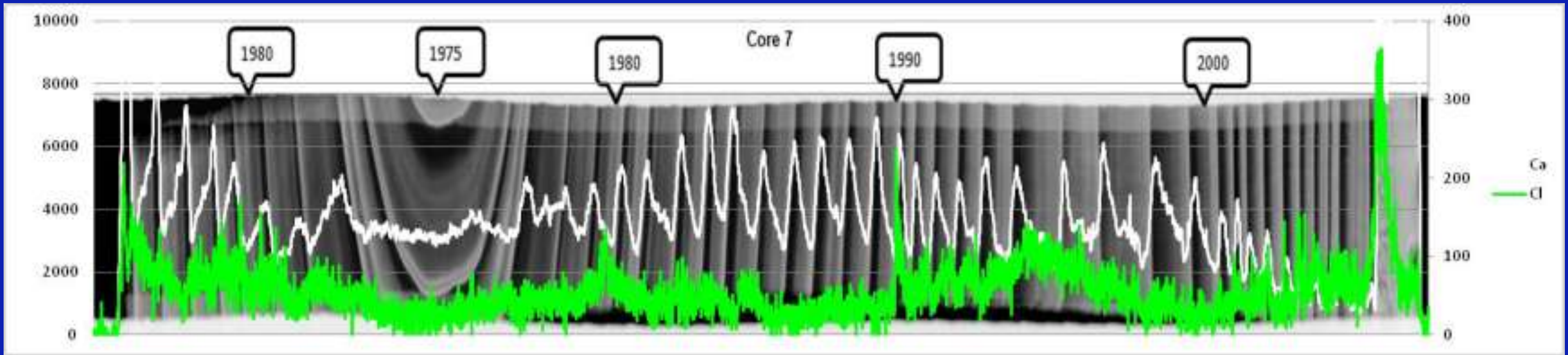
Case Study of Phyto-Forensics via Dendrochronology and Phytoscreening to clarify the "time-space" Context of a TCE-PCE-Groundwater Contamination



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Environmental Forensics

Scientific investigations that address contamination within the environmental media of air, water, soil and biota, and is subject to law court, arbitration, public debate, or formal argumentation.

Scientific studies that explore source, fate, transport and ecological effects of environmental contamination, with contamination being delineated in terms of chemical characterization, biological influence, responsible parties and legal consequences.

Pollution Investigation by Trees (PIT)

PIT is an international program, 6 nations, 18 members, led by Ademe, started 2010 and to be completed in June 2013.

PIT is to document and test Phytoscreening and Dendrochemistry methods, using trees as proxyrecorders, to delineate current and past distribution of pollutants : Fossil fuels, PAHs, HVOCs, metals, PCBs and dioxins.

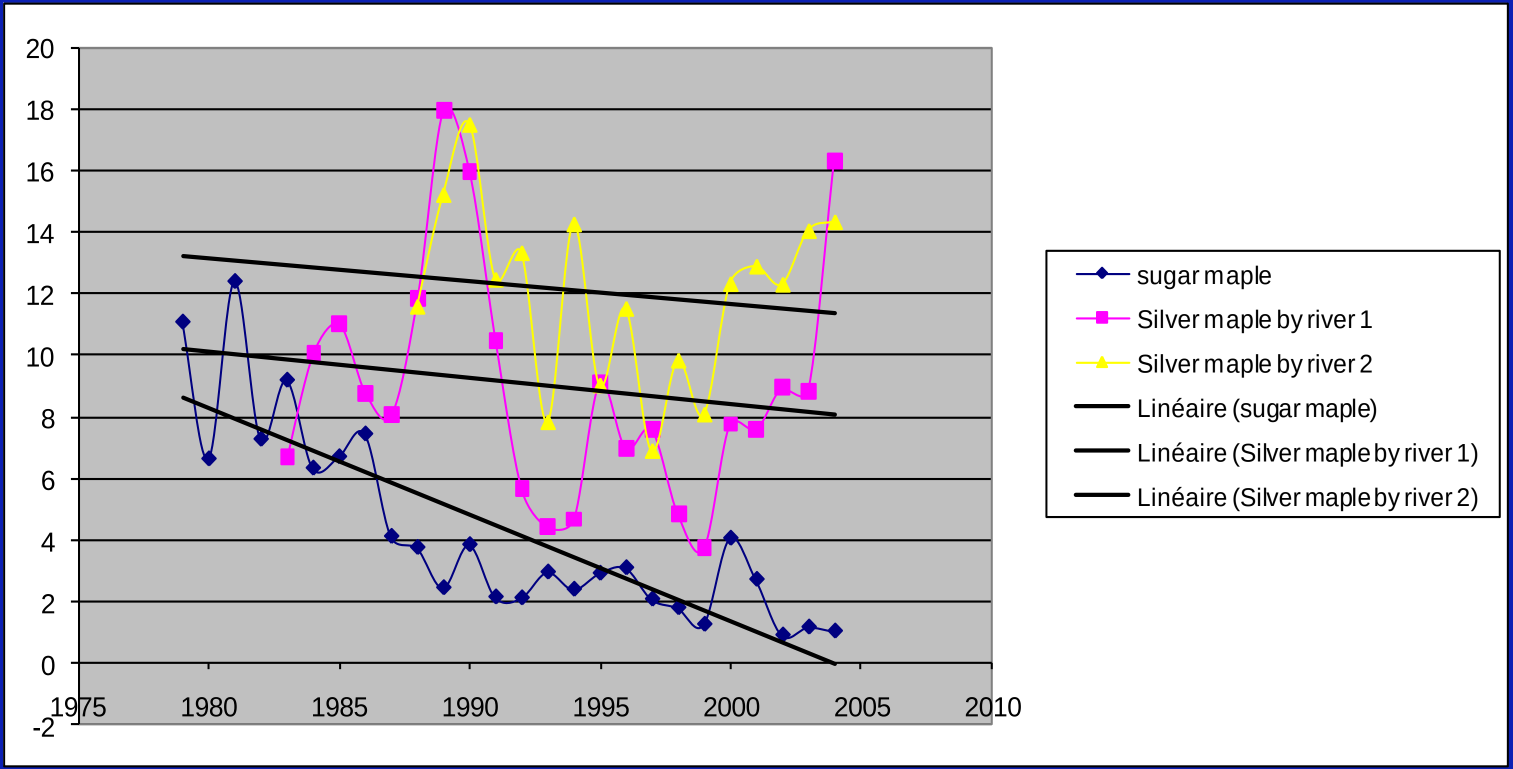
The following case is about a German HVOC site, investigated by HPC. *The cooperation between the HPC Group R&D Division and Dr. Balouet from Environment International showed the best Task-Force to tackle a difficult "Time-space" problem of understanding of the Groundwater contamination.*

Dendrochronology is about Tree rings !

Tree rings are not always circular or regular as taught in primary school, they tell us much more about the history of their environment, and can help age date floods, avalanches, rockfalls, earthquakes, fires, insect plagues, cold winter, storms, bullets… and when!

Dendrochronology and ring width

In this case , sampled 2004, a former sand and gravel pit, by Delaware river,. The pumping of groundwater at 50' deep, caused the groundwater level at neighbouring farm property to be lowered by > 7 feet. Growth suppression on pit's neighbouring sugar maple has been associated to the resulting lowering of water table at farmland and State of Delaware condemned.



