In-Planta Sampling & Dendrochemistry Fast, Cheap & Green Site Assessment &Phytoforensics

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NARPM Meeting

Cutting Edge Technologies

May 19, 2011

Collaborators: Coauthors

S&T students: Matt Limmer, Emily Sheehan, Kendra Waltermire Mikhil Shetty Sam Markus

USGS: Don Vroblesky, John Schumacher

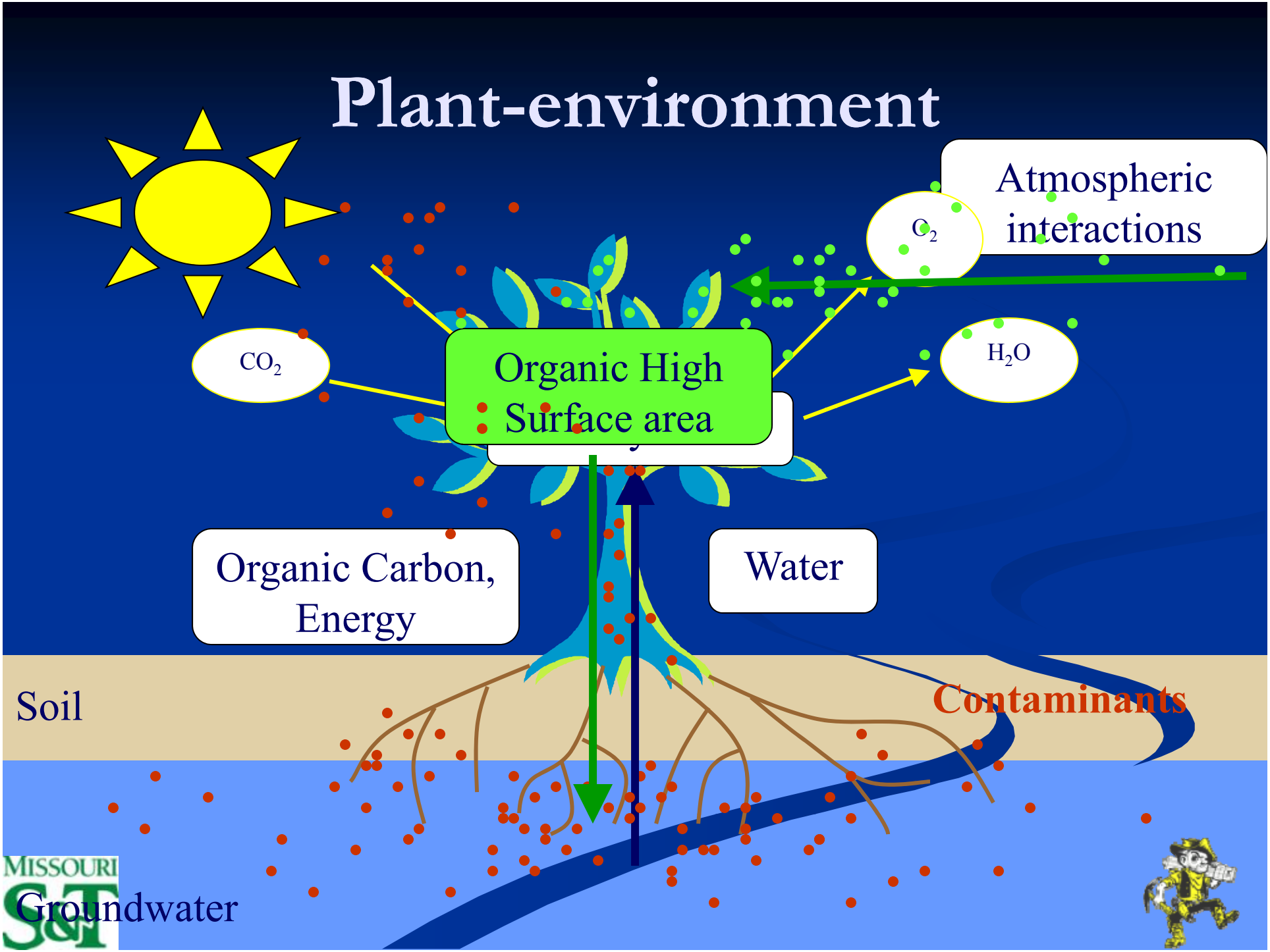
Ministry of the Environment: Camilo Martinez, Chris Watson, Bill Gizyn

Guelph University: Ryan Kroeker

Foth Environmental: Matt Shurtliff

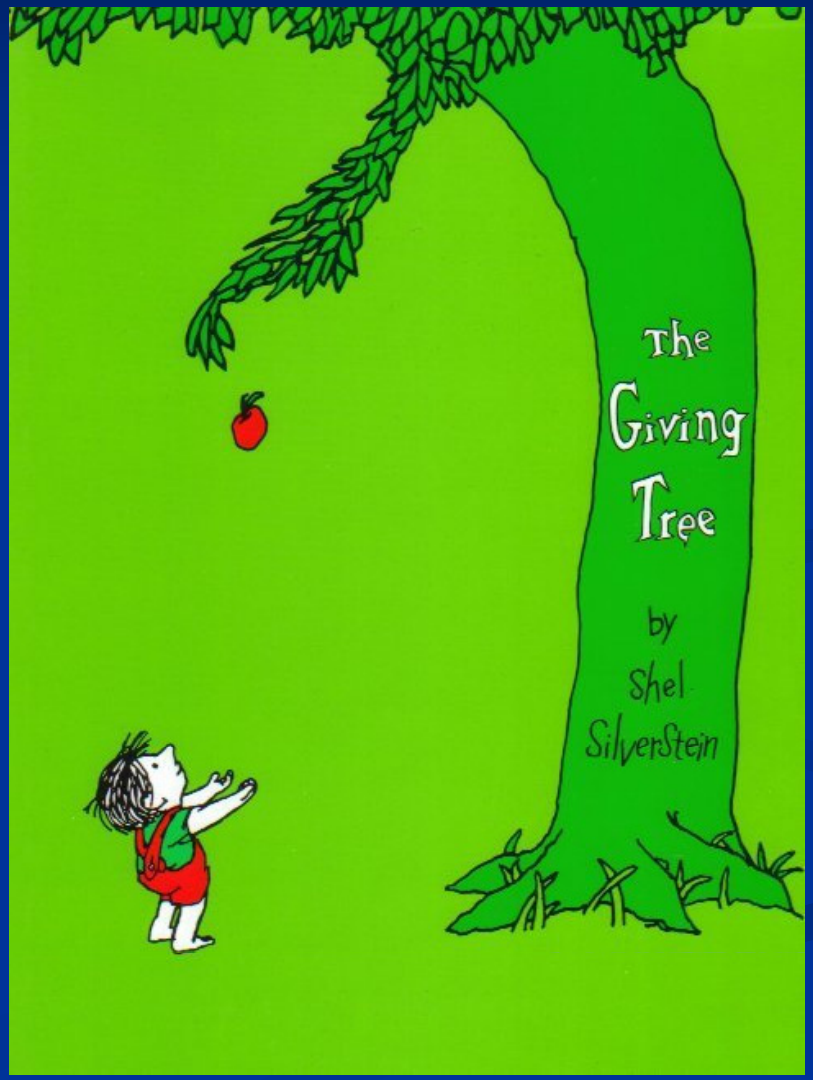
Denmark: Philipp Mayer, Uli Karlson (NERI), Stefan Trapp (DTU)

Plant-environment



Mother nature can tell us a lot…

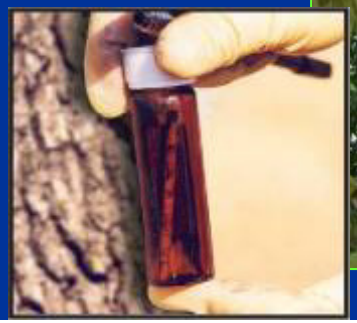
- The data is in there…
- How do we get it out?
- How do we interpret it… as groundwater, soil, vapor data?



Tree Coring

- Methods: D. Vroblesky - USGS
- Collect a core sample of the trunk/stem
- Core sample placed into vial
- After equilibration time headspace GC analysis
- Partition coefficients determine concentrations

Headspace Analysis



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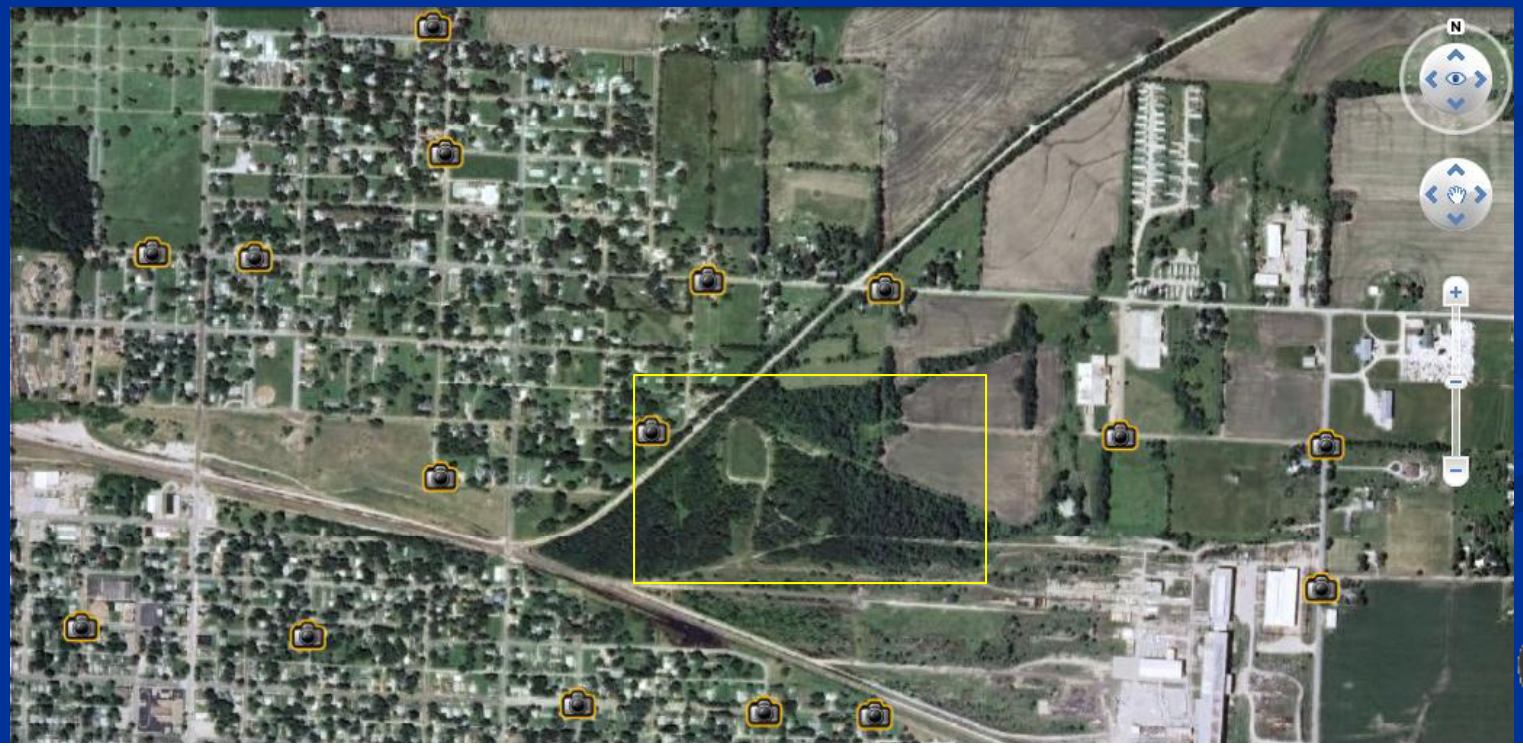
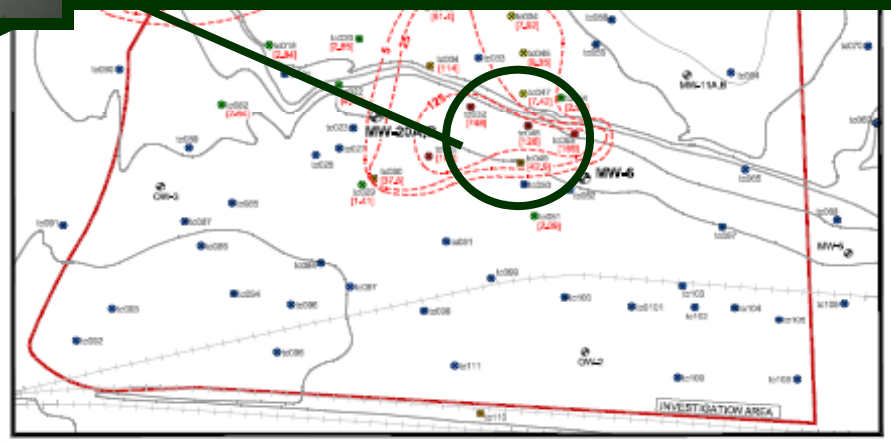
Field Site – Sedalia Missouri

