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317/319 Phytoremediation Site Monitoring Report – 2004 Growing Season

Energy Systems Division

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317/319 Phytoremediation Site Monitoring Report – 2004 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 2004.

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. Since the inception of the project, significant progress was made in the refinement and testing of the analytical method (for which no official method is available), the determination of the optimal tissue for sampling, and of the variability of the concentrations within a specific tree. An understanding has also been developed on background concentrations of VOCs, and how to discriminate between VOCs that are associated with plant tissue because of aerial or of soil/groundwater uptake pathways. Also, during the 2003 sampling campaign, core samples from tree trunks were collected for the first time (the trees were large enough to stand the procedure). Data collected from the French Drain area last year supported the hypothesis that a correlation was present between concentrations of VOCs in the soil and in corresponding branch tissue. During this year (2004), systematic data collection in the French Drain area further consolidated this correlation and indicated that trees are clearly in the condition to have reached the target rooting depth. Concentrations in the hundreds of ppb in branch and trunk samples confirm that uptake can be a quantitative way to remove VOCs from the contaminated media.

Additionally, laboratory studies were conducted in 2004 to determine mass recoveries from leaves and branches using the headspace method, and to determine if we could further modify our sample pretreatment method to ensure optimal recovery. Results showed that the recovery of TCE in leaves and branches with our current method ranged between 98 and 138%, indicating that most of the TCE present in the samples is recovered during the analysis. Freezing and heating had variable results in recovery rates, which resulted in no significant changes being introduced to the current SOP.

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. 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 TeeMediation® 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) 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 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.
- Conducting laboratory studies to determine contaminant recovery with the analytical method.

Monitoring Protocols

VOC Contaminant Uptake

Field Studies

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 2000-2003 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. In fact, this is still a very imprecise measurement because of unknown diffusion rates from the sap through cell walls into external air, and because it is still unknown how much of the total contaminant detected in tissue is in the freely moving sap and how much is adsorbed to the plant tissues, thus not flowing. 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. It is strongly related to a chemical's physiochemical properties, and principally to its log K_{ow}, or water-octanol partitioning coefficient. Most VOCs have relatively favorable K_{ow}s and thus TSCF (for TCE = 0.75, according to Dietz & Schnoor, 2001). A more comprehensive description of the relationship between tissue concentration and plant removal is described as:

Plant Removal = Tree Concentration x K_{ww} x Transpiration Rate

Where: K_{ww} = wood-water partitioning coefficient, 0.0217 (Ma and Burken, 2003);
Tree Concentration = concentration in tree conductive tissue, ng/g; and
Transpiration Rate = L/day (50-100).

Samples were collected by cutting leaves and branches with sharp scissors and placing them directly into headspace vials, which were crimped airtight immediately after. Trunk cores of 0.5 cm diameter and approx 2.5 cm length were collected using an appositely designed core sampler. 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 alternate tree (willows and poplars) at the 317 FD area, and downgradient hydraulic control area, starting with tree A10W and through row T, where non-detect were mostly found. Additional trees were sampled in rows V, Y, and Z.

Sampling and analysis began on June 4th, 2004 and ended on September 30, 2004. Background levels were determined on samples collected from trees around the ANL campus. 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. Core samples were collected in duplicate at 60 cm above ground level. Cores were collected only from selected trees that had an average diameter larger than 7-8 cm to minimize adverse impacts on the tree's health. Field data were processed for spatial regression using kriging techniques (discussed in the Results section).

Laboratory Studies

The objective of these experiments was to evaluate the accuracy of the analytical method by measuring the percentage of TCE recovered from the leaf and branch samples during the analysis. Pre-analytical conditions such as freezing or heating the leaf and branch samples for different time periods were changed to estimate the impact on chemical recovery from the plant.

In order to study recovery rates, known amounts of contaminants needed to be added to the plant tissue, and thus additional experiments were conducted to reliably "contaminate" clean tissue to be used in recovery studies. Several methods were tried, including direct injection of dilute VOC solutions directly into branches and leaves. When this was found not to be practical, adsorption from an aqueous solution was selected as the best method to spike the tissue with VOCs (TCE was chosen for these tests).

The leaves and branches were placed in a glass jar that was completely filled with distilled water. The jar was then sealed with a cap with a Teflon septum. Approximately 11,000 ng of TCE was injected into the water in the jar. The jar was then placed on shaker and the leaves and branches and the solution equilibrated for 3 days. The leaf and branch were then removed, patted dry, and placed in 20 ml vials sealed with an aluminum crimp-cap and Teflon septum. One ml of the water solution with TCE was also placed in the 20 ml vial and sealed immediately with the aluminum crimp-cap and Teflon septum.

The leaves, branches, and water solutions were analyzed using a 7694 Hewlett-Packard Headspace sampler and a Hewlett-Packard Model 5890 Series II GC equipped with an electron capture detector using the same settings as the tissue samples.

The plant species used to evaluate the accuracy of the method was crabapple (*Malus spp)* as higher background concentrations of TCE were detected in the willow and poplar plants found near the greenhouse.

The leaves and branch samples were analyzed under the following conditions:

1) Without any heating or freezing.
2) When frozen for 1 day at 4°C prior to analysis and heated in the oven at 90°C for 0 hours, 2.5 hours, and 4 hours, respectively.
3) When frozen for 0 days, 1 day, and 2 days, respectively, at 4°C prior to analysis and heated in the oven at 90°C for 4 hours.

A comparison of TCE recovery from leaf and branch samples collected from willow, poplar, and crab apple plants was also performed. In this comparison, the samples were frozen for 1 day and then heated in the oven at 90°C prior to analysis.

Equilibrium Relationships Between Water Solution and Plant Tissue

The objective of this part of the experiment was to estimate the relationship between the concentration absorbed in the plant tissue and the concentration in the water solution when equilibrium conditions were reached, at varying water solution concentrations. While needed to understand our test conditions, this relationship could also be used to evaluate the amount of chemical being absorbed by plants in the field.

The experimental setup used was the same as described above. The jars were equilibrated for 3 days. The leaf and branch samples were frozen for 1 day and then heated for 4 hours in the oven at 90°C prior to analysis. TCE concentrations used during the experiment were 2.4 ng/ml, 4.8 ng/ml, 12.2 ng/ml, and 24.4 ng/ml, respectively.

Tritium in Transpirate

Samples of transpirate were collected following the procedure established in the Year 2000 growing season on 17 test poplars. All samples were forwarded to an off-site lab that specializes in low-level tritium counting (Isotech Lab, Champaign, IL). Two sampling events took place during the test period: August 31st and September 29th, 2004. Trees selected for tritium analyses were located in the 317 and 319 hydraulic control areas, both within and outside the Radiologically Controlled Area. For the September sampling, arrangements were made with ANL/PFS (Secor) and a crew with a truck-mounted lift (Versalift) allowed us to obtain samples from apical branches approximately 30 to 40 ft above ground. Unfortunately by the time the arrangement was possible, most leaves in the lower branches had already fallen so a clean comparison between transpirate from leaves at different tree heights was not possible. Our hypothesis was that apical branches may receive water from the deeper tap root and thus better reflect groundwater concentrations.

Results

VOC Contaminant Uptake

Field Studies

Table 1 and Figs. 2 to 9 summarize the VOC tissue analysis results. The full set of data collected from field sampling is reported in Appendix 1.

In the French Drain, samples included willows growing in the soil and several TreeWell® poplars growing in groundwater at the southernmost edge of the French Drain area. Samples were collected from willows growing in parts of the FD area that had been previously treated with the mixing/steam and iron filings process in 1997 (“mixed soil”) and in areas that had not been previously treated (“non-mixed”). These two areas are expectedly different in contamination levels as the treatment had achieved more than 80% contaminant removal. In 2003 samples yielded average concentrations that were remarkably different between willows

growing in mixed versus non-mixed soil. Non-mixed soil trees showed dramatically higher contaminant concentrations in branches, probably reflecting the higher exposure levels of their root system. TreeWell® Poplars growing in the French Drain groundwater (DD row) also showed elevated concentrations of contaminants, further demonstrating that their roots were exposed to significant contamination from contact with the groundwater at depth. Groundwater analysis from nearby well 317322 showed significant concentrations of chloroform, carbon tetrachloride, TCE, PCE, but not 1,1,1 TCA.

VOC data in plant tissue during the 2004 season (Table 1) 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 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 studied at this time. Compared to the 2003 season, the number of trees with VOCs higher than background is similar and the region where the contamination (R and S rows) starts to be close to background is the same as 2003. Because of the elevated potential for retardation of VOCs in the organic-rich backfill material in the root zone of the TreeWell® trees, non-detects do not necessarily imply that the roots have not reached the groundwater, as VOCs may be adsorbed and/or degraded in the rhizosphere before they actually reach the roots.

This 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 data set consisted of 120 willows 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.

The optimal variogram found for this data set was a spherical variogram with a range of 37, nugget of 1,000, and a sill value of 4,257. ArcGIS v 8.0 was the software used to produce the Kriged maps. Cross validation, where the original concentrations from a small subset of the sample locations are tested against the results predicted by the kriging software, was used to verify the results. A standardized root-mean-square (RMS) error of 0.9 was obtained with this method, indicating that the predicted concentrations from the kriging technique are closely related to the original values and hence can be used in spatial mapping of the plume.

In order to compare tree and soil data, the following method was used. When soil borings were found within 5 ft of a tree, the concentration from that tree (the nearest neighbor) was used for the comparison. When no single “nearest neighbor” tree was found, the average concentration of all trees within a 10 ft radius was used for comparison. As the tree samples were collected on a 10 x 20 ft grid, the maximum distance between the soil borings and the trees would be 10 ft. Results are shown in Figs. 3 and 4 for TCE and in Appendix 3 for all other

contaminants. TCE is the compound for which we have the highest number of data in soil and groundwater and thus the one that allowed us to determine this correlation more effectively. As it is seen on the figures, spots with highest contamination are found in the French Drain along the NW corner, the eastern edge, and the southernmost rows (K and DD). The plume tends then to migrate 500 ft of the trenches going east and reaches non-detects before the end of the planting. Results for the other contaminants tend to be similar, but as less data points are available, the resolution is not as precise. However, as seen in Appendix 3, correlations between PCE in trees and soil and CT in trees and soil are significant with R^2, respectively of 0.86 and 0.92. Too few data for 1,1,1 TCA was available for processing, thus no results are available for this contaminant.

In summary, the correlation hypothesized in 2003 has been strengthened by this year's data to the point that it is conceivable for the 317/319 area to map the plume by analyzing tissue rather than groundwater or soil. It is important to note that tree roots are effectively "averaging," or integrating exposure to different contaminant levels, as they extensively explore soil regions and pockets that would be very difficult and expensive to sample individually with conventional soil sampling methods. Integrated exposure levels are then reflected in aboveground tissue.

Repeated samplings of the same tree were conducted to determine whether VOCs would accumulate in tree tissue with the progression of the growing season. Figure 6 depicts average concentrations of the VOCs on branches of one willow from May 28th to July 22nd, and Fig. 7 shows trends of TCE in branches of 10 different trees during the same timeframe. The data for the only tree sampled consistently through the growing season show concentrations rising and falling with time with no obvious pattern. Other trees were sampled less frequently and thus did not show this trend as clearly. However, concentrations were not increasing and decreasing consistently for each tree at the same time, which seems to exclude the potential for a correlation with site conditions common to all trees such as climatic conditions. In fact, 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).

