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317/319 Phytoremediation Site Monitoring Report – 2005 Growing Season

Energy Systems Division

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317/319 Phytoremediation Site Monitoring Report – 2005 Growing Season

by

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ANL 317/319 Phytoremediation Site
Monitoring Report –2004 Growing Season

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Abstract

In 1999, Argonne National Laboratory (ANL) designed and installed a series of engineered plantings consisting of a vegetative cover system and approximately 800 hybrid poplars and willows rooting at various predetermined depths. The plants were installed using various methods including Applied Natural Science's TreeWell® system. The goal of the installation was to protect downgradient surface and groundwater by hydraulic control of the contaminated plume by intercepting the contaminated groundwater with the tree roots, removing moisture from the upgradient soil area, reducing water infiltration, preventing soil erosion, degrading and/or transpiring the residual volatile organic compounds (VOCs), and removing tritium from the subsoil and groundwater. This report presents the results of the monitoring activities conducted by Argonne's Energy Systems Division (ES) in the growing season of 2005.

Monitoring of the planted trees began soon after the trees were installed in 1999 and has been conducted every summer since then. As the trees grew and consolidated their growth into the contaminated soil and groundwater, their exposure to the contaminants was progressively shown through tissue sampling. However, as trees grow larger, some of the findings obtained in the early years when trees were much smaller may not hold true now and need to be verified again. During the 2005 sampling campaign, data from the French Drain area confirmed the results obtained in 2004 and earlier, and the previously found correlation between soil and branch concentrations. During the 2005 summer, studies under controlled conditions (cartridges) have shown a generally linear dose response of PCE uptake, and have also shown that tree concentrations of PCE decrease after flushing with clean water in short times when trees are exposed to low levels of the contaminant. This data proves that tree concentrations are transient, and that with proper time levels can return close to background levels when exposure is removed. Further study of the results and additional future experiments under constant supply will also allow us to confirm that the oscillations found in the tree branches are indeed derived to changing supply of the contaminant in the soil solution or gases. They will also allow us to optimally estimate the amounts of chemicals that are removed from the system by plant uptake.

Introduction

The 317/319 Area at Argonne National Laboratory (ANL) (approximately 2 hectares of surface) contains several release sites used in the past to dispose of solid and liquid waste from various laboratory activities (Fig. 1). Because of these past activities, VOCs and tritium have been released in the groundwater at depths of approximately 6-9 m and have been detected in groundwater offsite. The U.S. Department of Energy (DOE) has funded ANL to deploy a phytoremediation system instead of the traditional technology of pump-and-treat on the basis of

phytoremediation being more cost effective and better suited than mechanical extraction wells (currently removing groundwater as an interim measure) and an asphalt cap to achieve project goals.

As part of the deployment efforts, approximately 800 hybrid poplars and willows were planted in the summer of 1999 in the 317/319 Area at varying, predetermined depths as an engineered plantation. These trees have been planted so that root development targets the areas of soil and groundwater contamination, using methods that include the TreeWell® and TreeMediation® system patented by Applied Natural Sciences, Inc. In addition, a vegetative cover of herbaceous plants has been seeded among the trees to control soil erosion and minimize water infiltration. Appropriate control cells have been set up at the ANL greenhouse area (a clean area on site nearby) to represent background conditions. Figure 1 depicts the remediation area: in the upgradient VOC source area French Drain (FD) hybrid willow trees were planted so that their roots could freely explore the contaminated soil from the surface throughout the 9 m depth and take up excess water and entrained chemicals. A few poplars were also planted at the southernmost edge of the FD area with the same technique used in the hydraulic control area (see below) to contain the contaminated groundwater. In the downgradient area of groundwater contamination (hydraulic control area, or HC), hybrid poplars were planted using the TreeWell® technology so that their roots were isolated from clean surficial aquifers and forced to extend downwards to the deeper, contaminated groundwater.

The monitoring efforts conducted by ES Division Personnel had the purpose of determining and documenting the system's effectiveness in achieving the remediation objectives. Activities involved:

- Determining the uptake of the volatile contaminants in the plant tissue to document source reduction and contact with groundwater.
- Determining tritium concentration in tree transpirate to document removal and rooting depth.
- Conducting greenhouse studies (cartridge) to determine contaminant uptake under controlled conditions.
- Begin investigating methods to determine contaminant partitioning and degradation in soil and groundwater.

Monitoring Protocols

Field Studies

VOC Contaminant Uptake

While it is known (Newman et al. 1997, and Gatliff et al. 1998) that trees such as poplars and willows are capable of taking up a number of organic compounds (including chlorinated solvents such as trichloroethene (TCE), tetrachloroethene (PCE), and carbon tetrachloride (CT), there are varying hypotheses on the fate of those compounds in the rhizosphere and plant systems. These compounds have been shown to be degraded in the root zone (Nzengung et al.

2001), taken into the plant and vented through the bark (Ma and Burken 2003), and degraded in leaf tissue (Newman et al. 1999). Portions of these contaminants have shown to be vented out by the trees into the air via the transpirative flow or, during winter, by gas diffusion through the plant's air conducting tissue (Nietch et al. 1999, Vroblesky et al. 1999, and Davis et al. 1998). Monitoring of the 317/319 area phytoremediation system during the 2000-2004 summers has provided clear indication that VOCs are taken up by willows and poplars, and that their concentration may be correlated with that in the medium they are exposed to. Background levels of the same analytes were found at concentrations above detection levels, and thus need to be considered when determining the originating pathway for the contaminants found in the tissue.

Plant tissue from the study area was sampled to determine the presence of VOCs. Finding VOCs in leaf and/or branch tissue above background levels provides a clear indication that the trees are indeed taking up the contaminants from soil or groundwater and translocating it to the aboveground tissues. In principle, by multiplying contaminant concentrations in the sap (ng/mL) by sap flow (L/day), a measure of contaminant removal by plant uptake can be obtained. The amount of contaminant in the soil that is taken up by the plant is dependent on that contaminant's transpiration stream concentration factor (TSCF), or the ratio of the concentration in the transpiration stream of the plant to the concentration in soil water. Mobile (flowing with the sap) and "fixed" (adsorbed on tissue) VOCs make up sap concentration.

Samples were collected by cutting leaves and branches with sharp scissors and placing them directly into headspace vials, which were crimped airtight immediately after. Gas chromatographic analysis was conducted after freezing the samples in the vials for a minimum of 1 day to facilitate cracking of the tissue and better analyte recovery. Samples were then thermally equilibrated at 90˚C for four hours before being analyzed via headspace according to the SOP developed during previous years. Analytes were trichloroethene (TCE), tetrachloroethene (PCE), carbon tetrachloride (CT), chloroform (CF), and 1, 1, 1, trichloroethane (TCA). Detection limits were 3 ng/g for chloroform and TCE, 0.04 ng/g for PCE, 2.6 ng/g for CT, and 2 ng/g for TCA.

Samples were collected from every fourth tree (willows and poplars) at the 317 FD area, and downgradient hydraulic control area, starting with tree A10W and through row P, where non-detect were mostly found. Sampling and analysis began on June 30th, 2005 and ended on September 30, 2005. In most sampling events, four samples were collected from each sampled tree, including two of branch tissue, and two of leaves growing on that branch. Field data were processed for spatial regression using kriging techniques (discussed in the 2004 Report).

Tritium in Transpirate

Samples of transpirate were collected following the procedure established in the Year 2000 growing season on 13 test poplars. All samples were forwarded to an off-site lab that specializes in low-level tritium counting (Isotech Lab, Champaign, IL). One sampling events took place during the test period this year (August 2, 2005). Trees selected for tritium analyses were located in the 317 and 319 hydraulic control at locations that had previously shown to be "hot spots", both within and outside the Radiologically Controlled Area. Arrangements were made with ANL/PFS, and a crew with a truck-mounted lift (Versalift) allowed us to obtain

samples from lower branches (4 to 8 feet above ground) and apical branches (approximately 30 to 40 ft above ground). Our initial hypothesis was that apical branches may receive water from the deeper tap root and thus reflect tritium concentrations differently than lower branches tapping more surficial soil moisture.

Laboratory Studies

Cartridge experiments

During the past several years since deployment, vegetation at the 317/319 area at ANL has been monitored for uptake and degradation of the VOC contaminants, and several hypotheses have been formulated regarding optimum sampling procedures, accumulation and fate of contaminants, presence of metabolites and overall removal rates from the source area. Given the heterogeneous conditions present in a real field situation however, some of our working hypotheses cannot be resolved without more controlled experimental conditions. In addition, many of the co-contaminants present at the site have common metabolic pathways making it difficult to determine whether a compound is present as an original contaminant or as a metabolite. A carefully dosed experiment using only one of the contaminants present is necessary to determine practical removal rates, correlation between medium and tissue concentrations, time elapsed from exposure to detection, and a sufficiently detailed dose response curve. In order to obtain this critical piece of information controlled experiments under predetermined conditions have been undertaken.

The experiment was conducted at the Argonne Greenhouse Area, using tightly sealed PVC tubes placed in sealed 55-gallon drums.