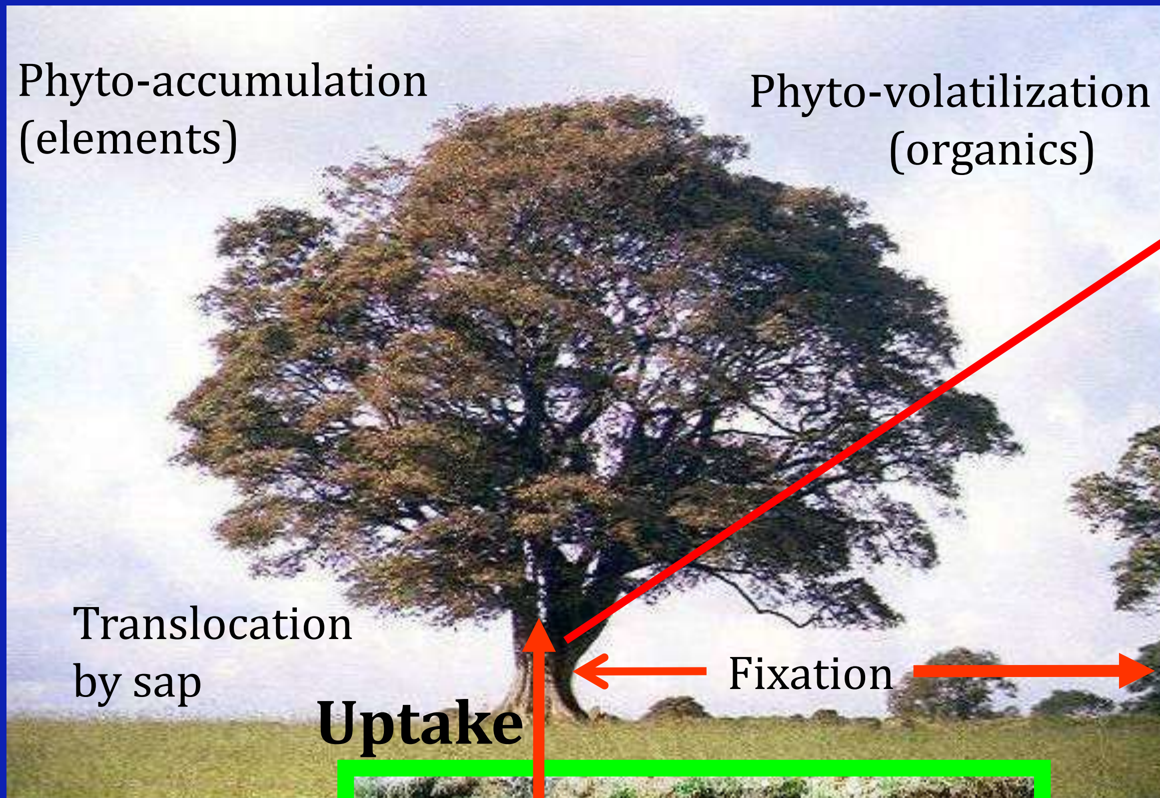
Other Forensics examples

Charles Lindberg's son kidnapping : wooden ladder and wood parts that were used to repair it were found at murderer 's garage shop. Saw marks and tree rings were used as legal evidence.

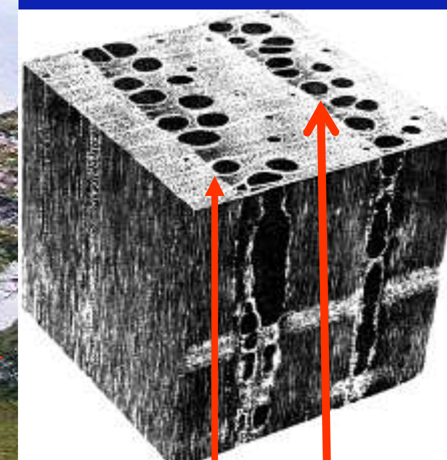
Did George Washington had dinner in 1669 in this house in Virginia? Dendrochronology on beams showed that the mansion was 71 years younger. A significant loss of value for this « historical « house sold for 750 000 $.

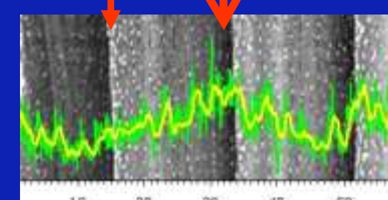
Is this a Stradivarius? Wood dates back to the little ice-age.

What trees do …



Phytoscreening as outer most ring(s) are sap-enriched





Phyto-extraction
Phyto-fixation
Rhizo-decomposition

Contaminant

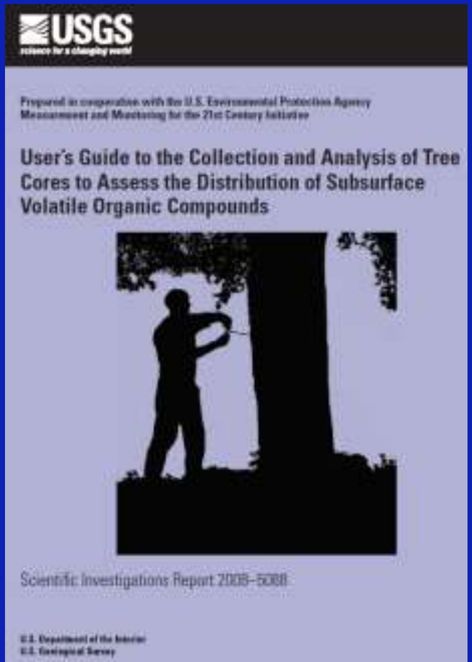
Dendrochronology : as annual rings reflect uptake at exposure times

Phytoscreening

Method’s basis established over the past decade, and « tested » at over 20 sites.

In our case, 49 trees sampled in may 2010, plus four double samples. 5 mm cores sampled by sampling hammer, sample mass > 0,2 g for volatiles.

Sampling tools.



Samples analysed by GC/ECD, at University of Missouri, in ppt. Transpiration stream.

General method was published in USGS guide by Don Vroblesky, in 2008.

Phase I site Assessment

Phytoscreening, other approaches

Trees rootball uptake contaminants from both soils and groundwater. As a result, sap /outer ring content can be assimilated to an integral $_{GW}\int^{Soil}$ exposures. In Planta methods by Joel Burken, allow to monitor trees in the field without making new samples. This method is well adapted to follow up mitigation.

Portable GC : allows to have about 30 trees monitored and data available within one day.

Other studies used branches.

