# OPTIMIZING MANAGEMENT OF PAH CONTAMINATED SEDIMENT FROM THE APPOMATTOX RIVER FEDERAL NAVIGATION CHANNEL[1]

G. Tracey[2], G. Berman, S. Insalaco, J. Swanko, S. Powell, R. Pruhs, R. Reali, W. Daniels, C. Carter

**Abstract**. The USACE-Norfolk District (NAO) and the City of Petersburg, VA are working toward restoring the former Appomattox River Federal Navigation Channel. In this effort, ~350,000 cubic yards of deposited sediment will be removed from -14 feet MLLW up to + 6 feet MLLW over a ~1 mile reach of the Appomattox River. Historical industrial uses have resulted in PAH contamination exceeding 500 mg/kg on average, with hotspots detected in excess of 5,000 mg/kg based on USACE 2004 analytical data. To support the NAO with its assessment of contaminant distribution, upland source control measures, dredge sequencing, sediment capping requirements to address residual contaminants and beneficial reuse options for the dredged material have been evaluated. In support of beneficial reuse as agricultural soil, a lab treatability study has been completed to assess biodegradation potential. Total PAH concentrations in three laboratory test pans after 46 weeks of treatment indicated an overall 80% contaminant reduction using an enhanced bioremediation process. The results of this bench-scale study were used as the basis for the design of a pilot field-scale landfarm study demonstration undertaken during July 2007. After five months of treatment, LMW PAHs in landfarm material appear to have degraded first while HMW PAHs are degrading more slowly, a process which generally mimics the results of the laboratory investigation. Conclusions based on the laboratory and landfarm activities as well as the technical and regulatory issues that must be resolved to allow eventual placement of the material at a mine reclamation site for revegetation purposes will be presented.

**Additional Key Words**: Biodegradation, Landfarm, Treatability.

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[2] Gregory A. Tracey, Ph.D is a Senior Scientist/Program Manager, SAIC, 221 Third Street, Newport, RI 02840; Gregory A. Berman, P.G., SAIC, 221 Third Street, Newport, RI 02840; Samuel E. Insalaco, SAIC, 8866 Commons Boulevard, Twinsburg, OH 44087; Jesse Swanko, SAIC, 221 Third Street, Newport, RI 02840; Stephen J. Powell, P.E., Robert S. Reali, P.E., Robert S. Pruhs, USACE-Norfolk District, 803 Front Street, Norfolk, VA 23510; W. Lee Daniels, Ph.D., Dept. of Crop and Soil Environmental Sciences, Virginia Tech, 244 Smyth Hall, Blacksburg, VA 24061; Charles R. Carter, Port Tobacco at Weanack, Weanack Land, L.L.L.P., 461 Shirley Plantation Road, Charles City, Virginia 23030.

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# Introduction

The Appomattox River Federal Navigation Channel constitutes a portion of the Appomattox River located in south-central Virginia, approximately 32 km (20 miles) south of Richmond. It lies within the city limits of both Petersburg and Hopewell, and spans both Chesterfield and Prince George Counties. The U.S. Army Corps of Engineers (USACE[1]) is responsible for maintaining federally authorized navigable waterways in the United States, and thus the USACE-Norfolk District (NAO) has been tasked with assisting the City of Petersburg in restoring the navigability of the channel up to an artificially terminating portion in the downtown section of the city. When dredging of the Appomattox River Federal Navigation Channel commenced in 1991, petroleum-related contamination in the form of Total Petroleum Hydrocarbons (TPH) was discovered in the sediment and operations were suspended indefinitely pending further investigation. Since that time, several site investigations have been conducted by the USACE and various contractors to evaluate the potential environmental risks posed by post-dredging contaminant impacts as well as to determine proper disposal versus upland placement scenarios for contaminated dredged sediments. These investigations included dredge sequencing and both laboratory and field-scale treatability testing for beneficial reuse options. Results of these activities, as well as descriptions of the technical and regulatory issues being resolved to allow eventual placement of the dredge material for use as revegetation media at a mine reclamation site, are presented in this paper.

## Site Description

The Appomattox River is a tributary of the James River that drains approximately 1,300 square miles of watershed in southeastern Virginia. Continuous siltation in this commercially important waterway resulted in the authorization of the Appomattox River Federal Navigation Channel during the 1870s, which begins at the head of the tidal reach and ends approximately 11 miles downstream at the confluence point with the James River. As shown in Fig. 1, the current major dredging site encompasses the artificially terminated section of the Navigation Channel beginning at the Pocahontas Island Bridge in Petersburg, Virginia (Station 0+00) and extending approximately one mile east parallel to the Norfolk Southern railroad tracks (Station 50+00). This area spans approximately 21 acres to the top of the projected side slopes,

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[1] A list of Acronyms and Abbreviations may be found at the end of this paper.

and contains a portion of Lieutenant Run, which is a small flowing channel tributary that lies to the west of Interstate 95. The western third of the project site resembles a tidally-influenced pond, the center third a forested wetland, and the eastern third a tidal marsh. The western pond-like region can only be accessed aquatically using a small shallow draft vessel launched from the riverbank at high tide.

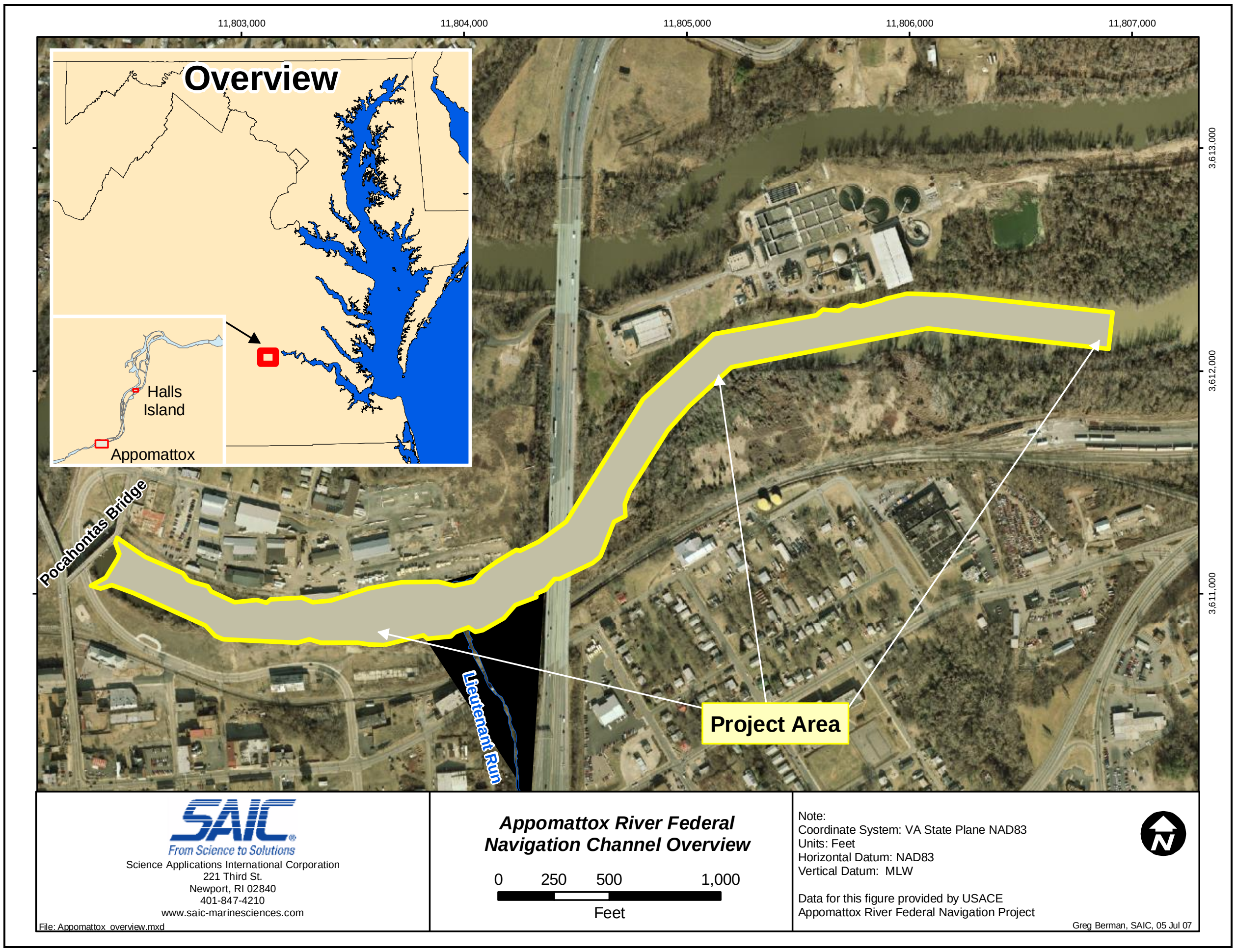

Figure 1. Location and boundaries of the Appomattox River Federal Navigation Channel dredging area in Petersburg, Virginia.

## Site History

Due to persistent sedimentation problems in the main portion of the Appomattox River Federal Navigation Channel following its federal authorization in the 1870s, a second channel was built in the 1920s to divert the natural flow of the river along with its heavy sediment load (ERDC, 2006). While the diversion channel successfully reduced siltation in the navigation area, it also blocked most freshwater flow coming into the channel from upstream, which reduced water exchange, increased seasonal water temperatures and lowered dissolved oxygen levels. After the cessation of maintenance dredging by the USACE in the 1950s, the Federal Navigation Channel once again became noticeably clogged with sediment. This problem is believed to have been exacerbated by the construction of Interstate 95 (Richmond-Petersburg Turnpike) which introduced bridge piers into the river that obstructed direct flow, slowed tidal wash and provided physical barriers (City of Petersburg, 2001). During October 1972, the Appomattox River watershed experienced the worst flooding in the history of Petersburg and tons of sediments were deposited into the upper reaches of the Federal Navigation Channel. After years of inactivity, the USACE-Norfolk District determined in 1990 that restoration of the channel could only be accomplished by separate tasks that included dredging, compensating for wetlands that now occupy the former channel footprint and repairing the breach that connects the diversion channel to the navigation channel at Halls Island (Fig. 1).

In 1991, dredging was planned for a 5 mile stretch of the Appomattox River beginning at the head of the Federal Navigation Channel (corresponding with the Pocahontas Island Bridge) and proceeding eastward. A number of site characterization investigations were performed in preparation of this dredging operation that included: WES (March 1990); ETS (March 1991); Virginia Water Control Board (November 1991); J. H. Carr & Associates (June 1992); and O’Brien & Gere Engineers (July 1993). During the November 1991 study, total petroleum hydrocarbons were detected in channel sediments at concentrations >1,000 mg/kg. During the July 1993 study, total petroleum hydrocarbons were detected at concentrations >2,500 mg/kg. As a result, dredging operations were suspended pending further investigation (USACE, 1996). Additional sampling was conducted by the USACE at the Appomattox Federal Navigation Channel project site in 1994 and 2004, during which several sediment borings were collected and analyzed for a variety of contaminants. Results from these investigations determined that Polycyclic Aromatic Hydrocarbon (PAH) contamination is present at high concentrations (up to 5031 mg/kg) within deeper layers of soil (up to 22 ft bgs).

Based on the results of all previous testing, a plan to dredge the Appomattox Federal Navigation Channel to between twelve and fourteen feet below Mean Lower Low Water (MLLW) and cap residual contaminants with clean material was developed to restore navigability to the waterway while also isolating potential ecological receptors from the PAH contamination (USACE, 2006). As defined, the dredge prism involves the removal of approximately 350,000 cubic yards of dredged material from a depth range of -14 feet MLLW to +6 feet MLLW (20 ft thickness) over a 1 mile reach of the Appomattox River. Capping material is to be obtained from a clean area downstream from the site where separate maintenance dredging is scheduled to occur (USACE, 2006).

### Nature of Contamination

Polycyclic aromatic hydrocarbons are a subset of TPH contaminants that consist of fused aromatic rings containing only carbon and hydrogen. They are typically formed and released to the environment during the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances and generally occur as complex mixtures (*e.g.*, part of combustion products such as soot) rather than as single compounds (USDHHS, 1995). The USEPA has specifically identified benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene and indeno[1,2,3-c,d]pyrene as probable human carcinogens (USDHHS, 1995).

Biological degradation is widely accepted as the primary natural dissipation mechanism for most organic pollutants in the environment, but the activity of degrading microorganisms is dependent upon many factors, including contaminant uptake and bioavailability, concentration, toxicity, mobility, access to other nutrients and activated enzymes (Cerniglia, 1992; Government of Canada, 1994). Being highly hydrophobic, PAHs tend to accumulate in solid phases and organic matter, thus becoming unavailable for microbial degradation (Johnsen *et al*., 2004). High molecular weight (HMW) PAHs (5- to 6-ring) are particularly recalcitrant and of special environmental concern (Johnsen *et al*., 2004).

