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LETTER AND RESPONSE TO THE U S EPA REGION I COMMENTS ON DRAFT REMEDIAL  
INVESTIGATION REPORT FOR OPERABLE UNIT 9 ( OU 9) FORMER NCBC DAVISVILLE RI  
01/02/2009  
NEW FIELDS



January 2, 2009

Mr. Curtis Frye  
U.S. Department of the Navy  
Remedial Project Manager  
Base Realignment & Closure  
4911 South Broad Street  
Philadelphia, PA 19112-1303

**Subject:        Response to Comments**  
**Davisville Draft RIR OU9 – Appendix F**  
**(Environmental Forensic Investigation)**

Dear Mr. Frye:

At your request, I prepared a response to comments (RTCs) sent by EPA on November 17, 2008 concerning the Davisville Draft RI Report for Operable Unit 9 (OU9). This RTC pertains exclusively to comments that related to Appendix F concerning environmental forensics investigation. The RTCs are presented in the same order used in the EPA comment letter.

***EPA 105a. Explain the forensic matching process with examples.***

*EPA requested an example of 1) a match between a source sample and a field sample and 2) a non-match between a source sample and a field sample.*

**RTC 105a. Match and non-match examples provided.**

One of the better matches was sample PIL16-01 (abbreviated PIL01) and SD16-AH-15-SD-0001 (abbreviated SD15) (Table 1). Pursuant to the tiered forensics approach (Figure 6), this conclusion is based on the concentration gradient, high resolution hydrocarbon fingerprint, PAH, and biomarker patterns. The concentration of PAHs was high in PIL01 (366,000 mg/kg EPAPAHs) and lower in SD15 (54.9 mg/kg EPAPAHs) due to dilution with native sediment (Table 7 and Figure 8b). The moderately weathered creosote pattern in PIL01 became heavily weathered in SD15 due to environmental weathering (Figure 10). The ratio of fluoranthene relative to pyrene (FL0/PY0) was 1.8 for both samples indicating good source signature fidelity (Figure 12a). The ratio of anthracene relative to phenanthrene (A0/P0) was 0.2 in PIL01 and 0.4 in SD15 (Figure 12a). This increase was likely due to mixing with native sediments (Figure 12b - the reference area sediments ranged between 0.3 and 0.6). The saturated hydrocarbon pattern of PIL01 resembled a middle distillate product while SD15 exhibited plant waxes mixed with lesser amounts of weathered distillate range hydrocarbons (Figure 13). These signatures demonstrated the strong influence of ambient hydrocarbons. The creosote sample PIL01 contained no detectable triterpanes while SD15 exhibited a BIO/GHI ratio of 0.3 (Figure 12d) with Pattern F (Figure 14) as evident elsewhere in Allen Harbor. The presence of triterpane Pattern F in SD15 was attributed to localized storm water runoff or petroleum products from docked vessels.

A poor match existed between samples 16TP-TP1-0509-Wood (TP1Wood) and the sheen sample AP16-AH-01-082807 (SH01) (Table 1). TP1Wood sample contained 32,300 mg/kg EPAPAHs and SH01 contained 2,960 mg/kg EPAPAHs (Table 7). The declining concentration gradient was consistent with a hydrocarbon release into a water body, so additional hydrocarbon analysis was pursued. Importantly, no other upland sample contained more PAHs than the sheen sample, so TP1Wood was the most significant candidate upland sample for this investigation based on PAH concentration and proximity to Allen Harbor sediments (Figure 8b). TP1Wood and SH01 exhibited weathered 4- to 6-ring pyrogenic PAHs (Figure 11); however, several important differences existed. In comparison to TP1Wood, SH01 contained lower proportions of retene and anthracene relative to phenanthrene (Figure 11). The double ratio plot demonstrated the different PAH source signatures between the TP1Wood (upper center) and SH01 (mislabeled SP01 – lower right) as evidenced by the pronounced lack of overlap between these samples in Figure 12a. These PAH source signature differences led to a non-match conclusion. The saturated hydrocarbon signature of the TP1Wood sample exhibited a late eluting UCM while the SH01 exhibited late eluting normal alkanes (Figure 13). TP1 Wood and SH01 samples both exhibited triterpane Pattern G (Figure 14). In summary, the systematic hydrocarbon fingerprinting method demonstrated that the PAHs in the sheen sample originated from a source that was distinct from the TP1Wood sample.