PIT will further test method for metals, PAHs and PCBS/dioxins. PCCD/F

Phytoscreening, other approaches

SPSs Placed Into Soil

Water Distribution Tube

Willows Growing in Greenhouse

Directionnal Studies by Prof Joel Burken UoM S&T

Phytoscreening, other approaches

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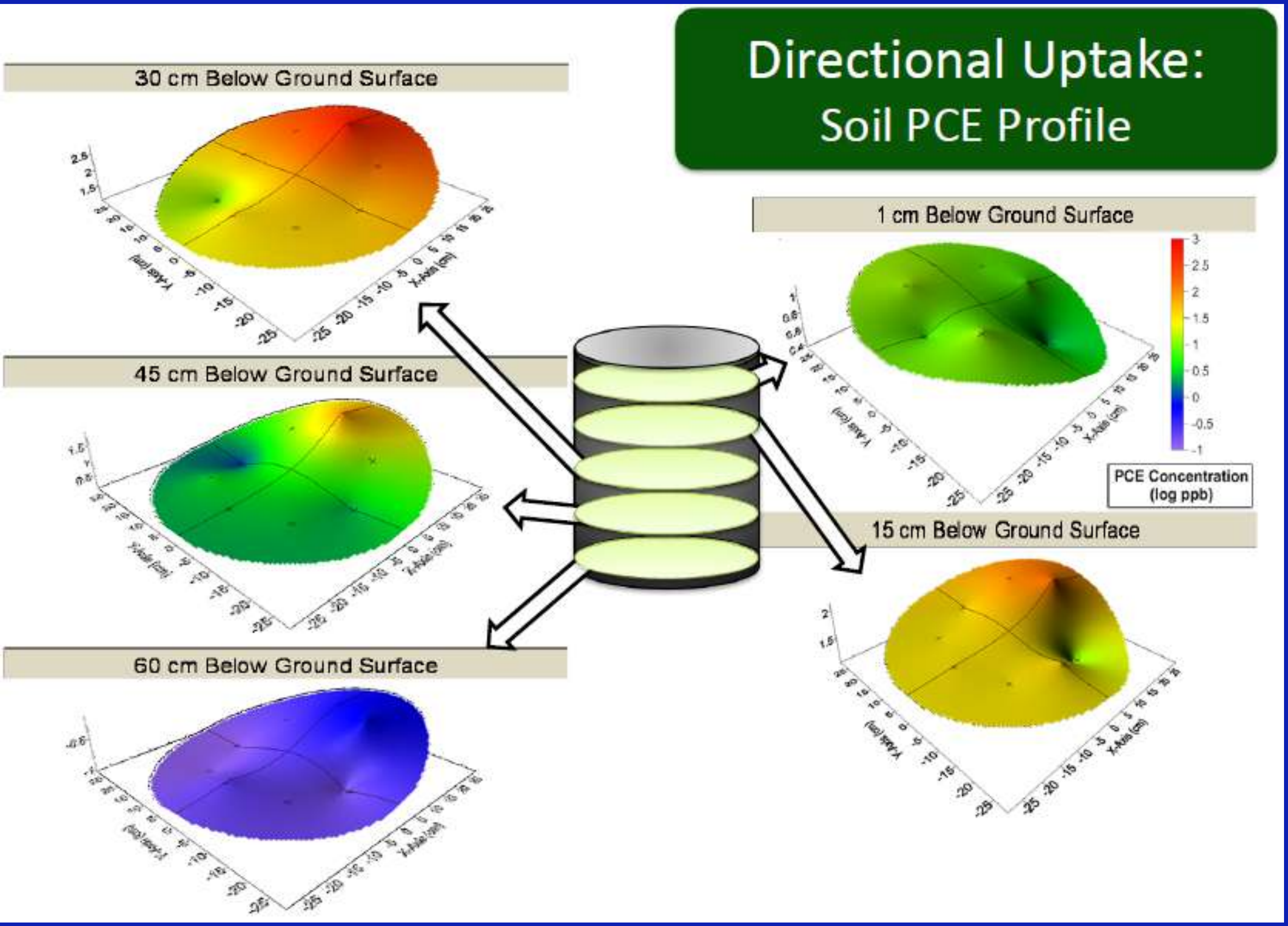
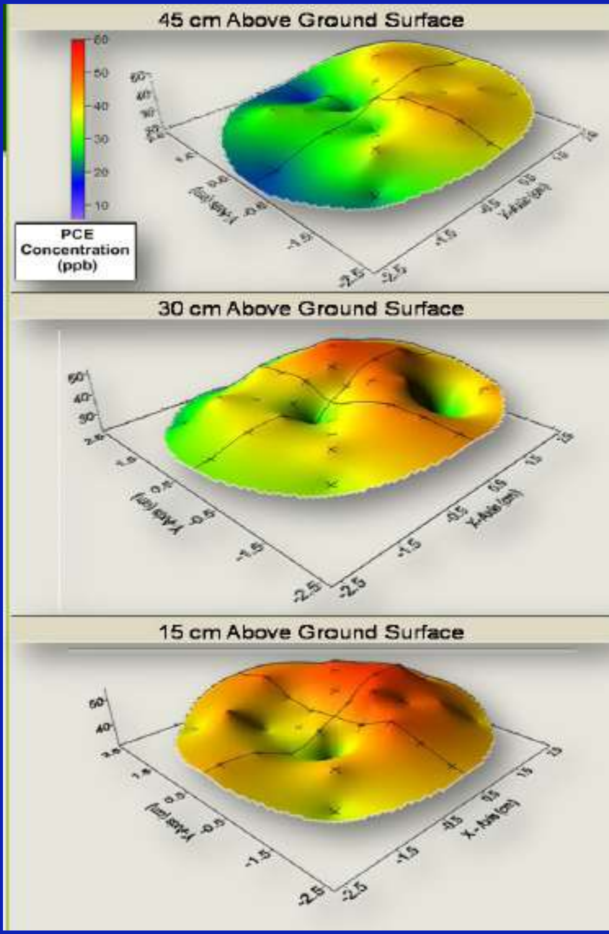
Phytoscreening, other approaches

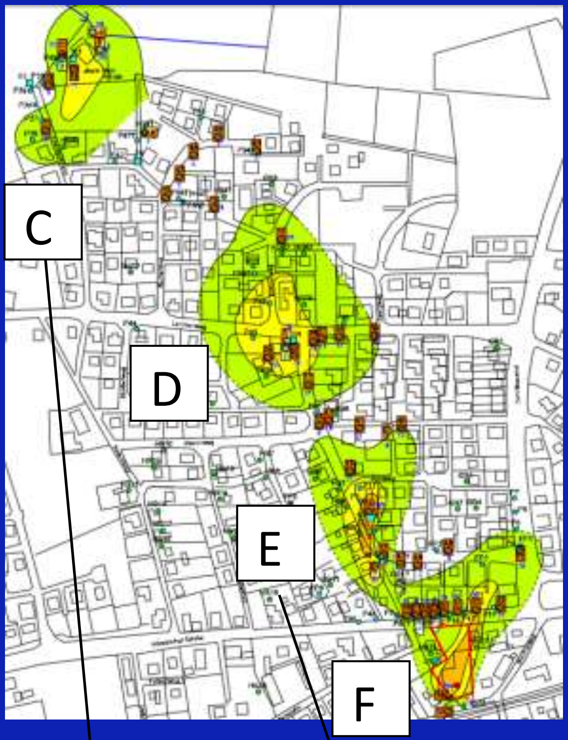


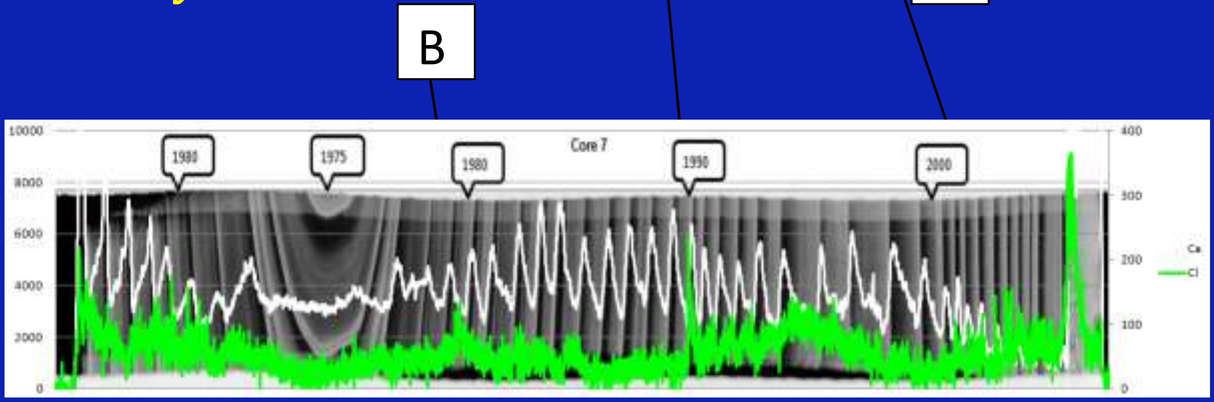


An HVOC case

Combining phytoscreening and dendrochemical methods, at an HVOC site in Germany for site assessment and history of environmental releases : a case by HPC, in association with PIT.

Pollution Investigation by Trees is an international program sponsored by Ademe, and joined by 13 organisations in Canada, France, Germany, Israel, Sweden, USA.





