ABSTRACT

COOK, RACHEL LOUISE. Phytoremediation of a Petroleum-Hydrocarbon Contaminated Shallow Aquifer, Elizabeth City, NC: Planting Methods and Preliminary Results. (Under the direction of Dr. Elizabeth Guthrie Nichols.)

The US Coast Guard Support Center former fuel facility is a phytoremediation demonstration site for the US EPA and North Carolina Department of Environmental and Natural Resource's 319 Program. The primary project goal is to prevent petroleum contamination in soil and ground water from entering the adjacent Pasquotank River. Gasoline, diesel fuel, and jet fuel released from aboveground and underground storage tanks lie 1.2-2.1 meters below land surface. A free product recovery system, operated since 1991, was replaced beginning in 2006 with a phytoremediation system. Over 3,000 bare root or unrooted cuttings of hybrid poplars (*Populus spp.)* and willows (*Salix spp.*) were planted across the two hectare site. Here we report the effect of three different planting methods on tree growth and mortality from 2006 to 2008. Method 1 in April and June 2006 used a direct-push rig to auger 8 cm diameter, 1.2 m holes that were backfilled with the excavated, *in situ* soil; Method 2 in 2007 and 2008 used a Bobcat rig to auger 23 cm diameter, 1.2 m deep holes that were backfilled with clean offsite topsoil; and Method 3 in 2007 used a 1.3 cm diameter rod to punch shallow holes between 15 to 30 cm deep with no backfill. Plant mortality was determined for each method after each growing season. In early 2008, total stem length was measured for all planted trees (n=2,984). This information was incorporated with global position system (GPS) locations into a geographic information system (GIS) for analysis and monitoring. Trees planted using Method 1 in June 2006 experienced higher percent mortality and did not grow as well as trees planted using Method 1 in April 2006. Trees planted in April 2007 using Method 2 demonstrated better survival and growth than trees planted using Method 3. Some differences in mortality and growth were observed between the four different hybrid poplar clones planted with Method 2. Overall, planting early in the growing season, augering a larger diameter hole, and backfilling with uncontaminated offsite topsoil allowed for greater survival and growth.

Preliminary results regarding concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX) and methyl *tert*-butyl ether (MTBE) in ground water and masses of total

petroleum hydrocarbons (TPH), BTEX, naphthalene, and other constituents in soil gas indicate dissolved contaminants have slowed their migration towards the river and show significantly decreased levels after planting. The effect of planted trees on residual petroleum contaminants in the vadose zone will continue to be assessed over time by monitoring soils for all 42 alkylated and non-alkylated polycyclic aromatic hydrocarbons (PAHs). Specific ratios between select alkylated PAHs will be used to continue to monitor PAH-contaminant weathering. Ground water wells, soil gas wells, and soil collection locations as well as all planted trees were spatially referenced using GPS. Once integrated into GIS, we used interpolated values between contaminant sampling points to evaluate interactions between trees and subsurface hydrocarbon contamination. Several patterns are evident in the spatial analysis. Areas with the greatest subsurface contamination appear to have smaller trees and higher mortality, while cleaner areas have distinctly taller trees and greater survival. This observation is reinforced by comparison of soil total polycyclic aromatic hydrocarbon concentrations and tree total stem length. However, field conditions complicate correlations between contaminants and tree performance likely due to such variables as depth to water table, soil heterogeneity, tree viability, and differing planting methods.

Phytoremediation of a Petroleum-Contaminated
Shallow Aquifer, Elizabeth City, NC:
Planting Methods and
Preliminary Results

by
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BIOGRAPHY

Rachel Louise Cook was born February 3, 1983 in Murray, Kentucky to James Michael Cook and Louise McGee Cook. She spent most her childhood in Western Kentucky and later Southern Illinois where she learned the joys of farm life before leaving for the Illinois Math and Science Academy for high school. It was there that Rachel discovered her love for biology and research science and first learned about phytoremediation. She participated in a heron rookery observation inquiry, cared for the school greenhouse plants, and started a botanical survey in Iowa through the mentorship program.

Rachel enrolled at Saint Louis University in August 2001 where she majored in Biology and minored in Anthropology. She gained experience in the laboratory, greenhouse, and field through her work study. She infected soybeans with parasitic nematodes, extracted their DNA, and learned how to run and develop electrophoresis gels and western blots. For three consecutive summers, she traveled to Portal, Arizona to camp in the desert and collect data on granivorous ant populations. During her time there she studied abroad in Madrid, Spain and spent the following summer traveling Europe by train. The following summer she took the opportunity to study Cave Biology at the Reis Biological Station in the Ozarks of Missouri and went to Nicaragua to study primate ecology.

These experiences led Rachel to pursue a Master of Science degree at NC State University researching phytoremediation. Her time at NCSU has inspired a greater interest in environmental sustainability, bioenergy, and permaculture. She has discovered the joys of pottery, felting, and spinning through the NC State Craft Center. In her spare time she also likes to go rock climbing, garden, feed the chickens, or sit on the porch with good friends or a good book.

Rachel plans to pursue her PhD, but first will take a semester in Brazil to study ecosystem services, learn Portuguese, and work on organic farms.

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The Effect of Planting Method on Hybrid Poplar and Willow Mortality and Growth at a Petroleum-Hydrocarbon Contaminated Shallow Aquifer

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ABSTRACT

Establishment of a viable plant community is integral to the success of any phytoremediation system. Here we report the effect of different planting methods on tree growth and mortality for hybrid poplars (*Populus spp*.) and willows (*Salix sp*.), planted from 2006 to 2008 at a site with by petroleum-hydrocarbon and methyl *tert*-butyl ether contaminated soil and shallow ground water. Bare root and unrooted 1.2 to 1.8 meter cuttings were planted using three different methods: Method 1 in April and June 2006 used a direct-push rig to auger 8 cm diameter, 1.2 m holes that were backfilled with the excavated, *in situ* soil; Method 2 in 2007 and 2008 used a Bobcat rig to auger 23 cm diameter, 1.2 m deep holes that were backfilled with clean offsite topsoil; or Method 3 in 2007 used a 1.3 cm diameter rod to punch shallow holes between 15 to 30.5 cm deep with no backfill. Plant mortality was determined for each method after each growing season. In 2008, total stem length and mortality were measured for all planted trees (n=2,984). This information was incorporated with global position system (GPS) locations into a geographic information system (GIS) for analysis and monitoring. Trees planted using Method 1 in June 2006 experienced higher percent mortality and did not grow as well as trees planted using Method 1 in April 2006. Trees planted in April 2007 using Method 2 demonstrated better survival (lower percent mortality) and yearly growth than trees planted using Method 3. Differences in mortality and growth were observed between the four different hybrid poplar clones planted with Method 2. Overall, planting early in the growing season, augering a larger diameter hole, and backfilling with uncontaminated offsite topsoil allowed for greater survival and growth.

KEY WORDS: phytoremediation, hybrid poplars, willows, planting method, petroleum hydrocarbons

INTRODUCTION

Petroleum-hydrocarbon spills and leaks from above and below ground storage tanks contaminate soil and ground water with hazardous substances such as benzene, toluene, ethylbenzene, xylenes (BTEX), methyl *tert*-butyl ether (MTBE), and polycyclic aromatic hydrocarbons (PAHs). In particular, benzene and PAHs are listed on the U.S. EPA's CERCLA priority list of 275 Hazardous Substances (USEPA/ATSDR, 2007) as numbers six and eight, respectively. MTBE fouls drinking water and is classified as a possible human carcinogen (USEPA/OTAQ, 2008). Widespread contamination and associated potential toxicological risks that follow the release of these compounds to the environment require an effective and economical method of remediation.

Phytoremediation systems can be a successful, competitive, and cost-effective means of cleaning up soil and ground water contaminated by petroleum hydrocarbons (Aprill and Sims, 1990; Cunningham and Ow, 1996; Schnoor *et al.*, 1995; Corseuil and Moreno, 2001; O'Neill and Nzengung, 2004). The most likely mechanism for the breakdown of petroleum-hydrocarbon contamination using phytoremediation is by the plant-associated enhancement of contaminant degradation by soil microorganisms in the rhizosphere (rhizodegradation) (April and Sims, 1990; Anderson *et al.,* 1993; Rubin and Ramaswami, 2001; Chen *et al*., 2003; Maila and Randima, 2005; Widdowson *et al.*, 2005; Dietz and Schnoor, 2001). Vegetation promotes greater microbial abundance in the rhizosphere (Chaineau *et. al*., 2000; Crowley *et al*. 1996; Jordahl *et. al*., 1997) and can encourage a greater diversity of PAH-degrading microorganisms (Muratova *et al.*, 2003). The release of plant organic material enhances contaminant degradation of more labile contaminants and cometabolism of more recalcitrant contaminants (Schwab *et al*., 1995). Other mechanisms for organic contaminant dissipation linked to phytoremediation include: the uptake and metabolism of contaminants within the plant (phytotransformation); the transpiration of contaminants into the atmosphere (phytovolatilization) (Dietz and Schnoor, 2001); or sorption of contaminants onto subsurface organic matter (Chen *et al*., 2003).

Trees, especially poplars (*Populus spp.)* and willows (*Salix spp.)*, can effectively dissipate (or attenuate) fuel contaminants such as BTEX, MTBE, and some PAHs in contaminated ground water and soils (Burken and Schnoor, 1998; Hong *et al*., 2001; Ma *et al*., 2004; O'Neill and Nzengung, 2004; Rubin and Ramaswami, 2001; Widdowson *et al*., 2005). In addition to increasing rhizodegradation, plants can also promote upward movement of ground water during evapotranspiration, drawing contaminants into aerobic soil where they can be oxidized (Karthikeyan *et al.,* 2003). This is especially important for BTEX and MTBE because their half-life in aerobic environments is relatively short compared to saturated, anaerobic conditions (Morgan *et al.*, 1993). Evapotranspiration by poplars and willow trees also provides hydraulic control of contaminated ground water and can prevent further dispersion and migration of the subsurface contaminant plume (Hong *et al.,* 2001; Ferro *et al.,* 2001, Vose *et al.,* 2000, Landmeyer, 2001).

Integral to the success of these phytoremediation processes is the establishment of a viable plant community. One means to improve tree survival and growth is to determine which plant species or clonal varieties perform better under similar field conditions (Zalesny *et al.,* 2005a, Zalesny *et al.,* 2005b*)*. Another way to improve tree survival and growth is by the choice of planting methods. Appropriate practices such as soaking cuttings in water prior to planting, the time of planting, irrigation, weed control, and fertilization all can have significant effects on tree survival and growth (Hansen, 1986; McKnight and Biesterfeldt, 1968; Hoag, 1995). The presence of phytotoxic, hydrophobic conditions at most contaminated sites where phytoremediation may be used requires adaptation of typical tree planting practices to increase survival (Zalesny *et al.*, 2005a).

Resources such as GIS (Porter *et al.,* 2006) and databases such as Phytopet© (2008) can help determine appropriate plant selection; however, they do not provide information on planting methodology. Published field-scale studies often give sparse details about tree-planting methods used and do not always report growth and mortality. The Hazardous Waste Clean-up Information database (Clu-in), administered by the U.S. EPA, provides a section for a description of planting at phytoremediation field projects (Hazardous Waste Clu-in, 2008), but often a full account of planting methods is not provided. This database has the potential to be a great resource for phytoremediation planting techniques and their results.

A summary of planting methods, growth, and mortality for field-scale studies using poplars and willows is shown in Table 1. Some studies for chlorinated solvents were included because planting methods often are contaminant independent. These studies show a wide range of planting methods resulting in great variability in mortality and growth. Establishing rapidly growing, thriving tree stands, with their rhizosphere-associated bacteria, is the most important prerequisite to the long-term degradation of petroleum contaminated soil and ground water (Zalesny *et al.*, 2005a). Additional studies are needed to establish appropriate planting methods and silvicultural practices for climatic, soil, water, and contaminant conditions on a regional basis.

This paper reports the results of three different planting methods developed successively during the implementation of a field-scale phytoremediation demonstration site contaminated with weathered, petroleum-hydrocarbons and free-product fuels in the vadose zone and ground water. A phytoremediation system was designed with the primary objective to prevent further migration of contaminated ground water off site towards the Pasquotank River by using trees to hydraulically retard ground water movement towards the river and decrease on-site recharge. A second objective was to enhance biodegradation of residual petroleum in the contaminated soil and ground water via rhizodegradation. To achieve this, a tree plantation was established.

This paper reports the results of planting methodologies used to establish a phytoremediation system. We report tree survival, tree growth, and cost effectiveness of each planting method during the first three years of project implementation (2006 to 2008). This field study was not designed to specifically test planting methods, but results should be of use to future phytoremediation efforts.

MATERIALS AND METHODS

Site Description. The study site is a former fuel storage facility at the US Coast Guard Support Center, Elizabeth City, NC (Figure 1). From 1942 to 1991, aboveground and underground storage tanks for aircraft refueling were located at this five-acre site (Figure 2A) 150 meters south of the Pasquotank River (Figure 2B). Leaks from these storage tanks have contaminated the soil and shallow ground water. An estimated 153,000 gallons of free-product, *i.e.* gasoline, diesel, and aviation jet fuel, remain at the site based on monitoring well measurements (ARCADIS, 2006). Benzene and MTBE concentrations in the groundwater were as high as 2,100 μg/L and 2,500 μg/L, respectively (ARCADIS, 2006). The most contaminated areas contain up to 85 cm of free-product floating above the water table (ARCADIS, 2006). Depth to water table can range from 61 to 335 cm depending upon well location (ARCADIS, 2006) and season.

Soil Characterization and Analysis. The soil is classified as Udorthent, loamy with 0-2% slope from 0-80cm (USDA/NRCS, 2007). Parent material is classified as loamy mine spoil or earthy fill and is well drained. Fill dirt has raised the elevation of the site to an average of three meters above mean sea level (NC State Climate Office, 2008). Native, fine gray clays and sand can be found approximately one meter below land surface.

To test for soil characteristics, soil was collected according to the procedures of the North Carolina Department of Agriculture and Consumer Services (NCDA&CS, 2008) and analyzed by the Agronomic Division. Triplicate soil samples were collected at 60 cm depths at three different locations across the site. Samples were sieved through a two millimeter screen, homogenized with a mortar and pestle, combined for each location, and submitted for analysis according to NCDA&CS protocol. The soils were classified as mineral soils with cation exchange capacities ranging from 4.7 to 11.7meq/100cm^3 (milliequivalents per cubic centimeter), percent humic matter from 0.18 to 0.32, and pH from 6.2 to 7.3. Hand augered soil profiles to a depth of 1 to 1.5 m and analytical results have shown great soil heterogeneity across the site, most likely due to backfilling and soil movement during construction and deconstruction of underground storage tanks, treatment systems, pipelines, and utilities.

Plant Selection. Phreatophytic trees, such as willows and poplars, can reach and extract water from the capillary fringe or saturated zone and are beneficial for ground water contaminated with biodegradable organics (Dietz and Schnoor, 2001; Landmeyer, 2001; Collins, 2007). Hybrid poplars (*Populus deltoides* Bartram ex Marsh. *x nigra* L.) were selected for their deep root systems, rapid growth, high water uptake rates, tolerance to contaminants, and well-documented success in phytoremediation systems (Ferro *et al.*, 2001; Widdowson *et al.*, 2005; Vose *et al.*, 2000; Hong *et al.*, 2001, Zalesny *et al.*, 2005b). Black, coyote, and sandbar willows (*Salix nigra*

Marsh., *Salix interior* Rowlee, and *Salix exigua* Nutt.*)* were selected for general tolerance for saturated conditions, ability to rapidly produce adventitious roots (Schaff *et al.*, 2002), and success in removing gasoline and PAHs from ground and surface waters (Corseuil and Moreno, 2001; O'Niell and Nzengung, 2004; Vervaeke *et al*., 2003). Planting unrooted cuttings is the standard method of propagating poplars and willows, because they are inexpensive to produce and easy to handle (Hansen, 1986; Zalesny *et al*., 2005a; Vose *et al*., 2000; Hoag, 1995; Schaff *et al.*, 2002).

Planting Methods. Planting methods over the three-year installation period were modified and adapted based on mortality or slow growth of trees and additional site characterization (i.e. soil-gas analyses). Commercial hybrid poplar cuttings, approximately one meter in length, included clones DN-34, OP-367, 49-177, and 15-29, and coyote or sandbar willows cuttings were obtained from Segal Ranch Hybrid Poplars© Grandview, WA. In 2007, in addition to the four poplar hybrids, black willows were also purchased from the Coastal Plain Conservation Nursery, Edenton, NC.

All cuttings were soaked, upright in less than 30 cm of clean water for approximately one week prior to planting for each method to increase adventitious rooting, survival, and growth rates (Hansen, 1986; Hansen *et al*., 1993; Schaff *et al*., 2001). Soaked cuttings should be planted within a day or two of the initial root emergence (Hansen, 1986). Once root primordia start to swell, respiration increases dramatically and if cuttings are not planted promptly, their stored energy reserves will be drained (Phipps *et al*., 1983).

Method 1. In the first year of planting (2006) a direct-push rig augered 8 cm diameter, 1.2 m deep holes that were backfilled with excavated, *in situ* soil once trees were placed in the borehole. All trees were mulched around the base. The same method was used for two separate phases of plantings in 2006: April 25th consisted of 114, 1.2 m long bare root poplars; June 5th & 6th consisted of 403, 1.2 m unrooted poplar and willow cuttings (Figure 3). All of these trees were planted on three meter centers.

Method 2. In the second year (2007) two new methods were used to plant the remainder of the site. From April 9-13th, 2,123 poplars, 43 willows, and 10 rooted loblolly pines were planted using a labor-intensive method consisting of augering larger, 23 cm diameter holes to a depth of 1.2 m, and backfilling with clean topsoil. Fourteen poplars in the Method 1, April area and 221 trees in the Method 1, June area were replaced using Method 2 as well. All trees were heavily mulched after planting to help control weeds. 1.2 m cuttings of the same four hybrid poplar clones were planted in four main sections with OP-367 repeated in one smaller section (Figure 4).

Method 3. On April 19th & 24th, 2007, an alternative, low cost, common planting method (Hansen *et al.,* 1993) was used to plant 65 poplars and 208 willows. A dibble was used to create a hole, 15 to 30 cm deep, with just enough diameter to insert a cutting, often called a "planting slit" (Frances and Hollis, 1988). Air gaps were filled by pushing soil against the cutting; no backfill was needed. Poplar clones and willows were planted at random with this method. All 2007 trees, both Method 2 & 3, were planted on a two meter center grid.

Stand Maintenance. While several studies have used composted manure or other organically rich soil amendments when plantings trees (Table 1), no nutrient amendments or irrigation were used in this study. The site is mowed regularly to control grass and weeds. Providing adequate weed control is of utmost importance for establishment of hardwoods (Hansen, 1986; Hansen *et al*., 1993) regardless of contamination. In fact, Zalesny *et al*. (2005a) found that poplar clones survived equally well on contaminated soil with proper weed control as they did on heavy clay soils with poor weed management. Additionally, proper row spacing facilitates better weed management and easier replanting by allowing equipment to maneuver without damaging trees.

Tree Mortality and Growth. Tree mortality was determined after the 2006 and 2007 growing seasons. In early 2008, all 2,984 tree locations were mapped using global positioning systems (GPS) and mortality was integrated with GPS information as well as species and/or clone variety. Surviving trees were measured for total stem length. To measure total stem length, all major stems were measured by hand from the base of the cutting to the apical bud (to the nearest 1.0 centimeter) and totaled for each living tree. Total stem length was measured, as opposed to height, to better represent tree growth. Simple height measurements do not account for the difference between trees which have only one tall stem versus many shorter stems. All field measurements and GPS locations were incorporated into a GIS database for monitoring and analysis of percent mortality and mean total stem lengths.

Soil Gas Analysis. Soil gas sampling and analysis were performed by W.L. Gore and Associates, Inc. of Elkton Maryland. Sixty-eight GORE™ passive sampling modules were placed in permanent soil gas monitoring stations consisting of 2.5 cm diameter, 75 cm long slotted PVC screens installed in borings of the same diameter and depth. These stations were located on 30 m centers for consistent, repeated sampling. Analysis reports a quantitative measurement of soil gas mass levels present in the vapor phase underground in the vicinity of the sample location. This vapor phase can be released from either soil or ground water contamination (ARCADIS, 2006; GORE™, 2007).