- PCE and TCE contaminated site in Old railroad yard. Site investigation over 10 years, 40 sampling points.



Chlorinated Solvents Sampling Project, Sed



Foth

- 114 samples = 1 day, 4 person crew

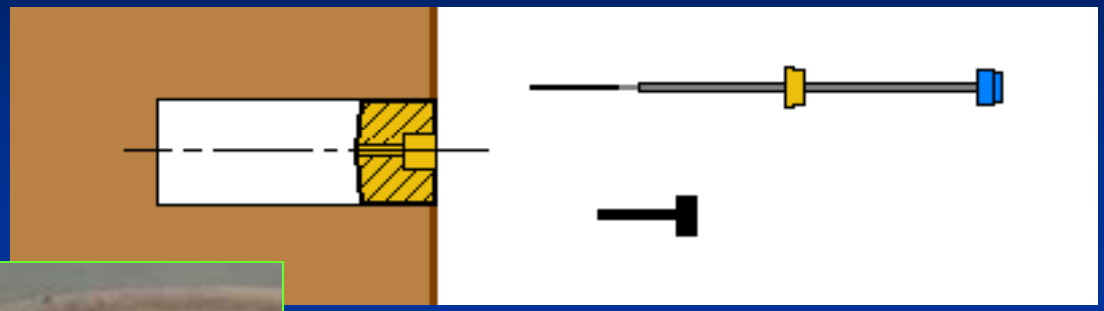
New Approaches

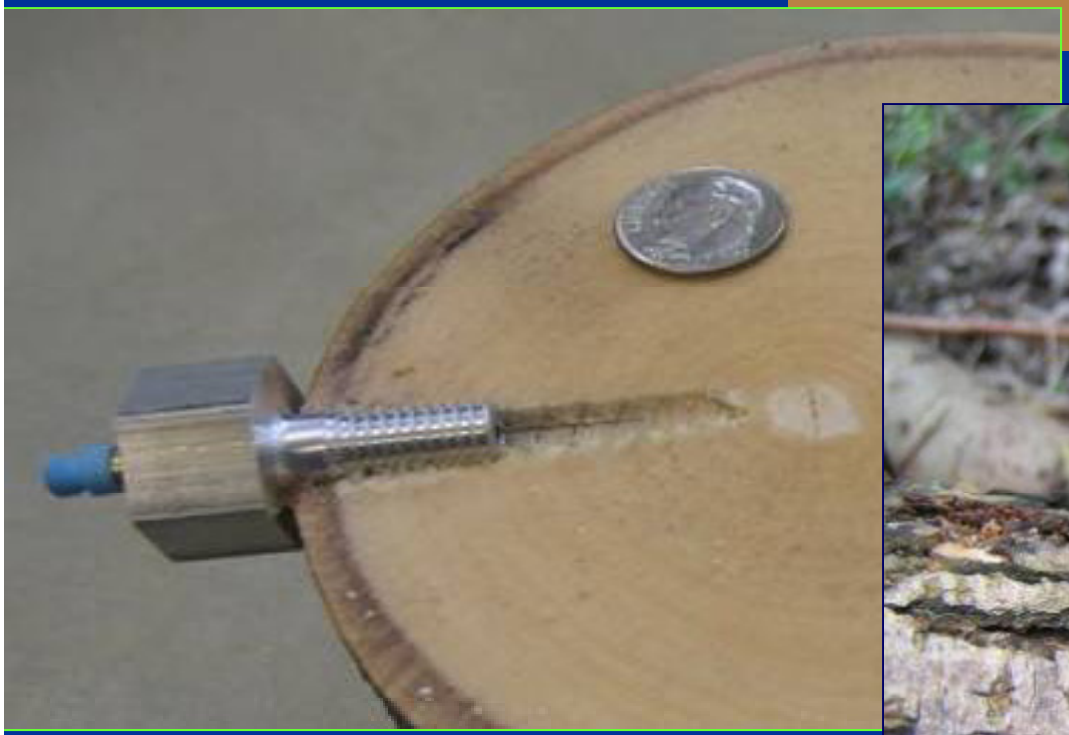
Sampling does not need to bring the tree into the lab.

Rather let's bring the lab to the tree!

In-planta sampling

In Planta SPME analysis





Patent Pending

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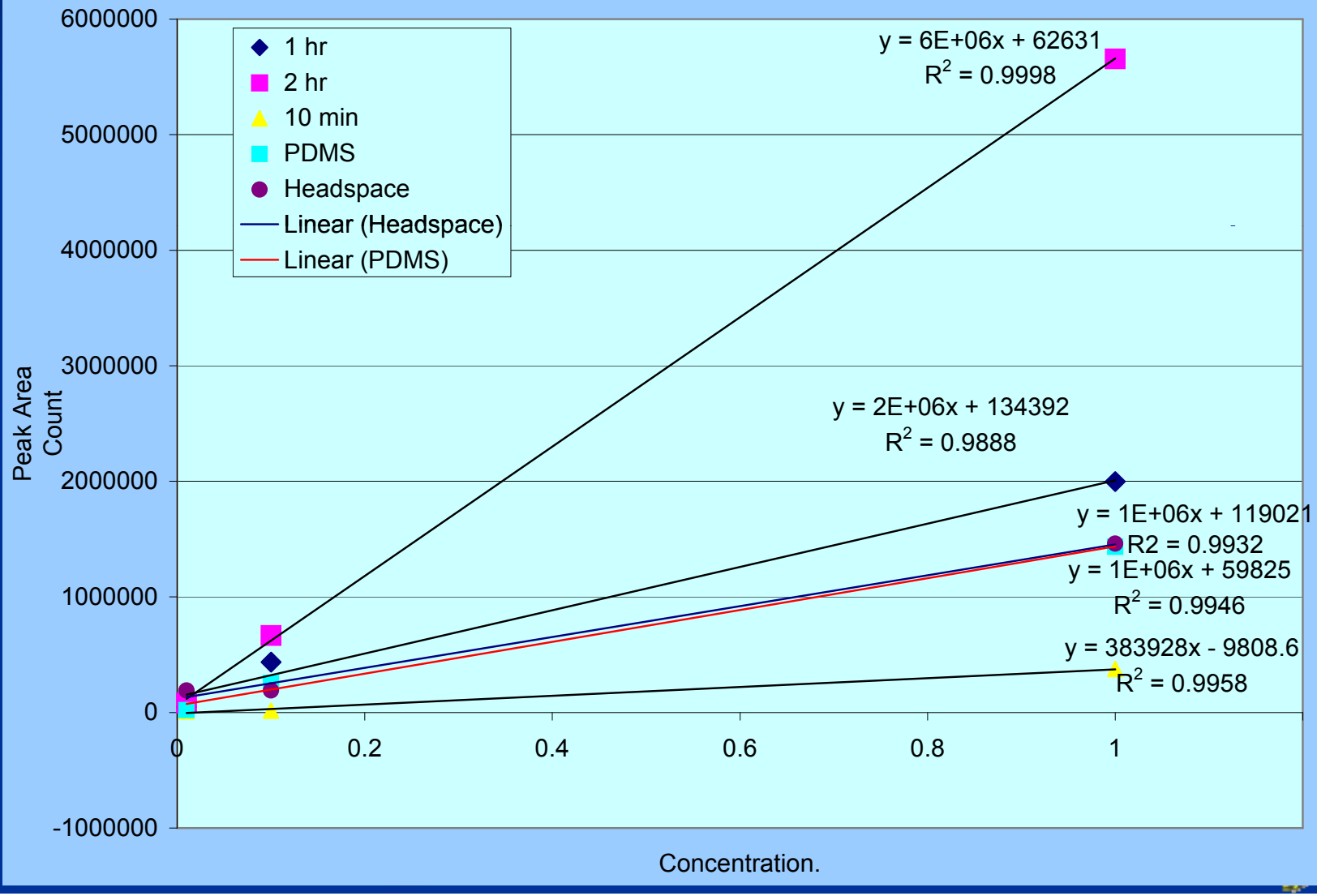
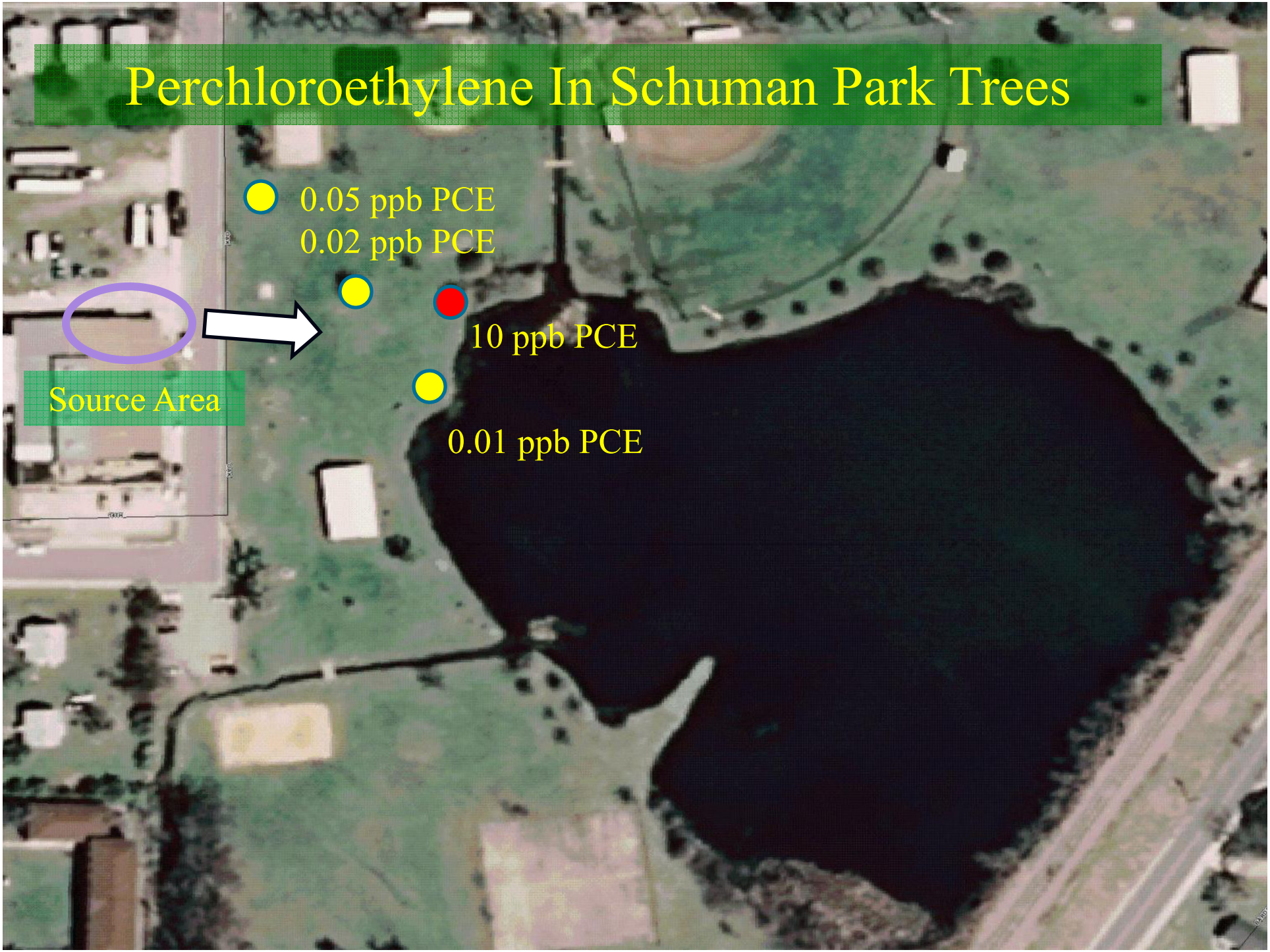
NERI

