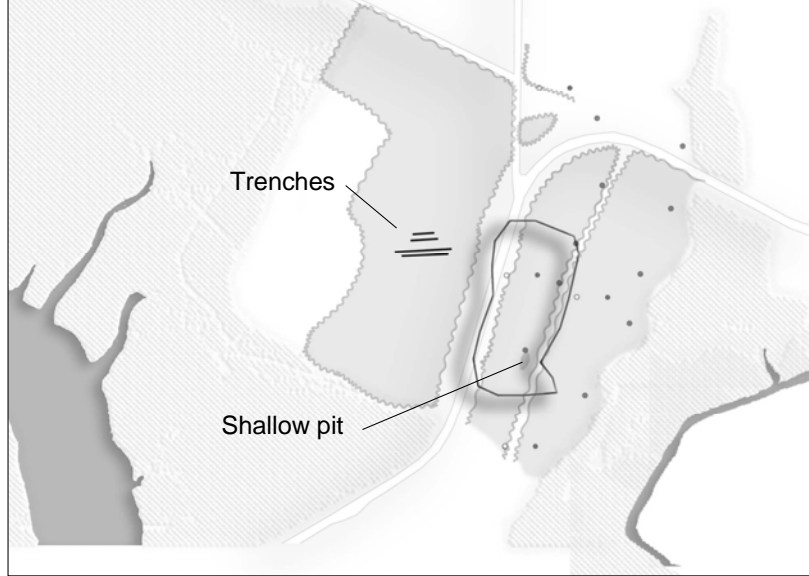


2001, 2002 wells SWMU17



Data from Tetra Tech NUS

Potential source areas, SWMU17



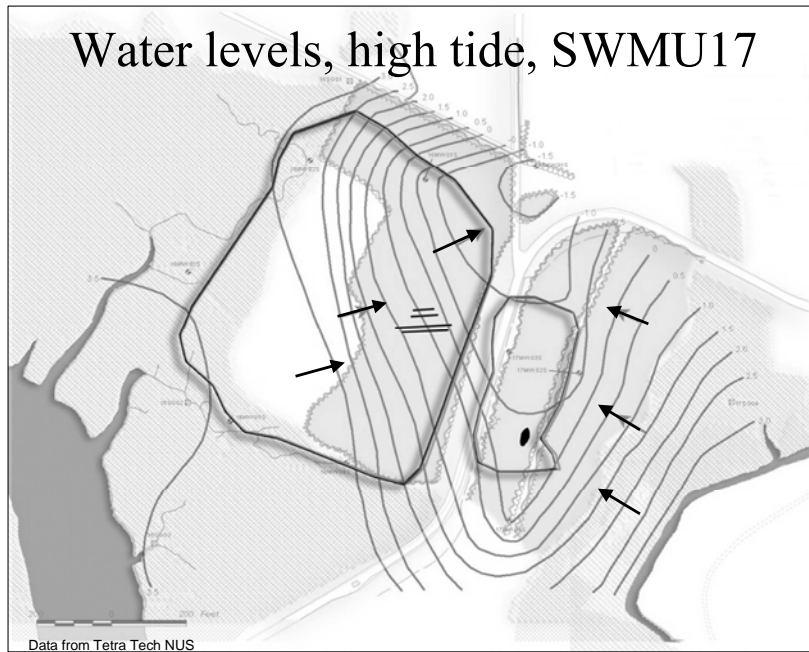
75

Water levels, low tide, SWMU17

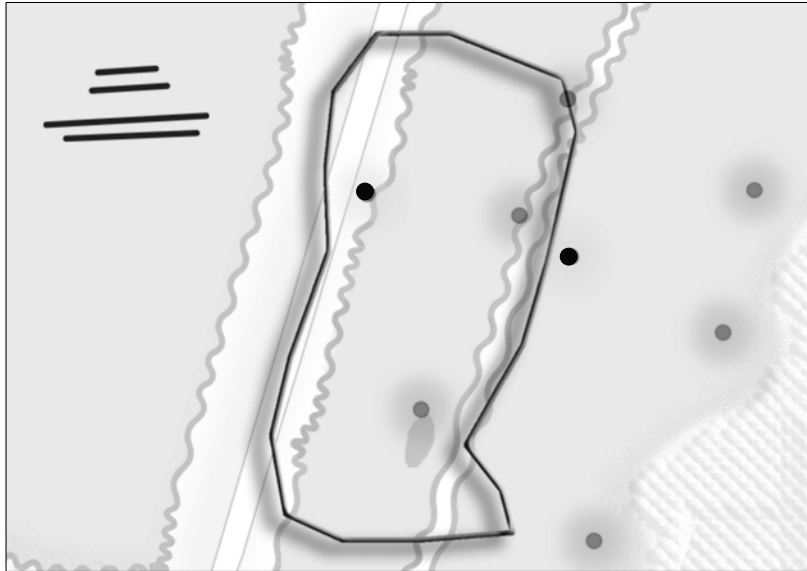


Data from Tetra Tech NUS

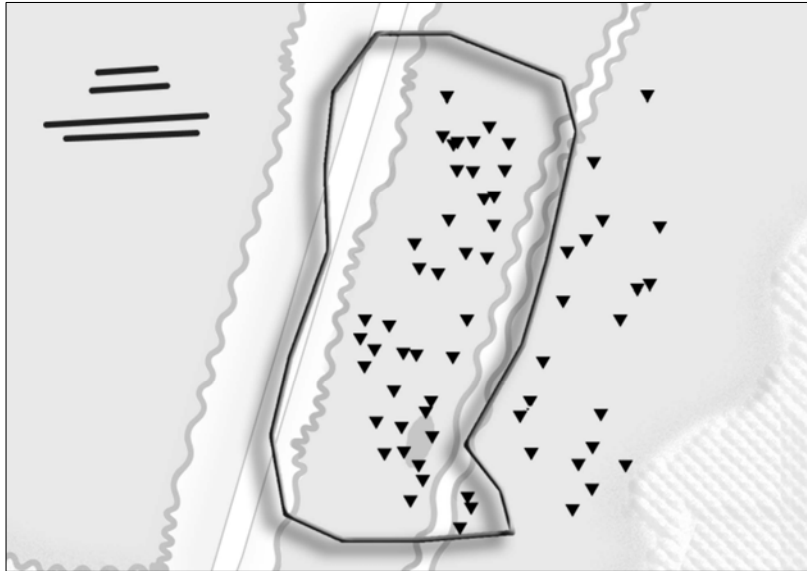
