5. RESULTS AND DISCUSSION

A. Site Characterization

The rationale behind site characterization was to document contaminant concentrations and distributions prior to occurrence of poplar phytoremediation effects. Collection of subsurface soil boring samples occurred along two lines that transected the primary PAH plume. Figure 7 for a diagram of the plume. Ground water samples were collected along a portion of transect one and along a line from ML-15 to ML-16. Figure 8 shows the location of both transects, ground water sampling lines and all sample Tables 2A and 3A in the Appendix list the distance points. between sampling points along both transects and ground water sampling lines. Using the analytical results, graphs containing soil and ground water concentration contours were developed in SURFER using the kriging calculation method. Soil and ground water PAH analytical results used to create the concentration depth profile figures are in Tables 4A thru 7A in the Appendix. Ground water flow is in a southeasterly direction towards Pine Creek (Geraghty & Miller, 1997). Average linear ground water velocity is approximately 0.63 - 1.4 cm/day (Appendix). Collection of transect data will allow a future time-dependent comparison of contamination levels, but most importantly, evaluation of overall site remediation and the effectiveness of the phytoremediation system can be assessed.

Figure 7: Extent of PAHs/BTEX/TPH(DRO) in Ground water (Geraghty & Miller, 1997) (figure7.gif, 56K)

Figure 8: Location of Sampling Transects Used for Site Characterization (figure 8.gif, 45K)

i. Transect One

The first transect was approximately 100 feet north-north-east of the reported source area. Acenaphthene and fluorene soil and ground water concentration depth profiles are shown in Figures 9 and 10, respectively. the Appendix, figures 1A thru 4A are soil and ground water depth profiles for the other PAHs and figure 5A is the ground water concentration depth profile for benzo(b)fluoranthene. Two different areas experienced PAH soil and ground water contamination. In the first area, soil contamination occurred from ML-4 thru SB-3. Creosote movement along bedrock from the known source area likely contaminated this region. PAH transport with ground water flow was likely and subsequent soil contamination had occurred along the flow pathway. The most severe PAH contamination was just above bedrock at SB-3. At SB-4, soil PAH contamination occurred from bedrock up to the 6 foot depth. Of the 6 PAHs, phenanthrene soil concentrations were the highest. Phenanthrene is a major component of creosote, 13% by weight of total PAHs. In addition to contamination from the source, another contaminated area was located. The contamination was located between ML-2 and SB-6 with the highest PAH concentrations in the depths of ML-3. This source was likely a dug pit used for creosote disposal.

Ground water samples collected along a portion of transect one allow comparison of soil and ground water concentrations in approximately the same locations. The sampling ports where ground water contamination was detected correlated well with soil boring contamination. PAH ground water concentrations were highest in the two source areas, ML-3 and -12. At ML-3, ground water

Figure 9: Transect One: Soil Concentration (mg/kg) Depth

Profile for Acenaphthene (top) and Fluorene at

t=0 (figure9.gif, 97K)

Figure 10: Transect One: Ground Water Concentration (ppb)

Depth Profile for Acenaphthene (top) and

Fluorene at t=4 Mos. (figure10.gif, 106K)

contamination appears to emanate from deep soil contamination. Within the primary plume area, ground water contamination is also more prevalent in the lower soil depths at ML-12. As PAH molecular weight increases, high PAH constituent concentrations appear to be more restricted to the lower subsurface. PAHs reside primarily in the residual oil phase and may partition into other organic phases, such as soil organic matter and soil water (Zemanek et al., 1997). Over time, constituents will separate from the creosote oil phase and disperse into soil pore water and soil. PAH dissolution/diffusion from the oil phase to water and soil phases has occurred in this system. presence of a very hydrophobic PAH, benzo(b)fluoranthene, in the ground water at ML-12 is indicative of significant contamination. Benzo(b)fluoranthene presence also suggests that transport and dissolution of most PAHs from the source area may eventually occur.