Bioremediation with PAH-degrading microbial lab strains has long been proposed as a treatment technology for the decontamination of PAH-contaminated soils. Numerous bacteria are known to catabolize PAHs as sole sources of carbon and energy, but the effectiveness of the bioremediation approach depends on overcoming any potential nutrient limitations within the soil system to be remediated (Bogan *et al.*, 2001). In the case of PAH contamination, the limiting nutrients are typically phosphorus and nitrogen, which can be ameliorated via the application of soluble nutrients. However, the resulting very high nutrient concentrations have been observed to lead to excessive localized microbial growth (Bogan *et al.*, 2001). Biosurfactants can enhance hydrocarbon desorption and solubility, but their effect on bioavailability and degradation are less straightforward.

## Dredge Sequencing

As part of the Appomattox River Federal Navigation Channel overall management strategy, the project area was divided into 17 segments, or cells (App-1, App-2, etc.), to optimize the handling of dredged material. The location of these cells, along with both current pre-dredging and planned post-dredging bathymetry, is shown in Fig. 2. The footprint of each cell (3,850-6,450 square yards with 3:1 side slopes) corresponds to ~20,000 cu-yd of dredged sediment as required to achieve the 12-foot depth.

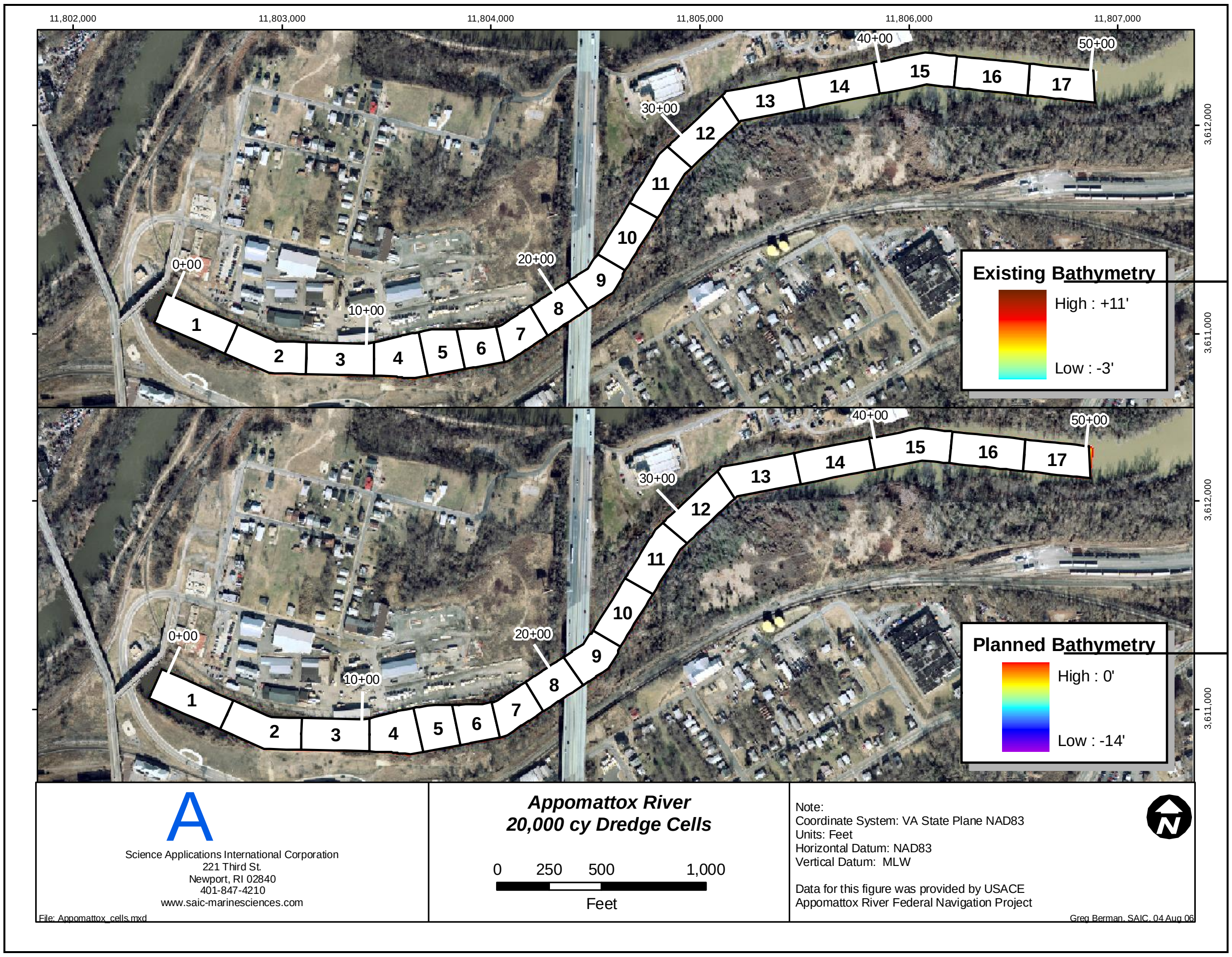

Figure 2. Current pre-dredging and planned post-dredging bathymetry within various cells at the Appomattox River Federal Navigation Channel project area.

A three-dimensional solid contaminant model was developed from existing 1994 core data to define the nature and extent of total PAH contamination in each cell. The results of this model are provided for three cross-sections across the project area in Fig. 3. As shown by the solid model cross-sections, a layer of relatively non-impacted material exists at the surface in each cell with various "hotspots" existing at depth. For management purposes, non-impacted dredged material was defined as all sediments from the surface to the first depth with total PAH >100 mg/kg. The weighted average total PAH concentration of all sediment in this horizon was 2 mg/kg (see Table 1). At this concentration, individual PAH levels (approximately 1-10% of total) were deemed unlikely to exceed even the most stringent USEPA Region III Human Health Risk-Based Concentrations (RBCs), including regulatory criteria for benzo[a]pyrene and dibenz[a,h]anthracene (0.39 mg/kg and 0.022 mg/kg for industrial and residential use, respectively). Thus all material removed from the non-impacted horizon would be considered suitable for beneficial reuse without treatment. As shown in Table 1, some cells do not feature any impacted sediment layers (*i.e.*, App-1, App-3, App-16 and App-17) and all dredged material from these areas would be considered non-impacted.

For the remaining cells, the volume of material between the "clean" depth and the final proposed navigation depth (-12 ft MLLW) was determined. Although additional "clean" layers of sediment may be present below the impacted material (total PAH < 100 mg/kg) in many of these cells, this material was included in the impacted volume because it would not be technically or economically feasible to dredge the various layers on an individual basis. In the majority of cells, the residual PAH concentration at the planned -12 ft depth was calculated to be non-impacted and therefore could be left in place without further treatment (see Table 1). For other cells (App-6, App-7, App-12) an additional 2 ft of dredging was planned to accommodate cap material needed to cover impacted sediment left in place. Volumes associated with this so-called "overdredge" are also shown in Table 1. On this basis, the overall volumes of both non-impacted and impacted dredged material were determined for the entire Appomattox River Federal Navigation Channel project (Table 1).

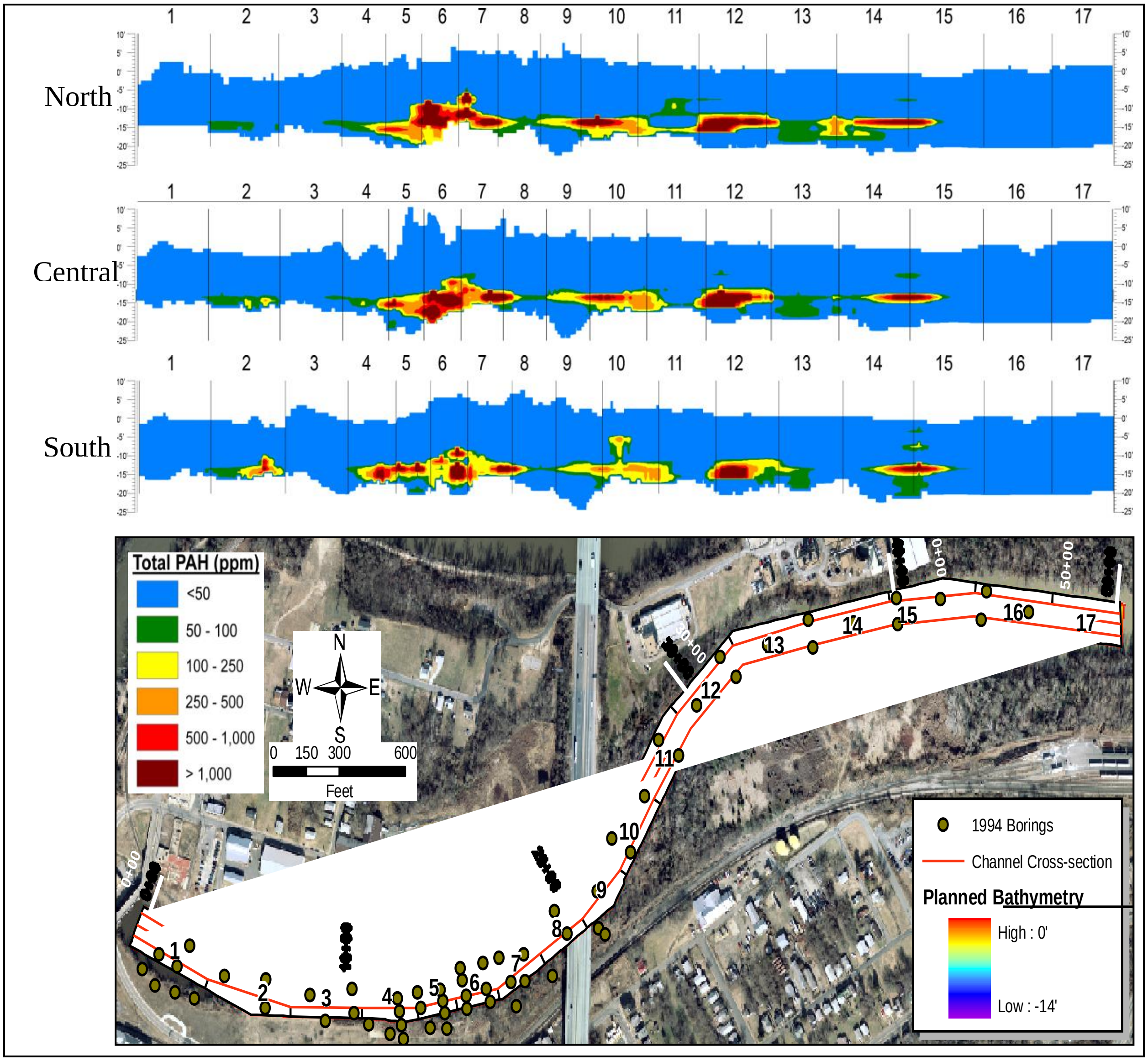

Figure 3. Results of the three-dimensional solid model for total PAH along three transects developed from 1994 boring data for the Appomattox River Federal Navigation Channel.

