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A User's Guide for Determining the Sources of Contaminants in Sediments

A Demonstration Study: Sources of PAH in Sediments in the Vicinity of the Norfolk Naval Shipyard, Elizabeth River, Norfolk, Virginia

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EXECUTIVE SUMMARY

Defining the nature and extent of anthropogenic contamination from naval facilities in sediments can be difficult. This is particularly true in waterways and coastal areas where multiple point sources co-exist along with persistent non-point sources (i.e., urban background), a situation that leads to complex mixtures of contaminants in nearby sediments. Navy policy on Sediment Site Investigations and Response Actions dictates that source identification is critical in determining the Navy's cleanup responsibility and the potential for site recontamination. Therefore, when non-Navy sources are suspected, all sources of Navy and non-Navy contamination at a site should be identified and "background" levels of contaminants established.

The objective of this document is to produce a guide for Navy Remedial Project Managers (RPMs) that will describe and demonstrate the process by which the Navy can defensibly determine the nature, extent, *and source(s)* of anthropogenic contamination in sediments near existing or former naval facilities.

This Guidance Document is divided into two sections. **Section 1** provides a "step-by-step" description of the investigative process that RPMs can use when considering or designing a study. These steps include (1) evaluation of the site's candidacy for a contaminant source study and development of a Watershed Contaminant Source Document (WCSD), (2) development of a conceptual site model, (3) development of a defensible study design, (4) field sample collection, (5) rapid sediment characterization (RSC) screening, (6) advanced chemical fingerprinting (ACF), and, finally, (7) synthesis and presentation of the results. Each of these steps, and the strategy involved in each, are discussed in detail. The cost effectiveness and utility of the "step-by-step" approach are highlighted in **Section 2**, which contains a demonstration study aimed at determining the source(s) of Polycyclic Aromatic Hydrocarbons (PAH) in sediments of the southern branch of the Elizabeth River near the Norfolk Naval Shipyard and surrounding naval properties.

After a thorough review of the operational history and existing chemical data for the Elizabeth River study area, four objectives were established for the demonstration study, namely,

1. To determine the potential impact of PAH derived from nearby historic tar refining and wood treatment operations on sediments proximal to naval properties,

2. To evaluate of potential fate and transport of PAH to/from areas proximal to Navy Installation Restoration (IR) sources,

3. To establish the PAH attributable to urban background within the study area, and

4. To distinguish PAH associated with creosote and related materials derived from the multiple wood treatment operations within the study area.

Approximately 200 sediment samples from the study area were analyzed using RSC for total PAH concentrations. Fifty samples were subsequently selected and analyzed via ACF, using modified EPA methods (SW-846) tailored for the "fingerprinting" PAH and related hydrocarbons. The results indicated that sediments throughout the study area are overwhelmingly impacted by PAH derived from variably weathered creosotes (or related creosote blends) that are superimposed on PAH attributable to urban background. While a few sediments also contained some petroleum products,

there was no recognizable contribution of PAH attributable to these evident in the PAH data. The creosote urban-background-derived PAH occurred in five recognized categories, namely,

1. Creosote- or related creosote-blend dominant,
2. Urban background with heavy creosote,
3. Urban background with moderate creosote,
4. Urban background with trace creosote, and
5. Urban background.

The concentrations and characteristics of the PAH attributable to these categories are summarized in Table 2-5 (p. 71).

Objective 1: There is strong evidence that creosote(s) or related tar distillates from the Creosote Site 1 and Creosote Site 2 area (see Figure 2-2 on page 28 for site locations) have impacted the western shoal sediments: (1) proximal to the South Gate Annex piers as far south as NS13 and (2) as far north as SB05. (See Figure 2-26 on page 73). Any impact to the sediments within the Main Shipyard of such materials is not evident in the available data.

Objective 2: The sediments within the western tributaries to the Elizabeth River that flank the various Navy properties (Paradise, St. Juliens, and Blows Creeks) contain low concentrations of PAH. The nature and concentration of these PAH (and associated hydrocarbons) are entirely consistent with urban background. There is no evidence for any point source of PAH derived from any of the Naval properties impacting sediments in these tributaries.

Objective 3: Twenty sediments were recognized to contain PAH derived exclusively from urban background, which collectively refers to PAH from a variety of point and non-point sources such as (1) stormwater runoff; (2) direct deposition (atmospheric fallout) of combustion particles (soot) from vehicle exhaust and factories; (3) surface runoff from proximal roadways, parking lots, and bridges; or (4) discharges from recreational, commercial, and military boat/ship traffic. Statistical analysis of these 20 sediment samples indicated that urban background contributes, on average, about 16 mg/kg (dry) total (priority pollutant) PAH or 26 mg/kg (dry) total PAH (43 analytes measured via ACF). In the study area, sediments containing more than 30 mg/kg total (priority pollutant) PAH should be considered to have been impacted by a source(s) of PAH other than what is readily attributable to urban background.

Objective 4: Distinct sources of creosote (and related products) were difficult to defensibly establish using the ACF data, which clearly indicated that the greatest chemical differences between creosotes in sediments from Creosote Site 1 and Creosote Site 3 areas were in their various degrees of weathering. However, the density of RSC data (n = 200), in combination with the ACF, indicated that PAH ‘hotspots’ existed proximal to all four creosote sites (see Figures 2-4 and 2-26; pages 44 and 73). This implicates a creosote contribution from each of these sites and underscores the added value of the combined RSC and ACF approach in a contaminant source study.

The results of this demonstration study clearly indicate that the sources of PAH to the southern branch of the Elizabeth River are dominated by creosote-like sources that are likely attributable to historic wood treatment operations. In addition, there is no evidence of Navy point sources of PAH to sediments in the western tributaries near naval IR sites (i.e., Paradise, St. Juliens, and Blows Creeks). In accordance with Navy policy, this information will be used to augment the WCSD for naval facilities, in which the documented evidence will be passed to the regulators for consideration.

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1. INTRODUCTION

Defining the nature and extent of anthropogenic contamination from naval facilities in sediments can be difficult. This is particularly true in waterways and coastal areas where multiple point sources co-exist along with persistent non-point sources (i.e., urban background), a situation that leads to complex mixtures of contaminants in nearby sediments.

The objective of this document is to produce a guide for Navy Remedial Project Managers (RPMs) that will describe and demonstrate the process by which the Navy can defensibly determine the nature, extent, *and source(s)* of anthropogenic contamination in sediments near existing or former naval facilities. Understanding the source(s) of contamination in sediments can provide Navy RPMs with greater ability to accomplish the following:

1. Define what contaminant signatures are site-related to determine the Navy's responsibility under Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and differentiate those contaminant signatures from other sources that are potentially not covered under the Navy's CERCLA responsibilities,

2. Define the ambient/background conditions for the study area[1], which should influence decisions surrounding a site's remedial action objectives (RAOs) and clean-up goals,

3. Provide insight to the fate of contaminants in sediments (e.g., evaluate the degree(s) of biodegradation or the propensity for other attenuation mechanisms, including natural recovery),

4. Provide insight to the transport of contaminants in sediments (e.g., evaluate degree(s) of dispersion away from sources, resuspension of sediments, tidal effects, weathering, etc.), and

5. Provide potential benefits to regional watershed investigations by providing supporting evidence for inclusion in a Watershed Contaminant Source Document (WCSD) to better delineate Navy-derived source contributions in a cost-effective manner.

Collectively, this information would be used to support Navy sediment management decisions. Further, this information could ultimately support cost recovery efforts from other non-Navy sources of contamination in cases where the Navy is not the only Potentially Responsible Party (PRP) involved in remedial actions.

Toward this end, this Guidance Document is divided into two sections. Section 1 provides a "step-by-step" description of the investigative process that RPMs can use when considering or designing a study. Section 2 provides the detailed description of a demonstration study that was conducted to assess the nature, extent, and source(s) of polycyclic aromatic hydrocarbons (PAH) in Elizabeth River sediments near the Norfolk Naval Shipyard and the surrounding naval properties.

[1] The term "study area" is used throughout this document to imply that the area includes the Navy *site*, as well as the surrounding areas including non-Navy source sites and background areas. Thus, the term "study area" is not limited to the Navy *site*.

1.1 PROBLEM STATEMENT

The management of contaminated sediments near existing and former naval facilities is a major issue facing the U.S. Navy. The monitoring, removal (e.g., dredging), or isolation (e.g., capping) of contaminated sediments in order to meet acceptable, risk-based cleanup levels requires that the nature and extent of any contamination be well-defined. The degree of understanding with respect to "*nature and extent*" is normally obtained in the course of a site's remedial investigation/feasibility study (RI/FS). However, defining the nature and extent is often complicated in waterways and coastal areas where multiple point sources co-exist along with persistent non-point sources (i.e., urban background), creating a situation where the contaminants from multiple sources are commingled or overlapping. Under such circumstances, it is prudent to also evaluate all source(s) of contamination to assess and recognize the potential contribution(s) from any non-Navy or non-point (ambient background) source(s) of contamination.

Recognizing and unraveling multiple sources of contamination typically requires more advanced chemical "fingerprinting" data than normally are acquired in a conventional RI/FS; however, advanced chemical "fingerprinting" of large numbers of sediments can be cost prohibitive. Thus, the need exists for a process by which the naval facilities' RPMs can cost-effectively collect the data necessary to recognize and distinguish the different sources of contamination to sediments proximal to former or existing Navy facilities.

1.2 GENERAL APPROACH TO PROBLEM

Unraveling the complexity of commingled or overlapping sources of contamination in sediments near any facility requires good spatial (and perhaps temporal) coverage of the impacted sediments and Advanced Chemical Fingerprinting (ACF). These two requirements can be cost-effectively achieved through the combination of the following:

1. Rapid sediment characterization (RSC) of a large number of sediments to identify contaminant trends, 'hotspots,' and key samples using fast, semi-quantitative, and typically field-deployed methods and subsequent

2. ACF of a selected subset of sediments to recognize and unravel distinct source "fingerprints" using more advanced laboratory methods.

Table 1-1 provides a summary of the properties of the RSC and ACF methods. The objective of combining RSC with ACF is to cost-effectively maximize the benefits of each method and to help offset the limitations of each method. For example, ACF normally requires specialty analyses beyond the scope of normal (RI/FS) regulatory requirements and beyond most commercial laboratory capabilities. For example, in the case of PAH, the Environmental Protection Agency (EPA) requires that the concentrations for only 16 priority pollutant PAH be determined and reported for regulatory purposes. However, ACF of PAH requires that approximately 50 PAH compounds (or compound groups) be determined at accordingly higher analytical costs (Table 1-1; e.g., Stout et al., 2001b). Comparable disparity exists between the analytical procedures used to meet regulatory objectives and the analytical ACF requirements with respect to other contaminants (e.g., metals, PCBs, etc.). When combined with historical and hydrologic/geologic information, the ACF data can provide a defensible basis of recognizing and allocating among different sources of contaminants, which is the objective of most environmental forensics investigations (Stout et al., 1998).

Table 1-1. Comparison benefits and limitations of RSC and ACF methods.

Rapid Sediment Characterization	Advanced Chemical Fingerprinting
Benefits Near-real-time results can guide sampling locations Potential for high data density for mapping Lower costs	Benefits Highly specialized, quantitative methods Can often remove interferences Can distinguish contaminant 'fingerprints'
Limitations Often non-specific Semi-quantitative Matrix-sensitive	Limitations Often reliant upon blind sampling Limited availability in commercial laboratories Slow turn-around time Higher costs
Cost per Sample XRF (metals): $75 UVF (PAH): $75 Immunoassay (PAH, PCB, pesticides): $100 QwikSed: $200	Cost per Sample ICP/MS (metals): $350 GC/FID (THC/fingerprinting): $275 GC/MS (full suite of alkyl PAH): $350 GC/MS (biomarkers): $150 GC/MS (PCB congeners): $400
Throughput XRF: 40 samples per day UVF: 20 samples per day Immunoassay: 40 samples per day QwikSed: 6 – 12 samples per day	Throughput Metals: 30 to 60 days TAT THC and PAH: 30 to 60 days TAT PCB: 30 to 60 days TAT

The strategy for combing RSC and ACF is that the higher analytical costs for ACF can be substantially reduced if the sediment samples are first 'screened' using inexpensive RSC technique(s). The RSC can cost-effectively provide the spatial (and depth) coverage that is necessary to perform the following:

1. Recognize concentration gradients (which speaks to the fate and transport processes at work in an area and perhaps changes in contaminant input over time),

2. Recognize contaminant "hotspots" (which often indicate source areas), and

3. Help define "background/ambient" conditions (which will impact clean up goals and methods).

Data from the RSC screening process are then synthesized to determine which samples are most appropriate for ACF analysis. Collectively, this combined approach provides a cost-effective method intended to (1) determine if distinct sources can be recognized and, if so, (2) determine the nature and extent of those contaminants in sediments near Navy facilities.

The combined use of RSC and ACF, however, are only two steps in the process of unraveling contaminant sources near naval facilities (Figure 1-1). The overall sequence of steps include (1) evaluation of the site's candidacy for a contaminant source study and development of a WCSD, (2) development of a conceptual site model, (3) development of a defensible study design, (4) field

sample collection, (5) rapid sediment characterization screening, (6) advanced chemical finger-printing, and, finally, (7) synthesis and presentation of the results. The details of and interaction between each step shown in Figure 1-1 are described in greater detail throughout Section 1.4.

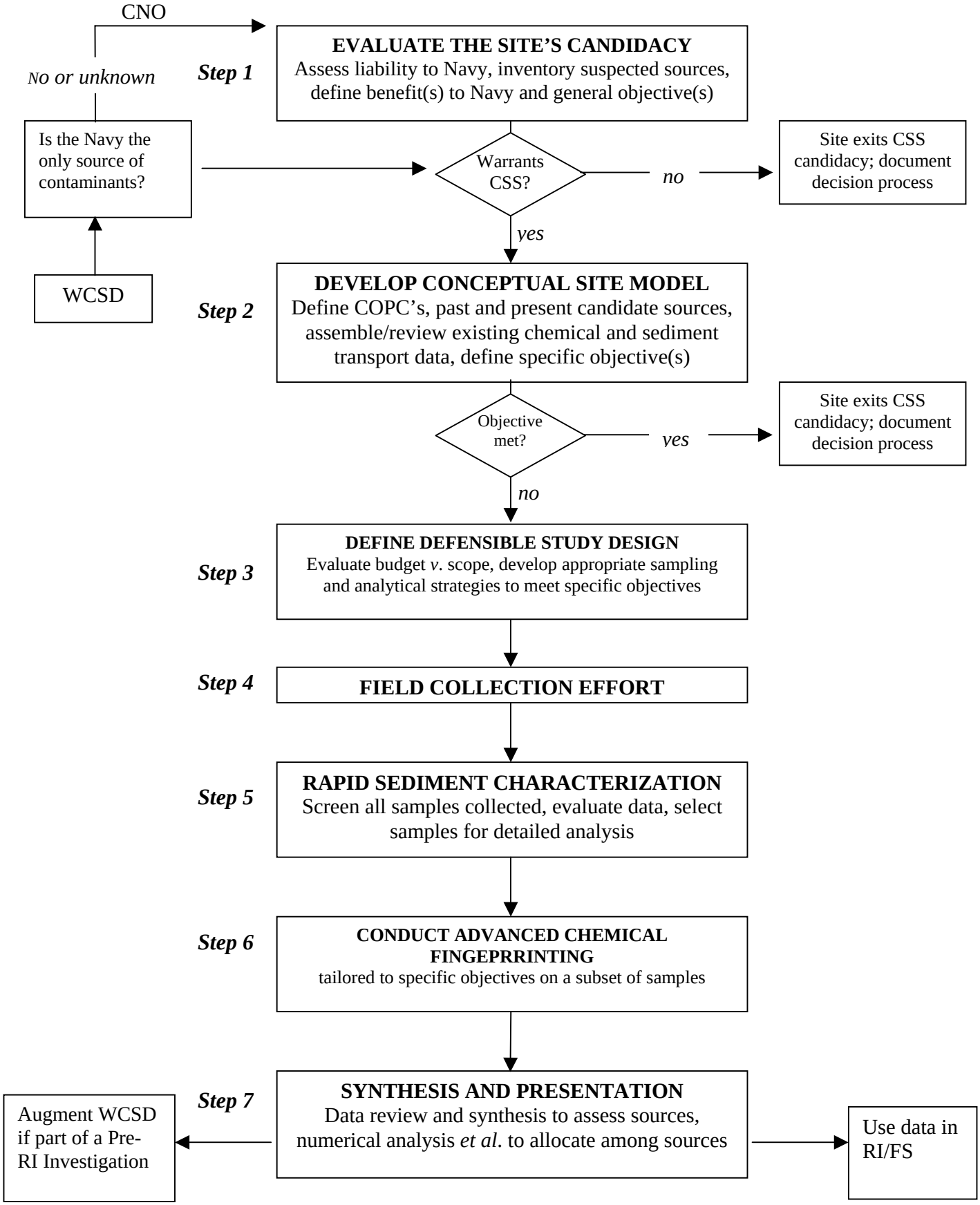

Figure 1-1. Flowchart showing considerations, steps, and decision points for conducting a contaminant source study (CSS).

1.3 BENEFITS TO NAVY AND NAVY RPMS

Contaminant source studies have particular application in industrial and urban waterways where multiple potentially responsible parties (PRPs) operate (or had previously operated) in the area. The benefits of contaminant source studies for the Navy RPMs include the following:

1. A clear definition of the ambient/background conditions of the sediments, particularly as these relate to previous or ongoing sources of contamination beyond the control of the Navy (e.g., urban runoff/fallout, discharges from neighboring properties, water vessel traffic, etc.),

2. The ability to refute or substantiate the contaminant source(s) and pathway(s) conceived in pre-existing conceptual site models (CSMs),

3. An evaluation of the effectiveness of any previous Navy-sponsored source control measures,

4. A basis to evaluate if there is a potential for future recontamination,

5. Provision of supplemental data to the RI/FS during the Human Health Risk Assessment (HHRA) and Ecological Risk Assessment (ERA),

6. Grossly assessing sediment conditions that may be amenable to natural recovery *versus* those requiring other remedial action,

7. Recognition of previously unknown sources of contamination, thereby allowing for early abatement (in the case of Navy sources) or gather policy mandated data (in the case of non-Navy sources),

8. Establishment of a detailed baseline before long-term monitoring via natural recovery, and finally,

9. If warranted, the option for liability reduction or cost recovery through identification of other non-Navy sources.

1.4 ROLE FOR CONTAMINANT SOURCE STUDIES WITHIN NAVY SEDIMENT POLICY

Contaminant “fingerprinting” using RSC and ACF methods has many applications within the RI/FS process relative to sediment investigations and response actions. The Navy sediment policy supports using innovative investigation and interpretation techniques such as rapid assessment, fingerprinting, and in-situ tools used to investigate sediments. The sediment policy also requires the development of a WCSD if there are other non-Navy sources contributing to the contamination of the sediment. Since source identification is important in determining the Navy’s cleanup responsibility, fingerprinting techniques applied early in the RI can be effectively used for source identification to augment the WCSD and or verification of background locations and concentrations. Although a WCSD is not required when the Navy is the sole source of the contamination, RSC methods can still be used to evaluate the nature and extent of contamination, and ACF procedures can still be used to document the potential for, and ‘baseline’ conditions for, monitoring and natural attenuation processes. Fingerprinting methods can also be used in the later stages of the FS to evaluate the

potential (and baseline) for natural attenuation in remedey selection and/or setting appropriate cleanup goals (see Figure 1.1).

Users of "fingerprinting" tools in the course of contaminant source studies must be aware of the applicability of implementing such tools funded under Environmental Restoration, Navy (ER,N) and Base Realignment and Closure (BRAC) activities. Navy policy on Sediment Site Investigations and Response Actions (February 2002) states that source identification is critical in determining the Navy's cleanup responsibility and the potential for site recontamination. Therefore, when non-Navy sources are suspected, the sources of Navy and non-Navy contamination at a site should be identified. As will be highlighted in the demonstration study (Section 2), this is particularly important for sediment sites contaminated with PAH, which are ubiquitous and persistent "background" contaminants in urbanized/commercialized waterways. Standard analytical methods cannot defensibly 'tease apart' the proportional contributions of "background" PAH from any PAH point-sources (see Section 2).