At ML-12, chrysene ground water concentrations exceeded aqueous solubility. Sufficient desorption time from the oil phase and augmentative cosolvency effects likely permitted dissolution of benzo(b)fluoranthene into the aqueous phase. Cosolvency refers to the presence/increased concentration of a constituent in the aqueous phase due to the presence of another aqueous phase constituent(s). In a creosote-contaminated soil, Zemanek et al. (1997) witnessed substantial PAH solubility enhancement in soil pore water. The authors observed the most substantial solubility enhancements for the more hydrophobic PAHs.

ii. Transect Two

The second transect was located about 200 feet north-north-east from the source area. Only soil samples were collected along transect two. Figure 11 contains the acenaphthene and fluorene soil concentration depth profile. Figures 6A and 8A in the Appendix contain the concentration depth profiles for the other PAHs. Along a line approximately 60 degrees southeast of transect two and 180 feet northeast of the source area, ground water samples were collected to evaluate PAH movement with ground water across the site. Figure 12 is the ground water concentration depth profile for acenaphthene and fluorene. Figures 7A and 9A in the Appendix contain concentration depth profiles for the other PAHs. Along the second transect, the highest degree of PAH soil contamination was located between SB-9 and SB-12. During the boring process at SB-9 and -10, creosote free product of varying concentrations and consistencies was present at depths of 6 to 7 feet and bedrock and 6 to 8 feet, respectively. Accordingly, high PAH soil concentrations were found in these regions. A MLS, ML-7, is adjacent to SB-9 and SB-10. Ground water in ML-7 was contaminated with 5 PAHs from a depth of 4.5 to 7 feet. Chrysene was not present in any ground water samples taken from ML-7. Apparently, insufficient contact time with the oil phase or insufficient aqueous phase concentrations of LMW constituents did not allow for aqueous phase partitioning of chrysene.

Another region of lesser soil PAH contamination was located between SB-16 and SB-17. Soil contamination through out the depth of the subsurface had occurred. When

Figure 11: Transect Two: Soil Concentration (mg/kg) Depth
Profile for Acenaphthene (top) and Fluorene at
t=0 (figure11.gif, 99K)

Figure 12: Ground Water Concentration (ppb) Depth Profile for Acenaphthene (top) and Fluorene along a line from ML-16 to ML-15 at t=4 Mos.

(figure12.gif, 110K)

the ground water collection trench was constructed in 1991, excavated soil was placed in 3 piles at the site. One of these piles (SP-1 thru SP-6) was located adjacent to transect two. In 1997, the soil piles were spread out over the grass phytoremediation study area. Weathering of creosote contaminants in the soil pile occurred, resulting in PAH soil contamination in this area.

In comparison to ML-7, ML-16 ground water PAH concentrations were greater. In addition to higher PAH concentrations at ML-16, chrysene is also present in the ground water. Cosolvency is probably responsible for the presence of chrysene in ground water.

In previous site investigations, soil and ground water contamination was solely attributed to creosote movement from the source area. In this study, multiple creosote/PAH sources were located. In addition, the areal extent of DNAPL along the bedrock was much greater than initially suspected. Approximate free product bedrock areal coverage prior to this study was 1064 ft². Bedrock areal DNAPL coverage has now been approximated to cover 6500 ft². The Geraghty & Miller, Inc. and Virginia Tech site soil concentrations (Σ 6 PAHs) ranged from below detection limits (BDL) to 944 mg/kg at X-1 (11-12 feet BLS) and BDL to 8,276 mg/kg at SB-12 (10 feet BLS), respectively. Different soil extraction procedures were used by each investigator, so analytical results may not be directly comparable. Ground water analytical results indicate that PAHs are in the aqueous phase along portions of transect one and at ML-7 and -16. Aqueous phase PAHs should be available for microbial and poplar uptake. Geraghty & Miller and Virginia Tech site ground water concentrations

(Σ 6 PAHs) ranged from BDL to 0.564 mg/L at MW-05 and BDL to 1.58 mg/L at ML-16 (8.75 feet BLS).

Subsurface behavior of DNAPLs, like coal tar and creosote, has been discussed by other researchers. is not uncommon for coal tar released into soil to migrate downward through the subsurface until a low permeability layer is encountered (Luthy et al., 1994). If a large mass of contaminant is present, the coal tar may then pool on the low permeability material or move laterally, following the geologic gradient of the confining or rock layer (Mercer et al., 1990). At this site, creosote is present along the bedrock at SB-3, -9, -10, and -12. From the source area to approximately transect one, bedrock elevations generally increase. See Figure 13 for a contour map of the subsurface bedrock elevations at the site. Creosote retention in the upper subsurface due to soil heterogeneity, i.e. low permeability layers, could have permitted lateral contaminant movement from the source area. Subsequent horizontal and vertical movement of creosote towards transect one is likely to have occurred. From transect one to transect two, bedrock elevations generally decrease in a southeasterly direction. contamination just above bedrock is likely due to gravitational movement of creosote (free product) along the bedrock surface.