**Table 1**. Final volumes for the Appomattox River Federal Navigation Channel dredging scenarios.

| Cell Parameter | App-1 | App-2 | App-3 | App-4 | App-5 | App-6 | App-7 | App-8 | App-9 |
|---|---|---|---|---|---|---|---|---|---|
| **Non-Impacted Dredge Material** | | | | | | | | | |
| "Clean" Depth (ft below MLW) | N/A | 9 | N/A | 11 | 9 | 7 | 4 | 11 | 11 |
| Avg Total PAH Above "Clean" Depth (mg/kg) | 3 | 1 | 2 | 1 | 2 | 1 | 1 | 1 | 1 |
| Sediment Vol Above "Clean" Depth (cy) | 20,400 | 16,800 | 20,500 | 16,100 | 14,500 | 13,300 | 10,500 | 16,500 | 16,500 |
| **Contaminated Dredge Material To Be Treated (No Capping)** | | | | | | | | | |
| Avg Total PAH From "Clean" Depth to 12' Dredge Depth (mg/kg) | - | 7 | - | 10 | 32 | 251 | 151 | 31 | 40 |
| Sediment Vol From "Clean" Depth to 12' Dredge Depth (cy) | - | 3,900 | - | 900 | 2,700 | 4,000 | 6,900 | 700 | 700 |
| **Additional Contaminated Dredge Material To Be Treated (Capping)** | | | | | | | | | |
| Avg Total PAH From 12' Dredge Depth to 14' Dredge Depth (mg/kg) | - | - | - | 12 | 83 | 416 | 217 | 37 | 32 |
| Sediment Vol From 12' Dredge Depth to 12' Dredge Depth (cy) | - | - | | 2,900 | 2,600 | 2,200 | 2,200 | 2,300 | 2,300 |
| **Residual Contamination at Post-Dredging Surface** | | | | | | | | | |
| Predicted Avg Total PAH at 12' Depth (mg/kg) | 3 | 9 | 9 | 14 | 65 | 487 | 330 | 38 | 50 |

**Table 1**. Final volumes for the Appomattox River Federal Navigation Channel dredging scenarios (continued).

| Cell Parameter | App-10 | App-11 | App-12 | App-13 | App-14 | App-15 | App-16 | App-17 | Avg / Total |
|---|---|---|---|---|---|---|---|---|---|
| **Non-Impacted Dredge Material** | | | | | | | | | |
| "Clean" Depth (ft below MLW) | 4 | 6 | 9 | 11 | 11 | 6 | N/A | N/A | **8** |
| Avg Total PAH Above "Clean" Depth (mg/kg) | 1 | 1 | 2 | 1 | 4 | 1 | 5 | 6 | **2** |
| Sediment Vol Above "Clean" Depth (cy) | 11,100 | 13,200 | 16,800 | 19,600 | 19,300 | 12,100 | 20,600 | 19,600 | **277,600** |
| **Contaminated Dredge Material To Be Treated (No Capping)** | | | | | | | | | |
| Avg Total PAH From "Clean" Depth to 12' Dredge Depth (mg/kg) | 12 | 35 | 471 | 11 | 19 | 11 | - | - | **83** |
| Sediment Vol From "Clean" Depth to 12' Dredge Depth (cy) | 9,200 | 6,800 | 3,400 | 1,100 | 1,200 | 8,600 | - | - | **50,400** |
| **Additional Contaminated Dredge Material To Be Treated (Capping)** | | | | | | | | | |
| Avg Total PAH From 12' Dredge Depth to 14' Dredge Depth (mg/kg) | - | - | 86 | - | - | - | - | - | **126** |
| Sediment Vol From 12' Dredge Depth to 12' Dredge Depth (cy) | - | - | 3,400 | - | - | - | - | - | **18,200** |
| **Residual Contamination at Post-Dredging Surface** | | | | | | | | | |
| Predicted Avg Total PAH at 12' Depth (mg/kg) | 31 | 41 | 725 | 13 | 24 | 20 | 9 | 11 | **101** |

## Laboratory Treatability Study

The main goals of the beneficial reuse investigations for the Appomattox River Federal Navigation Channel sediment were to determine the properties, treatability options and disposal versus upland beneficial reuse capabilities of material to be removed from the project area during dredging. The laboratory-scale treatability study for potential Appomattox River dredge material was conducted from February 2007 to January 2008. A summary of this investigation is provided in the following sub-sections.

### Methods and Materials

In February 2007, SAIC and ICOR personnel collected 20 gallons of sediment from the Lieutenant Run portion of the Appomattox River Federal Navigation Channel project area to be used in a laboratory treatability study designed to evaluate various methods for degradation of PAHs and TPH (DRO & HRO) in dredged sediments. The goal of this bench-scale effort was to determine the optimum amendment mixture that could be used to treat hydrocarbon-based contamination to achieve applicable thresholds for reuse in a mine reclamation project. Based on analytical results from previous cores, the aforementioned bulk sediment sample targeted 15 gallons of mildly impacted sediment (< 500 mg/kg total PAH) and 5 gallons of highly impacted sediment (> 500 mg/kg total PAH) in order to simulate the likely overall composition of the sediments to be removed during the full-scale channel dredging operation.

Sediments were collected from USACE 2004 coring stations BLAR15-0 (5 gallons mildly impacted sediment from 18-20 feet bgs) and BLAR15-3 (10 gallons mildly impacted sediment from 20-22 feet bgs; 5 gallons highly impacted sediment from 22-24 feet bgs) using a hydraulic drill rig and hollow stem auger. Samples were transferred from the auger blades into 5-gallon containers using decontaminated pans and stainless steel spoons. These sediments were then shipped, along with a reference sediment sample from the nearby Elizabeth River, to the Environmental Technologies (ETEC), LLC treatability laboratory in Portland, Oregon where they were composited for bench-scale testing. The “reference” sample was collected from an impacted sediment site in the Elizabeth River (Money Point) in order to assess the effectiveness of treating sediments representing the worst case conditions for bacterial degradation, including elevated contaminant levels (total PAH > 500 mg/kg), high organic content (TOC > 8%) and high silt/clay faction.

Upon receipt by the analytical laboratory, the samples were immediately placed in a refrigeration unit at 40°F. The Appomattox site sediments were removed from the plastic containers and homogenized (mixed) in a sterilized 50-gallon plastic container using a pre-cleaned shovel. This new sediment mixture was mostly sand, consisting of >95% medium-grained sand particles and featuring few gravel particles (< 2 inches in diameter) that were physically removed during the mixing process. The site sediment, as well as a homogenized reference sample, was then evenly distributed into five stainless steel pans (cleaned and sterilized with isopropyl alcohol) and weighed. The total mass of sediment in each pan ranged from 55 to 60 pounds.

After distribution into the pans, two composite baseline sediment samples were collected prior to the addition of any amendments. Biological products were then added to each pan based on experimental design specifications. These trademarked biological products included ETEC Laboratory's Custom Blended Nutrients (CBN$^{TM}$), PAH-degrading bacterial consortium (EZT-A3$^{TM}$), enzyme accelerator (EZT-EA$^{TM}$) and biodegradable surfactant solution. These amendments are all designed to enhance and support biological degradation of organic constituents, primarily gas-, diesel-, and heavy-range petroleum hydrocarbons (*i.e.*, PAHs).

The CBN$^{TM}$ product is a specific blend of macro- and micro-nutrients that are required for biological transformation of organic compounds. It includes the necessary nitrogen compounds (84.7%), phosphorus compounds (14.6%) and potassium compounds (1%) as well as a series of trace elements that are also important for cellular function and growth of microorganisms including S (< 0.1%), Mn (< 0.01%), Fe (< 0.01%), Zn (< 0.01%), B (< 0.001%), Cu (< 0.001%) and Mo (< 0.00001%). The volume of CBN$^{TM}$ mixture to be added is based on the mass and composition of PAHs in the test sediment. The selected endpoint ratio of carbon to nitrogen to phosphorus (C:N:P) for this study was 100:10:1, a mixture which had been found in previous studies to support > 80% reduction of total PAHs (Leys *et al.*, 2005). In the present study, the baseline TPH-DRO and HRO concentrations for the Appomattox site were approximately 1,880 mg/kg, which equates to a total TPH mass of approximately 47 grams per pan containing 55 lbs (25 kg) of test sediment. Assuming TPH is all carbon (a conservative estimate), the target nutrient ratio dictated a need for 4.7 grams N and 0.47 grams P in each pan. Accordingly, ETEC added 13 grams of CBN$^{TM}$ (28% elemental N and 12% elemental P, wet weight) to each pan, thus equating to 3.6 grams N and 1.5 grams P. A three-fold surplus of P was added above the desired ratio demand because previous experiments indicated that some P (>50%) is typically lost as abiotic phosphate species due to mineral speciation, thus making it unavailable to microbes and requiring compensation to preserve the 100:10:1 ratio.

The EZT-A3™ product is a PAH-degrading bacterial consortium made up of facultative (*i.e.*, can function in both aerobic and anaerobic environments) petroleum-degrading microbial strains that naturally occur in the environment (*i.e.*, not genetically engineered microorganisms). These strains are all non-pathogenic and have been shown via numerous independent research efforts to be extremely effective degraders of diesel- and heavy-range hydrocarbons. The microbes are grown on a diesel, phenanthrene, benzo[a]pyrene and chrysene substrate mixture (microbial carbon and energy source/electron donor solution fed with liquid nutrients and buffering agents) in order to facilitate production of the right enzyme structures capable of degrading diesel- and heavy-range hydrocarbons. The "raw" bacterial consortium is manufactured in a liquid form with a minimum microbial "strength" of $1\text{x}10^8$ colony-forming units per milliliter (CFU/mL). This concentrated product was then diluted 50-100 times with water prior to application to the dried sediment. The target concentration of $0.8\text{-}1.0\text{x}10^6$ CFU/mL ensures that a high quantity of bacteria will be applied to the sediment subsurface to help establish a healthy foundation population of hydrocarbon-degraders, which will accelerate overall remediation efforts.

The EZT-EA™ product is a diluted enzyme accelerator that enhances desorption of heavy-end petroleum hydrocarbons. It consists of a biodegradable rhamnolipid made up of oxymethyl fatty acid complexes, the main purpose of which is to decrease the hydrophobicity of recalcitrant hydrocarbon compounds, thus making them bioavailable for microbial degradation. The working solution is either injected slowly through a recirculation loop or directly applied to the test sediment.

In addition to these biological products, the control pan received sodium azide ($NaN_3$; 6 g/lb sediment), which has been previously used in open pan soil experiments to effectively inhibit ("kill") all microbial activity (Goel *et al.*, 2003). Though potentially useful, another control pan containing only untreated sediment from the project area was deemed impractical and not included in the experimental design because the natural PAH degradation rate is well known to be inherently slow (Government of Canada, 1994) and only negligible degradation would be expected over the timeframe of the treatability project. Overall, biological products were added to the pans as follows:

- **Killed Control (KC)**: Nutrients (CBN™), microbial consortium (EZT-A3™), enzyme accelerator (EZT-EA™), heavy biodegradable surfactant, sodium azide (sterilant).
- **Live 1 (LV1)**: Nutrients (CBN™) only.
- **Live 2 (LV2)**: Nutrients (CBN™), microbial consortium (EZT-A3™), enzyme accelerator (EZT-EA™).
- **Live 3 (LV3)**: Nutrients (CBN™), microbial consortium (EZT-A3™), enzyme accelerator (EZT-EA™), heavy biodegradable surfactant.
- **Reference (REF)**: Nutrients (CBN™), microbial consortium (EZT-A3™), enzyme accelerator (EZT-EA™), heavy biodegradable surfactant.

The biological products were thoroughly mixed into the sediment in each pan for 5-10 minutes. To ensure that moisture content of the sediments was ideal for biodegradation (>25% of field capacity) deionized water was added to the pans as necessary. The edges of the pans then had weather strip tape attached to them and were covered with plywood to limit volatilization and prevent any cross-contamination. The sediments in all pans (except KC) were mixed 2-3 times per week for periodic maintenance. Moisture levels in the pans were maintained through applications of deionized water.

Discrete sampling of each pan was conducted at the start of the experiment (baseline) and every three weeks (21 days) for an initial period of 18 weeks. Following Week 18, the sampling frequency was reduced from three weeks to six weeks through Week 30 of the project. The frequency was adjusted because the analytical data showed that low molecular weight PAH compounds had been largely degraded by Week 18 while the high molecular weight PAH compounds were degrading more slowly. The final end point was extended an additional 16 weeks (to Week 46) as asymptotic degradation rates were observed leading up to this point.

Also during the course of the study, another potentially promising treatment called Enzymmix™ was introduced to one test pan (LV1) after Week 26 and again after Week 30 to evaluate its effectiveness on degrading high molecular weight PAHs. This product, provided by Oil Free Technologies, Inc., is produced by earthworms that have been genetically modified to secrete mucus that contains an enzyme, or enzymes, capable of catalyzing mineralization reactions (*i.e.*, converting organic compounds into carbon dioxide and water). Based on the vendor's recommendations, 1 mL of Enzymmix$^{TM}$ was mixed with 1 L of water and applied evenly into the impacted sediment.

Inclusive of the baseline (Day 0) and final (Week 46) efforts, a total of ten independent sampling events for the control and the live pans were conducted. Final samples for the reference pan were collected after Week 30 (9 samples), as results leading up to that time indicated little ongoing degradation. Sediment samples from each pan were collected in unpreserved glass containers (4 or 8 oz.) and analyzed for PAHs, pH, heterotrophic hydrocarbon degrading plate count and inorganic nutrients (nitrate-N, total-N, ammonia-N, sulfate, Olsen extractable phosphorous-P). All sediment analyses were performed using the following methods:

- **PAHs** – Method USEPA 8270 SIM (modified)
- **Diesel and Heavy-End Petroleum Hydrocarbons** – Method NWTPH-Dx
- **Hydrocarbon-Degrading Plate Count** – Modified Pour Plate Method (Chapter 84 in the Manual of Environmental Microbiology)
- **Inorganic Nutrient Parameters** – Various Methods

After each sampling and analysis event, analytical PAH and nutrient data were tabulated and time series graphs were created to depict PAH reductions, nutrient utilization, microbial health and pH shifts due to microbial activity over time. For the PAH degradation analysis, Total Low Molecular Weight (LMW) PAHs were calculated as the sum of seven analytes (2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, fluorene, naphthalene, phenanthrene) and Total High Molecular Weight (HMW) PAHs were calculated as the sum of six analytes (benzo[a]anthracene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, fluoranthene, pyrene) based on USEPA guidance.