RESULTS AND DISCUSSION

Tree Mortality and Planting Methods

Substantial differences in mortality were observed for different planting methods and between tree species and/or clones within a specific planting method (Table 2). Comparatively low mortalities were observed for trees planted using Method 1 in April 2006 after the first growing season (12%) and in 2007 after the second growing season (11%). Recall that any dead trees from Method 1 plantings were replaced with trees using Method 2 during the second planting season. The lower mortality (compared to Method 1 June 2006) may be due to the fact that the area planted by Method 1 in April contains less TPH mass than the area planted in June according to the Gore™ soil gas map (Figure 2B). Low total mortality (13%) was also observed overall for trees planted using Method 2 (Table 2, Figure 4). Willow trees were interspersed throughout the Method 2 planting area, and they had the lowest mortality overall at 7%, though the number planted was considerably less (n=43) than poplars (n=2,123). Hybrid poplar clonal mortality ranged as follows: 9% for DN-34, 12% for 49-177, 15% for 15-29, and 16% for OP-367 (Table 2; Figure 4, shades of green). Percent mortality was equal for both OP-367 sections. The area planted using Method 2 encompasses most of the site and represents a large gradient of contamination (Figure 2B). A cluster of dead trees mainly in the larger OP-367 section (Figure 4) is clustered around the most contaminated soil gas well (GORE™, 2007) and is visually associated with one of the two former fuel bunkers (Figure 2A). This may explain the greater mortality of OP-367 clones for that particular area. The clean backfill likely contributed to greater survival success than refilling augered holes with contaminated, *in situ* backfill, as was done in Method 1. More research needs to be done to find an optimal backfill for phytoremediation systems.

Higher mortality (55%) was observed in the later June 2006 planting using Method 1. Unrooted cuttings planted in June using Method 1 had 49% mortality for willows and 57% mortality for hybrid poplars. Poplar clonal mortality ranged as follows: 42% for DN-34, 52% for OP-367, 64% for 49-177, and up to 67% for 15-29 (Table 2; Figure 3 outlined in dark purple). Visual inspection of the TPH soil gas map in Figure 3 (inset) shows this area to contain high masses of TPH. Differences in mortality data and TPH soil gas data between this area and the April 2006 area would suggest that use of 8 cm augered holes backfilled with excavated, *in situ* soil was acceptable for the less TPH contaminated area (April 2006) but problematic for June 2006 area that contains greater TPH contamination. In addition, excavated, *in situ*, backfill used in Method 1 was often barely enough to refill the holes due to the fact that much of the soil remained trapped in the grass onto which it had been excavated. Dead trees in the Method 1 area were replaced using Method 2 in 2007. Overall mortality was reduced for willows and poplars in this area to 28% after one year (Figure 4, dark purple background). Thus, increasing the size of the augered hole to 23 cm and backfilling with clean topsoil helped reduce mortality in the June 2006 area the following year.

The greatest total mortality (89%) for willows and poplars was observed in the area planted by Method 3, or by the dibble/planting slit method (Figure 4, orange background). This method is widely used to plant trees for fuel and fiber production in non-contaminated conditions (Hansen *et al.,* 1993). At this site, mortality for willows was 97% and 63% for poplars. The significant mortality prevented determination of specific poplar clones due to indistinguishable “dead stick” phenotypes. Trees in Method 3 were immediately surrounded by compacted and contaminated soil instead of loose, clean backfill and not planted as deeply as other previous methods. This combination of factors, based on mortality results, proved Method 3 an unacceptable method for phytoremediation planting.

Mortality in comparable phytoremediation studies have ranged anywhere from 0 to 90% (Table 1). Zalesny *et al.* (2005a) reported mortality ranging 0 to 74% across reps, genera, and cutting length for poplars and willows. They deemed the experiment wide mean mortality rate of 33% reasonable considering the hypoxia from periodic flooding and highly contaminated soils (25% petroleum-hydrocarbon by weight). Braun *et al.* (2004) found a 25% mortality rate in poplars planted over a TCE plume when ground water levels were three meters or shallower. However when groundwater dropped to 3.7 to 4 m from ground surface, mortality increased to 90%. Success of tree establishment can be directly related to contact with the low water table (Hoag, 1995). In riparian vegetation management, *Populus spp.* and *Salix spp.* mortality rarely exceeds 35%, even in extreme drought when deeply planted (Hoag, 1995). Coincidentally, 2007 was a year of extreme drought for this area of North Carolina with annual precipitation of 25.58 inches, 18.22 inches below normal (NOAA, 2008). Yet, mortality remained 16% or less for willows and poplars planted by Method 2. These results show that tree performance at phytoremediation sites can be highly variable depending on climate, site characteristics, planting methods, clones, and contaminant levels.

Total Stem Length and Planting Methods

Each surviving tree was measured for total stem length in January and February 2008; thus, results represent the entire population of trees at the site. Tree growth varied dramatically across the site and followed patterns similar to mortality. Trees planted by Method 1 in April 2006 grew larger than trees planted by Method 1 in June 2006 with 2-yr-old mean total stem lengths of 565 ± 340 cm and 363 ± 245 cm, respectively (Table 2). Trees planted in April were rooted while trees planted in June were unrooted. However, over time, Vose *et al.* (2000) found no apparent advantage over planting whips versus 1-yr-old trees so it is not likely that planting rooted versus unrooted cuttings necessarily impacted tree growth. However, rooted trees in small diameter holes did sometimes create air pockets which may have contributed to some mortality. Slower growth observed for trees planted in June may reflect higher TPH contamination in onsite soils used for backfill (Figure 2B). The later timing of planting also likely affected tree growth. Hansen (1986) found that poplar tree height declines when planting occurs later in the summer, or after soil has reached the optimal planting temperature of 10^{o}C.

Overall mean total stem length for trees planted by Method 2 (229 ± 143 cm) was greater than trees planted by Method 3 (163 ± 93 cm). Poor growth in Method 3 was mostly likely caused by the same factors affecting mortality: lack of loose, clean backfill and shallow planting depth during a drought year.

Total stem length varied a great deal for species and clones between each planting method with an average relative standard deviation of 51% $\underline{+}$ 16. The least amount of variation in tree growth was observed for willows (17%) and poplars (39%) planted by Method 3 due to the high mortality of most of these trees and very poor growth.

Stem lengths for willows planted by Method 2 were less variable (48%) than willows planted by Method 1 in June (60%). Stem length variability among all poplar clones planted by Method 2 was 62% which is lower than poplars planted by Method 1 in June 2006 (68%) and similar to poplars planting in April by Method 1 (60%).

Comparison of median growth between all four poplar clones in Method 2 shows very similar performance (Table 2 & Figure 5). However, while all the median total stem lengths fall very close together, several individual OP-367 trees outperformed all other 1-yr-old trees. This exceptional growth contributes to greater variability of total stem lengths observed for OP-367 clones (78%). The reason for the above-average performance by some OP-367 trees is still unclear. 15-29 and 49-177 clones had similar variations in stem lengths of 44%, while DN-34 clones had slightly greater variability of 54%.

The variability of stem lengths follows similar patterns to observed mortalities among planting methods across the site. The more consistent stem lengths by Method 2 may indicate this method provided more consistent initial growing conditions for trees and therefore better survivability.

Caution must be taken when comparing tree performance of clones and species across this site. While certain trends appear to be an obvious result of planting methods (Method 2 versus Method 3), results will also be affected by large variations in concentrations of petroleum contaminants (Method 1 April versus June), variations in depth to water table (Braun *et al.*, 2004), and variations in soil quality and heterogeneity, among other factors. In addition, the survival and growth of the tree can also be affected by 1) the diameter of the cutting, by providing the cutting with a reserve of energy (Hansen, 1986), and 2) the area from which it was cut from the parent tree (apical, middle, or basal section), by influencing quantity of rooting hormone (Zalesny *et al*., 2003). Understanding tree performance across a highly variable site can be difficult when confounded by genotype and environmental interactions (Zalesny *et al.*, 2005b). Further studies will be required, with more appropriate planting design to control variables, to better elucidate whether planting factors or contaminants most strongly influence tree growth and mortality.

Cost Analysis of Planting Methods

Cost effectiveness is often cited as a major incentive for using phytoremediation systems (Cunningham *et al.*, 1997; Glass, 2000). While the overall cost of phytoremediation is small compared to engineering systems, planting costs may be a consideration in method selection depending on the budget and/or time scale of the project. Choice of plants (rooted versus unrooted), required time, materials, equipment, and labor intensity must be balanced with acceptable initial survivability. Method 3 proved to be the most cost effective method in the initial planting at the unit price of the cutting ($1.15). Although Method 3 is certainly the least expensive and the most rapid method to plant trees (Figure 6), the high mortality (89% overall) clearly shows this method was not successful at this site.

Method 2 cost substantially more due to extra labor and equipment to auger 23 cm diameter, 1.2 m deep holes that were backfilled with clean topsoil; the total cost per tree for Method 2 was approximately $12/cutting ($26,892/2,166 trees; Figure 6). The cost of the cuttings and estimated cost of rental of a direct-push rig for Method 1 was approximately $9/cutting ($4,600/517 trees; Figure 6). Labor costs do not include researchers time, only additional hired labor.

At this site, a greater expenditure of time and energy in initial planting, especially in areas of higher contamination, proved to be a worthy investment in terms of growth and survival (Figure 6). Method 2 did show greater survival than the Method 1, June planting, but similar mortality was observed for the Method 1, April 2006 planting in the lowest TPH contaminated area (Table 2). Initial planting and replanting costs, survival, growth, and levels of contamination must all be considered when determining which planting method is most appropriate for any site. Regardless of the method employed, appropriate care must be taken when planting tree cuttings. Poor handling of cuttings can limit root development (Zalesny *et al*., 2003) and therefore affect chances of survival. Cuttings must be kept wet during planting and never left in direct sun or wind or new roots and leaves can be damaged from drying (Hansen *et al*., 1993; Phipps *et al*., 1983). In addition, only one bud should be left above ground, pointing upwards (Hansen *et al*., 1993), to allow for more vigorous root development, the first biological requirement for healthy stand establishment (Zalesny *et al*., 2005a). Promotion of root growth can help cuttings survive drought stress (Schaff *et al*., 2001; Phipps *et al*., 1983).

CONCLUSION

We found that augering large (23 cm diameter x 1.2 m deep) boreholes and backfilling with clean topsoil proved to be most effective for tree growth and survival under the petroleum-hydrocarbon contaminated conditions investigated. Common phytoremediation tree planting practices generally include either trenching or augering boreholes. The diameter, depth, soil characteristics of backfill, fertilization, and irrigation are all variables that need further study to optimize planting success. While some of these variables will be tree species and site specific, accepted protocols for tree planting would be beneficial to phytoremediation system designers.

Professionals, such as foresters, arborists, and other horticultural specialists, can be a valuable resource to engineers, hydrogeologists, or other environmental professionals not familiar with vegetation management. However, traditional forestry or horticultural techniques may require modification to adapt to contaminated, site-specific conditions. Attention to planting methods and plant care impacts the success of a phytoremediation project. Survival is a prerequisite for success. Creating healthier soil environments around cuttings to enhance initial survival and growth can promote more rapid stand establishment. Field-scale studies that report growth, survival, and cost are needed to establish more effective plantings methods for contaminated soil and ground water in phytoremediation projects.

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Figure 1 Satellite image of the former fuel farm and the aboveground tanks of the current fueling station [C]. The field site (orange outline) is located approximately 150 meters from the Pasquotank River.

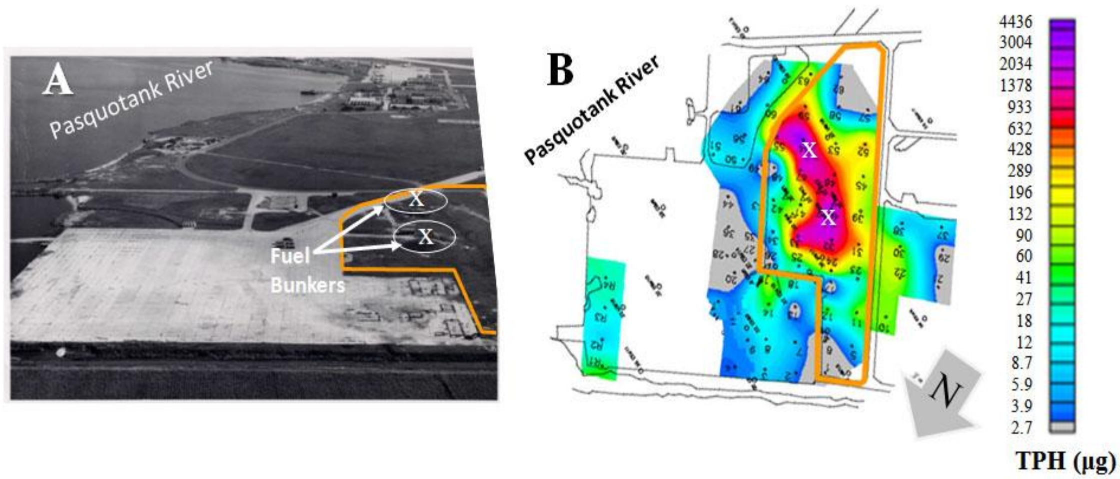

Figure 2 (A) Location of fuel storage areas in 1942 at the Former Fuel Farm Site, US Coast Guard Support Center, Elizabeth City, NC. **(B)** Soil gas analyses show greater Total Petroleum Hydrocarbon (TPH) mass (µg) in areas of former fuel bunkers (W. L. Gore and Associates, Inc., 2007). Note: Map turned upside down to match Figure 2A orientation.

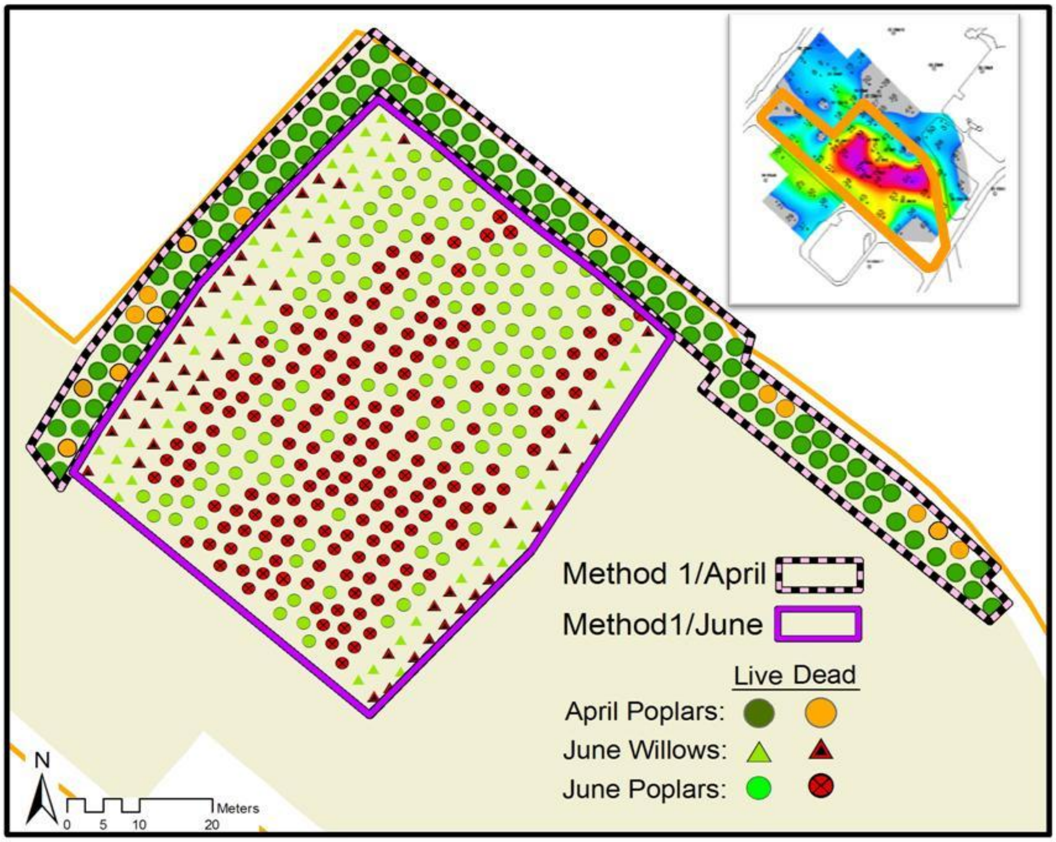

Figure 3 Mortality after 2006 growing season for willows (triangles) and poplar clones (circles) using planting Method 1 in April and June 2006. Red/orange circles indicate dead trees; green symbols indicate living trees. Mortality for April, Method 1 planting was 12% (all poplars) and for June, Method 1 was 57% (poplars) and 49% (willows).

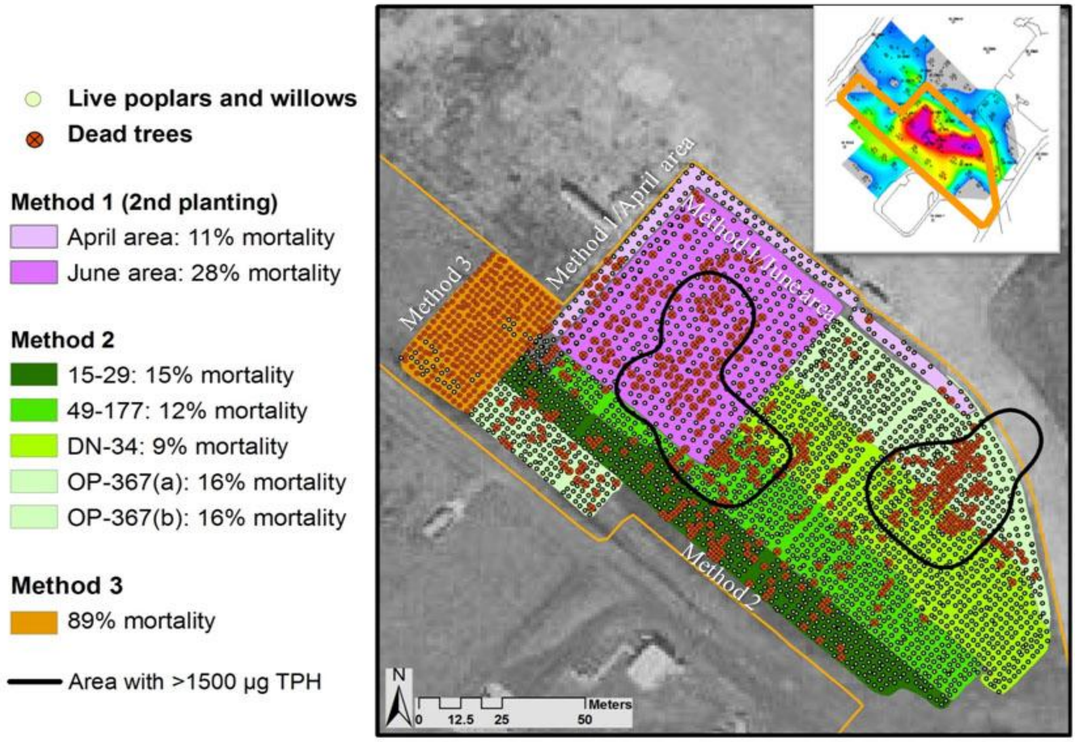

Figure 4 GPS map of tree mortality after 2007 growing season. Black contour lines indicate areas of soil gas TPH mass greater than 1500μg. Each dot indicates a GPS location for every tree and whether trees were alive (green) or dead (red) in 2007.

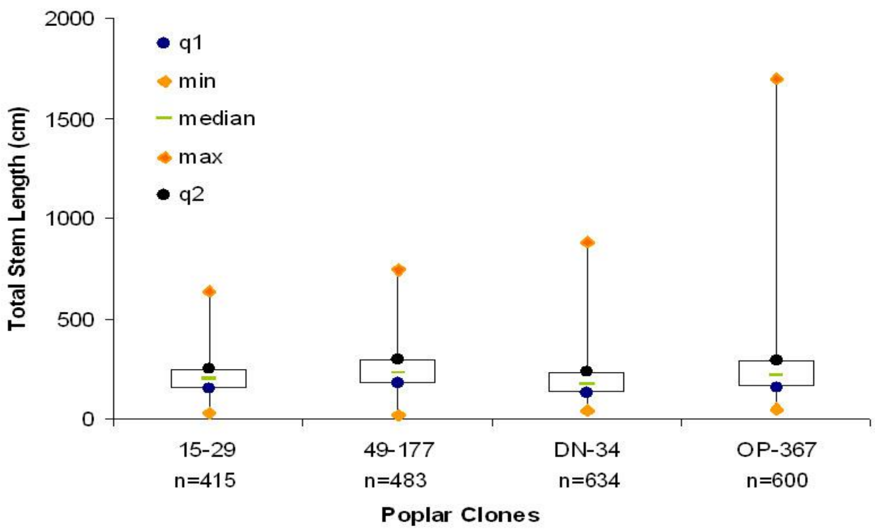

Figure 5 Box plot of total stem length medians, minimums, maximums, and first and third quartiles after one year of growth for hybrid poplar clones planted by Method 2.