The contaminant plume has been depicted to move across the site in the direction of ground water flow and generally decreasing subsurface bedrock elevations. The PAH soil and ground water analytical results from this study suggest a slightly different plume direction (Figure 14). The width of the plume from the source area to

Figure 13: Estimated Subsurface Bedrock Elevations at the Site (Geraghty & Miller, 1997)

(figure13.gif, 90K)

Figure 14: Extent of PAH Soil and Ground water

Contamination Based on Virginia Tech Analytical

Results (figure14.gif, 49K)

transect one is more narrow in comparison to the prior plume approximation. PAH movement from the source area to transect one appears to be in a southeast direction. From transect one to transect two, creosote movement likely follows bedrock contours in a northeasterly direction. The highest PAH aqueous concentrations were located at 8.75 to 9.75 feet BLS in ML-16. This may suggest that bedrock DNAPL is present at ML-16.

At this site, ground water concentrations of naphthalene, anthracene, phenanthrene, fluorene, and pyrene were typical to PAH concentrations found at other creosotecontaminated sites (Kiilerich et al., 1996). Kiilerich et al. (1996) also found concentrations of chrysene and benz(a)pyrene in ground water that exceeded maximum solubilities and suggested that some of the analyses could have somehow included nondissolved contaminants present in ground water. Zemanek et al. (1997) saw the same phenomena and concluded that cosolvency predicated the PAH water concentrations in excess of respective aqueous solubilities.

PAH phytoremediation and bioremediation should be at least partially successful at this site. Currently, sufficient amounts of PAHs are present in the aqueous phase. A viable, acclimated microbial community should be able to degrade the PAH contaminants if contaminant concentrations are not toxic to microbes/trees and dissolved oxygen levels are sufficient. Therefore, the areas of the site with moderate levels of water contamination are likely to be most rapidly bioremediated.

Contaminant concentrations have to be high enough to warrant microbial acclimation and growth in the presence of PAHs.

Plants typically enhance oxygen transfer to subsurface microorganisms by a direct and/or indirect route (Erickson et al., 1994). Plants can lower the water table/level in the neighboring soil, thus increasing the zone of aeration. However, PAHs in the aqueous phase may sorb back into surrounding soil if water levels are decreased. Once the poplar trees are fully-grown, the direction of ground water flow is likely to be altered. Ground water flow is likely to shift from the southeast to the northwest. However, the question of whether the poplar trees will eventually provide hydraulic control for the site, especially during the summer, has yet to be determined. At the site, tree survival is primarily dependent on weather conditions and subsurface contaminant concentrations.

Complete groundwater restoration may be technically impossible at many DNAPL-contaminated sites (Luthy et al., 1994). USEPA acknowledges that DNAPLs "often are particularly difficult to locate and remove from the subsurface" and "very long restoration time frames may be indicative of hydrogeologic or contaminant-related constraints to remediation (Luthy et al., 1994 from USEPA, 1993). Unforunately, full-scale site remediation activities conducted at MGP sites have emphasized the removal of source material (Luthy et al., 1994).

B. Grass Phytoremediation Field Study

Field data from PAH grass phytoremediation studies is limited and results are likely to be dependent on contaminant age and site conditions. If augmentative PAH degradation was experienced, then grass phytoremediation systems would be an inexpensive way to clean creosotecontaminated surface soils. The impetus behind the study was to evaluate performance of a grass phytoremediation system with the premise of implementation at sites with creosote or other PAH contamination.

i. PAH Reductions

PAH reductions were evaluated in two ways.

Probability charts (Eckenfelder, 1980) were used to assess overall changes in PAH concentrations over the 9 month period. See Figure 15 for the acenaphthene plot and Figures 10A thru 13A in the Appendix for other PAH plots. The probability plots of acenaphthene, fluorene, phenanthrene, fluoranthene and pyrene suggest that substantial reductions occurred over the nine month period. Conversely, the probability plot for chrysene suggests no reduction over the same period (Figure 16).