A set of 5 drums with 4 tubes in each was used in the experimental set-up to evaluate:

1) The level of contamination present in the tree trunks, branches and leaves when exposed to different levels of VOC contamination
2) The minimum contaminant level required in the medium for the contamination to be seen in the plant branches and cores and the time for the contaminant to be recorded in the tissue.
3) The change in contaminant accumulation in the plant as a function of time

As all the plants were exposed to the same existing environmental conditions, all tests were also used to evaluate the effect that temperature, barometric pressure and rainfall have on the contaminant concentrations, if any.

Each drum was designed to have up to 4 PVC tubes of 6” (15 cm) diameter, sealed at the bottom. Each tube contained two willows (of the varieties currently growing at Argonne’s 317/319 Area) approximately 4 feet tall with the roots at a depth of 50 cm to 75 cm. The tube was filled with clean clay from the 317 Area mixed with clean sand. Caps were used to ensure that rainwater did not infiltrate the cartridge. One irrigation tube was used to deliver the chemical contaminant solution to the plant in the tube. The water level was monitored through a small piezometer tube using a water-level meter to ensure that plants were constantly supplied with the

same volume of contaminant solution and to determine water usage rates. One soil gas probe was installed to monitor the volatilization of the contaminant from the soil, however it was later dropped as impractical. Figure 2 presents the design of a single tube.

Each cartridge was initially dosed with concentrations of TCE varying from 1 ppm to 20 ppm. As the background concentrations of TCE in the area were soon found to be elevated to the point of confounding our experiment, we switched to PCE, which has a much lower background and is a suitable surrogate of TCE.

Five drums containing 4 replicates of the same dose (treatment) each (0, 0.5, 1, 5 and 10 ppm PCE) were used. The dose 0 drum was given deionized water only during the entire experiment and functioned as the control. Sentinel trees (one each dose) were sampled (small branches and leaves) and analyzed every 2 days. On 7/25/05 all trees were sampled for baseline PCE concentrations and then dosed with their respective PCE spike. Cartridges were dosed with these PCE concentrations every 2 days (when depleted solution was replenished) until August 10, 2005. At this date, two replicates of each treatment were sacrificed (harvested), and the other two were left standing and flushed with clean water (10 L of water were given in 25 days, and then no water for the last week so that the cartridges could be more easily harvested) until September 16, 2005, when they were harvested, sampled and analyzed.

Branches and leaves were monitored every alternate day using the same techniques used in the field monitoring. The tree core (main stem) concentrations were evaluated only at the end of the experiment when the plants were sacrificed and each section of the plant analyzed separately.

Soil cores were also collected from the tubes in the cartridges at the end of the experiment to develop an understanding of the amount of chemical absorbed by the soil and the amount taken up by the plants.

Microbial degradation studies and Distribution Coefficient Studies

Experiments were set up in the lab using soil and groundwater from the 317/319 area to determine:

- The partitioning of TCE between water and soil (to determine to what extent the backfill or soil may be able to adsorb and retain TCE) – Kd studies
- The degradation of TCE in groundwater - Microbial degradation studies

K_d studies were conducted using a method adapted by Itakura and Airey (2001). Uncontaminated soil from the 317 area was dried at 105 C, sieved and autoclaved and then dosed, in a 1:4 soil:water ratio in 20 mL vials, with a single amount of TCE. After 24 contact, the TCE in the water was analyzed. Results were however inconclusive and are not included in this report.

Microbial Degradation studies were conducted in batch experiments according to the procedure developed by Bogner (2004). As results were inconclusive, detailed methods are not discussed here, but are available if requested.

Results

Field Studies

VOC Contaminant Uptake

Tables 1 and 2, and Fig. 3 summarize the VOC tissue analysis results. The full set of data collected from field sampling is reported in Appendix 1.

VOC data in plant tissue during the 2005 season (App. 1) were in general similar to the 2004 data and followed the established trend of being highest in the French Drain area (the source area), and decreasing as distance from the source area increased. Non-detects were found in the southernmost rows sampled in the hydraulic control areas. Many factors could contribute to these low values: low contamination levels in the groundwater, retardation by the backfill medium, and possibly biodegradation in the rhizosphere. None of these possible explanations has been thoroughly studied at this time. Because VOCs may be adsorbed and/or degraded in the organic-rich backfill rhizosphere of the TreeWell® trees before they actually reach the roots, non-detects do not necessarily imply that the roots have not reached the groundwater.

Similar to last year, the correlation between tissue and medium concentrations was further tested by correlating each tree tissue data with soil (data from SAIC sampling of 2002) and groundwater concentrations (data from quarterly monitoring) (Figs. 2 and 3) and by conducting geostatistical regression analysis (kriging). Kriging is a geostatistical tool often used in mapping spatial datasets as it predicts the concentration at unsampled locations using data from sampled locations. It provides the "best linear unbiased estimator" for the data set. Universal kriging was the method of choice for this analysis as the concentration data set from the willows showed a distinct spatial trend. The 2005 data set consisted of 78 trees and 31 soil borings. The results from the willow and soil data are compared as the willows are expected to be rooting in the area of soil contamination. Kriging methods used are described in the 2004 report.

In summary, the correlations between branch and soil concentrations found in 2004 have been confirmed in the 2005 data, as the plume maps look relatively similar to the 2004 ones, and the areas of highest contamination are still at the same locations. Average 2005 concentration levels in the tree branches were compared to the 2004 data (Table 1). TCE averages were higher in both the French Drain and the Hydraulic control-inside fence areas. PCE concentrations were comparable to 2004 in the French drain but higher in the Hydraulic control-Inside fence, while carbon tetrachloride was on average lower than 2004 in the FD but higher in the Hydraulic control-inside fence area. Leaf concentrations of TCE and CT were, in contrast, extremely elevated throughout the entire site, and quite higher than in 2004 signaling elevated background

concentrations for these two chemicals. PCE was present in leaves in much smaller amounts than other contaminants in both years.

Whether the changes in concentrations were related to the extreme drought that affected the Midwest in the 2005 summer, to changed contaminant concentrations in the soil or groundwater, or both, it is not clear at this time. During the summer the willows in the French drain were visibly stressed, while poplars in the hydraulic control areas showed a transient yellowing of leaves in July which quickly disappeared later. As no significant precipitation occurred that may have mitigated it, it is possible that poplar roots were able to respond to the drought stress by growing deeper and successfully reaching the receding water table. As this did not seem to have happened in the willows (the stress was sustained throughout the summer), it would be useful to determine moisture levels in the FD soil to ascertain if the stress was indeed due to the drought (directly by lack of moisture, or indirectly by more concentrated soil solutions and more gas diffusion of VOCs in dry soil pores). New soil sampling would help answer this question and also provide more updated information to relate to the tissue analysis.

Repeated samplings of the same tree were conducted at a few locations to determine whether VOCs would accumulate in tree tissue with the progression of the growing season. In all trees samples twice, concentrations were lower in July than they were in June (data in appendix 1). Attempts at correlating branch concentrations with climatic data (ambient temperature, rainfall, barometric pressure, global radiation, and relative humidity) from the ANL meteo tower provided no clear direct correlation with any of these factors individually (multiple correlation was not attempted).

Branch samples were also collected at different spatial locations in a few trees (bottom, middle and top branches growing on the N, S, E, and W side of the trunk). Vroblesky et al., (2004) showed that core samples collected at different radial locations had a marked difference in concentration. This potential source of variability was investigated in the past at our site when the trees were much smaller (2001), but no significant differences were found then within an individual tree. It is possible however that these differences may begin to show up when the trees become larger, roots spread out in a larger soil volume, and especially when branching and vertical distances increase significantly. In fact, the 2005 data (Table 2 and Appendix 1) show that mature trees may have quite varying concentrations in spatially different samples of the same tree.

Tritium in Transpirate

Results from the tritium analyses are reported in Figs. 4 – 6. An updated full set of data collected since the trees were planted is reported in Appendix 2. As reported in previous summaries, trees vary widely among each other in their concentration of tritium, and several of them growing immediately south of the 319 landfill have by now shown to be well above our established background (constant at approximately 14 TU, or 45 pCi/L). Concentrations during the 2005 summer in this area have been shown spanning from background to 201 TU (643 pCi/L). Trees with the highest levels of tritium in their transpirate were found in the first few rows south of the 319 landfill. By comparison, average tritium concentrations at the 317/319 monitoring wells have been decreasing from their peak in 2000 to levels around 500 pCi/L in the

summer of 2005 (data from N. Golchert), and are thus generally comparable to the transpirate concentrations.