Evaluation of the potential Navy source(s) of contamination should always precede a contaminant source study for sediments in an adjacent water body. It must be first verified that a CERCLA/RCRA release(s) has occurred on/from Navy property and that the migration/transport of that release to the water body is evident or has been empirically verified. Once a release has been confirmed, conducting a contaminant source study using RSC and ACF then can be used early in the RI process to defensibly determine if a chemical "link" exists between the contamination in the offshore (presumably impacted) area and the contaminated onshore Navy source. Very often, it will be necessary to identify the nature and extent of Navy and non-Navy contamination before the primary source(s) of the contamination can be verified. Any positive chemical "link" can be verified through an assessment of the hydrodynamics/bathymetry of the receiving water body, and consideration of whether other similar sources of contamination that may exist in the area, before making a final determination as to the primary source of contamination. If there is evidence that there are other non-Navy sources, but lack of sufficient quantitative evidence whether the Navy is the primary source, then the RPM and their respective management should follow the principles laid out in the sediment policy (i.e., notifying Chief of Naval Operations [CNO], cease ER,N funding for further investigation or remediation). Thus, a contaminant source study can be an important early step in the RI. The scope of a contaminant source study will always be site-specific and dependent upon the site's use history, size, and characteristics of the receiving water body, and other *a priori* information that may exist.

Contaminant source studies using RSC and ACF can also be used to establish "background" levels of contaminants in the study area, which necessarily extends beyond those sediments proximal to Navy facilities. The Navy Interim Background Policy (September 2000) and the Sediment Policy (February 2002) clearly specify that cleanup goals must be risk-based, but must not be below the "background" levels. Therefore, the combined use of RSC/ACF can be used to screen for and identify appropriate locations for background and reference (non-site, anthropogenic) sampling. Appropriate evaluation of "background" concentrations is essential in establishing appropriate cleanup goals relative to the potential for recontamination from non-Navy sources. Using RSC/ACF procedures can also assist the Navy in determining which appropriate cleanup program an area of concern should be handled (e.g. Underground Storage Tank (UST), Installation restoration (IR), etc.).

1.5 STEP-BY-STEP APPROACH TO PROBLEM

The sequential steps in a contaminant source study (Figure 1-1) can be applied at any Navy site. However, each site is unique and therefore the process will need to be tailored to the particular Navy site under investigation. In the following sections, we provide generalized guidance for an RPM to consider in the course of designing and conducting a contaminant source study.

1.5.1 Evaluating a Site's Candidacy for a Contaminant Source Study

The specific reason(s) for whether and why a contaminant source study should be considered will undoubtedly vary for each site. At some sites, the need will be obvious (e.g., the Navy is being held responsible for contamination for which it is not liable), whereas at others, the need will be less obvious (e.g., the Navy has agreed to clean up to 'background' levels, which are poorly established). Some considerations to help determine the need for a contaminant source study are discussed in the following sections. The result of this, the first step (Figure 1-1), is to determine whether or not to continue with the process.

1.5.1.1 Overall Assessment of Actions

Navy RPMs and their managers need to consider additional factors when considering the use of any environmental fingerprinting/forensics studies. There are potential liabilities that must be weighed against the potential benefits of performing a study where the Navy can defensibly establish its contribution to a potentially impacted waterway. First and foremost, the RPM must be consistent with the standing Navy sediment policy and other applicable guidance. Other factors that may influence the decision include (1) is the CERCLA site already a National Priorities List (NPL) (Superfund) site? (2) is there the potential for costly natural resource injuries to be assessed to Navy sources? (3) are there political or grassroots pressures to 'do something,' either now or later? and (4) how amenable will regulators and other stakeholders be to the use of such methods? Each question must be considered and weighed in determining if the site warrants a thorough understanding of the Navy's contribution to a known or suspected problem.

1.5.1.2 Assessment of Known or Suspected Navy and non-Navy Sources—Past and Present

An obvious consideration is whether or not it is reasonable to suspect that the historic or current naval operations have potentially impacted the nearby waterway. Due to the diversity of industrial marine operations and the ubiquitous nature of potential contaminants, it can be difficult to ascertain the relative contributions from multiple sources, including a CERCLA release to a receiving water body. However, in some situations where the contaminant of concern or the levels of contamination cannot be reasonably attributed to the Navy operations, then the Navy may be required to provide information identifying the existence of other sources of contamination by conducting a CSS.

Another obvious, and more common, consideration is whether or not it is likely (possible) that non-Navy sources may have contributed to the known or suspected contamination in the vicinity of the Navy site. This potential situation will be obvious in some locations where the Navy site is surrounded by other industrial and commercial properties with long operational histories (e.g., as in our demonstration site along the Elizabeth River; Section 2). This situation certainly favors that a contaminant source study be conducted to determine the potential contribution of the Navy to the 'total' contamination. Even at more isolated naval facilities, the potential exists for 'back-ground' levels of contamination to rival or even exceed any reasonable Navy contribution to the sediments. In this situation, the Navy may be prudent to defensibly define the background (ambient) conditions

(e.g., due to direct atmospheric fallout to a water body or natural 'background') and thereby limit their potential liability to only those areas where a CERCLA activity has impacted the water body above the background conditions.

Other considerations include (1) what known or suspected contaminant sources exist(ed) on the Navy property, (2) what known or suspected industries are (or were) located on nearby properties, (3) what are (or were) the known typical contaminants associated with those industries, and (4) what are the general sediment transport dynamics of the area—i.e., could contamination get from "*there to here*" and *vice versa*? The answers to these questions should each be considered in determining the candidacy of a particular Navy site for a contaminant source study as described in this guide.

1.5.2 Development of a Conceptual Site Model for Contaminant Source Studies

Once a site's candidacy has been established, a conceptual site model (CSM) for the ensuing contaminant source study must be developed, or an existing CSM must be modified. For example, a CSM developed for a baseline ecological risk assessment (BERA) may already exist that can be augmented to include a preliminary synthesis of the contaminants, their candidate sources for the study area, and the potential for transport of sediments/contaminants. At the completion of a CSM, an RPM should be in a position to accomplish the following:

1. Identify (or confirm the identity) the known or suspected contaminants of concern (COPCs) for the site,

2. Identify all of the known or suspected sources of the COPCs within the study area, and

3. Develop specific objectives (hypotheses) to be evaluated by the contaminant source study that address the greatest environmental risks, and provide the greatest potential benefit, for the Navy.

1.5.2.1 Assembly and Utility of Pre-Existing Data

An important step in the identification or confirmation of contaminants of concern is a review of the pre-existing data for the study area (and nearby areas, which might provide additional insight to regional background issues). Pre-existing data may reside in published and unpublished sources. Published sources of data will reside primarily within the scientific (journal) literature. Therefore, a library literature search of the study area could reveal published datasets related to earlier investigations by academic or industry researchers. In addition, inquiries to local universities may reveal that environmental studies have been conducted in the study area and unpublished data from M.Sc. and Ph.D. theses may already exist. Other sources of unpublished data will include the data submitted to Regional, State, or Federal regulatory agencies by other groups (e.g., consultants to nearby industries) working within the study area. Finally, data already collected by government entities, including different parts within the Navy or within the Army Corps of Engineers, should be sought and evaluated. In some instances, other groups within the Navy (e.g., Naval Research Laboratory or SPAWAR) may be conducting studies in the same area and collecting relevant data, but be unknown to the local RPM.

The primary problem facing the utility of the pre-existing data is that they normally represent different 'vintages' of data, collected at different points in time, and using different analytical methods and different laboratories. Each factor tends to introduce variables that limit the comparabi-

ity and any comprehensive interpretation of the pre-existing data as a whole. Furthermore, the pre-existing data need to be reviewed with a very critical eye with respect to the data quality. For example, vintage data may suffer from inadequate analytical methods (e.g., EPA 418.1) or, as is far too common the case, prove to be virtually useless due to significantly elevated detection limits. Thus, the utility of the assembled data need to be carefully evaluated and interpreted within the context of when and how the data were collected.

As a result of these shortcomings, pre-existing data can rarely be used in providing defensible interpretations surrounding the source(s) of contamination within the study area. However, in some instances, the pre-existing data may sufficiently address some of the considerations that had warranted the site's candidacy, such that the contaminant source study might be averted or delayed (Figure 1-1). This instance is probably a rarity, primarily because pre-existing data will only rarely include sufficient chemical detail to distinguish similar sources of contamination.[2] The reason for this is that most environmental data were collected to satisfy some regulatory requirement using standard EPA methods (Douglas and Uhler, 1993), which lack the chemical detail to distinguish similar sources of contamination. This shortcoming is discussed further in Section 1.5.3.3.

Thus, at the very least, the assembled pre-existing data should be reviewed to help confirm the contaminants of potential concern (COPCs), potentially identify trends and hotspots, potentially identify candidate sources, and generally guide the study design of the contaminant source study.

1.5.2.2 Historical and Published Records Review

The anthropogenic use history of the study area can reveal significant insight as to the potential environmental impacts on sediments in the area. This history applies to historic naval IR site activities at the subject site, or to the current and historic commercial and industrial activities of other properties in or near the study area. The use history of an area can be assembled from the local historical archives of a public library. Additional information will reside in city and county records of property owners and their business activities. Historic land use maps and fire insurance maps (e.g., Sanborn maps; www.lib.berkeley.edu/EART/snb-intr.html) can provide a historical picture of what facilities existed within the study area. Finally, the U.S. EPA and State regulatory agencies are also sources of information regarding the recent activities of other contaminated properties in an area.

An important consideration in the historical assessment of an area is the occurrence and extent of past dredging activities that may have occurred within the study area. This information is important because dredging activities will have influenced the distribution of contaminants, which will impact decisions surrounding where samples should and should not be taken. Unfortunately, the specific records of these activities often are poor (particularly non-Navy sponsored dredging), but the simple knowledge that they had occurred is sometimes important to know (and consider in assessing pre-existing data).

It is important to determine what National Pollutant Discharge Elimination System (NPDES) discharge permits exist in the study area. The discharges from permitted facilities can provide clues as to the current and historic 'loads' of potential contaminants entering the waterway and its sediments. And finally, the magnitude of any non-permitted, stormwater drainage should be considered,

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[2] If the electronic raw data files are available (e.g., gas chromatography coupled with mass spectrometer [GC/MS] acquisition data from EPA Method 8270), it is possible to qualitatively evaluate selected extracted ion profiles from these data to obtain useful 'fingerprinting' information.

particularly in large urban areas with sizable watersheds that are collectively drained and may enter the waterway at outfalls.

1.5.3 Development of a Defensible Study Design

1.5.3.1 Sampling Design Strategy

The development of a technically defensible sampling strategy requires a balance between meeting project objectives and data quality objectives within the budget of the project. The design is typically based upon either some sort of a statistically-based sampling (e.g., random, systematic, stratified, cluster, etc.) and professional judgment based upon the information assembled in the CSM. Sampling designs are often site specific and require consideration of many aspects of the study design. These types of considerations are addressed in many outside references (e.g., Gilbert, 1987, and references herein).

Professional judgment is a valuable tool in the study sampling design because it allows for site-specific knowledge to be incorporated into the design. For example, larger numbers of samples can be placed in the vicinity of known or suspected contaminant sources (e.g., NPDES, stormwater, marinas, or combined serwer overflow [CSO] outfalls), or in locations where historic releases are documented to have occurred, and fewer (or no) samples can be placed in areas where little sediment deposition is occurring or where dredging was recently completed. The climatic conditions may be important to consider. For example, particulate loading to surface sediments near outfalls may be highest in the time following heavy rains or snow melt.

As part of developing this strategy, the RPM needs to consider how well-represented are the potential contaminant sources. In many instances upland sampling of non-Navy properties will not be permitted. In the case of stormwater runoff, access to sediments within a catchment basin may simply require a permit from the city. However, in the case of a ‘hostile’ neighbor, access may be impossible and the sampling design strategy will require sampling in sediments proximal to the inaccessible properties, usually at some point below the mean high water line. Thus, the sampling strategy needs to include consideration of the legal issues balance with the best means of representing potential contamination from an inaccessible area.

The extent and density of sampling (i.e., spatial coverage) is usually the issue that requires the greatest consideration in developing a sampling design strategy. It is the number of samples that will largely determine the cost of the project (Section 1.5.3.4). In some budget-constrained investigations, it may be necessary to ‘back-in’ to a specific number of RSC screening and ACF samples first, and then distribute the allocated RSC screening samples among the locations that best address the specific objectives of the study using one’s professional judgment (see Section 1.5.3.4).

If it had been determined that an objective of the study was to access historical inputs to the sediments, then it is necessary for the sampling design to include collection of at least some sediment cores that are intended to capture “pre-anthropogenic” (or at least pre-naval operations) contributions to the sediments. Such cores need to be placed in areas that have been shown (or are believed to be) areas of sedimentary deposition and that have not been dredged. Radiogenic dating of core segments using radiogenic dating techniques (e.g., ^{210}Pb or ^{137}Cs) can yield sediments from particular ‘time intervals’ whose chemistry reflects conditions from those periods. This dating can be important in areas where historic (and now defunct) operations are considered to have been a significant source of the COC to the study area.

Whatever the number of samples determined available for RSC is determined to be, some of these need to be reserved as “samples of opportunity” to be determined in the course of field work. Such samples could include any samples related to interesting or peculiar observations made in the course of the field work.

In addition, most contaminant source study objectives will necessarily include some assessment of the ambient (background) conditions within the study area. Thus, careful consideration must be given to where representative background samples can be obtained, including areas beyond the immediate study area. Given the importance of background samples in demonstrating the concentrations of contaminants beyond the control of the Navy, the number of background samples needed to meet the objectives of the study should be carefully considered. Population statistics are vital to the defensibility of the conclusions and should be qualitatively and quantitatively considered.

The final sampling design should be recorded in a written project workplan that includes the locations of each sample to be collected for RSC. (Remember, the locations of the samples for ACF will not be determined until after the RSC data are acquired and interpreted.) The project workplan should include maps of the sample locations and GIS coordinates, which will expedite their location during the sampling event. Producing maps of the planned sample locations before the field operation provides an opportunity to visually assess (and modify if necessary) the adequacy of the spatial coverage of the sampling design to meet the project objectives.

1.5.3.2 Selection of RSC Techniques

Numerous RSC methods have been described in existing Navy guidance for other purposes (http://web.ead.anl.gov/ecorisk/issue/pdf/rsc.pdf), so the discussion here is brief. Several RSC options are available that primarily depend upon the contaminants of concern (COC; http://cluin.org/char1_tech.cfm). Briefly, the available RSC methods can be divided, depending upon the COC category of interest, namely, (1) metals and (2) semi-volatile organics (PAHs, PCBs, and pesticides).

RSC of metals can be conducted using x-ray fluorescence (XRF) spectroscopic techniques that rely upon the fluorescence emitted by different metals upon excitation by an x-ray beam. With proper calibration, the concentration of multiple metals can be screened for simultaneously. Before RSC analysis of metals via XRF, sample preparation may be as simple as placing wet samples in sample holders and running the analysis. Additional sample preparation (similar to standard laboratory techniques) may include drying, grinding, and sieving to obtain a more homogeneous matrix for better precision in replicate analyses (an important consideration for comparisons between screening and laboratory replicates).

RSC of semi-volatile organics can be conducted using various immunoassay or fluorescence techniques. The techniques for the RSC of PAH in sediments have been adapted from methods developed for use in soils. They require dewatering of the sediment to below about 30% moisture by placing on filter paper to remove excess water. Again, like with metals, sample preparation can be more involved and similar to standard laboratory methods, depending on the objectives of the project. For many applications, the more basic preparation methods that will still meet the project needs are usually selected so this initial step in the procedure can be conducted in a timely manner. The dewatered sediment is then extracted using solvent (e.g., methanol) and analysis of the extract is then conducted by either immunoassay or *uv* fluorescence techniques. In the case of immunoassay, the extract is then treated with specific antibodies that promote a color change depending upon PAH

concentration, which is measured against a PAH standard solution-calibrated spectrophotometer. Fluorescence techniques allow direct measurement of the emitted fluorescence following *uv* excitation of the extract. The fluorescence response is compared to that of a suite of PAH standard calibration solutions.

As discussed below (Section 1.5.5.2), RSC data interpretation of metals and semi-volatile organics can significantly benefit from additional physical properties data for the sediments, if available. For example, in the case of organics, these additional properties may include grain size or total organic carbon (TOC). In the case of metals, the cation exchange capacity (CEC) or surface area may be useful. Therefore, during the planning of the RSC phase of the study, some consideration should be given to obtaining useful physical properties data concurrently with the RSC data.

1.5.3.3 Selection of ACF Techniques

The selection of appropriate ACF analytical methods will also depend upon the nature of the COC for the study, and to a degree upon the objectives of the study. As with the RSC techniques, the ACF techniques can be divided into (1) metals and (2) semi-volatile organics (PAH, PCBs, and pesticides).[3]

The need for ACF methodology rests with the limitations of standard EPA methods (SW-846) to meet the objectives of a contaminant source study (Stout et al., 2002a). The fundamental shortcoming with virtually every conventional EPA SW-846 method of analysis, when used for measuring contaminants, particularly organic contaminants in sediments and other media, is a lack of detailed measurements of those *diagnostic* chemicals known to comprise these complex mixtures. Instead, these methods are focused on selected compounds identified as “priority pollutants,” which are quite pervasive in contaminant mixtures (e.g., different petroleum products) and generally insufficient to distinguish different sources of otherwise similar contaminants (Douglas and Uhler, 1993). Because of these limitations, chemists at some environmental laboratories have modified the standard EPA methods to yield the data necessary to support detailed contaminant source investigations. With respect to these modified methods, note that the EPA SW-846 guidelines allow flexibility in the deployment of the ‘standard’ analytical methods. While most commercial laboratories are not interested in modifying the standard methods, some laboratories have the experience and flexibility to modify standard methods to meet project goals without violating the standard method guidelines. When properly planned, most data generated by ACF methods can support contaminant source studies and convention regulatory assessment programs. In other words, the ACF data can generally be considered defensible and accepted by regulatory agencies if the data quality objectives are clearly defined and met by the effort.

The ACF techniques available for the assessment of semi-volatile organic contaminants in sediments (e.g., hydrocarbons, PCBs, and pesticides) are all based upon high-resolution gas chromatography, usually operated in conjunction with compound-specific detectors (e.g., ECD or MS). An inventory of some typical ACF methods available for “fingerprinting” semi-volatile organic contaminants, mostly hydrocarbons, is given in Table 1-2. More detailed descriptions of these methods are in Stout et al. (2002). Note that not all the target compounds listed in Table 1-2 are considered contaminants (e.g., petroleum biomarkers). However, these compounds are extremely

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[3] Note that ACF techniques also exist for volatile organics (e.g., gasoline and chlorinated solvents), but these are not discussed in this document. The reader is directed to Stout et al. (2002) for discussion on ACF techniques for automotive gasoline and other light petroleum fuels.

useful in characterizing different sources of petroleum (Peters and Moldowan, 1993; Stout et al., 2000) and when used in conjunction with contaminant fingerprinting (e.g., PAH), these compounds can be used to distinguish contaminant sources.

Table 1-2. Common analytical methods used for ACF of semi-volatile organic contaminants[4].