Phytoscreening : GC / ECD

Vial #	Wet Mass (g)	Dry Mass (g)	Vial Mass (g)	Water Mass (g)	Dry Wood (g)	Wet Wood (g)	% Water (by mass)	Volume of air (L)	PCE Mass Correction Factor			TCE Mass Correction Factor		
									Numerator	Denominator	Ratio	Numerator	Denominator	Ratio
1	19,027	18,449	17,910	0,578	0,539	1,117	52%	0,0187	0,86	0,55	1,57	0,77	0,55	1,38
1,1	18,891	18,399	17,944	0,492	0,455	0,947	52%	0,0189	0,78	0,46	1,68	0,68	0,47	1,46
4	18,703	18,123	17,698	0,580	0,425	1,005	58%	0,0188	0,75	0,44	1,72	0,65	0,44	1,49
5	18,572	18,034	17,498	0,538	0,536	1,074	50%	0,0187	0,86	0,55	1,57	0,76	0,55	1,39
5,1	18,438	18,049	17,665	0,389	0,384	0,773	50%	0,0191	0,71	0,39	1,81	0,61	0,39	1,55
6	18,277	17,832	17,553	0,445	0,279	0,724	61%	0,0191	0,61	0,29	2,11	0,51	0,29	1,75
6,1	18,364	17,881	17,520	0,483	0,361	0,844	57%	0,0190	0,69	0,37	1,86	0,59	0,37	1,58
7	18,638	18,232	17,859	0,406	0,373	0,779	52%	0,0191	0,70	0,38	1,84	0,60	0,38	1,56
7,1	18,340	17,965	17,593	0,375	0,372	0,747	50%	0,0191	0,70	0,38	1,84	0,60	0,38	1,57
9	18,338	17,911	17,588	0,427	0,323	0,750	57%	0,0191	0,65	0,33	1,96	0,55	0,33	1,65
10	18,652	18,330	17,984	0,322	0,346	0,668	48%	0,0192	0,67	0,35	1,91	0,57	0,35	1,62
11	18,825	18,372	18,104	0,453	0,268	0,721	63%	0,0192	0,60	0,28	2,16	0,50	0,28	1,78
12	18,473	18,153	17,929	0,320	0,224	0,544	59%	0,0194	0,55	0,23	2,40	0,45	0,23	1,95
12,1	18,241	17,882	17,560	0,359	0,322	0,681	53%	0,0192	0,65	0,33	1,97	0,55	0,33	1,66
13	18,926	18,440	17,993	0,486	0,447	0,933	52%	0,0189	0,77	0,46	1,69	0,67	0,46	1,47
14	18,541	18,252	17,905	0,289	0,347	0,636	45%	0,0193	0,67	0,35	1,91	0,57	0,35	1,62
15	18,639	18,245	17,807	0,394	0,438	0,832	47%	0,0190	0,76	0,45	1,71	0,66	0,45	1,48
16	18,706	18,250	17,808	0,456	0,442	0,898	51%	0,0189	0,77	0,45	1,70	0,67	0,45	1,47
17	18,896	18,233	17,711	0,663	0,522	1,185	56%	0,0186	0,85	0,54	1,58	0,75	0,54	1,39
18	18,573	17,971	17,576	0,602	0,395	0,997	60%	0,0188	0,72	0,41	1,77	0,62	0,41	1,52
19	18,401	18,076	17,502	0,325	0,574	0,899	36%	0,0189	0,90	0,58	1,55	0,80	0,58	1,37
20	18,815	18,407	18,046	0,408	0,361	0,769	53%	0,0191	0,69	0,37	1,86	0,59	0,37	1,58
21	18,411	18,085	17,680	0,326	0,405	0,731	45%	0,0191	0,73	0,41	1,78	0,63	0,41	1,53
22	18,475	18,139	17,704	0,336	0,435	0,771	44%	0,0191	0,76	0,44	1,72	0,66	0,44	1,49
23	19,184	18,447	18,002	0,737	0,445	1,182	62%	0,0186	0,77	0,46	1,68	0,68	0,46	1,46
24	18,520	18,149	17,686	0,371	0,463	0,834	44%	0,0190	0,79	0,47	1,68	0,69	0,47	1,46

Phytoscreening : GC / ECD

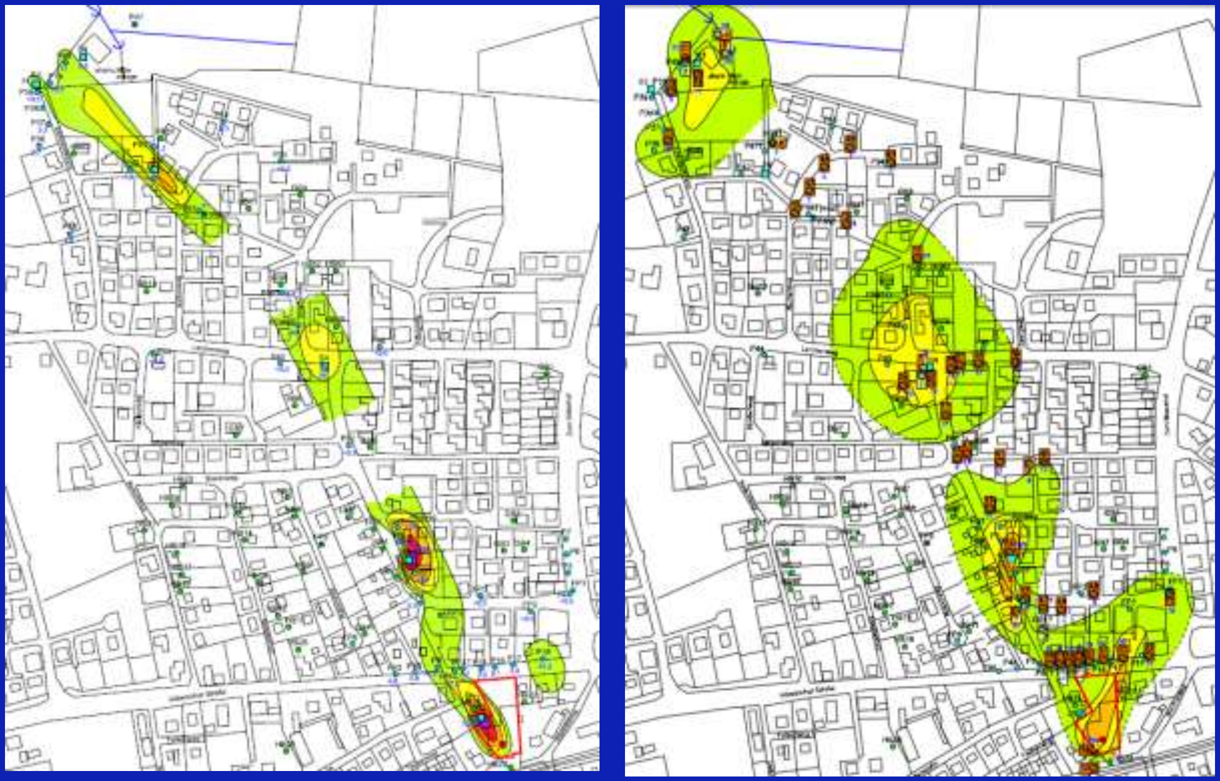
Vial #	Type	Duplicate?	Core Concentrations (ppt) (PDMS Fiber)				Location	Tree Type
			cDCE	TCE	PCE	Extrapolation?		
1	Core		-	825	80			*Aesculus*
1,1	Core	Yes	-	1 127	78			*Aesculus*
4	Core		-	676	36			*Quercus petraea*
5	Core		-	918	58			*Quercus robur*
5,1	Core	Yes	-	246	13			*Quercus robur*
6	Core		-	1 549	10			*Platanus*
6,1	Core	Yes	-	1 304	7			*Platanus*
7	Core		-	1 225	84			*Albies sp*
7,1	Core	Yes	-	1 138	79			*Albies sp*
9	Core		-	299	3	Yes		*Quercus petraea*
10	Core	reference	-	-	4			*Betula sp.*
11	Core		-	126	249		X	*Prunus avium*
12	Core	reference	-	107	7			*Aesculus*
12,1	Core	Yes	-	950	50			*Aesculus*
13	Core		-	430	15			*Tilia cordata*
14	Core		-	348	146			*Acer campestre*
15	Core		-	400	31			*Acer campestre*
16	Core		-	199	8			*Tilia cordata*
17	Core		-	547	31			*Quercus petraea*
18	Core		-	555	26			*Picea albies*
19	Core		-	95	6			*Pyrus sp.*

Phytoscreening : PCE

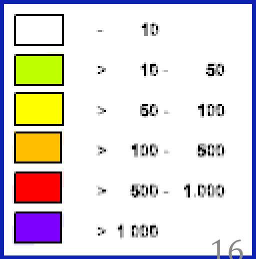
49 trees sampled in may 2010, plus four double samples.

Plumes mapped with Autocad.