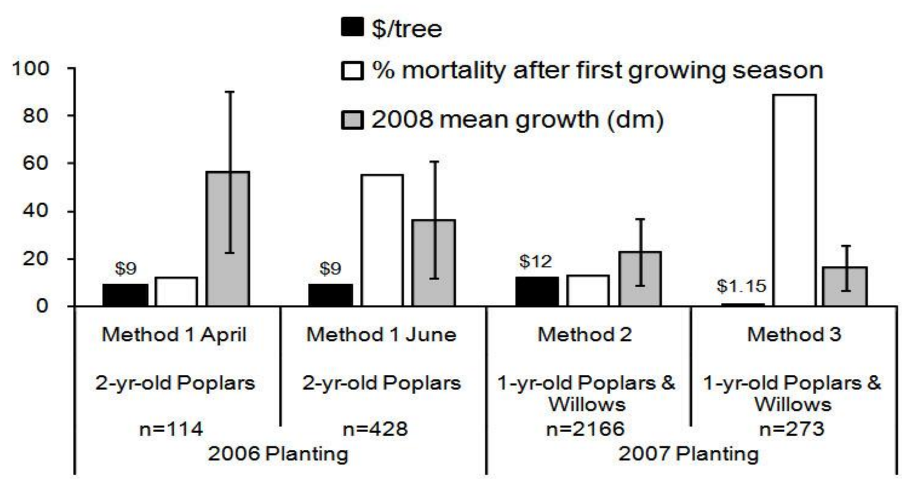

Figure 6 Comparison of cost per tree, tree mortality (after first growing season), and mean tree growth (February and March 2008) for each planting method.

Table 1 Review of published studies and planting methods for phytoremediation of petroleum hydrocarbons or chlorinated solvents using trees.

Site	Contaminant	Plant Species	#/Type Planted	Mortality	Growth	Method	Backfill	Reference
Ogden, UT	Petroleum hydrocarbons	Hybrid Poplars	40 9ft poles	No data	3yr ht= 7.9m	10in diameter x 8ft deep boreholes	Sand, compost, nutrients	Ferro *et al.*, 2001
Fort Worth, TX	TCE	Poplars	440 whips/ 224 seedlings	25-30% Up to 90%	3yr ht= 5.5-6.6m	1m deep x 1.2m wide trenches	Excavated, *in situ*	Braun *et al.*, 2004; Vose *et al.*, 2000
Belgium	PAH/ mineral oil	Willows	2m rods	48% (338,000 shoot/ha decrease)	2yr= 417,000 shoots/ha	Horizontally inlaid cuttings (SALIMAT)	Dredged sediment	Vervaeke *et al.*, 2003
Oneida, TN	PAH/ creosote	Hybrid Poplars	1146 2-3yr trees	No data	3yr ht= 4.89 m	No data	No data	Widdowson *et al.*, 2005
Gary, IN	Petroleum hydrocarbons	Poplars Willows	500 20&60cm cuttings	0-75% Ave=33%	1yr= 14-72cm	7.62cm diameter x 17 or 56 cm deep	Clean sand	Zalesny *et al.*, 2005
Orlando, FL	TCE/ PCE	Poplars Willows	2000 whips	No data	6mo ht= 5.5m	1.8m deep boreholes	Composted media	Rockwood *et al.*, 2004
Houston, TX	MTBE	Hybrid Poplars	100 whips	No data	1yr ht= 2.7m	1ft diameter x 6-9ft deep boreholes	60% sand 40% mulch & fertilizer	Hong *et al.*, 2001
Athens, GA	Gasoline	Willows	290 2m cuttings	No data	2yr ht= 6m	20cm boreholes	Composted peanut shells and manure	O'Neill and Nzengung, 2004

Note: Poles and rods tend to be more rigid and larger than whips. All types of cuttings are vegetative propagations.

Table 2 Percent mortality and mean total stem length (cm ± one standard deviation) for each tree planted by one of three different methods. Hybrid poplars are broken down into mortality and growth for each clone planted. Method 1 stem length only includes 2-yr-old trees.

			2006		2007		
	Date planted	**Tree type**	**# trees**	**% mortality**	**# trees**	**% mortality**	**Mean stem length (± 1 sd)**
Method 1[a]	Apr 2006	Poplars	114	12%	114	11%	565 ± 340
	Jun 2006	Willows	102	49%	55	33%	151 ± 91
		Poplars	301	57%	373	27%	363 ± 245
		OP-367	60	52%	----	----	----- -----
		DN-34	64	42%	----	----	----- -----
		49-177	61	64%	----	----	----- -----
		15-29	60	67%	----	----	----- -----
		Total	403	55%	428	28%	232 ± 164
Method 2[b]	Apr 2007	Willows			43	7%	176 ± 85
		Poplars			2123	13%	231 ± 143
		OP-367			600	16%	264 ± 207
		DN-34			634	9%	198 ± 108
		49-177			483	12%	251 ± 110
		15-29			415	15%	212 ± 94
		Total			2166	13%	229 ± 143
Method 3[c]	Apr 2007	Willows			208	97%	321 ± 53
		Poplars			65	63%	124 ± 48
		Total			273	89%	163 ± 93

[a] 8 cm diameter x 1.2 m deep hole backfilled with excavated *in situ* soil.
[b] 23 cm diameter x 1.2 m deep hole backfilled with clean offsite topsoil.
[c] 1.3 cm diameter x 15 to 30.5 cm deep hole with no backfill.

Phytoremediation of a Petroleum-Hydrocarbon Contaminated Shallow Aquifer, Elizabeth City, NC: Preliminary Results

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ABSTRACT

The US Coast Guard Support Center former fuel facility is a demonstration site for the US EPA and North Carolina Department of Environmental and Natural Resource's 319 Program. The primary project goal is to prevent petroleum contamination in soil and ground water from entering the adjacent Pasquotank River. Residual gasoline and fuel oil from aboveground and underground storage tanks exist in the vadose zone, 1.2-2.1 meters below land surface. A free product recovery system, operated since 1991, was replaced in 2006 and 2007 with a phytoremediation system. Over 3,000 hybrid poplars (*Populus spp*.) and willows (*Salix spp.*) were planted over the five acre site. Benzene, toluene, ethylbenzene, and xylenes (BTEX) and methyl *tert*-butyl ether (MTBE) concentration data in ground water and soil-gas samples appear to have slowed subsurface contaminant migration towards the river and decreased the contaminant levels in the soil and ground water in the planted area. The effect of planted trees on residual petroleum constituents in the vadose zone will continue to be assessed over time by monitoring soils for all 42 alkylated and non-alkylated polycyclic aromatic hydrocarbons (PAHs). Specific ratios between select alkylated PAHs will be used to continue to monitor PAH-contaminant weathering. Ground water wells, soil-gas wells, and soil collection locations as well as all planted trees were spatially referenced using global positioning systems (GPS). Each tree was inventoried for mortality or total stem length and species. Tree measurements and contamination data have been integrated into a mapping database through a geographic information system (GIS). Using interpolation in GIS, we examine relationships between contaminants and tree growth to evaluate interactions between trees and subsurface hydrocarbon contamination at this site. Several patterns are evident in the spatial analysis. Areas with the greatest subsurface contamination appear to have smaller trees and higher mortality. Field conditions complicate correlations between contaminants and tree performance due to such variables as depth to average water table, soil heterogeneity, tree viability, and differing planting methods.

KEYWORDS: phytoremediation, hybrid poplars, willows, pines, BTEX, MTBE, PAH, GIS, spatial autocorrelation

INTRODUCTION

Across the nation, over 478,000 underground storage tank (UST) releases have been confirmed as of March 31, 2008 with 107,000 still requiring clean up (USEPA/UST, 2008). In North Carolina, there are currently 16,247 regulated and 6,865 nonregulated UST sites. The state of North Carolina pays $7.6 million annually for commercial claims (ASTSWMO, 2008) and the average cost of clean-up per site was $121, 950 (ASTSWMO, 2008). The prevalence of this environmental contamination requires effective, yet less expensive means to relieve financial pressure on UST Trust fund dollars, ensure remediation, and protect public health and ground water resources.

Phytoremediation, the use of plants to clean up environmental contaminants such as petroleum hydrocarbons, currently is not approved for reimbursement by the UST Trust Fund. Therefore, few incentives are in place to explore this promising technology. The purpose of this project is to demonstrate the feasibility of using a phytoremediation system in North Carolina to 1) provide hydraulic control and prevent off-site migration of petroleum-hydrocarbon contaminated ground water and 2) to stimulate the *in-situ* biodegradation of the contaminants.

Located outside of Elizabeth City, NC on a US Coast Guard Support Center, the demonstration site consists of approximately two hectares surrounding a former fueling facility (FFF) operated from 1942-1991 that has been contaminated from leaking above and underground fuel storage tanks. Soil and ground water contaminants include benzene, toluene, ethylbenzene, and xylene (BTEX), methyl tertiary-butyl ether (MTBE), and polycyclic aromatic hydrocarbons (PAHs). Each of these contaminants poses significant environmental and health risks as well as challenges for remediation.

Contaminants. BTEX compounds are volatile organics that make up approximately 18% of gasoline and are most often found in the groundwater due to spills or leaking storage tanks. Of the four compounds in BTEX, benzene is the most harmful to human health. Long-term exposure affects bone marrow, causing a decrease in red-blood cell count and can affect the immune system or even lead to anemia and acute myelogenous leukemia, a cancer of the blood-forming organs (ATSDR, 2007). The other constituents of BTEX also present harmful health effects. Toluene may affect the nervous system and kidneys, but is not currently classified as a carcinogen, ethylbenzene may cause cancer in humans, and it is currently unknown if xylene causes cancer.

While fuels are primarily comprised of petroleum hydrocarbons (Douglas *et al*., 1996), MTBE can make up to 15% of gasoline composition (Suflita and Mormile, 1993). MTBE was introduced as a fuel-oxygenate to improve octane ratings in the late 1970's in the U.S.A. when alkyl lead additives were phased out (Johnson *et al*., 2000). In 1990, U.S. Clean Air Act Amendments caused increased use of MTBE in gasoline blends to reduce emissions and improve combustion of gasoline hydrocarbons (Ma *et al*., 2004). More complete combustion of gasoline hydrocarbons results in reduced hydrocarbon emissions from vehicles reducing the formation of ozone. Unfortunately, MTBE is now a common groundwater contaminant due to frequent gasoline spills and leaks from storage tanks. In groundwater, MTBE is essentially non-biodegradable and non-reactive with a half-life of two years (Suflita and Mormile, 1993). MTBE is generally found at the leading edge of a gasoline contaminant plume due to its high solubility and low retardation (Ma *et al*., 2004). MTBE is a known carcinogen to animals, and is currently classified as a possible carcinogen to humans by the EPA (USEPA/OTAQ, 2008).

PAHs constitute less than two percent of the bulk composition of fuels (Douglas *et al*., 1996), but are the most recalcitrant of the petroleum-based contaminants and of particular concern to human and environmental health because of their toxic, carcinogenic, and mutagenic properties (Lowe and Silverman, 1984; Szentpaly, 1984; Collins *et al*., 1998). PAHs are commonly found in the environment from industrial processing, petroleum spills, and incomplete combustion of fuel (Chefetz *et al*., 2000). They naturally occur in coal, coal tar, creosote soils, oils mists, and pitches formed from distillation of coal tars (ATSDR, 1996). More cost effective methods to remove PAHs from soils are needed considering they are found at 600 of the 1,408 National Priority List hazardous waste sites (ATSDR, 1996).

Treatment System. To remove these contaminants, the site was managed from 1991-2006 with a free product recovery system, pumping gasoline, diesel, and aviation jet fuel out of the ground water to control migration of the plume at the cost of $30,000 per year with an indefinite time span (ARCADIS, 2006). This technology did not address or remove recalcitrant PAHs. Phytoremediation was chosen as a Best Management Practice to provide an effective, economic alternative. Installation of the new phytoremediation system, including trees, labor, and equipment rental cost approximately $36,000 to install (including materials, equipment rental, and extra hired labor) and will only require mowing for weed control until canopy closure. This system should promote biodegradation and prevent off-site migration of contaminants into the Pasquotank River, located only 150 meters north. While phytoremediation is not appropriate for every site, it can provide a low cost, long-term, visually aesthetic, and effective remediation system. Commonly cited benefits to using phytoremediation besides lower cost include 1) greater public acceptance and aesthetic appeal, 2) avoidance of the need to transport contaminants which creates the risk of generating toxic air emissions, and 3) the process is solar-powered and requires very little energy input (Cunningham and Ow, 1996; Kuiper *et al.,* 2004).

Studies have shown that trees in particular can be effective in cleaning up ground water and soils contaminated with BTEX, MTBE, and PAHs (Burken and Schnoor, 1998; Hong *et al*., 2001; Ma *et al*., 2004; O'Neill and Nzengung, 2004; Rubin and Ramaswami, 2001; Widdowson *et al*., 2005). Hybrid poplars (*Populus deltoides* Bartram ex Marsh. *x nigra* L.) have shown great success in phytoremediation systems because they grow quickly, can have deep root systems, are easy to propagate, have high water uptake rates, and are tolerant to a variety of contaminants (Ferro *et al.,* 2001; Widdowson *et al.,* 2005; Vose *et al.,* 2000; Hong *et al.,* 2001, Zalesny *et al.,* 2005). Poplars have been used to remediate sites contaminated with nitrates, salts, landfill leachates, heavy metals, pesticides, solvents, explosives, and radionuclides (Zalesny *et al.,* 2005 and references therein). Willow trees (*Salix spp.)* have also shown success in removing gasoline from soil and groundwater (O'Neill and Nzengung, 2004; Corseuil and Moreno, 2001; Yu and Gu, 2006; Vervaeke *et al.,* 2003). These trees are often preferred because they can grow in saturated conditions and produce adventitious roots (Schaff *et al.,* 2002) creating healthier environments for microbial growth (Vervaeke *et al*., 2003). Trees that enhance soil aeration and create macropores should improve the capacity of soil microbes to biodegrade PAHs as well as BTEX.

Greater root biomass has been shown to be associated with greater phytoremediation efficiency (Banks *et al*., 2003) by creating larger, healthier rhizospheres. For this reason, grasses are often the vegetation of choice. While grasses such as fescue (*Festuca arundinacea*), alfalfa (*Medicago sativa*), and annual ryegrass (*Lolium multiform*) have proven successful in several phytoremediation studies (Aprill and Sims, 1990; Karthikeyan *et al*., 2003; Lalande *et al*., 2003; Maila and Randima, 2005; Parrish *et al*., 2004; Siciliano *et al*., 2003), for sites with ground water contamination, deeper root systems are needed. At this site, groundwater averages 2 to 2.5 meters in depth (ARCADIS, 2006) which indicates trees, especially deep-planted, phreatophytic trees (species capable of taking water directly from the saturated zone or capillary fringe), are more desirable. Grasses root about one third of a meter deep (O'Neill and Nzengung, 2004) and would be preferred for contaminants located at the soil surface level.

Hydraulic Control. *Hydraulic control* utilizes evapotranspiration of deep-rooted, phreatophytic trees for ground water removal and recharge reduction (Ferro *et al.,* 2003). Deep-rooted trees can be installed in dense rows perpendicular to plume migration to create a zone of capture where dissolved phase contaminants will be drawn into the rhizosphere of trees. Trees essentially act as solar powered, biological groundwater pumps. By taking up water from the capillary fringe, phreatophytic trees, such as willows and poplars, cause the upward wicking of ground water into the vadose zone. Hydraulic control is generally suitable where the water table is within 3 to 4 meters of ground surface and has a low hydraulic gradient (Ferro *et al.*, 2003). Hong *et al.* (2001) showed it was possible to significantly draw down the water table and create a cone of depression under a stand of poplars to control an MTBE plume after only 1.5 years of growth.

To determine the effectiveness of trees in controlling ground water, field measurements can produce a greater degree of accuracy compared to computer modeling or calculations based on leaf area. Periodically sampling the edge of the plume can indicate if the extent is changing. Samples should be obtained in spring to determine the maximum extent of the plume due to seasonality of plant evapotranspiration capabilities. A reversal of hydraulic head down gradient of the tree plantation can indicate hydraulic control has been achieved (Ferro *et al.,* 2003).

Vadose Zone Volatilization. Trees may enhance phytoremediation by promoting the mass transfer of volatiles from the saturated zone to the aerobic vadose done. Plants promote upward movement of water during evapotranspiration drawing contaminants into the aerobic, vadose zone where they can be broken down (Karthikeyan *et al.*, 2003). Volatilization into the aerobic zone above the water table can remove a significant mass of volatile organic compounds susceptible to aerobic biodegradation (Anderson *et al.*, 2008). By lowering the water table and creating a steeper diffusion gradient, biodegradation can speed volatilization out of the saturated zone and into the more microbially-active vadose zone (Anderson *et al.*, 2008). Additionally macropores created by decaying roots can enhance facilitated transport of volatilized contaminants into aerobic conditions where they can be degraded more quickly.

Atmospheric Dissipation. A suite of mechanisms can be involved in the phytoremediation of organic contaminants depending on their hydrophobicity (Burken and Schnoor, 1998). Because of MTBE's greater water solubility, phytovolatilization, or the release the contaminant into the atmosphere via transpiration, is the most likely mechanism for dissipation (Hong *et al.*, 2001; Rubin and Ramaswami, 2001; Zhang *et al.*, 2002). Ma *et al.* (2004) found that hybrid poplars take up and volatilize MTBE from the subsurface environment, retaining only an insignificant amount in the leaves. Rubin and Ramaswami (2001) showed that hybrid poplar saplings removed 30% of MTBE mass from water in only one week in a bench scale experiment. MTBE has not been shown to biodegrade in soil or groundwater and resists breakdown by plant enzymes, but when transpired into the atmosphere, it is susceptible to photo-oxidation and reacts with photo-chemically produced hydroxyl radicals, dramatically reducing its half-life to approximately four days as opposed to two years underground (Yu and Gu, 2006). Burken and Schnoor (1998) found that hybrid poplars, in short-term, hydroponic experiments did phytovolatilize BTEX compounds, though no soil sorption processes were in effect in that experiment.

Rhizodegradation. The most likely mechanism for degradation of more lipophilic organics, such as BTEX and PAHs, is *rhizodegradation*, the breakdown of contaminants by rhizosphere-associated bacteria (Aprill and Sims 1990; Chen *et al*., 2003, Binet *et al.,* 2000). Other common fates for organic contaminants include cometabolism, the oxidation of nongrowth substrates (*eg.* higher ringed PAHs) during the growth of an organism on another energy source (*eg.* lower ring PAHs) (Kuiper *et al*., 2004), or adsorption to organic matter (Chen *et al*., 2003; Cunningham and Ow, 1996; Schnoor *et al*., 1995, Dietz and Schnoor, 2001).

Compared to PAHs, BTEX is a much easier compound to remediate for three reasons: it degrades rapidly in aerobic conditions, it is more water soluble, making it more bioavailable, and it can serve as the primary electron donor for many bacteria found in nature (Frick *et al*., 1999). However, when leaking fuels and petroleum hydrocarbons reach deep into soil profiles, biodegradation can become difficult due to lack of oxygen (Karthikeyan *et al*., 2003). Plants can create aerobic conditions and enhance microbial activity, thus enhacing biodegradation in the vadose zone.

Plants, soil microbes associated with the rhizosphere, and soil organic matter all play integral roles in the degradation of organic pollutants. Plant root systems can increase below ground organic matter and distribute soil microbes as they are carried with growing root tips (Aprill and Sims, 1990). Root exudates, including carbohydrates, amino acids, and mucigel, which helps the root penetrate the soil during growth, provide microbial populations with substrates for healthy population growth (Anderson *et al*., 1993) and can increase PAH degradation (Reilley *et al*., 1996). Root decay may also enhance biodegradation of organic contaminants by releasing diverse aromatic compounds, such as flavonoids, from plant vacuoles. According to Olson *et al.* (2003), an estimated 90% of substances released by roots occur when they decay. This flux can stimulate the growth of soil organisms that are capable of metabolizing pollutants similar in structure to natural aromatics. Additionally, root growth and decay can create macro and micropores allowing for the facilitated diffusion of oxygen (Zalesny *et al*., 2005).

Studies have shown an increase of microbial populations within the rhizosphere from four up to one hundred times that of populations outside of the rhizosphere (Chaineau *et. al*., 2000; Crowley *et al*. 1996; Jordahl *et. al*. 1997). In one study, Binet *et al*. (2000) found that the percentage of PAH degrading bacteria was similar in and out of the rhizosphere and suggested that the presence of PAHs rather than the rhizosphere increases the number of PAH degrading bacteria. However, Muratova *et al*. (2003) found that vegetated soil had a greater *variety* of PAH degrading bacteria than unvegetated soil. They found six or seven different types of PAH-degrading microorganisms as opposed to only one type isolated from soil outside of the rhizosphere. Having a greater diversity of microorganisms creates a more effective degradative community with more catabolic possibilities, although results vary with plant species (Muratova *et al*., 2003). Interactions in the rhizosphere change with soil conditions such as moisture, temperature, the growth stage of the plants (Newman and Reynolds, 2004), the species of plant (Muratova *et al*., 2003; Siciliano *et al.*, 2003), and genetic variation within a species of plant (Banks *et al*., 2003).