Measurement Method	Target Compounds	Utility for ACF of Contaminants
Modified EPA Method 8015	• Total (extractable) hydrocarbons (THC) • C_8 to C_{44} normal and branched-chain hydrocarbons • Resolved vs. unresolved • High resolution "fingerprints"	• Accurate determination of total extractable hydrocarbons • Development of diagnostic indices • Accurate product identification in the light distillate to residual petroleum products • Evaluation of degree of weathering
Modified EPA Method 8270	• Priority pollutant PAH • Alkyl homologues of priority pollutant PAH • S-, N- containing PAH • Petroleum biomarkers	• Detailed chemical indices used for evaluation of product identification and differentiation • Mixing and allocation • Degree of weathering • PAH source differentiation
Modified EPA Method 680	• Homologue (level of chlorination) groups • Full list of 209 congeners	• Optimized preparation for low levels analysis of sediments • PCB source differentiation • PCB weathering/dechlorination monitoring
Modified EPA Method 8082	• 16-20 pesticides and degradation products • Standard PCB Aroclors • Limited congeners	• Optimized preparation for low levels analysis of sediments

In the case of metals, fewer ACF techniques are available. Standard methods that use ICP-MS (e.g., EPA Method 6010) generally can provide low detection limits and suitable suites of metals to permit 'fingerprinting' of their distributions, which in some instances can reveal distinct sources. Thus, standard EPA SW-846 methods for metals analyses are generally acceptable for source contamination studies in sediments.

1.5.3.4 Achieving a Balance of Scope/liability Versus Costs

Selecting the appropriate RSC and ACF analytical methods need to balance the project objectives *versus* the project costs. (In turn, the project costs need to be balanced against potential liability or benefit of the study to the Navy.) Some estimated costs for the typical RSC and ACF methods were given in Table 1-1. Factors that affect these costs can include the number of samples (e.g., fewer

[4] Reprinted from *Introduction to Environmental Forensics*, Stout et al., "Chemical Fingerprinting of Hydrocarbons," p. 148, ©2002, with permission from Elsevier. Table 1-2 was modified and amended from original table.

samples having higher unit costs) and whether or not the RSC is performed in the field or laboratory. The overriding strategy for a contaminant source study is to maximize the use of the less expensive RSC methods to achieve a broad understanding of the study area and reserve the more costly ACF methods for 'key' samples. The obvious benefit of this combined approach is to have little net effect on the total project costs while providing greater technical defensibility because of the broader (spatial and temporal) understanding obtained during the RSC screening phase and the higher data quality and utility achieved by the ACF phase.

The approximate unit cost for various RSC screening and ACF methods (Table 1-1) can be used to estimate the total analytical costs, if some assumptions on the number of samples for RSC and the percentage of these that will be analyzed by ACF are made using the following formula:

(X samples for RSC) x ($/sample) + (Y samples for ACF) x ($/sample) = analytical costs,

where X>Y.

Iterations of this exercise may be necessary to achieve a balance between the sampling strategy, analytical strategy, and scope/objectives for a particular study.

Additional costs for contaminant source studies need to consider the project management time, field mobilization and demobilization efforts, the field collection effort, field materials and supplies (including boat time if necessary), data analysis and interpretation, and report generation (including GIS support). Because the field collection effort can be a significant cost, it is prudent to explore the potential to 'team' or share boat time with other ongoing studies to achieve greater cost benefit.

1.5.4 Sample Collection

The collection of sediment samples for contaminant source studies is fairly routine. Sediment samples can be collected using a range of surface (~0-10 cm; grab) and subsurface (core) sampling devices. The selection of sampling device is dependent on the specific objectives of the project and numerous references are available to aid in this selection process; see Section 2.7 of Navy Sediment Guidance:

http://web.ead.anl.gov/ecorisk/related/, March 2003, and

http://www.epa.gov/waterscience/cs/collection.html, SEATAC 1997

Most RSC screening methods require approximately 10 grams of wet sediment whereas most ACF requires 50 grams (wet) or less. If additional physical properties methods are to be measured (e.g., grain size, TOC) then additional sediment should be collected.

Sediment samples from grab samplers should be transferred to the pre-cleaned glass jars. It is generally recommended that a minimum of one 8-ounce (glass) jar be collected to represent a particular sediment sample. The jars should be filled to minimize headspace, yet still allow for expansion after freezing. If required, grain size and TOC samples should be placed in clean ZipLock™ bags. Samples should be placed on ice and maintained at approximately 4ºC throughout the field operations. A continuous chain-of-custody (COC) should be maintained during field collections and subsequent laboratory processing. If the RSC and ACF are to be conducted at different locations, it may be prudent to homogenize and split the sediments during the field operations so that they can be sent to the appropriate laboratory. Alternatively, the samples can be

first sent to the laboratory performing the RSC, who then sends only the selected samples to the laboratory performing the ACF.

It has become commonplace to prepare sampling maps in advance of field activities in which target sample locations can be recorded using global positioning satellite (GPS) guidance. The preparation of sampling maps before the field collection effort provides an opportunity to assess the spatial coverage of the proposed sample locations. Of course, modifications can be made in the course of the field collection effort due to unforeseen difficulties or decisions based upon field judgement.

1.5.5 Sample and Data Analysis

1.5.5.1 Scheduling of Chemical (RSC and ACF) Analyses

Consideration must be given to the additional time associated with conducting RSC and ACF in a manner satisfactory for the technical objectives and regulatory requirements, particularly sample holding time. The latter is generally not an issue in the analysis of most metals (6-month; 28-day for mercury). However, with respect to semi-volatile organic analyses, it is prudent to discuss the RSC and ACF approach with all stakeholders to determine if 14-day holding times for the extraction of soils/sediments is warranted. Freezing of sediment aliquots is a technically viable option for extending the holding time of sediments for semi-volatile organic analysis, and thereby permitting adequate time for the RSC analyses and data evaluation before selecting samples for ACF. These types of decisions are often site- and project-dependent, so consideration should be given to allow for full discussion of options with all stakeholders.

In some instances, it may be necessary to have the RSC analysis conducted either in near real time in the field or nearby staging location. This analysis will usually increase the cost of the RSC operation, but has the added advantage of being able to alter the field sampling program on the basis of the RSC results as they become available (see Triad methods, http://www.epa.gov/tio/char.htm). If this real-time function is not required, samples can be simply sent overnight to a laboratory where RSC analyses can still be conducted in a relatively short time period (1 to 3 days, depending on required sample preparation). If keeping the 14-day holding time had been determined to be necessary, it is still possible to perform the RSC screening, ACF sample selection, and sample extraction within 14 days, so long as all parties are adequately prepared. This will require clear communication with the laboratories involved and may affect cost. As noted above, if such regulatory holding times are not a constraint, sediment samples may be frozen and held while the RSC screening is conducted and the results are comprehensively reviewed. It is reasonable that aliquots for grain size and TOC be removed before freezing. This removal avoids any issue surrounding the affect that freezing may have on grain size.

1.5.5.2 Analysis of RSC Data

Once the RSC data (and any supporting physical properties) are available, they need to be evaluated to identify samples for ACF. The first step is to evaluate the spatial relationships of the data. GIS-based maps with RSC results displayed with symbols or colors related to RSC concentrations can be used to delineate contaminant trends and ‘hotspots’ (potential sources?). This type of visual assessment can provide the technical basis for selecting representative samples for ACF that occur along a given trend or within a given ‘hotspot.’ If data density and structure allow, the RSC data may even be contoured to interpolate concentrations across the study area.

Since chemical variations often follow changes in sediment texture, evaluating any physical properties data (e.g., grain size or TOC) that are available also can be useful in evaluating the RSC results. Crossplots of RSC concentrations (y-axis) *versus* some physical property (x-axis) will often show that many samples fall along a single trend that, for example, demonstrates contaminant concentrations increasing proportionately with the percentage of fine-grained sediments. Such trends normally are representative of the "ambient" conditions within the study area. (Some examples of these are shown later in Section 2.6.1.) Samples that plot above any "ambient trend" are typically indicating the presence of 'hotspots' (potential sources ?). The ambient trend normally is only seen if a sufficient number of samples at ambient levels are measured across the range in physical properities (grain size) at the site. Thus, such trends may not always be apparent in the RSC data.

In the case of metals, the percentage of fine-grained sediments may not be the best physical parameter to use in assessing ambient trends. Instead, with metals, the cation exchange capacity (CEC), surface area, or other parameters may be better to compare to RSC concentrations.

As noted above, cost is an important consideration when large numbers of samples are analyzed by RSC methods. Therefore, if some physical properties are unavailable (due to the added cost) some simple proxies may suffice for evaluating the RSC data. For example, the percent moisture can be easily and inexpensively measured because it requires only wet and dry weight measurements that can be used as a surrogate for grain size (following adequate correlation verification). During XRF measurements for RSC of metals, major element compositions of Fe or Al will often show good correlations with grain size and can be used to assess ambient trends (in the absense of authentic grain size data). Determination of which physical properties are measured is often project-specific and determined by what is most efficient under site conditions and budget constraints.

Finally, in some studies, it may be prudent to use various statistical or numerical analyses (e.g., principal component analysis) of the RSC data to recgonize trends or anomolies, which might warrant consideration in the selection of samples for ACF.

1.5.5.3 Selection of Samples for Advanced Chemical Fingerprinting

Regardless of the approach(es) used in the evaluation of RSC data, it is important to remember that the goal of the RSC data analysis is to develop a sufficient set of visual displays to aid in the selection of samples for ACF (and not to alone achieve the objectives of the study). The analytical strategy and budget will largely determine the number (or percentage of the RSC samples) that will be selected for ACF. Of course, it is not necessary that all of the ACF budget be used if there is no technical basis to do so. For example, if the RSC data have demosntrated an overwhelm-ing consistency and predominance of 'back-ground' ambient conditions in the study area, the ACF may simply include a few selected confirmation samples. Therefore, the task of selecting samples for ACF is largely a matter of selecting a reasonable and justified subset from the complete set of RSC samples. Some guiding principles to remember and keep in mind in the selection of samples for ACF are as follows:

1. Select samples that provide ample spatial coverage of the entire study area (i.e., try to represent all areas of the study and do not completely ignore any area on the basis of RSC alone),

2. Select a sufficient number of samples from specific location(s) within the study area that address a specific project objective(s) (i.e., select sufficient samples in areas of

specific concern or interest, potentially including accessible upland sites of interest), and

3. Select samples that represent the range of RSC concentrations observed, including those that are (apparently) representative of the ambient/background conditions (i.e., do not exclude all the low concentration samples as they may provide important information on "background" conditions).

Of course, an underlying basis for the selection of samples for ACF to meet these guidelines is the cost (Section 1.5.3.4). Thus, a degree of professional judgment is still needed in the selection of samples for ACF.

1.5.5.4 Analysis of ACF Data

The specific method(s) for analyzing the ACF data will depend upon the type of data available and the objectives of the study. However, most analyses will generally include the following:

1. Visual inspection of the available "fingerprints" employing qualitative pattern recognition (sometimes compared to known standards),

2. Graphical analysis of COC concentration histograms or source-specific diagnostic ratios or indices (e.g., cross-plots or ternary diagrams), and

3. Quantitative chemometric analysis. Each ACF data analysis method is described in the following paragraphs.

There is tremendous value in visually examining the chromatographic "fingerprints" that were acquired and subsequently used to generate the concentration data. These "fingerprints" can include the gas chromatography (GC)/flame iconization detector (FID) or GC/electron capture detection (ECD) chromatograms or the total ion chromatograms (TICs) or extracted ion profiles (EIPs) from GC/MS analyses. These chromatographic data were usually not provided by the laboratory and must be requested. In the case of semi-volatile organic matter, it is valuable to examine the GC/FID "finger-print" of the total extractable organic matter present in a sediment sample. The "fingerprints" should be interpreted by experienced chemists who can provide insight as to the specific nature of any hydrocarbons (including the presence of mixtures or naturally occurring, "biogenic" hydrocarbons associated with modern biomass) and the degree(s) of weathering. This qualitative "fingerprint" assessment of the chromatographic data can be extremely useful in subsequent interpretation of the tabulated COC concentration data associated with a particular sample, and is normally the first step in the analysis of semi-volatile organic matter in sediments.

Tabulated COC concentration data, particularly for large datasets, are difficult to examine visually. Numerous standard graphing techniques (e.g., population or individual sample histograms, population box-plots, or bivariate cross-plots) can aid in such analysis and should be performed during initial data exploration. For example, histograms of the analyte concentration data for individual samples can be visually compared to provide a qualitative assessment of the variability within the samples. Box-plots of various parameters (concentrations or ratios) can be used to identify potential outliers and population quantiles. Finally, some COC concentration data can be used to generate source-specific ratios or other diagnostic indices that can be cross-plotted to further reveal similar or dissimilar samples.

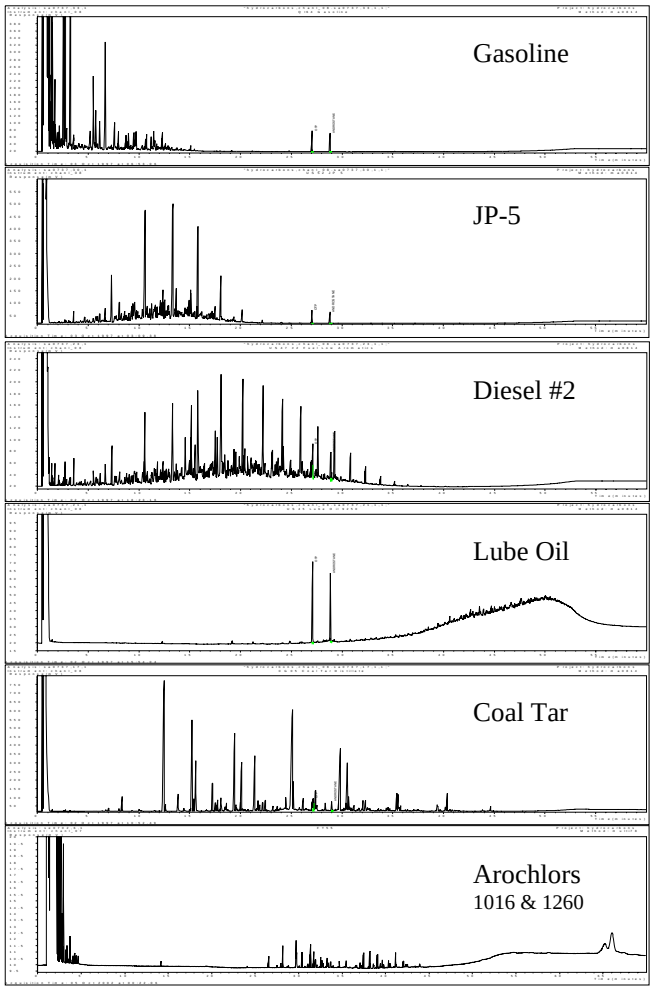

Figure 1-2. GC/FID fingerprints of common petroleum products and a PCB mixture. Knowledge of these materials, and their weathered equivalents, are required when interpreting chromatographic "fingerprints" of sediment extracts.

In recent years, these qualitative to semi-quantitative approaches to data analysis have been supplemented with various methods of statistical and numerical analyses performed on the tabulated concentration data (or ratios and other indices calculated from the concentration data). These methods are collectively referred to as "chemometrics."

Chemometric analyses have proven to be an especially effective means of comparing the chemical data from a large number of samples. Excellent summaries of statistical and numerical methods commonly used can be found in Gauthier, 2002) and Johnson and Ehrlich, 2002), respectively. One significant advantage of chemometric analyses is that they provide a strictly mathematical means of analyzing data, thus removing any biases of the interpreter. Chemometric analyses have the additional advantage of being able to convey the complex chemical differences among many samples with many individual chemical measurements in a visual manner that is more easily understood by the "non-expert."

Though others exist, two common chemometric techniques used in contaminant source studies include principal components analysis (PCA) and least-squares modeling. PCA is a powerful chemometric technique for visualizing intersample and intervariable relationships. It achieves this by reducing the "n" dimensionality of the data (where n = number of variables or samples, whichever is smaller) by finding linear combinations of the variables in the data set that account for the maximum amounts of variance. These linear combinations are called the principal components. The 1st principal component (PC) accounts for the maximum amount of variance and each successive PC accounts for less of the remaining variance.

PCA yields a distribution of samples (e.g., sediment samples) in n-dimensional space, where n is the number of variables (e.g., PAH analytes). The 1st PC is a line through this space upon which each sample point can be projected. The line's orientation is such that the variance of these projections is maximized. The 2nd PC is another line defining the next highest variance. These first two lines (i.e., the 1st and 2nd PC) define a plane. These planes are called '*factor score plots,*' which are one 'end product' of PCA (Gabriel, 1971). The Euclidean distances between sample points on these factor score plots are representative of the variance captured in each PC. In simpler terms, samples that cluster together are chemically similar and outliers are chemically distinct. Figure 1-3A shows an example of a factor score plot for nearly 100 sediments from an urban waterway in which three sources of PAH were recognized, namely, natural background (arising from pre-industrial, natural forest fires), urban runoff, and creosote (from a former coal tar distillation facility on the waterway; Stout et al., 2001a). Many sediment samples from this urban waterway contained only (or primarily only) one of these three end-members. These 'single-source' samples tend to plot as clusters at or near the apices of the trends revealed by the PCA factor score plot (Figure 1-3A). However, many other sediment samples tended to plot in locations intermediate between the three end-members indicating that they contain a mixture of these. Spatial relationships among samples on a PCA score plot (such at Figure 1-2A) can be used to estimate or determine the proportions of each end-member in each sediment sample. Additional calculations involving spatial distributions, concentrations, and volumes of impacted sediments of each sediment sample in the study could then be used to allocate responsibility among the three end-member sources.

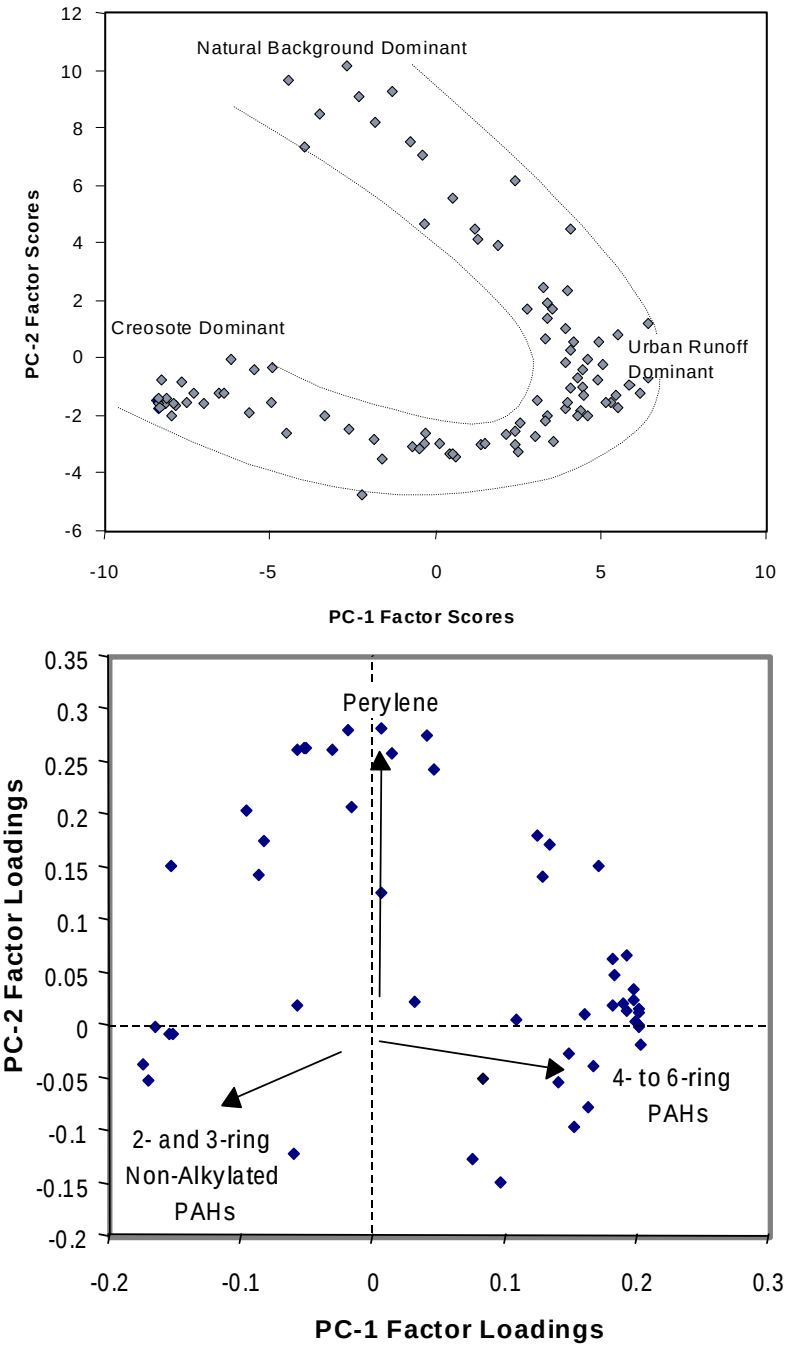

Figure 1-3. PCA factor score plot (top) and corresponding factor loading plot (bottom) for sediment PAH data. The PCA revealed three dominant PAH sources (natural background, urban runoff, and creosote) that were enriched in perylene, four- to six-ring PAHs, and two- and three-ring PAH, respectively. Samples plotting between the apices indicate a mixture of these dominant sources. Data from Stout et al. (2001).