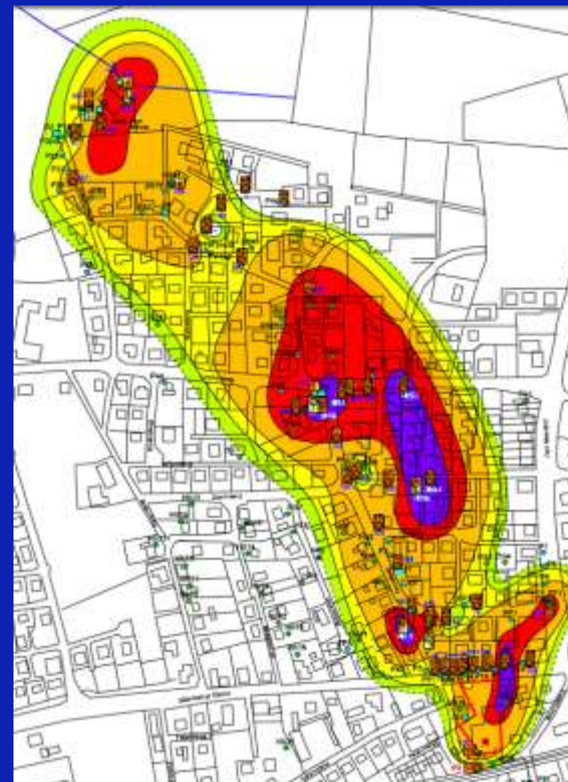
Match of Groundwater and phytoscreening data in delineating plume.

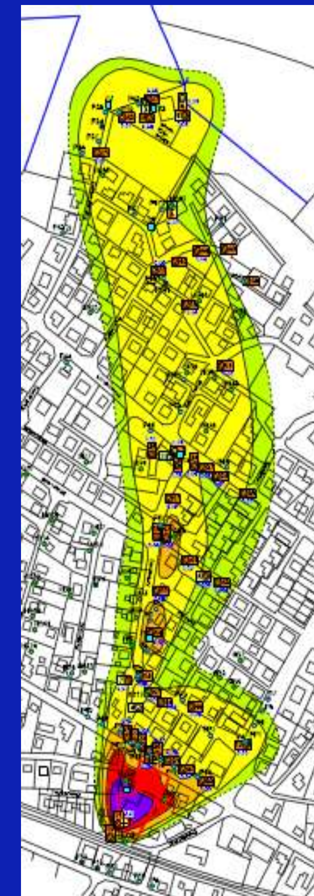


Groundwater data, left, in ppb (>5) , and phytoscreening data, right, in ppt. Transpiration stream. The plume areas appear larger in PS than from GW, as a result of units in ppb (GW) and ppt (PS)

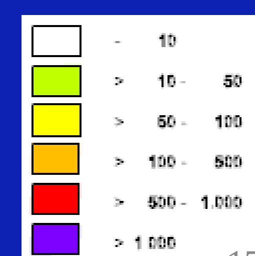


Phytoscreening TCE





Groundwater data, left, in ppb (>5) , and phytoscreening data, center, in ppt. Transpiration stream. The plume areas appear larger in PS than from GW, as a result of units ppb Right graph shows PCE to TCE ratio (PCE/TCE), confirming less decomposition of PCE to TCE by source.



Contamination spread and potential additionnal sources in unstarated zone were identified by the phytoscreening but not by the traditional (much more expensive) groundwater investigations

Other Analytical methods

- GC / MS for other organics
- Metals : Combustion / Trap Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) for Hg
- Inductively Coupled Plasma Mass Spectrometry : ICP /MS for other metals.
- PIXE, Neutronic Activation, Bio-Assay,
- EDXRF
- Detection limits from the ppm to the ppt. Sample mass > 1 mg.

Dendrochemistry

7 trees sampled in February 2010. Pressler borer, 10 mm Ø.

Samples checked for quality and age.

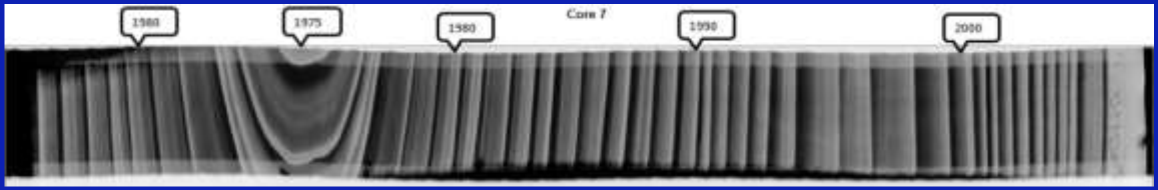
Sent to Dendrolab, Sweden, for making 2 mm thick laths (twin disk saw) and EDRXF analysis.

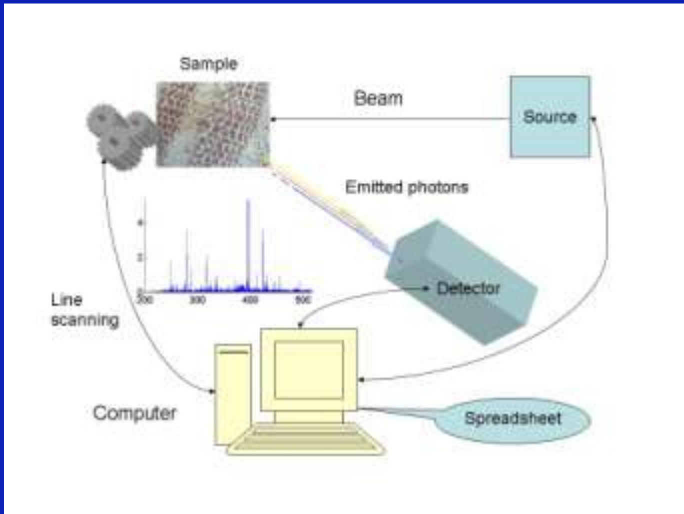
Sample is about 10 g : it takes about 15 minutes, to sample it.

Trees are selected for their location and age, and when possible, for their abundance at site.

EDXRF Line scanning

7 trees sampled in February 2010. Pressler borer, 10 mm Ø. Four samples checked for quality and age. Sent to Dendrolab, Sweden, for EDRXF analysis.

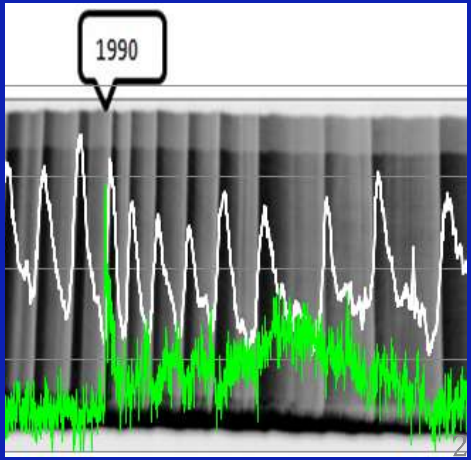




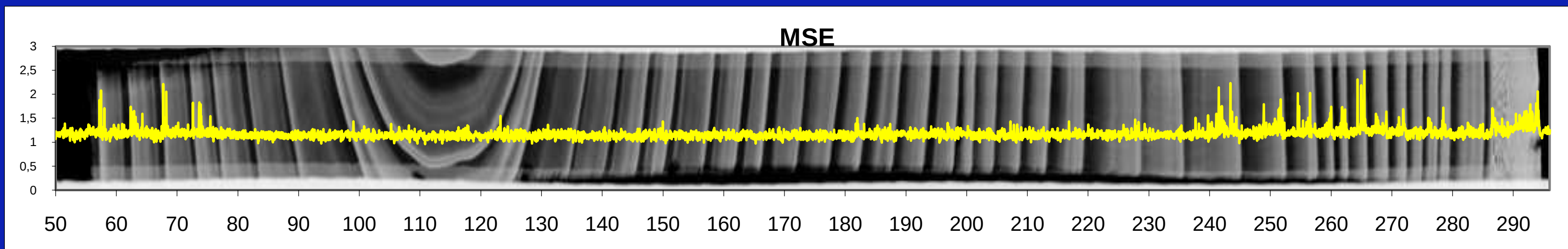
EDXRF data every 50µ, = 4000 data points /20 cm core). Microdensitometry at 20µm.