Laboratory procedures and sampling techniques were carefully reviewed and were found to be consistent over all the samples. All samples were collected on sunny days with temperatures greater than 60°F. Samples were collected from the lowest possible branch in all cases. After carefully reviewing lab procedures and the possibility of error in the lab the hypothesis of a correlation of tissue data with local, time dependent VOC supply in the soil and temporary depletion of available VOCs was considered. In favor of this hypothesis is the fact that the tree that is showing this trend is a large weeping willow, with expected high water use, which could create a condition of localized water depletion, causing a temporary dip in branch concentrations of VOCs at times of high water demand. Redistribution of water from surrounding areas and redissolution of VOCs would then reestablish the supply of chemicals to the plants and cause the levels to rise again. This hypothesis will need to be tested in the future with ad-hoc experiments. A second possibility is that the tree roots are sampling spatially different areas. Branch samples were collected at different radial locations in the tree, and the varying concentrations could be due to different contaminant levels seen by tree roots at the different radial locations and supplied to the branches. In favor of this hypothesis are results

from Vroblesky et al., (2004) who showed that core samples collected at different radial locations showed a marked difference in concentration. While this potential source of variability was investigated in the past when trees were much smaller (2001) with no significant differences found within an individual tree, it is possible that these differences may begin to show up when the trees become larger and roots spread out in truly different soil areas.

Branch concentrations did however seem to have some correlation (polynomial correlation with R^2 = 0.59) with branch diameter size (Fig. 8), as seen in 2003, and therefore sampling procedures continued to stress the importance of consistency in branch sample diameter size.

Data collected in 2003 showed that concentrations in trunk cores tended to drop with height from ground surface, and that this drop tended to be more sensible in the outer section. This confirms what previously reported by others (Ma and Burken, 2003). Core sampling, however, is an invasive procedure that can seriously damage small trees and represent a potential entry way for pests into older trees. It also cannot be replicated on the same tree to collect multiple samples and it is quite time-consuming and difficult to manually repeat exactly. In order to minimize damage to the trees, last year a number of plants were sampled so that a correlation between cores and branches could be established. A strong and positive correlation (R^2 = 0.97) was found for TCE and let us use branch data to correctly estimate plant removal rates with no harm to the tree. As a result of this work, this year only a limited number of tree cores were collected. However, this year we were not able to confirm the same trend (Fig. 9). After careful review of possible cases, we favor the hypothesis of errors in sample collection and handling. The trunks of the sampled trees were this year extremely large and difficult to sample, resulting in a very small sample being obtained using the coring equipment. Additionally, there was most probably loss of contaminants when the samples were transferred from the sampling equipment to the sample vials. The difficulty in replicating core sampling procedures between operators and the high operator error is another reason to use branch samples as the primary plant samples.

While this field site is especially suited for this approach because trees were planted so that their rooting would be highly controlled, biosampling techniques, when fully demonstrated, could be an economically viable alternative to conventional monitoring: for comparison, while in one day one or two operators can easily sample in duplicate approximately 20 trees, only a few groundwater samples are usually collected in the same timeframe.

Laboratory Experiments

The results from the experiments evaluating the analytical technique are presented in Table 2 and 3 and Fig. 10. Recovery of the TCE in the leaves and branches ranged from 98 (unreported) to 138%, indicating that most of the TCE present in the plant tissue is recovered during the analysis. The extra recovery is most evident in leaves, and may have to do in part with background.

Increasing the heating time from 0 to 4 hours resulted in an increase in the mass of TCE recovered. Maximum increase in mass recovery was obtained from heating till 2.5 hours and increasing the time period of heating to 4 hours resulted in a slight increase in mass recovery.

This would indicate that heating the sample for at least 2.5 hours and preferably for 4 hours resulted in higher rates of mass recovery.

Freezing the samples did not result in significant changes in TCE recovery from crab apple. A slight decrease in the mass of TCE recovered from crabapple branches was observed when the samples were frozen. This was unexpected when compared to results from freezing willow and poplar leaf and branch samples where the mass of TCE recovered increased on freezing. One possibility could be due to the differences between crab-apple and willow and poplar species. This would need further investigation.

The results from varying the equilibrium concentrations are presented in Fig. 10. It appears that there is a linear relationship between TCE concentrations in the branch and the water and a parabolic relationship between the leaf and water samples.

Tritium in Transpirate

Results from the tritium analyses are reported in Figs. 11 and 12. The full set of data collected since the trees were planted is reported in Appendix 2. As reported in previous summaries, when comparing data from individual trees it is difficult to show a clear increase in tritium levels in each individual tree with time. However, trees vary widely in their concentration of tritium, and several of them growing immediately south of the 319 landfill have now shown to be well above our established background (approximately 14 TU, or 45 pCi/L). Concentrations in this area have been shown spanning from background to 129 TU (413 pCi/L) this summer. Trees with the highest levels of tritium in their transpirate were found in the first rows south of the 319 landfill. The closest monitoring well (MW 319171) reported tritium concentrations around 2,500 pCi/L.

One important consideration is the extent of mixing of tritiated with clean water at depth and their uptake by different plant roots. As tritium levels are still not quite at the concentrations found in nearby groundwater, some mixing is evident. The recently discovered groundwater mounding pattern 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.

Segregated root “feeding” is well demonstrated in other disciplines, such as plant pathology, where bacterial or viral infections of the vascular system can be isolated on a specific side of the tree and relative branches. In order to determine if water taken up by the deeper tap root (fed by the groundwater) might feed the tallest branches, this year we collected samples from the tallest branch or tree apex (7.3 to 10.2 m) using a lift operated by ANL/PFS. Results do not show any clear difference attributable to this relatively short difference in height (Fig. 11). Compared to the samples collected earlier in the season however, the levels of tritium in transpirate from apical branches appeared in most cases higher than that collected previously from branches sufficiently close to the ground to be sampled with no ladder or other equipment.

Conclusions and Recommendations

As the trees completed their fifth 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 have begun to influence the cleanup area significantly.

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

- 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 and thousand 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.
- The majority of the sampled poplars have shown to be in contact with groundwater both at the French Drain and at the Hydraulic Control Areas, based on higher than background levels of VOCs and of tritium in transpirate.
- Tritium levels in some hydraulic control trees have been higher than background over the last several years. Sampling apical leaves may be a better way to sample transpirate in the future as these branches may transpire water with higher tritium concentrations.
- More controlled mass balance studies will need to be conducted to determine dynamics of plant uptake and temporary accumulation, and to estimate removal rates.
- Adsorption/desorption studies should be conducted to determine retardation factors by backfill material.

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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.

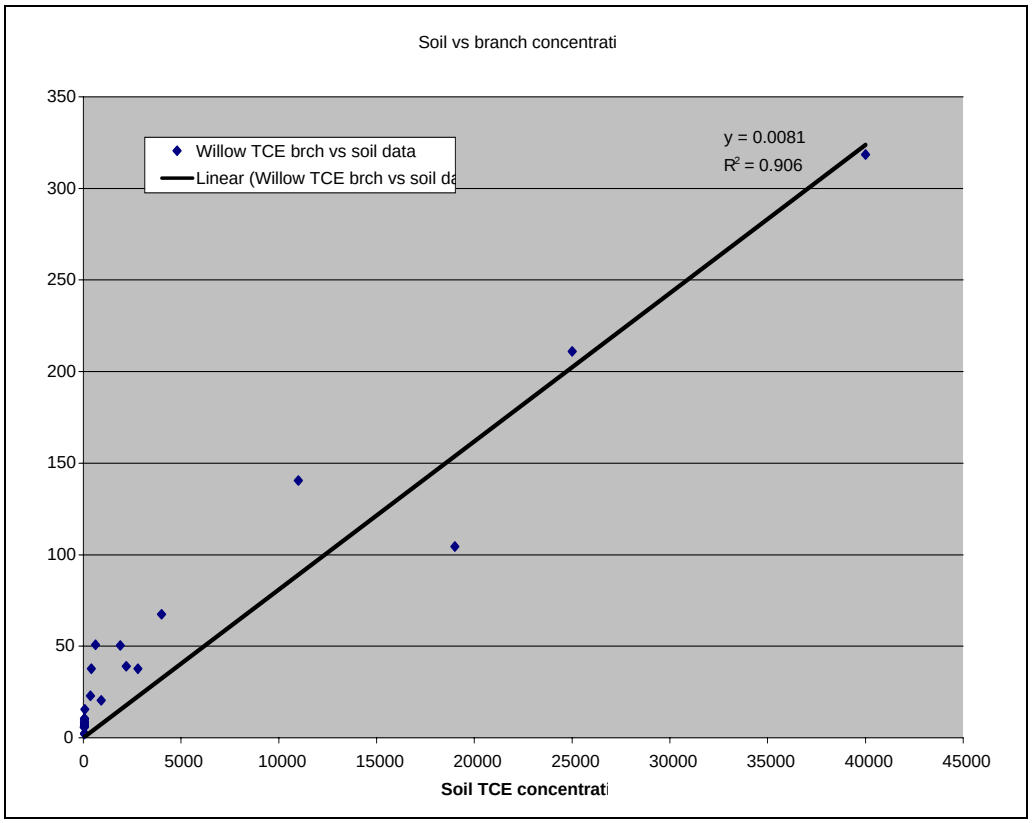

Figure 2. Correlation between soil and willow branch TCE concentrations.

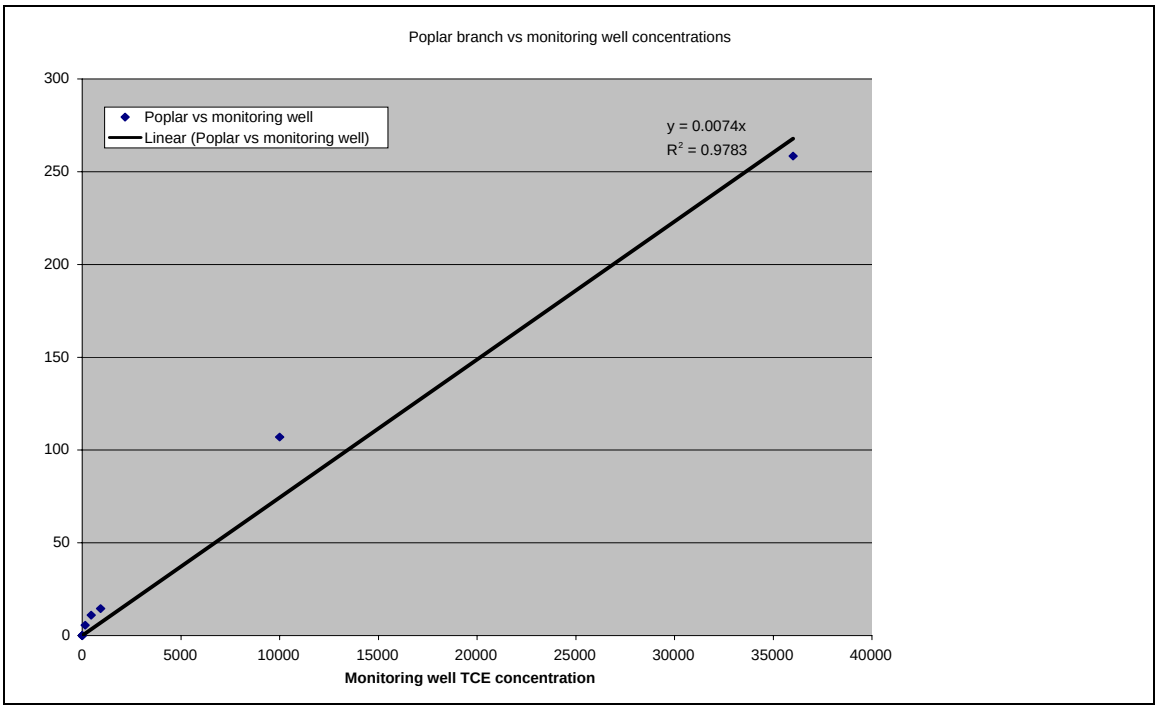

Figure 3. Correlation between groundwater and poplar branch TCE concentrations.