A factor loading is calculated for each variable (e.g., PAH analyte) contributing to each PC. A cross-plot of the factor loadings for the first few PCs reveals the individual chemicals responsible for the variance in each PC. These *factor loading plots* are another 'end product' of PCA, and they can be used to interpret the variables responsible for the clustering/separations observed on factor score plots. The corresponding factor loading plot for Figure 1-3A is shown in Figure 1-3B.

Representative GC/FID chromatograms and PAH histograms obtained for the three ‘end-members’ identified in the PCA are shown in Figure 1-4. These show that indeed the ‘end-members’ exhibited qualitative differences in their fingerprints (GC/FID and PAH) that were quantitatively depicted by the PCA. The combination of these two ACF techniques, interpreted in light of known product types and weathering (see below) were able to determine the sources that were represented (i.e., natural background, urban runoff, and creosote).

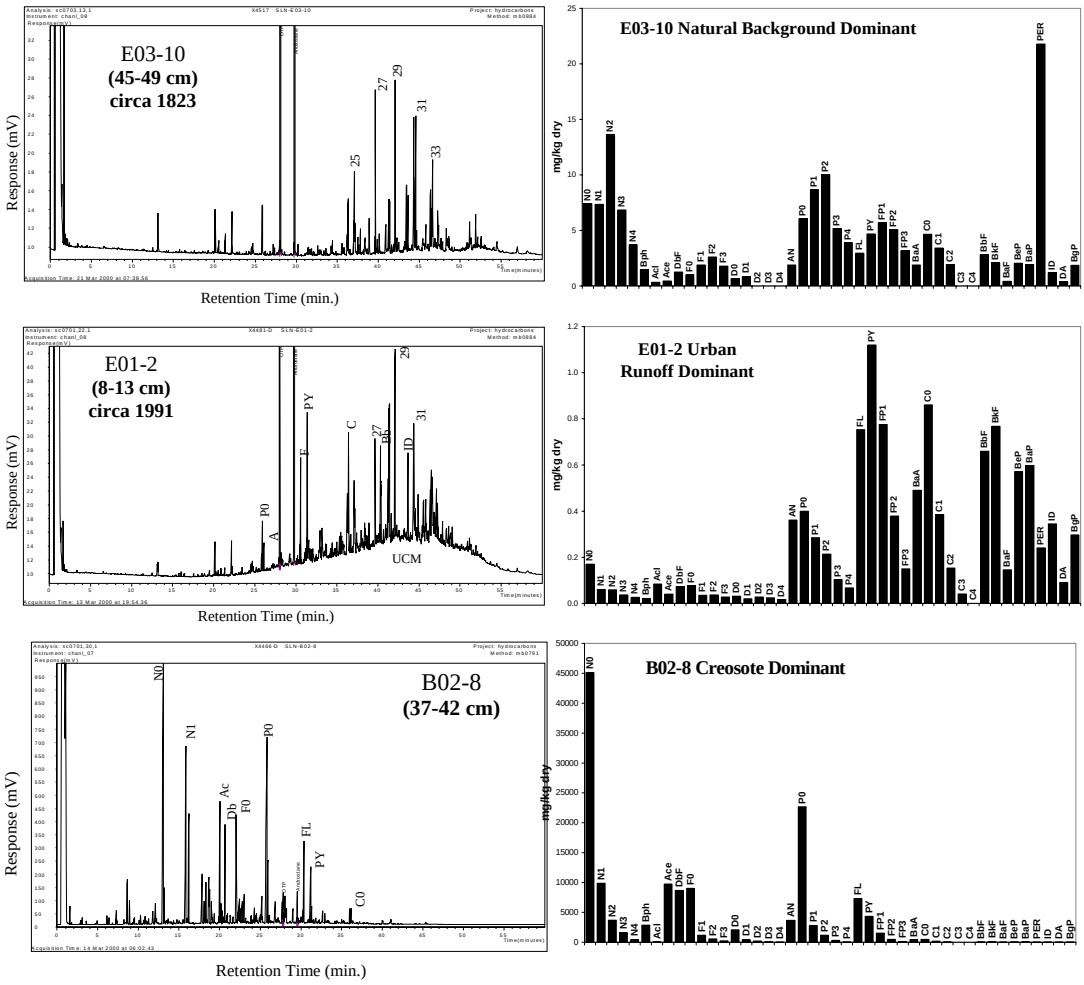

Figure 1-4. GC/FID chromatograms (left) and PAH histograms produced from ACF of sediments identified as ‘end-members’ in the PCA analysis shown in Figure 1-3A. Top: Sediment containing naturally occurring PAH, Middle: Sediment containing PAH derived from urban runoff, and Bottom: Sediment containing unweathered creosote. Data from Stout et al. (2001).

An important feature of any comparison among ACF data for sediment samples (whether it is qualitative or chemometric) is the effects that environmental weathering has had on the contaminant fingerprints. An overview of these effects was provided in Stout et al., 2002bb). Without an appreciation for the changes brought about by weathering, two identical source materials weathered to different degrees might be misinterpreted to represent two distinct sources. To minimize the difficulties related to differential weathering, it is common to focus any comparison upon parameters that are

considered the least affected by environmental weathering. In the case of organics, these parameters are often focused on the higher boiling, higher molecular weight compounds that tend to be less prone to the effects of weathering. Other studies can focus on highly recalcitrant compounds (i.e., petroleum biomarkers) that are resistant to biodegradation over most environmental timescales and conditions (e.g., Bence et al., 1996).

1.5.6 Synthesis and Presentation of Results

The manner by which the results and conclusions of a contaminant source study are conveyed needs to consider the audience, particularly whether they are technical or lay decision-makers. Naturally, the specific target audience will dictate the level of technical detail conveyed in a report or presentation. It is prudent to document the technical detail somewhere (e.g., a referenced summary report/package or as appendices to the non-technical summary) so that the detailed information can be quickly re-assembled at some future time without a considerable amount of effort. It should be emphasized that since fingerprinting and subsequent interpretations of that data may lead to crucial environmental decisions, proper maintenance of all data, field notes, reports, and calculations should be practiced.

Chemical ‘fingerprinting’ data in graphical and/or tabulate form can be very confusing to all but an experienced chemist. Their interpretation is much easier (and thereby useful) when the results of a contaminant source study are reported using numerous visual demonstratives that either convey the data spatially or some other easily interpreted visual (e.g., PCA score plots, as described above and in Figures 1-2 and 1-3). Such visuals can be more readily explained to and interpreted by technical and non-technical audiences. This is important since the value of any contaminant source study will be undermined if the audience cannot understand the results and conclusions.

Toward this end, Section 2 of this document conveys the results and conclusions of a contaminant source demonstration study that was performed in the vicinity of the Norfolk Naval Shipyard and St. Juliens Creek Annex (SJCA), in Portsmouth, Virginia. The reporting of this study is intended for a technical audience. Much of the detail of this demonstration study is found in appendices, as they detract from the results of this study. This is generally a good idea in presenting the results of a contaminant source study to any audience. The latter portions of the much shorter Executive Summar*y* that was provided at the beginning of this Guidance Document generally serves as an example of a non-technical manner to convey such results. The use of photographs and statistical graphing software is recommended to better communicate results to non-technical audiences.

2. DEMONSTRATION STUDY—SOURCES OF PAH IN SEDIMENTS NEAR NAVAL FACILITIES, ELIZABETH RIVER, NORFOLK, VIRGINIA

2.1 STATEMENT OF PROBLEM

Because of their toxic, mutagenic, and carcinogenic characteristics, the presence of polycyclic aromatic hydrocarbons (PAH) in sediments can warrant costly monitoring, removal (e.g., dredging), or isolation (e.g., capping). Many naval facilities are located along waterways flanked by multiple "point" sources of PAH (e.g., tar distillation, wood preservation, commercial petroleum storage and handling, aluminum smelting, manufactured gas production, rail yards, etc.). In addition, these waterways can receive PAH from "non-point" sources that include surface/storm water runoff and direct atmospheric fallout from the surrounding urban environment.

The occurrence of multiple point and non-point sources of PAH along a waterway can make it difficult to recognize and distinguish the contribution of PAH from any presumed Navy sources *versus* non-Navy sources surrounding the waterway. In addition, according to the National Oil and Hazardous Substances Pollution Contingency Plan (NCP), the term pollutant or contaminant as defined by 40 CFR 300 Section 101(33) of CERCLA, excludes petroleum, including crude oil or any fraction thereof and, by definition, a release specifically excludes emissions from engine exhaust of a motor vehicle, aircraft, or vessel from CERCLA. Therefore, since PAH are found in these types of sources, it is important to establish whether the PAH found in sediments near naval facilities falls within these exclusionary definitions and would thereby establish whether or not their presence constitutes a CERCLA release.

For the Navy to fairly assess its liability for the PAH in urban and coastal sediments, and to decide upon a prudent course of action, the contamination in the sediments attributable to a Navy source(s) should be recognized and distinguished from these other sources. Thus, the need exists for a process by which the naval facilities' RPMs can cost-effectively collect the data necessary to recognize and distinguish the different sources of PAH contamination in sediments proximal to IR sites at former or existing Navy facilities. This process was generically described in Section 1 of this report. In this section, a demonstration of this process is provided for PAH contaminated sediments near the Norfolk Naval Shipyard and nearby Navy properties where upland IR sites exist with known or suspected PAHs**.** In addition, in accordance with Navy policy, there are known or suspected migration pathways for the terrestrial PAH sources to reach the tributaries of the Elizabeth River.

2.2 STEP 1: EVALUATION OF DEMONSTRATION SITE'S CANDIDACY

2.2.1 Overview of Elizabeth River, Virginia

The Elizabeth River system is a sub-estuary of the southern Chesapeake Bay and is comprised of four tributaries that include the Lafayette River, Western Branch, Eastern Branch, and Southern Branch (Figure 2-1). The Elizabeth River system drains approximately 300 square miles of largely urbanized environments that include the cities of Norfolk, Portsmouth, Chesapeake, and Virginia Beach. Over the area's long commercial and industrial history, anthropogenic contaminants, particularly PAH, have accumulated in the river system's sediments.

The highly industrialized Southern Branch of the Elizabeth River system is home to several Navy properties, which include the Norfolk Naval Shipyard (NNSY), South Gate Annex, Scott Center Annex, Paradise Creek Landfill, and St. Juliens Creek Annex. Remarkably, the NNSY has operated at this location since 1801, i.e., more than 200 years.

The Navy properties co-exist among commercial and industrial activities along a short (~1.75 mile) stretch of the Southern Branch of the Elizabeth River, which is surrounded by a highly urbanized environment. Non-Navy historic activities in the area included at least four wood treatment facilities and 10 or more petroleum storage terminals. There have been at least two significant releases of creosote (20,000 to 30,000 gallons) from wood treatment facilities in the area (Lu, 1982) and one of the wood treatment facilities is currently a Superfund site (Section 1.3.3). Creosote is known to contain a significant mass of PAH. Thus, it is not surprising that, as will be shown below, the existing data indicate the PAH are prevalent in the area's sediments and are the most common class of chemical pollutants present in the Elizabeth River system (Section 1.3.3).

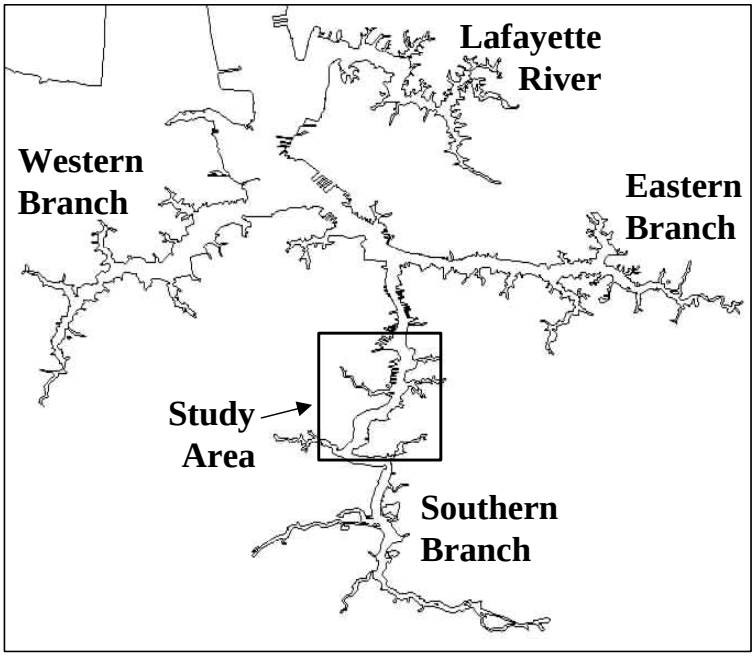

Figure 2-1. Map showing the three branches of the Elizabeth River, Virginia, and the general study area along the Southern Branch.

The hydrologic character of the Elizabeth River has done little to promote its natural recovery. For example, the entire Elizabeth River system is a tidally influenced sub-estuary with salinities ranging from around 25 0/00 near the mouth to 5 to 10 0/00 upriver (Virginia State Water Contol Board, 1983). Little fresh-water enters the system, thus, tidal action is the predominant control on water movement within the system. As a result, there are generally poor "flushing" characteristics and hydrologic sediment movement is limited. The combination of substantial PAH sources combined with the poor flushing characteristics of the tidal river means that contaminated sediments have largely remained trapped there.

Collectively, these conditions indicate that the anthropogenic PAH in the sediments of the Southern Branch of the Elizabeth River are likely to have a variety of sources, current and historic, which almost assuredly include non-Navy sources. However, the potential contributions of PAH from naval IR sites, if any, to the river's sediments currently are unknown. Thus, the Southern Branch of the Elizabeth River is a prime candidate for testing the approach and methods described in Section 1.

2.2.2 Assessment of Actions

The sediments within the Southern Branch of the Elizabeth River clearly contain high concentrations of PAH (see Section 2.3.3 below) that will undoubtedly promulgate remedial or restoration activities. For example, recent activities by the Elizabeth River Project (EPR), a non-profit citizens group, has publicized and promoted activities in the region that are directed at cleaning up the River's sediments. As a result, the U.S. Army Corps of Engineers already is planning a $2.4M feasibility study to clean up sediments in one area of the Elizabeth River.

The potential financial liability associated with any future remediation activities is likely to be substantial. As noted above, the NNSY and its predecessors have operated along the Southern Branch for more than 200 years. Furthermore, the Shipyard is adjacent to a property formerly used as a wood-treating facility (Creosote Site 1; see Figure 2-2 below). Previous research has revealed very high PAH concentrations in the sediments proximal to this facility (see Section 2.3.3), and it is currently a Superfund site. The tidal action of the study area has the potential to have distributed these PAH into the sediments proximal to nearby Navy properties and IR sites. Therefore, it is prudent to have a technical basis to assess the potential liability associated with the non-naval sources of PAH in the area surrounding the Naval properties. It is also prudent to understand the occurrence of any persistent, urban "background" source of PAH that could affect any decisions regarding removal of sediments adjacent to naval properties.

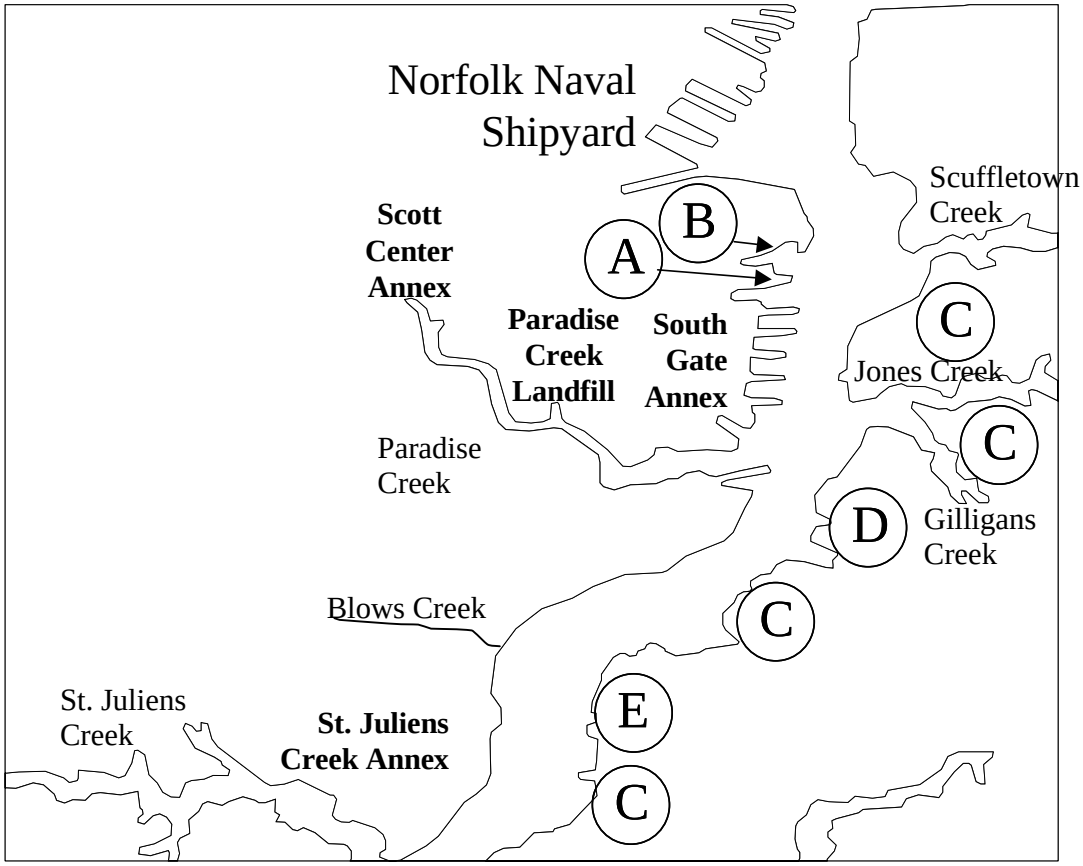

Figure 2-2. Map showing the demonstration study area along the Southern Branch of the Elizabeth River. Naval properties of interest are named and the approximate locations of commercial properties of interest include (A) Creosote Site 1, (B) Creosote Site 2, (C) multiple petroleum terminals, (D) Creosote Site 4, and (E) Creosote Site 3.

As an ancillary benefit, the Navy is always seeking new ways of increasing environmental stewardship with the community. Navy IR project managers are currently working closely with the ERP, a non-profit citizen group working towards restoration of the Elizabeth River. Coordination with the ERP during the fingerprinting project increased community relations and further solidified the Navy's goal of being an active environmental steward.

2.3 STEP 2: DEVELOPMENT OF A CONCEPTUAL SITE MODEL AND STUDY OBJECTIVES

A conceptual site model (CSM) provides the basis for the sampling strategy and specific objectives of a contaminant source study (Section 1.5.2). The CSM for a contaminant source study should include an understanding of the study area obtained from historic and other records and any pre-existing data. In the sections below, the relevant information assembled in preparation of the demonstration study is presented.