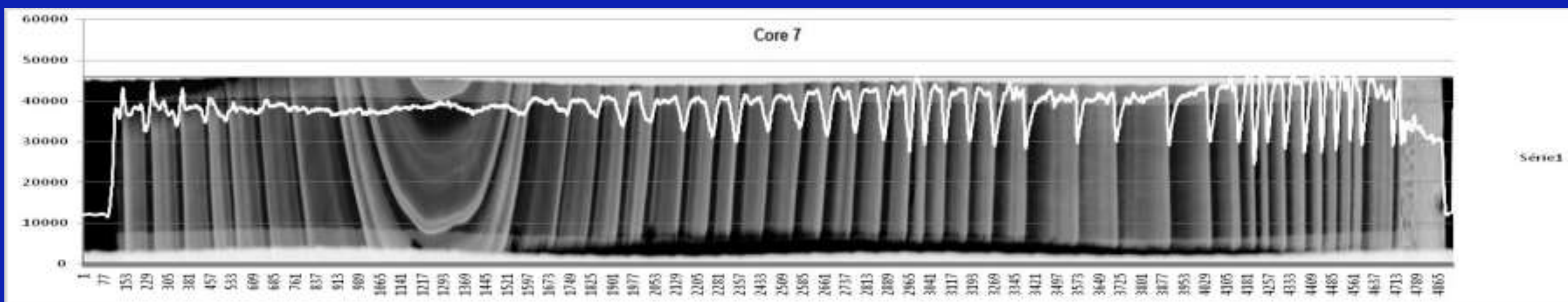
30 elements are simultaneously analized : Mg, Al, Si, P, S, Cl, Ar, K, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, I, Cs, Ba, Hg, Pb, Bi.

Detail of EDXRF profile in a spruce : Ca in white and Cl in green



EDXRF Quality Check





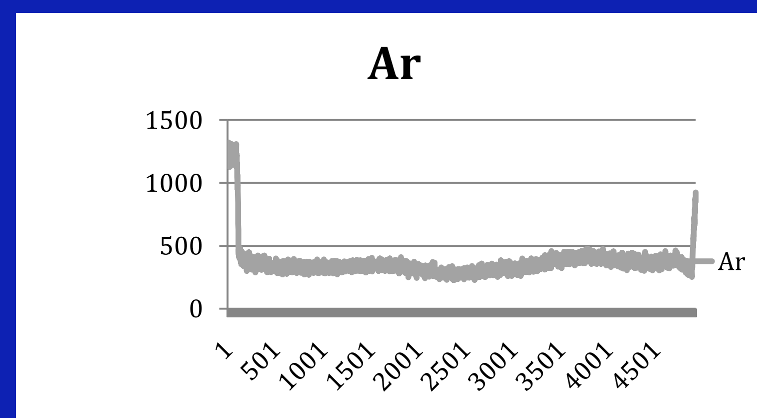
MSE : Mean Square Error

Total Coherent & scattered photons

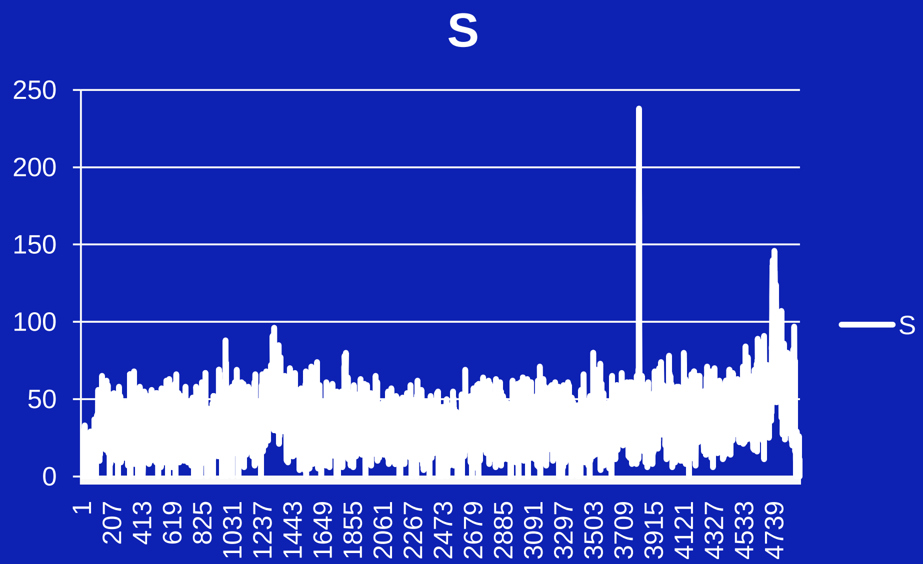
Argon profile = distance beam/core

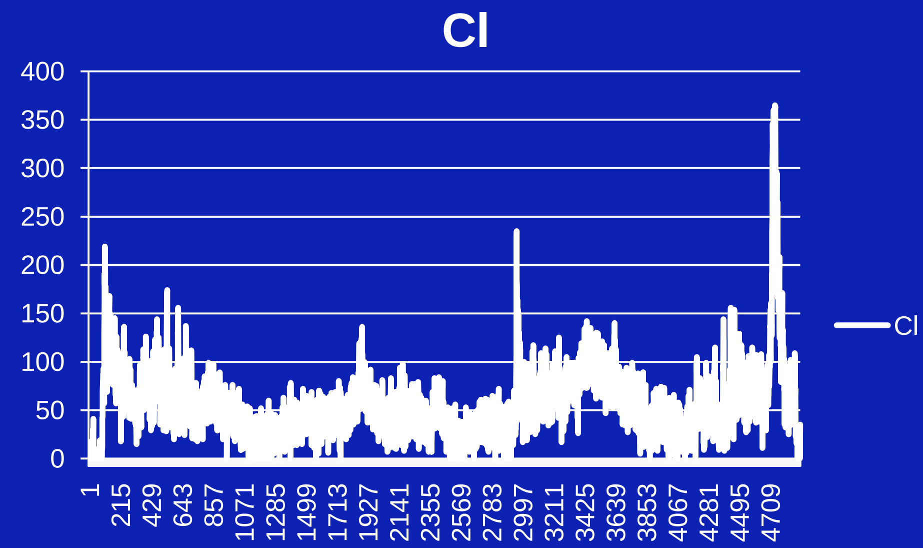
Repeatability = 1%

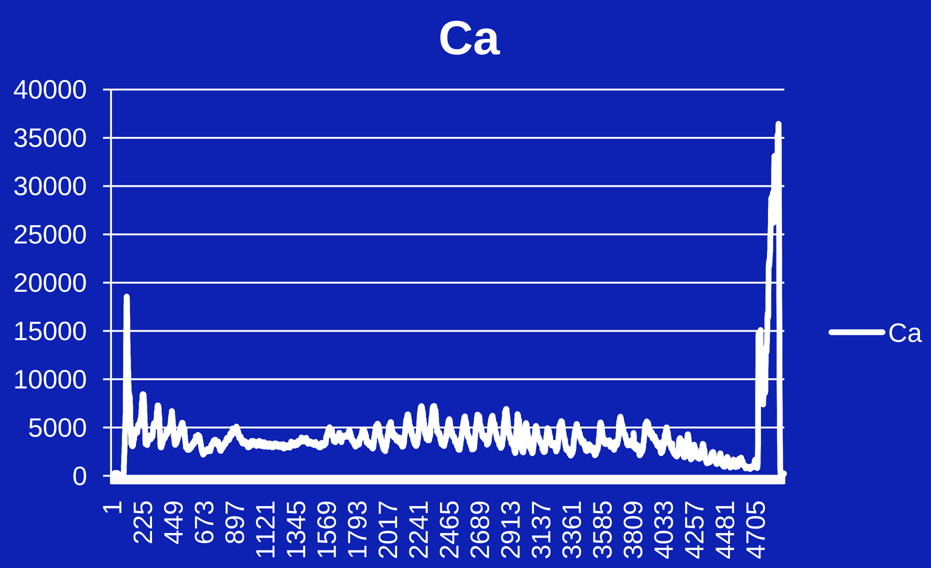
Cts = relative unit ; once density corrected translates to absolute concentrations

