

## **APPENDIX A**

### **Study area and sampling-Site Description**

This supplement is an updated version of Chapter 3 in the Masters Thesis by Helen Smartt: “Effects of the desorption and dissolution of polycyclic aromatic hydrocarbons on phytoremediation at a creosote contaminated site”, Virginia Tech, 2002. A.5-A.6 has new data and trend discussion. A.1-A.4 has not changed much, but A.5-A.6 is re-written.

#### **A.1 Introduction**

The study area and sampling-site for this research is the Norfolk Southern Tie Yard, which is located in Oneida, Tennessee, and was formerly used by Norfolk Southern Railway Company to treat railroad ties with creosote. When the site was active, creosote was discharged into the soil and groundwater below the land surface through various site operations. As a result, the site is highly contaminated with waste creosote. Supplement B presents a brief history of the Oneida Tie Yard site, a description of the remediation plan for the site, an overview of the uptake and rainfall data in the Oneida area, and a summary of the recent soil and groundwater contamination trends on-site.

#### **A.2 Site History**

Most of the site history outlined in chapter A is obtained from the ARCADIS Geraghty & Miller Remediation Progress Meetings from 2000 and 2001. The Oneida Norfolk Southern Tie Yard is located in the central-southern region of Scott County, Tennessee, which is approximately 50 miles northwest of Knoxville, Tennessee. The Norfolk Southern Corporation Currently owns this site.

The site was activated by the Tennessee Railway Company in the early 1950’s as a railroad cross-tie treatment facility. The tie yard was used continuously until the end of 1960 and then intermittently from 1960 to 1966 and 1968 to 1973. On-site operations were finally ceased in 1973 when Southern Railway Company purchased the Tennessee Railway Company. In 1990, Southern Railway Company changed its name to Norfolk Southern Corporation.

Figure A.1 shows a plan view of the Oneida Tie Yard site layout including the theorized locations the wood treatment processes. The site originally included an above ground storage tank (AST) to hold creosote, a pressurized wood treatment unit, and a spur track for transporting the treated railroad ties. The treatment unit was supposedly located about 100 feet north of Pine Creek. All the runoff from the plant was collected in sump pits at the property line; however, these pits are no longer discernible.

A holding pond was also located on-site, east of the treatment unit, and contained surplus creosote resulting from the pressure treatment process. Based on assessment of the contamination of the site the location of the treatment area is believed to be in the area west of the interception trench. A ruptured storage tank or spills during handling of the creosote at this location is suspected to be the source of the majority of the contamination. The holding pond is also a suspected source area for contamination at the site. All of the creosote treatment equipment was disassembled and removed from the facility when site operations were ceased. The region located adjacent to the tie yard houses an active rail yard including two diesel fuel AST's and fueling and maintenance facilities. In addition, Pine Creek runs along the southeastern border of the site and eventually feeds into larger bodies of water.

In 1990, the United States Army Corps of Engineers was performing drainage channel work along Pine Creek, when they discovered evidence of creosote contamination near the railroad bridge that crosses over the creek. The pollution was reported to the Tennessee Department of Health and Environment (TDHE), who decided to further investigate the site conditions. The TDHE analyzed groundwater and soil samples from the treatment areas as well as surface water and sediment from Pine Creek. The results from these samples showed that there was a presence of creosote in the subsurface soil and creek sediments based on the prevalence of benzene, toluene, ethylbenzene, and xylene (BTEX) and PAH constituents.

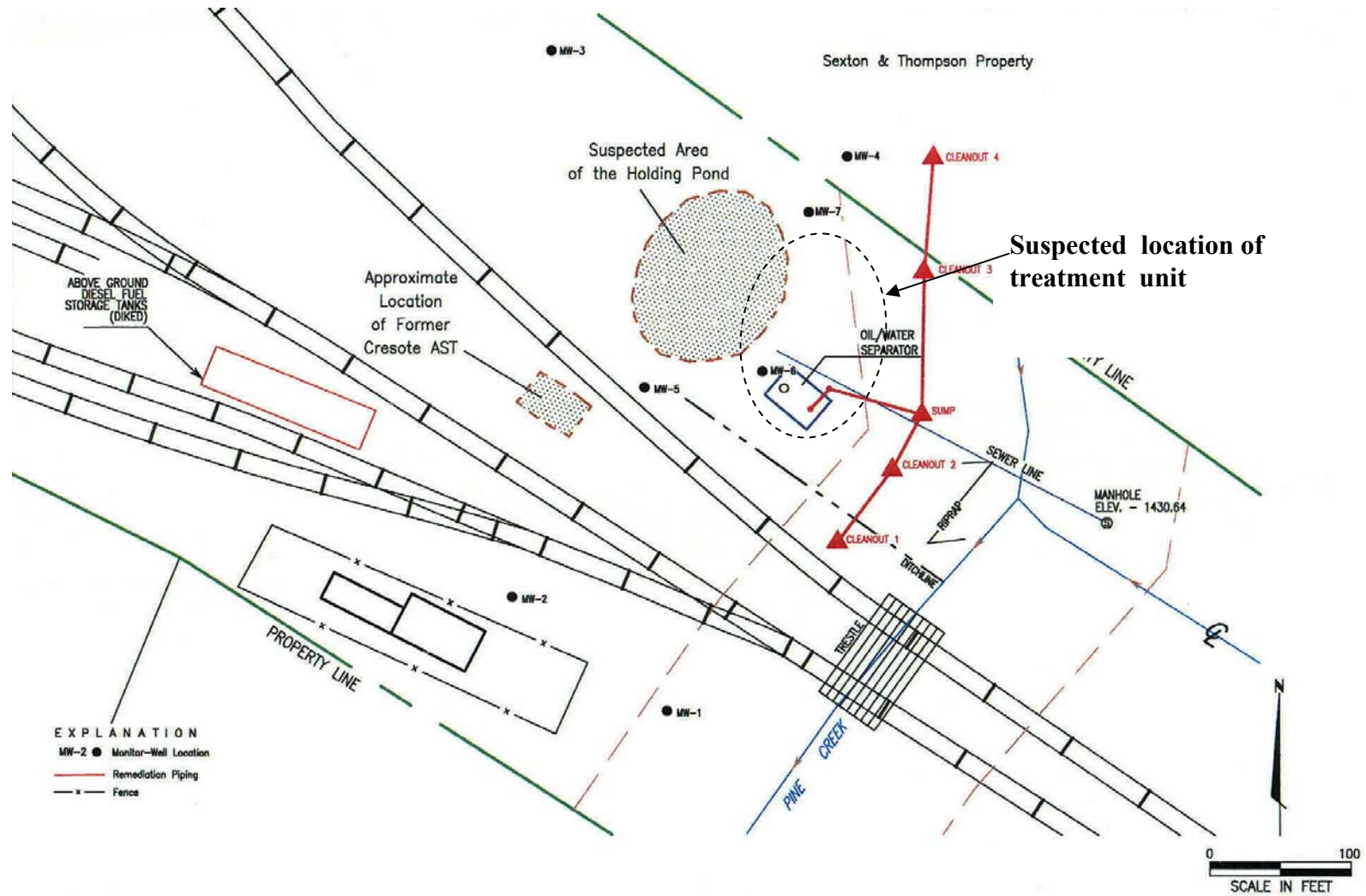


Figure A.1 Oneida Tie Yard Site Layout (ARCADIS Geraghty & Miller 2000)

Once it was established that contamination was present at the Oneida Tie Yard, the TDHE recommended the need for remedial action. The main goal of the initial remedial effort was to prevent any further creosote seepage into Pine Creek to keep contamination from moving off-site. From 1991 to 1995, several different consulting firms performed soil, groundwater, and surface water sampling and analysis. ARCADIS Geraghty & Miller, a consulting engineering firm, was hired by Norfolk Southern in 1997 to study the site and determine the appropriate method of remediation. Furthermore, Virginia Tech was also chosen to provide supplementary sampling and analysis and to assess the potential use of phytoremediation as a remedial technology.

### **A.3 Remediation Plan**

The initial cleanup strategy on-site was the installation of a groundwater collection trench and was conducted by ETI. In March of 1991, ETI conducted initial abatement and preliminary site assessment (PSA) activities to determine the soil and groundwater characteristics at the site. As part of the PSA, five soil borings were completed and five monitoring wells were installed. In addition, ETI created some test pits at the southeastern end of the site. Eventually these pits were connected to form a groundwater collection trench roughly 330-feet long, 20-feet wide at the top, and 3-feet wide at the bottom. A 4-inch slotted drain tile was positioned in the trench and attached to a 24-inch vertical standpipe. The groundwater interception system was updated in late 1997 and is still used intermittently as a method of hydraulic control to prevent creosote from traveling off-site and into Pine Creek. Groundwater from the site is collected by a submersible pump, situated in the standpipe, and sent through an on-site oil/water separator. The wastewater is then discharged to an 8-inch sanitary sewer line where it is treated at the Oneida public wastewater treatment facility. The oily free product is then separated and periodically removed.

In 1997, ARCADIS Geraghty & Miller performed additional sampling to further characterize the soil and groundwater at the tie yard. The results of this effort showed that PAH contamination was located mainly at the water table, which is approximately 7 feet below land surface, and on top of the bedrock, which is roughly 10 feet below land surface. After assessing the location and nature of the contaminants, ARCADIS

Geraghty & Miller proposed that an intrinsic cleanup process called phytoremediation, as well as bioremediation, be applied at the site. The TDHE approved the remedial action plan for the Oneida Tie Yard in 1997.

ARCADIS Geraghty & Miller planted 1,026 hybrid poplar trees at the tie yard in 1997 to induce phytoremediation. An additional 120 trees were planted down gradient of the original phytoremediation system in 1998. The trees were planted over roughly 2.5 acres of the site as displayed in Figure A.2. Phytoremediation was a feasible strategy because the interceptor trench located at the southeastern end of the site served as a hydraulic control to keep contamination from moving downstream. In particular, hybrid poplar trees were chosen for this site based upon their evapotranspiration potential, growth rate, depth and distribution of roots, biomass yield and degradative enzymes produced, and their ability to bioaccumulate contaminants (Al-Yousfi et al. 2000). Poplar trees can be used to remediate contaminants through direct and indirect phytoremediation. Through analytical testing, ARCADIS Geraghty & Miller indicated that anaerobic intrinsic bioremediation is also highly likely via increased bacterial populations around the roots of the trees.



**Figure A.2 Hybrid Poplar Tree Layout (ARCADIS Geraghty & Miller 2001)**

Contaminated soil from the excavation of the groundwater collection trench was spread over the top 2-feet of the surface of the site. A portion of the site was also covered by a layer of surplus coal from the adjacent rail yard activities. The coal layer is located a few feet below land surface and has caused stunted growth in some trees and/or caused

some trees to die because their roots cannot break through to the groundwater table. However, since they were planted many of the tree roots have been able to penetrate the groundwater table and reached the contaminated plume of creosote.

A series of groundwater monitoring wells, as well as over twenty multi-level samplers (MLS's) with ports located every foot above bedrock, were installed so that groundwater could be sampled. In addition to monitoring wells, piezometers and pressure transducers were fixed to measure the effect of the trees on groundwater flow patterns. The network of groundwater monitoring wells, multi-level samplers, piezometers, and pressure transducers allow sampling for a more accurate representation of the contaminated plume and soil and groundwater parameters.

In September 1998, 1,147 tons of soil was excavated from an identified shallow source area close to the above ground storage tank at the rail road tracks and backfilled with soil and gravel.

Based on monitoring after the implementation of the phytoremediation system in 1997 it have been discovered that the center of the plume is characterized by a significant free phase dense-non-aqueous-phase liquid (DNAPL) creosote plume located 8-10 feet below ground surface. PAHs from this DNAPL pooled on top of a confining bedrock layer continuously dissolves and spread to groundwater above and surrounding this creosote source. This deep source was not removed before implementation of the phytoremediation, because the extent and location of significant DNAPL pools was not discovered until 1998.