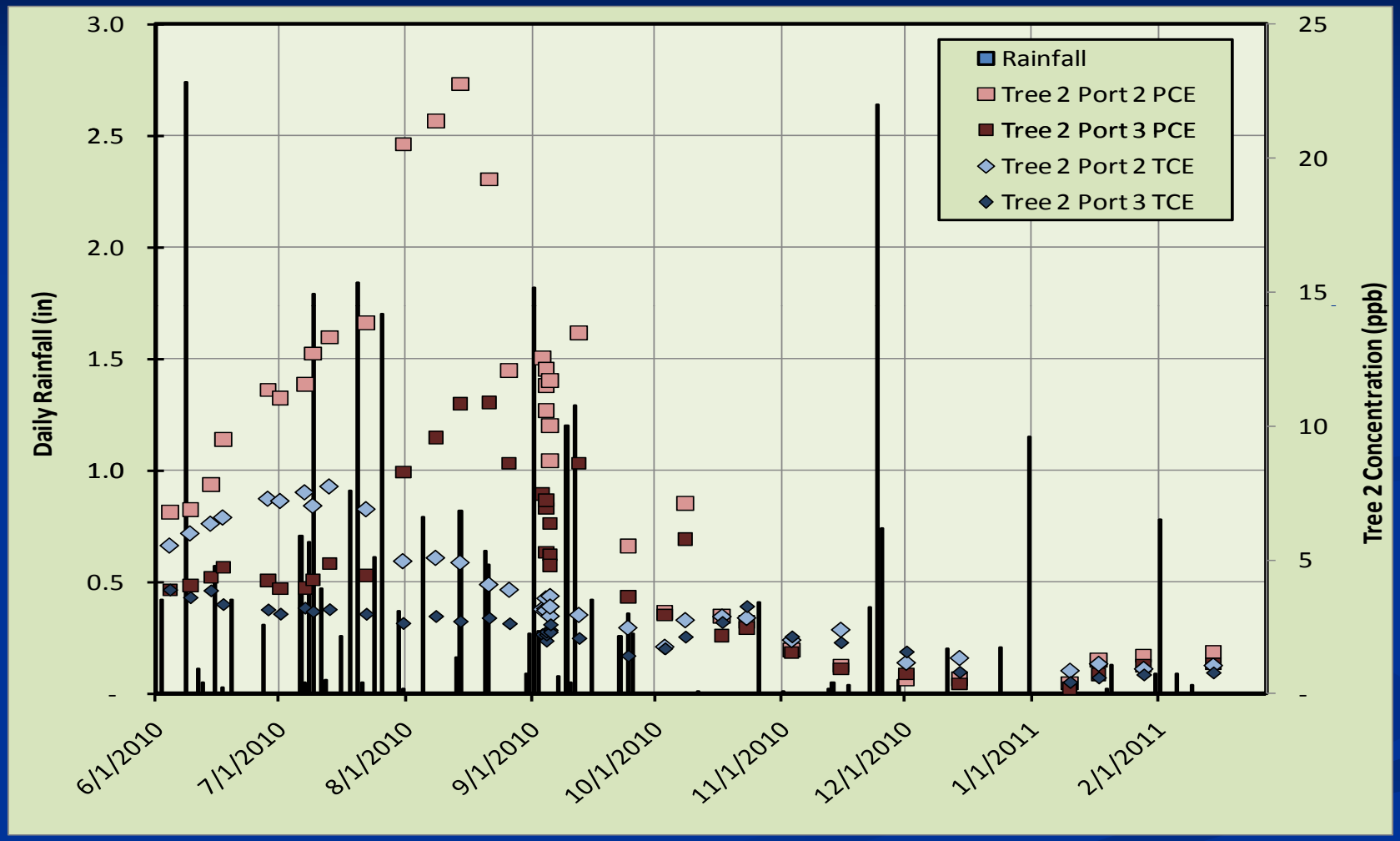
Methods Comparison: TCE



Perchloroethylene In Schuman Park Trees

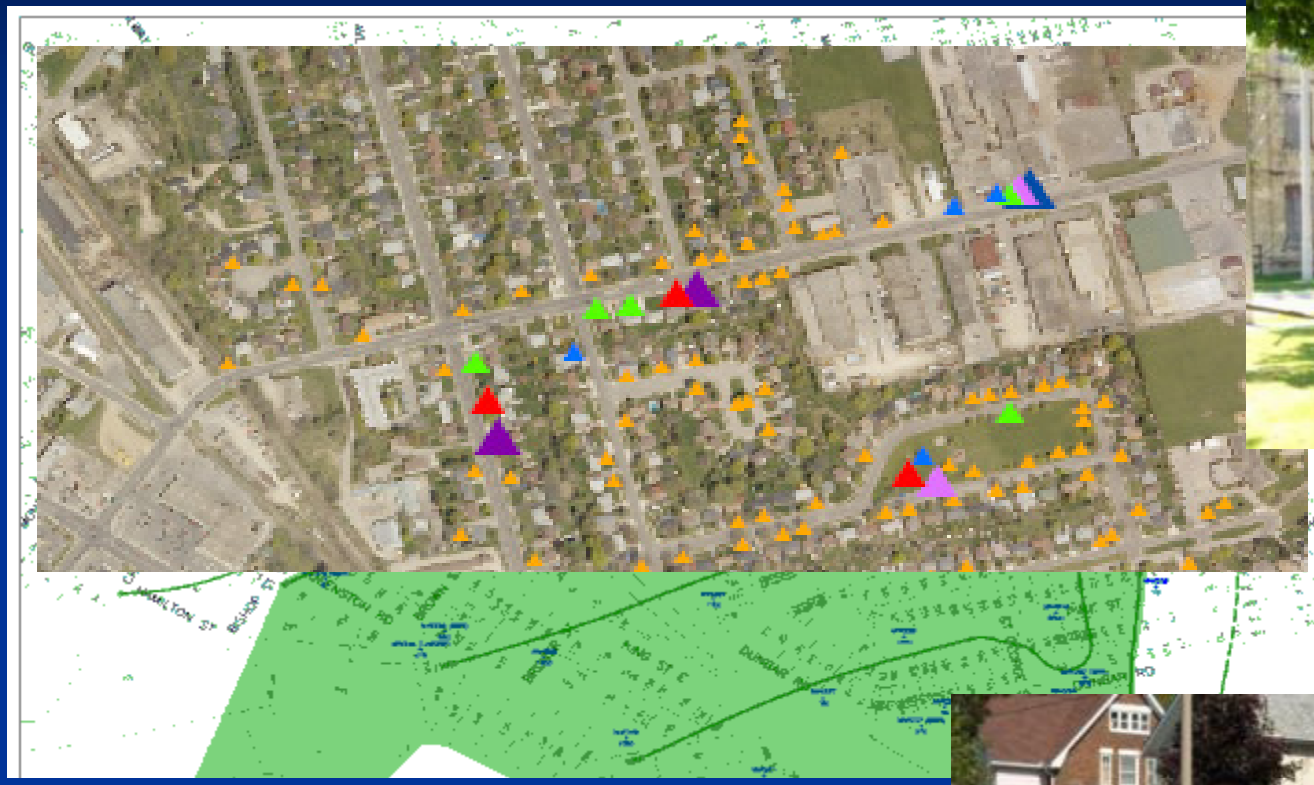


Variations in Tree Concentrations



The same SPME ports can be sampled over time to track contaminant- plant interactions.