Factors influencing tritium concentrations in plant transpirate are: (1) the extent of mixing of tritiated with clean water at depth, (2) the uptake of water by roots growing at different depths, (3) isotopic discrimination by the tree and (4) the vertical distance traveled (distance between the source of water and the point of branch insertion on the tree trunk). As tritium levels vary widely among tree locations, it is evident that one or more of these factors may be present and play a different role at each location. It is however clear that some trees have shown concentrations directly comparable to groundwater levels, and thus were in all likelihood tapping from the groundwater for most of their water needs. Tritium concentrations (maximum and averages) were quite higher this year compared to the last few years, a fact likely to be facilitated by the drought. The groundwater mounding pattern discovered in recent years near the SE corner of the radiologically controlled area may also need to be considered as a potential cause of the inconsistencies with tritium levels over the last few years (dilution of groundwater may explain the drop in tritium in the 2003 and 2004 transpirate samples) shown in Figs. 4 and 5.

In order to determine if water taken up by the deeper tap root (fed by the groundwater) might feed the tallest branches, and to determine if branch height might be correlated with different tritium concentrations in transpirate, this year we continued the collection of samples from the lowest and tallest branch or tree apex (7.3 to 10.2 m) using a lift operated by ANL/PFS. While results do not show any correlation between height from ground and tritium concentration in transpirate, this may be due to the confounding different exposure of the sampled trees to tritium in groundwater. When compared within each tree, there seemed to be higher tritium concentrations in the lowest branches compared to the highest, thus indicating a certain degree of discrimination of the heavier hydrogen isotope in transpiration processes (Fig. 5). As it is very difficult to separate all the possible factors contributing to these findings in the field, controlled uptake experiments should be undertaken to determine isotopic discrimination by trees as a function of branch height under constant tritium concentration supply.

Laboratory Studies

Cartridge Experiments

Cartridge experiment results are illustrated in Figures 7 – 10 and Tables 3 and 4.

PCE concentrations in cartridge trees during the dosing and flushing phases are shown in Fig. 7. This data shows that under high dosing (5 and 10 ppm) plant accumulation was heavily variable with time and continued, particularly for the highest dose, well into the flushing phase, probably as a result of PCE being temporarily adsorbed onto the clay and released for plant uptake with the flushing. Concentrations however seemed to drop later on and may have dropped further had flushing continued longer. At harvest the concentrations in the 10-ppm plants were above our analytical limits and thus are not reported. Concentrations of PCE in the 5-ppm plants were higher at harvest after the 5 weeks flushing period than when harvested immediately before the flushing (Fig. 9). It is important to note that these elevated doses are quite higher than what

actually present in the field and were chosen to study uptake under maximized supply. In fact, the highest dose showed clear signs of being phytotoxic. Comparing data from sentinel trees and harvest data (Figs. 7 and 10), concentrations are significantly different, however this may be an experimental artifact as the sentinel sampling was conducted on smaller branches than the ones at harvest (sampling the larger ones would have compromised end results) and as cartridges were left to dewater to facilitate the harvest their conditions may not be completely comparable to the other experimental phases. It is important to note that under field conditions the sampling resembles much more closely the conditions at harvest than the sentinel sampling. We have in the past determined that there may be a correlation between branch size and VOC concentrations (see 2003 report).

Trees dosed with the lower PCE doses (0.5 and 1 ppm) showed concentrations that were always below the 50 ng/g levels. At the end of the flush period main stem levels were approximately half of what they were when dosing was stopped, while branch levels dropped in the 1 ppm plants but stayed comparably at the same low levels in the 0.5 ppm plants. While concentrations may have dropped further had the flushing continued, levels were at this point getting closer to general experimental background noise and thus difficult to sort from it. At harvest, concentrations in the dose zero cartridges (controls) were consistently non-detects or below 2 ng/g.

The data from the cartridge experiment suggest that:

- Plants in phytoremediation systems can clean themselves as the site gets cleaned. Also, this data suggest that trees are dynamic indicators of subsurface contamination, reacting quickly to concentration changes.
- For all PCE doses, concentrations decreased with increasing branch heights, as expected from literature and previous studies.
- In any case, dose response of the PCE appears to have a linear dose-branch concentration correlation with a R^2 of 0.98 for day 3 and post-flushing, and of 0.79 for day 7 (Fig. 10), confirming field data obtained so far.
- Even at lower doses, increases in branch concentrations could be seen as early as two days after dosing (fig. 8)
- Under the tested conditions of background and respective volumes of soil and plant tissue, even the lowest dose tested gave measurable increases in branch concentrations.

Fluctuations in branch concentrations found in the field were thus confirmed by the cartridge experiment, indicating that indeed they may be caused by changes in contaminant supply. Future work where the supply is kept constant (such as using a hydroponic system) will be necessary to positively confirm this hypothesis.

Conclusions and Recommendations

As the trees completed their seventh growing season in the field, a significant amount of information has been collected to assess their performance at achieving the remedial objectives. From this data, the trees appear to be influencing the cleanup area significantly.

Based on this year's monitoring results, the following conclusions can be drawn:

- Like in 2004, willows growing in soil with higher contamination showed much higher concentrations than willows in cleaner soil, this correlation was confirmed by geostatistical analysis and utilized to generate plume maps based on tissue analysis, which correlated positively with maps generated with available soil and groundwater data.
- Concentrations in the order of hundreds ng/g in branch samples at the French Drain suggest a significant removal of VOCs by the plants in areas of higher contamination within the French Drain. A better quantification of this removal will be possible when we understand how much of the found concentration is flowing through the tissue and how much is fixed (adsorbed). Cartridge work has helped us do that but constant flow conditions will allow us to better model mass balances.
- Soil sampling at the 317 FD area could help in determining to what extent dewatering objectives have been met so far and possibly explain some of the symptoms exhibited by the willows in the 2005 growing season.
- Tritium in transpirate of poplars has shown that a number of the sampled trees is taking up tritium from groundwater. It is unclear if the ones that did not show elevated tritium levels were not at the target depth or they were growing in non-tritiated water
- Apical leaves tended to show lower tritium levels than lower leaves, suggesting that different factors, including isotopic discrimination, may play a role in transpirate tritium concentrations
- Controlled mass balance studies will need to be conducted to determine tritium uptake and isotopic discrimination as a function of branch height.
- Adsorption/desorption studies should be conducted again to determine retardation factors by backfill material and explain some of the flushing results obtained in the cartridge experiments.

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Figure 1. An Aerial Picture of the 317/319 Area in Summer 2001. Row lettering start from top and numbering increases from left to right.

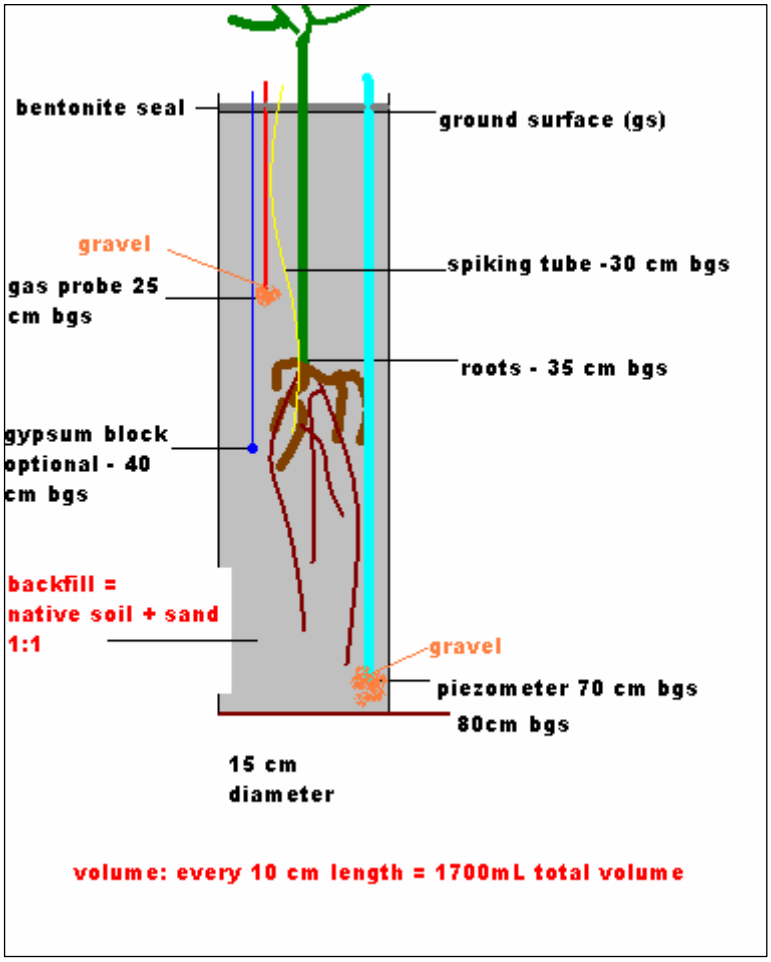
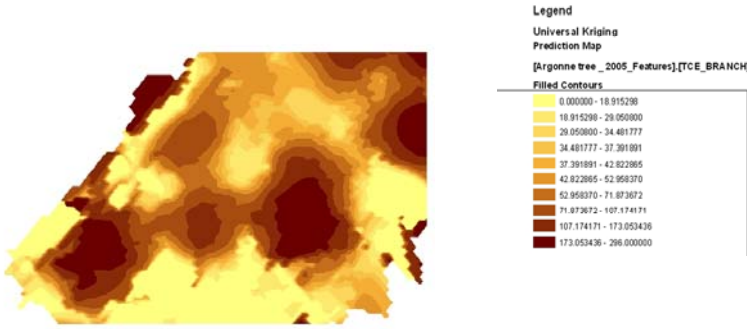