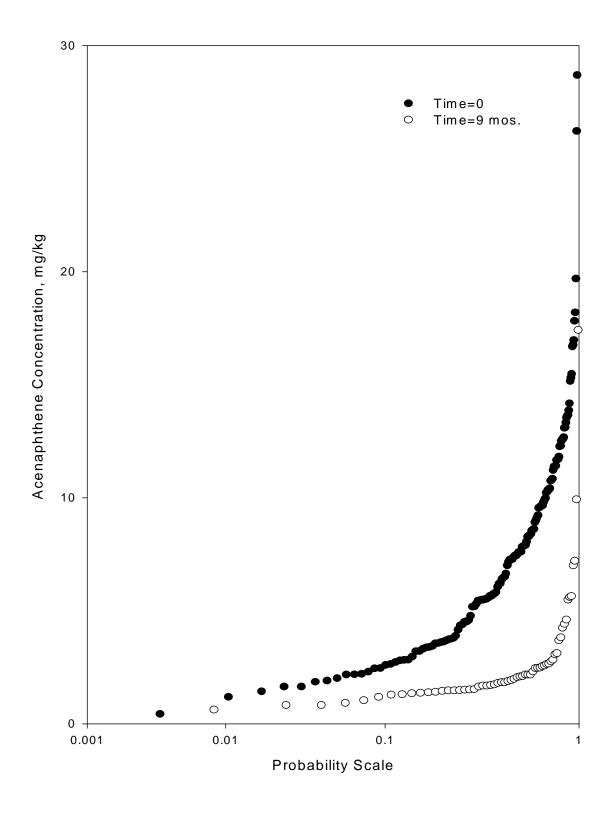


Figure 15: Acenaphthene Probability Plot Containing All t=0 and t=9 Mos. Grass Plot Data

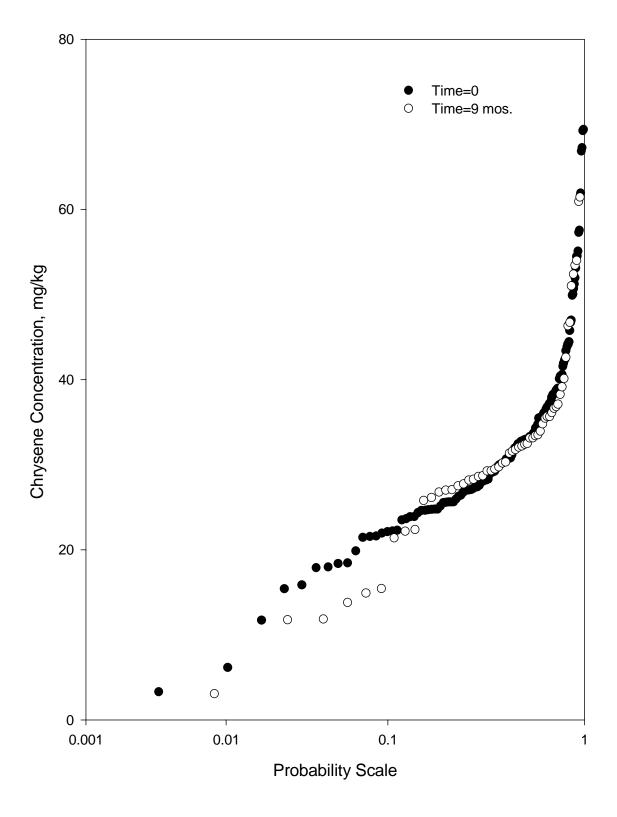


Figure 16: Chrysene Probability Plot Containing All t=0 and t=9 Mos. Grass Plot Data

Box plots also enabled assessment of overall PAH reductions over the study period (Figures 17 and 18). The $50^{\rm th}$ percentile concentrations were used to calculate percent reduction for each constituent over the nine month period (Table 12).

Table 12: Overall Reduction of PAH Constituents in the Grass Study 50th percentile concentrations, mg/kg							
PAH Constituent	t=0	t=9 mos.	Percent Reduction				
Acenaphthene	7.44	2.06	72.3				
Fluorene	7.63	3.81	50.1				
Phenanthrene	26.63	7.05	73.5				
Fluoranthene	56.6	25.13	55.6				
Pyrene	62.18	31.59	49.2				
Chrysene	32.73	32.19	*1.6				

^{*}Chrysene reduction is not statistically significant.

The box plots and Table 12 suggest the same conclusions as the probability plots. The 5 lowest molecular weight PAHs were significantly reduced while chrysene did not change.