Water levels, high tide, SWMU17



SWMU17, NWS Charleston SC



Locations of cored trees



VOCs from tree cores



80

Vroblesky and others, 2004, GWMR, v. 24, p. 124-138

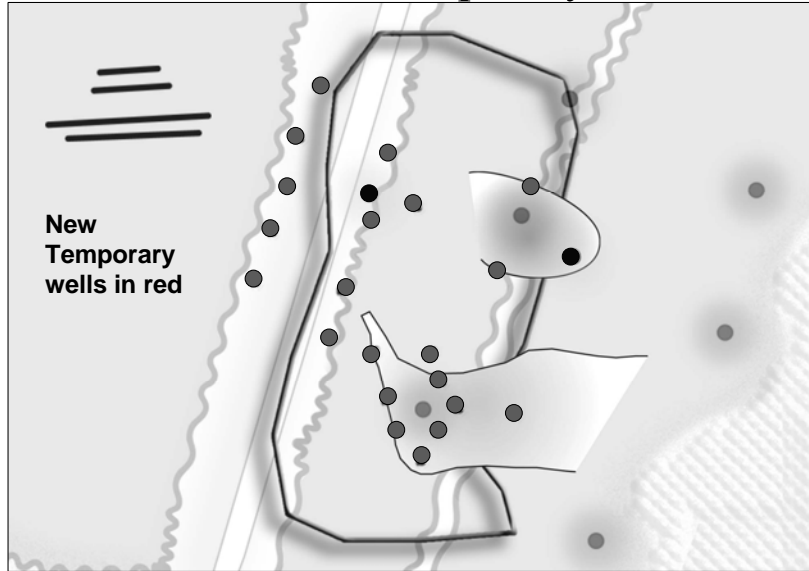
Plumes inferred from tree cores



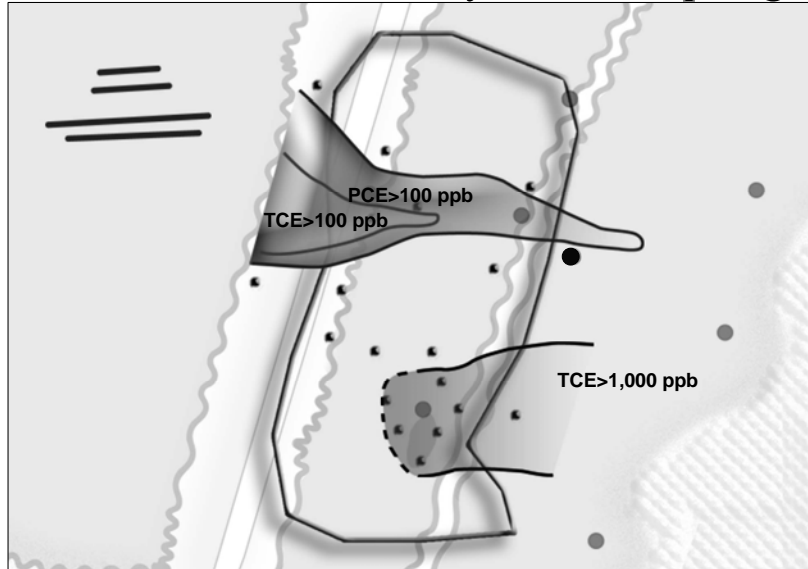
81