Figure 2: Experimental cartridge design

ARGONNE 2005 – ALL TREES
TCE PLUME



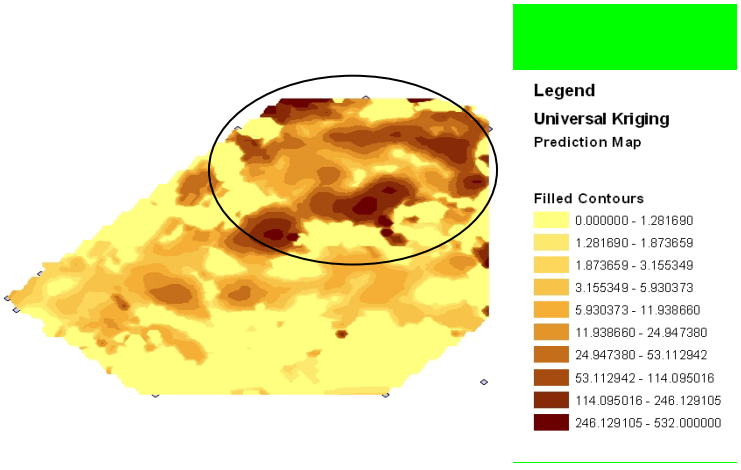


Figure 3. TCE map 2005 (top) and 2004 (bottom). The North is to the top and the East is to the left. These maps are difficult to compare because of the different number of samples used to make them, however the 2005 map depicts the area in the top part of the 2004 map (circled).

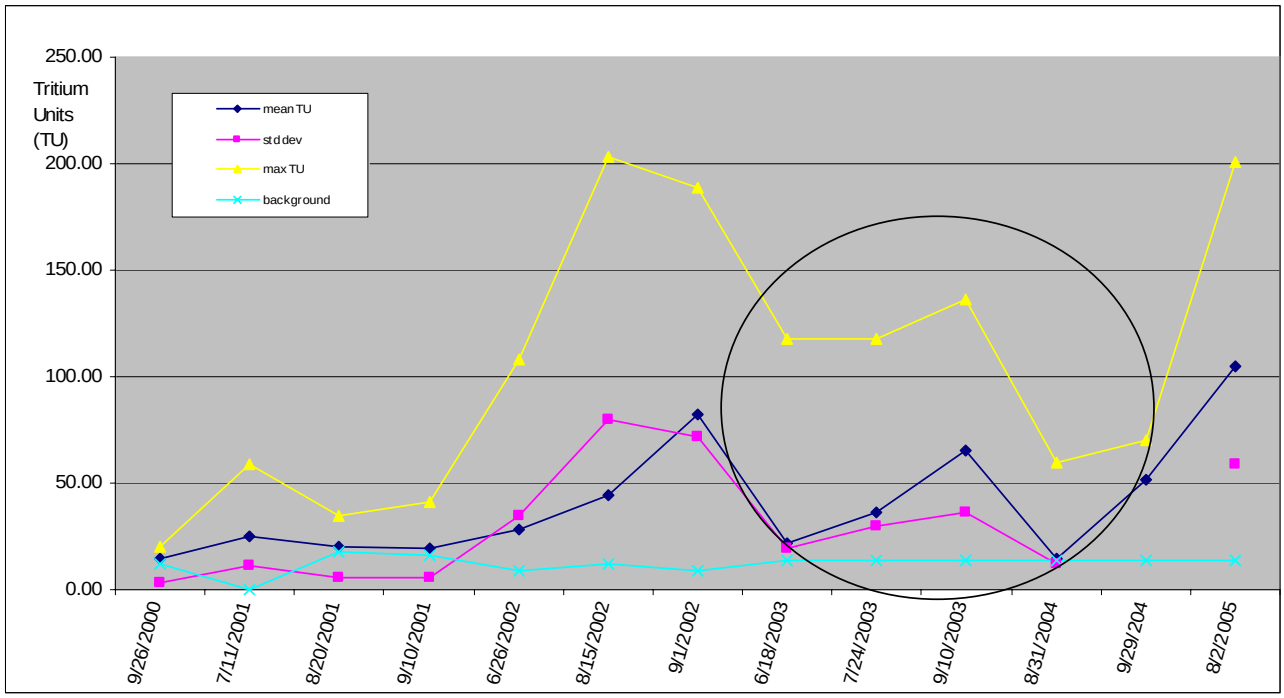


Figure 4. Tritium concentrations in transpirate (TU) 2000-2005. Mean values, standard deviation, max TU values and background values. 1 TU = 3.2 pCi/L. Circled area may have been affected by groundwater mounding and dilution.

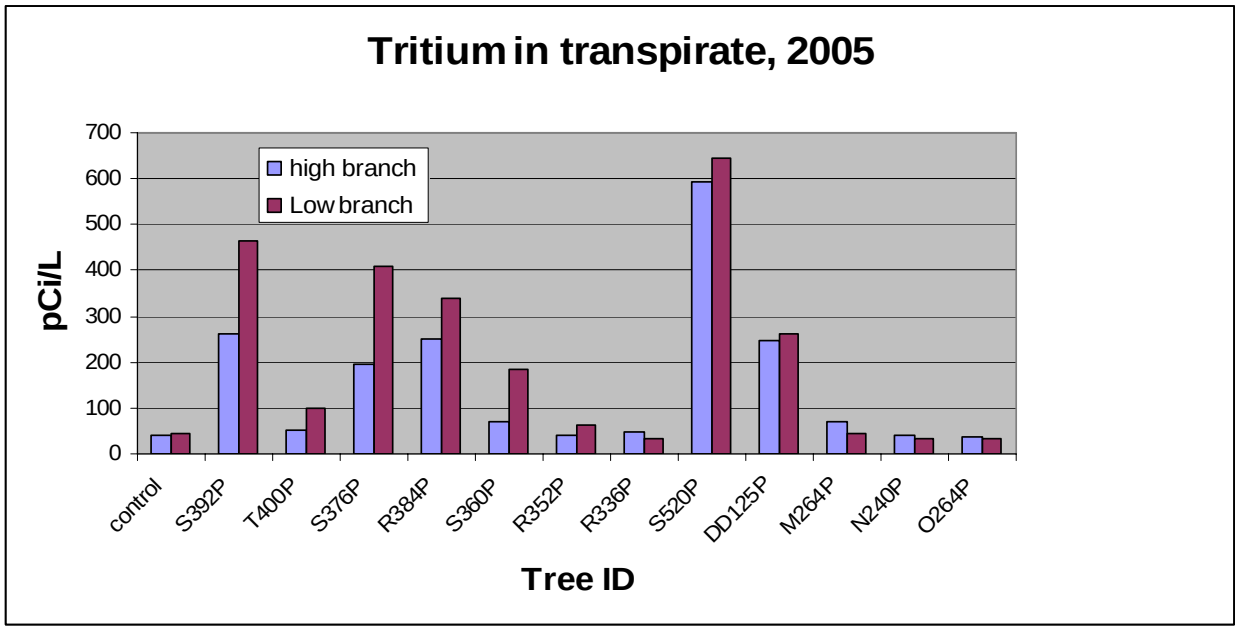


Figure 5. Tritium concentrations in transpirate (pCi/L) in low and high branch heights from ground of selected trees, August 2, 2005.

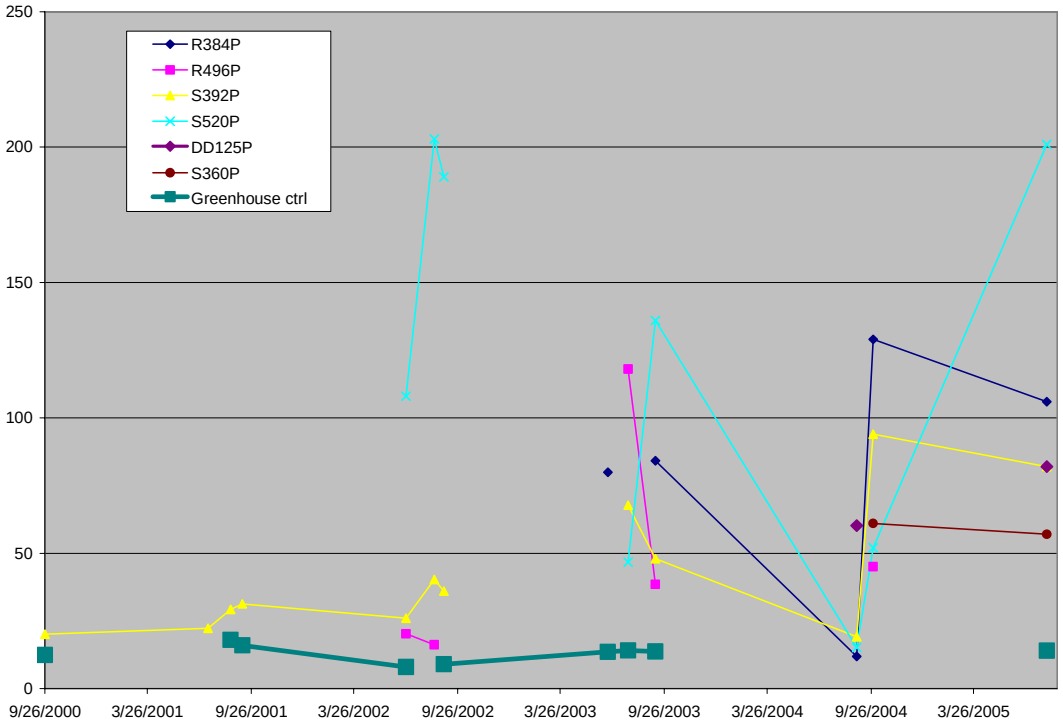


Figure 6. Tritium in transpirate sampled from selected trees, 2000-2005.