#### **A.4 Rainfall & Uptake Data**

The general direction of groundwater flow at the Oneida Tie Yard is from northwest to southeast toward Pine Creek. The flow direction remains constant despite the installation of the groundwater interception trench and the phytoremediation system. However, the hydraulic head and gradient have been affected by the remediation system. The estimated hydraulic gradient at the site ranges from 0.02 to 0.04 (Muck, 2000). According to Fetterolf, the average linear groundwater velocity is between 0.63 and 1.4 cm/day. The water table is usually located roughly 7 feet below land surface but is highly sensitive to

seasonal variability. According to seasonal data taken from the monitoring wells and multi-level samplers, ground water levels may vary from 4.5 feet below land surface (5.27 above bedrock highest sample to immeasurable depths. In some locations, groundwater is perched on shallow aquitards.

The climate in Oneida, Tennessee is generally mild with typically 55 inches per year of precipitation. Water levels in the monitoring wells and multi-level samplers are very sensitive to rainfall events because the aquifer saturated thickness is fairly shallow and the water table is generally close to the land surface. In addition, spatial variations in groundwater velocity also exist.

When fully grown, hybrid poplars can uptake and transpire over 50 gallons of water per tree per day which makes them useful for hydraulic control (Matso 1995). In some cases, poplar trees have even been found to transpire up to 350 gallons of water per day (Loftis 1999). According to Loftis, with approximately 1000 poplar trees on-site, this corresponds to an uptake rate of 4.6 gallons per tree per day.

## **A.5 Groundwater Characteristics**

After the addition of the groundwater interception trench in 1991, additional sampling was performed, the results of which showed that no contamination was moving to off-site drinking water wells. However, PAHs were still detected in surface water and sediment samples taken from Pine Creek and also the effluent from the oil/water separator located on-site. In 1993, another site investigation was conducted and more groundwater samples were taken. The outcome of this sampling event implied that PAHs were impacting Pine Creek sediments not only immediately adjacent to the site, but also further downstream. Off-site drinking water wells were still not affected. Samples were obtained once again in 1994 and 1995 indicating that PAHs were still present on-site. An investigation of the soil underneath the riprap along the northern bank of Pine Creek was also conducted but creosote was only discovered seeping from one area.

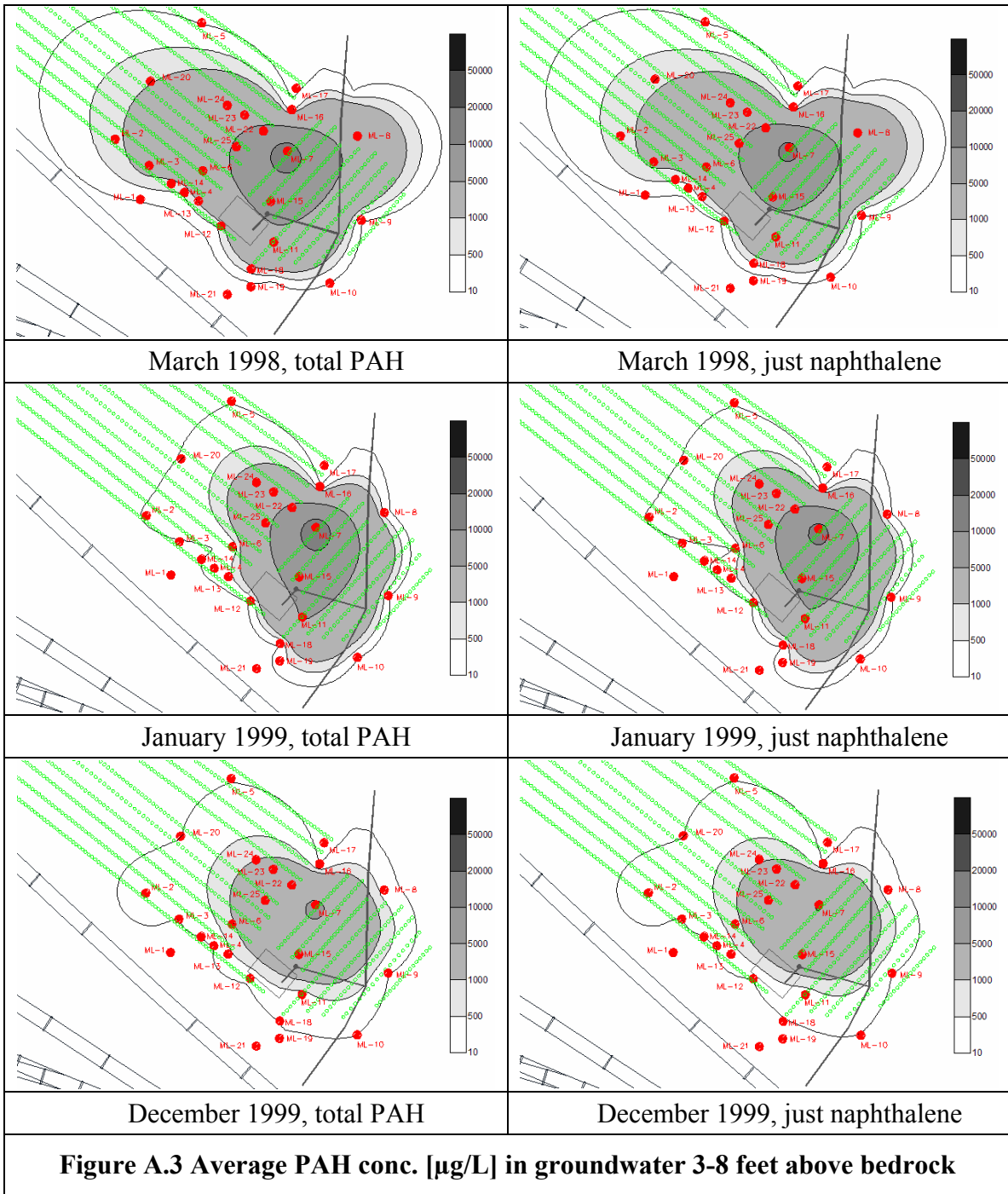
Since multi-level samplers were installed in 1997, groundwater samples have been analyzed by a Virginia Tech laboratory on a bi-annual basis. The selection of ten monitored PAHs was based on groundwater analytical results over a six year period

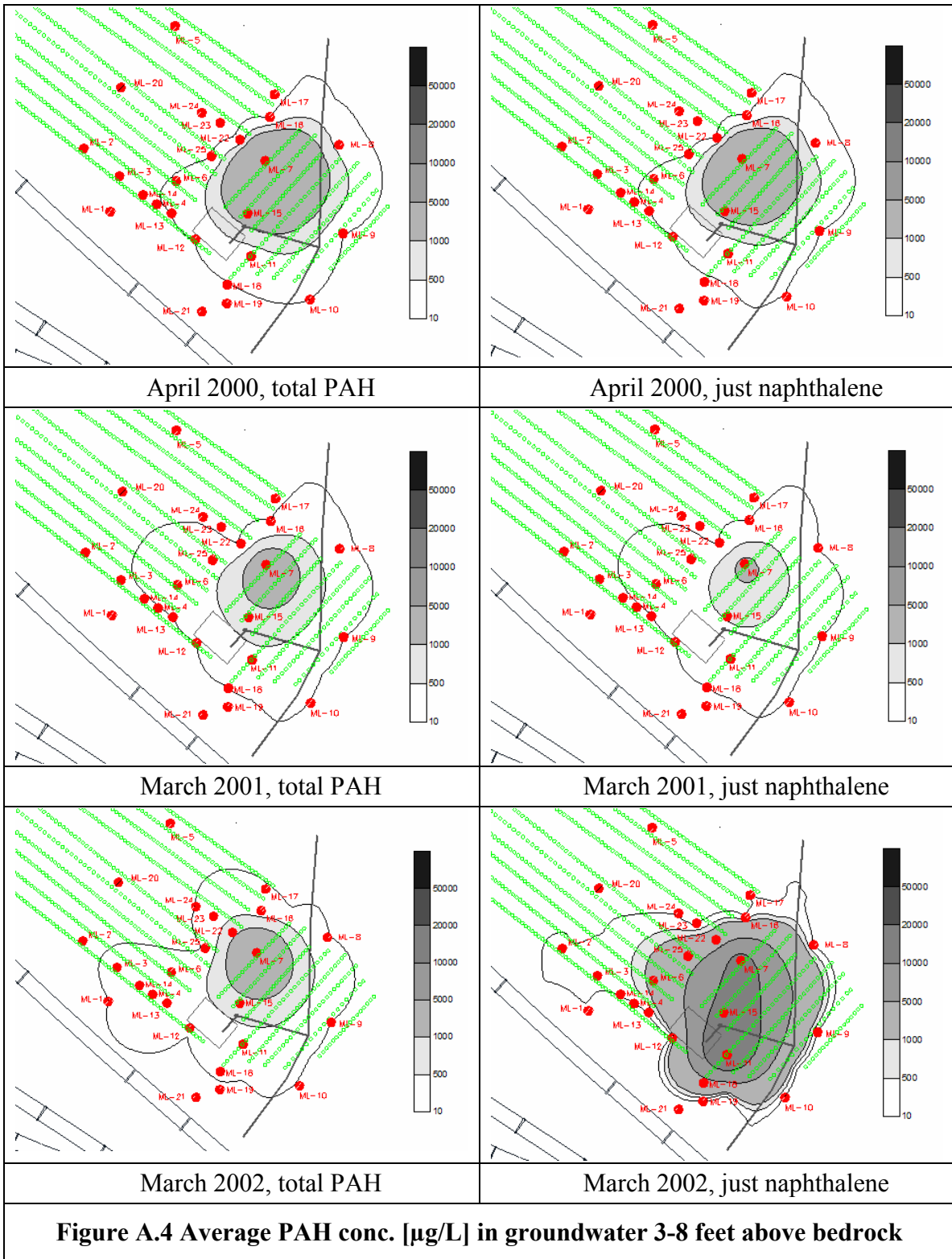
ending in 1997. The assessment of the remediation of groundwater is based on changes in plume size and the concentration of PAHs at multi-level samplers over time.

As shown in Figure A.3, Figure A.4 and Figure A.5, since monitoring began, the contaminant plume has been shrinking since monitoring began indicating that remediation is taking place at the Oneida Tie Yard.