## Results and Discussion

Baseline analytical results reflecting starting contaminant levels for the five treatments showed that the initial Diesel Range TPH concentration ranged from 970 to 1,400 mg/kg, the initial Heavy Oil Range TPH concentration ranged from 320 to 480 mg/kg and significant PAH concentrations were present in the sediment (total PAH concentration of approximately 250 mg/kg, excluding the KC result). The reported KC baseline PAH concentrations were unexpectedly approximately half of the live pans even though they were from the same source material. The analytical laboratory attributed this effect to an artifact from the addition of sodium azide causing an unknown temporary reaction in the sediment, as evidenced by a change in color from brown to dark brown and release of a free phase liquid (ETEC, 2008). Subsequent sampling events, however, showed that the PAH concentrations in the KC pan increased back to expected concentrations over time and were stable throughout the remainder of the study.

Baseline nutrient results for the live pans showed concentrations of total N at ~200 mg/kg (sum of 102-112 mg/kg ammonia-N and 95-122 mg/kg nitrate-N) and P (23-35 mg/kg) at ideal levels for baseline TPH-DRO and HRO concentrations (carbon) of approximately 1,880 mg/kg (C:N:P = 100:10:1). In contrast, the KC pan (2 mg/kg ammonia-N; 12.8 mg/kg nitrate-N; 32 mg/kg P) and REF pan (96 mg/kg ammonia-N; 165 mg/kg nitrate-N; 74 mg/kg P) showed substantially different nutrient concentrations even though an equal amount of CBN™ was added to each. The organic nature of the sediment in the reference pan (>8% organic matter as compared to 1.5-1.8% organic matter in the live pans) and the presence of the sodium azide in the killed pan may have reacted with the CBN™ to create these measured nutrient differences. Sodium azide has been shown to interfere with nitrate quantification and produce nitrate levels that were progressively lower with increasing azide concentrations (Goel *et al*., 2003). Accordingly, Week 3 data are presented as "baseline" for the killed control treatment because true baseline data were deemed unreliable as described above.

The baseline hydrocarbon-degrading microbial plate count results revealed a native population of 9.5 x $10^5$ CFU/g in the Live 1 pan, which received inorganic nutrients only. Treatments of the reference, Live 2 and Live 3 pans on Day 0 resulted in augmented microbial populations ranging from 4.2 x $10^5$ CFU/g to 1.1 x $10^6$ CFU/g. In contrast, the KC baseline microbial plate count was 1.7 x $10^4$ CFU/g with no significant increase or decrease observed throughout the remainder of the treatability test. This KC count an order of magnitude lower than the live pans represented a suitable population of hydrocarbon degraders that were not growing due to the sodium azide inhibition.

Final PAH concentrations relative to baseline are shown for twelve individual PAH compounds for the KC, LV1, LV2, LV3 and REF pans in Figs. 4-8, below; Table 2 provides the accompanying analytical values.

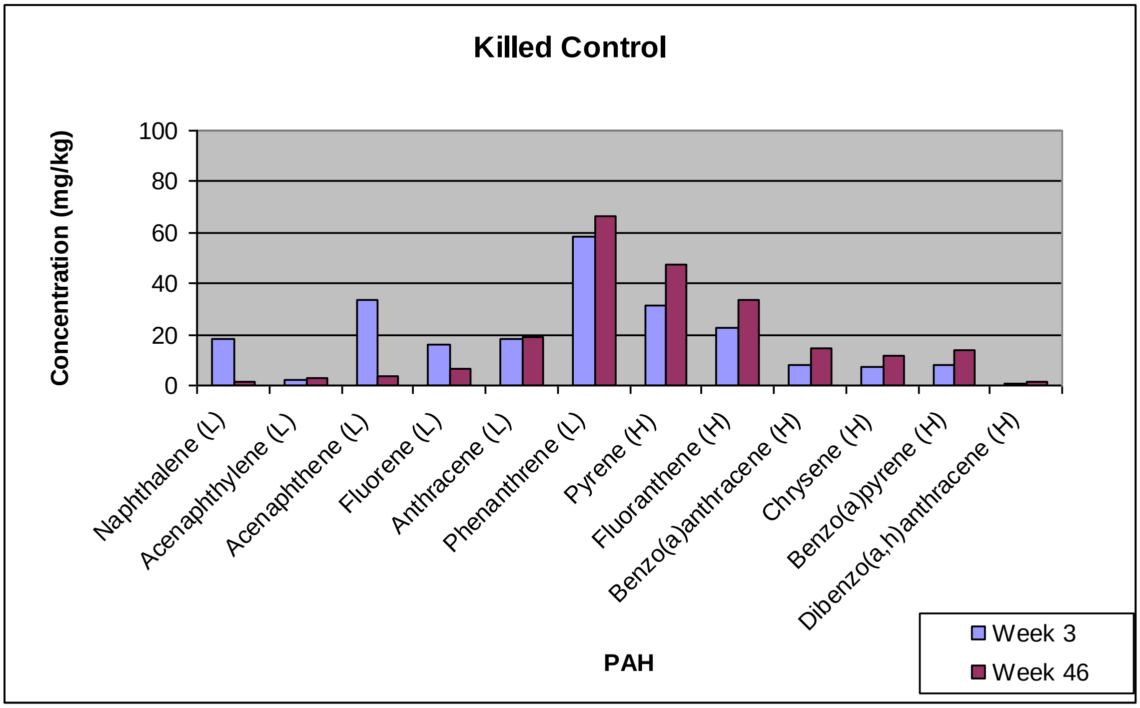

Figure 4. Degradation data for PAHs in the Killed Control pan of the laboratory study for treatment of potential Appomattox dredged sediments (baseline data excluded).

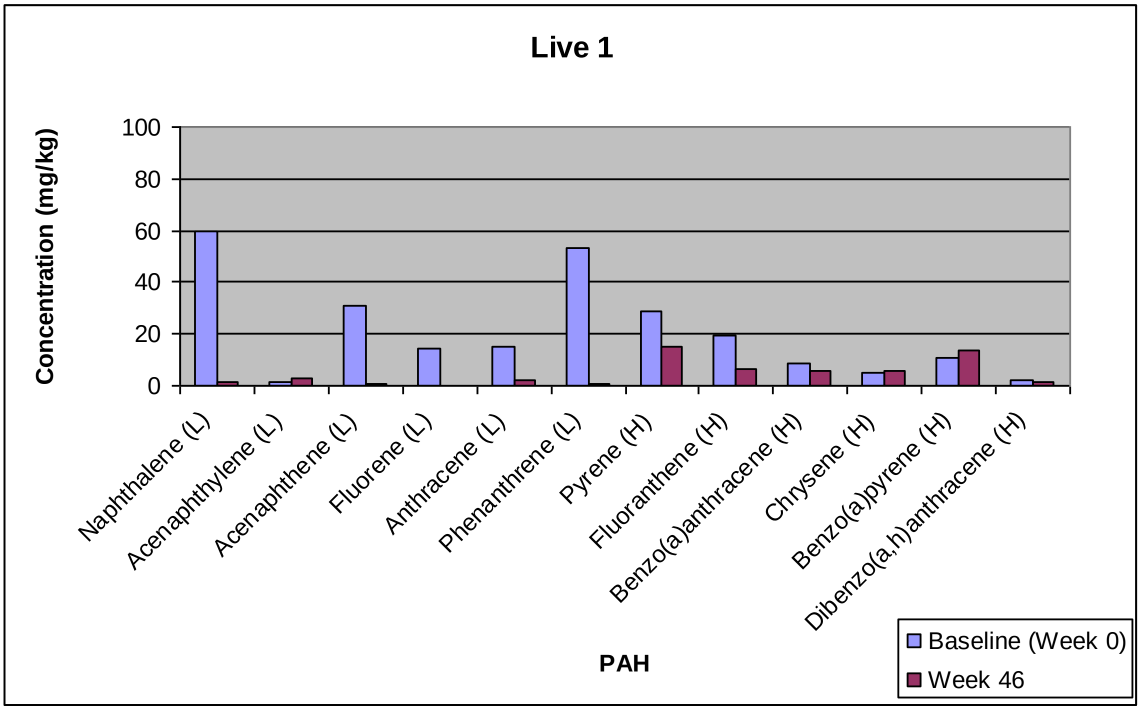

Figure 5. Degradation data for PAHs in the Live 1 pan of the laboratory study for treatment of potential Appomattox dredged sediments.

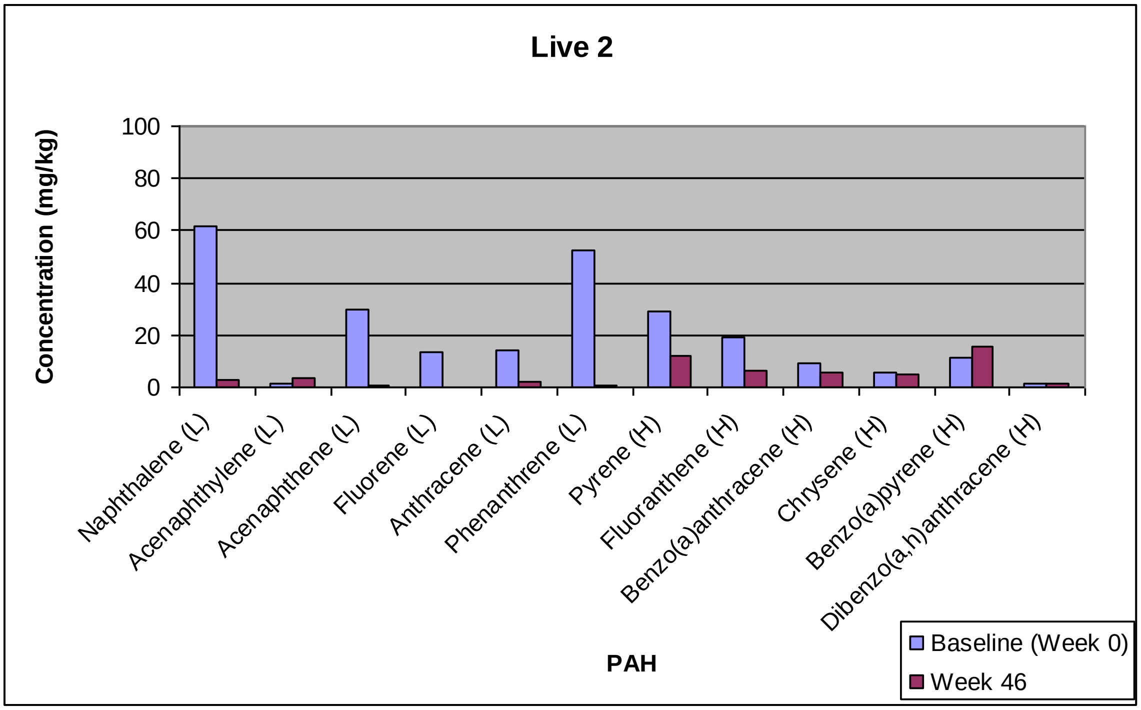

Figure 6. Degradation data for PAHs in the Live 2 pan of the laboratory study for treatment of potential Appomattox dredged sediments.

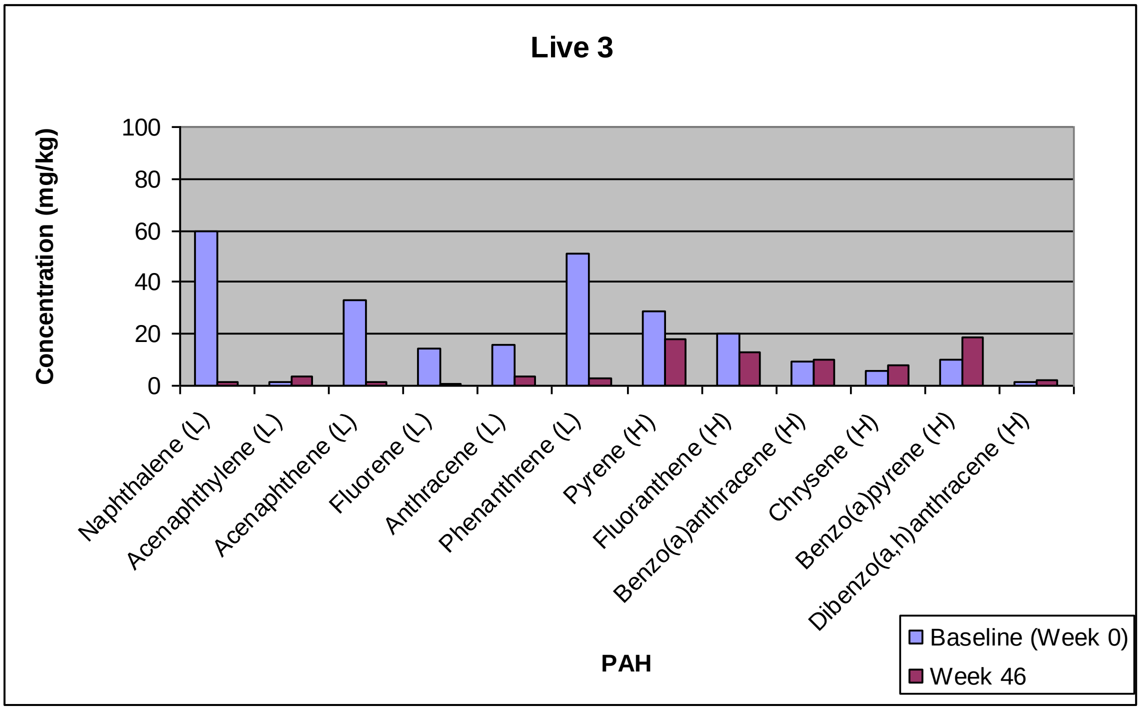

Figure 7. Degradation data for PAHs in the Live 3 pan of the laboratory study for treatment of potential Appomattox dredged sediments.