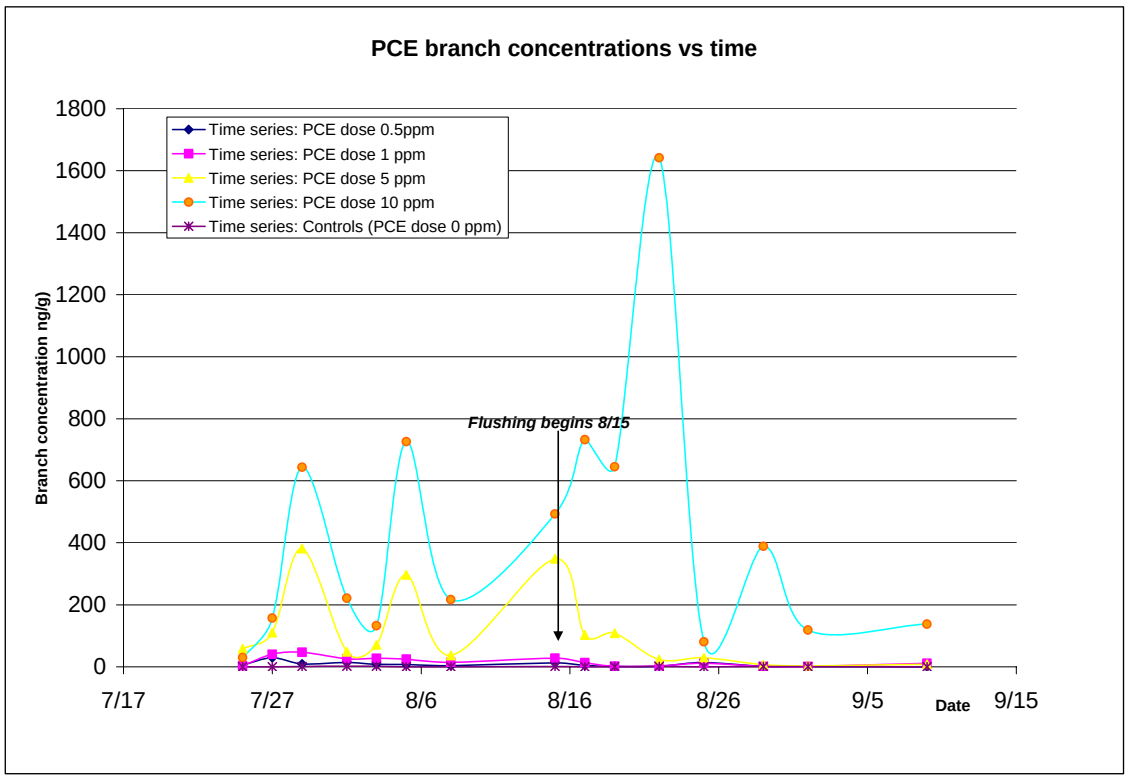


Fig. 7. Laboratory results: PCE in branches, cartridge experiment.

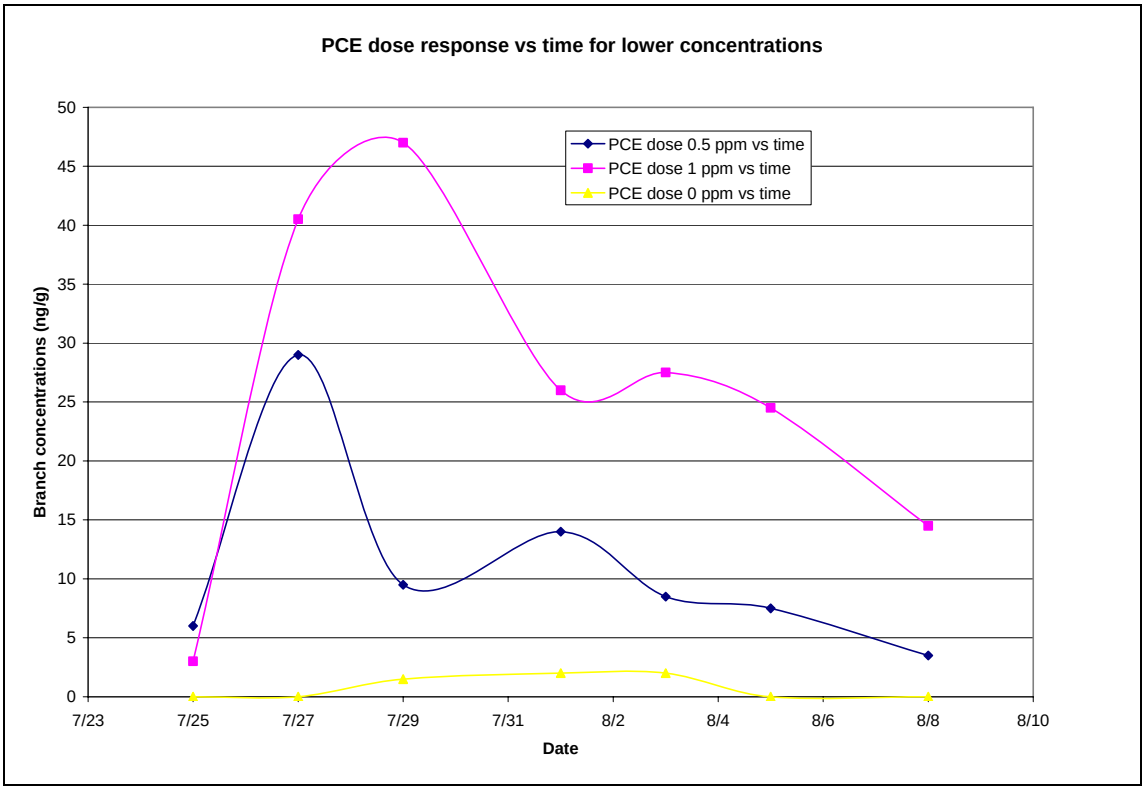
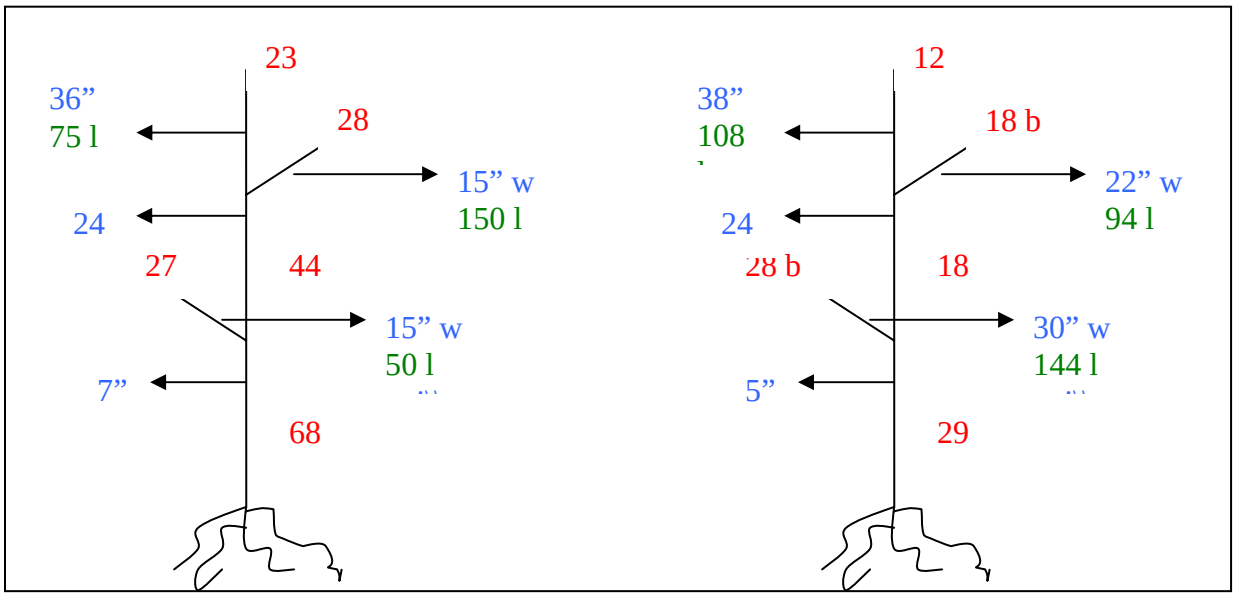


Fig. 8. Laboratory results: PCE dose response vs time for lower concentrations (dosing phase only).