Other upland source samples were systematically compared to the sheen and Allen Harbor sediment samples. No matches were observed.

***EPA 105b. Historical activities not represented in the forensic investigation.***

*EPA is not clear how the forensic data support the conclusion that historical activities at Site 16 are not attributable to PAHs in Allen Harbor.*

**RTC 105b. The forensic analysis is complete.**

The technical approach (Figure 6) for this investigation followed the Navy User's Guide for Determining the Sources of Contaminants in Sediment (Stout et al., 2003). This process has been peer reviewed, published in numerous textbooks, and employed on behalf of numerous entities, including U.S. EPA. The forensics investigation demonstrated that the concentration of PAHs in Allen Harbor were low and consistent with urban sediment. It must be remembered that background PAHs typically adsorb onto particles that settle out of the ambient water column, especially in quiet tidal environments. The central question for Allen Harbor is the degree to which historical activities at Site 16 caused significant and recognizable impacts above and beyond the concentrations of PAHs associated with the ambient background condition.

The initial forensic investigation conclusively determined that the PAHs in Allen Harbor existed at low concentrations and exhibited source signatures that did not match the hydrocarbon materials extracted from soil samples collected in Source Areas 1, 2, and 3. The supplemental forensic investigation demonstrated the representative nature of Source Areas 1, 2, and 3. It also demonstrated the absence of source material in the southern portion of Site 16 and the presence of blackened debris in several test pit areas in the central and northern portions of Site 16. The PAHs in several of these blackened areas were elevated; however, there was not evidence that the PAHs migrated into Allen Harbor using the systematic forensic approach described previously. Rather, the forensic results demonstrated the active and ongoing migration of PAHs from marina pilings and roadway runoff into Allen Harbor sediments. This conclusion is consistent with the hydrodynamics of the study area, the depositional nature of

the harbor, and the presence of contemporary PAH source signatures in the surficial sediments. The initial investigation indicated higher PAH concentrations in the surface sediment versus subsurface sediments (Core 1, Top = 10.4 mg/kg EPAPAHs and Bottom = 2.80 mg/kg EPAPAHs). This finding demonstrated the absence of historical Site 16 impacts associated with Navy activities.

**EPA 105c. Grain size**

*The grain size measurements do not correlate with PAH concentrations. Both marina pilings and roadway runoff apparently contributed PAHs to harbor sediment, but the concentration gradients from the shoreline are ambiguous and require further explanation.*

**RTC 105c. PAH concentration should not correlate strictly with grain size in all areas.**

Grain size data were collected to quantitatively evaluate the degree to which fine particles increased from the Narragansett Bay inlet to the sections of Allen Harbor with low energy water. This trend was observed by comparison of the grain size samples from the Narragansett Bay inlet and the sediment sample from the middle of Allen Harbor. The correlation broke down from the middle of Allen Harbor towards the marina and storm sewer, because commingling occurred with 1) leachate from the marina pilings and 2) abraded pavement from roadway runoff. The PAHs from these latter two sources were not correlated with particle size, because the piling leachate is not necessarily particle bound and the abraded pavement is highly variable in both particle size and PAH concentration.

**EPA 105d. Groundwater constituents.**

*It is unlikely that groundwater is a significant pathway for transport of pyrogenic 4- to 6-ring PAHs to harbor sediments.*

**RTC 105d. Navy concurs.**

**EPA 105e. Hydrocarbon fingerprinting for the non-specialist.**

*The mismatch between the hydrocarbon fingerprint (PAHs plus biomarkers) of the soils and the sediments is not easily discerned from the data by a non-specialist.*

**RTC 105e. Fingerprinting references provided.**

The Navy has produced numerous references and a flow chart that EPA can use to verify the conclusions of the forensic investigation. In addition, Navy will offer at least one additional opportunity to have NewFields explain in person any remaining specific EPA questions.