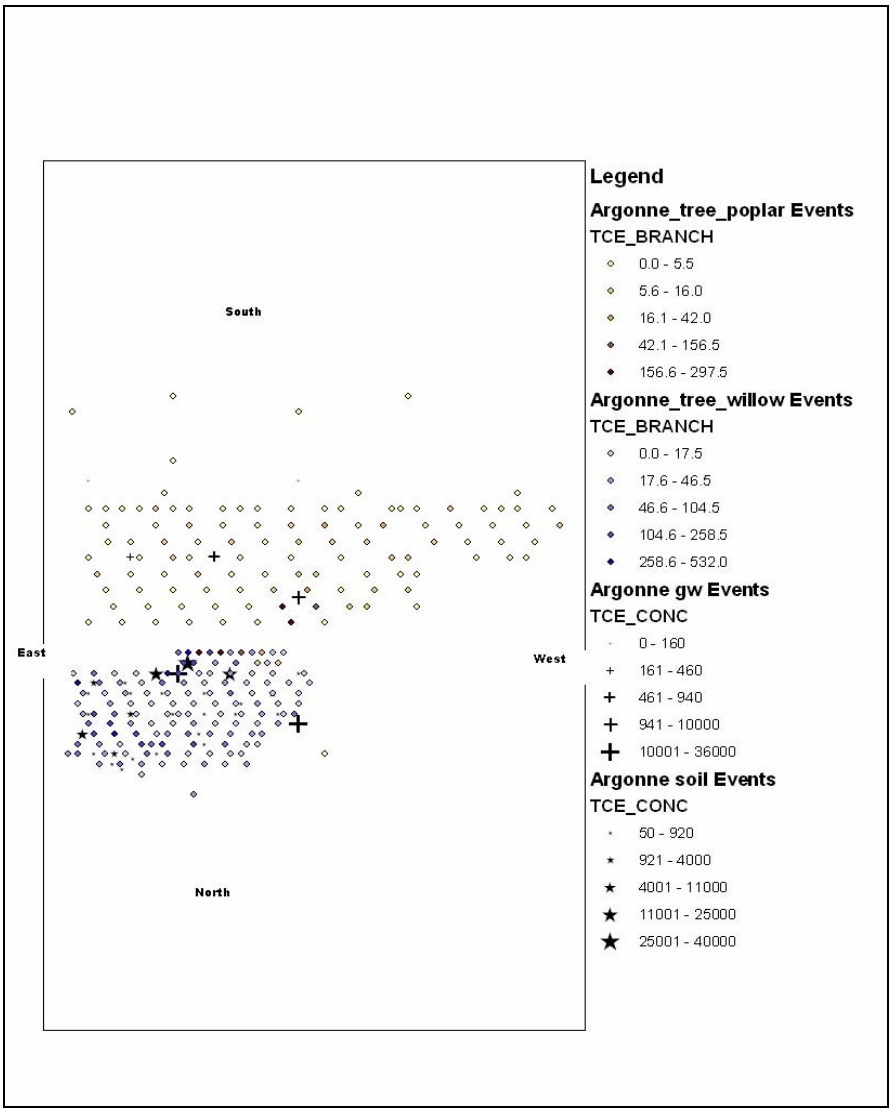

Figure 4. Spatial representation of tree branch soil and groundwater concentration data. Image is specular to normal, looking South.

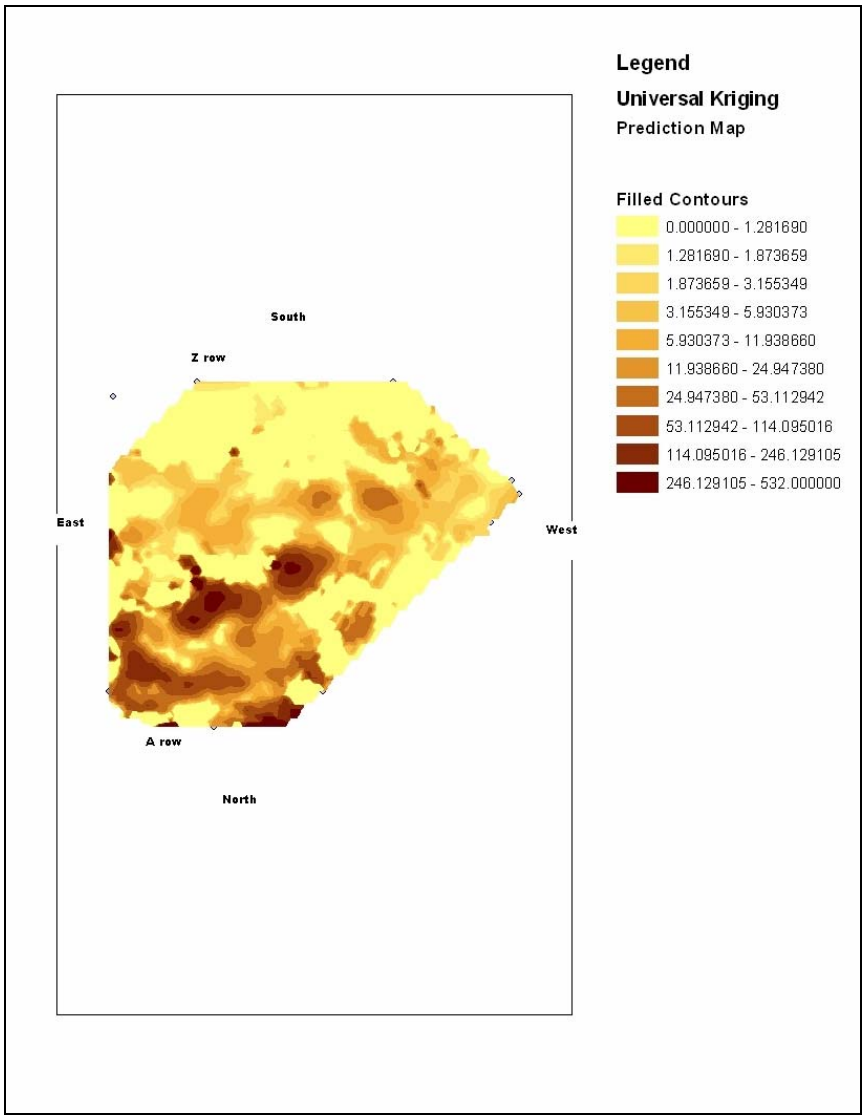

Figure 5. Prediction of plume concentration and location based on soil, groundwater, and all tree TCE data, image is specular to normal, looking South.

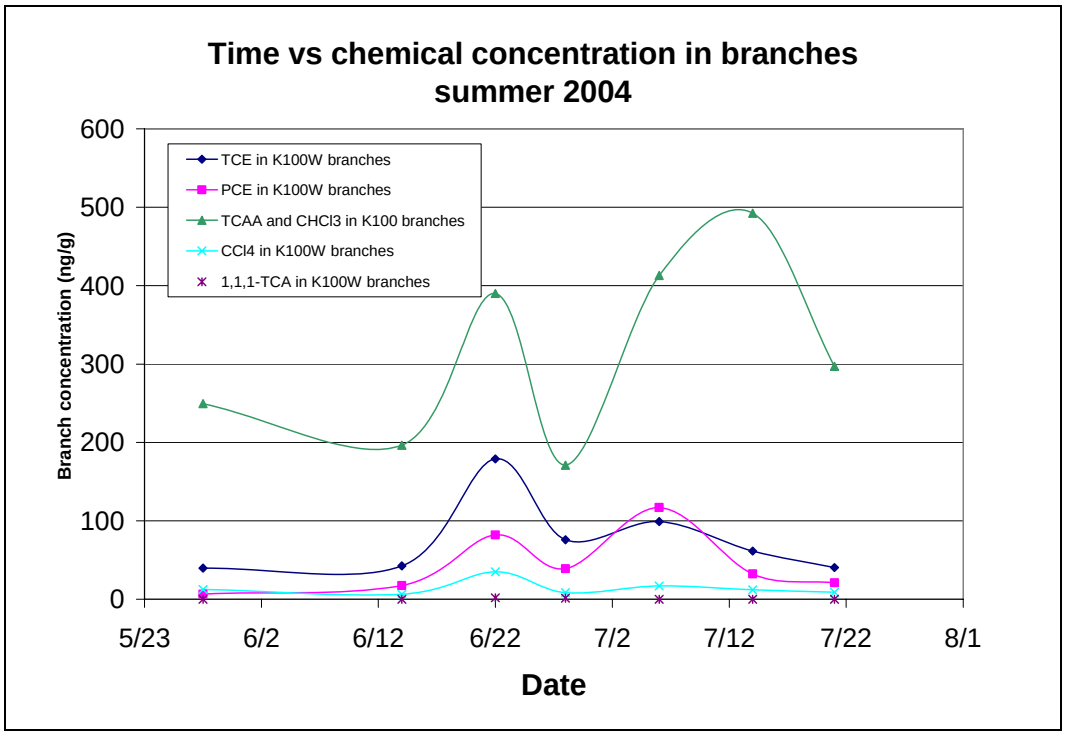

Figure 6. Variations in VOC concentrations in willow K100W from June to July 2004.

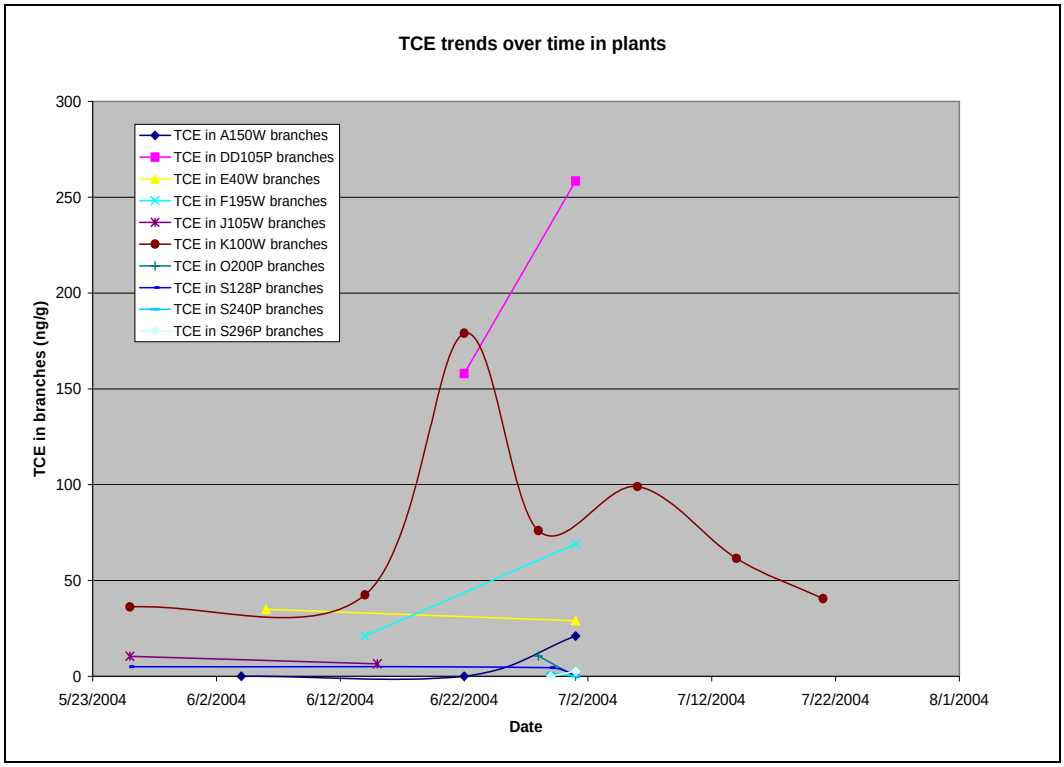

Figure 7. TCE trends over time in branches of different trees.