Assessment and comparison of PAH concentrations in planted-amended and unplanted-amended soils was conducted. Data from the clover plots was not used in this assessment, because clover growth was minimal. Box plots were used to assess differences between control (unplanted-amended), fescue, and rye plots at t=0 and t=9 months (Figures 19 and 20 and Appendix-Figures 14A thru 17A). The box plots suggest that rye and fescue did not improve PAH reduction. Except for chrysene, the 50th percentile PAH concentrations for the planted plots were higher than corresponding 50th percentile control concentrations at t=9 months. However, initial concentrations of the 5 PAHs were also higher in the fescue and rye plots than the control plots. Chrysene

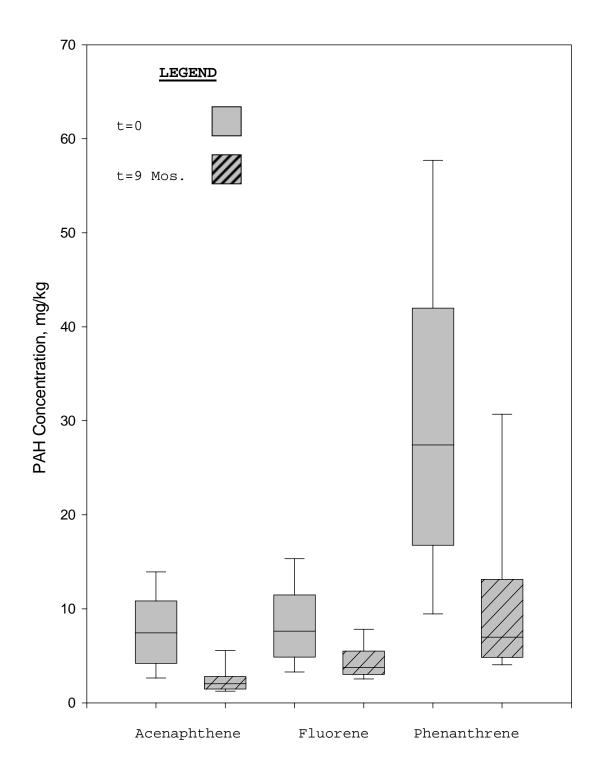


Figure 17: $5^{\rm th}/95^{\rm th}$ Percentile Box Plots: All t=0 and t=9 Mos. Grass Plot Data for Acenaphthene, Fluorene, and Phenanthrene

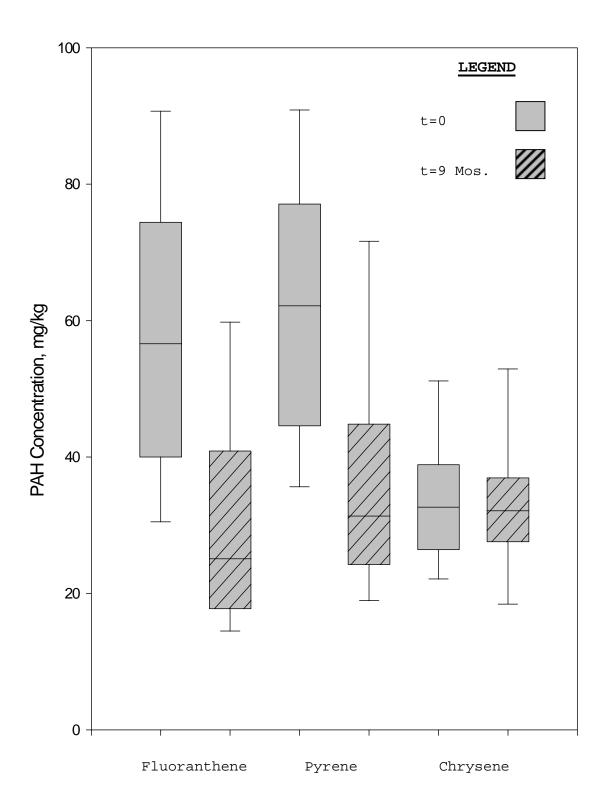


Figure 18: $5^{\rm th}/95^{\rm th}$ Percentile Box Plots: All t=0 and t=9 Mos. Grass Plot Data for Fluoranthene, Pyrene, and Chrysene