Aging. Organic contaminants are not only subject to biodegradation, but also to sorption into micropores in the soil matrix that can reduce their toxicity to living organisms by making them less accessible. Some soil pores are so small that neither bacteria nor root hairs can penetrate them to reach the contaminants (Alexander, 1995). Bioavailablity is a controlling factor in both biodegradation and toxicity (Shuttleworth and Cerniglia, 1995). Binet *et al*. (2000) found that after soil aging, there was less degradation of PAHs than in freshly spiked soils. As contaminants age in the soil, they tend to become less available (Parrish *et al*., 2004) to cross an organism's cellular membrane (Semple *et al*., 2004). Aging may involve humification, the process by which PAH metabolites are chemically bound to soil organic matter (Hurst *et al.*, 1996). Co-metabolism by microbes can enhance the soil sorption of partially metabolized PAHs and once covalently bound, they are unlikely to mobilize again (Eschenbach *et al*., 1998). Aging can also involve non-covalent binding of parent material via adsorptive and absorptive interactions with organic matter and soil micropores. Due to the non-polar structure of PAHs, they generally partition onto the hydrophobic surfaces in the soil (Aprill and Sims, 1990), and then slowly migrate to less accessible sites in the soil matrix (Conte *et al*., 2001). Many factors contribute to the capacity of soil to sequester organic contaminants, including the amount of organic matter in the in the soil, the clay content and soil structure, the pH, and the water flux through the soil profile (Cunningham and Ow, 1996). The humin fraction of soil, an extremely complex assortment of humic and fulvic acids and macromolecules, can strongly bind PAHs and their metabolites (Ressler *et al.*, 1999; Chen *et al*., 2003).

During phytoremediation, plant organic matter provides new carbon matrixes that sorb and bind PAHs (Chen *et al.*, 2003) or alternatively improves bioaccessability by destabilizing soil organic matter through microbial degradation, organic acids, and chelating agents (Gregory *et al.*, 2005). Plant exudates, made up of many aliphatic (non-aromatic) organic carbon compounds, build up labile carbon in the soil, making PAHs increasingly bioaccessible, for microbial degradation as this carbon breaks down. Some studies have shown an increase in PAH concentrations in the rhizosphere after planting due to this effect (Liste and Alexander, 2000). There may be a gap between when the PAHs are initially released due to the change in soil chemistry and when microbial populations degrade the released contaminants. The toxicity or bioavailability of these sequestered compounds needs further analysis over time to determine the real environmental impact or danger to human health. Toxicity studies are essential because metabolites of PAH have the potential to be more toxic than the parent compound, therefore measuring toxicity, such as the effect of contaminants on plants, can be a better indicator than simply monitoring the disappearance of PAHs (Shuttleworth and Cerniglia, 1995).

Weathering. To elucidate whether a reduction in PAH compounds is a result of sequestration (due to aging) or biodegradation (due to microbial activity), relative concentrations of alkylated homologues of PAHs can be compared to parent PAH compounds to indicate *weathering*. Biodegradation is the primary mechanism of weathering (Widdowson *et al.,* 2005), though other processes can include volatilization, evapotranspiration, photomodification, hydrolysis, and leaching (Frick *et al*., 1999). Alkylated homologues (*i.e.* 2-methylnapthalene*)* tend to weather more slowly than their parent compounds (*i.e.* napthalene) due to the extra alkyl groups, therefore increasing alkylation decreases rates of degradation (Douglas *et al*., 1996). Analysis of weathering patterns can be used to evaluate and determine indices of PAH weathering at phytoremediation sites.

Chemical Structure. Along with alkylation, size and shape (steric and electronic factors) also affect rates of PAH degradation. Smaller 2- to 3-ring PAHs have shown relatively faster rates of degradation compared to larger 5- to 6-ring compounds (Douglas *et al.,* 1996). Faster degradation of smaller PAHs most likely occurs because the larger PAHs are limited by low solubility, high rates of soil sorption and (Aprill and Sims, 1990), and greater clustering of rings (Ye *et al.*, 1996). Degradation may still be possible for larger PAHs. Binet *et al*. (2000) saw some disappearance of 5- and 6-ring PAHs in the rhizosphere of ryegrass, even after aging, while there was no decrease outside of the rhizosphere. However this decrease in PAH concentrations could have been due to binding to organic matter rather than actual degradation. Unfortunately, the larger PAHs are of greater health concern because of their greater carcinogenicity and higher persistence (Ye et al., 1996). Of the 16 priority PAHs listed by the EPA, the carcinogenic compounds generally include the larger, multi-ringed compounds such as, fluoranthene, pyrene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene (Hurst *et al.*, 1996).

PAHs, though a relatively small percentage of fuel contamination compared to BTEX and MTBE, often remain recalcitrant in soils and do not volatilize or dissolve into groundwater. A better understanding of the mechanisms of aging and degradation are needed to facilitate rhizodegradation in field scale situations. The array of biological, chemical, and physical interactions between plants, soils, and contaminants creates a complex system to understand and manipulate effectively.

GIS. While laboratory and greenhouse level experiments have helped to elucidate some mechanisms involved in phytoremediation, field demonstrations are critical to the progress of this technology as a viable method to clean up PAHs, BTEX, and MTBE. In order to facilitate field analysis, Geographic Information Systems (GIS) can provide an effective means to monitor and compile information within phytoremediation systems. GIS mapping has recently been combined with fuzzy logic models to inform plant selection decisions by integrating publically available soil, climate, and plant data (Porter *et al.,* 2006). When managing multiple contaminants, sampling points, plant species, clone treatments, and contaminant changes over time, this becomes an effective tool to integrate information and look for patterns. Creating interpolated surfaces from sampling locations can be used to visually compare changes in concentrations over time, note how those contaminants may be affected by plants, or look for general patterns in plant toxicity.

Objectives. Trees have been growing in this field phytoremediation demonstration site now for over two years. The main objectives of this paper are to 1) examine ground water BTEX and MTBE concentrations for indications of hydraulic control by trees, 2) establish preliminary soil total PAH concentrations and PAH weathering to provide a baseline for future indications of biodegradation in the rhizosphere, 3) examine soil gas analyses for indications of reduction in contaminants due to trees, and 4) explore effects of contaminants on trees.

MATERIALS AND METHODS

Field Methods

Ground Water Sampling. Ground water was collected by U.S. Geologic Survey and North Carolina State University researchers in February and November 2006 and December 2007 (Figure 1). Wells were purged and only sampled when a layer of free product was not present using a low-flow peristaltic pump and ¼-inch PFTE tubing. Duplicate samples from each well were collected in clean 40 ml volatile organic analysis (VOA) vials that were free of headspace and capped with Teflon-coated septa cap. Samples were transported back to NC State University campus on ice for laboratory analysis of BTEX and MTBE using Method SW 846 5030B and 8015B (USEPA, 1986) by the Civil Engineering Department. Historically, routine ground water samples have been collected by ARCADIS G&M of North Carolina, Inc. since June 2001 and tested for BTEX and MTBE (ARCADIS, 2006).

Soil Sampling. The first sets of soil samples were collected in February 2006 by hand auger, 30 cm north of selected ground water monitoring wells. When not impeded by rock fill, two sampling depths were collected, the first at the initial presence of gasoline odor, at approximately one meter depth, and the second at the capillary fringe above the water table, at approximately two meter depth. For sampling locations where hand augering was impeded, a direct-push drill rig was used to complete the sample set in April 2006. These locations were sampled again in November 2006, with the addition of 32RW2 and the exclusion of 32MW19.

In April of 2007 during replanting, a transect along one tree row was selected for soil sampling. Soil excavated by a Bobcat rig from a previously planted location was collected to represent soil in direct contact with tree roots. Later in December 2007, an additional transect was sampled to further explore the effect of TPAH concentrations on tree growth. The transect fell along a line of increasing contamination according to soil gas data (GORE™, 2007) and appeared to correlate to tree growth. For Transect 2, all soil samples were collected by augering to a depth of 0.5 meters below the surface at a distance of 0.5 meters from every other tree. All trees in Transect 2 were of a single hybrid poplar clone, OP-367.

All soil samples were collected in clean, 125 ml amber jars, and stored on ice for transportation back to NC State University. They were transferred to a -10° C freezer and stored overnight prior to laboratory analysis.

Soil Gas Sampling. Soil gas sampling and analysis were performed by W.L. Gore and Associates, Inc. of Elkton Maryland. In February 2007 and July 2008, Gore Module ™ passive membrane devices were placed in permanent soil gas monitoring stations consisting of 2.5 cm diameter, 75 cm long slotted PVC screens installed in borings of the same diameter and depth. These stations were located on 30 m centers for consistent, repeated sampling. Corks were used as caps and the sorbent modules were tied to a string and hung from a screw-in eyelet on the bottom of the cork. Four inch well boxes were placed over the soil-gas wells to complete the monitoring stations. The Gore Modules™ were placed in the soil-gas wells for approximately five days. These devices were then placed in glass vials and shipped back to GORE™ for analysis.

GPS and Field Measurments. Points were mapped using a hand-held Trimble GPS device. Four to eight satellites were available for positioning due to the open nature of the site and a minimum of thirty positions were recorded. Soil gas wells, groundwater monitoring and recovery wells, soil sampling locations, and all tree locations were all recorded. In early 2008, total stem length, survival, and species/clone were recorded for each tree. Planting areas and site perimeter were delineated. All GPS points were differentially corrected before incorporation into GIS. Total stem length was measured manually with tape measures, summing the length of all major stems to the nearest 1.0-centimeter. Total stem length was measured instead of height to compensate for difference between trees with a singular tall stem or many shorter stems.

Laboratory Methods

Ground Water Samples. Water samples analyzed by NCSU department of Civil Engineering for BTEX and MTBE used heated purge and trap gas chromatography with flame ionization detection (FID) (heated P&T – GC/FID). An inert gas was bubbled through a portion of the aqueous sample and the volatile compounds were transferred from the aqueous phase to the vapor phase. The vapor was swept through a sorbent column where the volatile compounds are adsorbed. After purging is completed, the sorbent column is heated and back flushed with inert gas to desorb the components onto a gas chromatographic column where the compounds are separated and quantified. Relative percent difference was calculated for wells sampled by both NCSU and ARCADIS for ground water analysis.

Soil Sample Preparation. Soil samples were freeze-dried in a Benchtop 3.3/Vacu-Freeze (VirTis Co., Gardiner, NY) then sieved through a 2 mm sieve to remove rocks and debris. Samples were then homogenized by hand with a mortar and pestle and returned to amber jars. Approximately 10 mg of each sample was weighed out three times and placed in three separate amber 40 ml VOA vials to produce triplicate samples. Two solvent extractions were then performed by adding 20 ml of dichloromethane (DCM) to each sample in the vials. These were allowed to shake for 24 hours then centrifuged for five minutes at 1000 RPMs. Supernatant was decanted into a new VOA vial and soils were solvent extracted a second time for another 24 hours and decanted again bringing the extraction volume up to approximately 40 ml.

Soil samples were then evaporated with blown nitrogen to concentrate solvent down to 5 ml. Concentrated extractions were cleaned by running them through activated neutral alumina columns. Columns were packed with glass wool, filled with DCM and layered with sodium sulfate, aluminum oxide, and another layer of sodium sulfate. Columns were conditioned by letting the DCM run through to the top of the sodium sulfate layer. Hamilton syringes were used to load 0.5 ml of sample into the column, followed by two rounds of 40 ml of DCM. These samples were allowed to evaporate under a fume hood until they were again concentrated to 1 ml. Samples of pre- and post-column extractions were archived.

Gas Chromatography/Mass Spectrometry. GC/MS select ion monitoring (SIM) mode analyses was conducted on a HP5890 Series II GC equipped with electronic pressure control connected to an HP5970 or HP5972 MSD using a Restek 30 m _ 0.25 mm Rtx-5 (film thickness 0.25 Ìm) MS w/Integra-Guard column. Before samples are analyzed, the linearity was determined with a standard curve consisting of known concentrations of 0.01, 0.1, 1.0, 5.0, 10 ng/ml of non-alkylated PAHs. Samples contained 501.0 ng/ml of d8 benzo[a]pyrene and 500.0 ng/ml of d10 phenanthrene as internal standards. All 42 alkylated and nonalkylated PAHs were quantitated for each triplicate soil sample using a modified method of EPA 8270 (USEPA, 1996). Concentrations of PAHs were normalized to micrograms PAH per gram dry soil using the average of all three triplicate sample totals and standard deviations were calculated.

Soil Gas Analysis. Analysis reports a quantitative measurement of soil gas mass levels present in the vapor phase underground in the vicinity of the sample location. This vapor phase can be released from either soil or ground water contamination (ARCADIS, 2006; GORE™, 2007). Sample preparation includes cutting the tip off the bottom of a sample module and transferring the absorbent to a thermal desorption tube. Instrumentation consists of gas chromatographs with mass selective detectors, coupled with thermal desorption units. The analytical methods are a modified EPA method 8260/8270 (USEPA, 1996). Before each run sequence, two instrument blanks, a sorber containing 5 µg Bromofluorobenzene (BFB), and a method blank are analyzed. The BFB mass spectra must meet the criteria set forth in the method before samples can be analyzed. A method blank and a sorber containing BFB are also analyzed after every 30 samples and/or trip blanks. Standards containing the selected target compounds at five calibration levels are analyzed at the beginning of each run. The criterion for each target compound is less than 25% RSD (relative standard deviation). If this criterion is not met for any target compound, the analyst has the option of generating second or third order standard curves as appropriate. A second source reference standard, at a level of 10 µg per target compound, is analyzed after every ten samples and/or trip blanks, and at the end of the run sequence. Positive identification of target compounds is determined by 1) the presence of the target ion and at least two secondary ions; 2) retention time versus reference standard; and, 3) the analyst's judgment (GORE™, 2007).

Spatial Relationships. Ground water BTEX and MTBE concentrations and soil gas contaminant masses were assigned to sampling locations through GIS using ESRI ArcMap 9.2™. To visually monitor these concentrations and discover patterns associated with plant growth, estimated concentrations between sampling locations were interpolated with inverse distance weighting (IDW). In Spatial Analyst, a variable search radius with 12 point option and a power of 2 was used. Surfaces are divided into ten value ranges by the Natural Breaks (Jenks) method. IDW uses a weighted average of a defined number of sampled points where the assigned weight diminishes as distance from that point increases (Chuanyan et al., 2005). Though this method creates a rougher surface than other methods such as spline, it was chosen for its simplicity and because it does not allow contaminant concentration values to fall below zero (the newly created surface must pass through input points) While kriging, a geostatistical procedure, can provide the most robust interpolation method and the best models for spatial analysis (Chuanyan et al., 2005), developing variogram models was beyond the scope of this project.

Interpolated values created using IDW were used to estimate values at each GPS point where trees were located. These raster data have a floating decimal number attached to each pixel in the surface. In order to spatially join tree points (vector data) to the newly created interpolated surface, the numbers assigned to the raster surface had to be converted to integer data and then turned into a polygon layer (also vector). Once the trees and the interpolated surface are both vector data, they can then be spatially joined and contaminant values can be assigned to each tree. This was done for all groundwater and soil gas contaminants to look for direct correlations between tree total stem length and contaminant concentrations.

Statistical Analyses. All constituents not normally distributed after log transformation were tested with the Wilcoxon paired signed rank test, which tests the null hypothesis that two related medians are the same and does not assume a given distribution (Gauthier, 2002). In the Wilcoxon test, ranks are based on the absolute value of the difference between the related variables, in this case 2007 and 2008 soil gas masses. The sign of the difference classifies it as positive rank, negative rank, or a tie (which is ignored). A Z-variable is a standardized measure of the distance between the rank sum of the negative group and its expected value. A two-tailed asymptotic significance estimates the likelihood of obtaining a Z-statistic that is as or more extreme in absolute value if there is truly no difference between the related groups. Statistics were performed using SPSS™ 16.0. The level of significance was considered to be $p<0.05$.

RESULTS AND DISCUSSION

Preliminary Post-planting Effects on Contaminants

Ground Water BTEX and MTBE. Historic ARCADIS ground water sampling results (Table 3A) show an overall decrease in MTBE (Figure 4) and BTEX (Figure 5) after trees were planted (Table 3B). From 2007 to 2008, both MTBE ($p=0.028$) and BTEX ($p=0.043$) decreased significantly ($p<0.05$). Average benzene concentrations decreased by 96% after trees were planted and average BTEX decreased by 88%. MTBE concentrations in well 32ESM14, located immediately down-gradient of the site, showed a 63% decline and BTEX showed a 98% decline after planting. The sharp declines in well 32ESM14 (Figure 5) indicate hydraulic control following the June 2006 planting.

The locations of the wells (Figure 1) and changes in concentrations indicate that some MTBE may have already moved offsite. Three wells located closest to the river show an average increase of 389% after 2006. MTBE is more water soluble than BTEX and therefore likely moved down-gradient and offsite before the phytoremediation system was installed.

Values for NSCU analysis of ground water contaminant concentration from February and November 2006 and December 2007 can be found in Table 1. Wells were chosen by USGS personnel in an attempt to delineate the plume and look for indications of hydraulic control. Additional wells were installed during the first planting and were sampled by NCSU in December 2007. Subsequent sampling was performed by ARCADIS in August 2008 (Table 2). These wells showed a significant decrease of 96% in MTBE ($p=0.018$; Figure 2) and 61% in benzene ($p=0.028$; Figure 3). Trees can enhance the upward movement of dissolved fractions of fuel into aerobic zones through water uptake and transpiration; this can increase biodegradation and volatilization (Karthikeyan et al., 2003). However, concentrations may have dropped in summer months when trees are fully transpiring. Additional comparative summer and winter sampling is needed to determine if indeed this effect is seasonal or a permanent decrease in contaminant concentrations.

GIS can be used to visually indicate how the ground water plume is changing over time. Concentrations for BTEX (Figure 6 A&B) and MTBE (Figure 7 A&B) were interpolated using inverse distance weighting (IDW) and show a reduction in overall contamination and indicate hydraulic control. However, this figure can be misleading because concentrations in wells containing a visible layer of free product, generally the recovery wells (indicated by RW), are not analyzed for BTEX and MTBE by ARCADIS for concentrations but are measured for product thickness (ARCADIS, 2006). Data concerning product thickness has not yet been reported for 2008.

NCSU and ARCADIS Relative Percent Difference. Four wells were analyzed for relative percent difference (RPD) to compare NCSU and ARCADIS ground water contaminant concentration results. Wells 32ESM1, 32ESM14, 32MW18, and 32MW20 were sampled and analyzed for MTBE and BTEX in November 2006 by NCSU and in June 2006 by ARCADIS. RPD resulted in 14, 18, and 20 percent differences for MTBE (32ESM1 & 32ESM14) and benzene (32MW20), respectively. Based on these results, it was assumed that NCSU and ARCADIS sampling could be compared.

Soil PAH Concentrations and Weathering. A map of all soil sampling locations can be found in Figure 8. Initial soil testing showed that deeper, two meter samples almost always had much higher TPAH levels than samples collected at one meter depths (Table 4 & Figure 9). This was expected based on field observations of soil odor. Variability between soil samples was often quite high. Soil heterogeneity across the site is likely a confounding factor as PAH recovery is generally higher in coarse textured soils, whereas fine-textured soils tend to facilitate PAH adsorption and therefore often have lower recoveries (Conte *et al*., 2001). Soils at this site are extremely heterogeneous due to the amount of construction and backfilling that have occurred in the past.

To evaluate initial weathering of fuels, the ratios specific alkylated PAHs such as C_3-naphthalene and C_2-phenanthrene can be examined. Later stages of crude oil degradation can require looking at the C_3-dibenzothiophenes/C_3-chrysene ratios (Douglas *et al*., 1996). However, use of these ratios can be complicated by the absence of alkylated constituents, such as chrysene, at this site. A cross- plot of the ratio of C_3-naphthalene to C_2-phenanthrene against TPAH concentrations in soil samples was constructed. These ratios provide data to analyze the impact of trees on the weathering of residual petroleum in the soil. Weathering may indicate biodegradation and could give support to the hypothesis that the trees will increase weathering of fuel oil in the soil. Weathering results of preliminary samples taken in November 2006 show a distinct pattern of shallower soils being more highly weathered (Figure 10). This is to be expected as shallower samples are exposed to more aerobic conditions and therefore more biodegradation by soil microorganisms (Hurst *et al*., 1996). When all soil samples from the two transects are plotted together, Transect 1 shows much greater weathering overall than Transect 2 (both collected at 0.5 m depths) (Figure 11). This follows the assumption that the leading edge of the plume, and therefore older constituents should be more highly weathered.

Soil Gas. Soil gas constituents were sampled and analyzed in February 2007 (Table 5) and July 2008 (Table 6). Only wells sampled in both 2007 and 2008 are shown, and include those in and around the planting area. Almost all soil gas masses decreased significantly from 2007 to 2008 (Figure 12). Total petroleum hydrocarbons decreased significantly ($p < 0.001$) after data were log transformed and analyzed with a paired t-test. BTEX, naphthalene, trimethylbenzenes all significantly decreased ($p < 0.001$) as did tridecane ($p < 0.011$), while undecane ($p < 0.002$) and pentadecane ($p < 0.213$) increased slightly. GIS was used to visualize the change in soil gas over time. TPH (Figure 13 A&B) and BTEX (Figure 14 A&B) show the contrast between February 2007 and July 2008. Inverse distance weighting was used to interpolate between sampling wells and the same scale was used for both years.