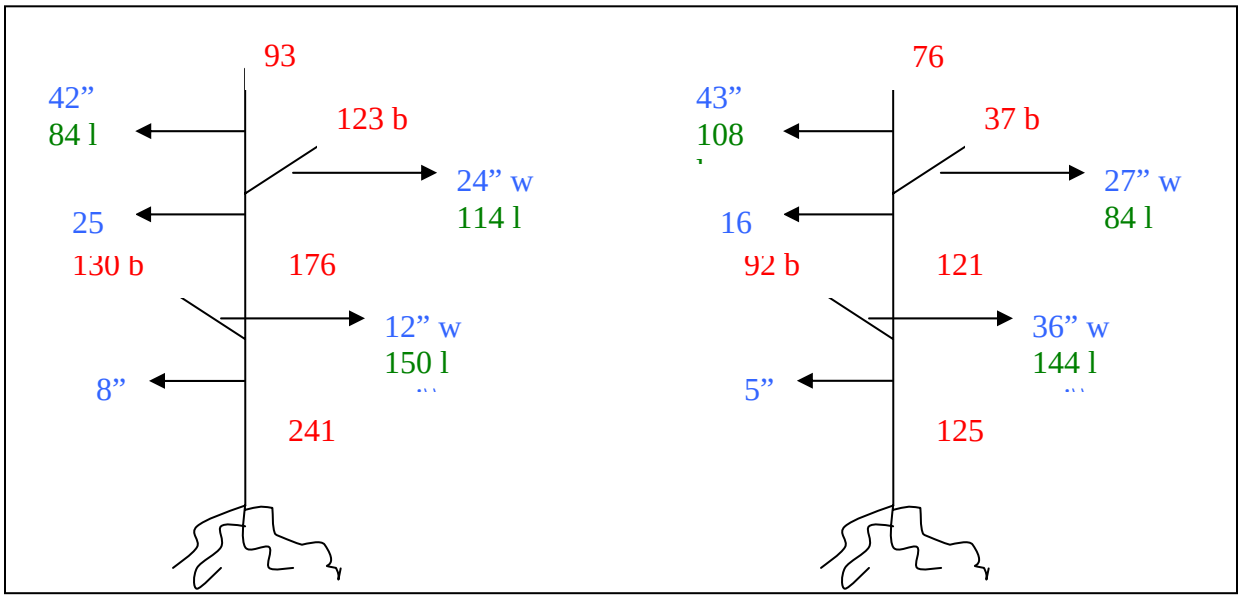
Fig. 9 A, B, and C: whole tree PCE concentrations at the end of the dosing (left) and flushing (right) phases, ng/g. A: 0.5 ppm dosed trees, B: 1 ppm dosed trees, and C: 5 ppm dosed trees. Concentrations in the 10 ppm dosed trees were above detectable range, and concentrations in the dose zero (controls) were all below 2 ng/g.

Legend:

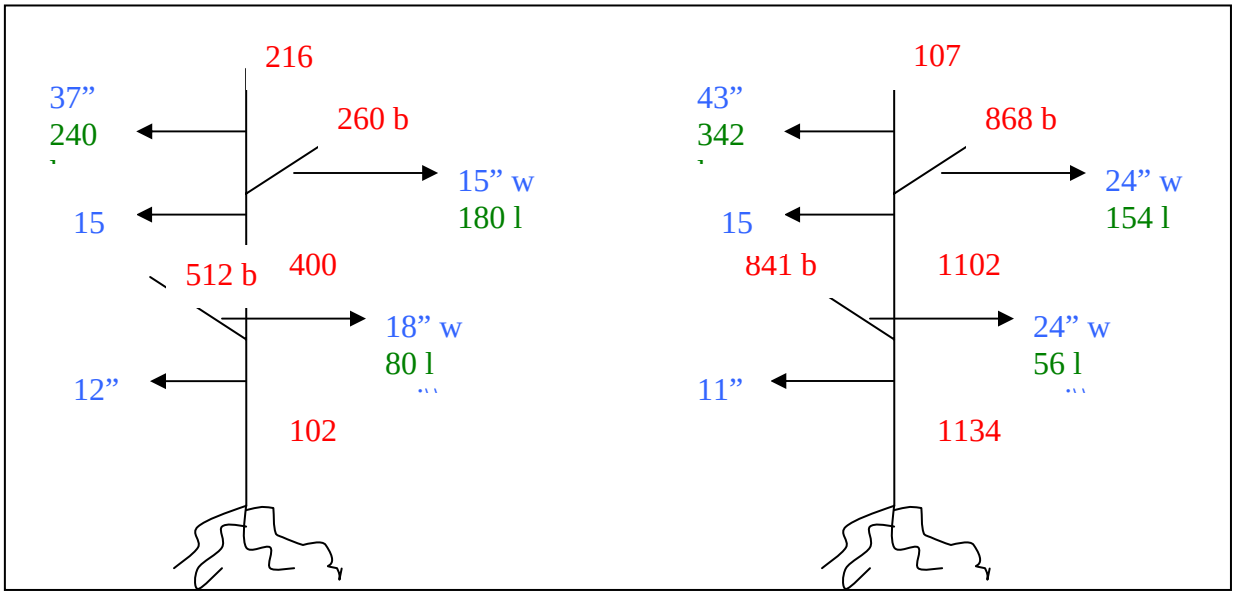
1020 = PCE concentration (ng/g)
312 b = PCE concentration in branches (ng/g)
12" = Distance above the ground that sample was taken (inches)
15" w = Length of the branch (inches)
80 l = Number of leaves on the branch



A: 0.5 ppm



B: 1 ppm



C: 5 ppm dosed trees

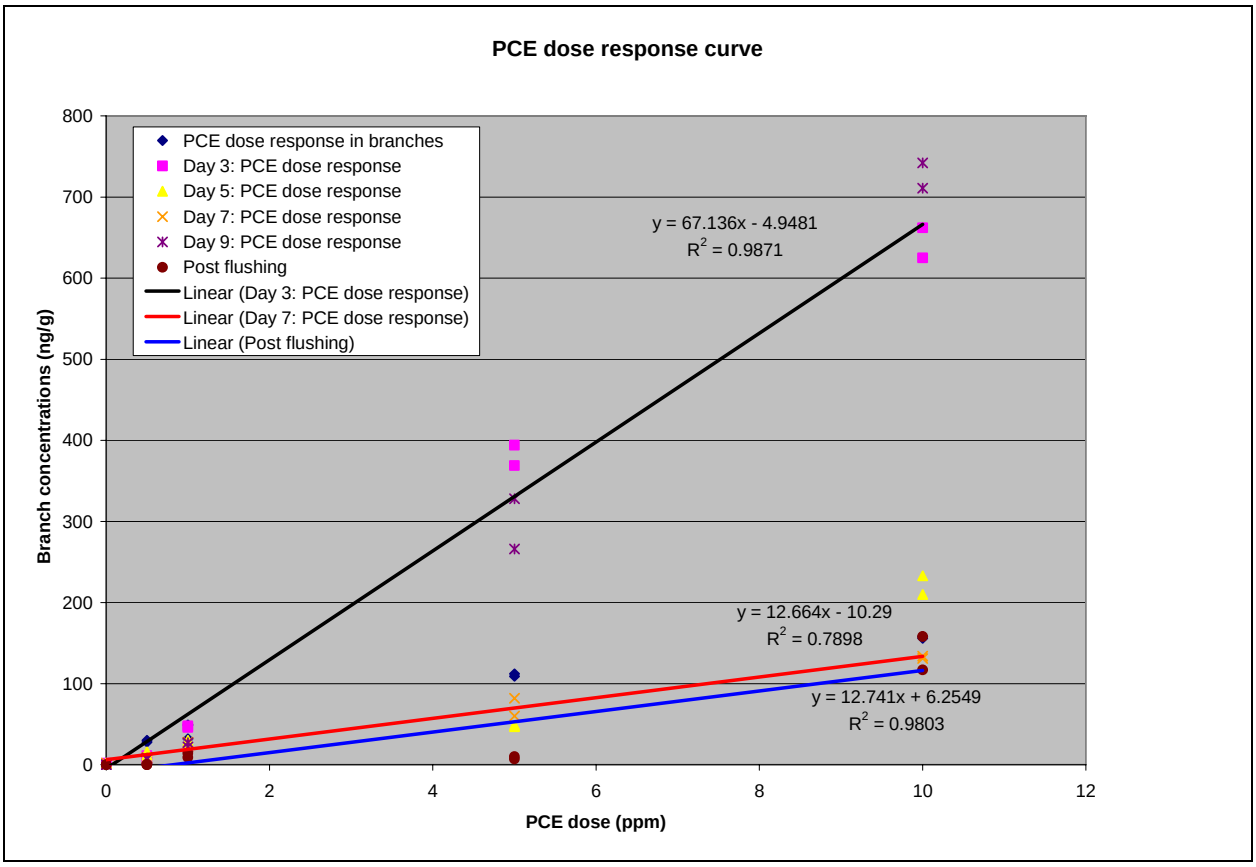


Fig. 10. Laboratory Results: PCE dose response in branches, cartridge trees.