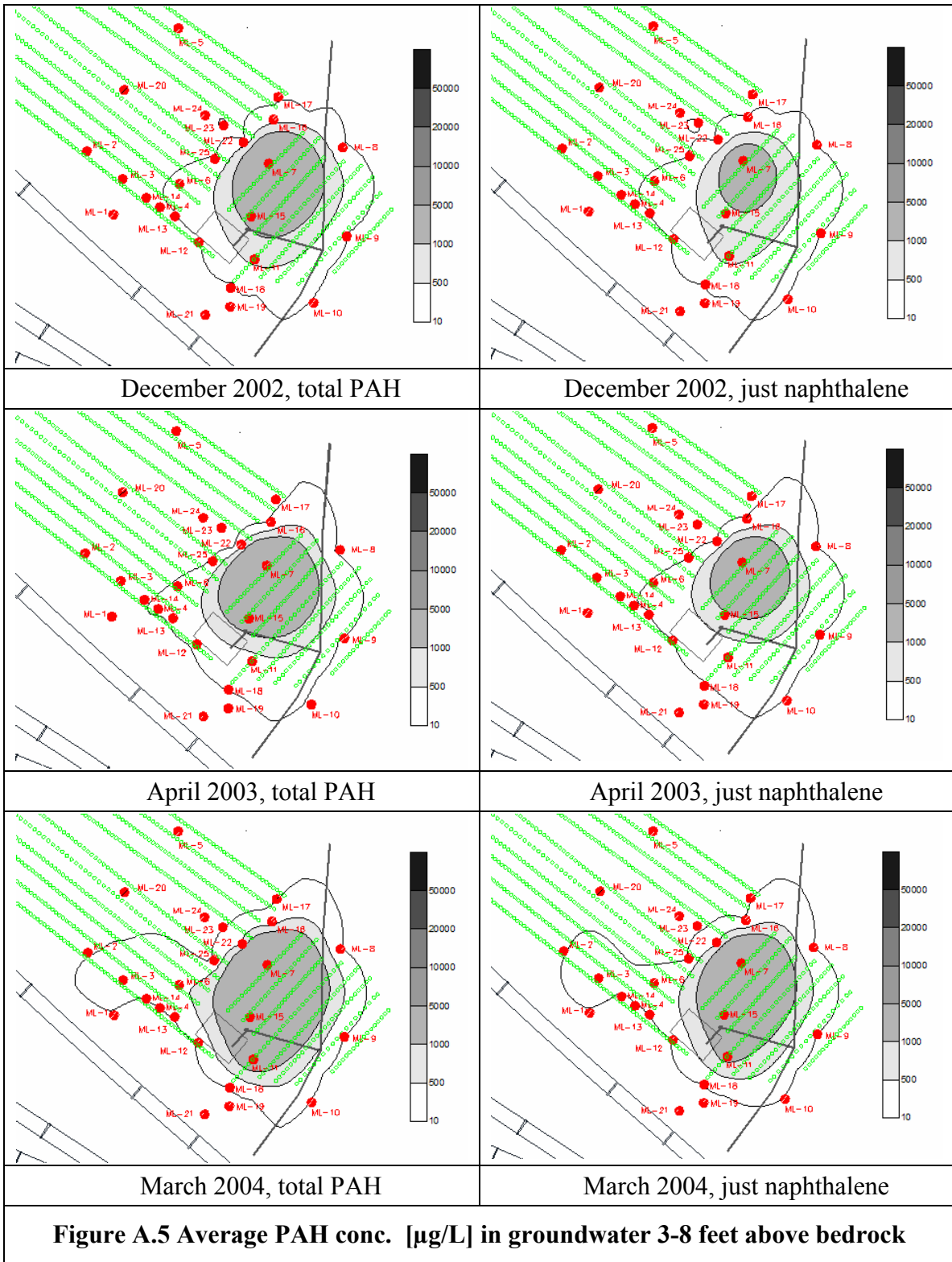
The plots displayed in Figure A.3, Figure A.4 and Figure A.5. were created using Surfer, a contouring program, which interpolates between the measured concentrations at different locations using a kriging method. Time interpolations of concentrations have been performed, in a few cases where data in an important sampling location is lacking, in order to avoid artificially distorted plume plots.

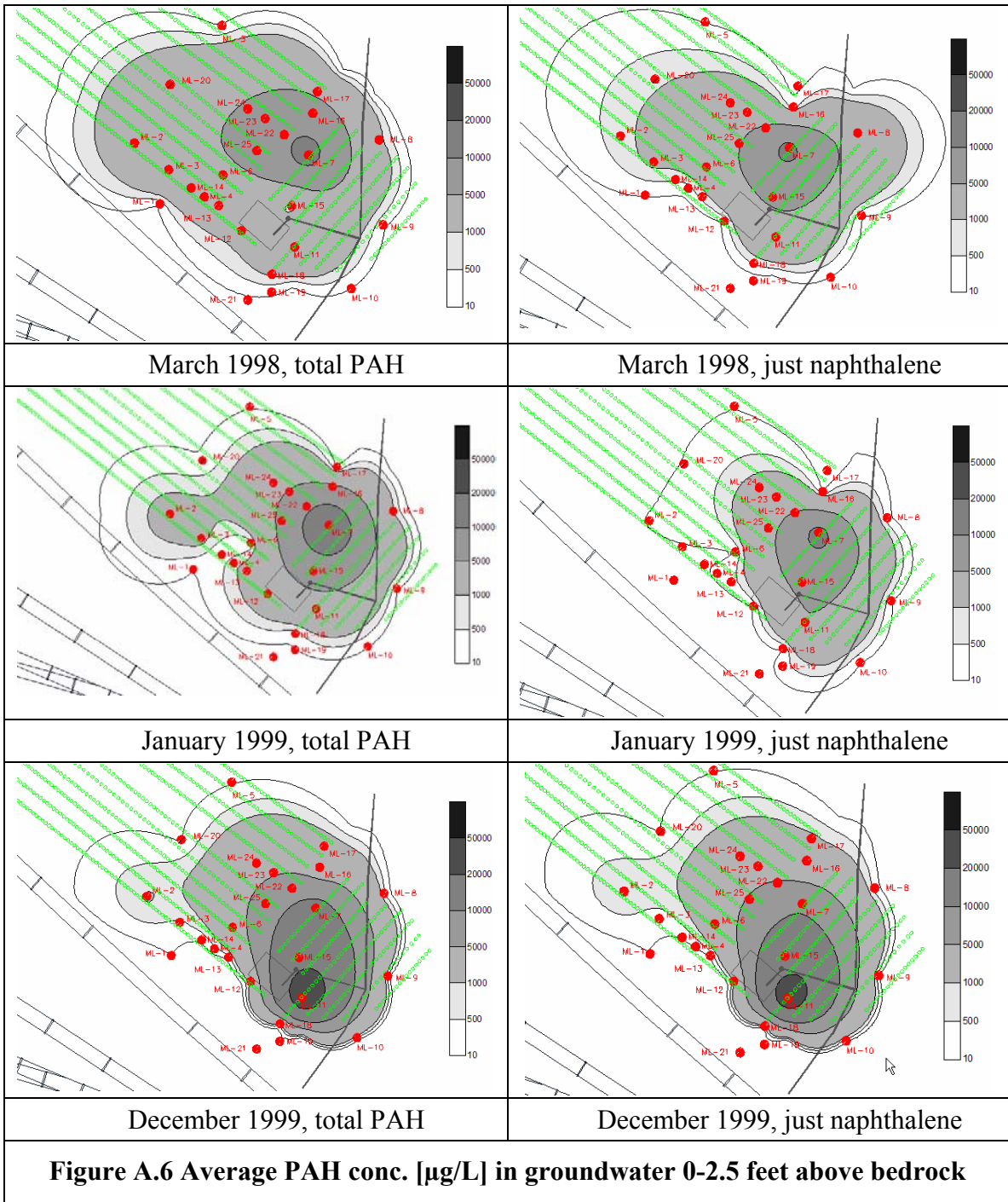
Each plot visualizes the distribution of the concentrations of total PAHs or naphthalene in the groundwater at sampling events conducted on the site. Figure A.3 to Figure A.6 shows results from sampling events in winters between growing seasons, in March 1998, January 1999, December 1999, April 2000, March 2001, March 2002, December 2002, April 2003 and March 2004. Figure A.3, A.4 and A5. represent shallow depth-averaged data taken from multi-level sampling ports between 3 and 8 feet above bedrock, while Figure A.6, A.7 and A.8 shows deep depth-averaged data from bedrock to 2.5 feet above bedrock. Figure A.9 and A.10 shows results from sampling events in summer seasons, July 1999, July 2000, July 2001, July 2002, August 2003 and July 2004. The March 1998 distribution of PAH's in groundwater signifies the baseline groundwater contamination. This sampling event occurred before the first growing season of the hybrid poplars; therefore, the impacts of phytoremediation had not yet gone into effect. All sampling events after December 1999 were obtained after the third growing season when, in theory, the tree roots had fully penetrated the water table.