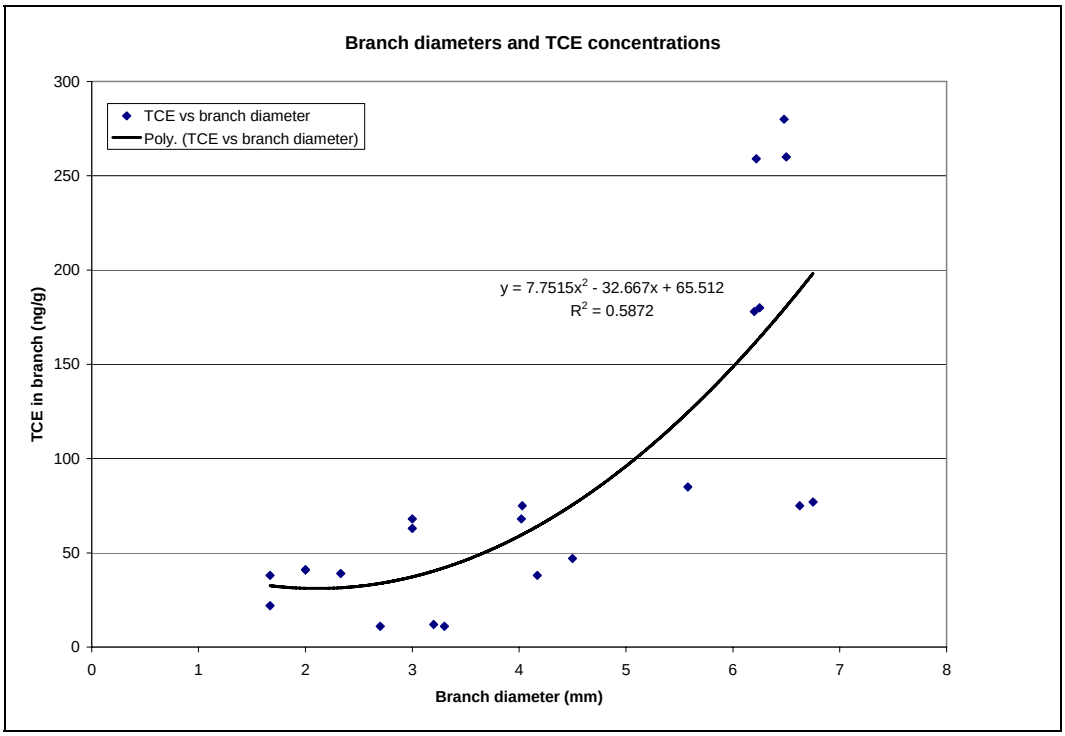

Figure 8. TCE concentrations correlation with Branch diameter.

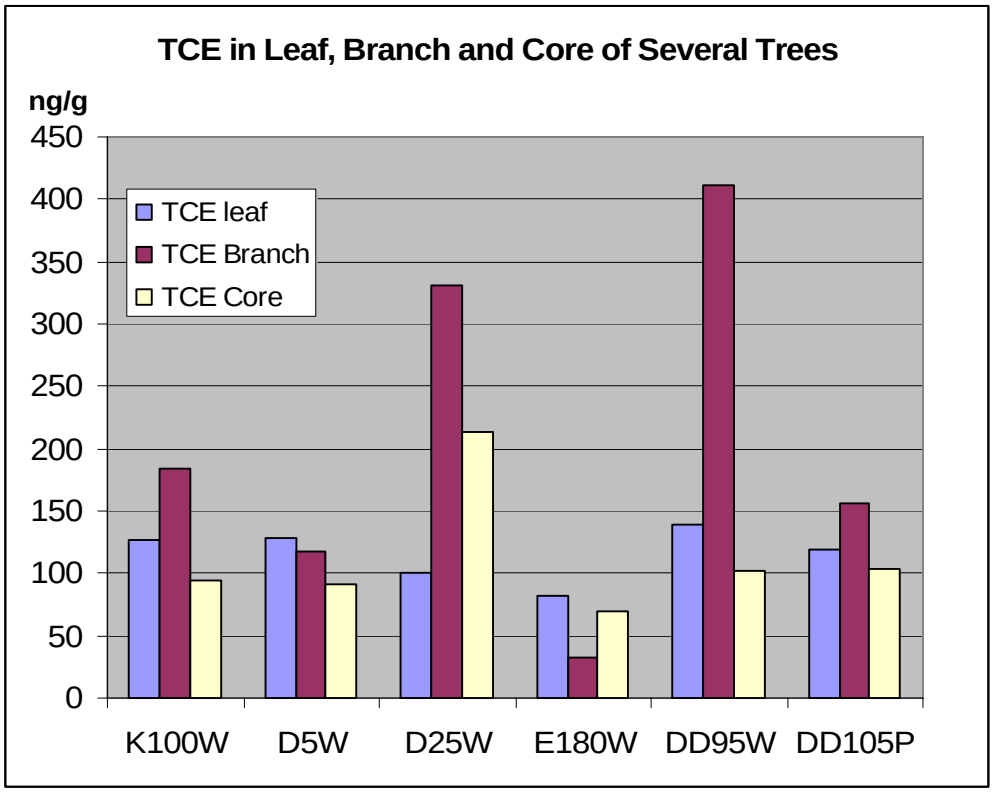

Figure 9. Concentrations in leaf, branch, and core of several trees in the French Drain.

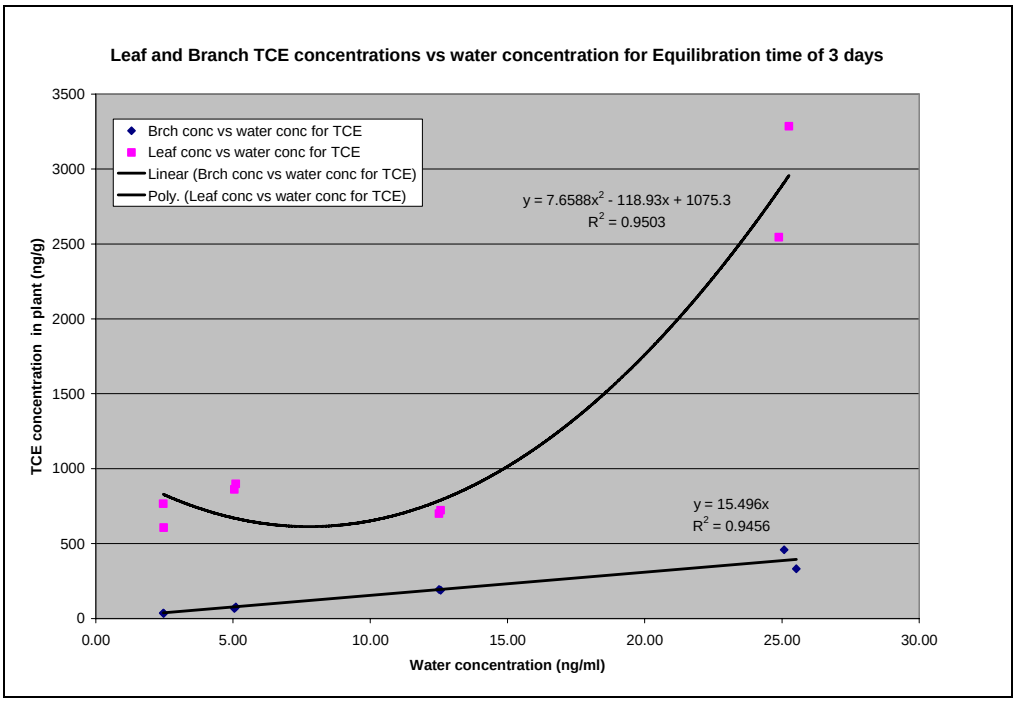

Figure 10. Correlation between concentration in water and relative concentration in leaf and branch in laboratory experiments.

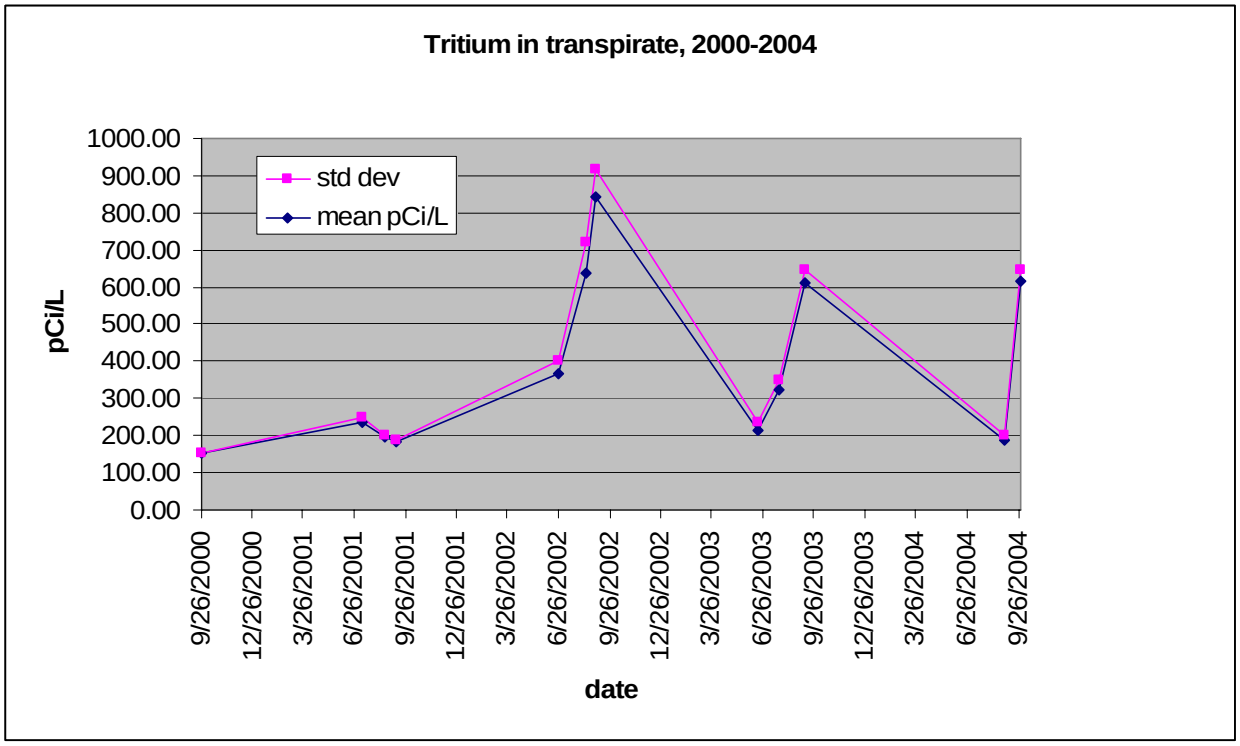

Figure 11. Tritium concentrations in transpirate (pCi/L) 2000-2004. Mean values and standard deviation.