**EPA 106a. PAHs by grain size fraction.**

*What is not clear from the grain-size work is an association of PAH concentrations with grain size fractions.*

**RTC 106a. Grain size data was collected to demonstrate the distribution of fines.**

The grain size data were collected to quantitatively evaluate the degree to which fine particles increased from the Narragansett Bay inlet to the sections of Allen Harbor with low energy water. This trend was clearly evident in the data collected. High energy areas exhibited high sand content (inlet and storm sewer) while low energy areas exhibited high fine content (middle harbor). The relationship between PAHs and percent fines is otherwise supported by the historical PAH concentration data (< 1 mg/kg EPAPAHs in Reference Areas 1 and 2, < 2.5 mg/kg EPAPAHs in Reference Area 3, and < 5 mg/kg EPAPAHs Middle Allen Harbor).

**EPA 106b. The conceptual site model (CSM) is oversimplified.**

*The forensic investigation only considers two sources of particulate influx to the harbor – Narragansett Bay and storm water outfall. This study oversimplified the complex hydrodynamics of Allen Harbor.*

**RTC 106b. The investigation focused on the significant PAH inputs.**

The initial forensic investigation established that Allen Harbor sediments contained pyrogenic 4- to 6-ring PAHs. The list of candidate sources of this material included numerous sources on Site 16 (creosote, fire fighter training, pavement) and around the perimeter of Allen Harbor (inlet, marina pilings, grit pile, pavement/roadway runoff). Other pyrogenic PAH sources in Allen Harbor (boat motor exhaust, building material runoff, etc...) were too diffuse to chase and potentially captured in the roadway runoff samples collected as part of the supplemental forensics investigation. As complex as the hydrodynamics of Allen Harbor may be, the sources evaluated in the study adequately represent the most significant PAH inputs to Inner Allen Harbor.

It should be noted for the record that Navy collected all of the additional forensic samples suggested by EPA during discussions about the supplemental forensics investigation work plan. EPA had ample opportunity to identify and suggest other PAH sources. Prior to this comment, EPA did not express any reservations about the PAH sources under consideration.

**EPA 106c. TPAH increases with finer grain size.**

*The distribution of grain size alone, with the central harbor sediments containing the largest proportion of fines, does not confirm the relationship between increasing PAH concentrations and abundance of fines as stated. Please provide support for the assumption that finer particulate sizes correlate with increasing PAH concentration. The data in Tables 5 (grain size) and 7 (hydrocarbon chemistry results) appear to show an inverse relationship between TPAH concentration and percentage of fines in the sediment.*

**RTC 106c. The investigation focused on the significant PAH inputs.**

As stated in the report, these samples contained storm sewer outfall material. This was demonstrated by the hydrocarbon concentrations and chemical fingerprints. Sediments impacted by roadway runoff were expected to exhibit variable trends; that is, variably sized, PAH enriched particles fall out of the storm water in a radial pattern around the point of discharge. The limited relationship discussed above (fines vs. TPAH) is inconsistent with the relationship between fines and more diagnostic hydrocarbon parameters, like TPH and EPAPAH concentrations, which vary independently of fine content among the sediment transect samples. In summary, these data strongly supported a CSM with localized influences from the marinas and storm water sewers in the Inner Allen Harbor.

**EPA 107. Dominant Hydrocarbon Signatures.**

*It is not obvious that the paired samples (marina piling and composited proximal sediment samples) demonstrate leaching. Other than for the PIL-01 and SD16-AH-15-SD-0001, there is no indication that the sediment samples show the expected loss of 2- to 3-ring PAHs during weathering. Please indicate specifically which data support this statement.*

**RTC 107. Hydrocarbon impacts by marina pilings are irrefutable.**

The marina pilings exhibited six irrefutable features. These include: 1) the creosote treated pilings contained the highest concentrations of pyrogenic PAHs (EPAPAH > 300,000 mg/kg), 2) they were physically located closer to Allen Harbor sediment than any other PAH source, 3) there was no impediment to the migration of PAHs from the pilings into the sediments, 4) the hydrocarbon fingerprints of pilings and sediments matched, 5) the PAH concentrations in sediment samples collected next to the creosote pilings were among the highest observed in Allen Harbor, and 6) pilings treated with preservatives other than creosote also leached into proximal sediments.