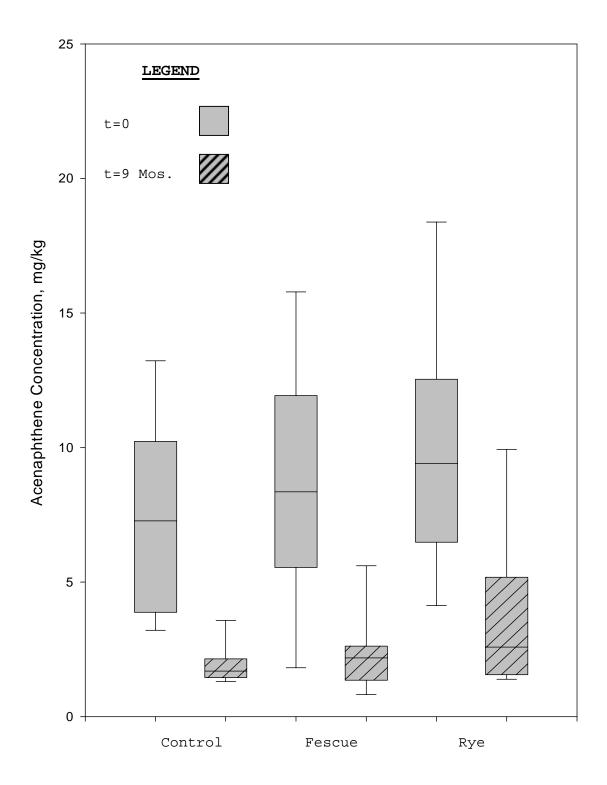


Figure 19: Comparison of Grass Plot Treatments: Acenaphthene Concentrations at t=0 and t=9 Mos.

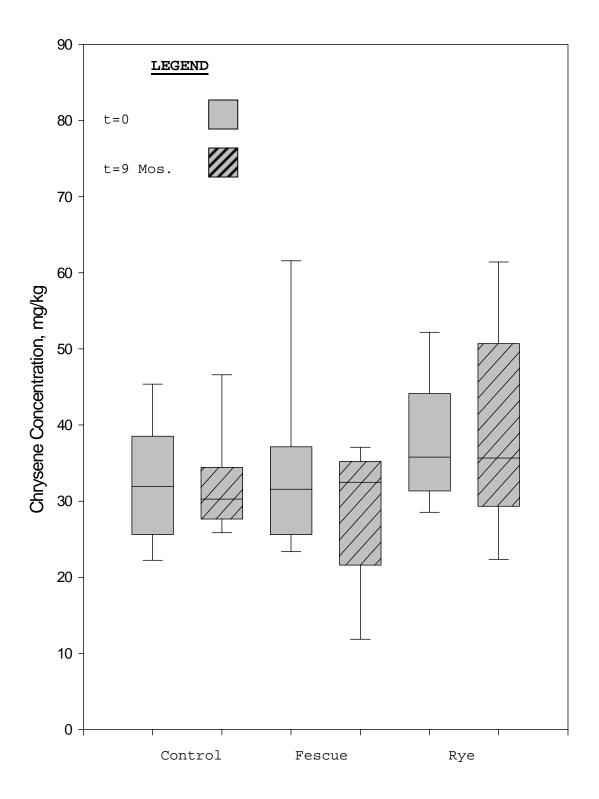


Figure 20: Comparison of Grass Plot Treatments: Chrysene Concentrations at t=0 and t=9 Mos.

concentrations did not vary across the treatments.

Besides other external factors, PAH reductions at the site were based on initial soil concentrations, aqueous solubilities and log K_{OW} values (Appendix-Figures 18A and 19A). The contaminant mass in the soil provides a driving force for partitioning into the aqueous phase and subsequent microbial degradation. Over the 9 month period, fluorene and pyrene 50^{th} percentile concentration reductions were about 50%. The aqueous solubility for fluorene is about 10 times greater than the aqueous solubility of pyrene, but pyrene is 9 times more abundant in the soil at t=0.

Contaminants should be in the aqueous phase for microbial degradation to occur (Mueller et al., 1989; Zhang et al., 1998). Accordingly, PAH solubility has a major influence on the bioremediation rate and extent. A plot of PAH reduction versus aqueous solubility generally indicated increasing reductions with increasing aqueous solubilities (Appendix-Figure 20A). Since much of the PAH loss was likely dependent on solubilization, the 5 LMW PAHs are all subject to bioremediation. At the end of 9 months, chrysene reductions were negligible. The bioremediation potential for the 5 LMW PAHs is certainly higher than the bioremediation potential for chrysene.

ii. Weathering of PAHs

Weathering mechanisms in contaminated soils include photooxidation, volatilization, solubilization, and biodegradation. The contaminated soil used for the grass plot study was exposed to the outdoor environment for approximately 4 years, so considerable weathering occurred. Over the 9 month study period, the data suggests that

reduction of the 5 LMW PAHs was not due to phytoremediation.