2.3.1 Description of Study Area

The study area selected for the demonstration study encompassed the Southern Branch of the Elizabeth River, ranging from approximately the Navy's Main Shipyard to the Upper Reach, the latter being the sharp easterly turn in the River East of St. Juliens Creek (Figure 2-2). This distance represents approximately 1.75 river miles. Included within the study area are various tributaries along the eastern (Scuffletown Creek, Jones Creek, and Gilligan Creek) and western (Paradise Creek, Blows Creek, and St. Juliens Creek) banks of the Southern Branch. Those tributaries located along the western banks were of particular interest because of their proximity to, or inclusion within (e.g., Blows Creek is entirely within St. Juliens Creek Annex), Navy properties of interest.

As noted above, the hydrologic movement of sediments in or out of the study area is limited. Thus, to maintain shipping access, sediments have been repeatedly dredged from the central channel of the Southern Branch, although the specific dredging history in the study area is unknown. Flanking the central channel are eastern and western shoals where sediments and the associated contaminants are expected to have accumulated. Water depths in the shoals are generally 1 to 2 meters or less. Any accumulation of sediment (or the associated contaminants) on the shoals, however, probably has been redistributed to some degree by tidal action and by the abundant anthropogenic activity (e.g., ship and tug traffic, etc.). However, given the general lack of hydrologic sediment movement in the river, any redistribution of sediment probably has not removed contaminant from the area. Dredging may be the primary mechanism by which sediment has been removed from the river.

2.3.2 Historical and Published Records Review—Candidate Sources

2.3.2.1 Naval Properties

The Main Shipyard, where most ship overhauls and repairs occur, is located at the northern end of the study area. Other Navy properties within the study area include South Gate Annex, Paradise Creek Disposal Area, and Scott Center Annex (Figure 2-2). South Gate Annex includes a ship anchorage and repair facility located along approximately 0.3 miles of the Elizabeth River. Upland portions of this annex contain some long-term storage facilities for radioactive materials. The Paradise Creek Disposal Area is a general disposal/landfill area along approximately 0.5 mile of the northern bank of the Paradise Creek (Figure 2-2). Further upstream within Paradise Creek is the Scott Center Annex, which is approximately 70 acres and flanks approximately 0.25 mile of the upper reach of Paradise Creek. Wastes from historic dry dock operations were stored here. Notably, dredged material from nearby waterways was reportedly placed in the Scott Center Annex to form the base of the landfill.

Another naval property within the study area, St. Julien's Creek Annex, is approximately 0.75 mile upriver from Paradise Creek (Figure 2-2). This 490-acre plus property includes Blows Creek toward the North and is flanked by about 0.75 miles of the Elizabeth River on the east and 0.5 miles of St. Julien's Creek on the south. The property was historically used as a munitions depot (1849-1970s), but now includes mostly administrative and storage facilities. Using the conceptual sites models and respective RI data from several upland Navy IR site investigations, it was determined that PAHs were identified as COPCs and that there was potential for these upland PAHs sources to reach tributaries of the Southern Branch including Blows Creek, Saint Juliens Creek, Paradise Creek, and potentially the main channel of the river itself. Remedial Investigations of Paradise Creek and Blow's Creek had both pre-dated the Navy Sediment Policy (February 2002) requiring the development of a WCSD. As of the writing of this guidance document, a WCSD is projected for the Southern Branch of the Elizabeth River in the Fall/Winter of 2003.

2.3.2.2 Non-Navy Properties

Industrial (non-military) activities along the Southern Branch also have had a long history. Evidence for degradation of the River's quality dates to at least 1925 when shellfish consumption from the River was first banned (Virginia State Water Control Board, 1983). The documents reviewed revealed that in 1983, 48 industrial and 15 domestic point discharges exist within the Elizabeth River system including several in the study area (Virginia State Water Control Board, 1983). A 1986 inventory of NPDES industrial discharge permits included 14 facilities within the study area (Table 2-1; Hampton Roads Water Quality Agency, 1986). As can be seen, most of these permits are for discharges from petroleum storage and/or handling facilities along the eastern shore and eastern tributaries of the study area (Figure 2-2). However, both dischargers that were identified as 'major dischargers' are located along the western shore, i.e., Norfolk Naval Shipyard and Atlantic Wood Industries. (Notably, the wood treatment facility representing Creosote Site 1 (Figure 2-2) is no longer operating and their discharges are reduced from 1986 levels.)

Table 2-1. Inventory of known industrial (non-municipal) NPDES point discharges (HRWQA, 1986) in the study area.

Property Operator	Operations	General Location
Amerada Hess	Petroleum handling	Eastern shore
Amoco	Petroleum storage	Scuffletown Creek
Atlantic Wood Industries* (Creosote Site 1)	Wood preservation	Western shore
BP NA Trading Company	Petroleum storage	Eastern shore
BP Oil	Petroleum storage	Paradise Creek
Cargill, Inc.	Petroleum storage	Jones Creek
Colonial Pipeline	Petroleum handling	Jones Creek
Colonial Pipeline	Petroleum handling	Upper reach
Continental Oil	Petroleum storage	Gilligan Creek
Crown Central	Petroleum storage	Eastern shore
Norfolk Naval Shipyard*		Western shore
Swann Oil	Petroleum storage	Upper reach
Tenneco Oil	Petroleum handling	Eastern shore
Texaco	Petroleum storage	Eastern shore

*Identified as major discharger by HRWQA

The current (2003) number and locations of industrial discharges is not known. However, URS Consultants, 1996) conducted a survey in the mid-1990s and reported that 14 NPDES permitted outfalls had existed within the study area. It is assumed that these are the same permits that are inventoried in Table 2-1.

In addition to these known industrial point discharges, an undetermined number of municipal discharges (e.g. sanitary wastewater, storm water runoff, publicly owned treatment works, and separate and combined storm sewer systems) exist in the study area. Our attempts to enumerate and locate these discharges during the conceptual design phase of this project were unsuccessful.

Historic operations along the study area are equally important as the current operations. Although no extensive study of historic operations along the river has been performed, it is notable that three wood preserving facilities have existed within the study area, though none of these are currently

operational. These facilities are notable because of their handling of PAH-rich materials used in wood preservation, e.g., creosote and coal tar. The Creosote Site 4 was formerly located on the eastern bank of the Southern Branch, directly across the river from the mouth of Paradise Creek (Figure 2-2). It reportedly had closed in 1971. Creosote Site 3 was formerly located on the eastern bank of the Southern Branch, directly across the river from the mouth of Blows Creek (Figure 2-2). This facility reportedly closed in 1981 (Merrill and Wade, 1985).

The third wood treatment facility, Creosote Site 1 was a 47.5-acre facility located along the western bank of the Southern Branch, just north of the South Gate Annex (Figure 2-2). Some additional information could be obtained regarding this property because it is currently listed on EPA's NPL (Superfund). The facility was opened in 1926 and reportedly closed in 1992. The original plant was used for various purposes, including a coal tar refinery, creosote wood treating plant, pentachlorophenol (PCP) wood treating plant, and a storage yard for treated lumber. The eastern portion of the site contains the currently inactive wood processing facilities and wood storage areas.

Any additional historic operations of potential relevance in terms of PAH sources within the study area have not been determined in the literature and documents reviewed.

2.3.3 Pre-Existing Published Data Review

Among the earliest studies of PAH in the Elizabeth River system was a survey of 28 sediments that was conducted by personnel from Virginia Institute of Marine Sciences (VIMS) in 1982. This unpublished report, and a subsequent published account (Bieri et al., 1986), provided some insight to the PAH concentrations in sediments within the study area. Three sediment samples collected in 1981 (Sites 15, 16, and 17) consisted of single grab samples representing only the upper 3 cm of sediment. The highest concentrations of total PAH[5] in the entire Elizabeth River system were recorded just downstream from the former Eppinger & Russell property (Creosote Site 3; Figure 2-2). The unpublished account concluded that the high concentration of PAH indicated a significant nearby source. Bieri et al. (1986) later attributed to two reported releases of "*thousands of gallons*" of creosote (or a creosote/coal tar mix) from the Eppinger & Russell property in 1960 and 1963 (Lu, 1982) as the likely source of elevated PAH observed just downstream. No chemical "fingerprinting" evidence was provided to support this contention.

Alden et al. (1984) and Alden and Butt, 1987) studied sediments from three locations within the study area (Sites M, N, O). Each sample was actually a composite of three sub-samples collected in 1982 using a bucket dredge in a transect across the river at three locations. The maximum concentration of total PAH recognized in these authors' survey of the entire Elizabeth River system was obtained proximal to the Naval Shipyard.[6] These authors suggest "*shipbuilding and repair operations and the associated shipping/anchorage activities are the most likely source of PAH in this area.*" Lower concentrations of PAH were found proximal to the Atlantic Woods (Creosote Site 1) and Eppinger & Russell (Creosote Site 3) properties. These concentrations were suggested to be the result of "*creosote spills and runoff are the most likely sources of PAH.*" No further evidence is offered to support these suggested sources of PAH.

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[5] Total PAH of 170 mg/kg (dry) includes the total of 14 individual priority pollutant PAH.

[6] Total PAH of 65.5 mg/kg (dry) includes the total of 14 individual PAH.

Huggett et al., 1984) surveyed PAH concentrations in sediments from the Elizabeth River, including four sites within our study area (Sites 17, 18, 19, and 20, which represented locations 17, 18, 19, and 20 km from the mouth of the Elizabeth River). Five cores or grab samples were collected at each location in a transect across the river. Some of these samples contained "*globular creosote inclusions, sometimes measuring several centimeters in diameter.*" Average PAH concentrations for each transect, which represented the upper 2 cm of these sediments, were reported to increase in an upstream direction.[7] This trend was generally consistent with the results of Bieri et al. (1982) and Alden et al. (1984). It is notable that Huggett et al. (1984) report "*that considerable variability in concentrations exist in any one segment (i.e. transect) of the river. This may be due to either different depositional patterns from one site in the river to another or perhaps past dredging activities that could have removed contaminated sediments*." This observation is interesting and speaks to the need to consider the affects of sediment transport/physical processes on the distribution of PAH within the sediments.

Merrill and Wade, 1985) reported on the PAH concentrations in four sediment grab samples (<10 cm) collected in the study area in 1983 and creosoted wood from the (then still operating) Atlantic Woods (Creosote Site 1) property. Similar to the previous studies, the maximum concentration of total PAH was obtained in sediments proximal to the former Eppinger & Russell (Creosote Site 3) facility[8]. After a comparison of the sediments to creosote standards, these authors attribute the PAH encountered in the sediments throughout the study area to "*carbonized coal products* [creosote and/or tar from] *point sources associated with creosoting facility sites.*" They acknowledge some contribution of petroleum to the sediments in the study area (as indicated by the presence of unresolved complex mixture of hydrocarbons), but do not suggest that petroleum is a recognizable source of the PAH.

The Virginia Water Control Board, 1987) reported on the concentration of a variety of contaminants in (effluents and associated) sediments at several outfalls within the Elizabeth River area collected in July 1985. Only one was near the study area, within the Main Shipyard of the Naval Shipyard (NS) property (NS Outfall 22). Although no data were reported, the sediment near this outfall reportedly contained "*an unusual distribution of PAH resembling weathered crude oil input, rather than the typical pyrogenic fingerprint of the Elizabeth River*."[9] This conclusion would appear markedly different from the earlier studies, which showed pyrogenic PAH associated with creosote and/or coal tar as the overwhelming source of PAH.

As part of a long-term monitoring program, Alden, 1990) sampled sediments proximal to (the then operating) Creosote Site 1 (SBE-2) and the former Creosote Site 3 property (SBE-3) in 1989. The PAH concentration data reported in these sediments is incomplete, and unfortunately, the concentrations that are reported have been normalized to total organic carbon content. Nonetheless, the SBE-2 and SBE-3 sediments contained about 8 and 12 mg of naphthalene/kg_{TOC} and 65 and 120 mg of fluoranthene/kg_{TOC}, respectively. No assessment as to the source of these PAH was discussed.

Alden et al., 1990) re-sampled sediment from the same sites as in the earlier studies (Alden and Butt, 1987), including two within the study area, Sites N and O, located proximal to Creosote Site 1 and the former Creosote Site 3 site, respectively. Samples representing the upper 150 cm of sediment

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[7] Total PAH ranged from 13 to 200 mg/kg (dry) includes the total of 11 individual PAH, including up to 36 mg/kg of benzo(a)pyrene in sediment proximal to the Creosote Site 3 (i.e., Site 20).

[8] Total PAH of 844 mg/kg (dry) includes the total of 16 individual PAH.

[9] Total PAH of 17.8 mg/kg (dry) includes the total of 14 individual PAH.

(intended to simulate what might be removed by dredging) were collected from the central channel and both shoals at each site. The channel at Site O had the highest concentrations of PAH observed anywhere in the Southern Branch in this study.[10] (Recall, the earlier samples from these same Sites revealed the maximum occurred at Site M, i.e., near the Main Shipyard; Alden and Butt, 1987). These authors point out that in this survey, the total PAH concentrations regularly decreased downstream from Site O (Creosote Site 3) and that concentrations were generally higher on the eastern shoal than corresponding channel or western shoal samples. No specific assessment as to the source(s) of PAH are discussed by Alden et al. (1990), however, general comments surrounding the potential sources at the Main Shipyard and the wood treatment operations are made. No chemical evidence was provided to support these comments.

Huggett et al., 1992) provides a synoptic review of about 10 years worth of sediment data on 225 samples collected in the Elizabeth River by the group at VIMS. These data collectively indicate that PAH concentrations are generally much higher (an order of magnitude or more) within the study area than they are in other parts of the Elizabeth River system. The high concentrations within the study area are attributed to the historic wood preservation activities along this stretch of the river. Overall, the concentrations of PAH generally decrease downstream for samples taken within the channel of the study area, indicating they are highest in the vicinity of the former Creosote Site 3 property. These authors suggest that the PAH distributions generally fall within two categories, namely a "*fresh creosote type*" and a "*weathered creosote or pyrogenic type.*" The creosote-type distribution is dominated by low molecular weight PAH (two and three rings) whereas the pyrogenic type is dominated by high molecular weight PAH (four to six rings). While the creosote-type PAH are readily attributable to wood treatment operations, they expect that the weathered creosote- or pyrogenic-type PAH are derived from weathered creosote and from incomplete combustion products (e.g., soot) derived from urban runoff and atmospheric fallout.

Alden and Winfield, 1993) report PAH for sediments re-sampled (again) at Sites N and O (as in the earlier studies by Alden and Butt [1987] and Alden et al. [1990]). The depth and collection date of these samples is unknown but appears later than the Alden et al. (1990) re-sampling. Notably, the highest total PAH concentration observed in this study was from Site N, i.e., adjacent to Creosote Site 1.[11] It is notable that in the three published accounts of samples collected from these same locations, the maximum PAH concentrations occurred at different locations each time. This testifies to the inhomogeneous distribution of PAH in the sediments within the study area, as was suggested by Huggett et al., 1992).

The concentrations of PAH in the 1988 through 1995 effluents from some of the permitted discharges were used to estimate PAH loads to the Elizabeth River (URS Consultants, 1996). Within the study area, only one of these was exceptionally high, i.e., permit #VA0005215 representing Norfolk Naval Shipyard. URS (1996) estimated a total PAH (n = 8) loading of 2185 pounds/year of PAH from this property. The URS (1996) study also attempted to estimate the contribution of non-point sources to the study area after considering rainfall, volume of storm water runoff, event mean concentrations, etc., to estimate that storm water could contribute almost 100,000 lbs/yr of total PAH (n=8) to the study area alone (i.e., river segments SB2 and SB3). This calculation, even if off by an

[10] Total PAH of 161 mg/kg (dry) includes the total of 16 individual PAH averaged over 150 cm. The upper 30 cm contained 520 mg/kg (dry) total PAH. The eastern shoal at Site O, closest to Creosote Site 3, had the second highest concentration of total PAH, 91 mg/kg (dry).

[11] Total PAH of 602 mg/kg (dry) includes the total of 16 individual PAH.

order of magnitude, suggests that non-point sources could be a significant source of PAH within the study area.

Mitra et al., 1999) collected and analyzed two 2.5-m sediment cores within the study area (Sites 1 and 2). Each core was analyzed for PAH and radioisotopes (^{210}Pb and ^{137}Cs) in 1-cm intervals throughout their lengths. (It is notable that radiogenic dating was confounded in this study, at least in part, due to dredging activities.) Site 2, located across the main channel from the Creosote Site 1, contained the highest concentrations of PAH. (Site 1 was located near the petroleum terminal near the mouth of Jones Creek; Figure 2-2). While tabulated concentration data were not reported, vertical profiles for both cores show that the concentrations of PAH in the sediment were highest near the surface and tended to decrease within increasing depth. The increase was gradual at Site 2 (near Creosote Site 1 and more abrupt at Site 1. The latter was suggested to have been caused by an 'unconformity' within the sediment profile caused by erosion at some point in the past that removed an interval of sediment.

Walker and Dickhut, 2001) analyzed the upper 2 cm of more than 70 sediments from the Elizabeth River system collected in 1998 and 1999; judging from the small-scale map(s) in this publication, about half of these appear to have come from within the study area. Approximately 13 sediments were collected adjacent to the Creosote Site 1 property and 12 were collected adjacent to the former Creosote Site 3 property. A sediment sample collected near Creosote Site 3 contained the highest concentration of total PAH of any sediment studied (1730 mg/kg $PAH_{\Sigma 25}$; surrogate corrected). However, average total PAH concentrations in sediments near both of these former wood treatment sites were comparable (approximately 200 mg/kg) and significantly higher than were observed in the other channel or shoal areas within the study area. These workers tried to unravel the source of PAH in sediment by comparison of selected PAH isomer ratios to published data for coal, creosote, coal tar, pitch, auto exhaust, and wood combustion. They also report some PAH distribution differences between these two suspected PAH source areas (Creosote Site 1 *versus* Creosote Site 3), which they use to suggest that most PAH in the shoals of the Southern Branch of the Elizabeth River are "*derived predominantly from Atlantic Wood* (Creosote Site 1) *and coal sources with little influence from Eppinger & Russell* (Creosote Site 3)." This finding is contrary to previous accounts that had suggested Creosote Site 3 was a notable source (e.g., Bieri et al., 1986). The coal sources recognized by Walker and Dickhut (2001) are suggested to be associated with historical and current coal sources, the latter potentially including a coal-fired power plant located upriver and coal storage downriver (at Lambert's Point) from the study area. More recently, these authors have supplemented their initial study with compound specific carbon isotope data, which was unable to distinguish fluoranthene in sediments from the Creosote Site 1 and Creosote Site 3 sites (Walker et al., 2002).

In summary, the available published data reviewed during the development of the conceptual site model clearly indicate that PAH are prevalent in the study area's sediments. There are numerous suspected point sources of PAH, the most notorious of these being related to historic wood treatment and related operations at multiple locations within the study area (Figure 2-2). Given the urbanized areas surrounding the study area, the impact of non-point source-derived PAH ("urban background") is also suspected to have contributed a significant PAH load to the study area's sediments. Potential contribution(s) of PAH are attributable to specific upland naval IR sites. The long operating history and proximity of various naval activities to the river and its western tributaries suggest the potential for PAH derived from naval operations. However, Navy inputs from non-CERCLA activities, if present, are still inclusive of anthropogenic background sources.

2.3.4 Defining Objectives for Study

The review of the Elizabeth River history and available PAH data (Sections 2.3.2 and 2.3.3) helped to focus the objectives for the contaminant source demonstration study. Clearly, the proximity of the Creosote Site 1 Superfund site, a suspected source of creosote(s) and related materials, to Paradise Creek, the Main Shipyard, and the South Gate Annex (Figure 2-2) warrants special consideration. This is particularly true since the potential for transport of PAH impacted sediments along the western shoal due to tidal action and anthropogenic activities is real. In addition, the notoriety of the sizable releases of creosote from Creosote Site 3 raises some concern for the potential for this material to have impacted a broad area, potentially including sediments directly across the channel along the western shoal, i.e., proximal to St. Juliens Creek Annex. Whether the PAH derived from the Creosote Site 3 creosote releases can be distinguished from the Creosote Site 1 creosote releases (as per Walker and Dickhut, 2001) is a very practical question regarding source attribution, the potential for transport of contaminants within the river, and the potential for future contaminant redistribution from creosote lenses.