EPA requested more information about the evidence supporting the match between the piling and sediment. The reader is directed to RTC 105a for a systematic analysis. The critical features of this systematic analysis for the paired piling and sediment samples are evident in Figures 10, 11, and 13. PIL01 (EPAPAH = 366,000 mg/kg) contained lightly weathered tar (creosote preservative with  $N0 > P0$ ) while SD15 (EPAPAH = 54.9 mg/kg) contained moderately weathered tar ( $N0 < P0 > PY0$ ). PIL02 (EPAPAH = 366,000 mg/kg) contained lightly weathered tar (creosote preservative with  $N0 > P0$ ) while SD16 (EPAPAH = 2,580 mg/kg) contained heavily weathered tar (weathered creosote preservative with  $P0 < PY0$ ) from the piling mixed with heavy petroleum (late eluting UCM) and plant waxes (likely leaf detritus) from background. PIL03 (EPAPAH = 3,660 mg/kg) contained lightly weathered diesel range petroleum (non-creosote preservative with normal alkanes > isoprenoid hydrocarbons) while SD17 (EPAPAH = 7.39 mg/kg) contained heavily weathered diesel range petroleum (normal alkanes < isoprenoid hydrocarbons) from the piling mixed with heavy petroleum (late eluting UCM) and plant waxes (likely leaf detritus) from background. PIL04 (EPAPAH = 1,600 mg/kg) contained moderately weathered diesel range petroleum (non-creosote preservative with normal alkanes ~ isoprenoid hydrocarbons) while SD18 (EPAPAH = 3.90 mg/kg) contained moderately weathered diesel range petroleum (normal alkanes ~ isoprenoid hydrocarbons) from piling mixed with heavy petroleum (late eluting UCM) and plant waxes (likely leaf detritus) from background. PIL05 (EPAPAH = 646,000 mg/kg) contained lightly weathered tar (creosote preservative with  $N0 > P0$ ) while SD19 (EPAPAH = 1,500 mg/kg) contained moderately weathered tar (weathered creosote preservative with  $N0 < P0 > PY0$ ) from the piling mixed with heavy petroleum (late eluting UCM) and plant waxes (likely leaf detritus) from background. In summary, the pilings contained a variety of preservatives and in each case the preservative signature is clearly evident in the proximal sediments. The migration of PAH containing hydrocarbons from the pilings into the sediments was irrefutably proven in the supplemental forensic investigation.

**EPA 108. Dissolved and particulate concentration units need clarification.**

*EPA would like to clarify the units for the filter/particulate fraction reported in Table 7.*

**RTC 108. Dissolved and particulate groundwater data were reported in ug/L.**

The supporting information can be found in the laboratory report attachments.

**EPA 109. Homogeneity of Marina Transect samples.**

*EPA would like to reconcile the discussion of relatively homogeneous PAH signatures discussed in Section 5.6 (5<sup>th</sup> paragraph) with the discussion of grain size in Section 5.3.*

**RTC 109. Inner Allen Harbor contains PAH mixtures from multiple inputs.**

As stated in RTC 106c, the Inner Allen Harbor sediments are influenced by the mixture of regional (Narragansett Bay) particulates, marina piling leachate, and storm sewer effluent. Prop wash likely helped mix these three inputs, especially around the marina structures.

**EPA 110. Differences between dissolved and particulate groundwater vary.**

*The difference between the dissolved and particulate concentrations in TW16-110S-NWG-081207 (16.2 ug/L and 0.19 ug/L, respectively) and TW16-111S-NWG-081207 (0.05 and 0.01 ug/L) vary. EPA believes the 100x difference in TW16-110S-NWG-081207 is substantial, but the 5x difference in TW16-111S-NWG-081207 may not be substantial.*

**RTC 110. The dissolved fraction contains more PAHs than the particulate fraction.**

The data addressed the purpose of the work plan and demonstrated the difference between the dissolved and particulate groundwater concentrations. See EPA 105d above. The groundwater is not a source of pyrogenic 4- to 6-ring PAHs or particulates from Site 16 uplands.