One explanation for the decrease in contaminants is that trees created a steeper diffusion gradient by lowering the water table and therefore brought oxygen into the soil to speed biodegradation (Anderson *et al.*, 2008). Alternatively, augering over 3,000 holes across the site during the large scale planting in April 2007, could have facilitated transport of volatile compounds out of the soil and allowed for greater diffusion of oxygen into the vadose zone. If macropores left by decaying roots are suspected to facilitate oxygen diffusion to the benefit of degradation, nine-inch diameter, four-foot deep holes, likely have an effect as well. If this is the case we will likely see a rebound of soil gases once this one-time effect dissipates. If soil gases remain at current levels and continue to decrease, then the trees may be the more likely mechanism.

Effects of Contamination on Trees

Groundwater and Soil Gas Spatial Analysis. A cross-plot of total stem length and interpolated values of soil gas TPH and ground water benzene shows that as total stem length increases, only lower concentrations of benzene and TPH are seen (Figure 15A&B). As the trees continue to grow the clustering below 500 cm should begin to spread and indicate long-term contaminant effects on tree growth. Exploratory analysis of all other contaminants and total stem length shows similar patterns of lower contaminant concentrations at the tallest trees. A GIS overlay of total stem length with soil TPH interpolation shows visually the pattern at the site, where the tallest trees tend to be in areas of lower contamination, while small, stunted, and dead trees often fall in areas of the highest contamination (Figure 16).

Soil TPAH and Total Stem Length. To further explore the toxicity effects of PAHs, two transects were selected to examine the relationship between soil TPAH concentrations and tree total stem length. Soil samples adjacent to trees were analyzed for soil contamination as compared to tree growth as measured by total stem length (Table 7). TPAH concentration patterns appear to have a relationship to tree total stem length (Figures 17&18). Vigorous growth tends to be associated with lower levels of TPAH concentrations (Figure 19&20) though it is not a linear relationship (Figure 21). Considering field conditions are highly variable, due to soil heterogeneity, depth to water table, and differing planting methods, these results still appear to show soil contamination influencing tree growth. However, the correlation coefficient indicates that other factors are involved in determining tree total stem length besides soil TPAH contamination.

CONCLUSION

Significant reductions in ground water contaminant concentrations and soil gas masses after planting indicate the phytoremediation system is successfully initiating hydraulic control of the contaminated plume and *in situ* degradation of contaminants. Continued monitoring will indicate if results are temporary, seasonal, or a permanent reduction in contaminants. Initial soil PAH weathering shows more weathering has taken place at the edge of the plume and closer to the soil surface, as would be expected. This study provides baseline data for comparison of later studies to see the effects of trees on PAH soil concentrations and weathering. Negative effects of contaminants on tree growth as measured by total stem length were observed in the field.

GIS has been an effective tool in the integration and monitoring of contaminants, tree growth, and spatial data by allowing for easy visualization of patterns. It is highly recommended that it be used in other phytoremediation systems to compile information. In-depth spatial statistics, semivariogram modeling, and kriging will be required to fully elucidate the relationships of contaminant toxicity on tree growth due to the complex nature of field studies. Bench scale studies are currently underway to test the relative toxicity of contaminated ground water versus soil PAHs to poplar cuttings taken directly from the site. These relationships will help to elucidate whether contaminated ground water or soil has a greater influence on tree toxicity.

Overall, preliminary results after only two years of tree growth have exceeded any initial expectations for hydraulic control and contaminant degradation. If future monitoring continues to report these initial trends, there will be a strong case to include phytoremediation as a viable, and even preferable, low cost alternative to traditional remediation techniques for the clean-up of petroleum-hydrocarbon contaminated soil and ground water due to leaking underground storage tanks. So far, this site has successfully demonstrated the ability of poplars and willows to significantly reduce petroleum-hydrocarbon contamination in a shallow aquifer.

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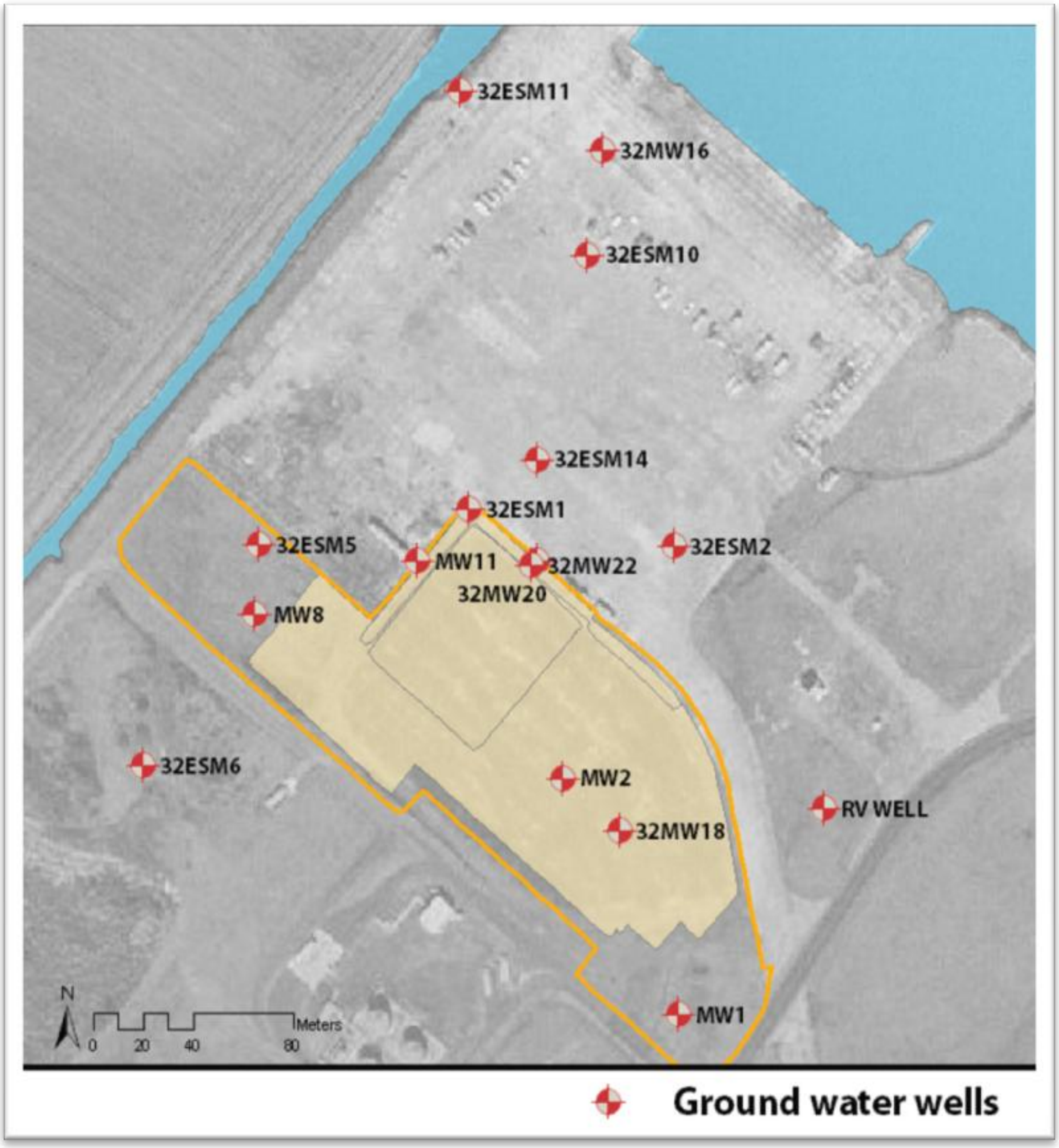

Figure 1 GIS map of ground water monitoring wells used in ARCADIS and ARCADIS/NCSU concentration analysis.

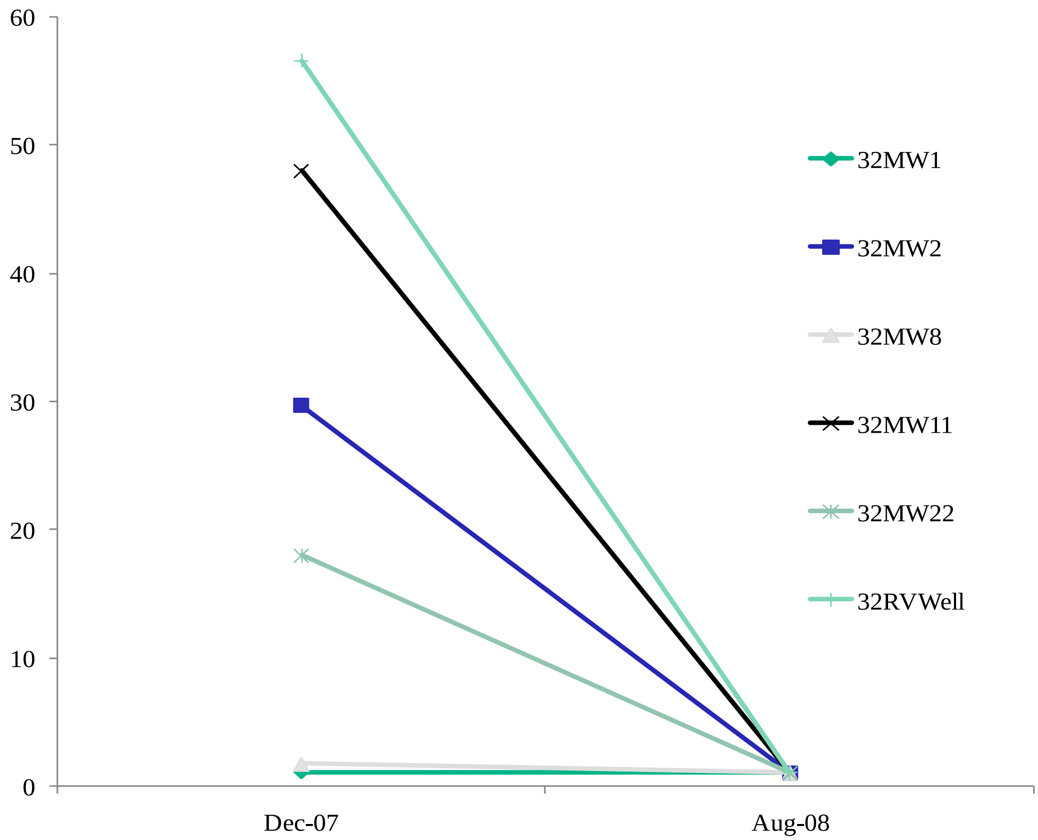

Figure 2 Ground water MTBE concentrations decrease 96% from 2007 to 2008. All wells were put in place during phytoremediation installation and first sampled and analyzed in Dec 2007 by NCSU; 2008 samples were collected and analyzed by ARCADIS in Aug 2008. Relative percent differences indicated comparison was feasible (<20%RPD).

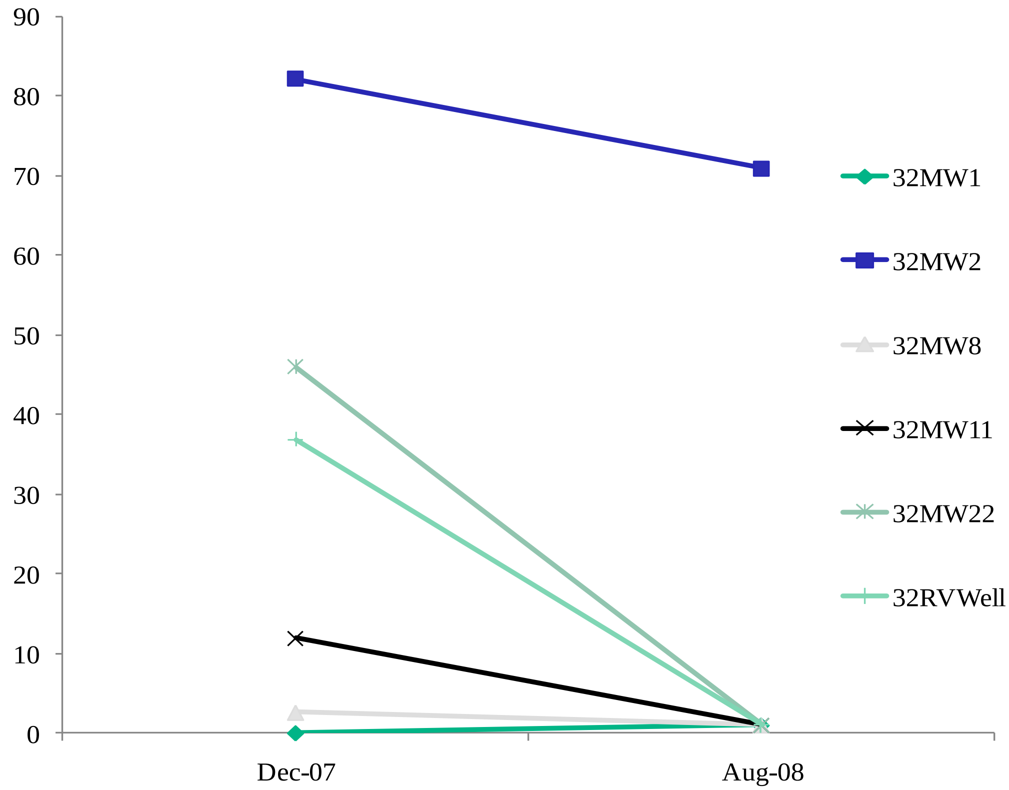

Figure 3 Ground water benzene concentrations decrease 60% from 2007 to 2008. All wells were put in place during phytoremediation installation and first sampled and analyzed in Dec 2007 by NCSU; 2008 samples were collected and analyzed by ARCADIS in Aug 2008. Relative percent differences indicated comparison was feasible (<20%RPD).

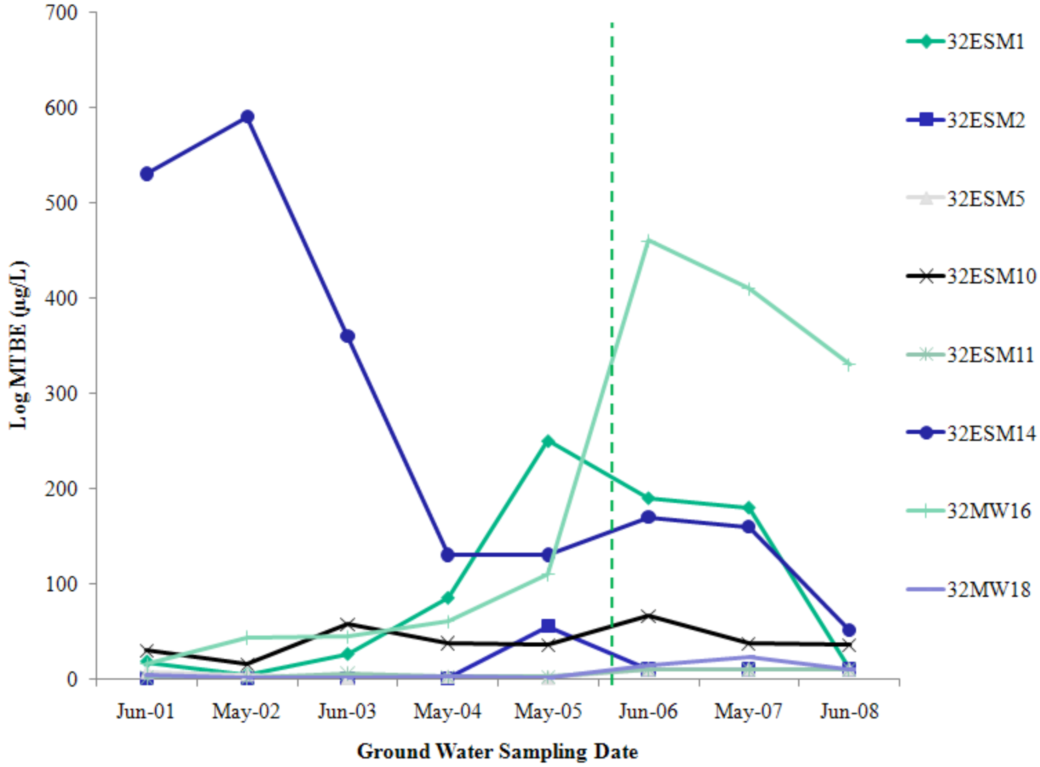

Figure 4 Ground water concentrations of MTBE, 2001 to present. Initial planting (April 2006) is indicated by the dashed line. Average MTBE concentration decreased 35% in planted area after tree planting. MTBE concentration in 32ESM14, located directly down-gradient of tree planting decreased 64% after planting indicating hydraulic control of plume. Average concentration after 2006 in wells nearest river jumps 389% due to prior offsite MTBE plume migration.

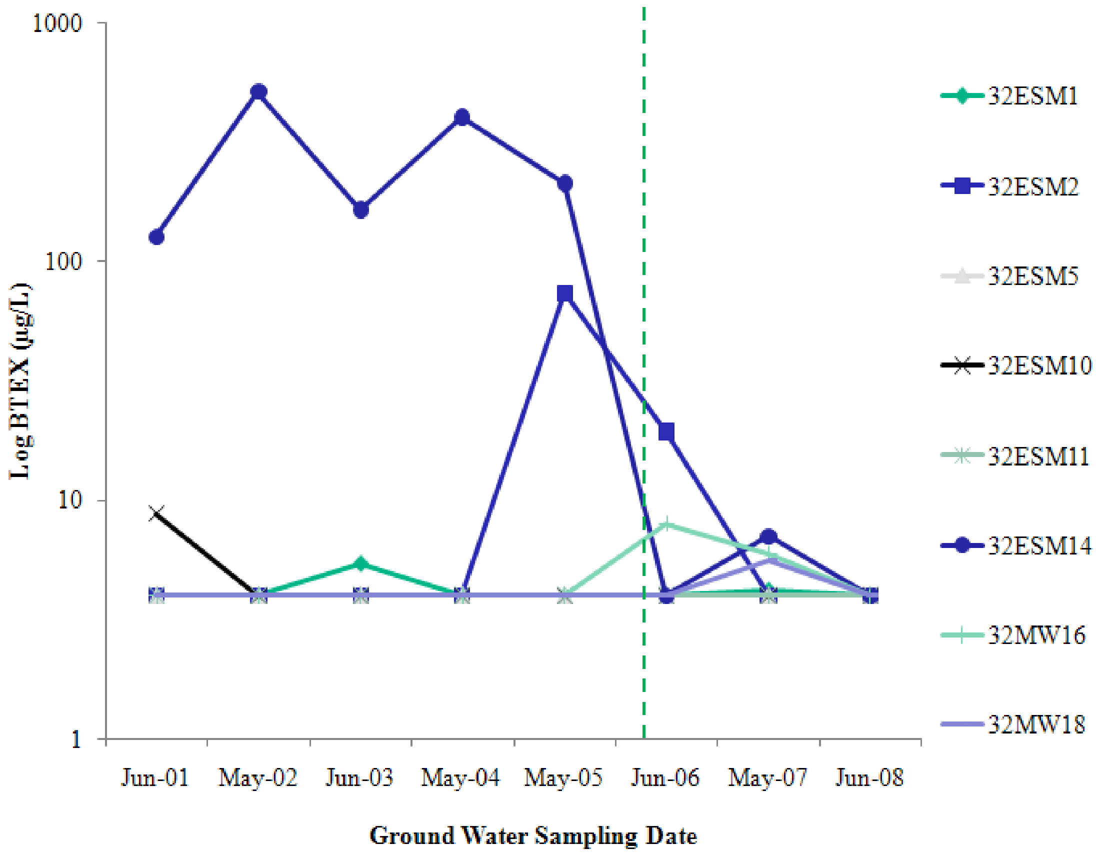

Figure 5 Ground water concentrations of BTEX, 2001 to present. Initial planting (April 2006) is indicated by the dashed line. Average BTEX concentration decreased 88% after planting. BTEX concentration in 32ESM14, located directly down-gradient of tree planting decreased 98% after planting.