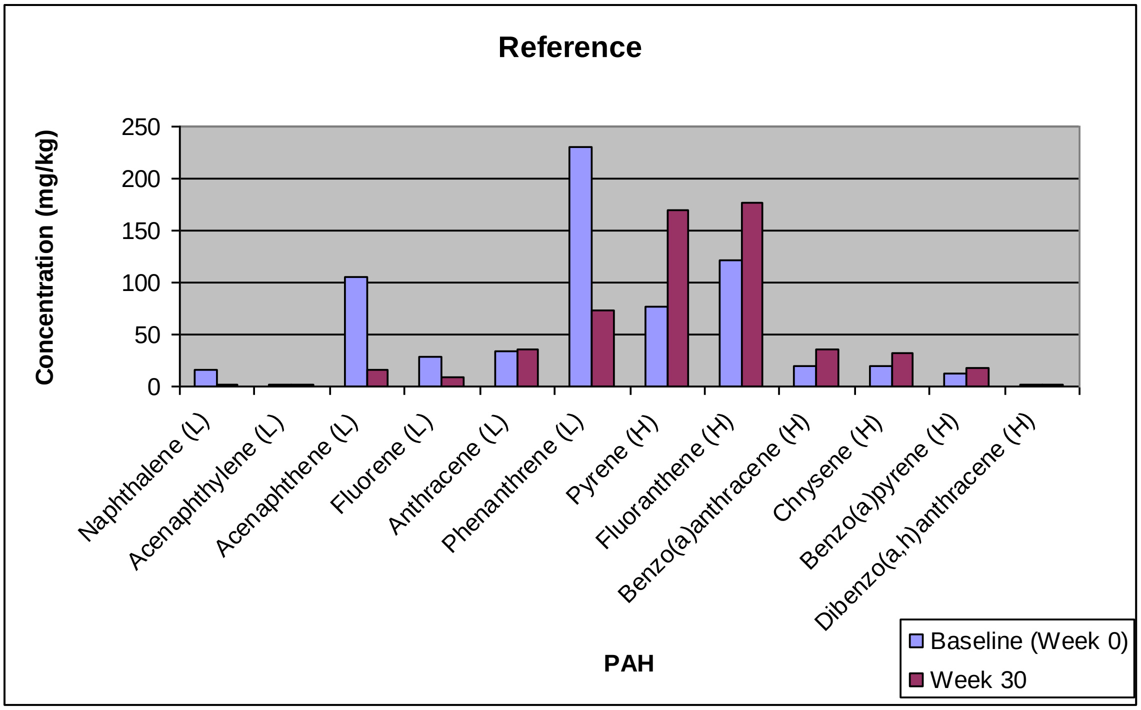

Figure 8. Degradation data for PAHs in the Reference pan of the laboratory study for treatment of potential Appomattox dredged sediments.

The stability of the KC data illustrate that biodegradation is the major process responsible for the declines of most PAH constituents in the live pans (Fig. 4). The only individual PAHs that were found to have volatilization as the major degradation mechanism in both the control and live pans were naphthalene and acenaphthene. Volatilization and photolysis were ruled out as the major degradation mechanism or else similar results would have been observed in the KC pan where these processes are assumed to occur.

In contrast to the KC pan, comparison of baseline and final concentrations for the LV1, LV2 and LV3 test pans showed that most of the PAH compounds exhibited at least some reduction after 46 weeks of treatment (Figs. 5-7). Total PAHs ranged from 55-83 mg/kg as compared to approximately 220 mg/kg in the baseline samples (Table 2) thus indicating an overall 80% contaminant reduction using the enhanced bioremediation process. Individual PAH reductions in the live pans were greatest for pyrene and anthracene (one HMW PAH and one LMW PAH, respectively) when compared to baseline values after 46 weeks, whereas the KC pan showed concentrations similar to the baseline. Overall, the degradation results suggest that the three LV treatments all appeared to have been effective in degrading PAHs.

Table 2. Comparative baseline and final PAH concentrations for various laboratory treatments.

| Analyte | Units | Killed Control | Live 1 | Live 2 | Live 3 | Reference |
|---|---|---|---|---|---|---|
| **Baseline (Day 0) Concentration / Week 3 (Day 21) for KC** | | | | | | |
| Naphthalene (L) | mg/kg | 18.6 | 59.7 | 61.6 | 60.0 | 16.2 |
| Acenaphthylene (L) | mg/kg | 2.3 | 1.1 | 1.1 | 1.1 | 1.6 |
| Acenaphthene (L) | mg/kg | 33.3 | 30.7 | 29.7 | 33.4 | 106 |
| Fluorene (L) | mg/kg | 16.1 | 14.1 | 13.7 | 14.5 | 28.8 |
| Anthracene (L) | mg/kg | 18.0 | 15.2 | 14.1 | 15.5 | 34.5 |
| Phenanthrene (L) | mg/kg | 58.5 | 52.9 | 52.8 | 51.4 | 230 |
| Pyrene (H) | mg/kg | 31.6 | 28.5 | 29.0 | 28.9 | 76.5 |
| Fluoranthene (H) | mg/kg | 22.5 | 19.3 | 18.8 | 19.8 | 122 |
| Benzo(a)anthracene (H) | mg/kg | 8.3 | 8.6 | 9.1 | 9.4 | 20.2 |
| Chrysene (H) | mg/kg | 7.2 | 5.0 | 5.4 | 5.7 | 18.8 |
| Benzo(a)pyrene (H) | mg/kg | 8.3 | 11.1 | 11.0 | 10.2 | 11.8 |
| Dibenzo(a,h)anthracene (H) | mg/kg | 0.4 | 1.9 | 1.7 | 1.3 | 2.1 |
| Total LMW PAHs | mg/kg | 147 | 174 | 173 | 176 | 417 |
| Total HMW PAHs | mg/kg | 78.3 | 74.4 | 75.0 | 75.3 | 251 |
| Total LMW+HMW PAHs | mg/kg | 225 | 248 | 248 | 251 | 669 |
| **Week 46 (Day 301) Concentration / Week 30 (Day 210) for Ref** | | | | | | |
| Naphthalene (L) | mg/kg | 1.1 | 1.4 | 2.5 | 1.5 | 1.2 |
| Acenaphthylene (L) | mg/kg | 2.6 | 2.6 | 3.2 | 3.9 | 2.0 |
| Acenaphthene (L) | mg/kg | 3.9 | 0.7 | 1.0 | 1.2 | 16.2 |
| Fluorene (L) | mg/kg | 6.9 | 0.2 | 0.3 | 0.4 | 9.1 |
| Anthracene (L) | mg/kg | 18.8 | 1.8 | 2.0 | 3.3 | 35.6 |
| Phenanthrene (L) | mg/kg | 66.3 | 0.9 | 1.0 | 2.9 | 72.6 |
| Pyrene (H) | mg/kg | 47.2 | 15.0 | 12.1 | 18.1 | 169 |
| Fluoranthene (H) | mg/kg | 33.9 | 6.2 | 6.5 | 12.8 | 176 |
| Benzo(a)anthracene (H) | mg/kg | 14.4 | 5.8 | 5.9 | 9.9 | 36.4 |
| Chrysene (H) | mg/kg | 11.5 | 5.5 | 5.1 | 8.1 | 32.8 |
| Benzo(a)pyrene (H) | mg/kg | 13.7 | 13.4 | 15.3 | 18.7 | 17.6 |
| Dibenzo(a,h)anthracene (H) | mg/kg | 1.5 | 1.6 | 1.6 | 2.2 | 1.5 |
| Total LMW PAHs | mg/kg | 99.6 | 7.6 | 10.0 | 13.2 | 137 |
| Total HMW PAHs | mg/kg | 122 | 47.5 | 46.5 | 69.8 | 433 |
| Total LMW+HMW PAHs | mg/kg | 222 | 55.1 | 56.5 | 83.0 | 570 |

The REF pan behaved very differently from the LV treatments in that little to no biodegradation of HMW PAHs was observed after 30 weeks (Table 2). This discrepancy was most likely due to the rich organic nature (8% organic matter) of the reference sediment compared to the test sediments (1.5-1.8% organic matter) as PAHs can be absorbed into small pores located inside of organic particles, thus limiting the availability of dissolved phase contaminants to the bacteria (Johnsen *et al*., 2004). In addition, the reference sediment was composed almost entirely of silt, which provided poor aeration compared to test sediments that were composed mostly of medium-grained sand. The REF pan also had an anaerobic odor and the moisture content was found to be very high throughout the experiment. In conclusion, the lack of biodegradation in the REF pan was most likely caused by the high sorption of the PAHs onto the rich organic silt, which prevented them from being bioavailable to the bacteria.

### Summary and Conclusions

The specific biological products used for the live pans were able to increase contaminant bioavailability and catalyze oxidation/reduction reactions that maximized breakdown and mineralization of the PAH constituents, including the carcinogenic 5- and 6-ring PAH compounds. The full-scale degradation of HMW PAHs would likely require additional biological amendments as potentially indicated by the difference in pyrene reductions. Since benzo[a]pyrene and dibenz[a,h]anthracene are the primary constituents of interest with the most stringent remedial standards and were not treated effectively in the present study, these products may become critical over time. The baseline plate count data indicate that hydrocarbon degraders were present in the native soils that are capable of degrading the majority of the PAHs in the sediment, but it was undetermined if they have the capacity to degrade benzo(a)pyrene.

According to PAH, nutrient and plate count results from the laboratory treatability study, significant biological degradation of petroleum constituents in the Appomattox River sediment was deemed possible, thus making bioremediation a potentially effective treatment option for dredged material. The laboratory results indicate that full-scale sediment treatment would require an estimated minimum of six months to reach desired levels for all PAHs based on *ex situ* landfarming application of the specified biological products, though degradation of most of the PAH compounds (>75% of the total mass) would occur within the first four months.

With regards to potential landfarm construction, laboratory results suggest a 12-18 inch deep treatment cell to minimize water loss through evaporation which would effectively inhibit biodegradation. Due to differences in organic content and overall consistency, the treatability study also advocated mixing future dredged material with on-site background sediments in a potential landfarm to aid in both moisture control and tilling ability as well as to achieve better overall degradation rates.

## Landfarm Pilot Study

The field-scale landfarm pilot study for potential Appomattox River dredged material was started in July 2007 and will be ongoing through November 2008. A summary of results obtained during the first year of this investigation (July-December 2007) is provided in the following sub-sections.

### Study Background

Due to a lack of an economically-feasible confined upland sediment management option for potential Appomattox River Federal Navigation Channel dredged sediment, the USACE is evaluating beneficial use sediment management options which would facilitate the full-scale remediation effort. A pilot-scale landfarm study was initiated in July 2007 to further characterize the benefits of the laboratory-tested biodegradation treatments as an effective means of reducing contaminants to levels allowing beneficial reuse as a surface revegetation medium for former sand and gravel mines. Due to the substantial volume of sediment that would ultimately be dredged during channel restoration (360,000 cy), the material handling requirements and associated costs of a potential full-scale biodegradation effort needed to be evaluated at a level greater than the laboratory setting (bench-scale).

In order to develop this potentially beneficial treatment option, SAIC is providing scientific, engineering and operational services in support of a biodegradation and beneficial use (*i.e.*, landfarming) pilot study being conducted at the Weanack Land LLP property in Charles City County, Virginia. Weanack operates a facility on the James River approximately 18 miles downstream from the head of the navigation channel that has been permitted to accept dredged materials from several other projects for conversion to substrate suitable for beneficial upland reuse. The primary purpose of this facility is to provide material to reclaim land areas that were formerly mined for aggregate product, thus restoring them to full agricultural use. Dredged material, by its nature, provides an excellent substrate that can augment these areas and result in a highly productive soil composition, assuming contamination and other agronomic issues (*e.g.*, entrained salts) can be adequately addressed.

The pilot study design includes two landfarming cells each containing soil (dried sediment) over an area measuring 30 feet long, 11 feet wide, and 1.0 foot deep, thus accommodating approximately 12 cubic yards of soil. These cell sizes were selected to be large enough to allow for a tractor/tiller to run through and add water and amendments while still minimizing initial sample collection volume requirements. The overall goal of the field-scale treatability study is to determine if the planned bioremediation approach will effectively reduce PAH concentrations in test sediments below beneficial use standards (*e.g.*, below USEPA Region III Soil RBCs).