Vroblesky and others, 2004, GWMR, v. 24, p. 124-138

Locations of temporary wells

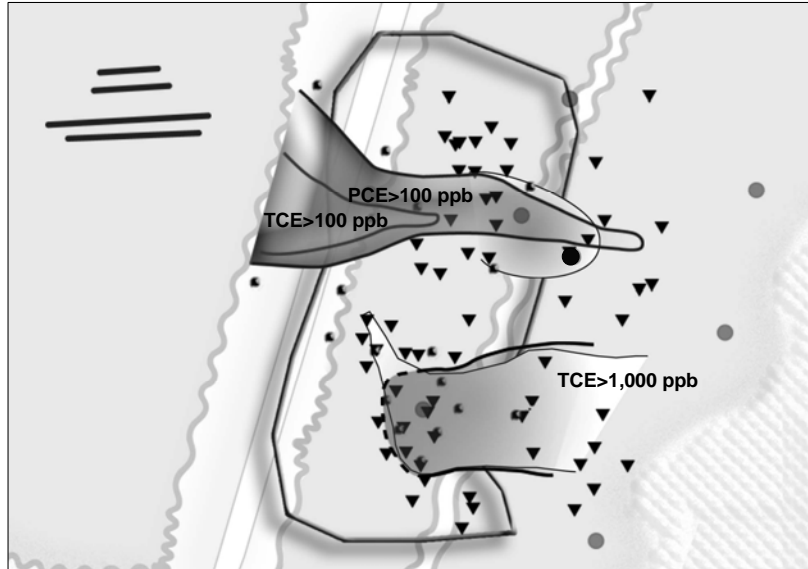


Plumes determined by well sampling



Data from Columbia Technologies

GW plumes detected in wells and tree cores



Merriam Manufacturing Company Property,
CT (tree cores and soil gas)