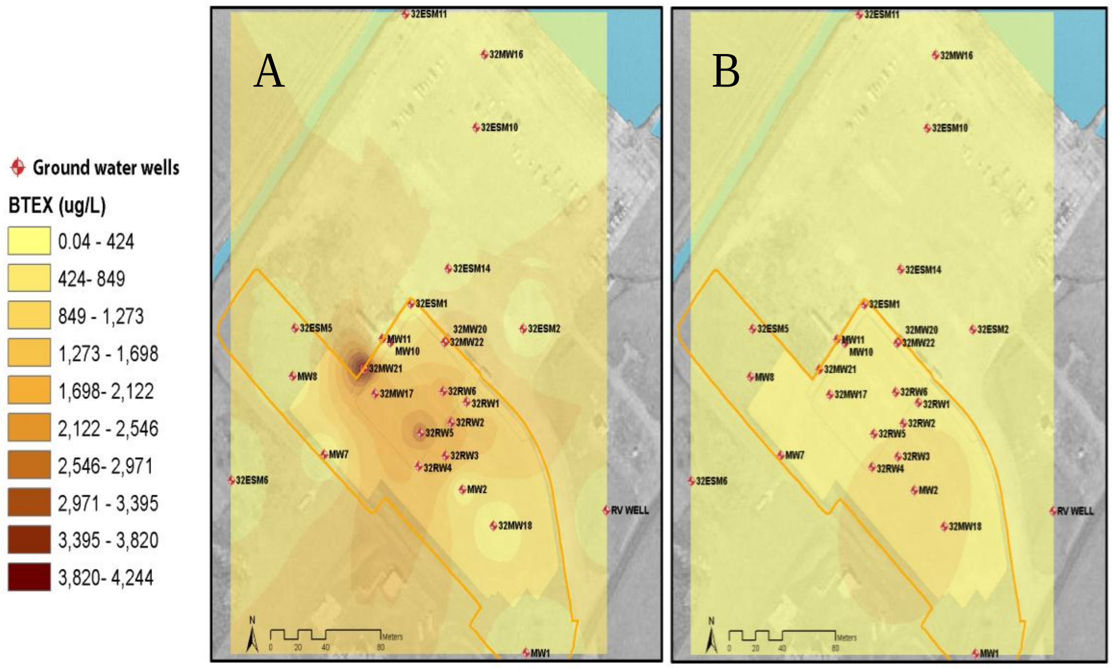

Figure 6 GIS visualization of reduction in ground water concentrations (µg/L) of **A)** BTEX in 2007 and **B)** BTEX in 2008. 2008 sampling by ARCADIS does not include recovery wells that have a measurable amount of free product floating above the water table and this data has not yet been reported for 2008.

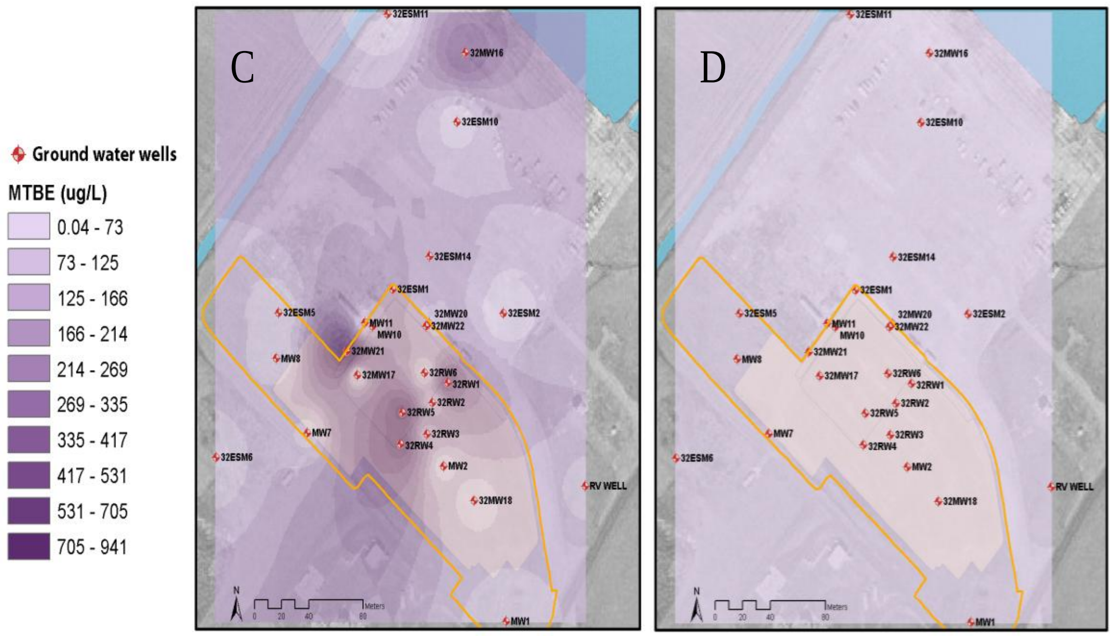

Figure 7 GIS visualization of reduction in ground water concentrations (µg/L) of **A)** MTBE in 2007 and **B)** MTBE in 2008. 2008 sampling by ARCADIS does not include recovery wells that have a measurable amount of free product floating above the water table and this data has not yet been reported for 2008. Notice the high concentration around 32MW16 near the river showing MTBE that had already migrated offsite prior to tree installation.

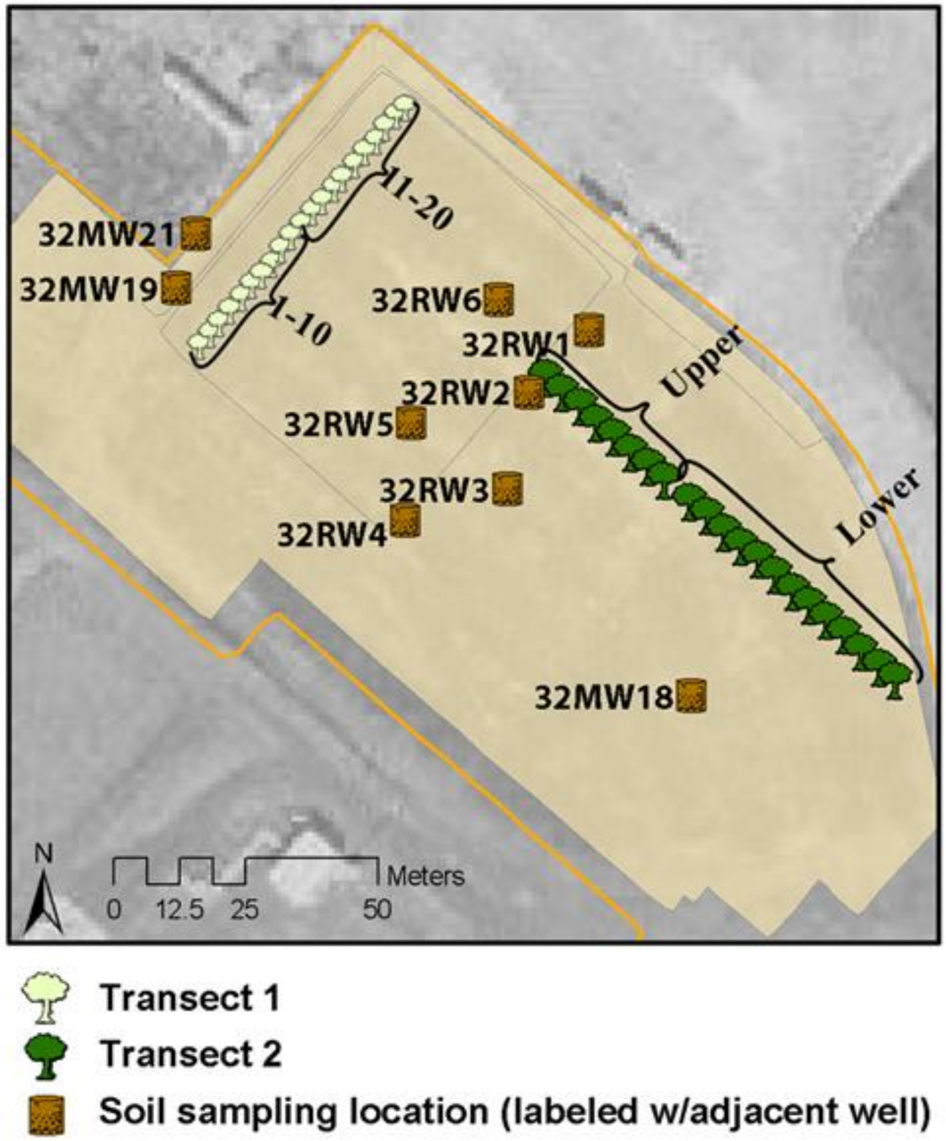

Figure 8 Soil samples collected at 1 and 2 meter depths in Feb/Apr. 2006 and Nov. 2006 are labeled according to adjacent ground water monitoring wells. Transect 1, collected Apr. 2007, and Transect 2, collected Dec. 2007, paired 0.5 meter deep soil samples with total stem length measurements of adjacent tree.

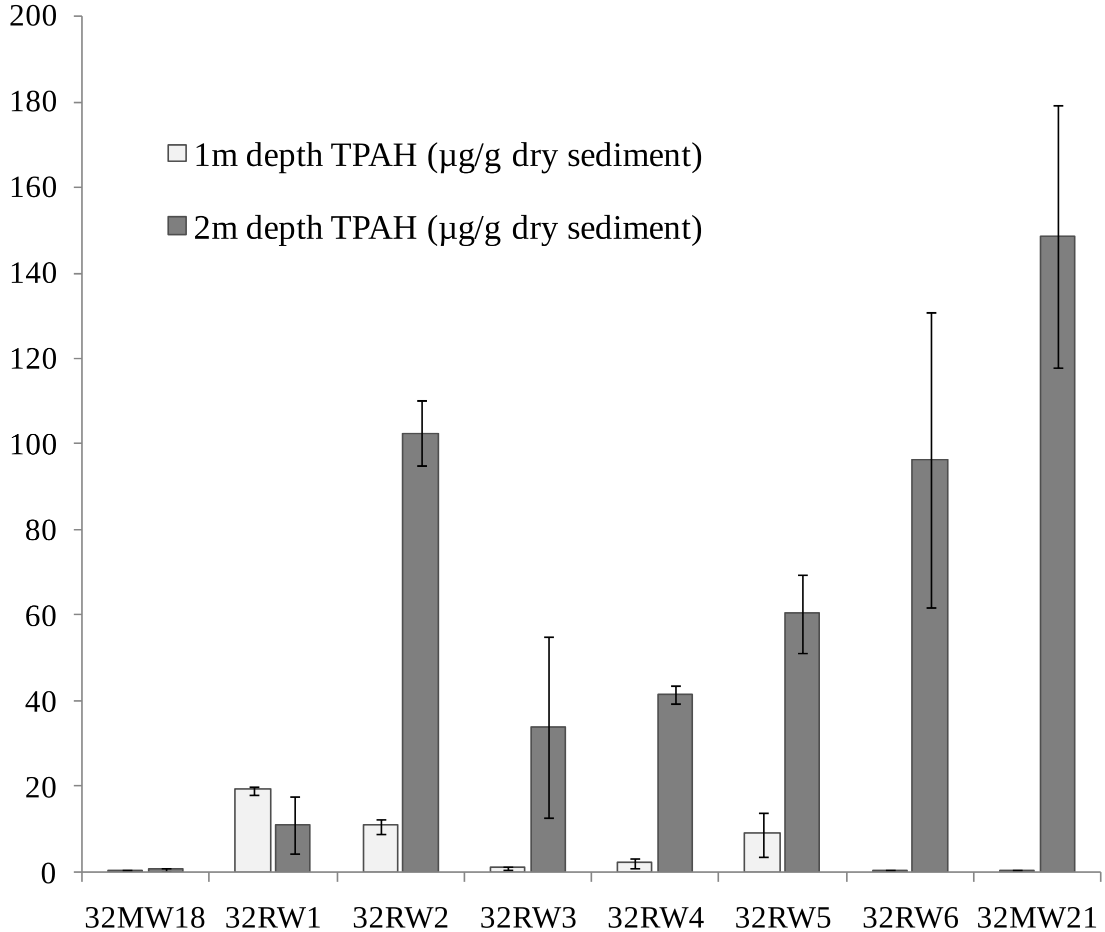

Figure 9 Total PAH concentrations in soil samples collected next to ground water recovery and monitoring wells in November 2006. TPAH concentrations are for 42 alkylated and non-alkylated PAHs. Values represent mean ± 1 standard deviation (n=3).

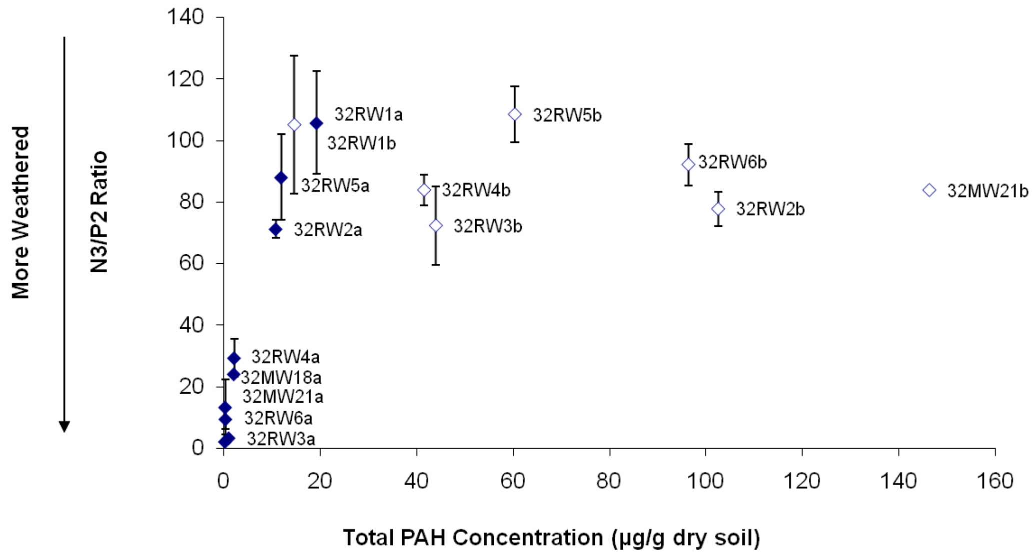

Figure 10 Cross plot of the PAH weathering ratio C_3-naphthalenes/C_2-phenanthrenes (N3/P2) to TPAH concentration at 1 m and 2 m depth from soil samples collected in November 2006. Soils from 1 m depths were more weathered and had lower TPAH concentrations than soils at 2 m depths.

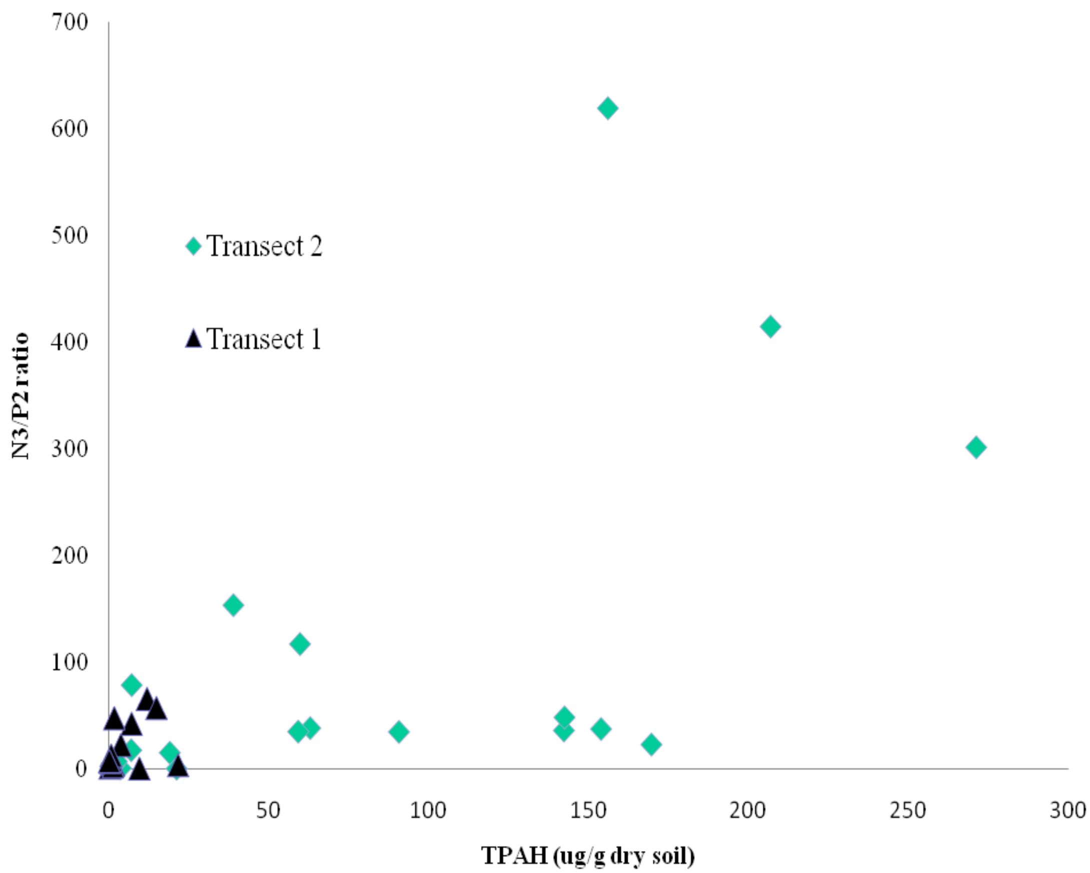

Figure 11 Cross plot of the PAH weathering ratio C_3-naphthalenes/C_2-phenanthrenes (N3/P2) to TPAH concentration soil samples collected from two transects. Transect 1 is located closer to the estimated leading edge of contaminant plume and shows greater weathering than Transect 2.

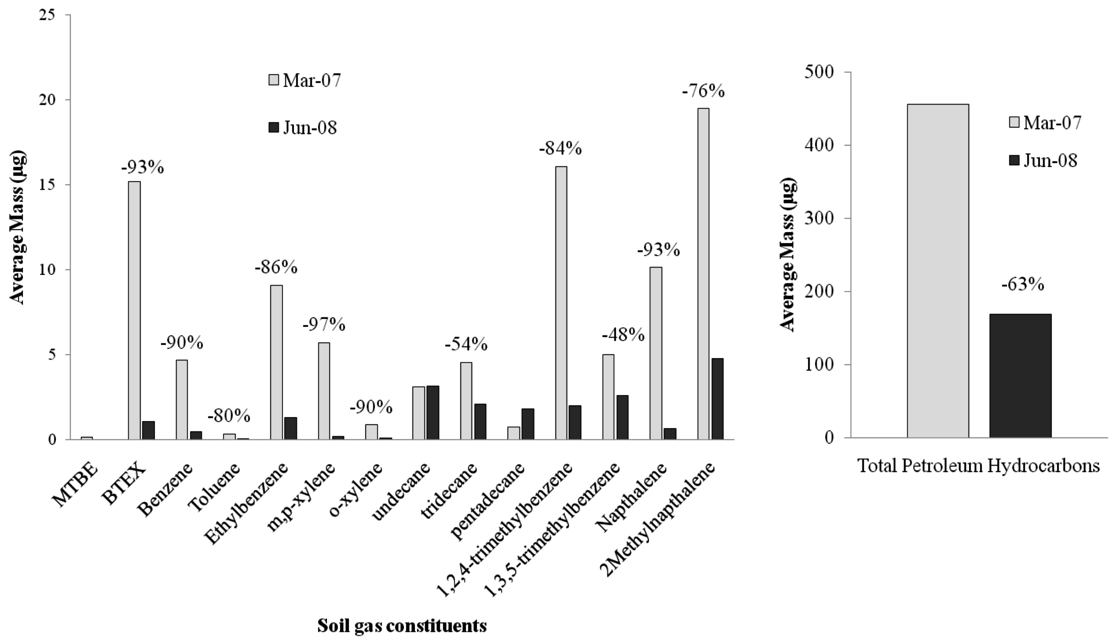

Figure 12 Average soil gas masses decrease from 2007 to 2008. Total Petroleum Hydrocarbon mass is pulled out for scale. All constituents labeled with percent decrease are statistically significant ($P<0.001$). Pentadecane and undecane are the only constituents to increase in mass. Significance based on Wilcoxon Signed Ranks test.

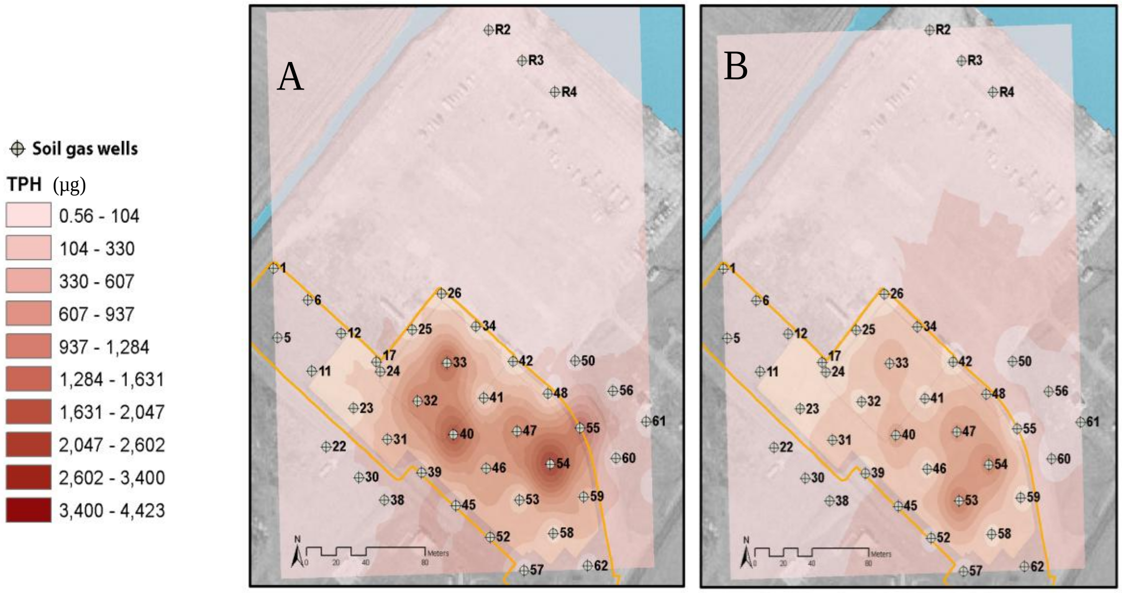

Figure 13 GIS visualization of reduction in soil gas masses of TPH (µg) in **A)** 2007 and **B)** 2008. Soil gas TPH decreased significantly (P<0.001) by 63% from 2007 to 2008.