Another potential concern identified in the review is the contribution, if any, of PAH derived from the western tributaries of the Elizabeth River, namely, Paradise Creek, Blows Creek, and St. Juliens Creek (Figure 2-2). Since these tributaries are flanked by various Navy and other urban properties, it is important to determine if the PAH contained in these sediments have been impacted by PAH. If so, it is important to establish if these PAH can be reasonable attributed to Navy IR activities/sources, or if they are consistent with “urban background,” which is significant in this urbanized and industrialized area (URS Consultants, 1996). Defining what urban background is, in terms of both concentrations of PAH and a chemical “fingerprint(s),” is important since the origin of PAH from these types of sources usually cannot be attributed to any particular party, including the Navy. Furthermore, the potential contribution of this persistent source of PAH would need to be considered in any future remedial designs.

In summary, the conceptual site model for a contaminant source study in the study area has identified four particular objectives for the demonstration study, *viz*., to determine the following:

1. Potential impact of PAH derived from Creosote Site 1 (and adjacent Creosote Site 2 and Creosote Site 3) historic tar refining and wood treatment operations on the sediments proximal to the Main Shipyard and South Gate Annex (or beyond),

2. Evaluation of potential fate and transport of PAH to/from areas proximal to Navy IR sources,

3. Concentrations and chemical character of PAH attributable to urban background within the study area, i.e., the nature of a persistent PAH source(s) not attributable to a specific source, and finally,

4. If the PAH associated with creosote and related materials derived from Creosote Site 1 and 2 area can be distinguished (either chemically or spatially) from the PAH associated with these materials near the former Creosote Site 3 or Creosote Site 4 areas.

2.4 STEP 3: DEVELOPMENT OF A DEFENSIBLE STUDY DESIGN

2.4.1 Sampling Strategy

As noted in Section 1.5.3.1, the sampling strategy for the demonstration study required a balance between meeting the study's objectives (noted above) within the available budget of the project. The cost estimates for the RSC and ACF analyses (based upon Table 1-1) yielded an analytical program that afforded approximately 200 samples for RSC and 50 samples for ACF analyses. Using 200 RSC samples as a benchmark, a strategy for the vertical and horizontal distribution of these samples was developed.

An important matter to consider first was the vertical distribution of PAH in the sediments. This distribution is critical because the impact on cost can be significant, depending on the need for surficial sampling *versus* coring (i.e., less expensive *versus* more expansive). Cores are more expensive to collect and generate multiple samples from a single location, thereby limiting the number of samples available at another location. The results of previous Elizabeth River sediment studies (Section 2.3.2.2) indicated that most PAH contamination resided in the surficial sediments (approximately 0 to 10 cm). Furthermore, cleanup of sediments is often driven by the nature of the surficial sediment where the risk to higher level ecological receptors exists via the food web and/or human health risks from ingestion of potentially exposed aquatic animals. This information allowed our study to focus on the nature of the PAH in the surficial sediments (0 to 10 cm) throughout the study area. However, results from the previous Elizabeth River studies (e.g., Mitra et al., 1999; Huggett et al., 1992) warranted consideration of weathering effects on the PAH signatures of any creosote-impacted sediments. Toward this end, it was warranted to include at least one shallow (1 m) core of the sediments near the two known creosote point sources, *viz*., Creosote Site 1 and Creosote Site 3 (Figure 2-2). This limited need for coring allowed for a greater number of surficial sediment samples in the study.

The spatial distribution of the surficial sampling was largely driven by the specific objectives determined for the study (Section 2.3.4). In other words, the sampling locations were largely driven by professional judgment, rather than any statistically based design. Importantly, the previous studies and a general knowledge of historic dredging of the river's main channel argued that the contaminant source study focus on sediments along the shoal areas of the Elizabeth River (rather than the within the main channel). Thus, the strategy was to generally focus on sediments within these assumedly depositional shoal areas.

To meet the first two project objectives, each suspected point source (Creosote Site 1/2, Creosote Site 3, and Creosote Site 4) had to be sufficiently represented within the sampling design. A particular need for sampling existed for sediments proximal to the potential source of PAH nearest to the naval properties, namely Creosote Site 1 (Figure 2-2), in order to achieve the first objective of the study. To determine the potential impact of creosote on the western shoal sediments proximal to the Main Shipyard and South Gate Annex, sediments from these areas also needed to be well-represented. Unfortunately, with respect to the Main Shipyard, access was somewhat problematic due to the tightened security following September 11, 2001. Thus, surficial sediment sampling within the Main Shipyard was somewhat minimized. To achieve the second objective, it was necessary to fully characterize the sediments proximal to the Creosote Site 3 property, i.e., which had sizable, historic releases of creosote in the early 1960's (Section 2.3.3).

The third objective (Section 2.3.4) required transect-sampling up the western tributaries (Paradise Creek, Blows Creek, and St. Juliens Creek). The interval between sample locations needed to be small enough to recognize a location where a specific source of PAH might exist (e.g., as evidenced by an elevated concentration). In addition, in the wider parts of Paradise and St. Juliens Creeks it seemed important to characterize both sides of the Creeks, since PAH concentration differences might reveal a source on one side *versus* the other. (Blows Creek was narrow and totally within the St. Julians Annex; therefore, this was not necessary.) Although it may have been prudent to include some surface soils or stormwater catchment basin sediments from Navy properties to objectively determine the potential for Navy IR sources, such samples were not included in this study.

The fourth objective, defining "background," required that no part of the study area be completely ignored. This requirement meant that some samples needed to be collected from the eastern tributaries (Scuffletown, Jones, and Gilligans Creeks; Figure 2-2) and regularly along the shoals of the Elizabeth River within the study area. Collection of the sediments from the eastern tributaries provided a basis to (1) recognize any potential contributions from the petroleum handling operations along these creeks (Figure 2-2) and (2) compare any urban background signature to that found in the western tributaries. For example, similar PAH distributions and concentration on opposite sides of the river could indicate a pervasive urban background signature, whereas disparate results could indicate a difference between the eastern and western drainage areas or specific PAH sources along the tributaries. Finally, several samples were necessary at the upriver boundary of the study area, in an area not likely to have been impacted by sources within the study area. Such samples have a greater chance of defining "background" conditions.

The strategy described in the proceeding paragraphs led to the selection of approximately 200 sample locations that are shown in Figure 2-3. Approximately 10 samples were reserved for "*samples of opportunity*" that were determined during the sampling event. In addition to the surface samples, two cores were collected near the Creosote Site 1 site and one core was collected adjacent to the Creosote Site 3 properties. The sample locations provide good spatial coverage within the study area. A higher density of sample locations was placed in the vicinity of Creosote Site 1, given the importance of the first objective (Section 2.3.4). Some modifications to the original sampling locations were made during a preliminary site visit that occurred 2 months before the actual field event. The coordinates for these sample locations and associated chain-of-custody documents are in Appendix A.

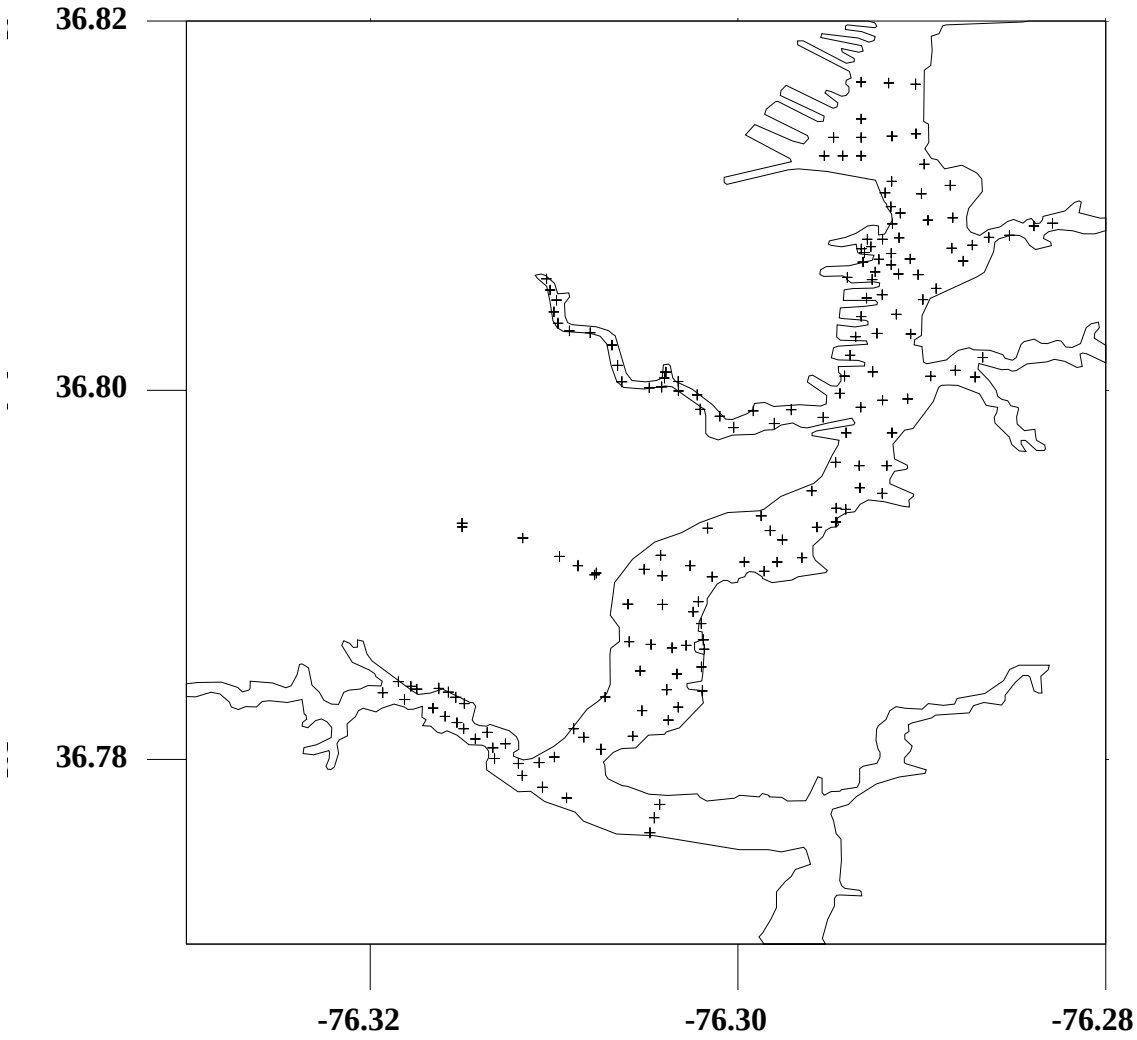

Figure 2-3. Location map showing distribution of approximately 200 samples collected for RSC in demonstration study.

2.4.2 Analytical Strategy

Since PAH were the focus of the demonstration study, the RSC and ACF methods focused on these chemicals. These methods are described in the following sections.

2.4.2.1 RSC Methods

The Rapid Sediment Characterization (RSC) screening method that was used has been demonstrated to be appropriate for PAH in sediments (see past RITS seminar series on NAVFAC website, Fall 2000). The RSC screening method relies upon enzyme-linked immunosorbent assays (ELISAs) that are based on combining selective antibodies with sensitive enzyme reactions to produce analytical systems that can detect very low levels of PAH (or depending on the enzyme, other chemicals; Strategic Diagnostics Inc.; www.sdix.com). Although possible, in this study, the

samples were not analyzed directly in the field, but were first shipped to the Navy's SPAWAR facility in San Diego for RSC (see Section 2.6).

The sediment samples were prepared for analysis by first homogenizing each sample by hand mixing. A 10-g aliquot of the homogenized, wet sediment was dewatered on filter paper and transferred to a 50-ml centrifuge tube with 20 ml of high-grade methanol. Samples were placed on a shaker table for 30 minutes and then centrifuged to separate methanol extracts. The remaining steps followed standard soil immunoassay analyses using Strategic Diagnostics Inc. immunoassay kits and procedures that have been approved by the EPA and have procedures listed in SW-846 manuals (EPA method 4035). Samples were run in batches of 40 samples with each run calibrated by the average of two replicate standard series (phenanthrene for PAH immunoassays). Samples were diluted to run over the calibrated range of 500 to 10,000 ppb for PAH, so the method detection level was set at the lower end of this range. Higher range samples can be run (as was done with most of these Elizabeth River samples) by running further dilutions and calibrating over a higher range. Precision and accuracy were evaluated in a fashion similar to standard immunoassay procedures. The QA/QC followed for the RSC analyses includes 10% of the samples having replicate analyses to determine %RSD. These QA samples include extract and method (separate splits sampled, extracted, and assayed) replicates with the goal being %RSDs <20%. Accuracy was judged by performance of SDI reference standards (phenanthrene) with the goal being 80-120% of expected levels.

In addition to the PAH immunoassays, RSC screening included a measurement of the percent moisture (%moisture) of each sample. This %moisture value will be used to screen for textural variations in the sediment samples, with higher %moisture values corresponding to higher fines content. This measurement allowed for a simple cross-plot of the immunoassay PAH values *versus* the %moisture content to evaluate for an ambient trend in PAH values. Inspection of spatial distribution of the immunoassay PAH and %moisture values, along with the cross-plots of these values, were used to select a subset of samples for ACF (Section 2.4.2.2). As noted above, approximately 200 samples were analyzed by RSC screening.

2.4.2.2 ACF Methods

Samples selected for ACF analysis were shipped to Battelle's Duxbury (MA) Laboratory. All of the processing of the samples was conducted in a clean laboratory environment to minimize contamination. The surficial grab samples were thoroughly homogenized by stirring, using pre-cleaned stainless steel, Teflon®, and Kynar®-coated spatulas. Aliquots of homogenized sediments were removed for analysis for sediment grain size and TOC. These 'bulk' analyses are useful. They provide a basis to normalize and compare the PAH concentrations to determine any effect on PAH concentrations. Grain size was determined as percentages of gravel:sand:silt:clay using Puget Sound Estuary Program (PSEP) protocols and TOC was determined as percent carbon via catalytic combustion after acid removal of inorganic carbonates according to EPA Method 9060.

Aliquots of homogenized sediments were also prepared for ACF via the following:

1. Modified SW-846 EPA Method 8015 and
2. Modified SW-846 EPA Method 8270 (see Table 1-2 and descriptions below).

Before analysis, an aliquot of approximately 50 g (wet weight) was taken from the homogenized samples for ACF analysis and 5 to 10 g (wet weight) for dry-weight (%moisture) determination. The appropriate concentrations of surrogate internal standards (SIS) were added to the samples to be extracted to allow accurate measurement of target organic compounds. The SIS compounds included *o*-terphenyl, naphthalene-d_8, phenanthrene-d_{10}, and chrysene-d_{12}.

Sodium sulfate was then added to absorb water from the sample and facilitate extraction with dichloromethane (DCM). The samples were shaken/tumbled once for a minimum of 12 hours, and then twice for at least 1 hour, using fresh aliquots of 100 mL DCM for each extraction. The combined extract was filtered and dried through a glass fiber filter containing sodium sulfate. The extract was then concentrated to 1 mL using Kuderna-Danish and nitrogen evaporation (*N*-Evap) techniques. The extracts were gravimetrically weighed and processed through a 10-g alumina column in order to obtain a combined aliphatic and aromatic hydrocarbon/unsaturated fraction (F1+F2). Extracts were eluted with 100 mL of DCM, and the combined F1+F2 eluent was then concentrated to 10 mL using the Kuderna-Danish and *N*-Evap techniques described above. Activated copper was added to sediment sample extracts at this point to remove any sulfur that may have been present in the sample. The extracts were then further concentrated to 1 mL and spiked with appropriate concentrations of recovery internal standard (RIS, containing 5α-androstane, fluorene-d_{10}, acenaphthene-d_{10} and benzo[a]pyrene-d_{12}) in preparation for the two ACF analyses.

The following quality control laboratory samples were processed along with each batch of sediment samples:

X 1 procedural blank (PB)
X 1 laboratory control sample (LCS)/ duplicate (LCSD)
X 1 matrix spike (MS)
X 1 laboratory duplicate (DUP)

The combined F1+F2 fractions of sediment extracts were analyzed by GC/FID using a modification of EPA Method 8015 (Table 1-2). The objectives of this analysis were to (1) provide a detailed, high-resolution chromatographic "fingerprint" of the total extractable hydrocarbons fraction of each sediment, and (2) determine the concentration of total extractable hydrocarbons (THC) in each sediment.

This method employs a HP 5890 gas chromatograph containing a 30-m x 0.32-mm i.d. capillary column with a 0.25-µm DB-5 coating. The split/splitless injector was operated in the splitless mode and the oven program is 35°C (5 min) then 6°C/min to 320°C (10 min). Hydrogen was the carrier gas. Before sample analysis, a five-point response factor calibration established the linear range of the analysis and determined the individual response factors (RF_{IX}) of each analyte in the calibration solutions. The calibration solutions were composed of selected C_8 to C_{40} *n*-alkanes, pristane, and phytane. Analyte concentrations in the calibration standard solutions ranged from 1.0 to 100 µg/mL. A mid-level calibration check was performed for every 10 samples. The individual response factors (RF_{IX}) at each calibration solution analyte was used to determine the THC response factor (RF_T), which was based on the average response factors of all the target analytes in the calibration solutions.

The THC in the samples was calculated based on the area response of all the resolved peaks and the unresolved hump from *n*-C_8 to *n*-C_{40}, adjusting for the area response of the SIS and RIS compounds and baseline rise due to column bleed. The THC concentrations in sediments are reported on a mg/kg dry-weight basis.

The combined F1+F2 fractions of sediment extracts were also analyzed by gas chromatography/ mass spectrometry (GC/MS) using a modification of EPA Method 8270 (Table 1-2). The objective of this analysis was to determine the concentration of 43 PAH analytes in each sediment (Table 2-2).

Table 2-2. Inventory of PAH commonly used to distinguish PAH sources. Abbreviations are used in figures later in this section.

Analyte/Analyte Group	Abbr.	Ring #	Analyte/Analyte Group	Abbr.	Ring #
Naphthalene*	N0	2	C3-dibenzothiophenes	D3	3
C1-naphthalenes	N1	2	C4-dibenzothiophenes	D4	3
C2-naphthalenes	N2	2	Fluoranthene*	FL	4
C3-naphthalenes	N3	2	Pyrene*	PY	4
C4-naphthalenes	N4	2	C1-fluoranthenes/pyrenes	FP1	4
Biphenyl	Bph	2	C2-fluoranthenes/pyrenes	FP2	4
Acenaphthylene*	Acl	3	C3-fluoranthenes/pyrenes	FP3	4
Acenaphthene*	Ace	3	Benz(a)anthracene*	BaA	4
Dibenzofuran	DdF	3	Chrysene*	C0	4
Fluorene*	F0	3	C1-chrysenes	C1	4
C1-fluorenes	F1	3	C2-chrysenes	C2	4
C2-fluorenes	F2	3	C3-chrysenes	C3	4
C3-fluorenes	F3	3	C4-chrysenes	C4	4
Anthracene*	AN	3	Benzo(b)fluoranthene*	BbF	5
Phenanthrene*	P0	3	Benzo(k)fluoranthene*	BkF	5
C1-phenanthrenes/anthracenes	P1	3	Benzo(e)pyrene	BeP	5
C2-phenanthrenes/anthracenes	P2	3	Benzo(a)pyrene*	BaP	5
C3-phenanthrenes/anthracenes	P3	3	Perylene	Per	5
C4-phenanthrenes/anthracenes	P4	3	Indeno(1,2,3-c,d)pyrene*	ID	6
Dibenzothiophene	D0	3	Dibenz(a,h)anthracene*	DA	5
C1-dibenzothiophenes	D1	3	Benzo(g,h,i)perylene*	BgP	6
C2-dibenzothiophenes	D2	3			
* Priority pollutant PAH					

Before this analysis, a five-point response factor calibration was run with analyte concentrations in the standard solutions ranging from approximately 0.01 to approximately 10 µg/mL. The samples were bracketed by standard checks analyzed no less frequently than every 10 samples and at the completion of the sequence.