SPS sampling of Northstar, Cambridge Ontario



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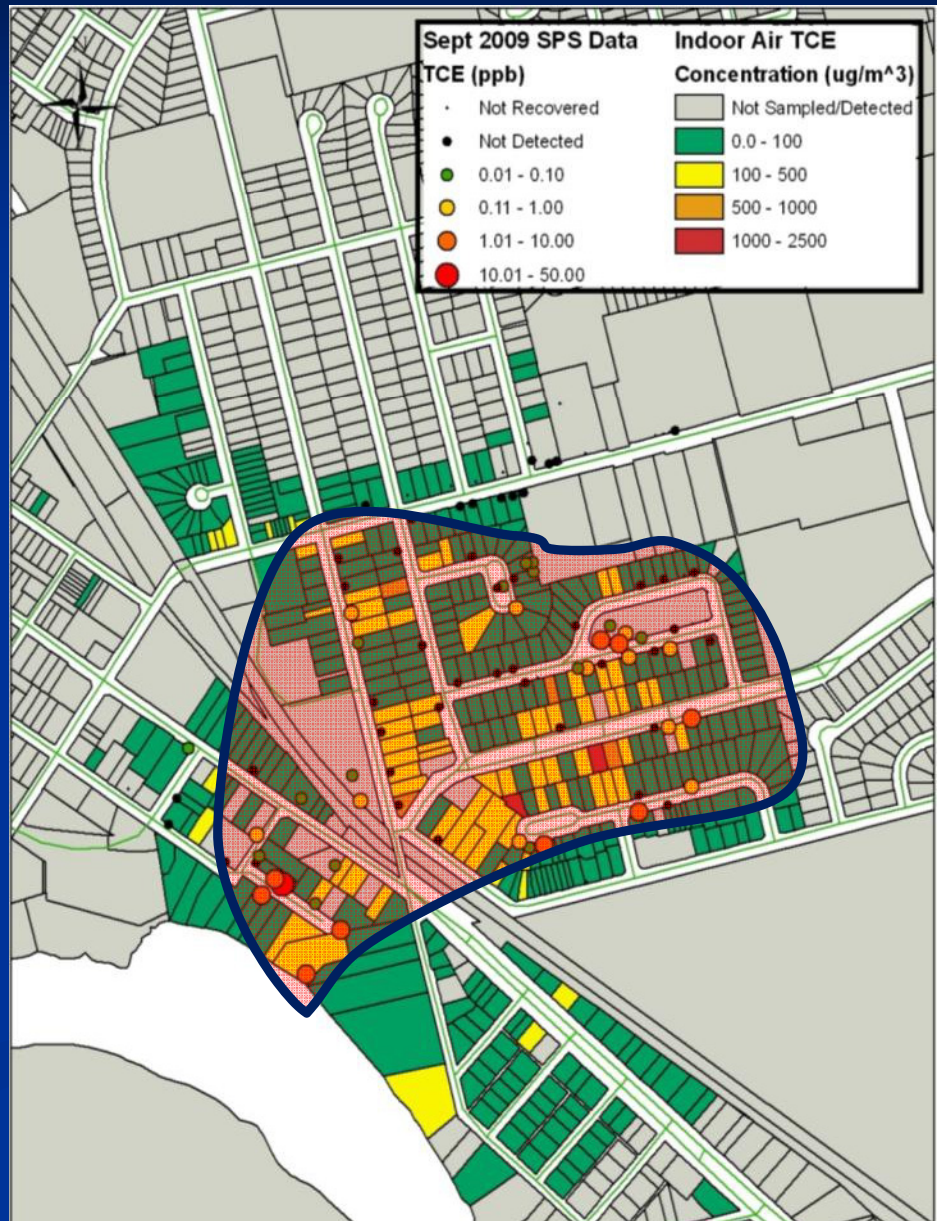
Ontario

Comparison of SPS & Indoor Air

- SPS testing and Indoor Air studies in Cambridge showed that *in-planta* sampling can indicate potential indoor air contamination, i.e. vapor intrusion



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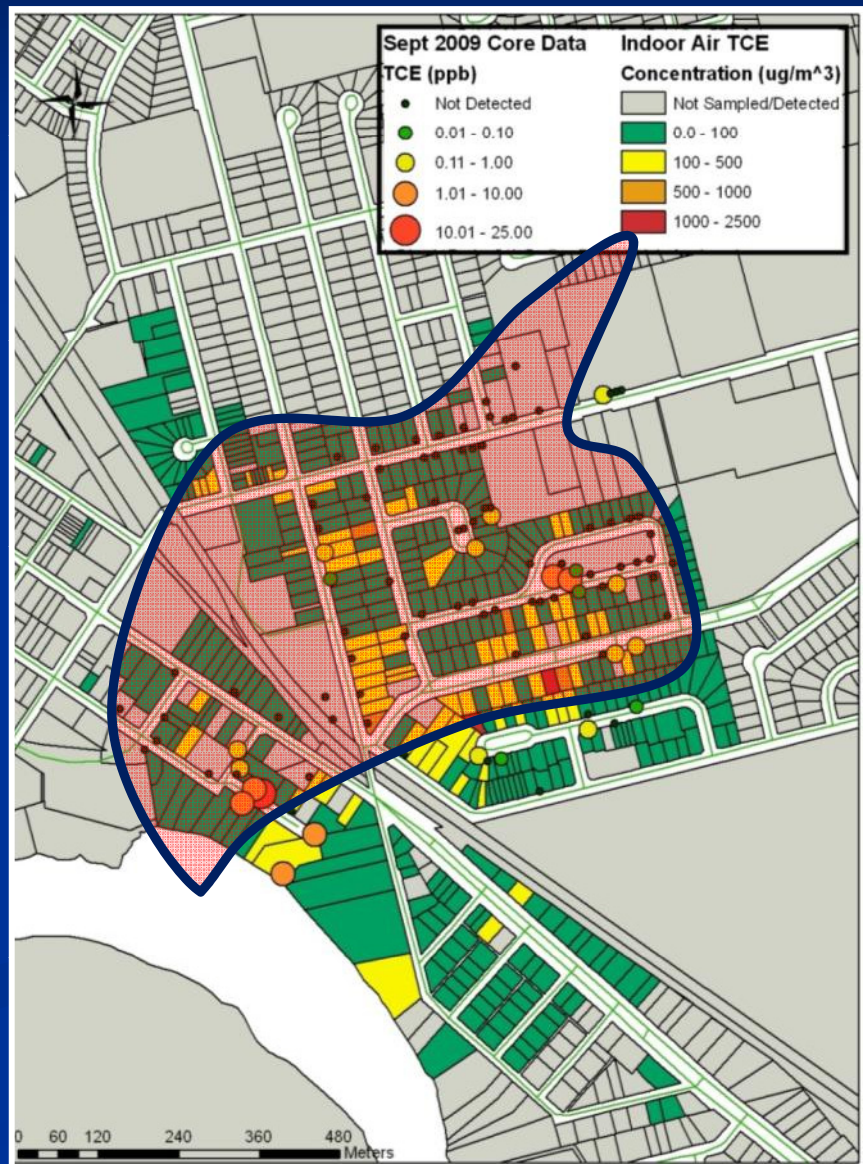
Core analysis & Indoor Air

- Very similar profile
- About 90 of the 'above action level' homes in the tree core indicated area
- All sampling = 1 day



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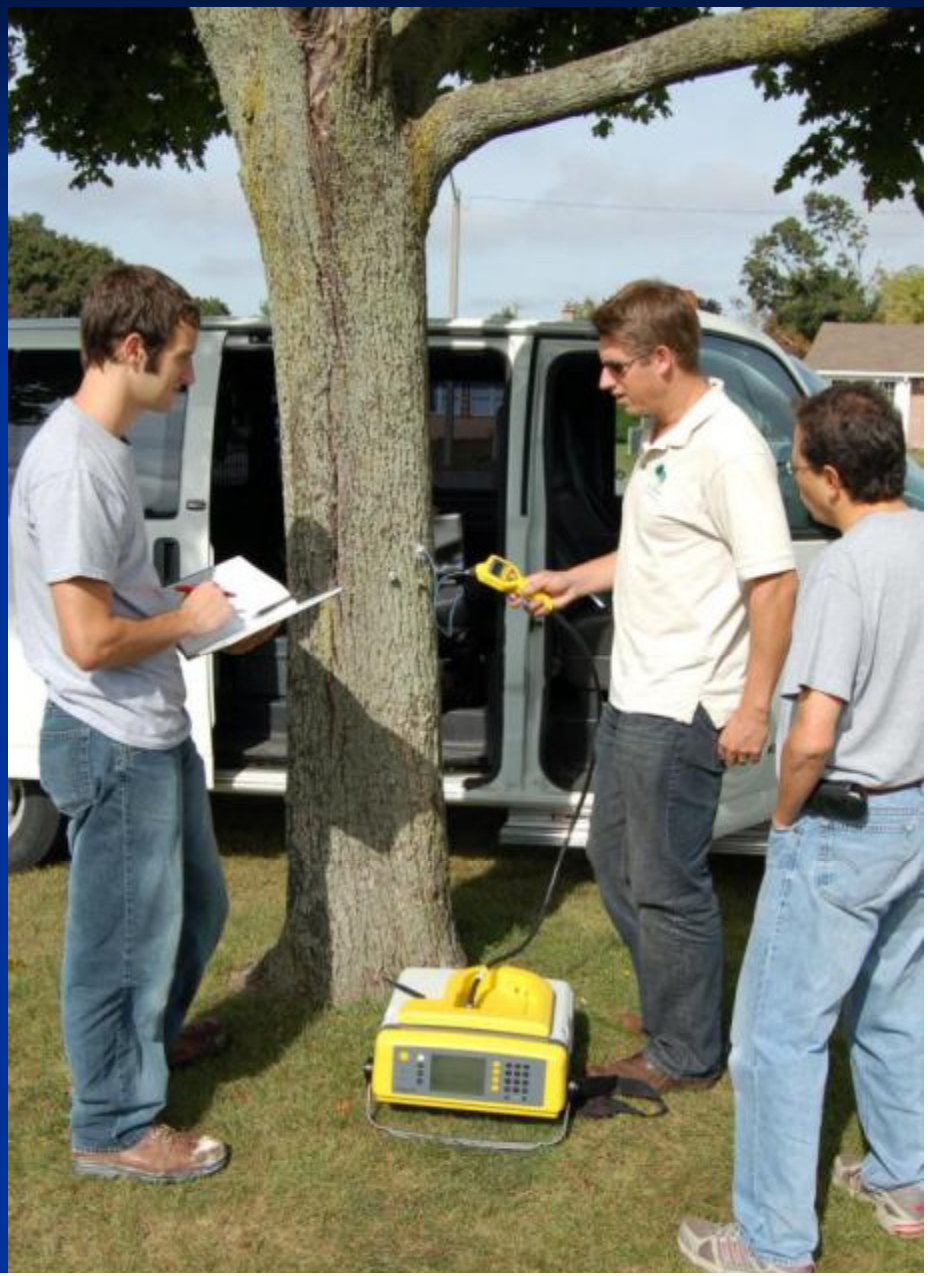
In Field Analysis