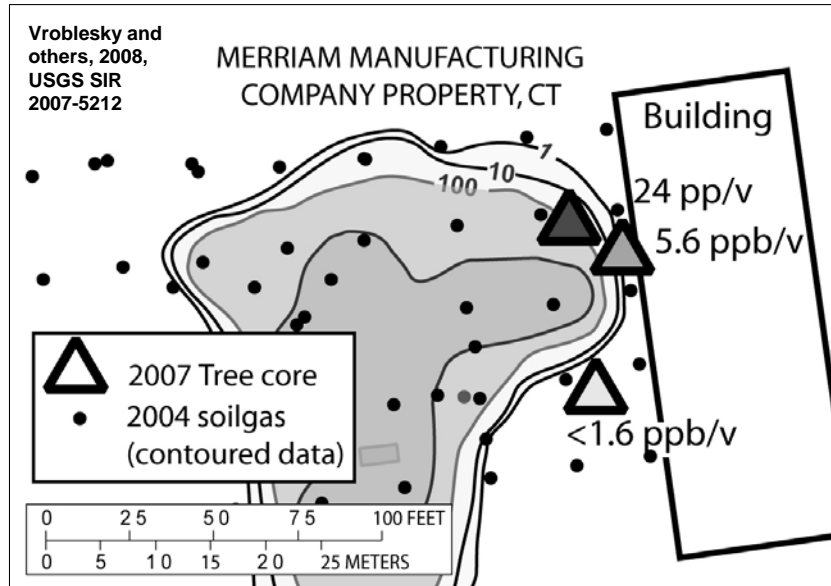


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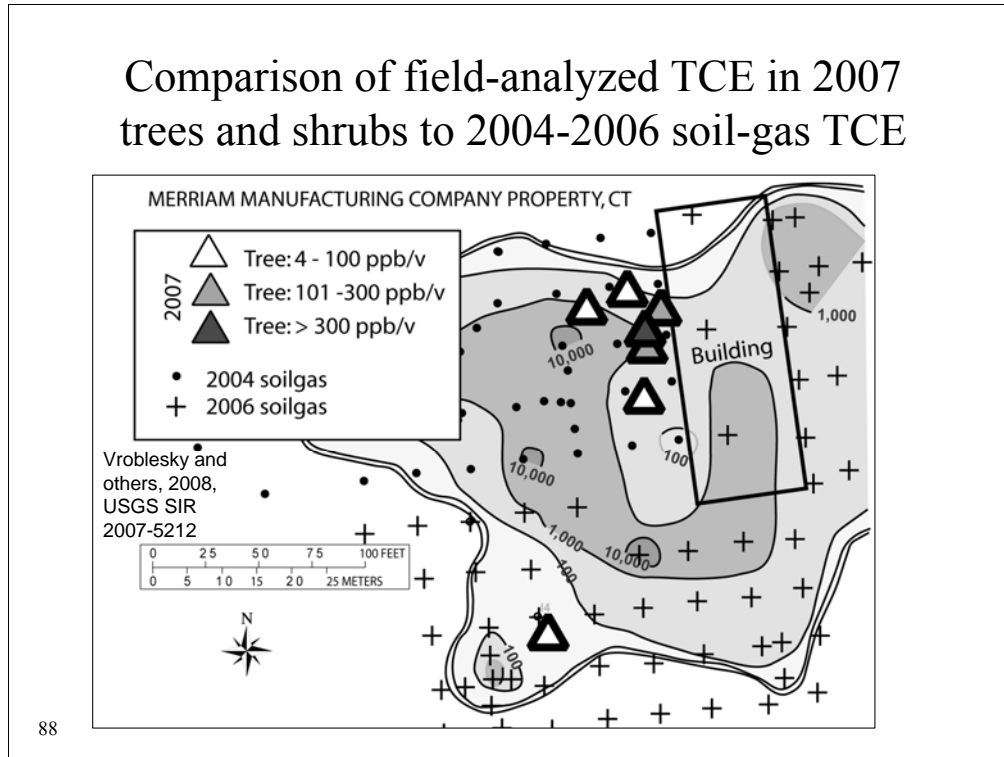
Property information

- Types of trees and shrubs
 - Maple, Catalpa, Mulberry, Sumac
 - Mostly small trees and shrubs
 - (diam=2.2 to 4 inches) (one tree was 40 inches)
- Depth to water= 15 to 20 ft
- Rooting depth of Mulberry
 - 1-2 ft in well drained soil (Peper, 1998)
 - 7.9 ft (but 70% of roots were in the top 2 ft) (Bunger and Thompson (1938)
 - 3.9 ft (but 70% of roots were in the top 2 ft)(Olson and Fletcher, 1999; Olson and others, 2001)
 - Mulberry TCE probably from vadose contamination (Struckoff and others, 2005); less likely to be hydraulic lift (Richards and Caldwell, 1987)

Comparison of field-analyzed 111TCA in 2007 trees and shrubs to 2004 soil-gas 111TCA



Comparison of field-analyzed TCE in 2007 trees and shrubs to 2004-2006 soil-gas TCE



Analyzing the tree onsite with field heating provided sufficient concentrations to identify zones of relatively high and low VOC concentrations.

The tree-core VOC concentrations in the shallow-rooted species probably were derived from horizons shallower than the water table.

Merriam Manufacturing Company Property

- Analyzing the tree onsite with field heating provided sufficient concentrations to identify zones of relatively high and low VOC concentrations.
- The tree-core VOC concentrations in the shallow-rooted species probably were derived from horizons shallower than the water table.

SUMMARY

- Tree coring is a simple, rapid, inexpensive reconnaissance tool for examining VOC contamination in ground water
- It has application in a variety of environments

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