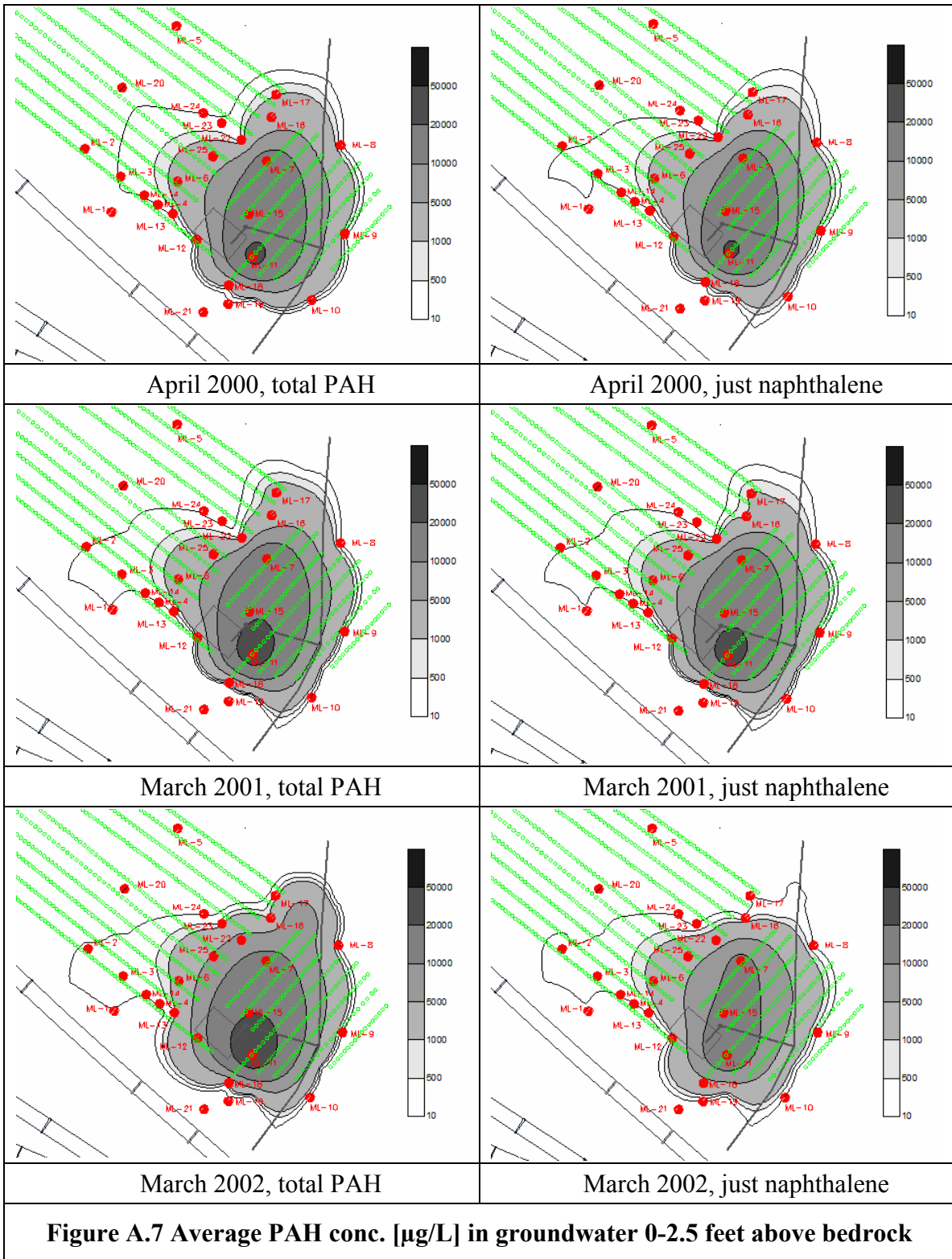




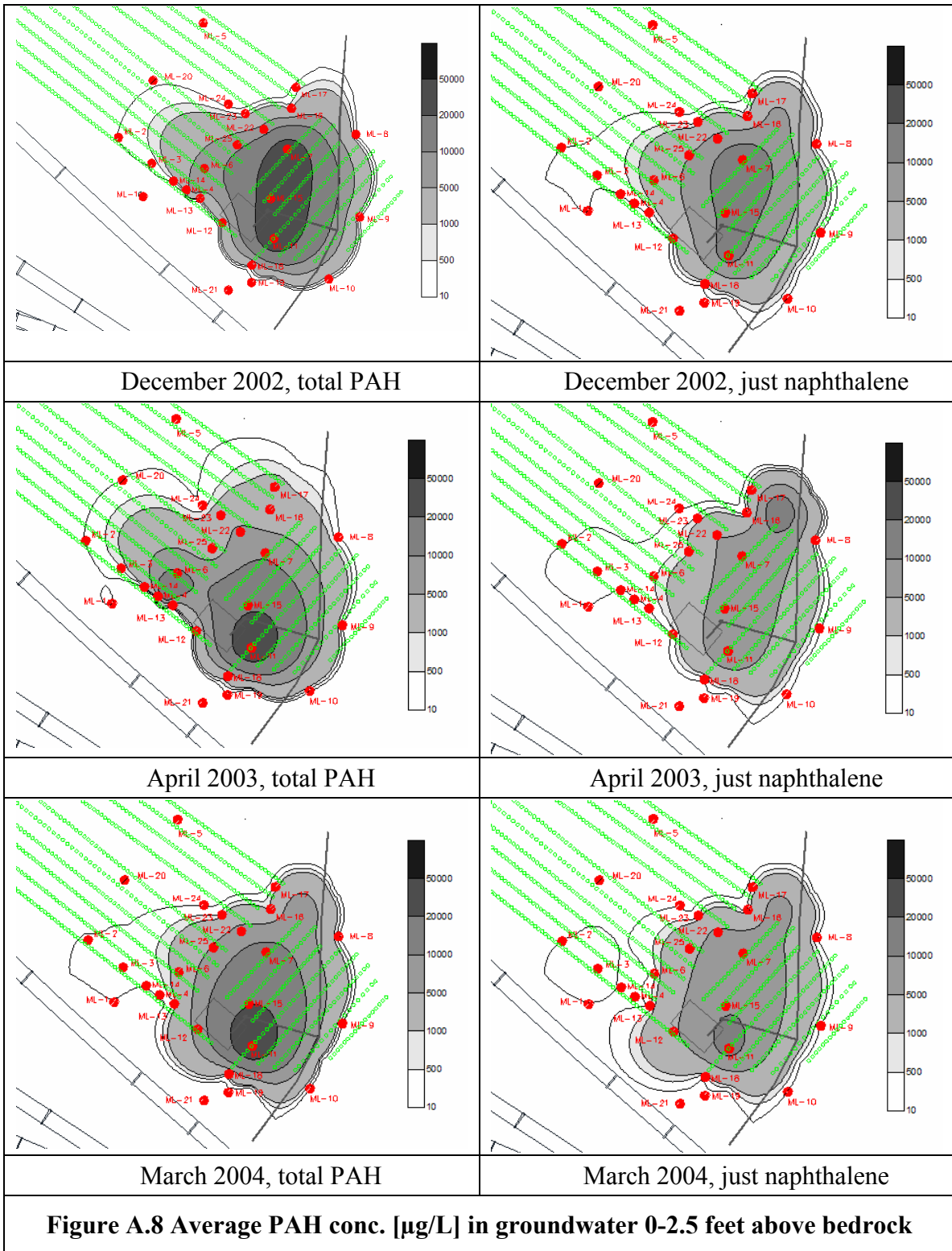
**Figure A.4 Average PAH conc. [ $\mu\text{g/L}$ ] in groundwater 3-8 feet above bedrock**

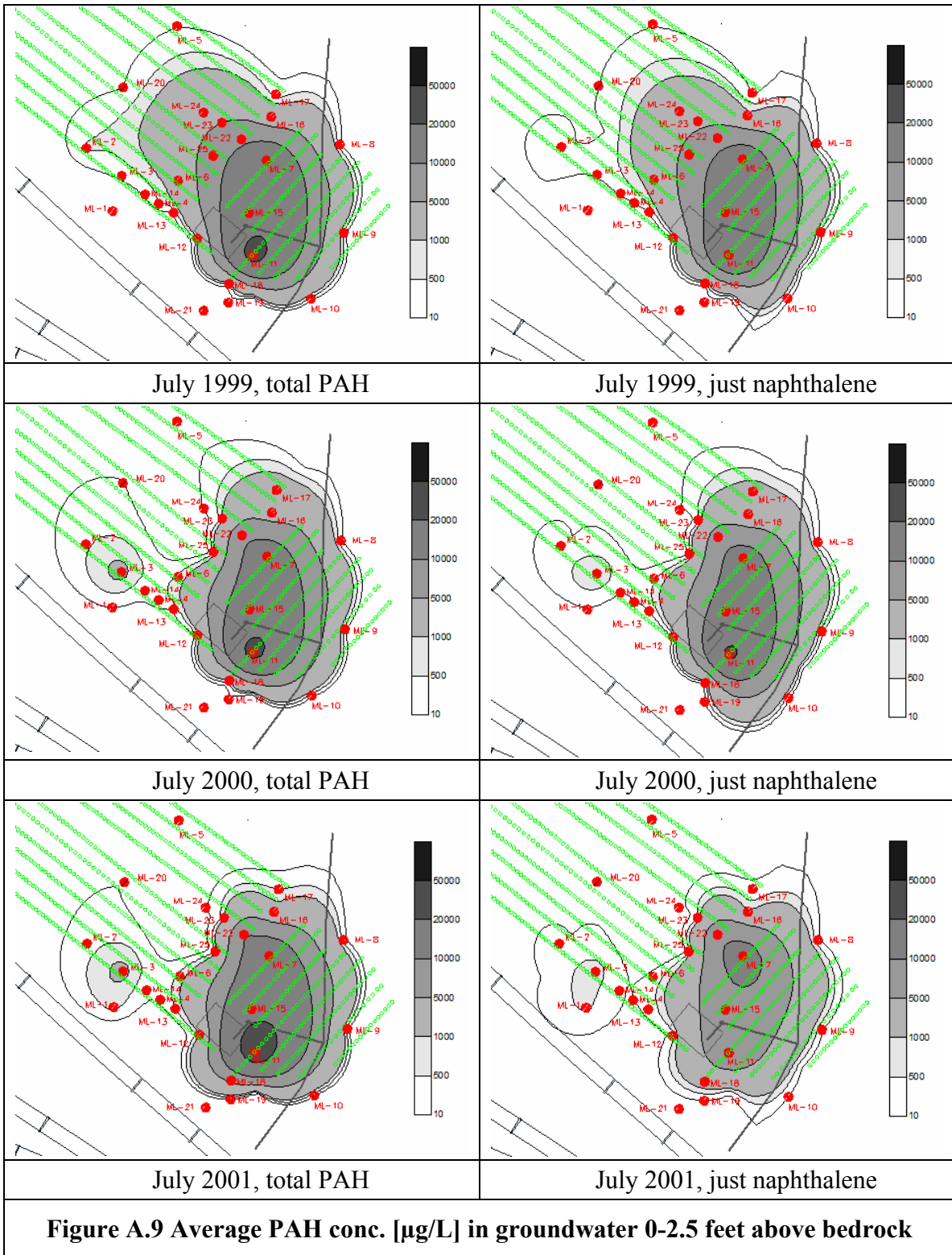


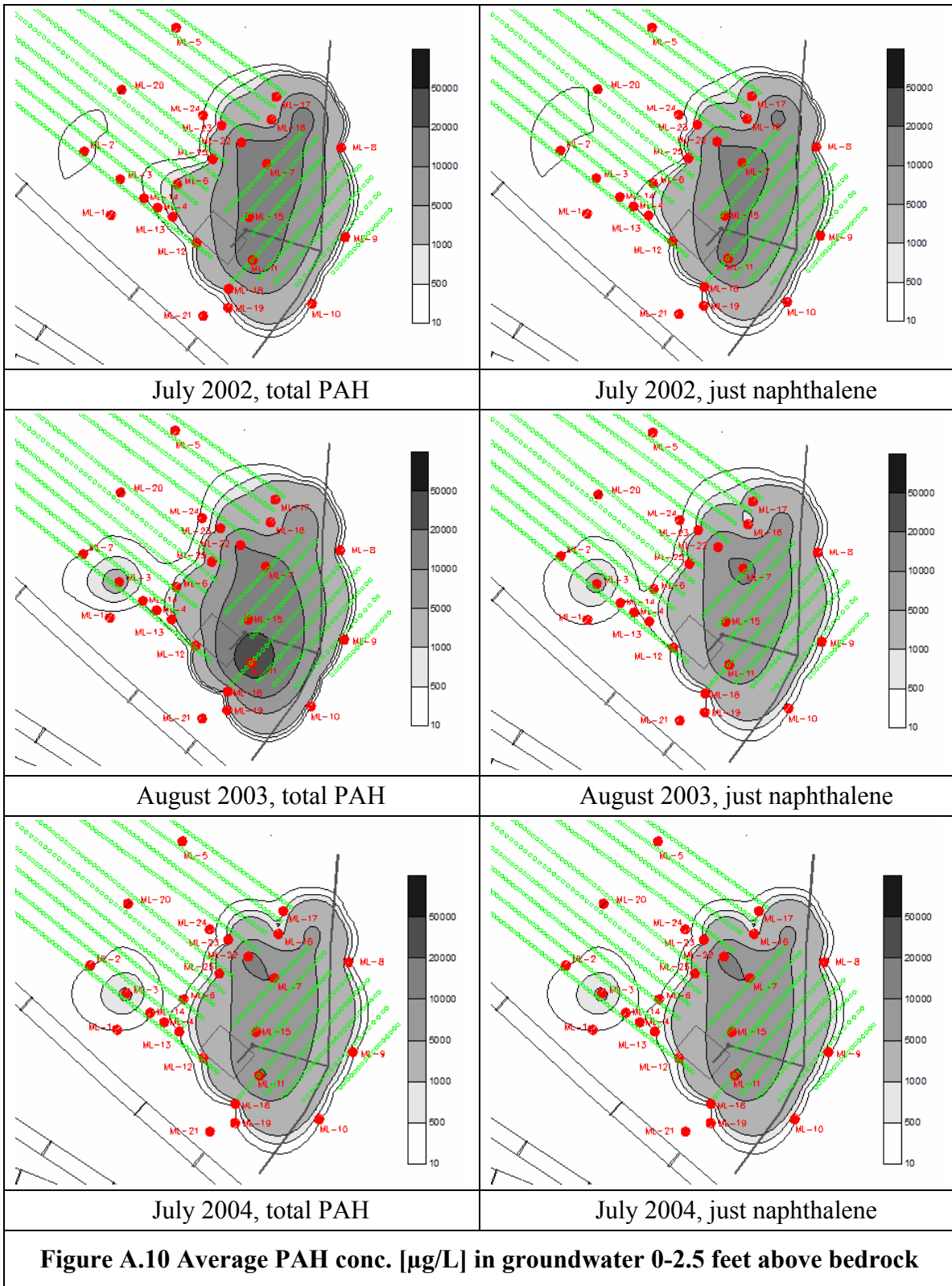




**Figure A.7 Average PAH conc. [ $\mu\text{g/L}$ ] in groundwater 0-2.5 feet above bedrock**







Overall, the plume is observed to be shrinking consistently over time in the shallow regions of the subsurface as well as in the deeper regions until year 2001. A major contribution to the reduction in the northern end of the plume was the removal of a more than 1000 tons contaminated soil in September of 1998 in an area just south of MLS-1, MLS-2 and MLS-3, where a creosote AST used to be located. Total PAH concentrations in MLS-2 and MLS-3 were greatly reduced due to the removal of this source. The greatest reduction in PAH contamination is evident along the fringe of the plume closest to the railroad tracks. At MLS-12 along the outer portion of the plume, total PAH concentrations in the shallow ports decreased from an average of 570  $\mu\text{g/L}$  in March 1998 to below detection limit in April 2003. In the deeper ports, total PAH concentrations at MLS-12 decreased from 1432  $\mu\text{g/L}$  in March 1998 to below 432  $\mu\text{g/L}$  in March 2003. Figure A.11 indicates the changes in the log of the total PAH distribution with depth over time for MLS-12 and MLS-7.

In recent years (2001-2003) the plume size and concentrations appear to have stagnated. This is believed to be due to equilibrium between the continuous release of contaminants from the DNAPL source and continuous removal due to groundwater flushing, volatilization, plant uptake and biodegradation in the saturated and unsaturated zones.