### Landfarm Construction

Sediments were obtained from the Lieutenant Run portion of the planned dredging area (see Fig. 1). Approximately 31 cubic yards (45 tons) of impacted sediment were excavated from a depth extending to 12 feet below MLLW so as to be representative of the material to be removed during full-scale dredging. Excess overburden material above the target sediment was stockpiled at an adjacent lay down area and subsequently used to backfill upon completion of the excavation activities. In order to maintain the integrity of the excavation walls, movable shorings (trench boxes) were used to facilitate sediment removal to required depths while minimizing sloughing back into the hole. Target sediments were then loaded directly into staged dewatering roll-off boxes and allowed to drain prior to transportation, with excess pore water being pumped to an on-site storage tank. The fluids generated during the excavation and dewatering processes were collected into an on-site frac tank (10,000 gallons), handled, and disposed/treated in accordance with Federal Solid Waste and Hazardous Waste Management Regulation 42 USCA §§ 6921-6931 and Commonwealth of Virginia Solid Waste and Hazardous Waste Management Regulations 9VAC20-60 and 80. Once dewatering was complete, the roll-off boxes were covered and transported via flatbed truck to the landfarm site at the Weanack property. Monitoring of organic vapors in the breathing zone was conducted during the excavation and placement process using a photoionization detector (PID). Because the PID indicated negligible real-time total volatile organic vapor levels even during contact with the most highly impacted sediment, further air monitoring was deemed unnecessary at the landfarm site.

Located in the middle of a corn field, the native Yoepim soil (fine-silty, mixed, semiactive, thermic aquic hapludults) at the landfarm site consists of a mostly fine grained silty loam substrate with a considerable clay fraction. This material has been used to build successful containment dikes for two previous dredged material placement projects, the Woodrow Wilson Bridge in 2004 and the Naval Weapons Station Earle in 2006. Thus prior to the placement of the impacted Appomattox sediment, the native soil was compacted in each landfarm cell with a vibratory compactor to create an impermeable layer so as to prevent runoff and leachate from contaminating the surrounding area. Intact core samples of the compacted liner layer were analyzed for saturated hydraulic conductance ($K_{sat}$) using a constant head apparatus with the average $K_{sat}$ being $< 10^{-6}$ cm/sec (W.L. Daniels, VT, personal communication). Three background soil samples were also collected from the native material used to construct each landfarm cell (six samples total) in order to establish contaminant levels at the site prior to the placement of any impacted material.

The final as-built layout of the entire landfarm pilot site is provided in Fig. 9. On 2 August 2007, the test sediments were spread over the compacted soil in each of the two landfarm cells, which were labeled “Landfarm Cell A” and “Landfarm Cell B.” These laydown areas were bounded and separated by a 2-foot berm constructed from the native soil as shown in Fig. 10. Prior to test sediment placement, a zero-tension lysimeter was installed in each landfarm cell to accumulate leachate during the landfarm process for analytical water quality testing. These lysimeters, labeled “Lys-A” and “Lys-B” to correspond to the individual cells in which they are located, were subsequently buried by the impacted material. Sampling points for the lysimeters are shown in Fig. 10 as the white PVC piping extending from the berm. A downgradient leachate and runoff pipe connected to a collection tank surrounded by a secondary retention dike was also installed along the boundary of the entire landfarm to control surface water flow resulting from prolonged rain events (see Fig. 10). Furthermore, an irrigation tank was installed adjacent to the landfarm to hold water to be dispersed for maintaining moisture levels during dry conditions as needed for optimum biodegradation rates to occur. Water for the irrigation process was either obtained from on-site wells or more commonly recirculated from the leachate collection tank. Because the leachate tank is located down gradient from the landfarm, water is pumped from the tank and sprayed over the test cells through a garden hose. Finally, a down-gradient monitoring well, labeled SEW 57, was constructed near the landfarm in order to assess whether contaminants are breaching the designed aquitard and permeating the local groundwater (see Fig. 9). Samples from this new well, as well as from existing up-gradient monitoring well SEW 51, were collected monthly. Analytical water quality testing was performed on the well and lysimeter samples in accordance with permit requirements to ensure that groundwater contaminant levels are not exceeding appropriate regulatory levels (*i.e.*, USEPA Region III Tapwater RBCs). Landfarm sampling and analytical methodologies are described in the “Performance Monitoring” section of this report.

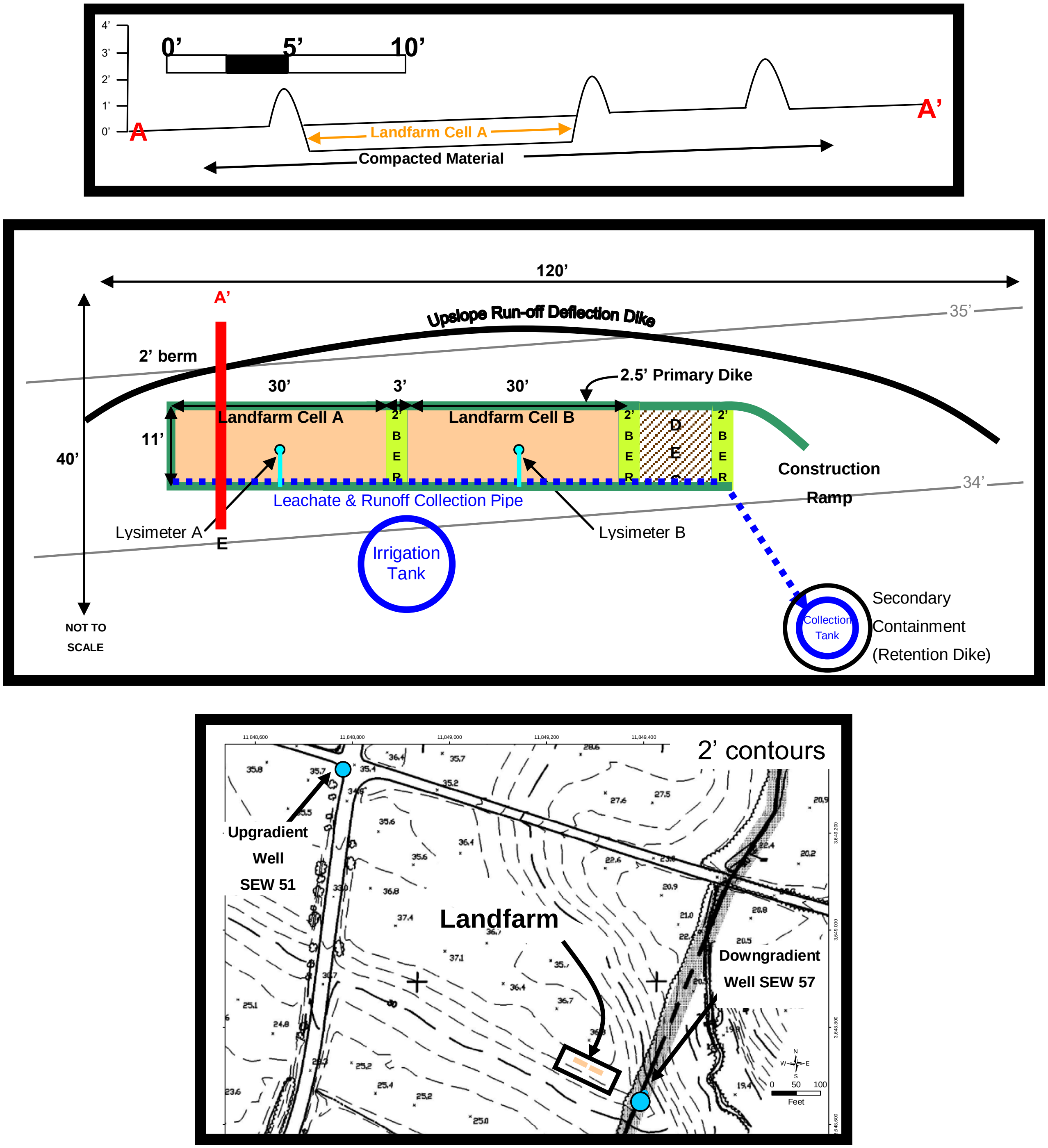

Figure 9. Final as-built layout of the entire landfarm pilot site at the Weanack facility.

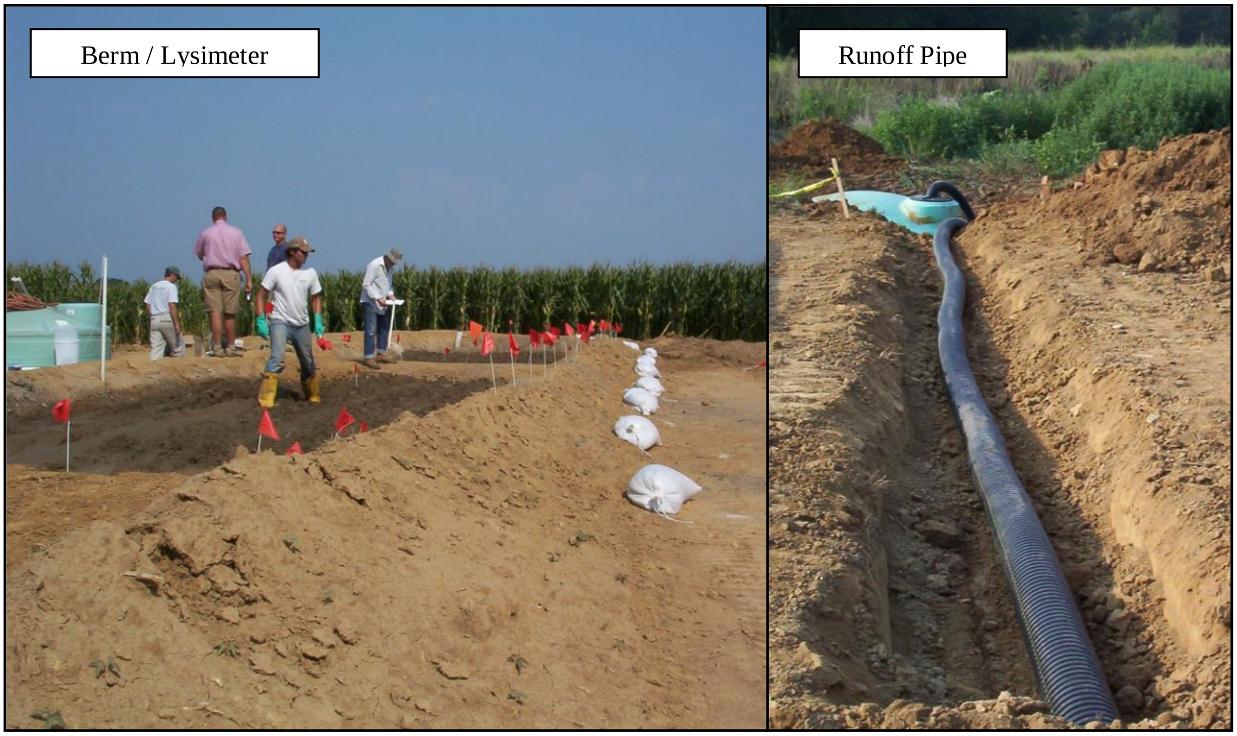

Figure 10. Construction of the Appomattox River Federal Navigation Channel pilot-scale landfarm at the Weanack facility.

Sampling Strategy

Given considerable spatial variation in PAH concentration at the sediment collection site, initial contaminant levels both across and within the two landfarm cells were expected to be quite dissimilar. Hence, a sampling strategy was developed involving the collection of composite samples (each made up of three discrete samples) at randomized locations within each cell. Based on the surface area of the test plots (300 $ft^2$), the random sampling process consisted of selecting five locations from a 3 ft by 10 ft grid (30 potential sites) using a random number generator. This strategy was deemed an appropriate approach for supporting the test of statistical significance between months (time effect) and cells (concentration effect).

Treatment Application

Following baseline sampling, ETEC Laboratory's Custom Blended Nutrients ($CBN^{TM}$) mixture, PAH-degrading bacterial consortium ($EZT\text{-}A3^{TM}$) and $PetroSolv^{TM}$ enzyme accelerator solution were added to the cells. The $CBN^{TM}$ and $EZT\text{-}A3^{TM}$ amendments are the same products used in the laboratory treatability study as described above, but $PetroSolv^{TM}$ was used in place of $EZT\text{-}AE^{TM}$. These two enzyme accelerators consist of the same biodegradable rhamnolipid (glycolipid surfactant) components but differ primarily in concentration, with PetroSolv™ being a more highly concentrated product designed for aggressive recovery of light non-aqueous phase liquids (LNAPL). PetroSolv™ is generally applied rather than EZT-AE™ when the more recalcitrant compounds (*i.e.*, 4-6 ring PAHs) comprise the bulk of the contaminant load, as was determined to be the case with the Appomattox landfarm sediments.