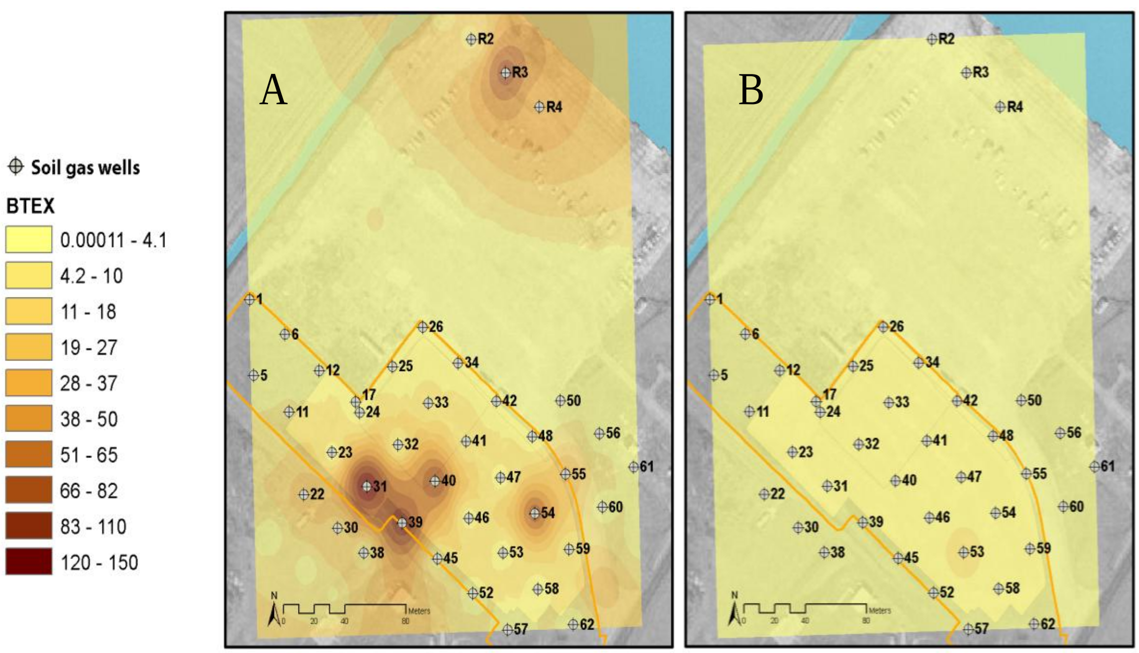

Figure 14 GIS visualization of reduction in soil gas masses of BTEX (µg) in **A)** 2007 and **B)** 2008. Soil gas BTEX decreased significantly (P<0.001) by 93% from 2007 to 2008.

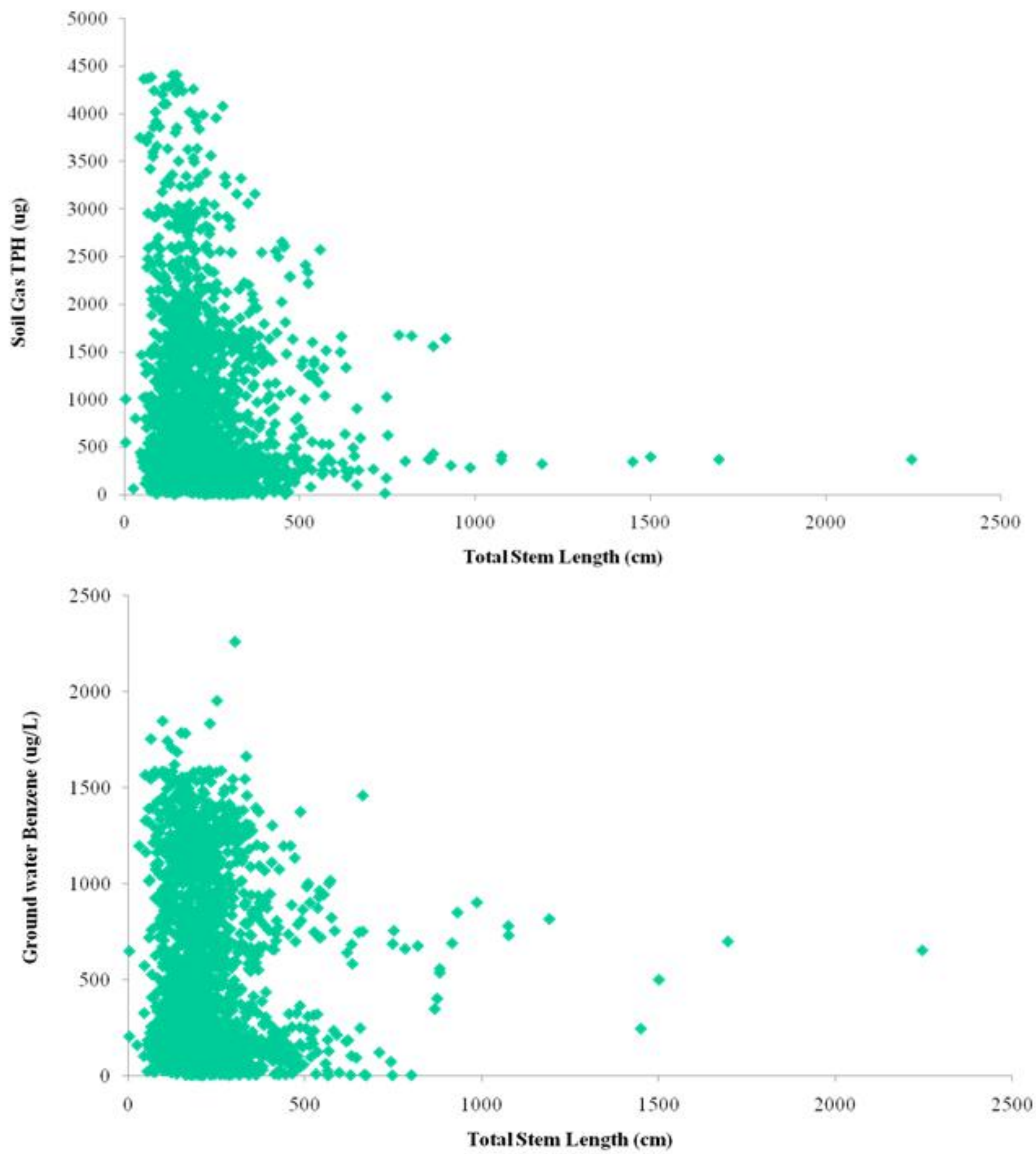

Figure 15 A) Cross-plot of soil gas mass of TPH (µg) and **B)** ground water benzene concentrations (µg/L) assigned to each tree based on inverse distance weighting interpolation between sampling points and total stem length values (n=2,016).

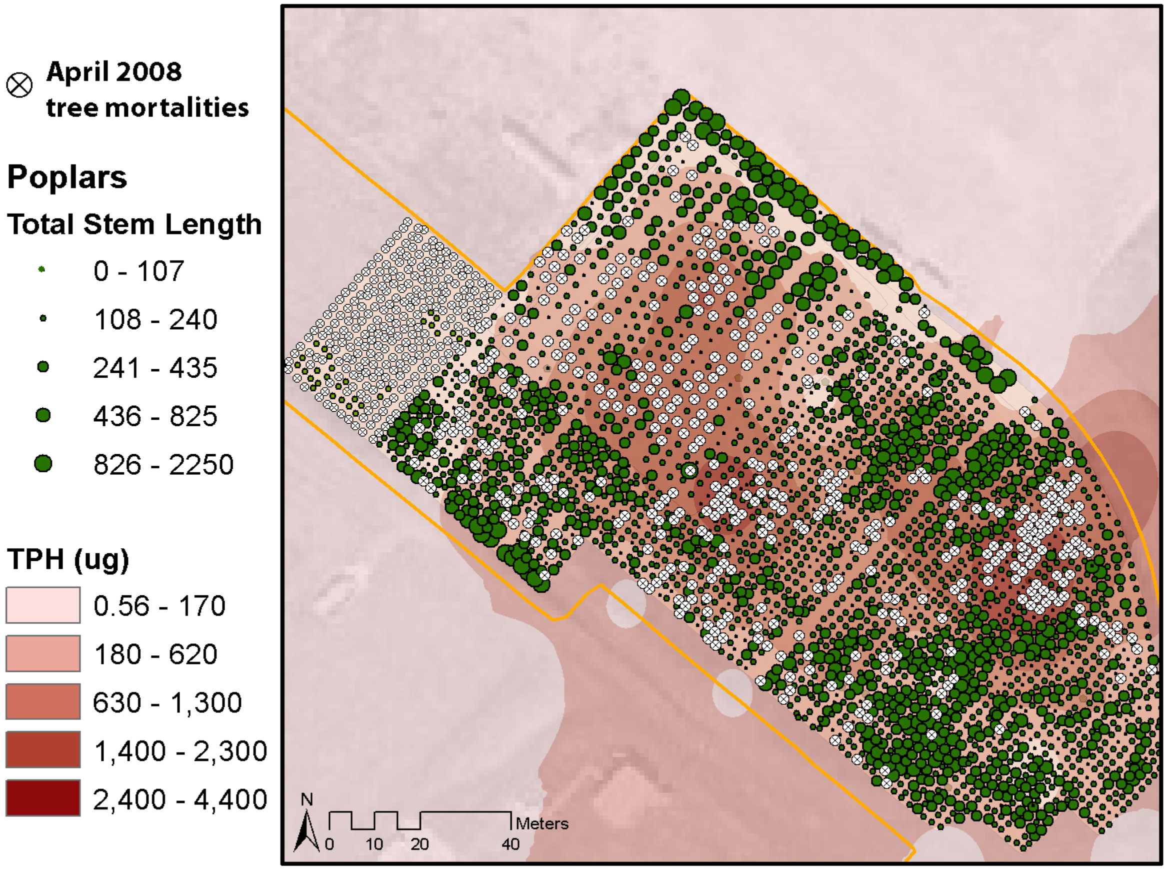

Figure 16 Soil gas TPH (2007) overlaid by tree mortality and total stem length (cm). Notice the areas with the best growth correspond to areas with the least amount of contamination and the areas of highest mortality correspond to those with the highest contamination.

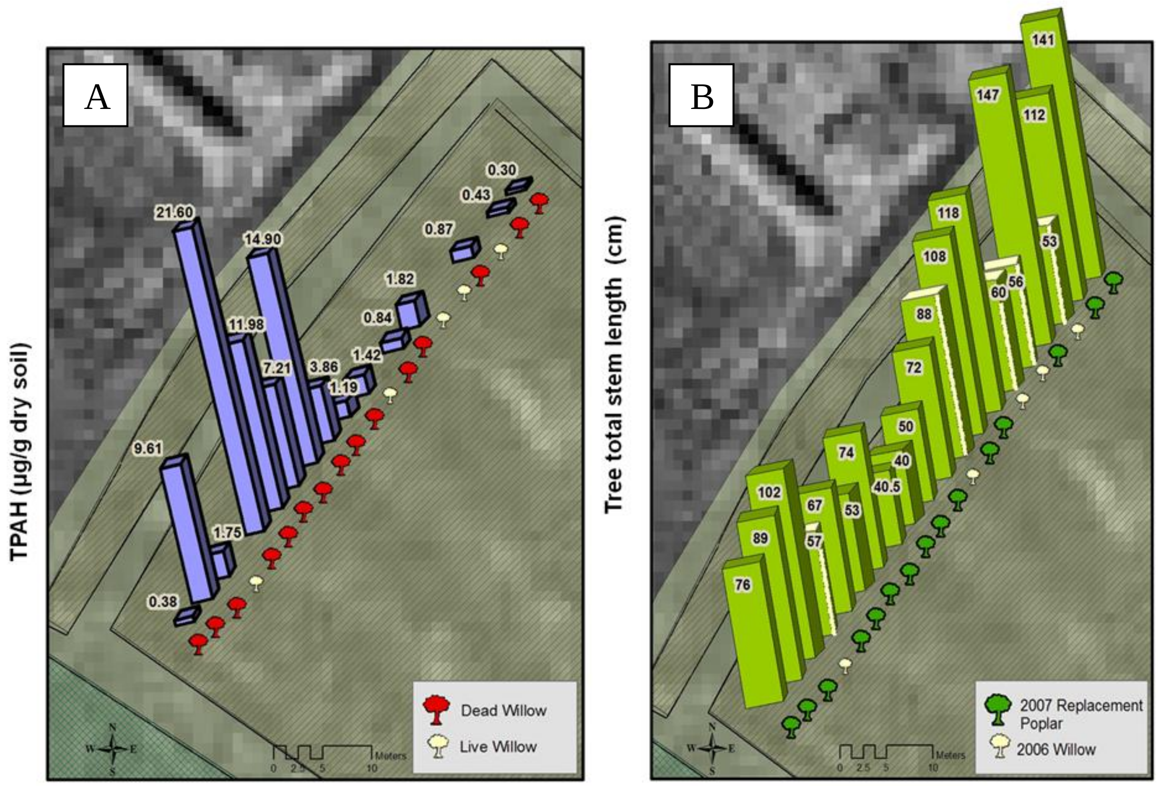

Figure 17 A) Tree mortality from April 2007 occurred in areas with high fuel oil contamination. **B)** Tree height of replacement trees (2007) and highlighted surviving first-planting trees (2006) appears correlated to fuel oil contamination. Surviving 2006 willow trees had not been backfilled with clean soil and appeared stunted even with an extra year of growth compared to poplars.

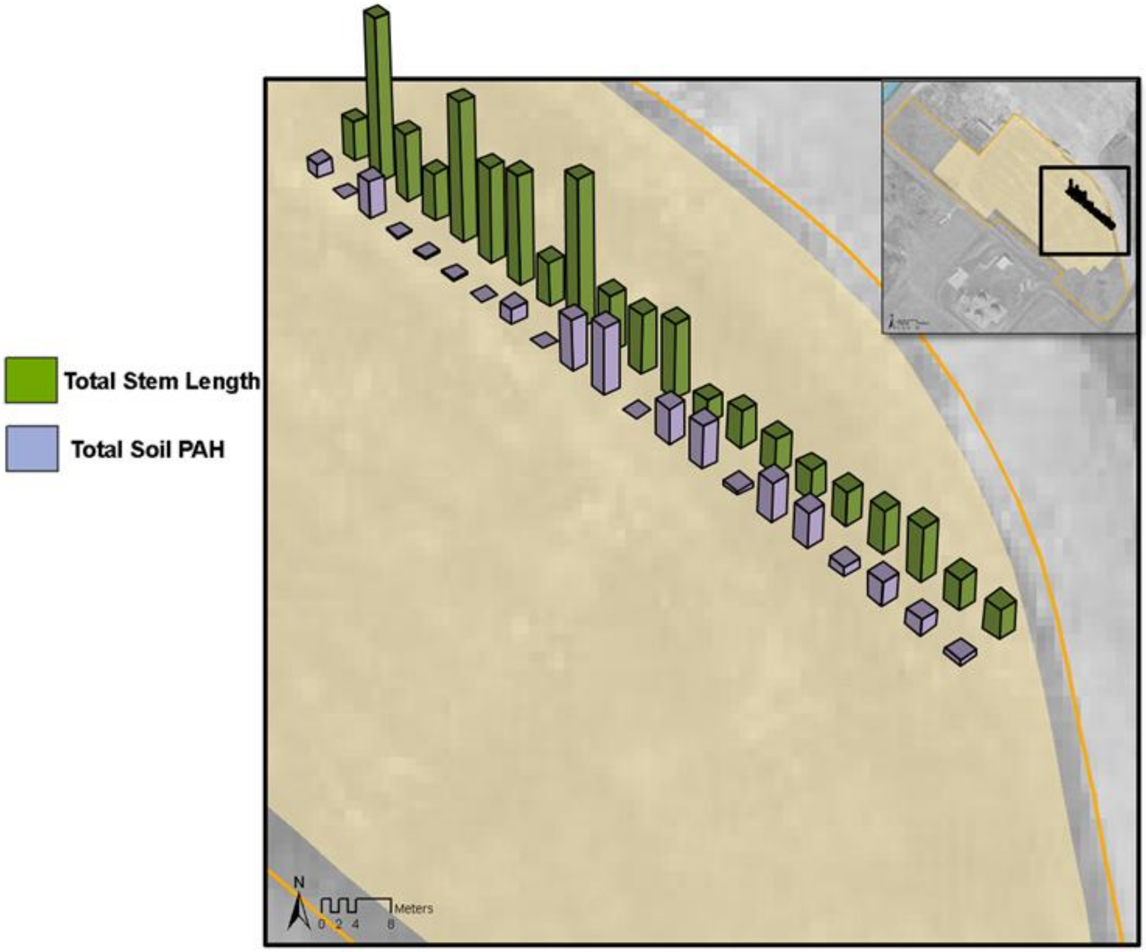

Figure 18 Total stem length (cm) of trees and associated TPAH concentrations (µg/g dry sediment) for Transect 2.

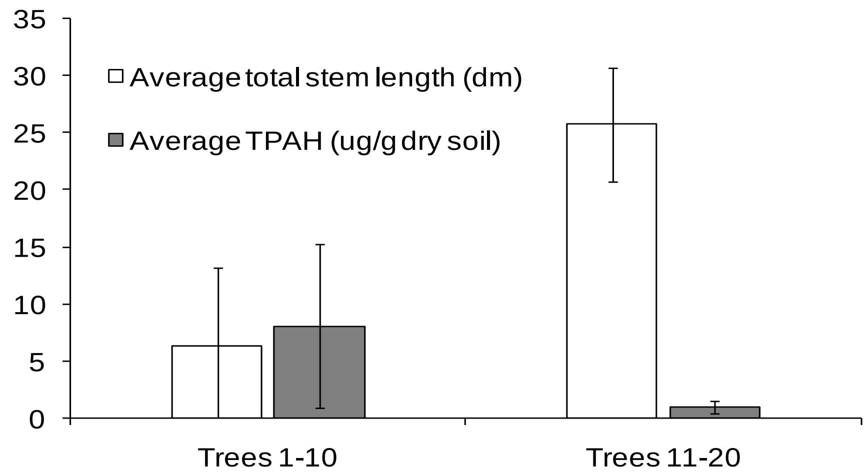

Figure 19 Transect 1 consisted of trees replanted with Method 2 in June Method 1 area. Transect was divided in two between trees 1-10 (poor growth) and trees 11-20 (better growth). Total stem length (dm) was measured after one year of growth. Soil for TPAH (µg/g dry sediment) was sampled at time of planting.

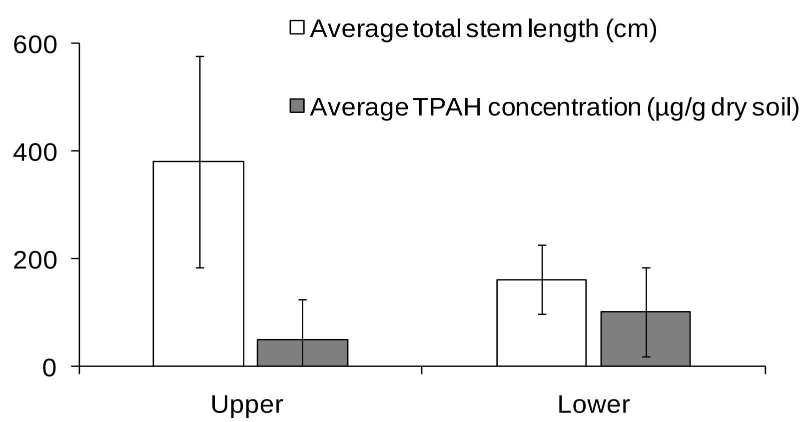

Figure 20 Transect 2 was divided between the “upper” half which showed better growth than the “lower” half. Lower half is approximately 0.5 m closer to ground water and showed twice the level of TPAH concentration on average.