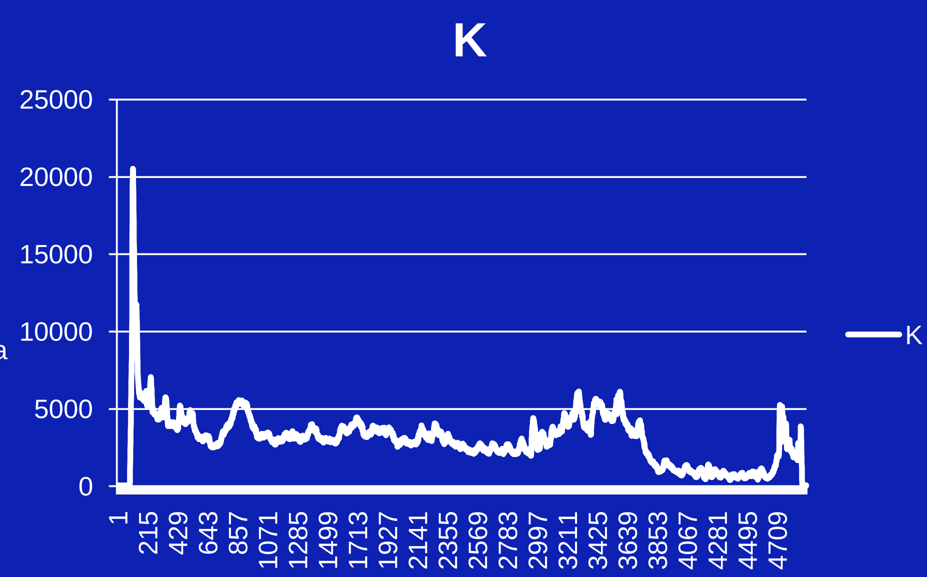


The EDXRF data : elemental graphs & Anomalies



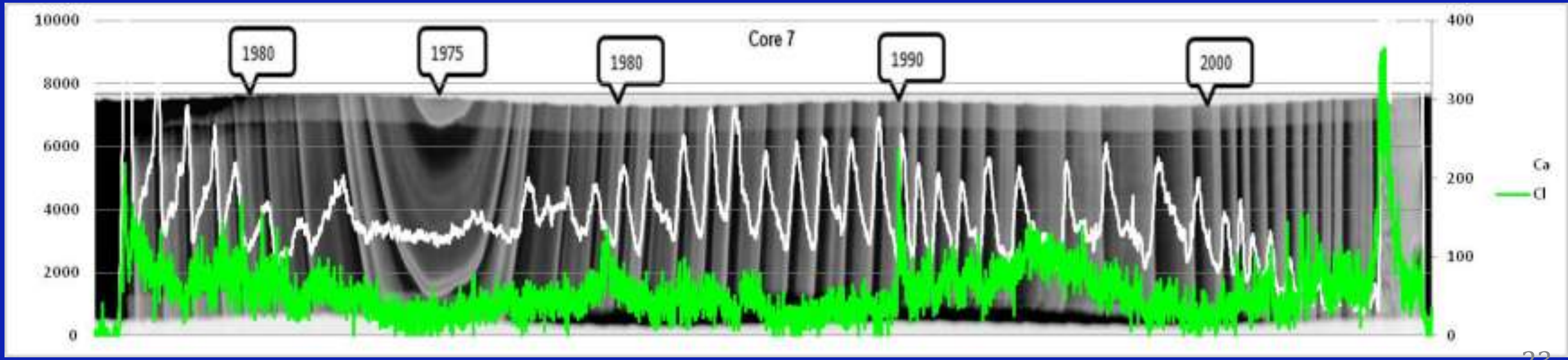




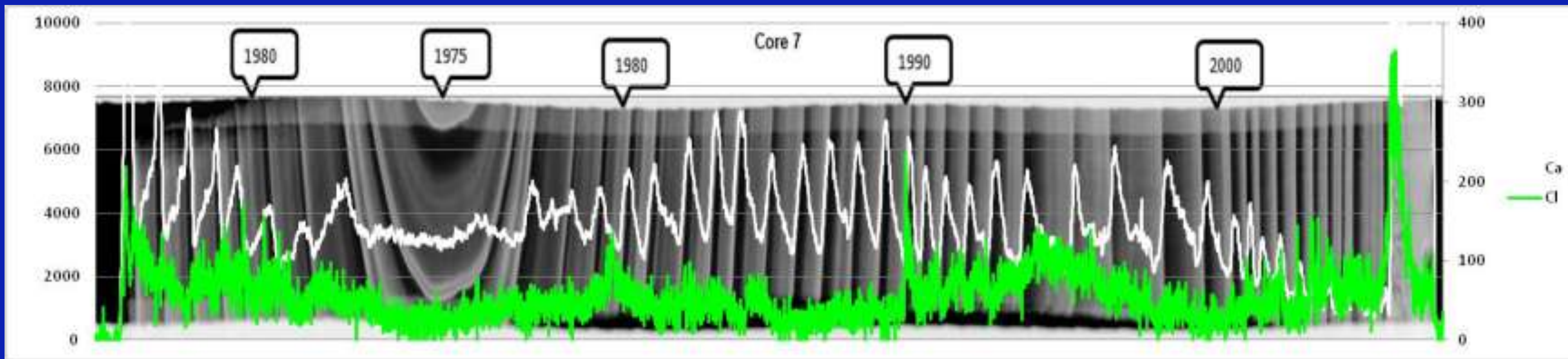


Tree physiology
& Natural versus anthropic impacts

- Uptake mechanisms (root / shoot) & metabolism
- Contaminant mobility * Age / Size trends
- Heartwood sapwood boundary (retranslocation)
- Background noise * Intraring and ring-boundary patterns
- Tissue / cell (apoplast / symplast) * tree species
- Protective barriers (infection). * Climate and wound effects



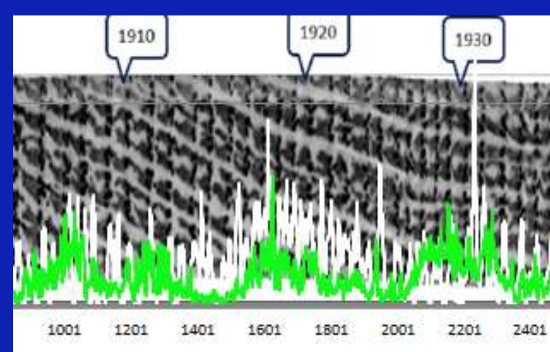
Chlorine anomalies

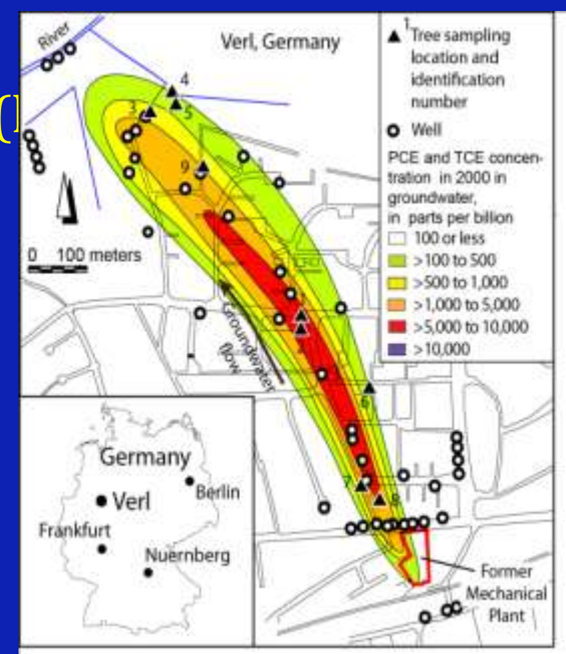


Above : graphed EDXRF for calcium (white) and chlorine green. Note the quasi symetry both sides of pith.