**EPA 111. Reference request.**

*EPA requests a reference for the weathering of A0 and P0.*

**RTC 111. References provided in the forensics report.**

Both A0 and P0 weather in the environment. See references in the forensics report. The use of the A0 and P0 ratios can also be found in: Yunker et al (2002) PAHs in the Fraser River Basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* 33: 489-515 and references therein.

**EPA 112. PAH and biomarker matches between pavement and sediments conflict.**

*The biomarker pattern for selected reference pavement samples matched the biomarker pattern found in harbor sediment at the storm sewer outfall, but the PAH pattern did not. Please reconcile this finding with the statement suggesting that the migration pathway for hydrocarbons and PAHs from the road to sediments is possible.*

**RTC 112. Roadway runoff contained heavy petroleum and pyrogenic PAHs.**

Most of the pavement samples were collected as abraded fragments from existing roadway courses (layers). Several samples (PAV13, PAV18, PAV19, and PAV20) were collected from piles or accumulations of roadway particulates. In this way, the forensic investigation captured discrete and composite samples. One of these composite samples, PAV19, contained roadway material with tar and petroleum components (EPAPAHs = 3,660 mg/kg). This sample demonstrated the use of tar binders on the Allen's Harbor Road. Importantly, the 2004 sediment sample collected at the storm sewer outfall (AH49 = 28 mg/kg EPAPAHs) exhibited

PAH ratios that plotted within the insert box ( $FL0/PY0 = 1.1$  and  $A0/P0 = 1.18$ ) (Figure 12b). The PAHs in AH49 were likely impacted by tar pavement binder from a different storm water runoff event. In short, PAV19 and AH49 collectively demonstrated a range of compositional variability with a high potential for matching Allen Harbor sediments.

**EPA 113a. Transect 1 EPAPAH concentrations decline with distance from Site 16.**

*Transect 1 EPAPAH concentrations decrease linearly with increased distance from the shoreline while the TPH C9-C44 concentrations increase along this profile.*

**RTC 113a. There is no concentration gradient along Transect 1.**

Transect 1 EPAPAH concentrations varied from 14.9 mg/kg (shoreline) to 9.5 mg/kg (midpoint) to 12.4 mg/kg (offshore). This is not a concentration gradient. The correlation of EPAPAHs with distance is poor ( $R^2 = 0.36$ ). It is disingenuous for EPA to claim there is a significant concentration gradient in Transect 1 while claiming that a difference of 500% between dissolved and particulate groundwater may not be significant (EPA 110 above). The report narrative is accurate as written.

**EPA 113b. Transect 2 EPAPAH concentrations decline with distance from the outfall.**

*Transect 2 spatial trends are not as apparent along Transect 2; however, concentrations of both EPAPAH and TPH C9-C44 are highest in the sample closest to the outfall. Please explain this observation.*

**RTC 113b. Navy concurs.**

As stated in the forensics report, Transect 2 concentrations varied from 15.1 mg/kg (shoreline) to 8.18 mg/kg (nearshore) to 14.8 mg/kg (midpoint) to 8.89 mg/kg (offshore). The correlation of EPAPAHs with distance was poor ( $R^2 = 0.14$ ). The variability in concentration and composition discussed in the report was attributed to episodic fluxes of hydrocarbons into Allen Harbor from Allen's Harbor Road.

**EPA 114. Figure 10 annotations are not understood.**

*What is the significance of the different colored lines superimposed on the chromatograms shown in this figure? Does the green line on the plots for PIL16-03 and adjacent sediment sample SD16-AH-17-SD-0001 show identical peaks for these two samples (thus supporting the conclusion regarding source and sediment)?*

**RTC 114. The annotations illustrate the dominant hydrocarbon features.**

The red line helps identify the pattern of pyrogenic EPAPAHs with inflection points for N0, P0, PY0, C0, BAP, and GHI (Table 2 for specific analyte identities). The green line helps identify the isoprenoid hydrocarbons with inflection points for pristine, phytane, and three other isoprenoid hydrocarbon compounds. The blue line below the chromatographic baseline helps identify the petroleum derived unresolved complex mixture (UCM). The blue line above the chromatographic baseline helps identify petroleum derived normal alkanes. "Q" identified peaks associated with laboratory quality control compounds.