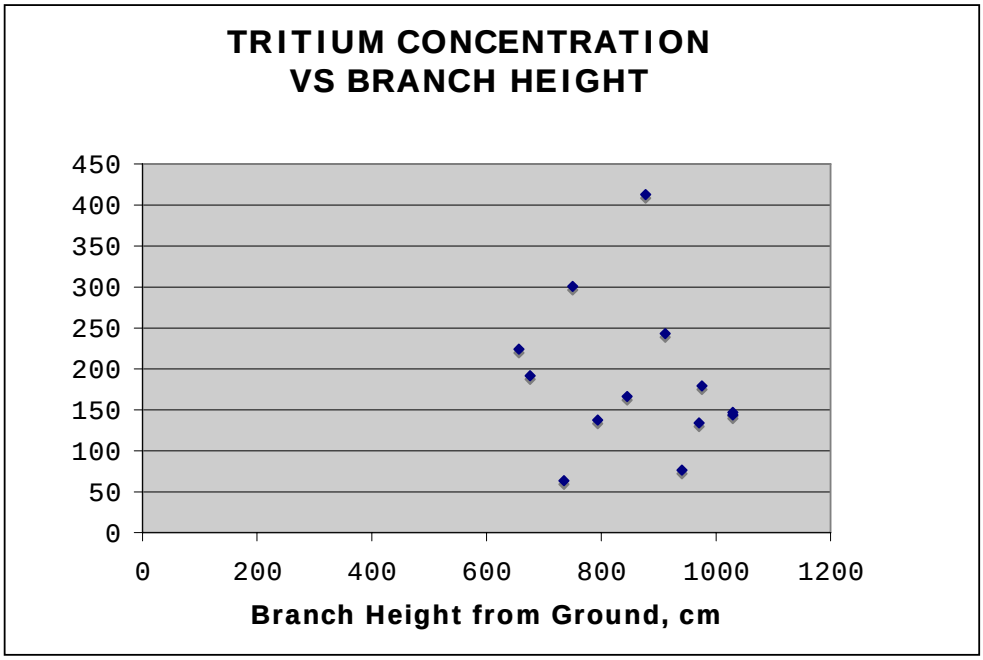

Figure 12. Tritium concentrations in transpirate (pCi/L) at different branch heights from ground, September 30, 2004.

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

Plant Tissue	Contaminant	Mean French Drain	Mean Hydraulic Control Inside Fence	Mean Hydraulic Control Outside Fence
Leaf	Mix TCAA + CHCl3	150	109	85
	TCE	17	39	27
	PCE	3	2	1
	1,1,1,TCA	Nd	Nd	1
	CCl4	21	22	20
Branch	Mix TCAA + CHCl3	318	46	30
	TCE	53	13	2
	PCE	63	14	1
	1,1,1 TCA	2	4	1
	CCl4	80	13	5

Table 2. TCE mass recovery from spiked willow, poplar, and crabapple leaves and branches.

TCE Concentration Branches (ng/g)	Mass Recovery Branches (%)	TCE Concentration Leaves (ng/g)	Mass Recovery Leaves (%)
Crab apple			
147	108	508	124
145	111	576	138
Willows			
384	108	92	123
315	107	89	132
Poplars			
368	123	308	122
350	121	359	123

Table 3. TCE concentrations determined at varying heating and freezing times.

	Crab apple (from ANL grounds)					
	TCE Concentration (ng/g)					
Time heated (hrs)	***Branches***	***Leaves***				
0	152	1,889				
2.5	213	2,464				
4	314	2,042				
	Crab apple (from ANL grounds)		**Willows** (from field)		**Poplars** (from field)	
	TCE Concentration (ng/g)					
Time frozen (days)	***Branches***	***Leaves***	***Branches***	***Leaves***	***Branches***	***Leaves***
0	275	289	1,262	26	31.5	38.5
1	223	563	1,766	26	62	46.5
4	233	610				

APPENDIX 1. Summary of Field Data, Summer 2004

Tree ID	Date	TCAA + CHCl3	TCE	PCE	111-TCA	CCl4	TCAA + CHCl3	TCE	PCE	111-TCA	CCl4
Average Concentrations (using dry weights)											
		Leaves	Leaves	Leaves	Leaves	Leaves	Branches	Branches	Branches	Branches	Branches
FRENCH DRAIN											
A010W	6/4/2004	76	12	0	0	10	31	47	20	0	9
A030W	6/4/2004	161	27	5	0	28	65	68	114	0	10
A050W	6/4/2004	95	22	4	0	16	53	42	122	0	8
A070W	6/4/2004	99	10	2	0	17	24	8	6	1	12
A090W	6/4/2004	98	10	2	0	19	23	3	3	0	4
A110W	6/4/2004	0	8	3	0	26	71	23	9	0	23
A130W	6/4/2004	104	6	3	1	15	56	2	2	0	8
A150W	6/4/2004	98	5	2	0	16	1087	0	2	14	823
A150W	6/22/2004	92	12	2	0	18	2157	0	2	22	1350
A150W	7/1/2004	397	0	0	0	0	1791	21	1	25	0
AA050W	6/29/2004	149	14	4	0	21	25	4	2	0	4
AC100W	7/1/2004	352	93	0	0	41	66	19	1	0	9
B-010W	6/4/2004	115	13	4	0	15	44	60	50	0	2
B015W	6/4/2004	144	11	3	0	15	32	21	22	0	4
B-020W	6/4/2004	108	18	5	0	14	47	44	100	0	8
B035W	6/4/2004	124	21	3	0	21	46	11	49	0	6
B055W	6/4/2004	138	18	5	0	21	85	58	122	0	7
B075W	6/4/2004	140	12	3	0	18	63	74	195	0	7
B095W	6/4/2004	213	27	5	0	32	78	3	14	0	15
B115W	6/4/2004	181	26	3	0	19	54	17	22	0	9
B135W	6/4/2004	109	10	3	0	17	42	6	6	0	7
B145W	6/4/2004	164	14	4	0	19	292	3	3	0	6
BB224P	7/1/2004	60	8	1	0	13	46	0	6	4	0
C010W	6/4/2004	136	22	57	0	25	47	20	57	0	6
C-010W	6/4/2004	97	7	3	0	10	52	83	132	0	7
C030W	6/4/2004	49	10	3	0	19	30	6	28	0	5
C050W	6/6/2004	255	14	8	0	26	228	137	692	0	6
C060W	7/1/2004	399	0	1	0	18	93	76	353	0	10
C070W	6/6/2004	410	21	6	0	33	104	173	440	0	4
C100W	6/6/2004	258	33	11	0	36	48	143	471	1	5
C130W	6/6/2004	176	10	5	0	23	97	94	56	0	5
C150W	6/6/2004	325	0	5	0	21	44	10	175	0	3
C160W	6/6/2004	107	5	4	0	16	33	2	7	0	4
D025W	6/6/2004	275	0	6	0	14	69	393	403	0	4
D045W	6/6/2004	222	5	5	0	14	60	129	453	0	3
D05W	6/6/2004	178	15	5	0	30	47	200	546	0	4
D065W	6/6/2004	153	0	5	0	26	52	10	36	0	2
D075W	6/6/2004	269	0	4	0	13	40	22	94	0	3
D095W	6/6/2004	262	28	5	0	28	55	51	128	0	7
D115W	6/6/2004	184	15	4	0	31	53	40	69	0	6
D135W	6/6/2004	112	36	4	0	36	34	19	62	3	2
D155W	6/6/2004	219	27	5	0	13	31	22	181	0	7
D165W	6/6/2004	107	20	4	0	29	33	45	149	2	0
DD085W	6/22/2004	265	12	2	0	24	742	92	5	0	310
DD095W	5/26/2004	180	8	0	0	24	666	57	7	0	33
DD095W	6/22/2004	171	13	0	0	18	2274	532	146	16	451
DD105P	6/22/2004	347	32	5	0	25	750	158	46	5	84
DD105P	7/1/2004	298	101	1	0	33	1015	259	72	10	151
DD115W	6/22/2004	97	10	4	0	18	1025	177	65	9	126
DD125P	6/22/2004	157	20	3	0	20	2615	224	101	24	748
DD135W	6/22/2004	148	7	5	0	18	1003	32	67	7	125
DD145P	6/22/2004	324	10	4	0	14	7088	157	132	0	1517
DD155W	6/22/2004	134	18	5	0	20	744	26	60	4	124
DD165P	6/22/2004	102	16	3	0	13	993	30	27	11	10
DD175W	6/22/2004	93	7	3	0	15	28	1	3	0	8
DD185P	6/22/2004	186	24	2	0	30	2074	0	1	0	1579
DD185W	7/1/2004	195	23	1	0	18	1565	0	1	0	1126
E020W	6/6/2004	98	19	5	0	31	38	141	152	0	3
E040W	6/6/2004	200	12	4	0	25	37	35	42	0	4
E040W	7/1/2004	425	37	1	0	15	107	29	39	0	7
E060W	6/6/2004	270	0	4	0	32	121	9	20	0	5
E080W	6/6/2004	277	14	4	0	36	134	9	58	0	3
E0W	6/6/2004	0	0	4	0	40	37	62	46	1	4
E100W	6/6/2004	217	15	5	0	36	47	39	73	0	2
E120W	6/6/2004	227	17	4	0	25	66	18	26	0	3
E140W	6/6/2004	93	0	4	0	27	30	10	35	3	2
E160W	6/6/2004	72	0	4	0	29	34	10	77	9	0
E180W	6/6/2004	207	0	3	0	14	23	18	16	11	0
F025W	6/6/2004	57	25	5	0	42	29	51	54	0	4
F045W	6/14/2004	110	21	3	0	22	44	3	4	0	8
F05W	6/6/2004	156	18	5	0	25	32	259	289	0	4
F-05W	6/6/2004	129	0	3	0	26	26	23	2	0	4
F075W	6/14/2004	90	17	2	0	16	25	8	18	0	3
F085W	6/14/2004	71	19	1	0	15	31	12	32	0	4
F095W	6/14/2004	33	9	31	0	5	104	11	4	0	2
F125W	6/14/2004	107	12	2	0	10	22	5	15	0	6
F145W	6/14/2004	102	16	0	0	17	30	16	22	4	0
F165W	6/14/2004	0	46	0	0	27	66	23	21	38	0
F185W	6/14/2004	113	14	4	0	22	32	6	2	6	0
F195W	6/14/2004	73	15	1	0	14	32	21	21	6	2
F195W	7/1/2004	361	44	1	0	15	103	69	61	8	16
G-010W	6/14/2004	62	8	1	0	15	11	5	3	0	7
G020W	6/14/2004	125	17	3	0	20	27	29	27	0	5
G040W	6/14/2004	108	21	3	0	19	24	3	5	0	4
G060W	6/14/2004	131	19	4	0	15	19	11	13	0	3
G080W	6/14/2004	70	8	3	0	14	19	3	6	0	3
G100W	6/14/2004	109	32	0	0	14	62	7	20	0	10
G120W	6/14/2004	95	12	3	0	13	26	3	4	0	4
G140W	6/14/2004	202	21	4	0	16	32	15	27	4	2
G160W	6/14/2004	113	13	4	0	20	147	39	25	62	0
G180W	6/14/2004	101	25	3	0	28	27	4	2	4	3
G200W	6/14/2004	102	9	2	0	18	26	6	11	2	4
H015W	6/14/2004	98	12	1	0	18	24	4	4	0	3
H035W	6/14/2004	85	20	0	0	31	29	23	13	0	9
H055W	6/14/2004	110	31	0	0	28	24	8	18	0	5
H-05W	6/14/2004	92	12	3	0	18	28	21	3	0	5
H075W (N)	6/14/2004	92	25	0	0	19	33	4	13	0	6
H095W (N)	6/14/2004	102	22	0	0	23	33	8	12	0	6
H115W	6/14/2004	114	16	3	0	19	28	6	10	0	4
H135W	6/14/2004	88	22	4	0	17	36	68	181	5	2
H155W	6/14/2004	119	18	4	0	24	31	16	70	7	7
H175W	6/15/2004	91	30	0	0	22	78	15	38	1	9
H200W	6/15/2004	103	13	2	0	24	28	16	28	4	0
I010W	6/15/2004	121	17	4	0	25	56	55	19	0	4
I-010W	6/15/2004	149	20	4	0	23	141	392	12	0	5
I030W	6/15/2004	117	10	3	0	29	37	26	6	0	7
I050W	6/15/2004	105	13	2	0	17	36	7	4	0	7
I070W	6/15/2004	111	13	4	0	19	116	62	28	0	4
I090W	6/15/2004	95	10	22	0	23	32	22	3	0	2
I110W	6/15/2004	104	12	2	0	13	61	5	3	0	8
I130W	6/15/2004	158	12	3	0	6	31	28	37	2	2
I150W	6/15/2004	104	24	3	0	19	70	8	31	2	5
I170W	6/15/2004	132	15	4	0	22	60	18	80	1	4
I190W	6/15/2004	122	12	4	0	23	23	6	4	0	3
I210W	6/15/2004	95	6	3	0	18	42	4	2	0	4