Phytoremediation is only a feasible strategy at this site because the groundwater interceptor trench served as a hydraulic control to keep contamination from moving into Pine Creek. Therefore, three multi-level samplers were located between Pine Creek and the trench to confirm the success or failure of the interception and phytoremediation system. As soon as the groundwater interception trench was functional, the PAH concentrations in groundwater at ML-9 and ML-10 were reduced drastically. Groundwater contours look as if they continue outside of the interception trench in most of the Surfer contour plots. Although concentrations at these two multi-level samplers are generally BDL, interpolation using kriging methodology incorrectly depicts the plume as extending to MLS-9 and MLS-10. Conversely, the third multi-level sampler located beyond the interception trench, MLS-8, has fluctuated in PAH concentration. In addition, the presence of NAPL has been occasionally detected in Pine Creek.

Much of the creosote DNAPL is still located in a pooled region right above bedrock causing deep groundwater PAH concentrations to remain high in the central portion of the plume. The most contaminated location on-site, as indicated by the darker regions in Figure A.3 through Figure A.10, is believed to be where the former holding pond was located. This area is situated east of the former treatment unit and close to the original location of Pine Creek. MLS-7 is located directly in the center of the most contaminated region of the plume. From March 1998 to April 2003, total PAH concentrations in the shallow ports of MLS-7 decreased from 12.7 mg/L to 4.1 mg/L, while there was no significant reduction in total PAH concentration in the deeper ports due to the presence of free product. Figure A.11 indicates the changes in the log of the total PAH distribution with depth over time for MLS-7. A logarithmic scale was chosen to emphasize the difference in PAH concentration between the shallow and deeper ports at MLS-7.

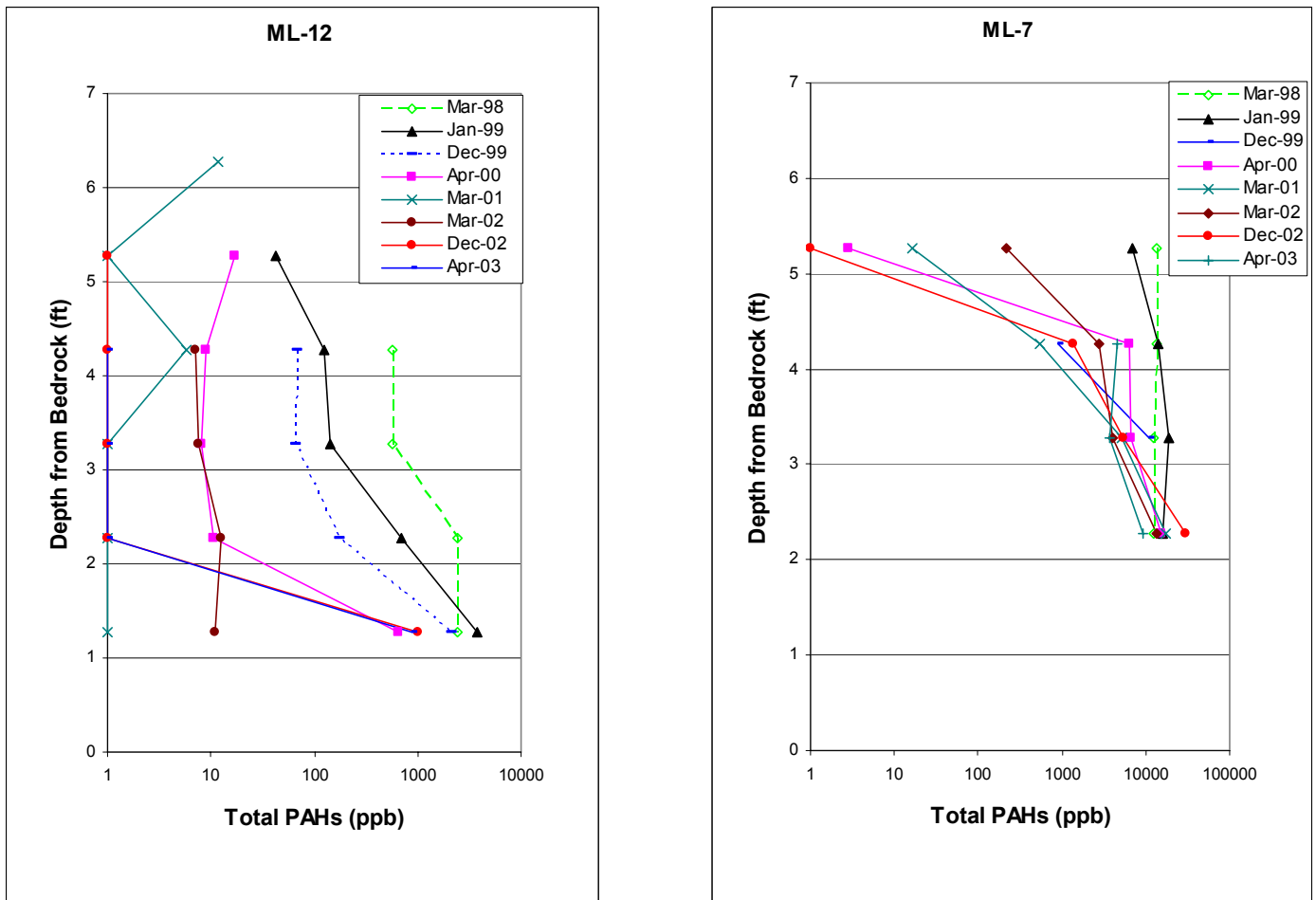


Figure A.11 PAH Concentration in Groundwater Changes with Time and Depth at MLS-7 & MLS-12

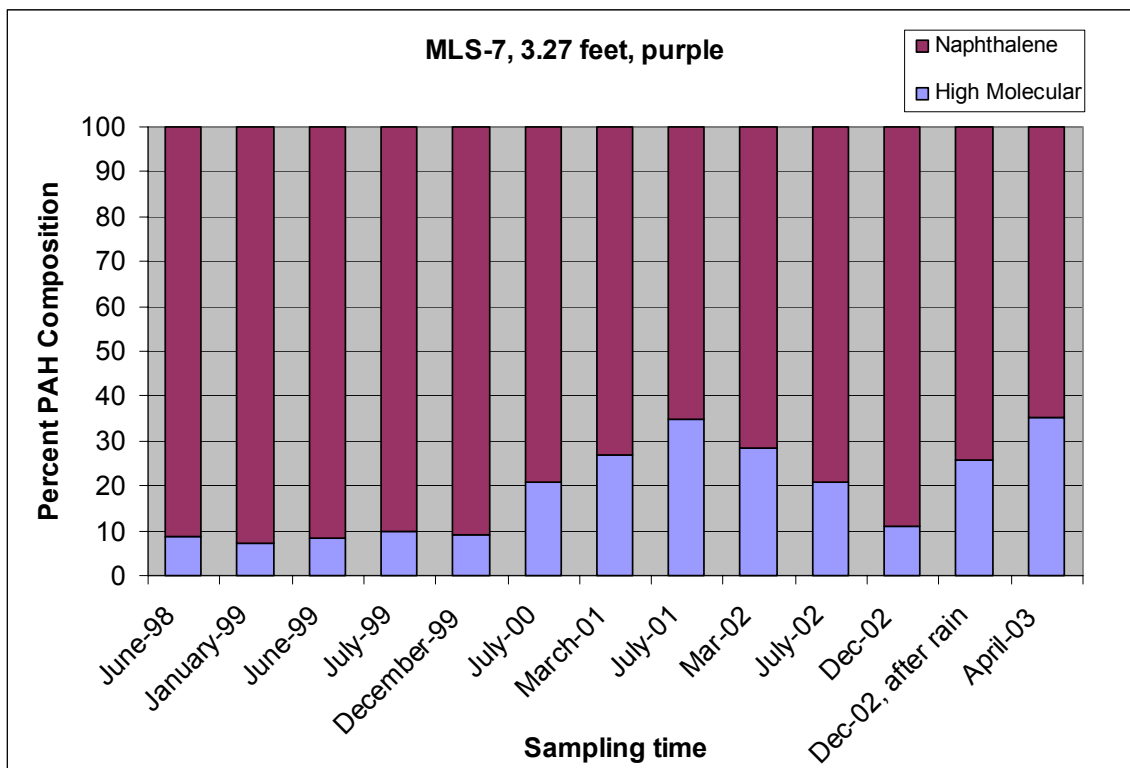
Overall, remediation has progressed significantly at the Oneida Tie Yard over the time period in which PAH concentrations have been monitored by Virginia Tech. In general, the contaminant plume has decreased in size and migrated downgradient towards Pine Creek but is interrupted by the groundwater interception trench. Creosote DNAPL has traveled downward in the soil until reaching an impermeable layer, which is for the most part bedrock. In some areas, the plume appears to follow the gradient of the confining layer rather than the hydraulic gradient.

Many of the individual multi-level samplers have shown steadily declining PAH concentrations in groundwater with time. In some areas, such as near MLS-2 and MLS-3, this decrease is due to source removal. The reduction in PAH concentration near MLS-9 and MLS-10 is due to the removal of contaminated groundwater by the interception trench. On the other hand, in the other areas of the site, PAH reduction is most likely due to a combination of phytoremediation and natural attenuation.

The flushing of clean groundwater through the creosote contaminated areas causes desorption and dissolution of creosote constituents ultimately resulting in the generation of a PAH contaminated groundwater plume. Similarly the contact of clean air at the interface of the groundwater and vadose zone facilitates volatilization of the most volatile PAHs, causing a contaminant plume in the soil gas. Creosote is a complex matrix of contaminants and each of its components will fractionate at different rates into the air, water, or soil as a function of physical and chemical properties. Furthermore the different components in creosote have different biodegradation rates and different tendency for uptake by plants. While low molecular weight PAHs such as naphthalene are more soluble and volatile and can be directly taken up by the roots of plants and/or bioremediated, many of the high molecular weight PAH's such as chrysene have a strong tendency to sorb onto subsurface particles and have slower biodegradability rates.

The different properties of the PAHs causes an aging creosote plume to get enriched in the high molecular weight PAHs over time, while the lighter more soluble, volatile and biodegradable compounds are remediated faster. As illustrated in Figure A.6-A.10, the percentage of low molecular weight contaminants, namely naphthalene, is decreasing faster with time than the overall total PAH in the deep portion of the groundwater.

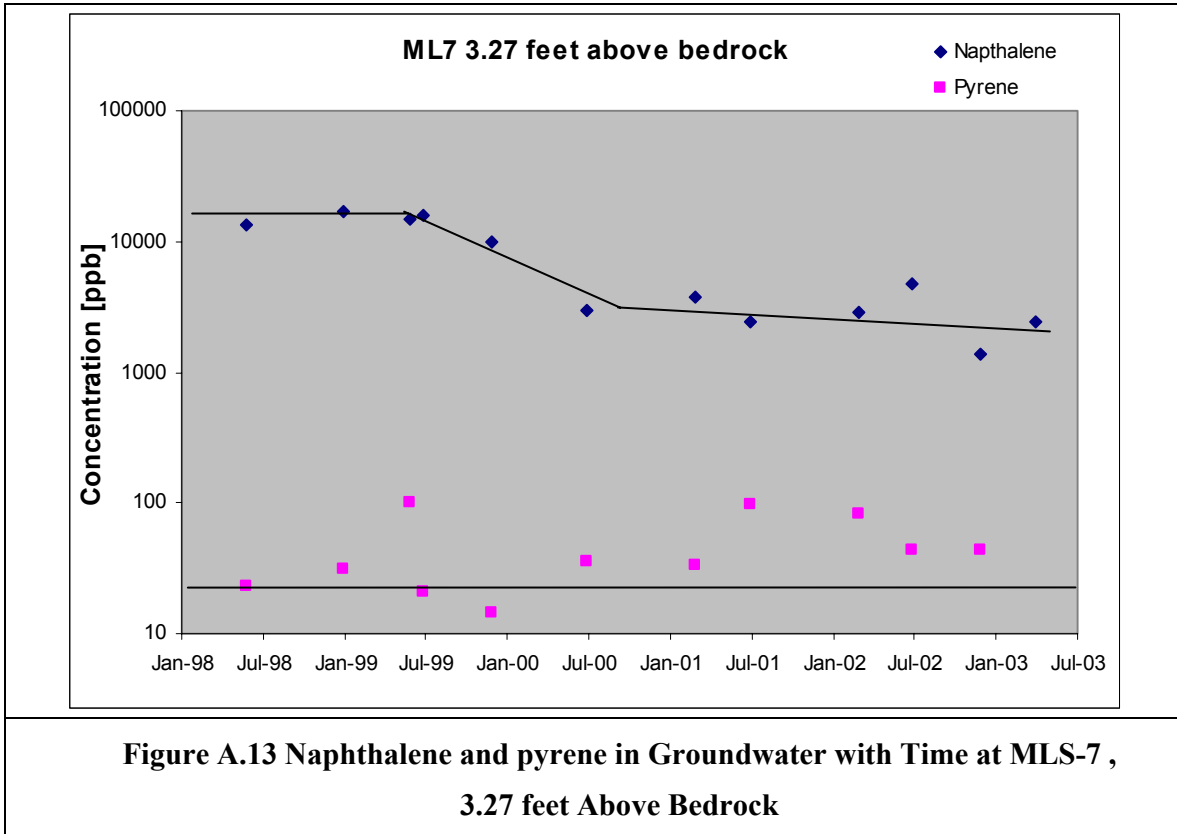
The percentage of higher molecular weight PAH's are increasing with time indicating the change in composition of the contamination as illustrated on Figure A.12 for MLS-7 at 3.27 feet above bedrock. The bar-chart also shows data from before and after a rainfall in December 2002 and the percentage of naphthalene is clearly reduced by dilution or flushing with the clean water introduced by the rain. As the lower molecular weight compounds dissolve, the DNAPL becomes enriched in high molecular weight PAH's which are less susceptible to water-based technologies such as phytoremediation and bioremediation. The rate at which water-based technologies function is often controlled by the pace of desorption and dissolution.