- Skip the sample collection, Direct Analysis to Tree



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In Field Analysis

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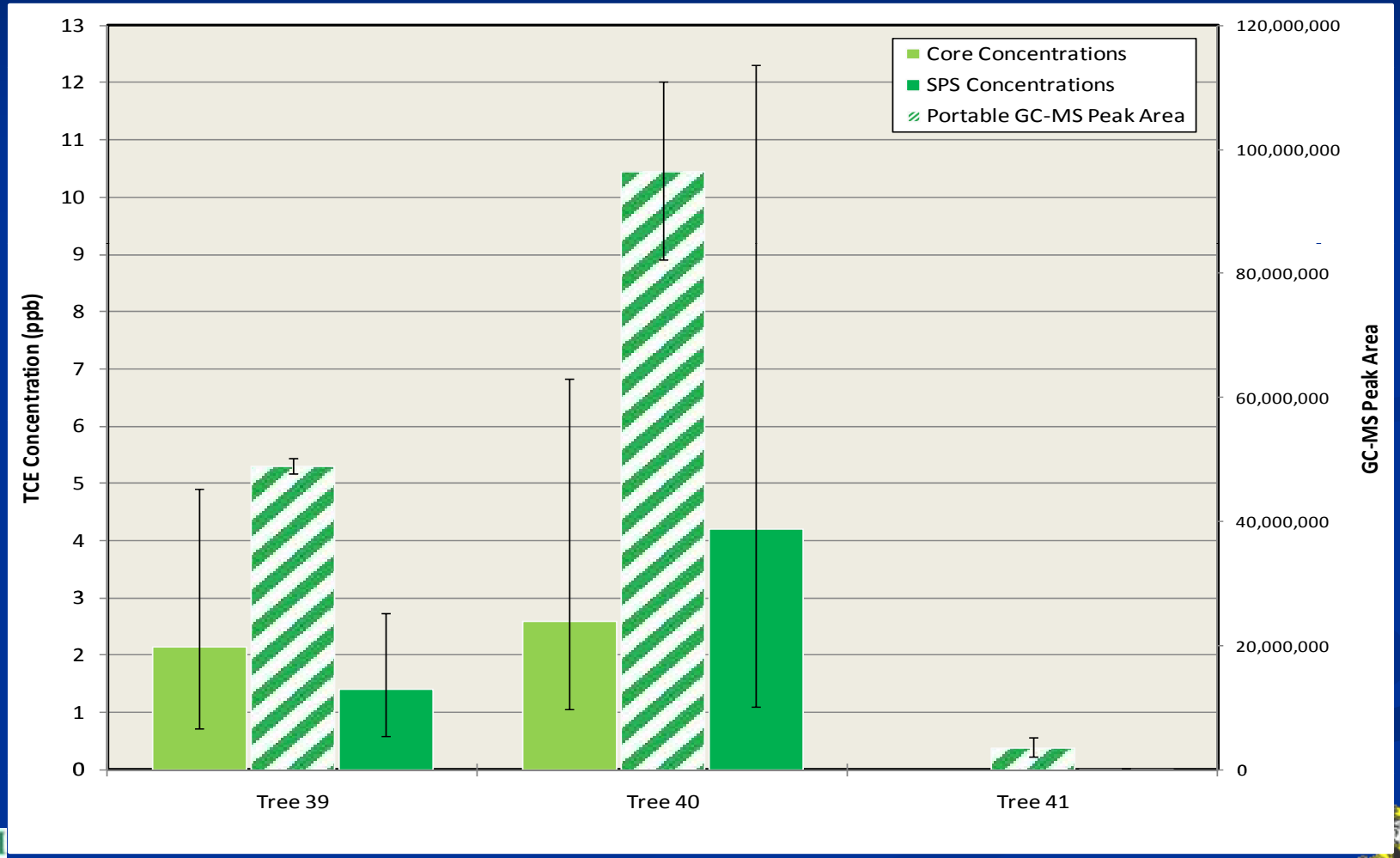
Ontario

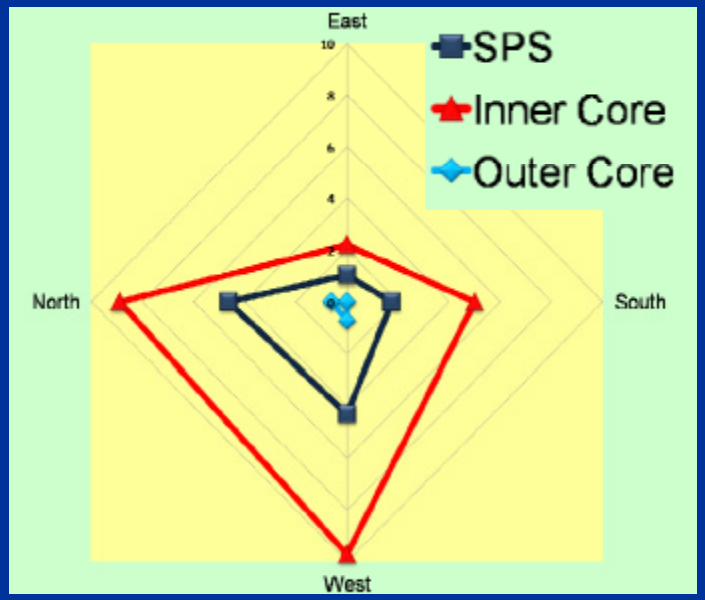
Field GS/MS results

Comparison of SPS, Cores and GC-MS

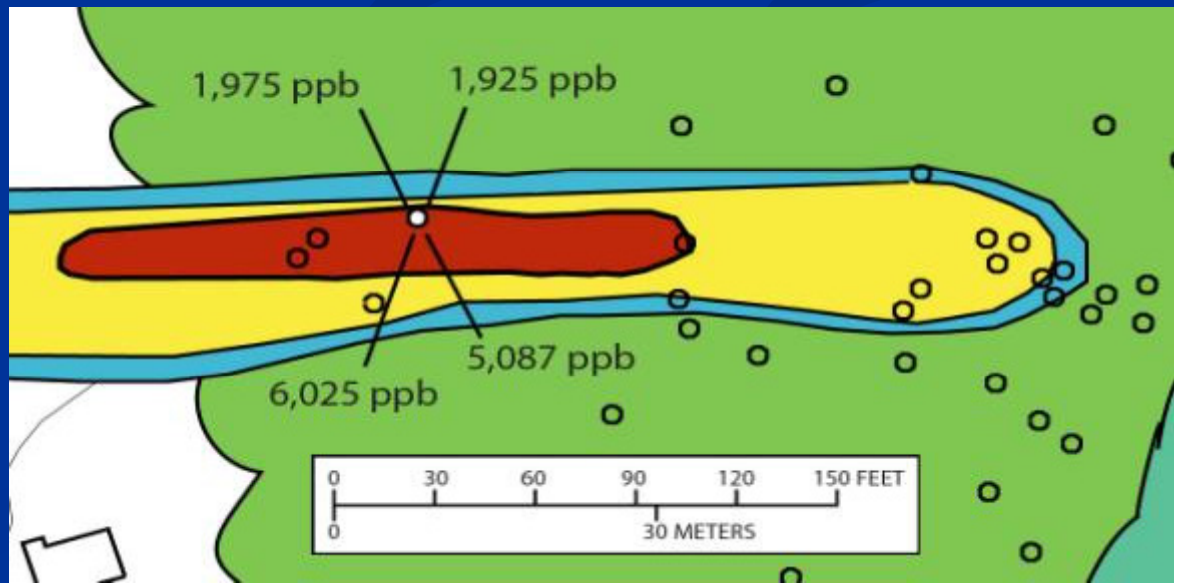


Directional Sampling Possibilities

- Field observations in Tree Coring has shown that sampling around a single tree can correlate to groundwater trends

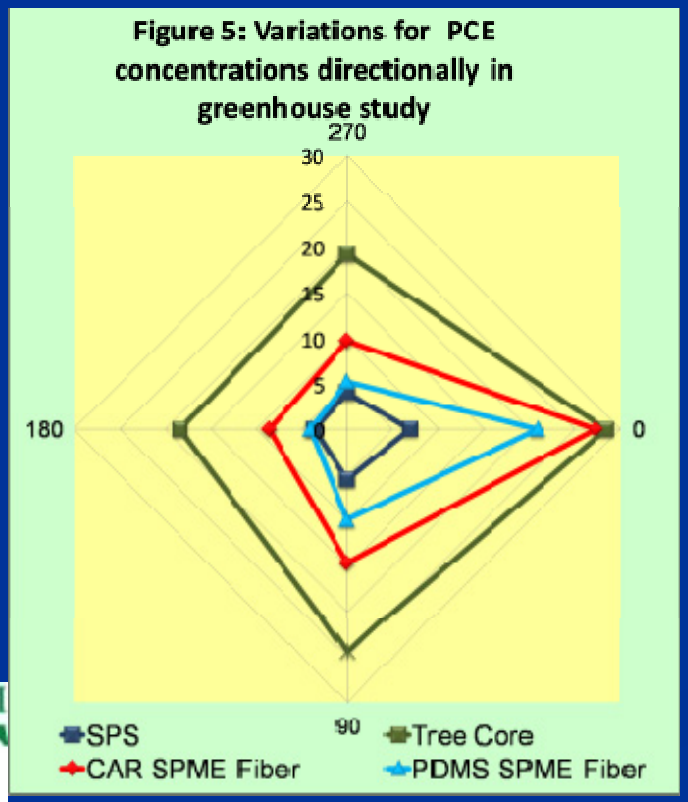


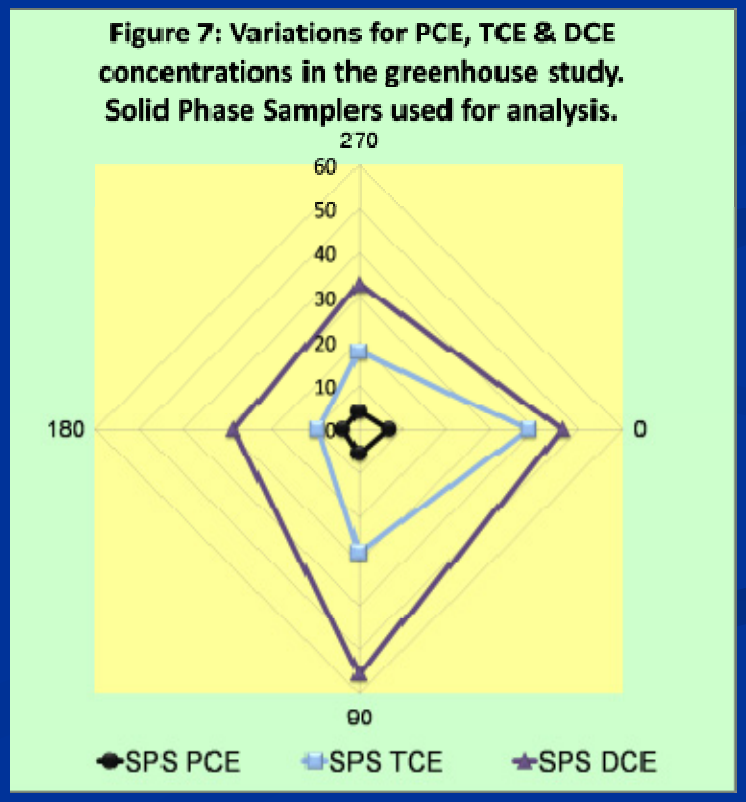
Vroblesky, D.A. et al. (2004) *Ground Water Monit. Rem,*