Table 1. Summary of French Drain and hydraulic control (inside and outside fence) results, ng/g on dry weight, average values of varying numbers (n) of duplicate samples.

Plant Tissue	Contaminant	Mean French Drain		Mean Hydraulic Control Inside Fence	
Leaf		**2004**	**2005**	**2004**	**2005**
	TCE	17	154	39	160
	PCE	3	1	2	2
	CCl4	21	68	22	24
	n	140	57	81	21
Branch					
	TCE	53	80	13	37
	PCE	63	55	14	34
	CCl4	80	48	13	41
	n	140	57	81	21

Table 2 . VOC concentrations in tree branches and leaves collected on the same tree (DD95W) in different parts of the tree (N, S, E, W facing branches at bottom, middle and top of tree height) (ng/g on dry weight, each value is mean of two replicate samples).

	TCE			PCE			Carbon Tetrachloride		
	Top	**Mid**	**Bottom**	**Top**	**Mid**	**Bottom**	**Top**	**Mid**	**Bottom**
North	121	92	52	8	10	5	42	64	38
South	101	189	109	5	24	12	28	91	164
East	302	51	63	27	4	2	67	29	23
West	127	391	35	17	108	1	35	283	15

Table 3: TCE concentrations in sentinel cartridge trees. The elevated concentrations found irrespective of dosing resulted in TCE being dropped as the contaminant used in the experiment, in favor of PCE.

Cartridge #	Date	Leaves ng/g	Branches ng/g	TCE dose (ppm)
1	7/6/2005	288	115	0
6	7/6/2005	246	126	0
9	7/6/2005	268	158	0
14	7/6/2005	254	125	0
19	7/6/2005	192	86	0
1	7/8/2005	283	177	1
6	7/8/2005	252	379	5
9	7/8/2005	191	152	10
14	7/8/2005	199	246	20
19	7/8/2005	251	212	0
1	7/11/2005	344	138	1
6	7/11/2005	362	260	5
9	7/11/2005	245	210	10
14	7/11/2005	224	99	20
19	7/11/2005	226	160	0
1	7/15/2005	197	85	1
6	7/15/2005	304	317	5
9	7/15/2005	287	227	10
14	7/15/2005	227	108	20
19	7/15/2005	199	88	0

*

Table 4. PCE concentrations in branch samples from cartridge trees.

PCE dose	Dosing begins 25-Jul	27-Jul	29-Jul	1-Aug	3-Aug	5-Aug	8-Aug	Flushing begins 15-Aug	17-Aug	19-Aug	22-Aug	25-Aug	29-Aug	1-Sep	9-Sep
0	0	0	2	2	2	0	0	2	0	1	2	0	1	1	0
0	0	0	1	2	2	0	0	1	0	0	1	0	1	0	0
0.5	6	30	11	16	9	8	4	14	5	1	2	15	1	1	0
0.5		28	8	12	8	7	3	12	4	1	2	13	1	1	0
1	3	32	46	30	27	27	11	33	16	2	4	13	1	1	14
1		49	48	22	28	22	18	23	11	2	2	10	2	1	9
5	58	109	394	47	60	266	35	391	105	134	27	35	10	4	10
5		112	369	49	82	328	39	305	101	83	20	23	4	2	7
10	30	156	662	210	131	742	247	591	552	731	1655	94	493	137	158
10		158	625	233	134	711	187	395	913	559	1628	67	285	100	117

*

APPENDIX 1. Summary of Field Data, Summer 2005

	Leaves	Branches	Leaves	Branches	Leaves	Branches	Leaves	Branches	Leaves	Branches
Tree ID	TCAA + CHCl3	TCAA + CHCl3	TCE	TCE	PCE	PCE	111-TCA	111-TCA	CCl4	CCl4
PGH_top	82	0	100	109	0	0	67	109	1	49
PGH_bot	0	170	149	108	0	0	0	0	53	31
S392P_top	180	131	109	128	0	0	0	0	26	35
S392P_bot	256	163	141	72	0	1	0	4	30	19
T400P_top	205	158	69	70	0	0	0	0	0	34
T400P_bot	187	217	104	93	0	0	0	0	25	26
N240P_top	279	324	67	109	1	49	0	0	0	66
O264P_top	194	230	79	85	2	2	0	0	13	43
DD95W-S_top	419	840	92	101	0	5	0	0	21	28
DD95W-W_top	407	967	144	127	0	17	0	0	25	35
DD95W-N_top	408	1508	124	121	0	8	0	0	21	42
DD95W-E_top	447	1893	112	302	0	27	0	0	20	67
DD95W-S_mid	374	1971	126	189	0	24	0	0	22	91
DD95W-W_mid	414	2765	125	391	0	108	0	0	14	283
DD95W-N_mid	442	2276	139	92	0	10	0	0	27	64
DD95W-E_mid	454	1216	122	51	0	4	0	0	31	29
DD95W-S_bot	347	1170	132	109	0	12	0	0	35	164
DD95W-W_bot	421	299	188	35	0	1	0	0	34	15
DD95W-N_bot	419	1240	178	52	0	5	0	0	29	38
DD95W-E_bot	358	1080	157	63	0	2	0	0	31	23

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Tree ID	Numerical ID	Date	TCE leaf	TCE branch	PCE leaf	PCE branch	CCl4 leaf	CCl4 branch
A010W	1	6/30/2005	151	107	0	143	63	20
A050W	2	6/30/2005	141	152	0	375	52	14
A090W	3	6/30/2005	192	38	4	1	90	12
A150W	4	6/30/2005	171	43	0	1	81	263
B-010W	5	6/21/2005	182	230	0	250	73	21
B005W	6	6/21/2005	166	166	0	231	62	21
B055W	7	6/30/2005	162	129	0	324	75	17
B075W	8	6/30/2005	162	46	3	50	91	19
B115W	9	6/30/2005	156	46	0	3	111	21
C-010W	10	6/30/2005	182	52	0	14	86	20
C050W	11	6/30/2005	168	70	0	201	227	29
C100W	12	6/21/2005	193	47	0	4	127	23
C160W	13	6/30/2005	197	36	0	3	89	22
D005W	14	6/30/2005	153	49	0	14	157	26
D045W	15	6/30/2005	165	59	0	233	86	14
D075W	16	6/30/2005	159	38	0	5	81	16
D115W	17	6/30/2005	132	51	0	2	104	27
E020W	18	6/30/2005	143	39	0	1	73	11
E060W	19	6/30/2005	136	42	0	2	87	28
E100W	20	6/30/2005	170	38	0	37	116	25
E160W	21	6/30/2005	167	49	0	0	140	28
F005W	22	6/30/2005	139	296	0	49	60	14
F045W	23	6/30/2005	163	40	0	1	62	23
F095W	24	6/30/2005	139	38	0	3	44	11
F165W	25	6/30/2005	145	52	0	41	46	0
G020W	26	6/30/2005	176	105	0	110	51	12
G080W	27	6/30/2005	143	34	2	1	38	10
G120W	28	7/1/2005	249	42	16	7	62	19
G160W	29	7/1/2005	106	161	5	101	29	142
H-005W	30	7/1/2005	144	272	0	69	51	25

H055W	31	7/1/2005	149	38	0	1	56	10
H095W (N)	32	7/1/2005	134	28	0	12	56	8
H135W	33	7/1/2005	147	24	0	15	60	13
H200W	34	7/1/2005	132	37	0	10	43	9
I-010W	35	7/1/2005	133	151	0	95	28	50
I050W	36	7/1/2005	169	43	0	1	121	30
I090W	37	7/1/2005	128	165	0	7	94	18
I150W	38	7/1/2005	171	40	0	3	71	11
J005W	39	7/1/2005	87	36	0	10	50	15
J045W	40	7/1/2005	139	62	0	13	12	29
J085W	41	7/1/2005	123	130	0	174	49	109
J135W	42	7/1/2005	108	30	1	1	33	15
J205W	43	7/1/2005	147	23	0	1	40	8
K100W	44	7/1/2005	68	45	0	34	37	17
K120W	45	7/1/2005	145	29	0	5	65	12
K140W	46	7/1/2005	132	33	0	23	71	36
K160P	47	7/1/2005	162	63	0	88	40	638
DD095W	48	7/1/2005	172	91	0	12	53	37
DD105P	49	7/1/2005	155	106	0	45	28	73
DD115W	50	7/1/2005	142	57	0	31	50	48
DD125P	51	7/1/2005	132	64	0	10	14	33
DD145P	52	7/7/2005	197	114	0	151	54	319
DD175W	53	7/7/2005	165	37	0	2	57	11
K100W	44	6/21/2005	187	64	0	36	0	25
DD095W	48	6/21/2005	170	258	0	22	44	119
DD105P	49	6/21/2005	150	168	0	46	41	78
DD115W	50	6/21/2005	171	59	0	2	77	17
L032P	54	7/7/2005	138	15	0	0	22	13
L128P	55	7/7/2005	122	29	0	3	20	10
L160P	56	7/7/2005	130	196	0	2	26	7
L192P	57	7/7/2005	96	23	0	1	25	22
M024P	58	7/7/2005	122	24	0	0	25	11
M152P	59	7/7/2005	119	14	0	1	20	10