After initiation of the study, precipitation amounts were very low in comparison to 30 year normal rainfall data. During the months of January thru March 1998, precipitation amounts increased substantially resulting in prolonged periods of subsurface saturation. Several heavy rain and snow storms fully saturated soil from the land surface to the sampling depth. On February 17, 1998, grass plot soil sample collection was attempted and terminated due to highly saturated site conditions. On March 12 and 13, 1998, t=9 month samples were collected. However, sample collection was restricted due to very saturated subsurface conditions in many plots and positions. Over the 9 month study period, subsurface moisture conditions were generally either under- or over-saturated with respect to optimal moisture levels for microbial communities. At t=0 and t=9 months, the average soil moisture content was 7.1 and 12.6 %, respectively. Loehr (1992) states," At moisture levels below 30% to 40% (of field capacity), activity is restricted due to low water concentrations, while at high moisture levels, aerobic microbial metabolism is reduced because the soil pores are near saturation and transfer of oxygen is inhibited." High soil moisture conditions can limit oxygen diffusion into the soil (Sorenson et al., 1997; Loehr, 1992). At the sampling depth, photooxidation and volatilization were likely negligible routes for PAH loss. PAH biodegradation may have also been affected by nutrient limitations. The plots were only fertilized twice during the first month of the study. Extreme subsurface moisture conditions and limited

nutrient availability may have negatively affected microbial communities capable of PAH degradation.

In a greenhouse study with rye grasses, Ferro et al. (1997) witnessed comparable concentrations of acenaphthene, fluoranthene, pyrene, and chrysene in unplanted-amended and planted-amended soils after 258 days. The soil was obtained from a Superfund site and contained a high percentage of sand. At t=258 days, mean reductions of acenaphthene, fluoranthene, pyrene, and chrysene in the unplanted-unamended, unplanted-amended and planted-amended were: 52.4, 93.4, 86.8, and 80.1 %; 84.8, 94.1, 94.6, and 80.1 %; 94.5, 94.3, 94.7, and 84.7 %, respectively. At t=64 days, concentrations of the 4 PAHs were the lowest in the planted-amended soils. At t=258 days, the unplanted-amended soils achieved concentrations similar to the planted-amended soils.

In a 3-year field study with buffalograss, Sorensen et al. (1997) experienced slow naphthalene degradation due to persistence of high soil moisture conditions from abovenormal precipitation and ponding of water on-site. During the third week of a field comparison between land application and a patented soil treatment process, Tremaine et al. (1994) experienced increased TPAH concentrations during heavy rains which saturated soils to greater than 80 percent field capacity. In the last 3 weeks of the experiment, TPAH concentrations decreased due to improved soil moisture conditions. The authors stated, "Environmental conditions of poor soil drainage and heavy precipitation as well as nutrient depletion tended to slow down biodegradation."

iii. Paired Data

Chrysene, the PAH with the highest molecular weight and lowest aqueous solubility in the study, was the only PAH to exhibit recalcitrance. To reduce statistical variability, only paired sample data, samples taken at the same plot and position at t=0 and t=9 months, were used to create Figure 21, 22A, and Table 13. Chrysene ratios were calculated by dividing the concentration of one of the 5 LMW PAHs into the corresponding chrysene concentration.

Concentration-based ratios of the 5 LMW PAHs with respect to chrysene were calculated to assess PAH weathering. Ratios were determined for paired data at t=0 and t=9 months and graphically expressed as a function of initial chrysene concentration (Figure 21). Differences between average chrysene ratios is evident graphically and statistically for the 5 PAH ratios (Table 13). Average chrysene ratios for all PAH constituents are less at t=9 months than at t=0.