Similar to the laboratory treatability study, the combination of the selected bacterial consortium with the surfactant and nutrients was designed to establish a very large, healthy *in situ* microbial soil population while also maximizing contact between these microbes and the sorbed petroleum constituents bound to the sediment matrix. Because bioremediation is a contact technology, the bacteria must physically contact both the PAH (carbon) food source in solution and the electron acceptors in surrounding inorganic compounds (oxygen, nitrate, sulfate) to biochemically oxidize the petroleum to carbon dioxide and water. Critical nutrients such as N and P support ongoing biological growth while also acting as secondary electron acceptors during temporary absences of dissolved oxygen to ensure a favorable environment for contaminant degradation.

Because nutrients were not consumed as quickly as anticipated in the laboratory investigation, the desired C:N:P nutrient ratio for the landfarm was increased to 400:10:1 in accordance with USEPA guidance to minimize nutrient loading while maintaining optimal performance (USEPA, 1994). The baseline TPH concentration for the landfarm sediment was estimated at 4,000 mg/kg, which equates to a mass of approximately 146 kg TPH in the 31 cy (36,500 kg) of sediment used in both landfarm cells. Assuming TPH is all carbon (a conservative estimate), the new target nutrient ratio dictated a need for 3.7 kg N and 0.37 kg P. However, non-aqueous phase liquid (NAPL) was observed in the landfarm sediments at the time of construction, which was expected to substantially increase the nutrient demand on the system due to decreased carbon bioavailability in the non-aqueous phase (Swindell and Reid, 2006). As a result, the target nutrient ratio was decreased to 40:10:1. Accordingly, 113 kg (250 lb) of CBN™ product (28% elemental N and 12% elemental P, wet weight) was added to both landfarm cells, which equates to 31 kg N and 13 kg P and represents a nearly 10-fold increase in the originally planned nitrogen level. Similar to the laboratory study, a surplus of P was added to compensate for expected losses (>50%) due to mineral speciation while preserving the 40:10:1 ratio.

## Landfarm Maintenance

Throughout the course of the landfarm process, watering from the onsite leachate or irrigation tanks occurred up to two times per week as needed to maintain optimal moisture levels between 60-85% of field capacity (soil clumps possible). Spraying was also performed as necessary prior to tilling in order to reduce wind erosion. Microbial populations and nutrient levels were monitored during the regular sampling activities. The target C:N:P ratio of 40:10:1 was monitored throughout the project and additional nutrient applications were not required. A pH value between 6 and 8 SU was desired for optimal biodegradation activity and was maintained through the addition of lime (pH increase) as needed. One lime application was performed during Month 3 sampling.

## Performance Monitoring

Samples for monitoring the PAH degradation performance of the bacterial treatments were collected from each cell at the beginning of each month immediately (1-2 days) after the tilling activity was completed. Such sampling occurred every month for five months (Sept-Jan) to be followed by additional sampling to occur in the coming spring-summer season (May-Nov). Seven independent sampling events (including baseline) are available to date to characterize PAH degradation trends in the landfarm cells. As described above, each sampling event consisted of five composite soil samples (made up of three discrete samples each) collected from each cell (10 samples total) and placed within pre-cleaned (unpreserved) glass containers to be sent to Xenco Laboratories in Houston, Texas and analyzed for 24 PAHs/SVOCS, TPH-DRO (diesel range), TPH-ORO (oil range), total organic carbon and percent moisture. A sixth single composite sample from each cell was also collected and analyzed for nutrients including nitrate-N, nitrite-N, ammonia-N, sulfate and total P as well as pH and heterotrophic hydrocarbon degrading plate count. All sediment analyses were performed using the following methods:

- **PAHs/SVOCs** – Method USEPA 8270SIM (GCMS)
- **TPH-DRO** – Method SW846-8015
- **TPH-ORO** – Method USEPA 8015M
- **TOC** – Method Walkley Black
- **Inorganic Anions** – Method USEPA 300
- **Nitrogen Ammonia** – Method USEPA 350.2

- **Phosphorus, All Forms** – Method USEPA 365.3
- **pH** – Method USEPA 9045C

Concurrent with the monthly sediment samples, low-flow water samples were also collected from the lysimeters and the external monitoring wells and analyzed for Ba, Pb, 24 PAHs/SVOCs, TPH-DRO (diesel range), TPH-ORO (oil range) and total organic carbon. They were also analyzed for inorganic nutrients by a second analytical laboratory (Virginia Tech). All water analyses were performed using the following methods:

- **ICP-MS Metals** – Method SW6020A
- **PAHs/SVOCs** – Method USEPA 8270SIM (GCMS)
- **TPH-DRO** – Method SW846-8015
- **TPH-ORO** – Method USEPA 8015M
- **TOC** – Method USEPA 415.1

General PAH degradation trends were quantified in the same manner as the laboratory study. Benzo[a]pyrene and dibenz[a,h]anthracene were also evaluated independently as they are the two most carcinogenic compounds with the lowest human health RBC values according to USEPA Region III guidance (available online at http://www.epa.gov/reg3hwmd/risk/human/index.htm).

## Results and Discussion

A summary of the landfarm results after five months of treatment is provided in the following section. Although landfarm cells A and B contained composite sediments obtained from the same region of the Appomattox River project area and were treated with the same amendments, detailed evaluations of the analytical data from the two cells were treated separately as the initial concentrations both within and between the two cells were found to differ substantially. For example, baseline analytical results showed that the initial Diesel Range TPH concentration across the 10 samples collected from cells A and B ranged from 38 to 290 mg/kg, while the initial Heavy Oil Range TPH concentration ranged from 40 to 158 mg/kg. Significant variations in PAH concentrations were also present in the sediment with total PAH concentrations ranging from 9.7 mg/kg to 34.5 mg/kg across both cells.

Average baseline soil nutrient results across the two landfarm cells following addition of the CBN$^{TM}$ product (as determined from one composite sample from each cell) showed an ideal P concentration (24.2 mg/kg), but elevated levels of ammonia-N (1340 mg/kg) and nitrate-N (1195 mg/kg). The average baseline carbon level (conservatively estimated as total TPH concentration) across the two landfarm cells was 145 mg/kg (85 mg/kg HRO + 60 mg/kg ORO), thus producing a baseline C:N:P ratio of approximately 6:100:1, which is substantially different from the target ratio of 40:10:1. The decreased carbon factor was a result of an actual TPH concentration (145 mg/kg) approximately 28 times less than the estimated TPH concentration (4,000 mg/kg) used to determine the mass of the initial CBN$^{TM}$ application (113 kg). The nitrogen level was high due to NAPL observed in the test soil during landfarm construction suggesting the need for more nutrients, but effects of NAPL on carbon availability did not materialize in the baseline analytical data. Regardless, the resulting nutrient ratio was not considered inhibitory and could be rectified by adding smaller doses of CBN$^{TM}$ over time.

A graphical summary of the overall landfarm performance data for PAH degradation in cells A and B combined after five months relative to baseline contaminant levels is provided in Fig. 11. As shown in this chart, LMW PAHs appear to have degraded first while HMW PAHs degraded more slowly, a process which generally corresponded to the expected results as identified in the laboratory investigation. The Month 3 results proved suspect as total PAH concentrations were significantly lower than the two subsequent months due mainly to non-detect results for a majority of the individual analytes. These results did coincide with the timing of a lime and heavy biodegradable surfactant addition to the soils which may have interfered with subsequent PAH extraction or quantification as evidenced by abnormal matrix spike/matrix spike duplicate (MS/MSD) recovery results compared to other months. Correspondence with the ETEC treatability laboratory indicated that similar analytical interference caused by the presence of biodegradable surfactant had previously been observed for hydrocarbons in the TPH range though not for hydrocarbons in the PAH range. Similarly, this analytical interference was not observed in the laboratory study (LV3 treatment), which also received the biodegradable surfactant. Thus, analytical interference due to the presence of surfactant was ruled out as a possible explanation for the anomalous Month 3 results, though the lime addition still remains suspect. Following an initial review of the Month 3 landfarm data, the Xenco laboratory was asked to perform additional sample clean-up to achieve lower detection limits in order to report concentrations that would previously have been considered non-detect. These adjustments had the effect of decreasing the need for sample dilutions and hence the number of non-detect data. Total PAH concentrations for subsequent months were found to conform to more expected levels (see Fig. 11).

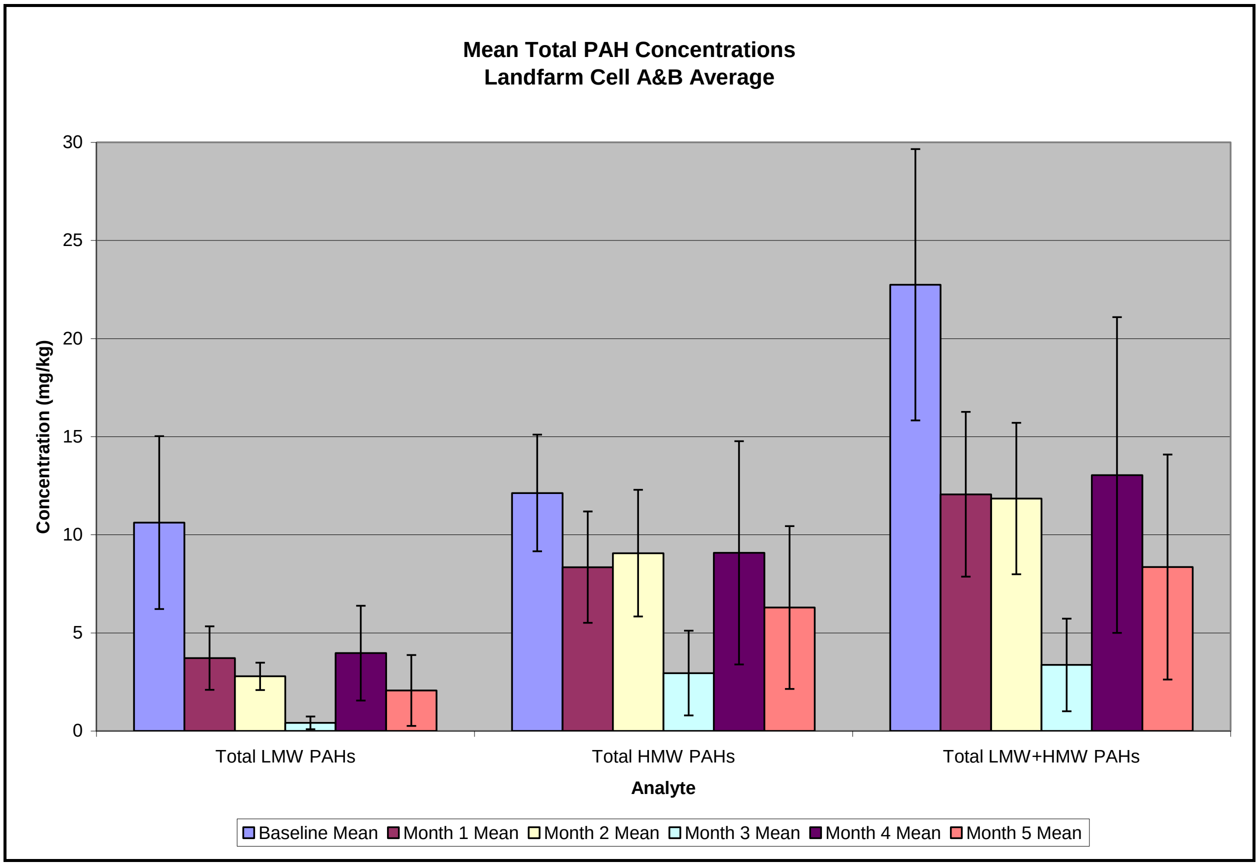

Figure 11. Summary of combined PAH degradation data (mean +/- SD) from landfarm cells A and B after five months of the field-scale pilot study for the treatment of potential Appomattox dredged sediments.

Landfarm data for four months of treatment (excluding Month 3) were ultimately used to determine degradation rates as the slope of the calculated linear regressions for PAH concentration versus time in Cell A and Cell B separately as well as averaged across both cells. The resulting regression lines are shown in Figure 12 along with associated linear equations and coefficients of variation ($R^2$ values), which denote the strength of linear association between the two variables and determine how certain one can be in making predictions from the trendline. As shown, the slopes of the regression lines were fairly consistent (0.052-0.064 mg/kg/day) as evidenced by the three regression lines being approximately parallel to each other. Cell A had the most robust linear association between mean total PAH degradation and treatment time

($R^2 > 0.8$). Using the Cell A equation and baseline concentration and assuming a steady biodegradation rate (rather than asymptotic degradation), it was predicted that approximately 233 days (8 months) of treatment would be required to reach 1 mg/kg total PAH, which is the lowest available ecological soil benchmark for total PAH (USEPA Region IV screening value) that is considered the acceptable criterion for beneficial reuse (USEPA Region III human health benchmarks for total PAH are not available).