The middle range petroleum distillate in PIL16-03 contained compounds that elute in the diesel range (see ranges on bottom of Figure 10). The high proportion of normal alkanes relative to isoprenoid hydrocarbons indicated little weathering. When these hydrocarbons leached into the

adjacent sediment (SD16-AH-17-SD-0001 a.k.a., SD16), the normal alkanes were biodegraded leaving middle distillate residues enriched in isoprenoid hydrocarbons and the diesel range UCM. SD17 also contained a late eluting UCM (heavy petroleum) and late eluting resolved peaks (plant waxes). The presence of these late eluting hydrocarbons demonstrated the presence of ambient sediments. Important constituents, like PAHs, saturated hydrocarbons and triterpane biomarkers were present, but the patterns of these compounds required mass spectrometry for accurate resolution (Figures 11, 13, and 14, respectively).

**EPA 115. Why do PIL16-03 and SD17 PAH histograms differ (Figure 11)?**

*The PAH histogram for PIL16-03 appears to show a petrogenic signature while that for SD16-AH-17-SD-0001 is characterized as "mixed." Please explain.*

**RTC 115. The difference demonstrates mixing of piling leachate and ambient sediment.**

PIL03-03 contains a diesel range petroleum distillate (see RTC114). The unweathered PAH signature of this middle distillate petroleum is presented in Figure 11. It primarily contains alkylated 2- and 3-ring PAHs. Once released into the sediments, environmental weathering reduces the proportion of 2-ring alkylated PAHs, which results in the enrichment of alkylated 3-ring PAHs (phenanthrene/anthracenes and dibenzothiophenes). Notice how the alkylated 3-ring PAHs dominate the PAH histogram of the adjacent sediment sample SD16-AH-17-SD-0001 (SD17). The additional pyrogenic 4- to 6-ring PAHs in SD17 came from the ambient sediments.

**EPA 116. Figure 12 shows similarities among samples in the magnified box.**

*It is interesting to note that all but two of the harbor sediment samples plot within the blue box, along with the Uplands Source Soil samples. What is the magnitude of uncertainty (i.e., error bars) that should be associated with these points, in both the x- and y-directions on this plot? Could these samples share a common origin?*

**RTC 116. The PAH source signatures are one of many lines of evidence.**

The insert box in Figure 12b was used to portray all of the samples clearly, not to cluster samples by common origin. The precision was approximately +/-5% on this plot as evidenced by the laboratory duplicates ("D" suffix). Samples outside of this range contained varying mixtures of particles with distinct PAH origins. See RTC 111 for comments on the use of A0/P0.

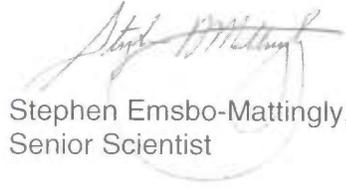
This plot demonstrated that the upland samples with the highest concentrations of pyrogenic PAHs (the most significant candidate sources) were very distinct from the sediment samples. EPA observed that the PAH signatures of several uplands samples plotted within the insert box along with many sediment samples. Most of these upland soils contained lower concentrations of EPAPAHs than the Allen Harbor sediments. The one upland sample with elevated PAHs (SO5506 = 139 mg/kg EPAPAHs) contained other hydrocarbons (saturates and biomarkers) that were not observed in the sediments. The tiered forensic approach requires agreement among multiple lines of evidence to determine a match, not just a passing similarity to a single double ratio plot. The tiered forensic evaluation of the available data demonstrated no matches between Site 16 upland soils and Allen Harbor sediments.

Importantly, the insert box also contains all of the background sediment samples in the study; specifically, the NIST standard reference material (SRM) from the New York City area plus

Narragansett Bay Reference Area Samples 1-4, 2-1, and 3-2. None of these background samples were affected by Site 16. Not surprisingly, the Allen Harbor sediments exhibited pyrogenic PAH signatures, heavily weathered petroleum residues, and plant waxes found in regional background samples.

Please let me know if you have any questions about these responses.

Sincerely,

A handwritten signature in cursive script, appearing to read "Stephen Emsbo-Mattingly". The signature is written in dark ink and is positioned above the printed name.

Stephen Emsbo-Mattingly, M.S.  
Senior Scientist