APPENDIX 2. Tritium in Leaf Transpirate, 2000-2004 Data

HYDRAULIC CONTROL OUTSIDE FENCE											
S016P	6/28/2004	70	28	1	0	10	27	4	1	2	3
S032P	6/28/2004	80	39	1	0	15	24	4	1	1	6
S032P	7/1/2004	0	22	2	0	27	38	0	1	0	5
S048P	6/28/2004	78	41	2	7	19	28	4	1	0	4
S064P	6/29/2004	0	17	3	0	19	32	6	1	1	6
S080P	6/29/2004	90	12	2	0	9	7	2	1	3	0
S096P	6/29/2004	156	36	3	9	15	20	1	1	1	3
S0P	6/28/2004	126	52	0	0	21	35	4	2	0	7
S128P	5/26/2004	107	48	0	0	23	57	5	1	0	8
S128P	6/29/2004	44	44	3	0	26	14	5	1	0	7
S128P	7/1/2004	0	14	2	0	18	22	0	1	0	6
S144P	5/26/2004	106	29	0	0	21	13	0	1	0	7
S160P	6/29/2004	0	23	2	0	26	17	1	0	0	3
S192P	6/29/2004	0	24	3	0	30	26	2	1	1	4
S224P	6/29/2004	33	14	2	6	13	22	2	1	0	4
S240P	6/29/2004	102	8	2	9	6	8	2	1	2	2
S240P	7/1/2004	97	57	1	0	32	15	0	1	0	8
S288P	6/29/2004	312	64	2	0	18	22	4	1	2	2
S296P	6/29/2004	192	22	3	0	28	31	0	3	0	5
S296P	7/1/2004	0	29	1	0	13	34	3	2	0	6
S312P	6/29/2004	0	25	4	0	30	37	0	1	0	5
S344P	6/29/2004	104	25	2	0	32	26	10	1	0	3
S376P	6/29/2004	206	46	2	0	21	26	3	1	5	0
S392P	6/29/2004	53	19	2	7	14	24	4	1	2	0
S408P	6/29/2004	56	16	1	0	19	21	2	1	4	0
S440P	6/29/2004	0	9	0	0	10	28	2	1	4	0
T072P	5/26/2004	108	31	0	0	20	1	1	0	0	10
T256P	5/26/2004	99	15	0	0	18	59	1	1	0	7
T408P	7/1/2004	105	34	0	0	28	71	0	0	0	9
V080P	5/26/2004	102	27	0	0	16	45	0	1	0	2
Y-016P	7/1/2004	134	0	3	0	15	43	0	1	0	6
Y200P	7/1/2004	95	19	2	0	18	32	0	1	0	6
Z080P	7/1/2004	82	0	2	0	15	20	2	1	0	5
Z304P	7/1/2004	164	35	0	0	34	88	0	0	0	13
AVERAGE HC-OUTSIDE		**85**	**27**	**1**	**1**	**20**	**30**	**2**	**1**	**1**	**5**
Tree ID	**Date**	**TCAA + CHCl3**	**TCE**	**PCE**	**111-TCA**	**CCl4**	**TCAA + CHCl3**	**TCE**	**PCE**	**111-TCA**	**CCl4**
Average Concentrations (using dry weights)											
		Leaves	Leaves	Leaves	Leaves	Leaves	Branches	Branches	Branches	Branches	Branches
Mean FD		150	17	3	0	21	318	53	63	2	80
AVERAGE HC-INSIDE		109	39	2	0	22	46	13	14	4	13
AVERAGE HC-OUTSIDE		85	27	1	1	20	30	2	1	1	5

APPENDIX 3. Additional Plume Mapping

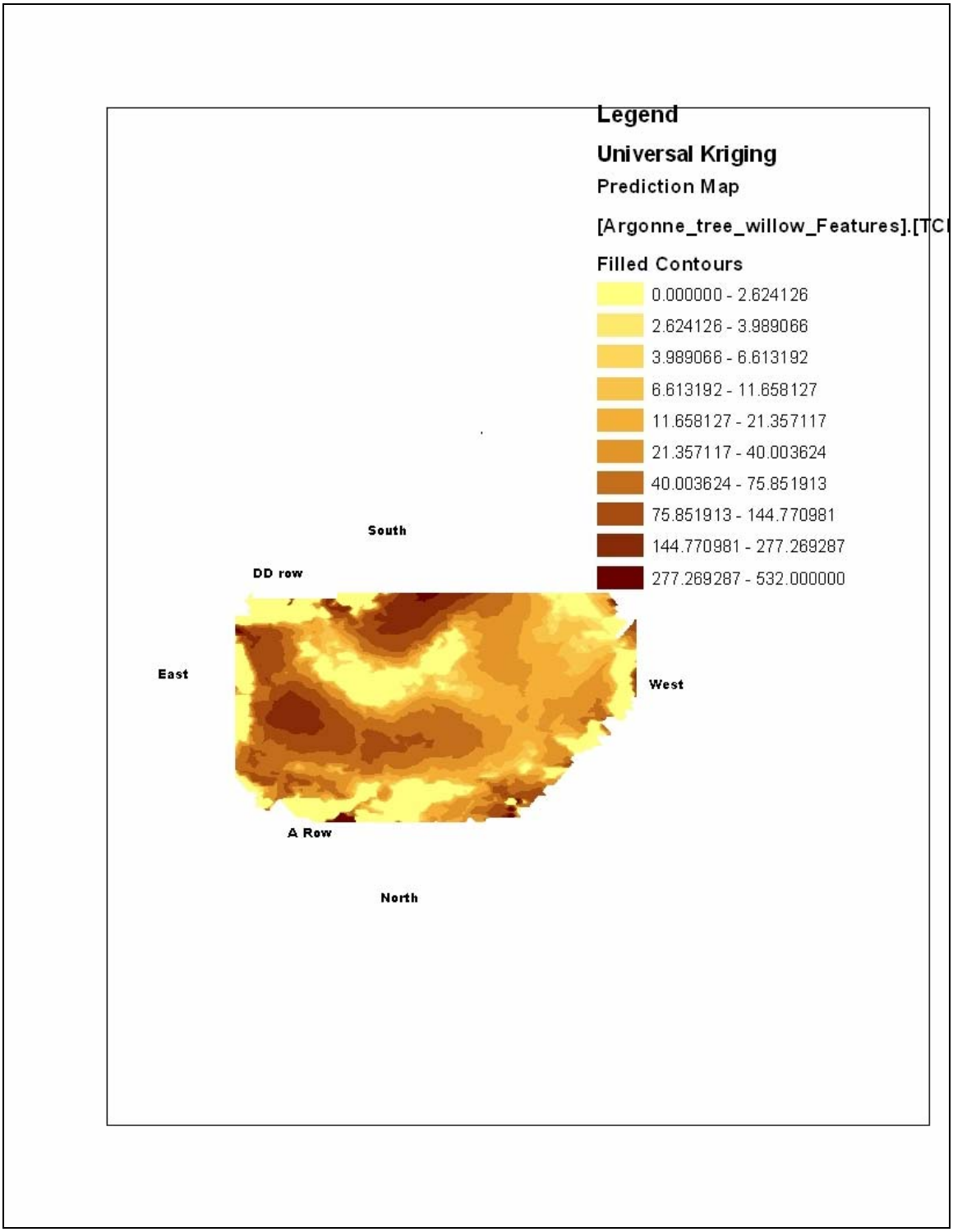

Figure 3-1. TCE plume delineation in French Drain using willow branch data.