**Figure A.12 Percent High Molecular Weight Polycyclic Aromatic Hydrocarbons in Groundwater with Time at MLS-7 , 3.27 feet Above Bedrock**

Figure A.13 shows the enrichment in the center of the plume 3.27 feet above bedrock, which is right above the deep zone which is dominated by NAPL (ML7 purple). It appears that pyrene concentrations persists, while naphthalene is being removed (dissolved, volatilized

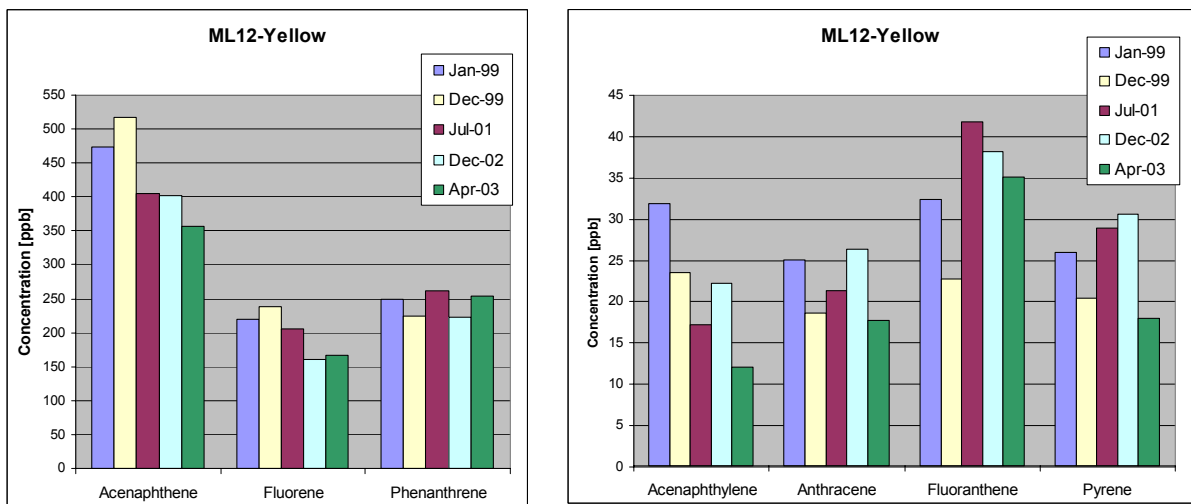
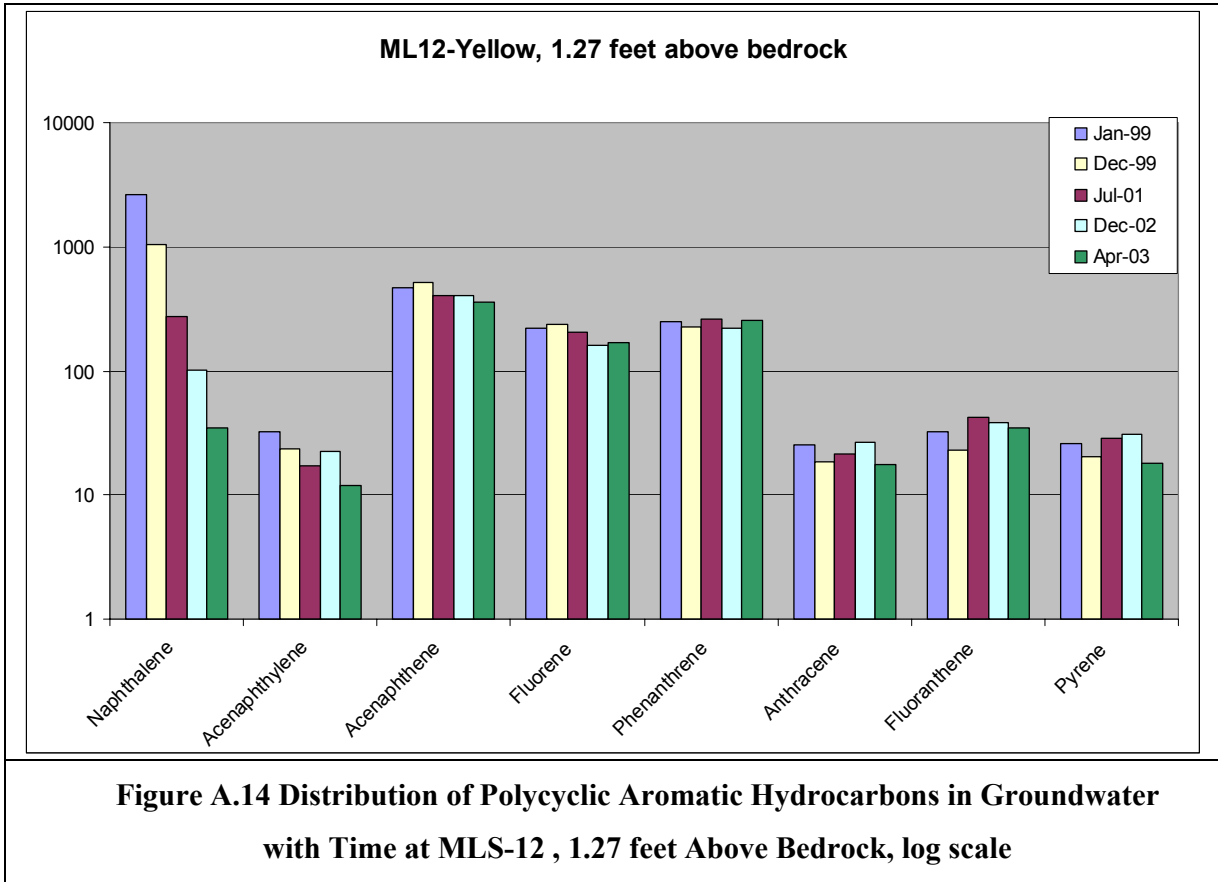
and biodegraded). There is an apparent lag phase until first growing season, then rapid decline in naphthalene followed by slower decline due to equilibrium between removal kinetics and dissolution/desorption kinetics at the lower naphthalene concentrations.



The average distribution of eight PAHs in a deep port in ML12 at the edge of the plume is shown on Figure A.14 on a logarithmic scale. The concentrations of the lighter PAHs, naphthalene, acenaphthylene, acenaphthene and flourene are decreasing over time, while the concentrations of the heavier compounds, phenanthrene, antrachene, flouranthene and pyrene do not change significantly.

The development in concentrations of acenaphthylene, acenaphthene, flourene, phenanthrene, antrachene, flouranthene and pyrene from the same well are shown on an arithmetic scale on figure A.15. The PAHs with fewer rings and lighter molecular weight are removed faster than the high molecular weight PAHs. A closer look at the data reveals that naphthalene and acenaphthylene appear to be removed and/or biodegraded

with first order kinetics, while acenaphthene and flourene apparently are degraded with zero order kinetics.



**Table A.16 Properties of the eight Polycyclic Aromatic Hydrocarbons**

	Removal rate [ppb/day]	Log $K_{ow}$	$C_w$ [mg/l]	$K_H$
Naphthalene	First order: 0.0011	3.36	31	0.017
Acenaphthylene	First order: 0.0003	4.1	3.93	0.0048
Acenaphthene	Zero order: 0.083	3.92	3.42	0.006
Flourene	Zero order: 0.046	4.18	1.98	0.0041
Phenanthrene	Not detected	4.57	1.2	0.0016
Anthracene	Not detected	4.54	0.041	0.0024
Flouranthene	Not detected	5.22	0.21	0.0005
Pyrene	Not detected	5.18	0.14	0.00044

Table A.16 shows the removal rates partitioning coefficient between octanol and water ( $K_{ow}$ ), water solubility ( $C_w$ ) and partitioning coefficient between water and air ( $K_H$ ) for the eight compounds in ML12 at 1.27 feet above bedrock. The lower the tendency to sorb (lower log  $K_{ow}$ ), higher solubility ( $C_w$ ) and volatility ( $K_H$ ), the faster the compounds are removed and/or biodegraded.

The shallow groundwater is not directly in contact with free phase creosote and is therefore dominated by naphthalene dissolving from the deeper zone as can be observed on Figure A.10, where the surfer plots of total PAH are almost similar to the surfer plots with naphthalene alone. A similar trend can be observed along the fringes of the plume in the deep groundwater, where the edge for naphthalene and total PAH is generally coinciding (Figure A3 through Figure A.10). Naphthalene is the contaminant most likely to possess a risk for the aboveground ecosystem and/or exposure to humans due to the higher mobility in water and gas. It is important that this compound is controlled and reduced over time. Fortunately the chemical structure and higher mobility of naphthalene also makes this contaminant more susceptible for removal mechanisms such as biodegradation and plant uptake. This agrees with the observation that the contamination in shallow groundwater and the groundwater along the fringes of the plume is being remediated faster. The heavier PAHs are not a direct risk as long as they stay immobilized sorbed to soil deep under the ground surface, while slowly being remediated over time.

Another reason for the faster remediation along the fringes of the plume and in the shallow groundwater, besides naphthalene being the dominant contaminant, is that the oxygen levels are higher in these areas and can promote aerobic biodegradation. The deep center of the plume tends toward anaerobic conditions and support anaerobic biodegradation, which is typically slower than aerobic for PAHs. Aerobic and anaerobic biodegradation rates as well as the influence of trees on the biodegradation rates have been investigated for this site in a laboratory setting as well as in field, which is described in Supplement C.

The groundwater contamination tend to be lower in the summer than the following winter, that is there seems to be a slight rebound in the contamination levels in the winter. Comparison of summer data (Figure A.9-A.10) with winter data (Figure A.6-A.8) indicates this trend. A reason for the summer concentration to be lower could be that the trees are actively transpiring during the summer, thereby lowering the groundwater table at the site. This probably increases the volatilization of naphthalene from the groundwater and DNAPL exposed to air. Furthermore the lowering of the groundwater table will increase aeration of the unsaturated zone and thereby facilitate increased aerobic biodegradation in this zone. The rhizosphere microbial populations are also likely to benefit from increased exudates from roots as the trees are actively growing in the summer.