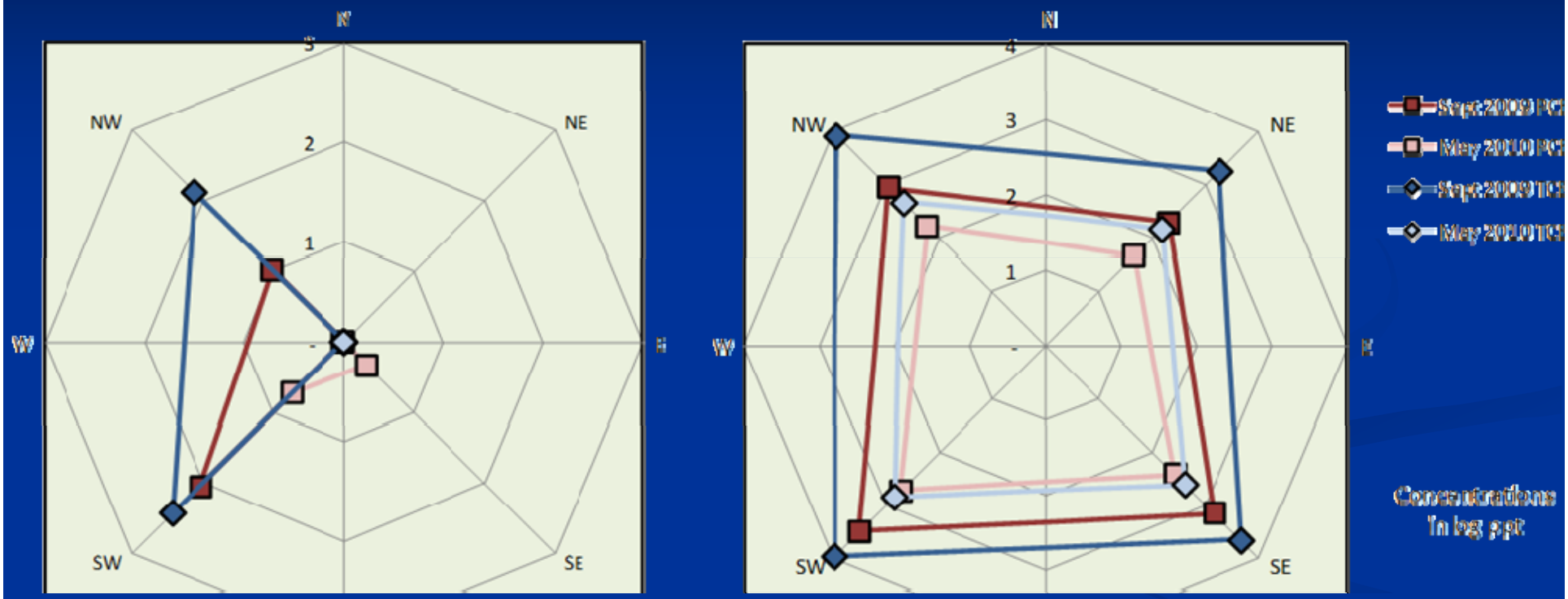
Comparison of Methods

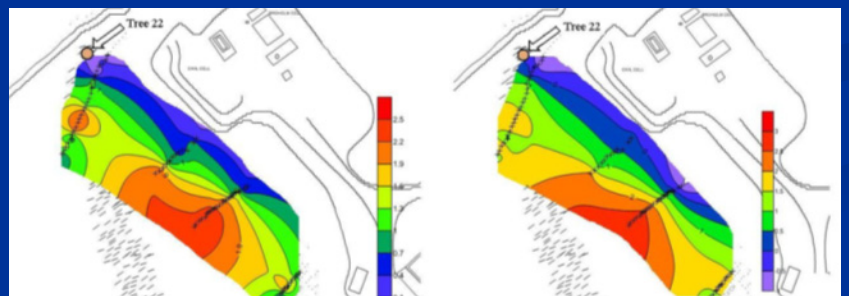
- SPS
- SPME- EQ
- Tree Coring
- SPME-TWA





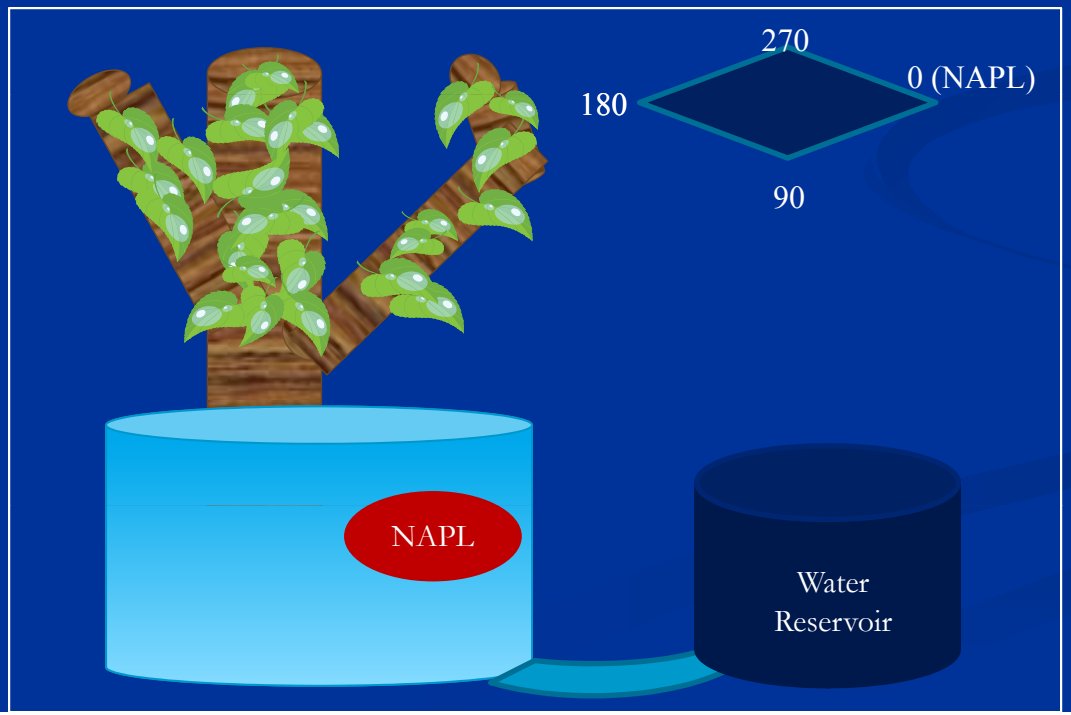
Directional Field Data: Borden ON



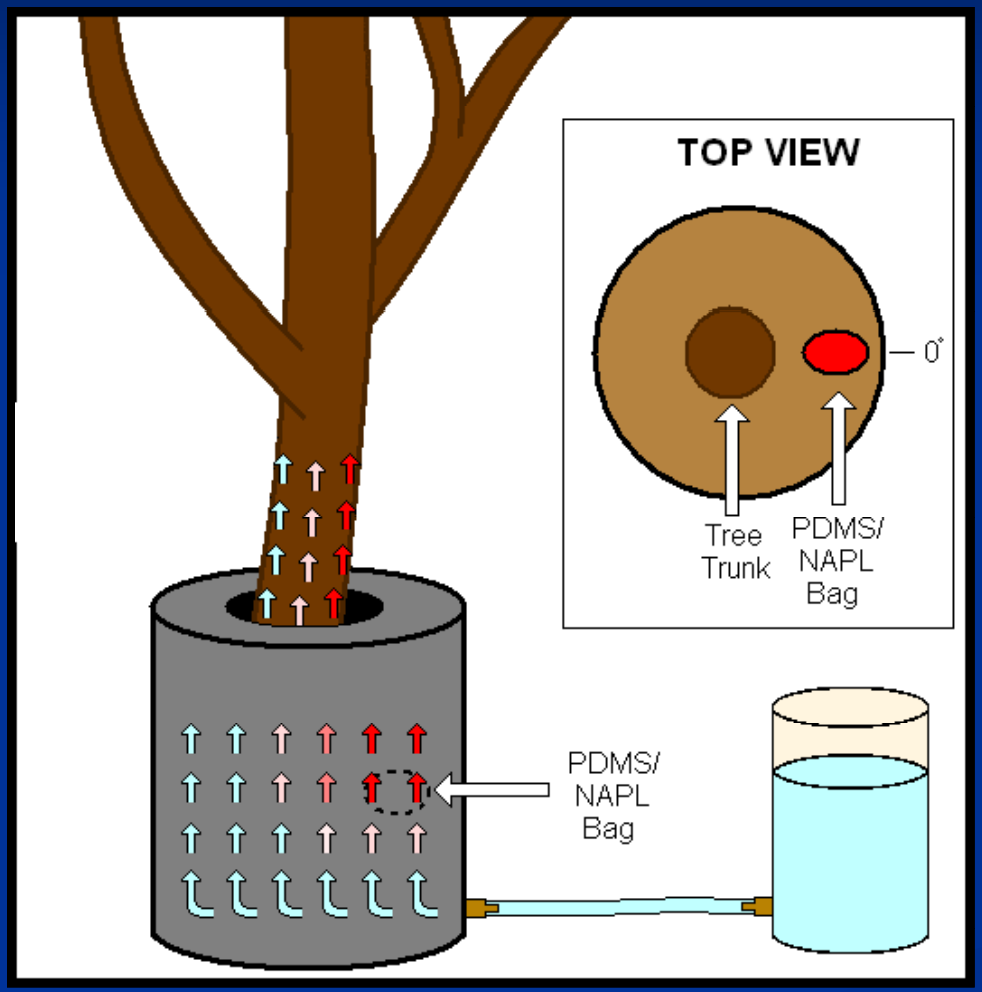


Directional Sampling Possibilities

- Laboratory study conducted by off center placing a NAPL phase PCE in polyethylene membrane
- Dosed with clean water, upflow reactor

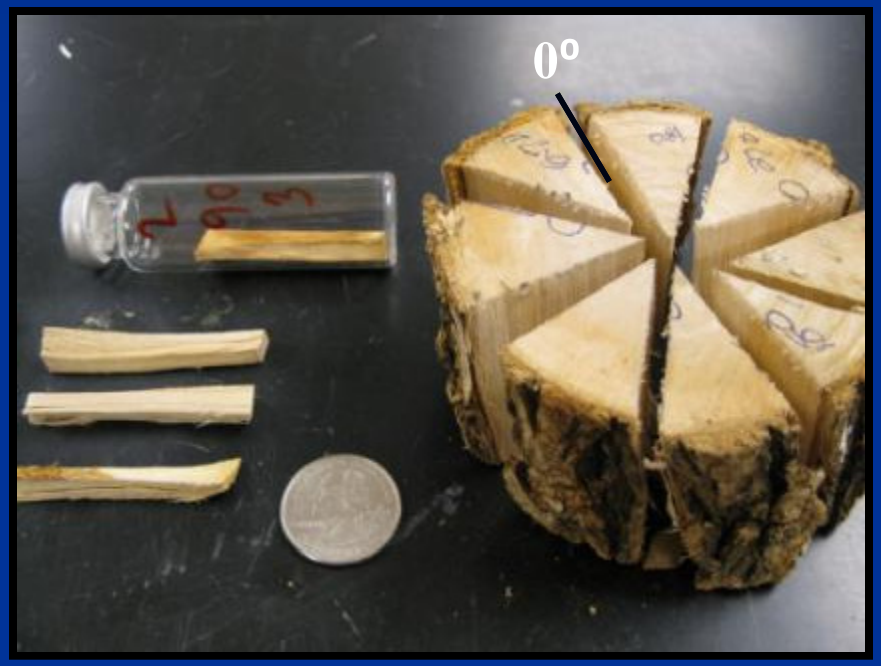


Experimental Setup



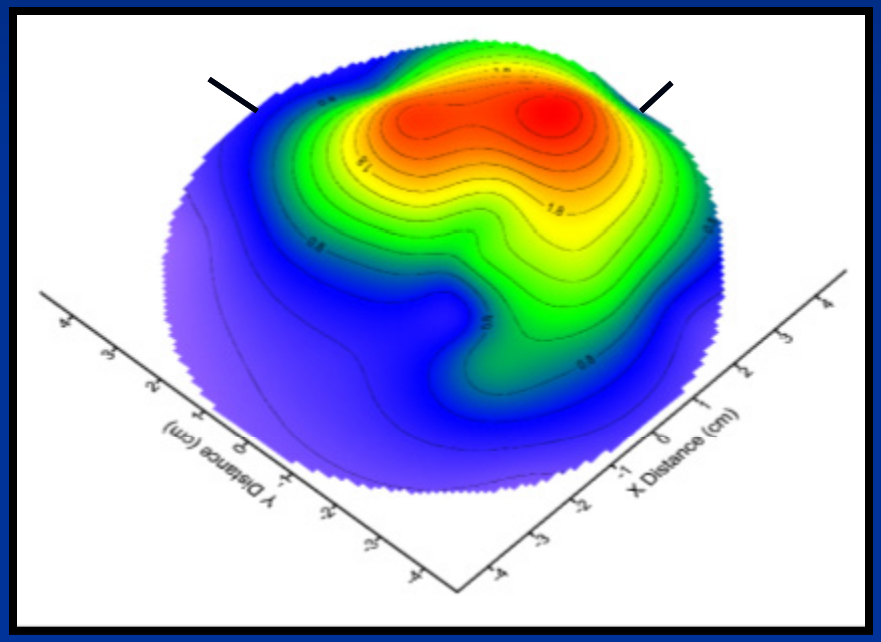
- Zip top bag contaminant reservoir
  - 400 mL of PDMS
  - 6 mL PCE
  - 4 mL TCE
- Cutting watered from below
- 2 month equilibration time