Quantification of individual compounds was done by the method of internal standards, using the RIS compounds as quantification internal standards. Total PAH was determined as the sum of the 43 PAH target compounds (Table 2-2). The homologous series of the various alkylated PAH analytes were quantified by using the straight baseline integration and the response factor of the appropriate parent PAH compound.

The data quality objectives (DQO) for the ACF analyses are outlined in Table 2-3. Quality control sample data that are accepted outside these criteria will be indicated with the appropriate data qualifier, and the rationale for accepting the analysis will be documented.

Table 2-3. Summary of data quality objectives.

QC Measurement	Frequency	Acceptability Limits	Corrective Action
Surrogate recovery	Per sample	40-120% (8015M; 8270M)	Reanalysis or justification documented
Procedural blank	1 per batch of 20 samples	No target analytes > 5X RL	Reanalysis or justification documented
Blank Spike	1 per batch of 20 samples	40-120% (8015M; 8270M)	Reanalysis or justification documented
Matrix Spike	1 set per batch of 20 (sed.) samples	40-120% (8015M; 8270M)	Reanalysis or justification documented
Laboratory Sample Duplicate	1 per batch of 20 (sed.) samples	+/- 25% PD for 90% of the target analytes that are present at concentrations >10x MDL	Reanalysis or justification documented
Instrument Calibration	Initial 5-point	±20% RSD single compound average of 15%	Re-calibration or justification documented
Instrument Calibration	Continuing checks every 10 samples and at completion of sequence	±25% PD for 90% of the target analytes	Remedial maintenance, new initial calibration, or justification documented

RL = reporting limit, the concentration of the lowest calibration standard run for initial calibration. Where a compound or element is detected below the RL the result is qualified with a “J” to indicate that the value is below the lower limit of the linear range.

2.5 STEP 4: SAMPLE COLLECTION METHODS

Most sediment samples were collected over a 3-day period of 24–27 June 2002. Two small (16-foot) flatbottom boats were rented locally to provide access to the sampling areas. Before the sampling event, sampling grids were mapped with navigational software on two laptop computers. One computer and GPS unit were carried on each boat to allow positioning. Since these boats did not have power winch capabilities, small surface grabs (Petite Ponars and similar lightweight grabs) were used to collect the sediment. Multiple grabs (2 to 4 at each location) were composited in a large stainless steel bowl to provide a sufficient homogeneous sample for RSC and ACF analyses. Two cores were collected at Creosote Site 1 (at AW03) and one core was collected at Creosote Site 3 (at ER01). Two-inch core liners were hammered into the sediment in shallow water to recover 30- to 50-cm cores, and each core was sectioned into 10-cm intervals. Due to some access problems, some

of the NS series samples and Blows Creek (BC) series samples were collected after the June 2002 sampling period, but used the same equipment and protocols.

The complete chain-of-custody documents for the samples included in this study are found in Appendix A.

2.6 SAMPLE ANALYSIS LOGISTICS

The sediment samples collected were all shipped to the Navy's SPAWAR facility in San Diego, California, for RSC analysis under the controlled conditions of a laboratory. Upon arrival, the samples were stored refrigerated at 4°C until the time of their analysis. Unused aliquots from each sample were immediately frozen at -20°C until the RSC results for all the samples were complete. Because of the extended interval of time between the main sampling event (24–27 June 2002) and the Blows Creek sampling event (22–23 August 2002), it was necessary to delay selection of the final set of samples for ACF until early October 2002. The basis for the selection of samples for ACF followed a review of the RSC data as described in Section 2.7.1.1).

The samples selected for ACF were shipped frozen to Battelle's laboratory in Duxbury, Massachusetts. The complete set of samples arrived in Duxbury in two batches on 21 and 30 August 2002. These sediments had been collected as early as 24 June, and thus, were approximately 2 months 'old' upon arrival at the laboratory. This arrival was well beyond the standard 14-day holding time for semi-volatile organics in sediments. However, this was considered adequate for this demonstration study since the samples were stored frozen (-20°C) during most of the time between their collection and analysis by Battelle. Further discussion on this point was given in Section 1.5.5.1.

2.7 STEPS 5 AND 6: SAMPLE RESULTS

2.7.1 RSC Data

The RSC results are depicted in Figure 2-4. In this figure, the site symbol sizes are proportional to the screening value as calibrated to the sum of the 16 priority PAH compounds. Figure 2-5 shows the relationship between the concentrations of PAH determined via screening (RSC) data and the ACF data on the samples run in the laboratory for this study. The good correlation (r-squared >0.9) confirms the results seen at other locations, and indicates that RSC data can be used to screen for concentration gradients around the site to assist in selection of samples for ACF. The most apparent concentration gradient relationships seen in Figure 2-4 are the obvious locations of the former creosote sites, *viz*., Creosote Site 3 to the south and Creosote Site 1 to the north. There are strong concentration gradients away from these two sites. The majority of Elizabeth River sites outside these two former creosote-handling sites show an ambient PAH level of 20 to 30 mg/kg. The tributary creeks also have significantly lower concentrations of RSC TPAH relative to these two former creosote-handling facilities.

The original study design had a grid of samples laid out along the South Branch of the Elizabeth River and associated side creeks, with higher density grids around suspected source areas such as the former creosote-handling operations at Creosote Sites 1 and 3 (Figure 2-3). It was intended that by placing a higher density of samples in specific areas it would be possible to have sufficient numbers of samples to make contour maps. Due to wind and current conditions, the actual sampling locations do not exactly match the original grid locations but still allow contouring by interpolation methods such as Kriging. The latter ACF sections will concentrate on the Creosote Site 1 and 2 area and show

additional maps. Figure 2-6 shows a contour map of RSC TPAH concentrations around the Creosote Site 3 location. This map is provided as an example of how this type of map can provide more spatial detail and aid in the selection of samples for ACF. The former Creosote Site 3 location on the eastern shoal of the river shows apparent high concentrations of PAH to the north and south of the original site. These high concentrations could be due to re-suspension of sediments due to tidal dispersion, episodic storm events, or ship/tug movements. The main point is that mapping the 200 RSC TPAH data points allows spatial relationships to be revealed, which leads to obvious questions that can be tested with ACF. For example, there appears to be a "plume" of high PAH sediment downstream from Creosote Site 3 that extends all the way to the former Creosote Site 4 (Figure 2-4). How much contribution might be assigned to each potential source? These are the types of questions that can be raised by these types of maps, and form the basis for sample selection for ACF samples to address these questions.

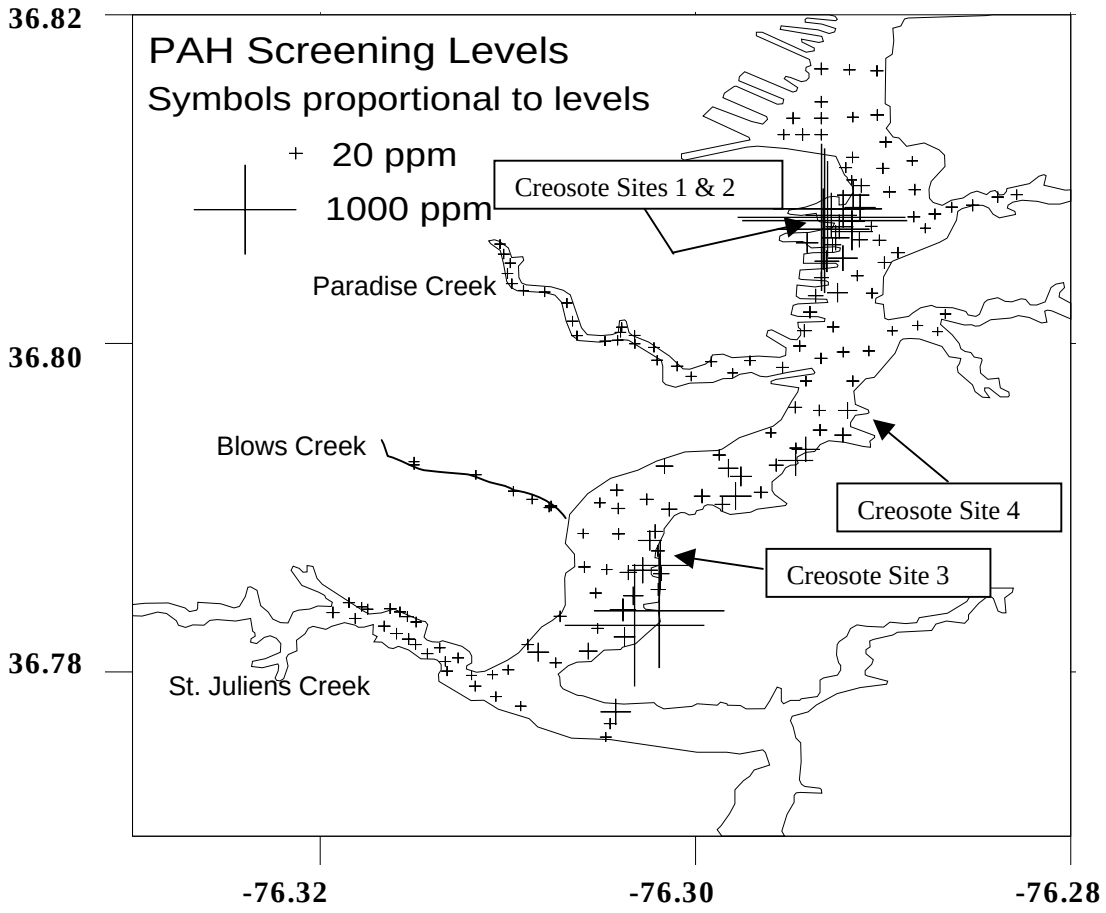

Figure 2-4. Map showing PAH concentrations determined by RSC screening of sediments. Map symbols are proportional to screening levels calibrated to the sum of 16 priority pollutant PAH.

2.7.1.1 Selection of Samples for ACF

As discussed above, there are obvious spatial and concentration relationships in the RSC data that will assist in selection of ACF samples. Out of approximately 200 RSC samples, 50 samples were selected to continue on for full ACF analysis. There were many objectives for this fingerprinting study that played into the selection process. One objective was to obtain coverage over the spatial and concentration ranges observed in the data. Spatial representations like the graduated symbol and contour maps discussed in the previous section can help with this concern. Another concern was to demonstrate the effects of the former Creosote Site 1 creosote site on sediments adjacent to Naval properties. Due to concerns about possible weathering effects interfering with fingerprinting, two cores from Creosote Site 1 (at AW03) and one from Creosote Site 3 (at ER01) were collected and sectioned into 10-cm layers. It was decided to put more effort into looking at the relationships between the former Creosote Site 1 creosote facility and the surrounding naval properties; so more samples were needed in these areas. To assist in sample selection, additional cross-plots of RSC chemical and physical properties may be useful. One plot plotted RSC chemical values (PAH corrected to the sum of 16 priority PAH) on the Y-axis *versus* physical properties (% moisture, Fe content, etc. as proxies for sediment texture or grain size) on the X-axis (Figure 2-7). This type of plot gives PAH concentration correlation information related to a physical and/or easily measurable surrogate parameter, so some measure of the ambient level of PAH is possible. The short dashed line shows the relationship of South Branch (SB) Elizabeth River samples that are away from suspected source areas, and serves as a measure of the "ambient trend." In industrial waterways like the Elizabeth River, contaminants are mixed out away from distinct source areas to an elevated, ambient level that exists throughout the region. In this case, it appears that finer-grained sediments throughout this section of the Southern Branch have up to approximately 30,000 μg/kg of $TPAH_{RSC}$ (sum of 16 priority PAH; Figure 2-7). In addition to obvious source areas like the Creosote Site 1 and Creosote Site 3 facilities, a sufficient number of sediment samples outside known or suspected areas of impact were also selected to represent this ambient trend. Note that many of the NS samples on this plot are at or just above the 30,000 μg/kg $TPAH_{RSC}$ level (Figure 2-7). This raises the question of the impact of the adjacent Creosote Site 1 creosote site on sediments proximal to the Navy properties, and if these shipyard samples are elevated above ambient levels, what is the source of these additional PAH? Since it was decided to focus on the Shipyard and Creosote Site 1 areas, 9 out of 18 NS samples (50%) and 7 out of 12 AW samples (58%) were selected for ACF characterization. Lower percentages of RSC-screened samples were selected from the other areas, although each area was given some representation in order to cover the spatial and concentration ranges observed in the data.

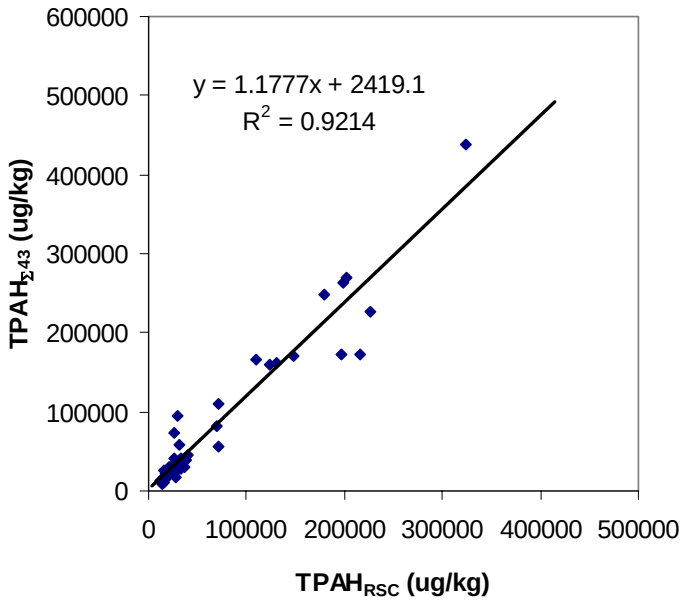

Figure 2-5. Correlation between total PAH determined by RSC ($TPAH_{RSC}$; corrected to sum of 16 priority pollutant PAH only) and by ACF ($TPAH_{\Sigma 43}$, includes sum of 43 PAH analytes in Table 2-2). Reduced scale here does not include AW and ER surface and core samples from obvious source areas that were above the calibrated RSC range of 500,000 μg/kg.

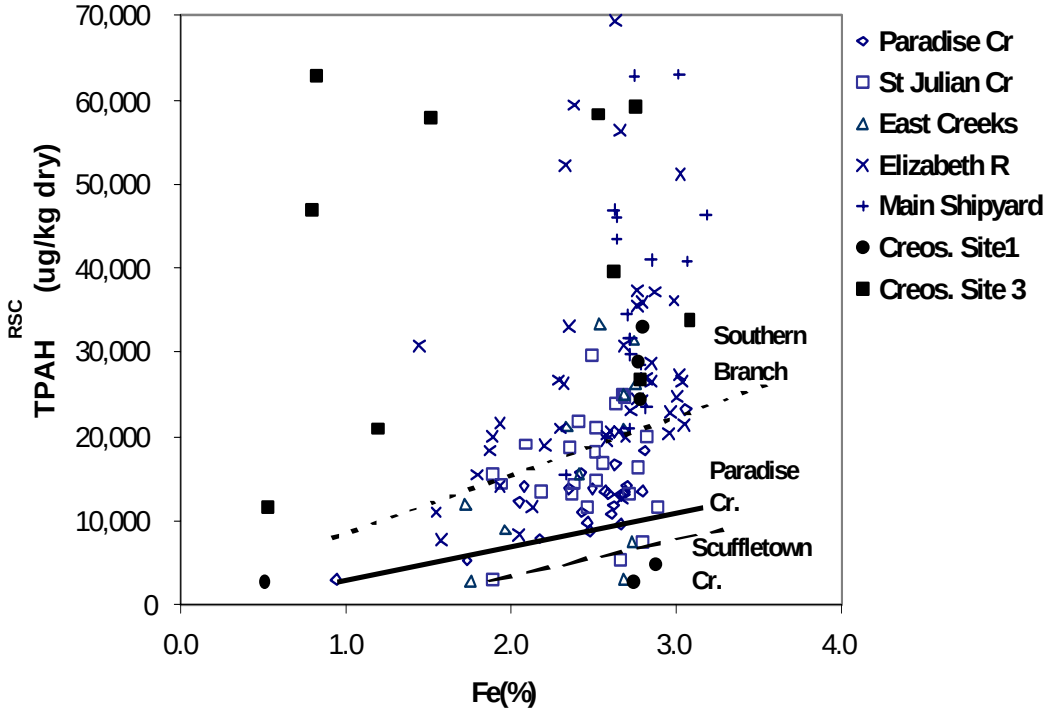

Figure 2-6. Example of a contour map showing spatial relationships in total concentrations of 16 priority pollutant PAH determined through RSC ($TPAH_{RSC}$) for sediments near and downriver from the former Creosote Site 3.

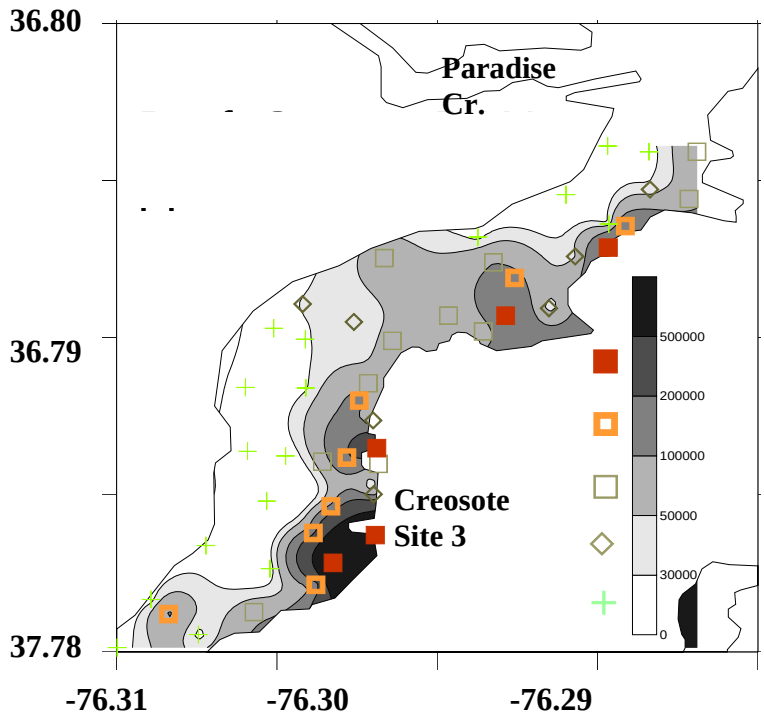

Figure 2-7. Example cross-plot of RSC chemical versus physical properties to assist in sample selection for ACF (see discussion in text).

2.7.2 TOC and Grain Size

Tabulated grain size and TOC data for the 50 sediment samples analyzed via ACF appear in Appendix C. (Note that there was insufficient sample for grain size analysis at one location, SB20.) Most samples (n = 28) contained between 50 and 90 percent of fine-grained sediments (defined as sum of silt and clay fractions < 62.5 μm). Eight of the nine samples containing more than 90% fine-grained sediments occurred within the western shoal sediments between Creosote Site 1 and the mouth of Paradise Creek (NS03, NS05, NS09, NS10, NS11, NS13, SB03, and PC24), perhaps suggesting that this area is depositional and relatively quiescent. The 12 coarsest grained sediments (<50% fines) were widely distributed throughout the study area, but the four coarsest sediments occurred within the cores from the area proximal to the Creosote Site 1 (AW03-C2-1, -2, and -3) and Creosote Site 3 properties (ER01-C-1). These cores also contained notable concentrations of creosote (see below), perhaps indicating that their "coarse" nature was (at least in part) attributable to the 'clumping' of mineral grains due to the presence of creosote. Finally, it was evident that grain size tended to increase downstream (i.e., finer grained near the headwaters) within Paradise and Scuffletown Creeks, whereas no trend was evident in St. Juliens Creek.