## **A.6 Soil Characteristics**

The subsurface conditions at the Oneida Tie Yard were determined during soil sampling events in 1998. Hand auger borings were taken as well as visual soil classifications of the different soil conditions on-site. The result of this investigation was an improved understanding of the extent of creosote DNAPL contamination, as illustrated in Figure A.17. The hydrogeology on-site is characterized by a shallow unconfined aquifer consisting of three layers. A mixture of gravel and coal, which was placed over the site during rail yard and remediation activities, is located in the first few feet under the ground surface. The first layer of native soil, which consists of 5 to 6 feet of silty clay, is located underneath the coal and gravel mixture. A silty sand layer which is 4 to 5 feet

thick underlies the top native soil layer and overlies bedrock. Shale bedrock is typically located 8 to 12 feet below land surface. The majority of free-product creosote is located in the silty sand layer 6 to 8 inches above bedrock. According to a sampling investigation by Muck, this layer is a non-plastic silty sand (Unified Soil Classification System - SM) and has a percentage of fines between 10 to 30%.

Soil samples have been taken with a hand auger and analyzed for PAH contamination by a Virginia Tech laboratory on an annual basis as of 1997. Soil borings (SB) are sampled along two transects of the site as shown in Figure A.15. Transect one is located parallel to the railroad tracks on the western end of the site, while transect two is located in the center of the site within the interior of the NAPL plume. Subsurface conditions at transect two are represented in Figure A.14. Six of the most prevalent PAH's on-site were selected for monitoring based on analytical results from a soil sampling event in 1997. High molecular weight PAHs generally have low water solubilities and tendency towards adsorption to soil and sediments. Therefore, six three and four ring compounds of high molecular weight were chosen as the focus of soil remediation at the Oneida Tie Yard site.

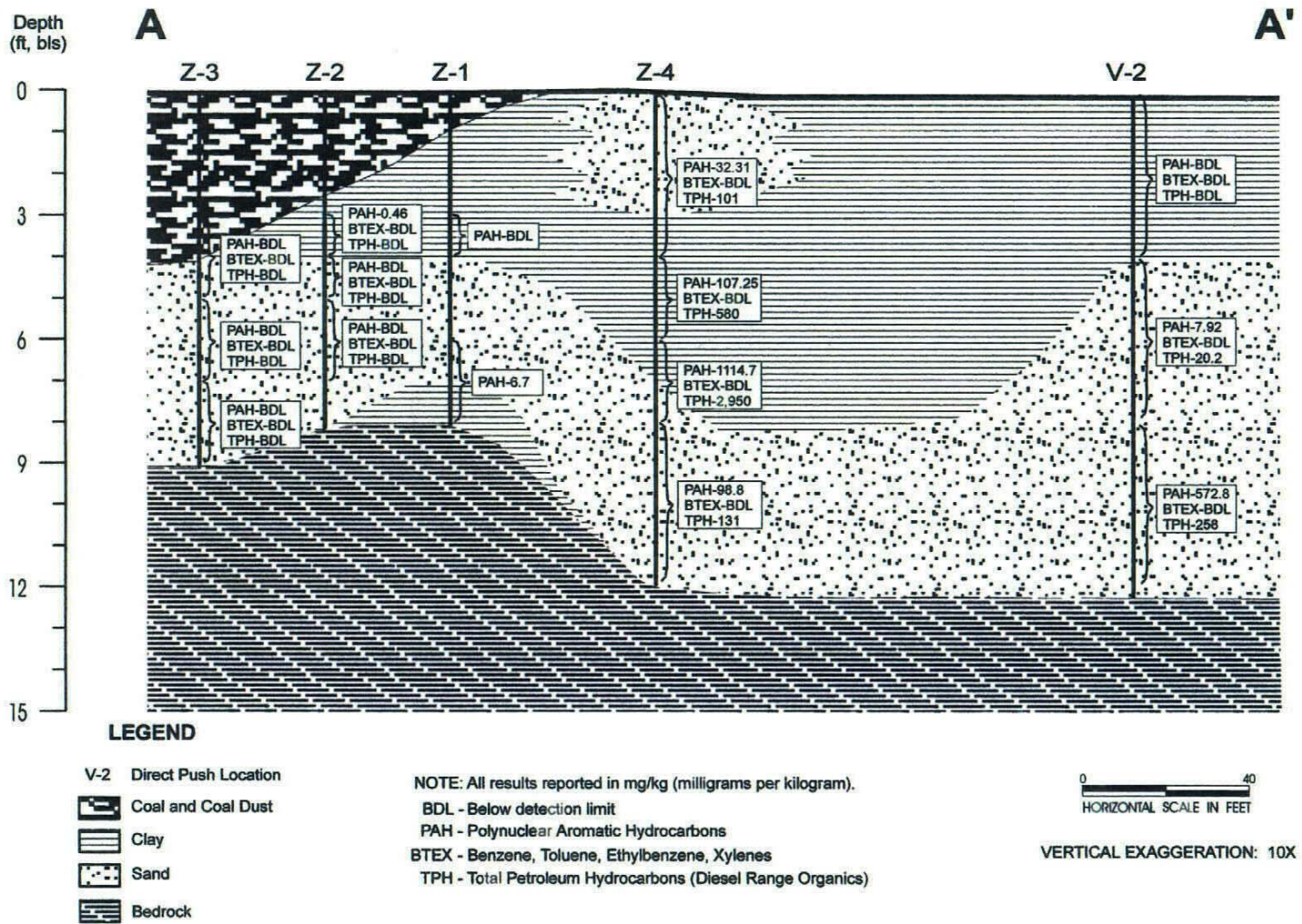
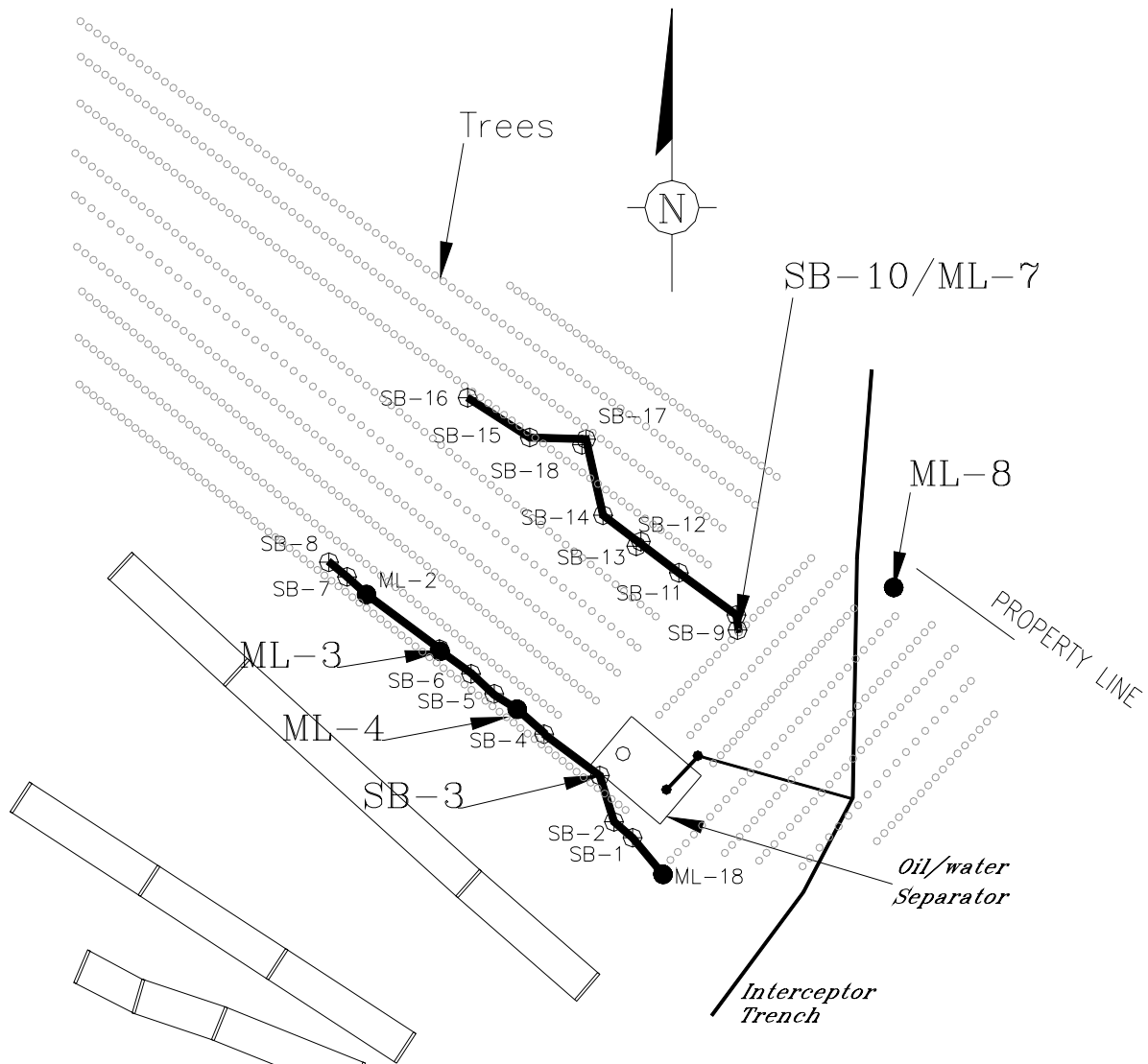


Figure A.17 Cross Section of Soil Transect Two (ARCADIS Geraghty & Miller 2000)



**Figure A.18 Multi-level sampler and soil boring locations at the Oneida Tie-Yard site**

The cross-sectional plots displayed in Figure A.19 and A.20 were created using Surfer. Each plot coincides with hand auger soil sampling events conducted on-site in June 1998, October 1999, March/April 2000, July 2001, March 2002 and April 2003. Samples were taken from a range of three to ten feet in depth below land surface.

The decrease in concentration of PAH's in soil with time is noticeable although not as marked as the reduction of PAH's evident in groundwater. At both transects, soil PAH concentrations with depth are not always consistent emphasizing the heterogeneity of the soil on-site. Human error in accurately gauging the depth of soil samples also contributes to the irregularity of the measurements of PAH contaminants in the soil.

The concentration of total PAHs over time in soil along transect one is shown in Figure A.19. Along the fringe of the groundwater plume, at the northern end of transect one (at SB7), depth-averaged total PAH concentrations generally diminished with time. For example, depth-averaged total PAH's at a soil boring near MLS-3 decreased from 173.3 mg/kg in July 1997 to 10.85 mg/kg in April 2003. This reduction could be due to the removal of a large source of creosote by excavation in September of 1998. In contrast to the northern end of transect one, total PAH concentrations remained fairly steady in the southern half close to the location of the oil/water separator (SB3). An exception is the sampling event in April 2003, which showed surprisingly low levels of PAHs in transect one and this needs to be confirmed with the next sampling event.

In Figure A.20 is shown the concentration of total PAHs over time in soil along transect two. Overall the soil contamination along transect two appear to have been shrinking from October 1999 to April 2003. As shown by the plot, from June of 1998 to October 1999, the center of the NAPL plume appears to be moving northwest along transect two. Free product just above bedrock may be following the geologic gradient of the confining layer rather than the hydraulic gradient. From October 1999 to April 2003, the center of the NAPL plume appears to be stabilized near SB-11. The concentration of total PAHs close to bedrock upstream from the center (ML-23) have been reduced from 4390 mg/kg in June 1998 to 3236 mg/kg in April 2003, while the concentration close to bedrock in the stabilized center appear to have stayed constant from October 1999 to April 2003.