Sampling



- Cross-section of tree (4 cm tall)
- Split into slices with hatchet
- Split into equal size pieces
- ~9 samples in each radial direction

Results



Cross-sectional concentration map of TCE (in ppb)

- Headspace of vial analyzed using SPME-GC
- Data krigged in Surfer®
- Highest concentration of TCE near 0 degrees

Dendrochemistry

Trees act as proxy-recorders by ring accretion. This method is used to age-date environmental impacts, and has been tested at 13 polluted sites *.

- Cores are made with Pressler borer, 10 to 12 mm in diameter.

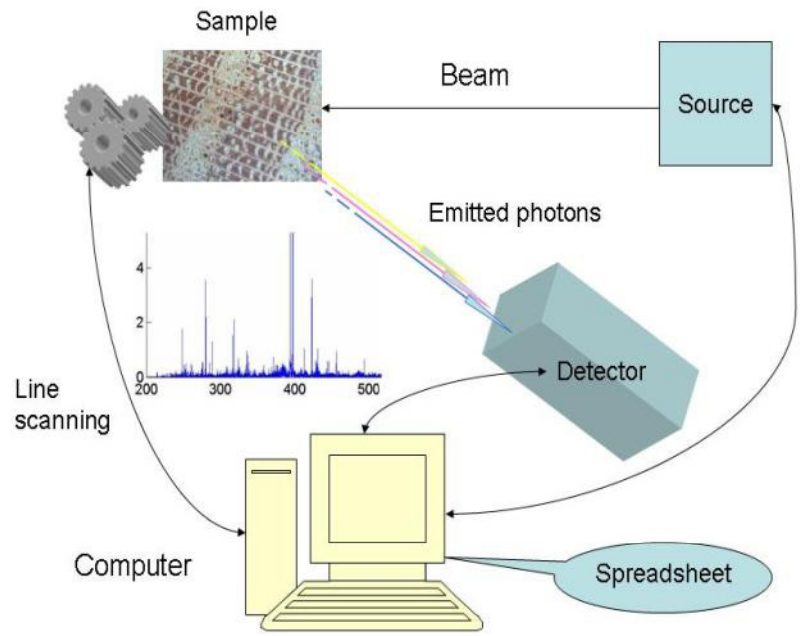
Rings can be analyzed by EDXRF, LA-ICP-MS, … giving access to elemental and non volatile pollutants.

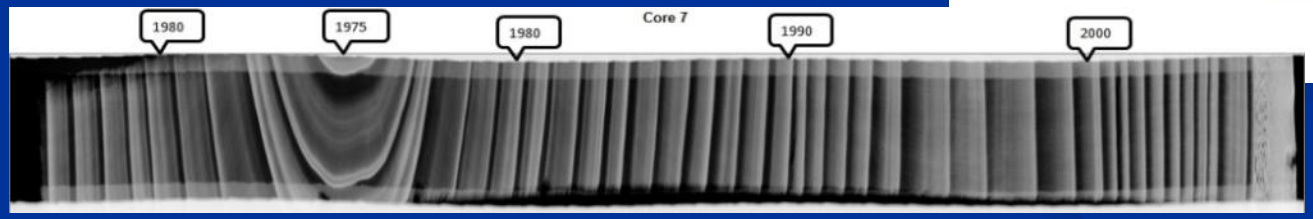
Balouet, Jean Christophe, Smith, Kevin T., Vroblesky, Don and Oudijk, Gil(2009) 'Use of Dendrochemistry in Environmental Forensics: Does It Meet the Daubert Criteria?', *Environmental Forensics*, 10: 4, 268 — 276,

EDXRF Line scannin

7 trees sampled - Pressler borer, 10 mm

Samples checked for quality and age. Sent to Dendrolab, Sweden, for EDRXF analysis.





EDXRF data every 50µ, = 4000 data points /20 cm core).

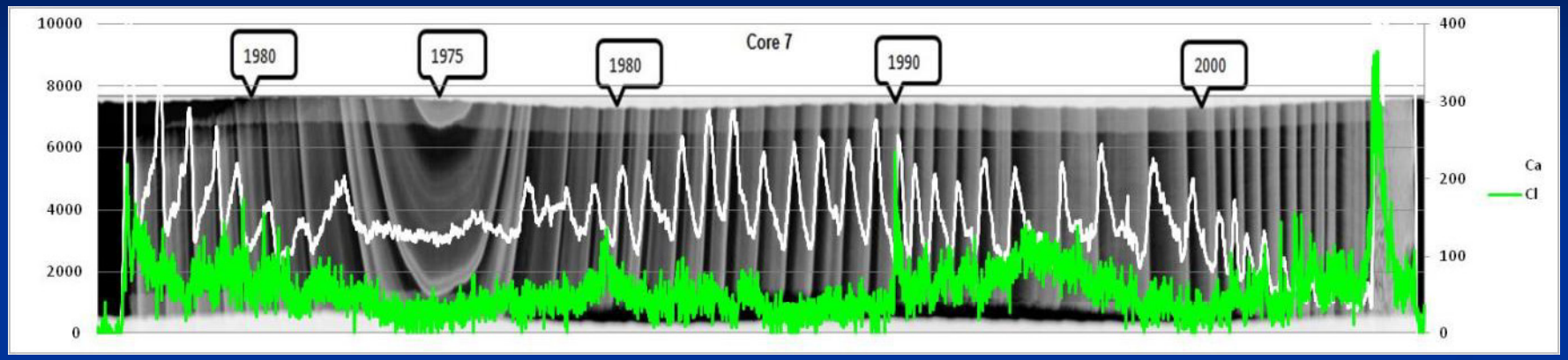
30 elements . Microdensitometry at 20µ ©

kc MS

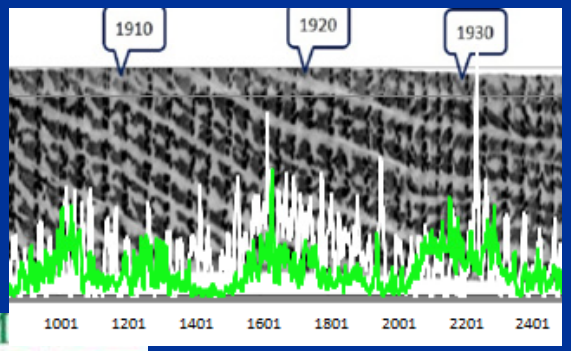
Cr

50,01	9670	1,07	33	19	0	0	13	0	1275	9	148	36	40	93	102	4	0	72	357	0	0	51	23	103	22	390	0	13	21	0	37	70	56	6926	5461
50,06	9689	1,22	39	20	0	8	18	0	1184	15	120	53	53	247	50	13	14	52	371	0	0	0	87	156	0	227	0	7	0	0	71	5	0	7085	5101
[illegible]	[illegible]	1,18	26	0	0	0	0	0	1250	0	131	0	9	127	83	25	0	26	349	0	0	0	140	181	0	381	0	10	31	25	26	55	46	6658	5389
[illegible]	[illegible]	1,16	45	30	4	0	0	0	1292	28	110	33	48	123	77	22	35	78	372	0	36	47	74	183	0	418	0	4	12	0	46	89	0	6980	5323
[illegible]	[illegible]	1,13	20	21	0	0	0	6	1281	18	150	16	40	151	82	34	37	66	371	0	0	60	133	145	0	351	0	13	25	0	79	0	61	6868	5036
[illegible]	[illegible]	1,2	38	33	12	0	26	8	1245	68	194	15	22	158	101	22	32	83	369	0	0	0	194	173	7	476	5	11	44	42	35	31	15	6622	5193
50,31	972[illegible]	1,2	28	27	0	0	21	7	1277	40	172	84	44	213	108	11	0	31	384	0	0	8	82	15	0	440	0	0	0	0	41	25	0	6738	5248
[illegible]	[illegible]	1,2	17	16	0	0	22	0	1244	26	159	49	24	158	118	32	47	73	335	0	32	0	118	66	0	271	0	0	14	24	7	0	0	6619	5359

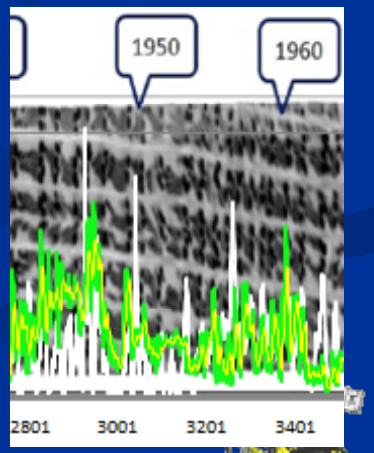
Chlorine anomalies (EDXRF)