M184P	60	7/7/2005	162	0	0	189	30	260
M216P	61	7/7/2005	83	226	1	1	28	19
M312P (by fence)	62	7/7/2005	162	0	0	189	30	260
N048P	63	7/7/2005	134	38	28	1	32	14
N144P	64	7/7/2005	116	30	0	1	24	12
N208P	65	7/7/2005	105	21	0	1	21	12
N272P	66	7/7/2005	102	37	0	255	12	93
O008P	67	7/7/2005	74	29	3	0	13	11
O072P	68	7/7/2005	71	15	0	1	12	15
O104P	69	7/7/2005	1064	18	0	0	40	14
O264P	70	7/7/2005	134	11	0	6	24	13
P064P	71	7/7/2005	93	22	0	5	36	18
P144P	72	7/7/2005	147	2	0	0	21	13
P240P	73	7/7/2005	71	26	0	61	12	33
P304P	74	7/7/2005	114	11	0	1	24	5

Tritium in Leaf Transpirate, 2000-2005 Data

	A	B	D	F	H	J	L	N
1								
2	**Tritium in leaf transpirate - 2000-2005 data**							
3								
4		**9/26/2000**	**07/11/01**	**08/20/01**	**09/10/01**	**6/26/2002**	**8/15/2002**	**9/1/2002**
5	**Tree ID**	**TU**	**TU**	**TU**	**TU**	**TU**	**TU**	**TU**
6	AA563P		22	24.9	12.4			
7	M216P			11.8	11			
8	P000P			22	16.6			
9	P064P		23.7	26.9	15.1			
10	P256P			21.4	17.4			
11	P480P							
12	Q056P		28.4	25.8	21.7	14.1	<22	
13	Q344P			23.3	20.4			
14	Q392P							
15	Q424P							
16	R000P		58.9			52.8	40.2	56.4
17	R384							
18	R416P			22.6	24.4			
19	R496P					20.3	16.2	
20	R512P	11.5						
21	R512P							
22	R528P							
23	R544P							
24	S016P	15.1	14.7	14.3	16.4			
25	S032P		18.7	15.4	11.6			
26	S048P	13.3						
27	S112P	12						
28	S128P	19.1						
29	S144P		<13	14.6	12.8			
30	S176P		17.5	12	15.2			
31	S328P			14.6	9.4	13.3	<25	
32	S344P							
33	S392P	20.1	22.3	29.3	31.3	26	40.3	36
34	S408P	12.2						
35	S520P					108	203	189
36	T000P		19.7	18	26	16.7	12.6	
37	T016P		13.9	20.1	15.7			
38	T096P		18.1	16.5	21.8			
39	T160P		23.9	15	16.8			
40	T256P		20.3	17.6	21.7			
41	T400P		27.1	17.5	23.7	17.3	27.7	
42	T512P							
43	T528P		51.7	34.8	41.3	20.6	38.3	48
44	T544P							
45	T560P							
46	U424P							
47	V016P					12.9	6.4	

	A	B	D	F	H	J	L	N
4		9/26/2000	07/11/01	08/20/01	09/10/01	6/26/2002	8/15/2002	9/1/2002
5	Tree ID	TU	TU	TU	TU	TU	TU	TU
48	W424P		20.6	16.9	21.8			
49	WT Poplar §		36.6		14.4			
50	X194P		11.7	<60	11.7			
51	X416P		27.6	19.8	24	9.82	12.3	
52	Z448P	14.3						
53	D5W							
54	D-15W							
55	K100W							
56	DD95W							
57	DD125P							
58	DD115P							
59	L192P							
60	L176P							
61	O256P							
62	P288P							
63	S288P							
64	Y216P							
65	R336P							
66	S360P							
67	R352P							
68	S504P							
69	S488P							
70	M232P							
71	M264P							
72	N208P							
73	N248P							
74	O264P							
75	S376P							
76	Greenhouse ctrl	11.4						
77	Greenhouse ctrl	12.4	N/a	18	16	<8.6		<9.05
78	Rainwater 317							
79	Rainwater GH					n/a	<12	
80								
81	mean backgrour	stdev background						
82	14.24	1.924						
83	background +2 stdev							
84	18.09							
85								
86		9/26/2000	7/11/2001	8/20/2001	9/10/2001	6/26/2002	8/15/2002	9/1/2002
87	mean TU	14.76	23.24	19.27	17.77	35.89	62.46	82.35
88	mean TU w/o bc	14.70	25.13	19.79	18.98	28.35	44.11	82.35
89	std dev	3.521	11.411	5.246	5.670	34.593	79.631	71.591
90	min TU	11.4	11.7	11.8	9.4	9.82	6.4	<9.05
91	max TU	20.1	58.9	34.8	41.3	108	203	189
92	n	10	20	25	26	12	11	5
93	background	11.9	n/a	18	16	9	12	9
94	mean pCi/L	47.22	74.36	61.65894737	56.88	114.83	199.87	263.52
95	1 TU = 3.2 pCi/L							

	A	P	R	T	V	X	AA	AD
1								
2	**Tritium in l**							
3								
4		**6/18/2003**	**7/24/2003**	**9/10/2003**	**8/31/2004**	**9/29/2004**	**8/2/2005**	
5	**Tree ID**	**TU**	**TU**	**TU**	**TU**	**TU Middle branch**	**TU low branch**	
6	AA563P							
7	M216P							
8	P000P							
9	P064P							
10	P256P							
11	P480P			82.7				
12	Q056P		11.6					
13	Q344P							
14	Q392P	21.8						
15	Q424P	29		48				
16	R000P		37.2					
17	R384	79.9		84.2	11.9		106	
18	R416P							
19	R496P		118	38.5		43		
20	R512P							
21	R512P	9.9						
22	R528P	11.6						
23	R544P	12.8						
24	S016P							
25	S032P				<10			
26	S048P							
27	S112P							
28	S128P				12.4			
29	S144P							
30	S176P							
31	S328P		10.2					
32	S344P	9.9						
33	S392P		67.8	48	19.2		82	
34	S408P							
35	S520P		46.7	136	15.2	60	201	
36	T000P		31.2					
37	T016P							
38	T096P							
39	T160P							
40	T256P							
41	T400P		25.5				31	
42	T512P	25.1		54.1				
43	T528P		16.5	31.8				
44	T544P	12.1						
45	T560P	14.2						
46	U424P	11.6						
47	V016P		13.6					

	A	P	R	T	V	X	AA	AD
4		6/18/2003	7/24/2003	9/10/2003	8/31/2004	9/29/2004	8/2/2005	
5	Tree ID	TU	TU	TU	TU	TU Middle branch	TU low branch	
48	W424P							
49	WT Poplar §							
50	X194P							
51	X416P		18					
52	Z448P							
53	D5W				21.9			
54	D-15W				13.8			
55	K100W				16.6			
56	DD95W				25.9			
57	DD125P				60.2		82	
58	DD115P				10.3			
59	L192P				17.4			
60	L176P				10.6			
61	O256P				11.1			
62	P288P				15.3			
63	S288P				20.3			
64	Y216P				12			
65	R336P						10	
66	S360P					70	57	
67	R352P						20	
68	S504P							
69	S488P							
70	M232P							
71	M264P						14	
72	N208P							
73	N248P						10	
74	O264P						10	
75	S376P						128	
76	Greenhouse ctrl							
77	Greenhouse ctrl	13.6	14.1	13.7			14	<13
78	Rainwater 317		14.3					
79	Rainwater GH		14.7					
80								
81	mean backgrour							
82	14.24							
83	background +2 s							
84	18.09							
85								
86		6/18/2003	7/24/2003	9/10/2003	8/31/2004	9/29/204	8/2/2005	
87	mean TU	20.96	31.39	59.67	18.38	57.67	58.85	
88	mean TU w/o bc	21.63	36.03	65.41	14.68	51.50	105.00	
89	std dev	19.589	29.817	36.400	12.012		58.987	
90	min TU	9.9	10.2	13.7	10		10	
91	max TU	118	118	136	60	70	201	
92	n	14	14	9	17			
93	background	14	14	14	14	14	14	
94	mean pCi/L	67.06666667	100.4342857	190.93	58.82	184.53	188.31	
95	1 TU = 3.2 pCi/L							

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