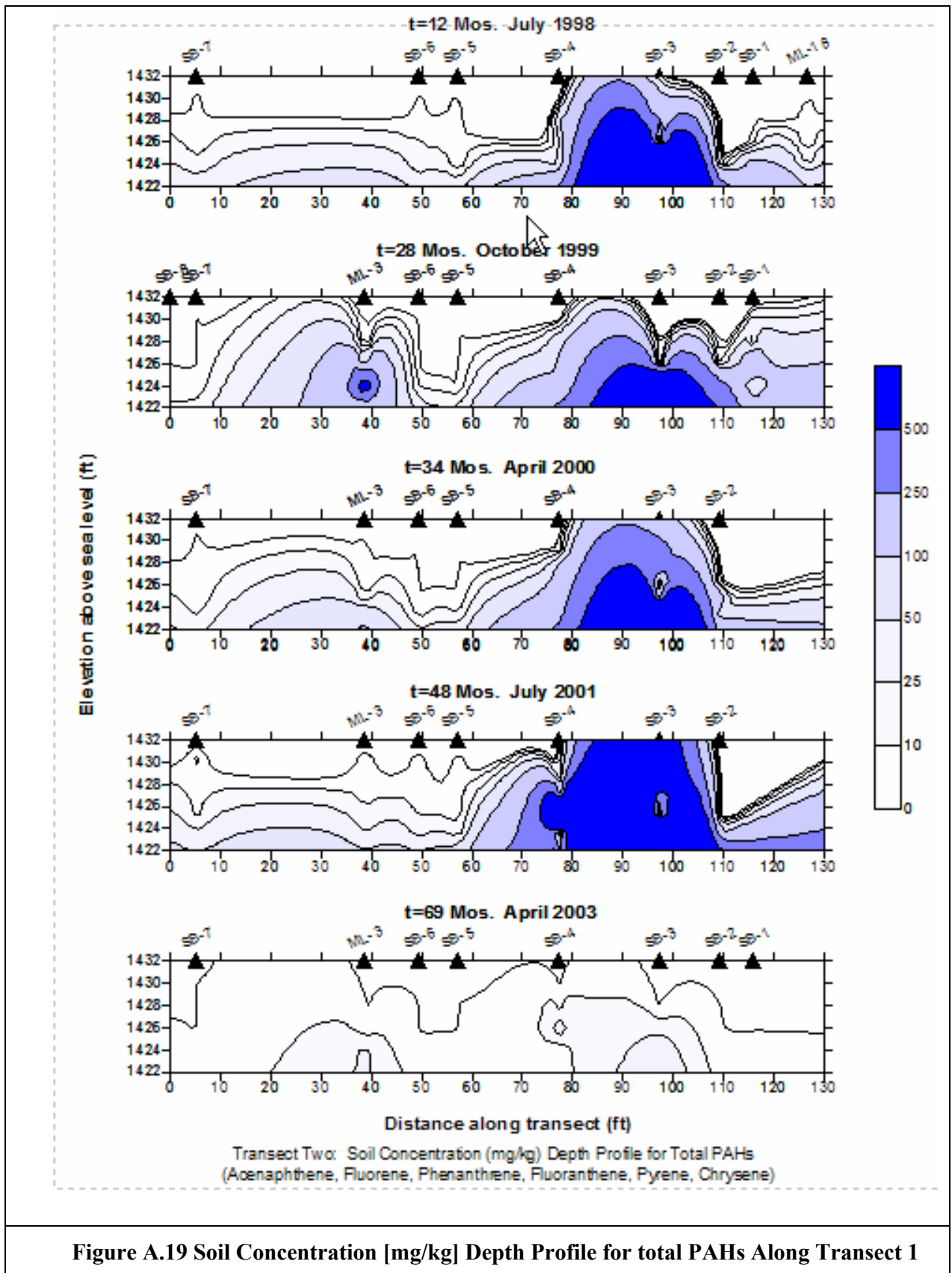


Figure A.19 Soil Concentration [mg/kg] Depth Profile for total PAHs Along Transect 1

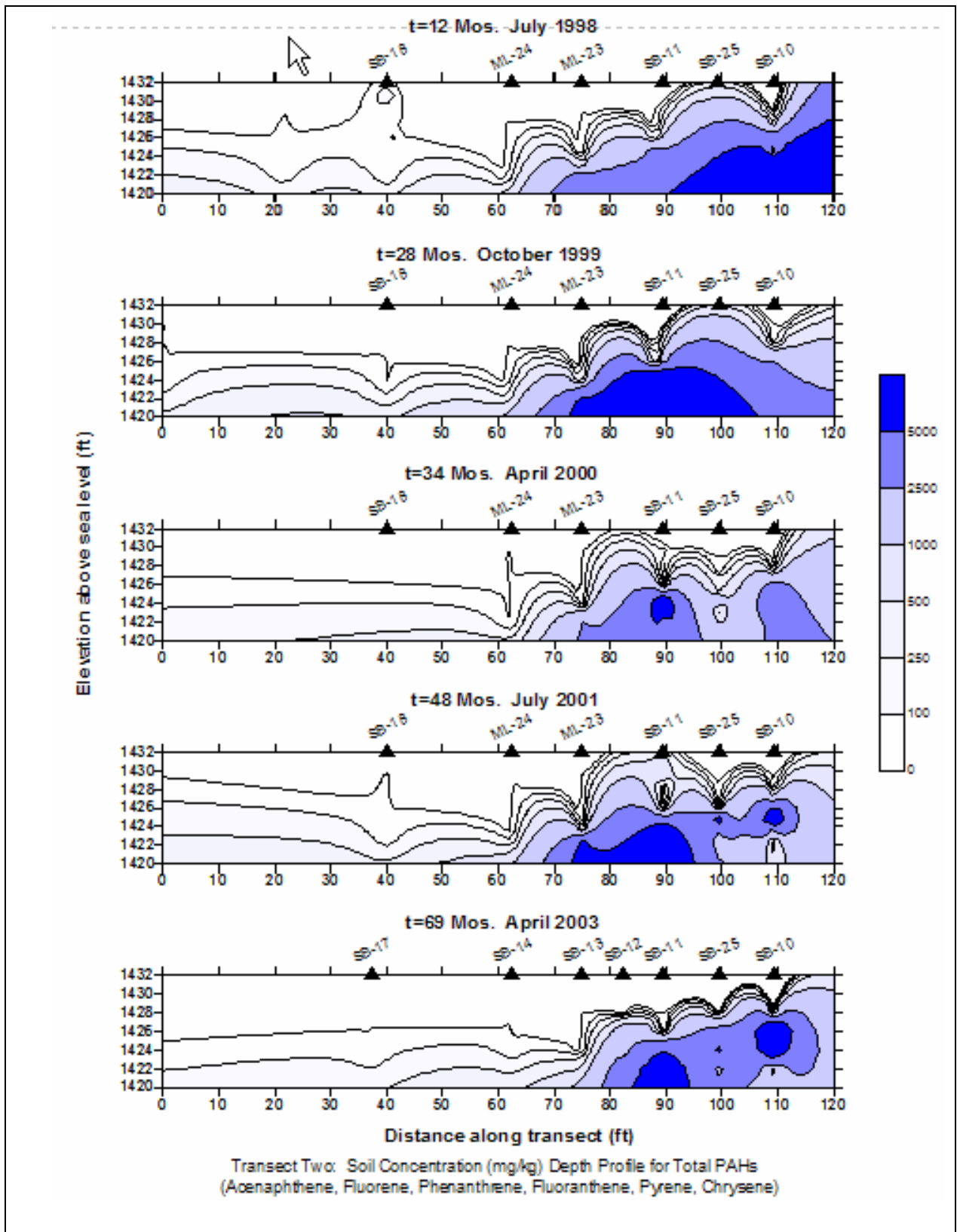
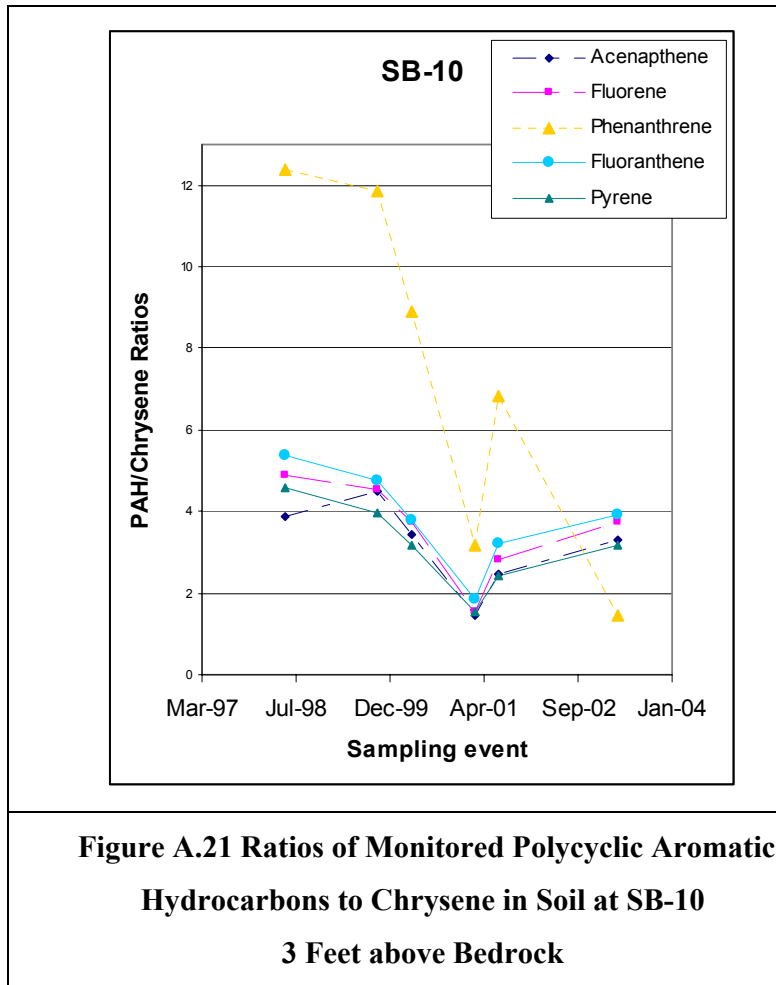


Figure A.20 Soil Concentration [mg/kg] Depth Profile for total PAHs Along Transect 2

The PAH contamination in the soil can be expected to be enriched in high molecular weight, low solubility compounds similarly to the groundwater contamination. The ratios of monitored PAH's in soil at SB-10 were calculated to determine the change in creosote composition with time. SB-10 is located at the center of the NAPL plume close to MLS-7; therefore, the PAH concentrations in soil at SB-10 can be compared to PAH concentrations in groundwater at MLS 7. The ratios of three-ringed PAH's, namely acenaphthene, fluorene, and phenanthrene, are shown in Figure A.21. For the most part, the ratios of three-ringed compounds to chrysene were reduced from approximately 5 to 3. Conversely, phenanthrene decreased in ratio from 12 to less than 2. The ratios of the four-ringed compounds fluoroanthene and pyrene are also shown in Figure A.18. Concentrations of fluoroanthene and pyrene behaved similar to those of the three-ringed compounds with a reduction in ratio from 5 to 3. The large reductions in ratio of PAH's to chrysene occurred during sampling events in late 1999 and early 2000, which were obtained after the third growing season once the poplar tree roots had penetrated the water table. The increased reductions at this time indicate that the trees are contributing to a reduction of the soluble PAH compounds.

Chrysene was chosen for comparison with the other PAH's in the soil because it has the lowest solubility and highest molecular weight of all of the monitored PAH's thereby making it fairly recalcitrant and prone to sorption. Due to natural attenuation and phytoremediation, the soluble PAHs are removed quickly from the subsurface by means of direct uptake and biodegradation. If the most water soluble contaminants in a NAPL are removed by contact with water, the less soluble higher molecular weight compounds are left in the NAPL or sorbed phase. In some circumstances, these high molecular weight compounds do not pose an appreciable risk to human health or the environment because they have limited mobility. However, in certain situations, these sorbed compounds may continue to leach contaminants after the low molecular weight compounds have been treated. For this reason, NAPL compositional changes with time, as demonstrated by the long term monitoring data at this site, must be accounted for in order to estimate aqueous PAH concentrations and the ecological and public health risk.



In summary poplar trees appear to enhance the remediation of creosote related PAHs at the Oneida site based on six years of monitoring. Increased removal rates of naphthalene as well as total PAHs has been observed after three growing seasons. This increased removal could be due to enhanced bioremediation due to rhizosphere effects or aeration of the subsurface and volatilization increased by transpiration (chapter 3). Naphthalene is the dominating PAH found dissolved in the groundwater. Naphthalene has the highest solubility and volatility and thus is the most likely to migrate off site or escape untreated to the atmosphere. Fortunately naphthalene typically has the fastest biodegradation rate of the PAHs.