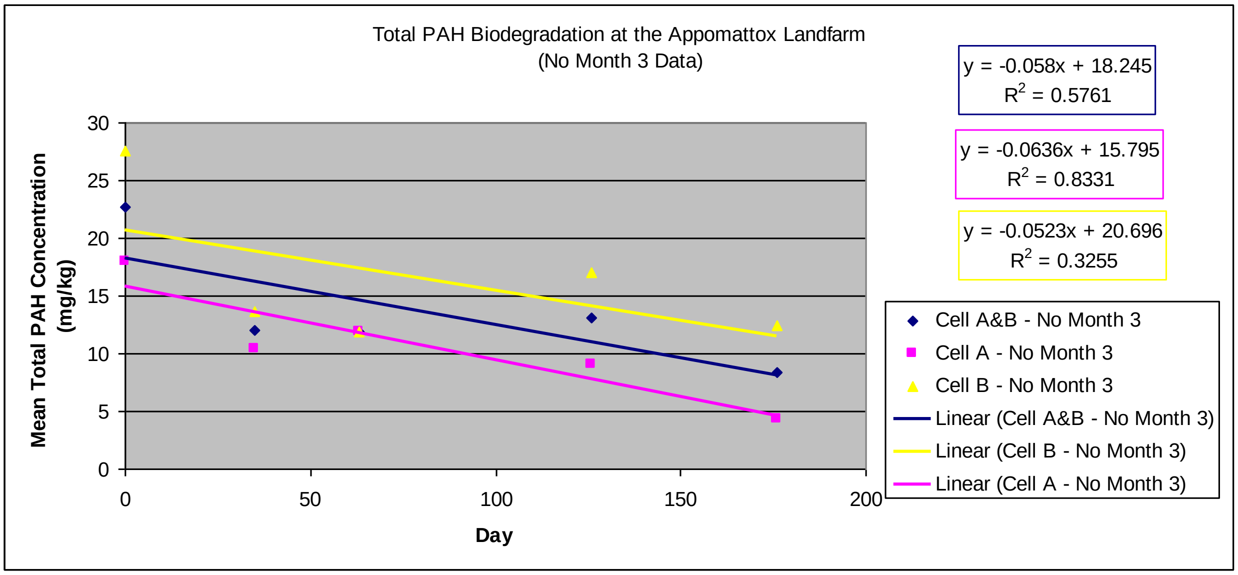

Figure 12. Linear regression equations for PAH biodegradation after five months of landfarm treatment for potential Appomattox dredged sediments.

## Technical and Regulatory Issues

The main regulatory goal of the Appomattox River Federal Navigation Channel landfarming effort is to degrade contaminant concentrations in potential dredged sediments below acceptable levels established in the Virginia Pollution Abatement Permit to the Weanack Land LLP. For PAHs in sediment, these criteria include USEPA Region III BTAG Human Health RBCs for both industrial soil use and recreational soil use. Because benzo[a]pyrene and dibenz[a,h]anthracene are the most carcinogenic contaminants with the most stringent soil RBCs for both industrial site use and residential site use (each at 0.39 mg/kg and 0.022 mg/kg, respectively), the concentrations of these compounds are considered the limiting factors for successful PAH degradation. The mean and associated 95% confidence limits (UCL, LCL) for the concentrations of these two compounds at Month 5 are shown in Figure 13.

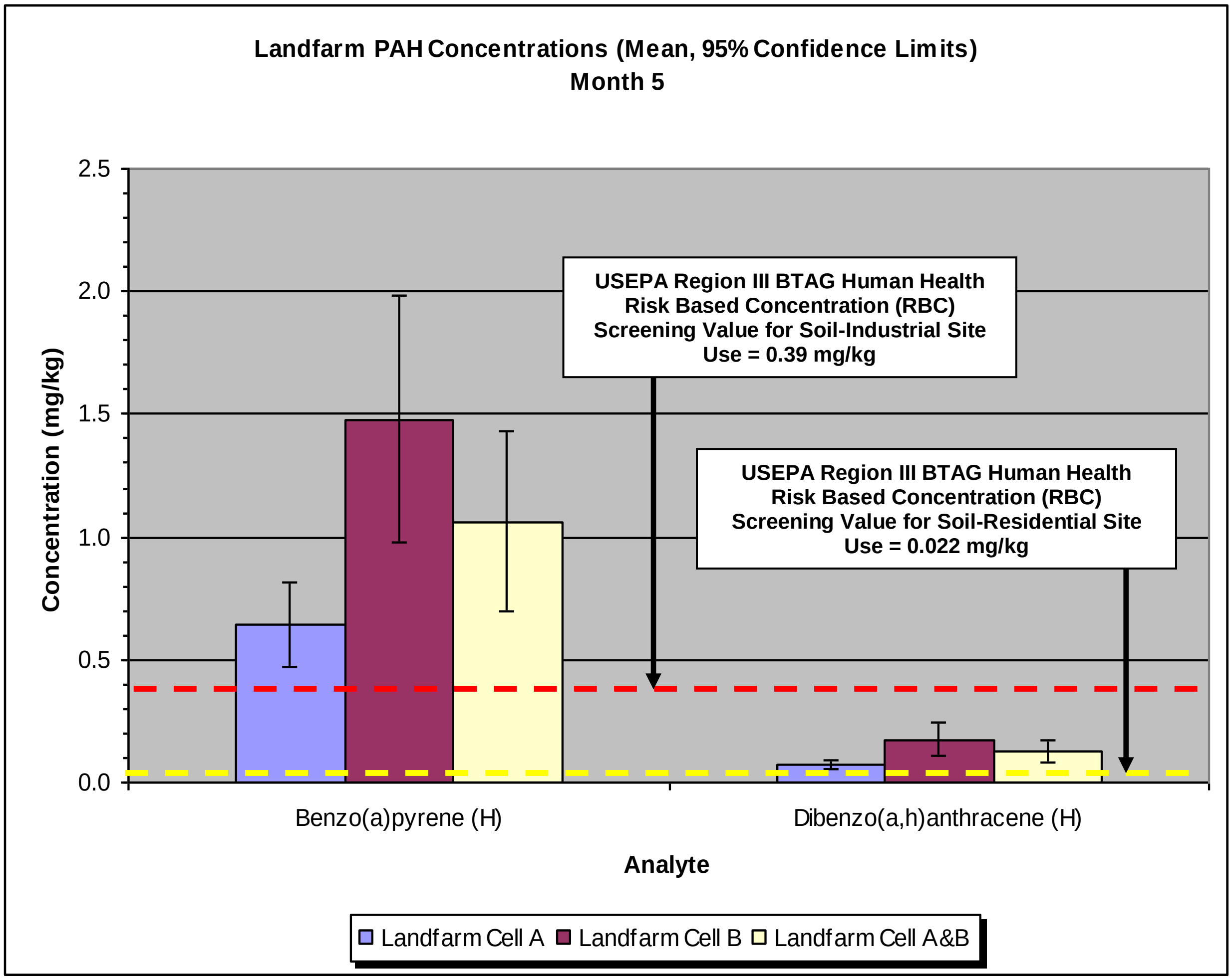

Figure 13. Concentrations of limiting factor PAHs in landfarm sediment relative to appropriate regulatory concentrations.

Comparative baseline and Month 5 landfarm concentrations for benzo[a]pyrene and dibenz[a,h]anthracene are provided in Table 3, below. As shown by this data, neither compound exhibited substantial degradation over the course of the landfarm investigation. Such results are consistent with the laboratory investigation where both compounds were not degraded in the live pans over a 46 week (11 month) timeframe. Extension of the landfarm treatment process or additional experiments using other treatment methods (*e.g.*, phytoremediation) are being implemented at the pilot study site to assess whether degradation of benzo[a]pyrene and dibenz[a,h]anthracene below regulatory levels can be achieved.

Table 3. Comparative baseline and Month 5 landfarm concentrations for PAH compounds of regulatory concern.

| Analyte | Units | Cell A (Mean) | Cell B (Mean) | Cell A&B (Mean) |
|---|---|---|---|---|
| **Baseline (Day 0) Concentration** | | | | |
| Benzo(a)pyrene | mg/kg | 1.4 | 1.9 | 1.6 |
| Dibenzo(a,h)anthracene | mg/kg | 0.12 | 0.15 | 0.13 |
| **Month 5 Concentration** | | | | |
| Benzo(a)pyrene | mg/kg | 0.65 | 1.5 | 1.1 |
| Dibenzo(a,h)anthracene | mg/kg | 0.08 | 0.17 | 0.13 |

A second regulatory goal of the Appomattox River Federal Navigation Channel landfarming effort is to maintain leachate and local groundwater contaminant and nutrient concentrations below acceptable levels as also established in the Virginia Pollution Abatement Permit to the Weanack LLC. For PAHs in water, these criteria include USEPA Region III BTAG Human Health RBCs for tap water. Similar to the sediment criteria, benzo[a]pyrene and dibenz[a,h]anthracene also have the lowest RBC for tap water (0.003 µg/L). Month 5 concentrations for these compounds exceeded this RBC in both the lysimeters (0.015 µg/L for benzo[a]pyrene; 0.012 µg/L for dibenz[a,h]anthracene) and the monitoring wells (0.031 µg/L for benzo[a]pyrene; 0.024 µg/L for dibenz[a,h]anthracene). However, these concentrations represent only slight increases from the baseline samples and because the sample quantitation limits (used as the analytical value for non-detect concentrations) were above the RBC criteria, compliance could not be directly assessed. In general, Month 5 water quality analyses from the lysimeters and the external monitoring wells yielded non-detect data for the majority of individual PAHs. These results confirm that petroleum-based contaminants from impacted sediments are not likely to escape into surrounding soils at levels that would adversely affecting groundwater quality.

In terms of Month 5 nutrient data, water samples from the zero-tension lysimeters did indicate very high (>900 mg/L) nitrate-N and ammonium-N levels and associated high electrical conductivity (>10 mmhos/cm) in shallow leachates, thus suggesting that excessive N-based fertilizer was added to the system during the initial months of the field study. If left unchecked, these increased nutrient and salt levels at the bottom of the sediment treatment system may actually inhibit microbial degradation activity. The elevated nutrient and salt levels in leachate are being addressed by a lime addition in Spring 2008.

If analytical samples collected at the end of the landfarm pilot study indicate that PAH concentrations and nutrient levels meet all soil and leachate regulatory requirements, the landfarm will be deemed successful, decommissioned and tilled under as agricultural soils. The bioremediation approach will then be scaled up to an eventual landfarm design for treatment of Appomattox River dredged sediments. A risk assessment will be conducted to determine the site-specific levels of residual contaminant that would pose no risk to human health or the environment. If acceptable levels cannot be obtained, the landfarmed sediments will be removed (with an 0.5 ft undercut) and transported to a local landfill to be disposed of as solid waste. Any associated leachate will also be collected in a tank and properly disposed.

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# List of Acronyms and Abbreviations

| | |
|---|---|
| bgs | Below Ground Surface |
| BTAG | Biological Technical Assistance Group |
| CBN | Custom Blended Nutrients |
| CDF | Confined Disposal Facility |
| CFU/mL | Colony Forming Units Per Milliliter |
| BTEX | Benzene, Toluene, Ethylbenzene, Xylene |
| DRO | Diesel Range Organics |
| ERDC | Engineering Research and Development Center |
| GC/MS | Gas Chromatography/Mass Spectrometry |
| HMW | High Molecular Weight |
| HRO | Heavy Range Organics |
| KC | Killed Control (Laboratory Test Pan) |
| Ksat | Saturated Hydraulic Conductance |
| LMW | Low Molecular Weight |
| LNAPL | Light Non-Aqueous Phase Liquid |
| LV1 | Live 1 (Laboratory Test Pan) |
| LV2 | Live 2 (Laboratory Test Pan) |
| LV3 | Live 3 (Laboratory Test Pan) |
| mg/kg | Milligrams Per Kilogram |
| µg/kg | Micrograms Per Kilogram |
| µg/L | Micrograms Per Liter |
| MLLW | Mean Lower Low Water |
| MS/MSD | Matrix Spike/Matrix Spike Duplicate |
| NAPL | Non-Aqueous Phase Liquid |
| NAO | Norfolk District |
| ORO | Oil Range Organics |
| PAH | Polycyclic Aromatic Hydrocarbons |
| PID | Photoionization Detector |
| REF | Reference (Laboratory Test Pan) |
| RBC | Risk Based Concentrations |
| RCRA | Resource Conservation Recovery Act |
| SAIC | Science Applications International Corporation |
| SU | Standard Unit |
| SVOC | Semi-Volatile Organic Compounds |
| TCLP | Toxicity Characteristic Leaching Procedure |
| TOC | Total Organic Carbon |
| TOX | Total Organic Halogens |
| TPH | Total Petroleum Hydrocarbons |
| USACE | U.S. Army Corps of Engineers |
| USEPA | U.S. Environmental Protection Agency |