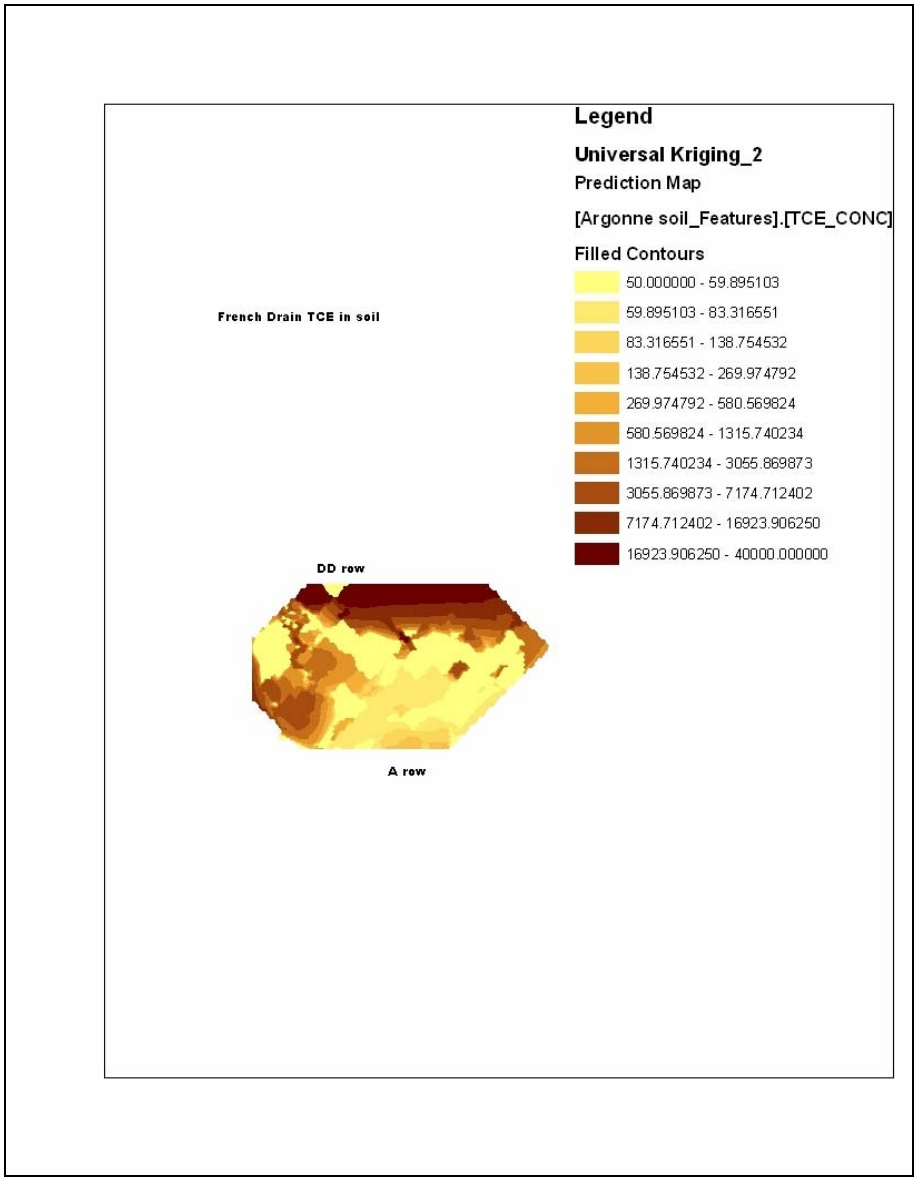

Figure 3-2. TCE plume delineation in the French Drain, using soil data.

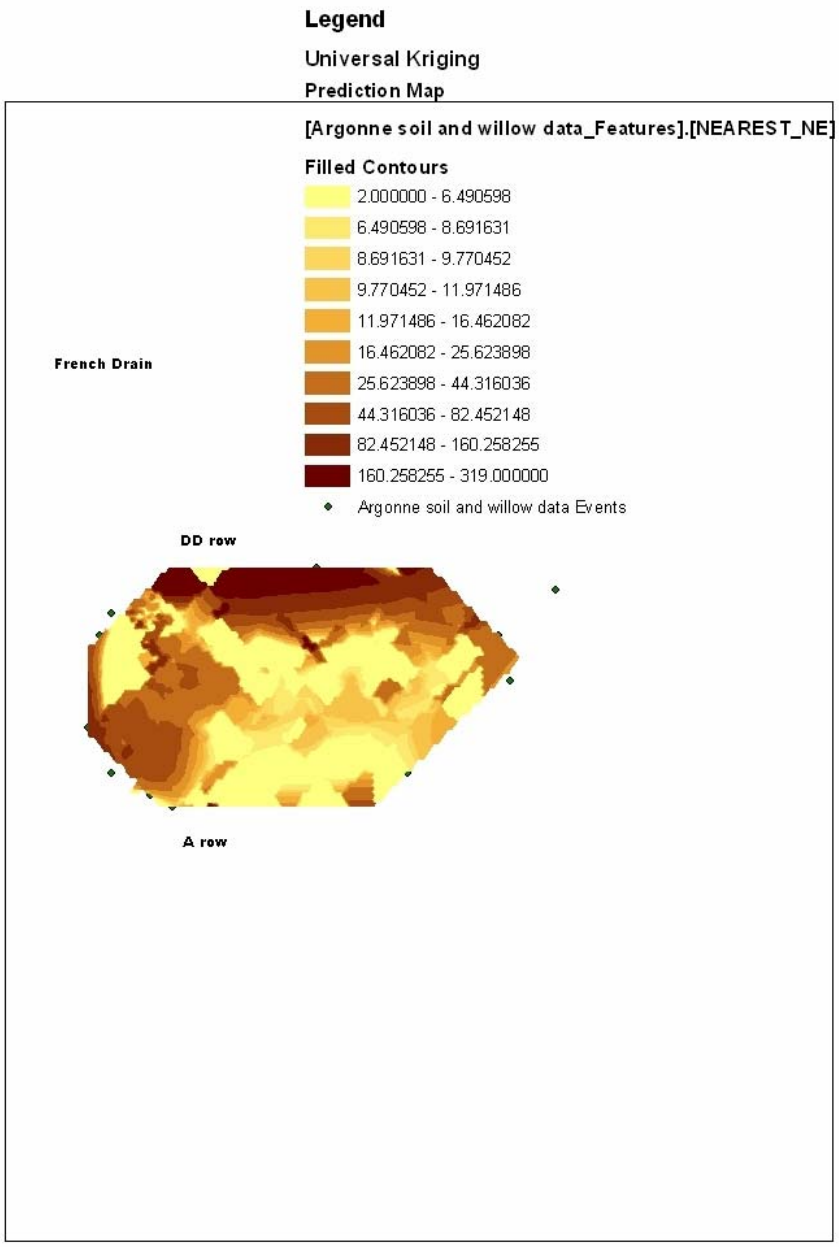

Figure 3-3. TCE plume delineation in French Drain using soil and willow branch data.

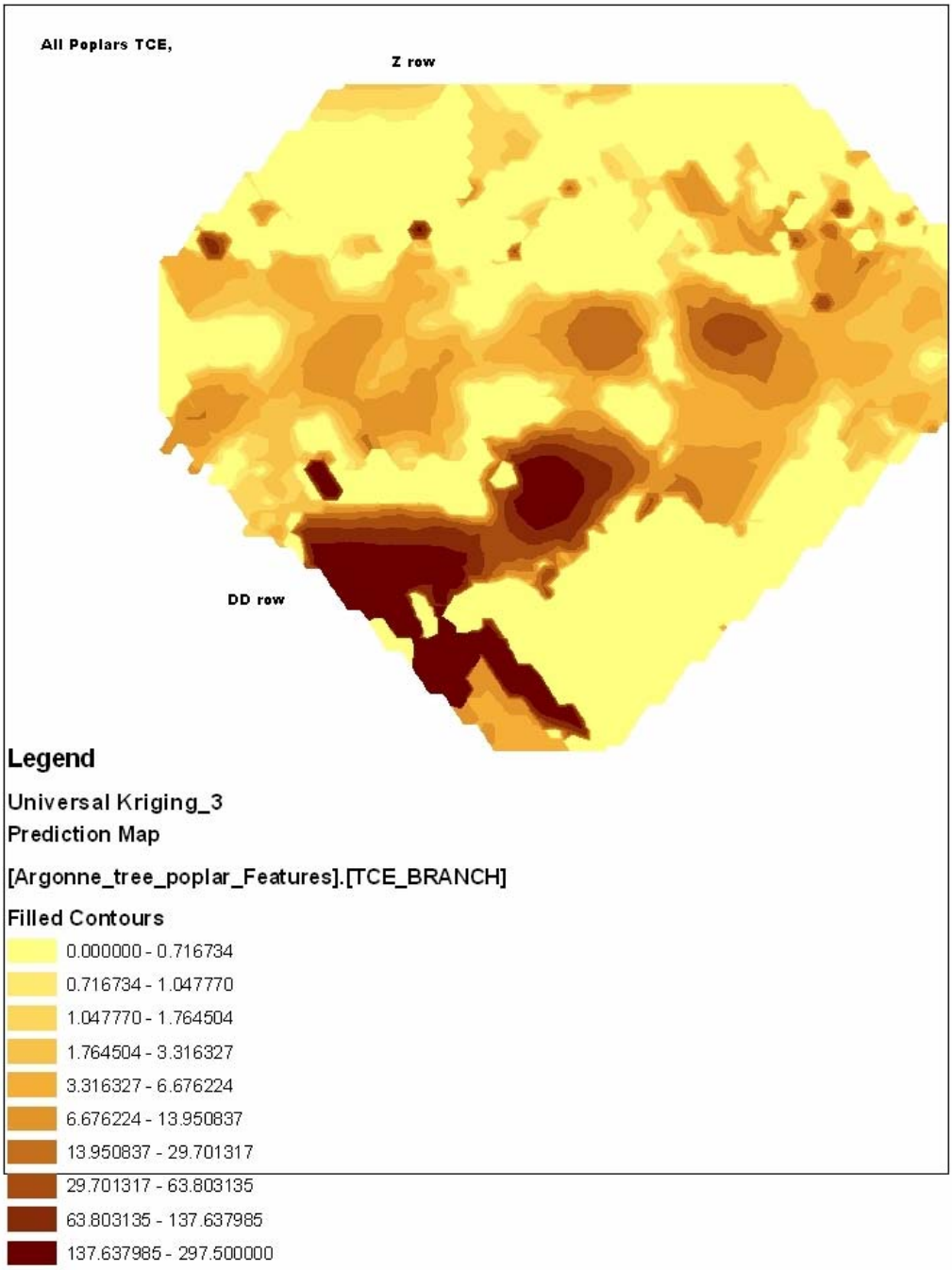

Figure 3-4. TCE plume delineation in French Drain and hydraulic control areas, using poplar tree branch data.

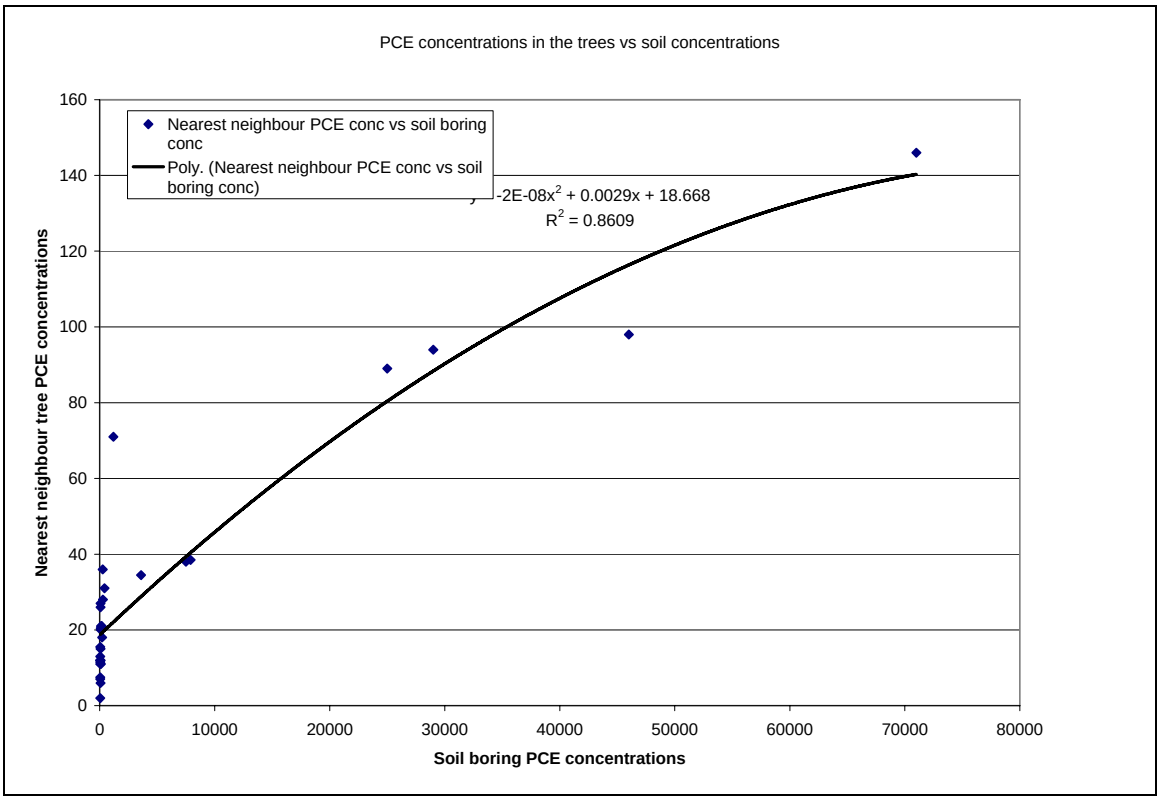

Figure 3-5. Correlation between branch and soil PCE concentrations.