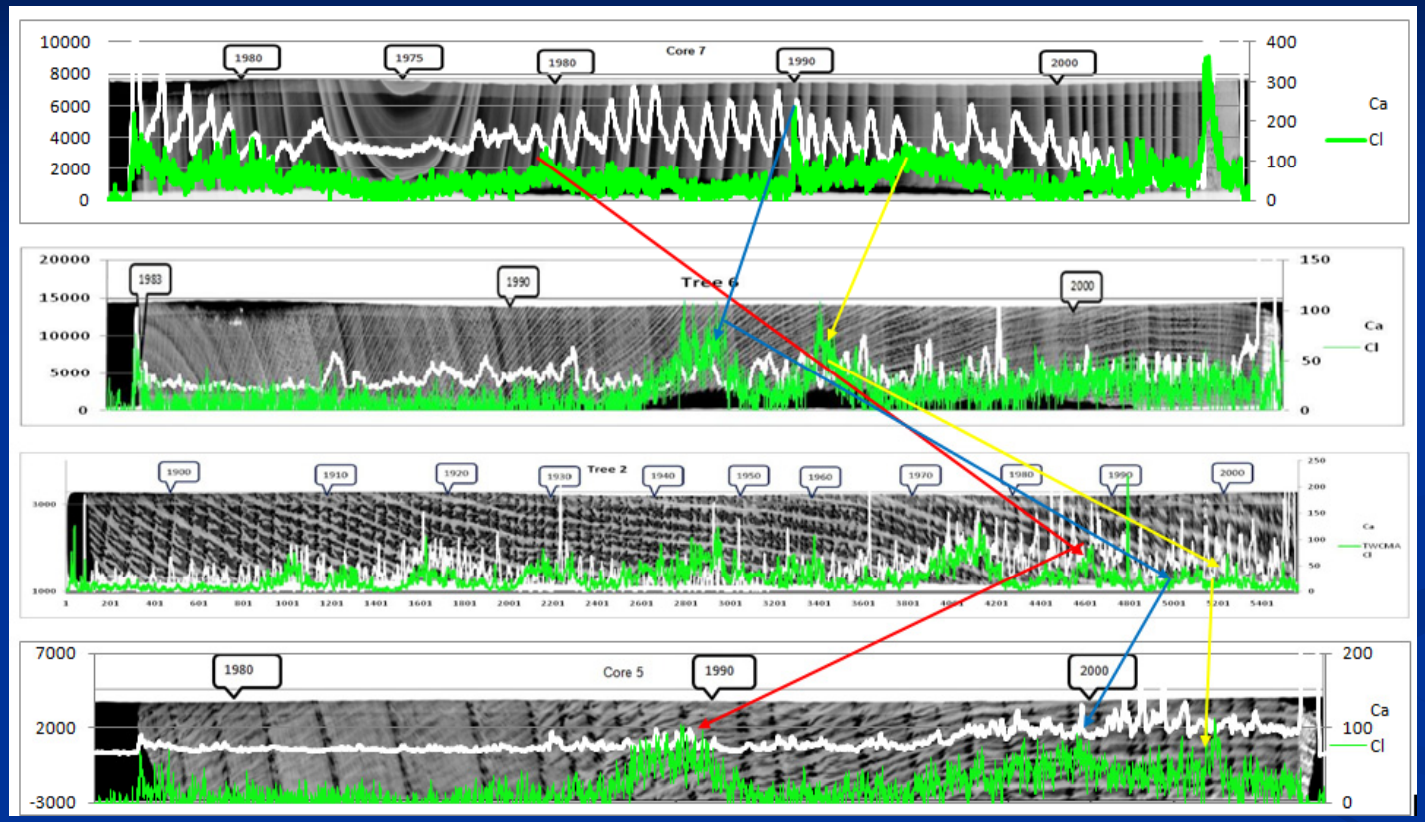
Above profile shows four Chlorine anomalies. Whilst HVOCs have evaporated, elemental chlorine remains available.



Below graphs show multimental (Ca + Cl) anomalies : this signature is associated to drought events

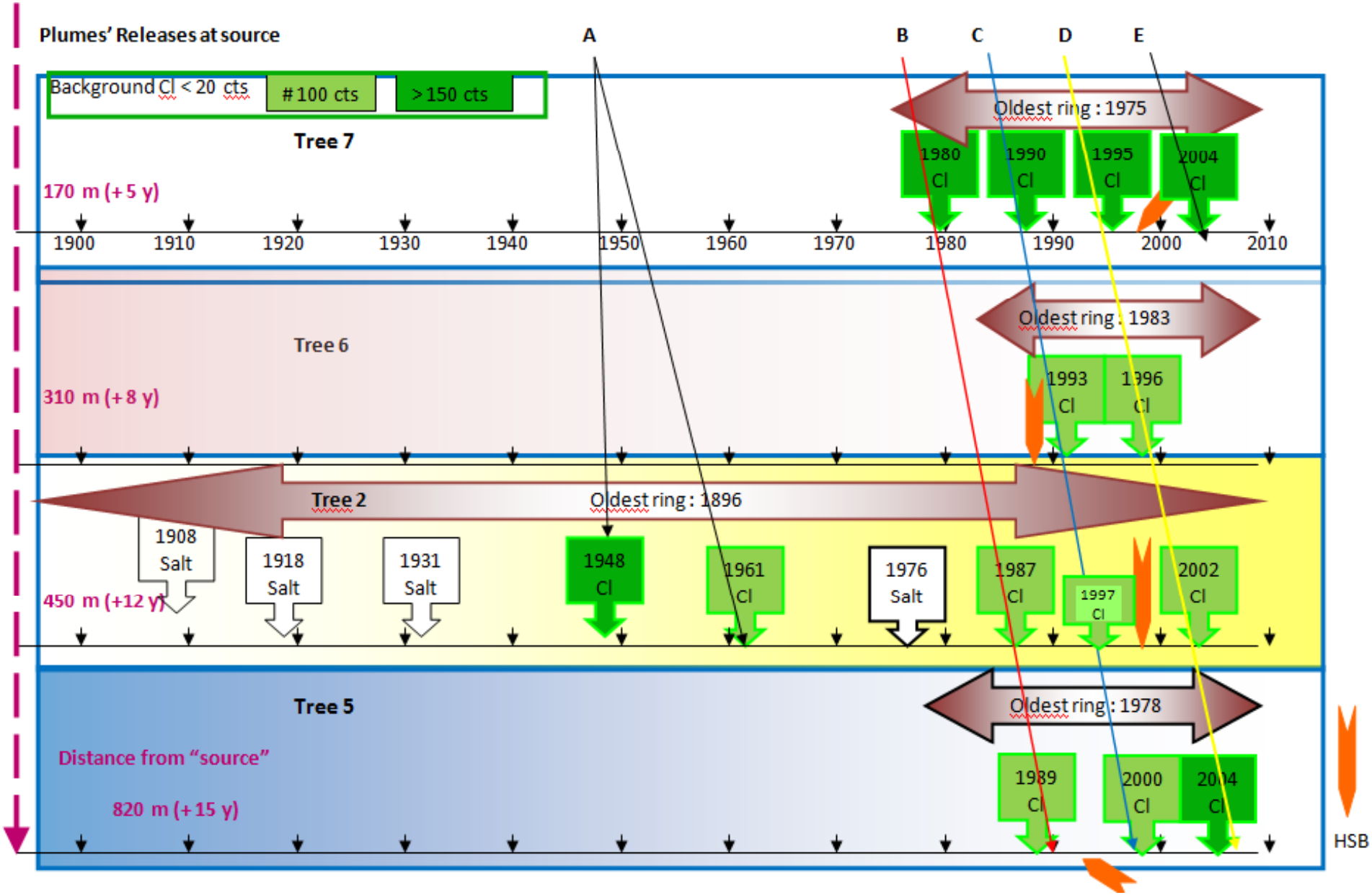


Dendrochemistry at Verl site



Calcium and Chlorine profiles are generated for each of the four analyzed cores and correlated (parsimony principle) the different pulses / impacts.

Reconstruct: History of plumes



Benefits

Phytoforensics Tech Transfer

EPA-USGS User's Guide

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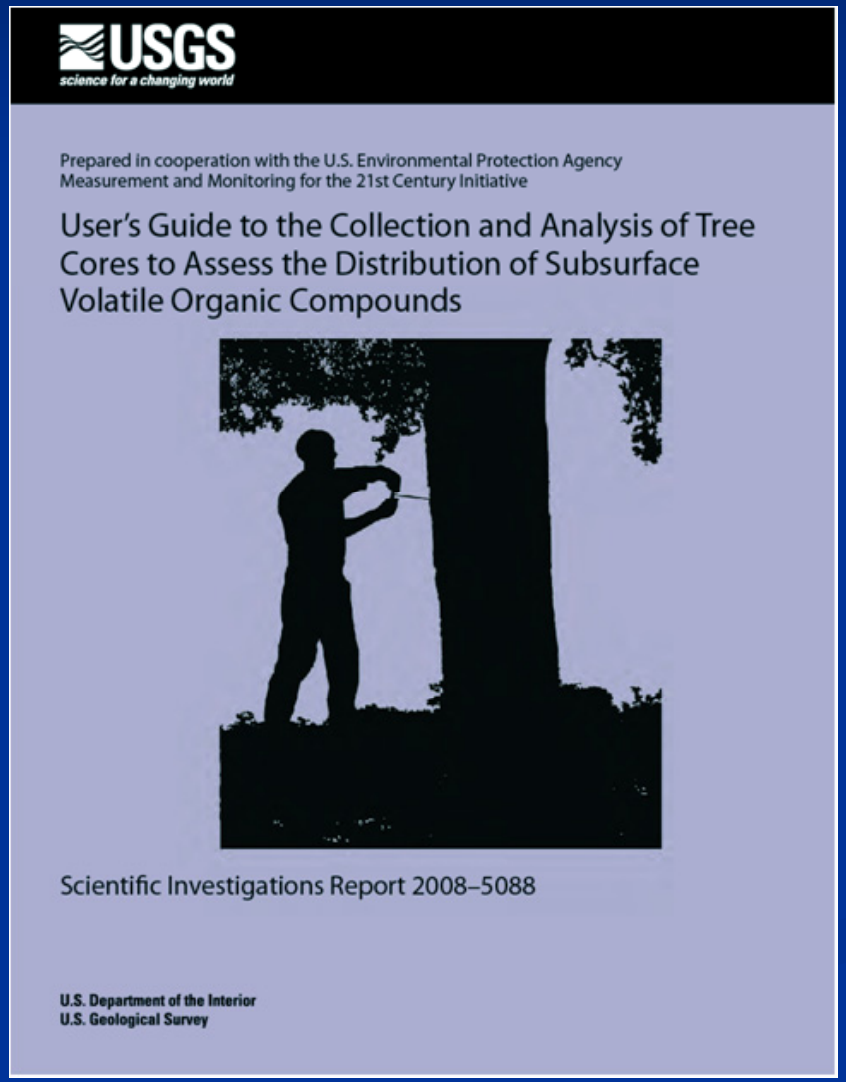
vroblesk@usgs.gov



USGS
science for a changing world

Prepared in cooperation with the U.S. Environmental Protection Agency
Measurement and Monitoring for the 21st Century Initiative

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

EU supported Biotool

Biotool

BIOTOOL project GOCE 003998 December 2007

A Guide to Vegetation Sampling for Screening of Subsurface Pollution

Stefan Trapp, Morten Larsen, Charlotte N. Legind, Joel Burken, Jiřina Macháčková and Ulrich Gosewinkel Karlson (addresses see backside)

Background. Measurement of vegetation samples is an alternative, cheap method to drilling for exploring sub-surface pollution. The objective of this manual is to transfer the experience gained within the EU project BIOTOOL into a concise guide for practical work.

Short description. Vegetation samples are taken and analyzed to find subsurface contamination. The occurrence of compounds like chlorinated solvents in vegetation is mapped. There is a relation, but not necessarily a linear correlation, between concen-

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In-planta PhytoForensics

Fast and Cheap….. FAST

Little, NO Ecological or Personal Property impacts.

Repeat Analysis in the same borehole.

Greater ability to rapidly screen greater areas… Protecting water quality and human health

The End

- Those that Pay:
  - Ministry of the Env. Ontario BiS
  - National Science Foundation, (BES: MRI & CAREER)
  - OECD (Faculty Fellowship)
- Great Colleagues!!!
- Those that listen

Thanks for your valued time!