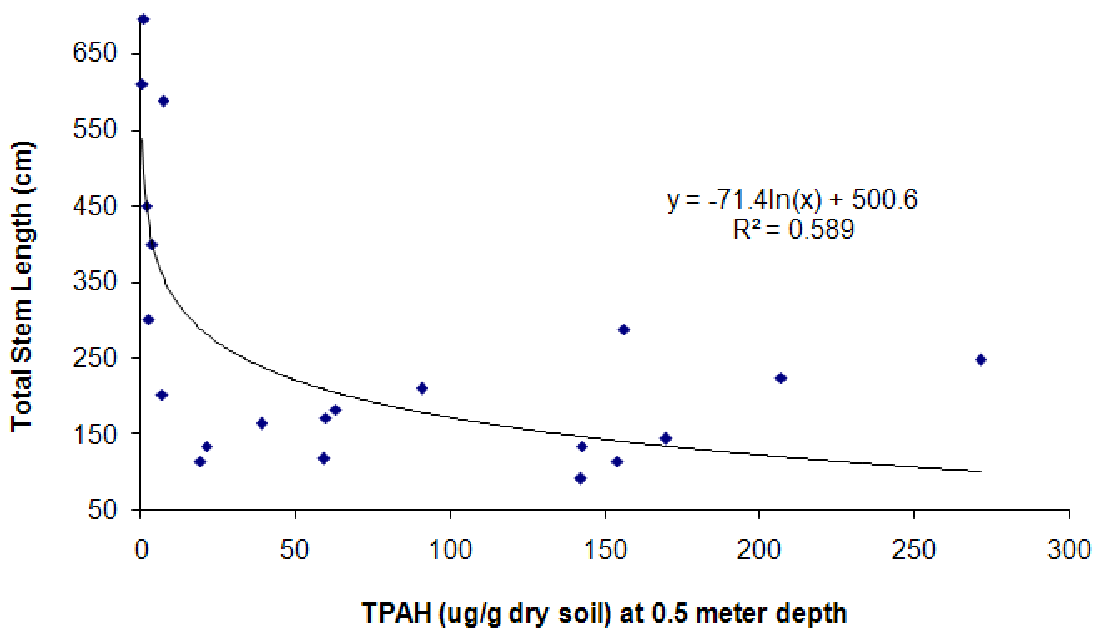

Figure 21 Scatter plot of total stem length (cm) of Transect 2 trees versus associated TPAH soil sample concentration taken at 0.5 m

Table 1 Ground water sampling results from Feb 2006, November 2006, and December 2007 by NCSU, Department of Civil Engineering. All units are in µg/L (ppb).

Date	Well	MTBE	Benzene	Toluene	Ethyl benzene	m+p-xylene	o-xylene	Total xylenes	1,2,4-trimethyl-benzene	1,3,5-trimethyl-benzene	1,2,3-trimethyl-benzene	Trimethyl-benzenes
Feb06	**32MW18**	0.0	0.0	0.0	2.9	2.3	1.9	4.2	2.3	2.7	2.9	7.9
	32RW1	68.0	679.3	7.1	20.5	210.4	0.0	210.4	55.2	164.4	69.4	289.0
	32RW2	99.4	1590.9	20.7	55.5	582.7	19.7	602.4	109.1	355.0	155.9	620.0
	32RW3	129.0	1047.0	33.0	48.3	893.1	9.2	902.3	106.7	322.6	168.2	597.5
	32RW4	506.2	1214.9	16.4	16.0	389.8	12.5	402.3	80.1	328.4	108.9	517.4
	32RW5	600.4	1589.4	22.5	216.7	984.0	14.2	998.2	119.3	372.2	152.5	644.0
	32RW6	48.3	1076.9	10.9	96.3	829.5	21.6	851.1	59.8	176.8	89.1	325.7
	32ESM 1	232.9	5.7	0.0	5.3	15.0	1.3	16.3	2.6	6.4	3.0	12.0
	32MW17	42.9	1330.3	10.8	7.5	355.6	6.2	361.8	122.4	84.4	153.7	360.5
	32ESM14	148.4	68.2	0.0	3.8	12.2	2.2	14.4	2.8	5.2	3.3	11.3
Nov06	**32RW1**	420.8	491.8	10.0	0.0	297.7	2.4	300.1	73.8	33.3	115.0	222.1
	32MW18	1.2	12.2	0.0	0.0	1.3	0.0	1.3	0.0	0.0	1.0	1.0
	32ESM1	9.0	11.0	0.0	0.0	1.6	0.0	1.6	0.0	0.0	0.0	0.0
	32MW20	25.8	1195.3	3.7	0.0	6.4	2.1	8.5	0.0	0.0	1.1	1.1
	32MW22	199.1	826.1	0.0	2.4	6.7	0.0	6.7	0.0	0.0	0.0	0.0
Dec07	**MW1**	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	MW2	29.7	82.1	4.7	3.0	0.0	3.2	3.2	0.0	245.5	193.1	438.6
	MW7	44.6	5.5	**	4.7	6.5	0.0	6.5	7.2	0.0	18.0	25.2
	MW8	1.7	2.6	**	0.0	1.5	0.0	1.5	0.0	3.9	3.0	6.9
	MW10	145.5	99.8	9.1	2.7	32.9	6.5	39.4	21.3	35.0	43.9	100.2
	MW11	48.0	11.9	49.7	0.0	1.4	0.0	1.4	0.0	3.8	3.4	7.2
	32MW21	944.4	3243.8	14.4	477.1	518.4	3.0	521.4	133.3	630.2	436.5	1200.0
	32MW22	18.0	45.9	**	14.1	40.4	3.6	44.0	7.1	23.6	13.6	44.3
	MW23	46.8	30.3	10.5	1.2	4	0.0	4.0	1.5	1.5	3.5	6.5
	RV Well	56.6	36.9	103.4	0.0	3.9	0.0	3.9	0.0	3.5	2.3	5.8
	32ESM6	1.7	1.2	0.0	0.0	0.0	0.0	0.0	0.0	3.5	2.2	5.7

** Large interference peak prevented quantification of toluene.

Table 2 December 2007 ground water concentration data analyzed by NCSU Civil Engineering Department. August 2008 ground water data analyzed by ARCADIS. All units are in µg/L (ppb).

Date	Contaminant	32MW1	32MW2	32MW8	32MW11	32MW22	32ESM6	RVWell
Dec07	**Benzene**	< 1.0	82.1	2.6	11.9	45.9	1.2	36.9
	Toluene	< 1.0	3	< 1.0	< 1.0	14.1	< 1.0	< 1.0
	Ethylbenzene	< 1.0	4.7	**	49.7	**	< 1.0	103.4
	Xylenes	< 1.0	3.2	1.5	1.4	44	< 1.0	3.9
	MTBE	1.1	29.7	1.7	48	18	1.7	56.6
Aug08	**Benzene**	<1.0	71	<1.0	<1.0	<1.0	<1.0	<1.0
	Toluene	<1.0	<1.0	<1.0	2.1	<1.0	<1.0	<1.0
	Ethylbenzene	<1.0	5.2	<1.0	1.4	<1.0	<1.0	<1.0
	Xylenes	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	4.6
	MTBE	<10	<10	<10	<10	<10	<10	<10

** Large interference peak prevented quantification of toluene.

Table 3A Historical ARCADIS ground water monitoring data before phytoremediation installation. All units in µg/L.

Date	Contaminant	32ESM1	32ESM2	32ESM5	32ESM10	32ESM11	32ESM14	32MW16	32MW18
Jun01	**Benzene**	<1.0	<1.0	<1.0	5.8	<1.0	120	<1.0	<1.0
	Toluene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Ethylbenzene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Xylenes	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	MTBE	18	<1.0	7.3	30	<1.0	530	16	4.1
May02	**Benzene**	<1.0	<1.0	<1.0	<1.0	<1.0	510	<1.0	<1.0
	Toluene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Ethylbenzene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Xylenes	<1.0	<1.0	<1.0	<1.0	<1.0	3.5	<1.0	<1.0
	MTBE	4.7	<1.0	4.7	16	<1.0	590	44	<1.0
Jun03	**Benzene**	2.4	<1.0	<1.0	<1.0	<1.0	160	<1.0	<1.0
	Toluene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Ethylbenzene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Total xylenes	NA	NA	NA	NA	NA	5.4	NA	NA
	MTBE	26	<1.0	<1.0	58	5.9	360	45	<1.0
May04	**Benzene**	<1.0	<1.0	<1.0	<1.0	<1.0	400	<1.0	<1.0
	Toluene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Ethylbenzene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Xylenes	NA	NA	NA	1.0	NA	NA	NA	NA
	MTBE	85	<1.0	2.5	38	2.2	130	61	2.4
May05	**Benzene**	<1.0	31	<1.0	<1.0	<1.0	210	<1.0	<1.0
	Toluene	<1.0	1.5	<1.0	<1.0	<1.0	<10	<1.0	<1.0
	Ethylbenzene	<1.0	4.3	<1.0	<1.0	<1.0	<10	<1.0	<1.0
	Xylenes	<2.0	37	<2.0	<2	<2.0	<20	<2.0	<2.0
	MTBE	250	55	1.4	36	2.2	130	110	1.4

Table 3B ARCADIS ground water samples after phytoremediation installation (32MW20 installed April 2006 in tree line). All units in µg/L.

Date	Contaminant	32ESM1	32ESM2	32ESM5	32ESM10	32ESM11	32ESM14	32MW16	32MW18	32MW20
Jun06	**Benzene**	< 1.3	<1.0	<1.0	< 1.3	<1.0	< 1.3	5.0	<1.0	1000
	Toluene	< 1.2	2.5	<1.0	< 1.2	<1.0	< 1.2	< 4.8	<1.0	< 12
	Ethylbenzene	< 2.4	<1.0	<1.0	< 2.4	<1.0	< 2.4	< 9.4	<1.0	< 24
	Total xylenes	< 3.3	15	<2.0	< 3.3	<2.0	< 3.3	< 13	<2.0	< 33
	MTBE	190	<10	<10	66	<10	170	460	14	250
May07	**Benzene**	4.2	< 1.0	< 1.0	< 1.0	< 1.0	3.9	3.0	1.8	2,800
	Toluene	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	1.0	< 1.0	1.8	< 20
	Ethylbenzene	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	1.2	< 1.0	< 1.0	< 20
	Total xylenes	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 40
	MTBE	180	< 10	< 10	37	< 10	160	410	23	200
Jun08	**Benzene**	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	750
	Toluene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Ethylbenzene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Total xylenes	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
	MTBE	<10	<10	<10	36	<10	51	330	<10	63

Table 4 Soil samples collected adjacent to ground water wells to analyze total 42 alkylated/nonalkylated PAHs and monitor weathering C3-napthalene/P2-phenanthrene (N3/P2) ratios.

	Feb/Apr 2006		Nov 2006	
Well ID	**TPAH (µg/g dry sediment) (± 1 SD)**	**N3/P2 (± 1 SD)**	**TPAH (µg/g dry sediment) (± 1 SD)**	**N3/P2 (± 1 SD)**
32MW18a	0.95 ± 0.41	3.32 ± 0.15	0.35 ± 0.20	13.43 ± 8.83
32MW18b	0.84 ± 0.65	4.61 ± 0.35	0.64 ± 0.39	NA
Abn RW*	NS	NS	2.20 ± 0.39	29.43 ± 6.06
32RW1a	1.03 ± 0.04	4.35 ± 2.45	19.26 ± 0.96	105.74 ± 16.66
32RW1b	101.63 ± 16.91	87.45 ± 6.03	14.66 ± 3.70	105.10 ± 22.53
32RW2a	NS	NS	10.81 ± 1.66	71.30 ± 2.95
32RW2b	NS	NS	102.54 ± 7.59	77.80 ± 5.49
32RW3a	47.72 ± 15.43	54.48 ± 3.49	1.09 ± 0.35	3.47 N/A
32RW3b	12.61 ± 5.67	36.20 ± 5.62	33.94 ± 21.11	72.40 ± 12.78
32RW4a	59.44 ± 8.15	80.46 ± 7.53	2.14 ± 0.98	24.21 N/A
32RW4b	17.37 ± 7.78	31.91 ± 10.40	41.57 ± 2.10	83.93 ± 5.01
32RW5a	31.35 ± 5.93	71.47 ± 3.36	11.94 ± 0.16	88.07 ± 13.90
32RW5b	126.58 ± 7.38	69.70 ± 1.23	60.38 ± 8.99	108.50 ± 9.05
32RW6a	1.54 ± 0.21	8.85 ± 0.97	0.32 ± 0.14	2.27 N/A
32RW6b	22.26 ± 10.79	15.44 ± 3.46	96.38 ± 34.35	92.19 ± 6.71
32MW19a	4.71 ± 0.76	36.34 ± 0.18	NS	NS
32MW19b	41.04 ± 26.47	22.15 ± 1.84	NS	NS
32MW21a	16.68 ± 1.59	14.48 ± 0.32	0.42 ± 0.11	9.58 ± 3.23
32MW21b	43.61 ± 26.02	24.20 ± 0.87	146.35 ± 6.55	83.91 ± 0.62

Note: a=one meter sampling depth; b=two meter sampling depth;
N/A= P2 equaled zero for two out of three triplicate samples.
*Abandoned recovery well

Table 5 Soil gas analysis in March 2007 (GORE, 2007). Wells included in table are those sampled again in 2008**.**

Well	TPH	Benzene	Toluene	Ethyl benzene	m+p-xylene	o-xylene	MTBE	Trimethyl-benzenes	Napthalene	2-methyl napthalene
1	0.77	0.03	0.03		0.02			0		
5	3.28	0.01	0.01					0		
6	0.68	0.01	0.02					0		
11	62.99	0.51	0.03	0.08	3.93	0.05		1.31		
12	59.06	0.02	0.03	0.02	0.05	0.02		0		
17	0.64	0.01	0.01					0		
22	80.34	9.11	0.05	0.96	13.05	0.28		6.13	0.35	0.04
23	14.15	0.13	0.01	0.06	0.12			0.16		
24	187.47	0.02	0.02		0.04			0.06	0.07	0.01
25	10.22							0		0.08
26	0.54		0.02		0.02			0		
30	68.4	8.2	0.03	0.29	4.23	0.04		4.33	0.03	
31	444.84	40.87	0.18	66.03	41.34	0.26		89.09	7.68	2.79
32	1632.28	0.04	0.04	0.35	0.09	0.05		9.78	5.35	17.45
33	2367.33	7.04	0.09	1.49	0.59	0.12		61.04	8.57	77.74
34	4.39	0.01	0.03		0.05			0		
38	4.12	0.12	0.02	0.17	0.68	0.02		0.44		
39	78.49	77.5	0.09	10.59	9.27	0.14	0.19	7.65	0.39	0.13
40	3040.11	3.78	0.1	45.08	33.98	0.37		129.85	51	86.31
41	56.31	0.28	0.46	0.92	2.31	0.52	0.06	10.62	0.84	0.97
42	21.13	0.02			0.02					
45	95.41	0.18	0.1	0.22	0.26	0.03		0.19	0.07	0.03
46	787.09	0.05	0.06	0.03	0.09	0.1		0.07	0.22	0.05
47	1680.82	0.01	0.11		0.05	0.02		0.03	0.16	0.06
48	0.82									
50	7.99	0.02	0.01	0.02	0.07			0.41	0.08	0.07
52	406.14		0.04		0.01			0		
53	91.35	0.02	0.04	0.02	0.1	0.04		0.06	0.21	0.47

Blank cells indicate measurements of “no detect” or “below detect limit.”

Table 5 (continued)

Well	TPH	Benzene	Toluene	Ethyl benzene	m+p-xylene	o-xylene	MTBE	Trimethyl-benzenes*	Napthalene	2-methyl napthalene
54	4431.96	10.38	0.04	62.07	1.11	0.38		44.15	33.18	108.15
55	1997.34	0.02	2.02	4.8	22.02	0.21		111.19	81.93	66.03
56	3.01	0.01	0.01		0.01			0.04	0.06	0.03
57	1.01	0.01	0.01		0.01			0		
58	1.5	0.02	0.03	0.01	0.02			0		
59	539.68	0.02	0.03	4.83	0.08	0.12		8.08	2.01	29.2
60	13.5		0.04	0.06	0.17	0.04		0	0.03	0.05
61	1.22	0.02	0.02		0.01			0		
62	1.59	0.01	0.03		0.01			0		0.01
R2	5.31	0.01	0.98	1.52	4.53	1.12		0.01		
R3	15.18		3.29	12.81	44.49	11.01		0.11		
R3	19.04	0.02	4.18	5.67	16.89	4.05		0.04		

*Trimethyl-benzenes include: 1,2,4-trimethyl-benzene and 1,3,5-trimethylbenzene.

Table 6 Soil gas analysis in July 2008 (GORE report not yet available).

Well	TPH	Benzene	Toluene	Ethyl benzene	m+p-xylene	o-xylene	MTBE	Trimethyl -benzenes	Napthalene	2-methyl napthalene
1	0.12									
5	0.02									
6	0.03									
11	0.49									
12	0.10									
17	0.06									
22	102.76						0.02		0.28	0.02
23	0.02									
24	32.49									
25	25.78									
26	0.01									
30	0.79									
31	322.25			0.01	0.15	0.09	0.03		3.05	0.16
32	60.51									
33	622.24		0.02						0.14	0.24
34	209.73									
38	1.58									
39	1.43									
40	739.05				0.08	0.06	0.04		2.26	1.76
41	0.07									
42	2.20									
45	193.48			0.05			0.05		0.02	0.02
46	3.42									
47	1021.58				0.04	0.16	0.07		7.32	0.62
48	0.00									
50	0.84									
52	4.12									
53	3.03									

Blank cells indicate measurements of “no detect” or “below detect limit.”

Table 6 (continued)

Well	TPH	Benzene	Toluene	Ethyl benzene	m+p-xylene	o-xylene	MTBE	Trimethyl-benzenes*	Napthalene	2-methyl napthalene
54	1674.49	1.76	0.01	7.53	0.19	0.22		12.02	1.98	37.49
55	1482.96	0.01		0.02	0.12	0.05		16.06	1.09	0.20
56	0.31									
57	6.71									
58	0.82									
59	248.73	0.01								0.01
60	0.14									
61	0.24									
62	0.03									
R2	0.01									
R3	0.08		0.16	0.07	0.52	0.21		0.46	0.03	0.01
R3	0.05		0.11							

*Trimethyl-benzenes include: 1,2,4-trimethyl-benzene and 1,3,5-trimethylbenzene.

Table 7 Two transects of soil total PAH concentrations (cm) and N3/P2 ratios **(**± one standard deviation) and associated tree stem length.

Transect 1			Transect 2		
TPAH (ug/g dry sediment) (± 1 SD)	**Total Stem Length (cm)**	**N3/P2 (± 1 SD)**	**TPAH (μg/g dry sediment) (± 1 SD)**	**Total Stem Length (cm)**	**N3/P2 (± 1 SD)**
0.38 ± 0.09	125	1.73 ± 0.37	59.91 ± 28.11	172	116.98 ± 22.63
9.61 ± 3.70	0	0.81 ± 0.22	0.97 ± 0.03	696	4.96 ± 1.61
1.75 ± 1.11	156	4.71 ± 0.45	156.19 ± 52.59	288	618.87 ± 78.41
NS	W	NS	7.14 ± 2.48	203	17.51 ± 1.33
21.60 ± 3.11	W	4.03 ± 1.27	7.26 ± 1.76	588	78.52 ± 2.60
11.98 ± 3.93	91	65.91 ± 1.84	3.85 ± 0.73	400	0.66 ± 0.36
7.21 ± 1.77	128	42.66 ± 3.28	1.76 ± 0.58	450	3.08 ± 0.20
14.90 ± 2.02	0	57.39 ± 6.99	63.09 ± 8.45	183	38.22 ± 4.40
3.86 ± 1.34	0	22.70 ± 5.41	0.59 ± 0.13	610	2.57 ± 0.45
1.19 ± 0.66	0	5.27 ± 1.05	207.08 ± 26.16	225	414.33 ± 22.90
1.42 ± 0.55	149	3.00 ± 0.16	271.40 ± 108.85	248	301.27 ± 37.66
NS	278	NS	2.64 ± 0.42	301	6.97 ± 0.87
0.84 ± 0.09	257	8.56 ± 2.33	142.44 ± 17.07	92	36.01 ± 2.63
1.82 ± 0.04	262	47.87 ± 1.08	169.81 ± 18.44	145	22.84 ± 3.69
NS	W	NS	21.33 ± 7.45	135	0.29 ± 0.04
NS	W	NS	154.05 ± 8.63	115	37.35 ± 1.45
0.87 ± 0.09	298	12.97 ± 2.73	142.64 ± 22.00	135	48.26 ± 3.89
NS	W	NS	39.10 ± 11.23	165	153.39 ± 13.43
0.43 ± 0.13	284	7.16 ± 1.78	90.87 ± 9.66	210	34.61 ± 2.32
0.30 ± 0.05	273	7.88 ± 2.94	59.34 ± 0.52	119	34.87 ± 1.83
			19.20 ± 8.34	115	15.15 ± 6.41

W=willow tree that was still alive at time of sampling and was therefore not sampled (NS) for TPAH