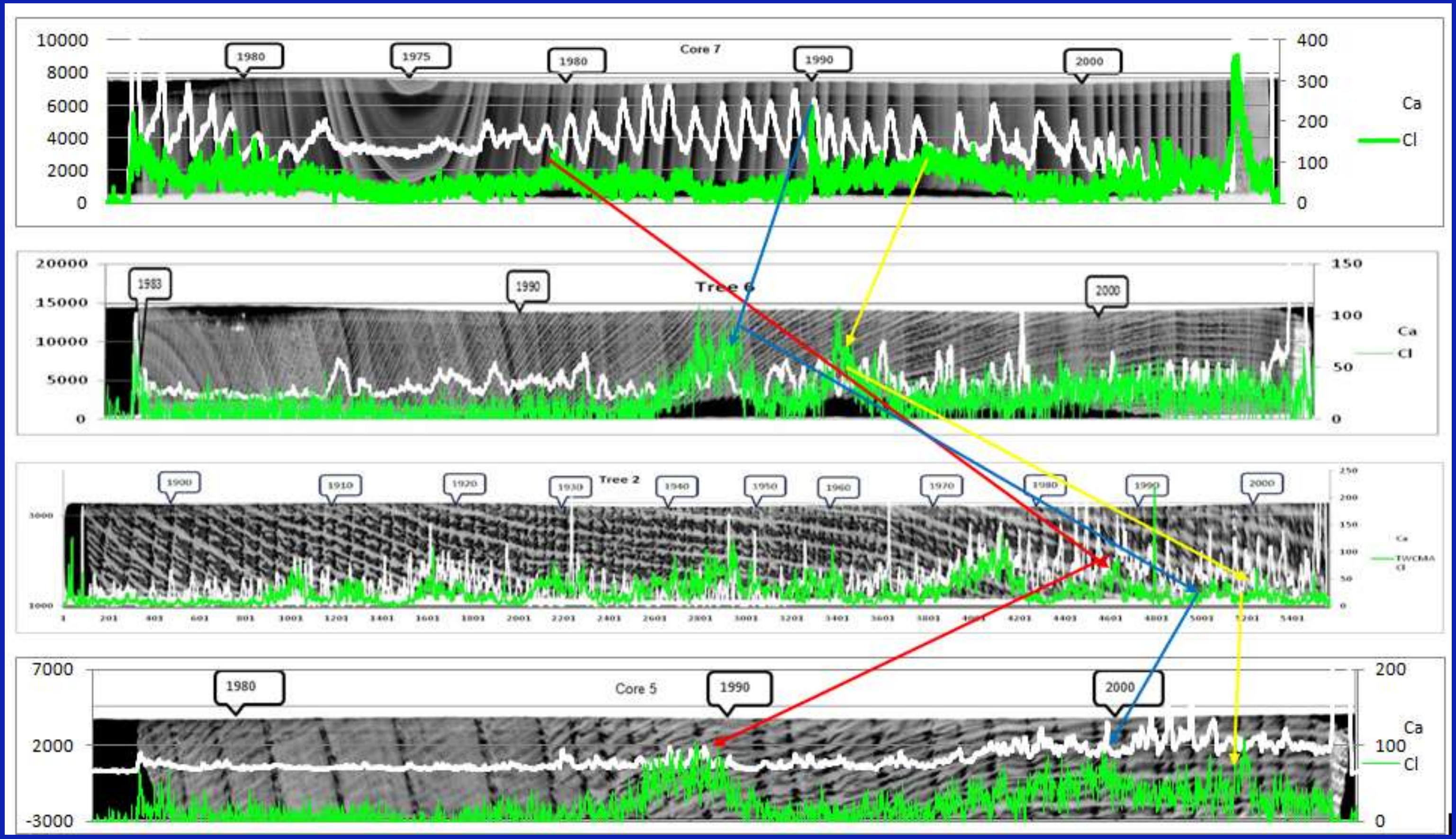
Multielemental check allows to distinguish chlorine only anomalies (right), from multielemental anomalies (l

Cl only anomalies are associated to HVOCs, as for its dechlorination undeRground, by rootball, or even within tree.





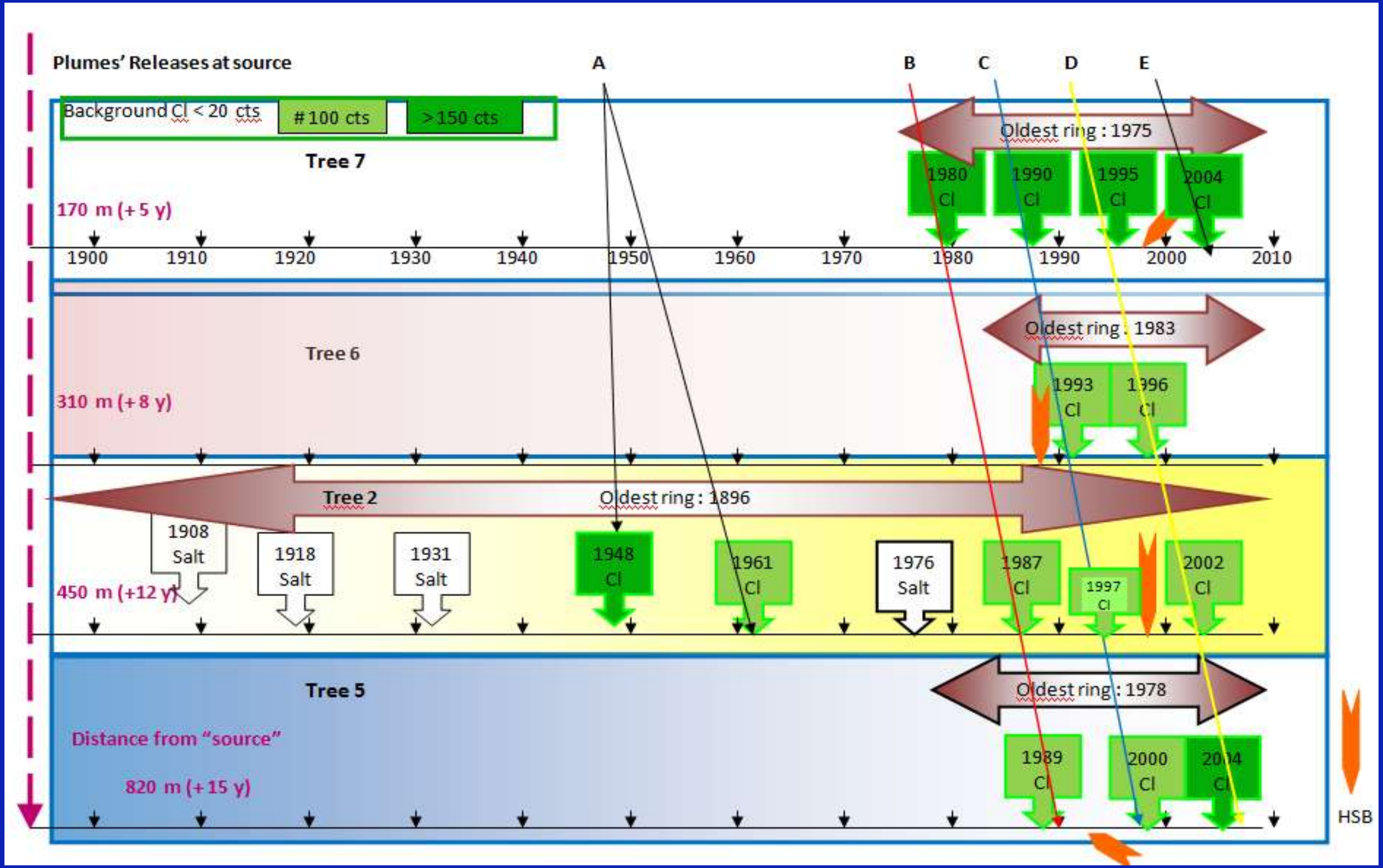
Dendrochemistry at site



Calcium and Chlorine profiles

Correlating (parsimony principle) the different pulses / impacts.

Dendrochemistry at site



Dendrochemistry allowed to distinguish and age-date six asynchronous releases.

Health benefits of plant sampling

- Detecting pollutants with greater speed and accuracy leads to more rapid responses, protecting human health as groundwater contamination has been positively linked to increased cancer.

- Dendrochemistry allows the potential to look back in time, potentially relating previous health problems to environmental contaminants

Conclusions

Phytoscreening is a simple, cheap and fast method to document polluted sites. It is a non invasive sampling method, most adapted to inhabited areas, or areas of difficult access. Used for phase 1 site assessment. PS allows ideal positionning of well rig.

Dendrochemistry, or the use of annual rings to document past impacts, is an essential forensics tool when to age-date environmental impacts.

Balouet, Jean Christophe, Smith, Kevin T., Vroblesky, Don and Oudijk, Gil(2009) 'Use of Dendrochronology and Dendrochemistry in Environmental Forensics: Does It Meet the Daubert Criteria?', *Environmental Forensics*, 10: 4, 268 — 276, First published on: 16 December 2009 (iFirst)

Consecutive and asynchronous releases?

"The Truth,
The Whole Truth, and Nothing But The Truth."

Whilst Trees don't lie… *Thank you*

…

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