Table 13: Comparison of Average Chrysene Ratios at t=0 and t=9 month								
		Chrysene Ratios						
Time=0	Acenaphthene	Fluorene	Phenanthrene	Fluoranthene	Pyrene			
Average	0.189	0.217	0.735	1.638	1.777			
Std. Dev.	0.111	0.115	0.440	0.492	0.412			
Time =9 mos.								
Average	0.077	0.147	0.320	0.897	1.089			
Std. Dev.	0.046	0.092	0.229	0.355	0.301			

Chrysene ratios for pure creosote and site concentrated creosote in the subsurface at SB-10 were calculated. Chrysene ratio comparison suggests prior and substantial weathering of the surface soils (Table 14). Acenaphthene, fluorene, and phenanthrene ratios were reduced in excess of 85% prior to initiation of the grass

Figure 21: Grass Plot Acenaphthene and Pyrene:Chrysene
Paired Data Ratios at t=0 and t=9 Mos.

(figure21.gif, 50K)

plot study (Appendix-Figure 21A). Chrysene may have experienced some degradation during the weathering process, but it is likely that weathering of the 5 LMW PAHs was more severe than chrysene weathering. At this time, chrysene ratios accurately depict the grass plot soil weathering process and clearly indicate concentration reductions of the 5 LMW PAHs. PAH reductions are clearly dependent on aqueous solubility (Appendix-Figure 22A). This may suggest that further degradation of some components of creosote, especially the LMW PAHs, may not be experienced. A lack of LMW PAH availability may decrease microbial degradation of the HMW compounds due to decreased cometabolic activity.

PAH Constituent									
Source	Acenaphthene	Fluorene	Phenanthrene	Fluoranthene	Pyrene				
Literature*	2	4	6.5	2	1				
Conc. site creosote	2.77	3.11	7.51	3.41	2.76				
Grass Plots;t=0	0.23	0.23	0.81	1.73	1.90				
Grass Plots;t=9 mos.	0.06	0.12	0.22	0.78	0.98				

Previous researchers also encountered chrysene stability in weathered chemical mixtures and used ratios for determination of cooxidation effects. After assessing the stability of PAHs in weathered and biodegraded crude oils, Douglas et al. (1994, 1996) reported substantial biodegradation of two- and three-ring PAH compounds in lab and field studies. Only twenty percent of chrysene was degraded, while there was complete degradation of naphthalene, fluorene, phenanthrene, and fluoranthene. In a PAH cooxidation study, Keck et al. (1989) used a ratio of $3\text{-ring}:\Sigma(5+6\text{-ring PAHs})$ to evaluate substrate: cosubstrate ratios for different wastes.

iv. Other Issues Concerning PAH Reductions

Several PAH biodegradation/sorption studies suggest PAH adsorption onto organic matter significantly reduces contaminant bioavailability (Loehr et al., 1996; Weissenfels et al., 1992). A reduction in bioavailability has been correlated to a decrease in microbial biodegradation. Chemical aging also restricts extractability and contaminant bioavailability (Hatzinger et al., 1995). Hatzinger et al. (1995) found that the extractability of fresh phenanthrene was greater for soils with lesser organic matter contents. The soils used in the study were lima loam and edwards muck which contained 4 and 19.3 % TOC, respectively. Phenanthrene extraction recoveries also decreased in both soils with increasing contact time between soil and phenanthrene. containing a high clay fraction may limit contaminant bioavailability (Pollard et al., 1994).

At t=0 and t=9 mos., average TOC in the grass plots was 5.3 and 4.9 %, respectively. The difference in TOC is indicative of the dissolved organic carbon fraction that has either been transported or utilized by plants or microorganisms. A soil grain distribution was performed on seven t=0 and t=9 month paired samples. Sand and silt/clay fractions were consistent over the study area and at both time intervals. Average sand and silt/clay fractions were 69 and 31 %. TOC and silt/clay levels in grass plot soils do not appear to limit desorption/solubilization of the 5 LMW PAHs. Creosote age and weathering prior to the study are likely to have the most negative influence on bioavailability.

In this study, differentiation between solubilization/transport, solubilization/biological bioremediation, and solubilization/phytoremediation of the PAHs could not be assessed. Low root mass in most planted plots and concentration similarities between control and planted plots suggest that phytoremediation has not contributed to PAH reduction over the first growing season. At the beginning of the study, nutrient addition likely augmented the population of indigenous microorganisms, but non-optimal moisture conditions likely hindered microbial growth and activity. PAH losses occurred by solubilization /microbial uptake and/or solubilization/downward transport of the 5 LMW PAHs. Nutrient limitations may have occurred after initiation of the study. Subsurface conditions may not have allowed development and growth of an adequate population of acclimated, PAH-degrading microorganisms.