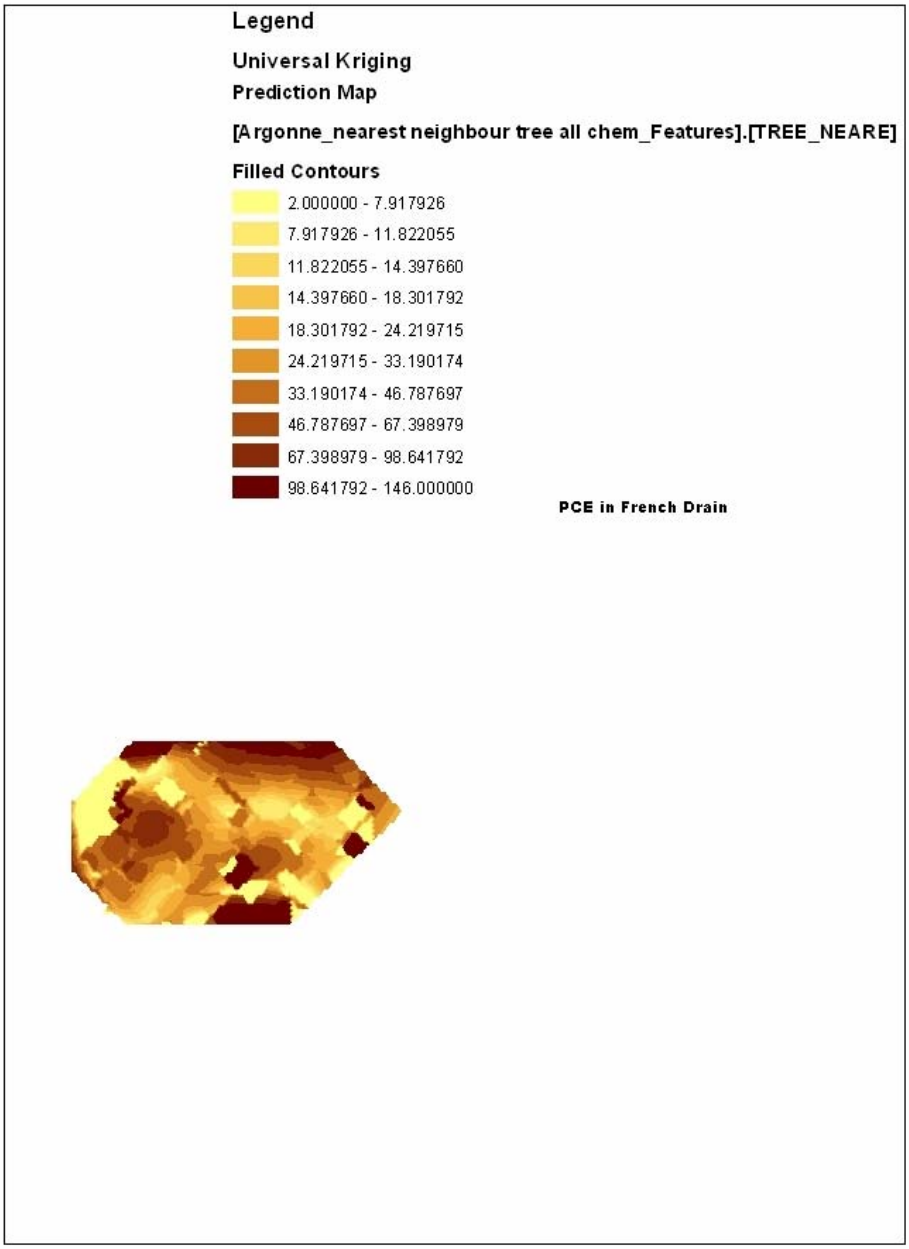

Figure 3-6. PCE plume delineation in French Drain using willow and poplar branch data.

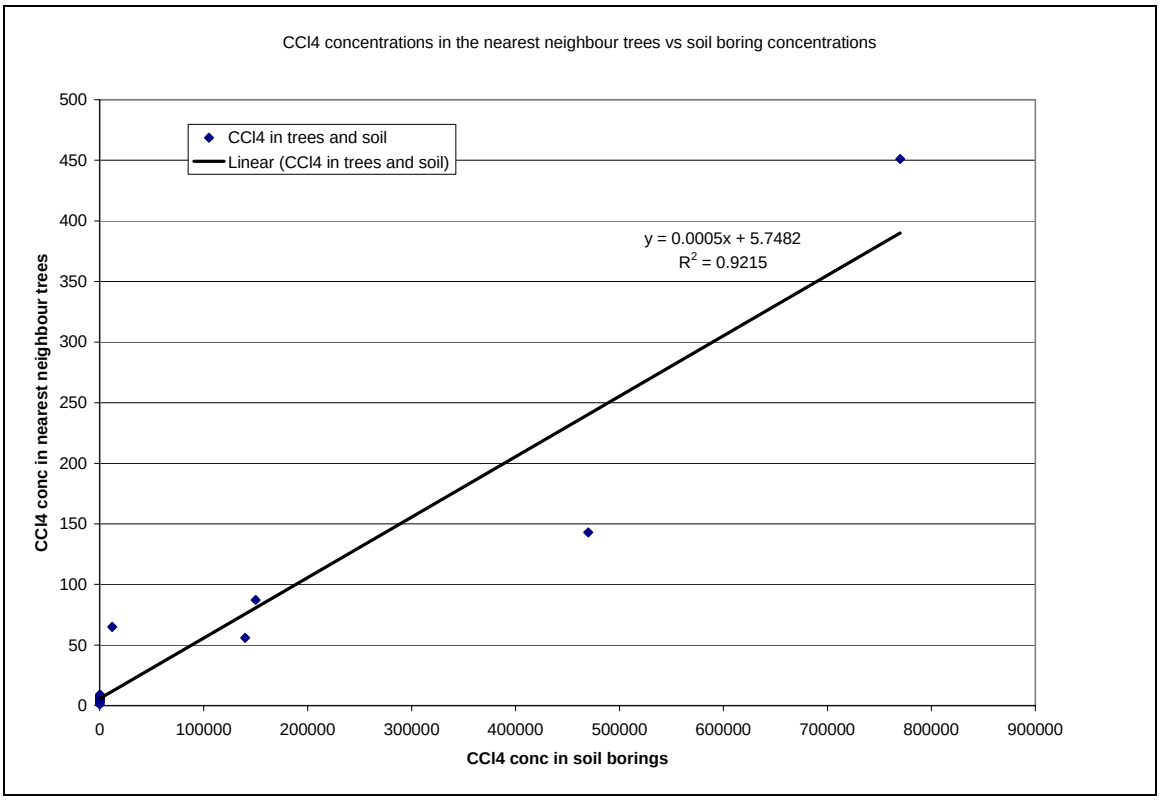

Figure 3-7. Correlation between branch and soil CCl_4 concentrations.

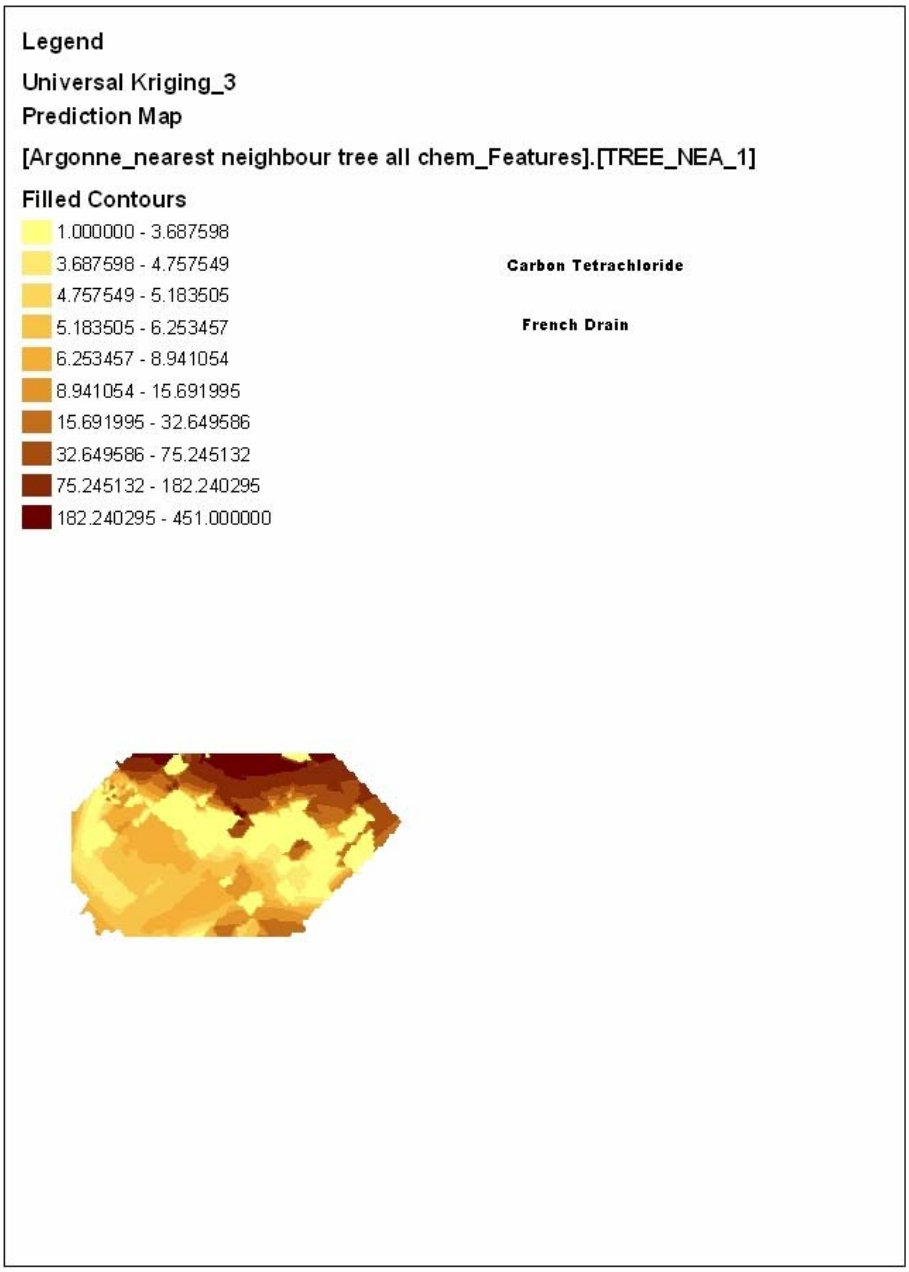

Figure 3-8. CCl_4 plume delineation in French Drain using willow and poplar data.

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