TOC values for the sediments studied ranged from 0.86 to 10.44 percent, although most sediments contained between 2.0 and 5.0 percent (n = 33). The highest TOC contents were found in the creosote-laden cores from sediments proximal to the Creosote Site 1 and Creosote Site 3 properties. Excluding these core sediments, there was a weak positive relationship between the %TOC and %fines among the remaining sediments studied (Figure 2-8). This weak relationship indicates that the %fines was a generally poor proxy for TOC. No obvious differences could be observed between the tributary sediments or shoal sediments, however, it is notable that the two Blows Creek sediments (BC#2 and BC#5) generally contained higher %TOC than other sediments of similar grain size. The reason for this is likely to be due to a greater abundance of plant debris in the Blow Creek sediments (as is evident in the THC fingerprints; see below).

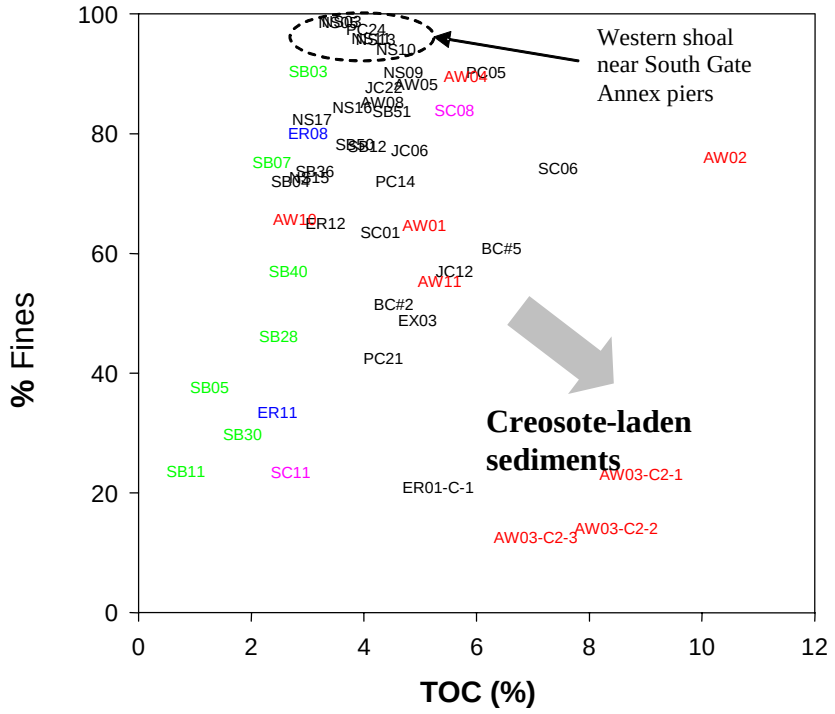

Figure 2-8. Cross-plot of percent TOC versus percent fines in the Elizabeth River sediments studied.

2.7.3 Assessment of THC Concentrations

GC/FID analysis provides an excellent basis for assessing the distribution and concentration of total extractable hydrocarbons (THCs) that are present in sediment samples. The tabulated THC concentrations for each sample studied are in Table 2-4 (discussed later in this Section and in Appendix D). Some generalities regarding these concentration data are described in the following paragraphs.

The THC concentrations for the sediments studied (n = 53, including duplicates) ranged from 13,090 to 142 mg/kg (dry weight). Half of the sediments contained THC between 560 and 2175 mg/kg, with the median value of all sediments of 913 mg/kg (Figure 2-9). The six samples that contained more than 5000 mg/kg of THC were all from sediments located near the Creosote Site 1 (AW02, AW03-C2-1, AW03-C2-3, AW04) and Creosote Site 3 properties (EX03 and ER01-C-1).

These same samples had the elevated %TOC (described above) that suggests the presence of weathered creosote (a feature that further is supported by the GC/FID fingerprinting data described below). The highest of these samples contained 13,090 mg/kg THC (or 1.3 wt%), which suggests the presence of pure phase creosote in these sediments. A generally poor correlation between THC and TOC ($r^2 = 0.37$) indicated that TOC is not a good proxy for the total concentration of extractable hydrocarbons in these sediments.

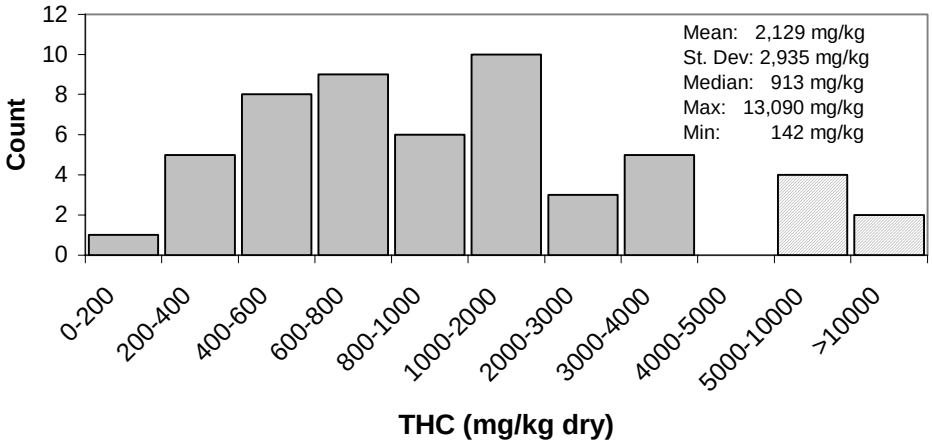

Figure 2-9. Histogram showing population of THC in sediments studied. Hatching indicates sediments obviously containing creosote.

The spatial distribution of THC in sediments within the study area is shown in Figure 2-10. The symbol sizes shown in Figure 2-10 are proportional to the THC concentrations, and thereby give a visual assessment of the locations where the highest and lowest THC concentrations occurred. The highest THC concentrations were observed in sediments proximal to the former wood treating facilities of Creosote Site 1/Creosote Site 2 and Creosote Site 3 (Figure 2-10). Other sediments containing higher THC concentrations were observed in the sediments near the South Gate Annex (near the retired fleet) south of the Creosote Site 1 property. Recall that sediments along this part of the western shoal were also relatively finer grained, potentially suggesting that this was an area of deposition (see above). Notably, the THC was generally low in the sediments within and nearest the NNSY, i.e., around the point of land (railroad bridge) from Creosote Sites 1 and 2. This spatial distribution of THC suggests that the Creosote Site 1 and/or Creosote Site 2 operations may be a source of hydrocarbons that have impacted the western shoal sediments proximal to South Gate Annex, but may not have impacted NNSY sediments. This question is further addressed below using the more detailed fingerprinting data.

The tributaries to the Southern Branch of the Elizabeth River contained sediments with THC concentrations mostly lower than were observed within the shoals of the main river. The highest concentrations of THC were observed in sediments nearest the heads of the tributaries (Paradise Creek, PC05, 2250 mg/kg; and Scuffletown Creek, SC08, 1406 mg/kg) and these decreased toward their mouths (Figure 2-10). The St. Juliens Creek and Gilligans Creek sediments studied contained very low concentrations of THC (<569 mg/kg). Collectively, these observations argue against a significant source(s) of hydrocarbons entering the main river's sediment from any of the tributaries studied.

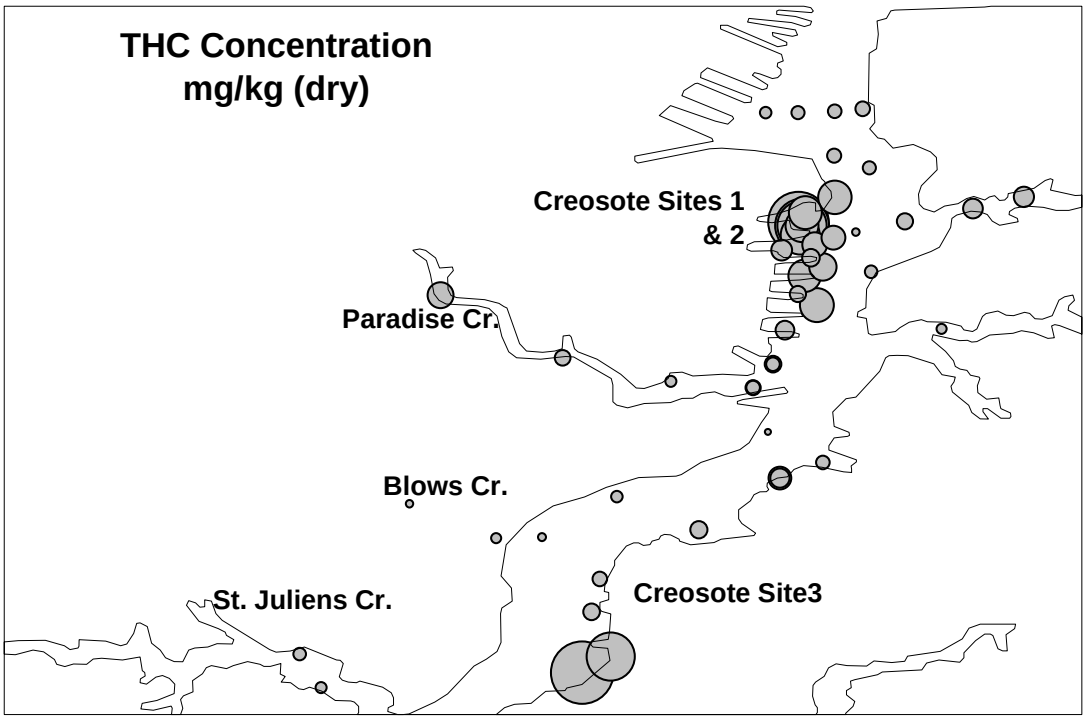

Figure 2-10. Map depicting THC measured in sediments studied. Bubble size increases with THC concentration. See text for description.

2.7.4 Assessment of THC Chromatographic "Fingerprints"

Examination of the detailed chromatographic fingerprints provided significant insights to the specific nature of the extractable hydrocarbons. Copies of the GC/FID chromatograms for each sediment appear in Appendix D. Visual inspection of these chromatograms revealed that they generally fall into three broad categories, namely,

1. Urban background dominated,
2. Creosote or creosote-tar blend dominated, or
3. Mixtures of these.

Examples of these categories are shown in Figures 2-11, 2-12, and 2-13, respectively.

Figure 2-11 shows the GC/FID fingerprints for three sediments that exhibit features consistent with those attributable to urban background. These sediments each occur within tributaries to the Southern Branch of the Elizabeth River and exhibit two characteristic chromatographic features, namely, (1) numerous later-eluting resolved peaks, and (2) an unresolved complex mixture (UCM) 'hump,' mostly within the residual oil range. These gross features have been previously observed in sediments impacted with urban background from many areas (Hostettler et al., 1999; Wade and Quinn, 1979; Barrick et al., 1980; Eganhouse et al., 1982). The resolved peaks represent various non-alkylated three to six-ring PAH, which are indicative of the combustion-derived particles in engine exhaust (Laflamme and Hites, 1978; Westerholm et al., 1988; Oahn et al., 1999). The UCM 'hump' is characteristic of a (mostly) residual range petroleum, such as lubricating, hydraulic, and waste oil(s), which also are expected to occur in urban runoff (Gogou et al., 2000). Clearly, most of the mass of THC occurs within the UCM, whereas the PAH represent a fairly small fraction of the mass. Also present in some sediments (e.g., BC-02; not shown) are numerous odd-dominated normal hydrocarbons (n-C_{27}, n-C_{29}, n-C_{31}) associated with plant waxes derived from modern leaf debris in the sediments (Prahl and Carpenter, 1984). (Recall that the Blows Creek sediments had slightly higher TOC due to such plant debris; see above.) Although there are minor differences among the sediments exhibiting these "urban background features," these differences are not unexpected, given the different drainage areas in the region.

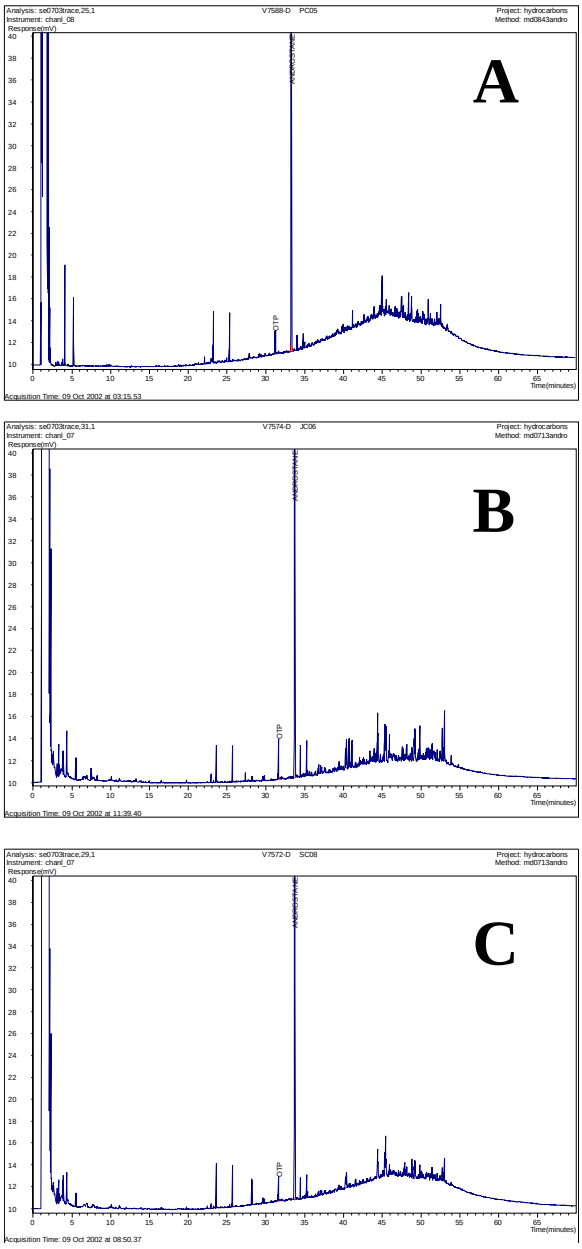

Figure 2-11. GC/FID chromatograms of extractable hydrocarbons in sediments containing hydrocarbon attributable to urban background; (A) Paradise Creek (PC05), (B) St. Juliens Creek (JC06), and (C) Scuffletown Creek (SC08). ***** = Int. Stand.

Figure 2-12 shows the GC/FID fingerprints for five sediments that exhibit chromatographic features consistent with variably weathered creosote or a related tar distillate. Each sediment's fingerprint is dominated by discrete peaks that (upon confirmation with the GC/MS data described later in this section) are identified as various PAH. No significant UCM is present, indicating the

absence of a significant petroleum-derived component. The chromatographic character of the extractable hydrocarbons in these sediments is typical of various liquid products formed during the liquefaction/conversion of coal (Zander, 1995). Coal tar, the primary coal-derived liquid generated during the production of manufactured gas (Gas Research Institute, 1987), was commonly distilled into numerous fractions that varied principally in the boiling range. Among these products was creosote, a common wood preservative, which normally exhibits a predominance of two- and three-ring PAH compounds (Hale and Aneiro, 1997). Creosote and various creosote-coal tar blends were commonly used by the wood preservation industry in the last century (Broese van Groenou et al., 1951). Thus, given the operational history of the Creosote Site 1, Creosote Site 3, and Creosote Site 4 wood preservative facilities (Section 2.3.2.2) and the results of previous studies (Section 2.3.3), the presence of creosote or creosote-tar blends in sediments of the Southern Branch is not unexpected. In addition, since it is also reported that some tar distillation occurred early in operations at the Creosote Site 1 property, it is also possible that other related tar distillates or residues might occur in this area.

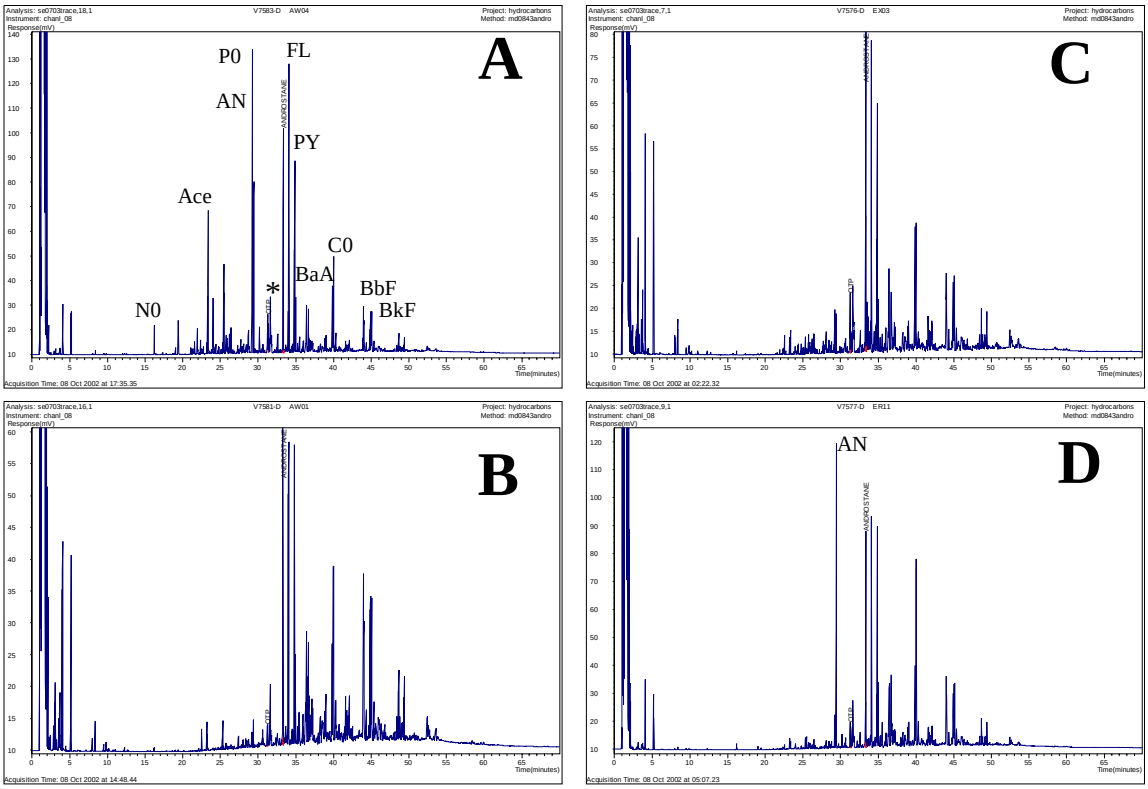

Figure 2-12. GC/FID chromatograms of extractable hydrocarbons in sediments containing creosote; (A) moderately weathered creosote near Creosote Site 1 (AW04), (B) severely weathered creosote near Creosote Site 1 (AW01), (C) severely weathered creosote near Creosote Site 3 (EX03), and (D) moderately weathered creosote near Creosote Site 4 (ER11). * = Int. Stand. For other compound abbreviations, see Table 2-2.

Comparisons among the sediments containing creosote-dominated hydrocarbons (e.g., Figure 2-12) reveal differences in their boiling ranges that, although these differences may be partly controlled by the particular type of creosote or creosote-tar blend, are most likely attributable to environmental weathering. Figures 2-12 A and B show two creosotes from the Creosote Site 1 area

that exhibit the range of weathering observed. Notably, even the least weathered example encountered (Figure 2-12 A; AW04) had relatively low concentrations of two-ring PAH compared to unweathered creosote (e.g., Merrill and Wade, 1985; Brenner et al., 2002), indicating that these have been preferentially removed/lost. With increased weathering (Figure 2-12 B), there are additional losses of the lower molecular weight PAH (e.g., naphthalenes, acenaphthalene). As a result, all the creosotes and creosote-blends from the entire study area have relatively low abundances of two- and three-ring PAH. Based upon the scale of creosote weathering reported by Brenner et al. (2002), the sediments studied can be said to contain only moderately to severely weathered creosotes or creosote-tar mixtures. Thus, it is notable that there was no unweathered (fresh) or even mildly weathered creasote observed, which is contrary to what was indicated by Huggett et al. (1992). These findings are not unexpected since wood treatment operations have ceased in the area, upland sources have been eliminated, and the fact that the current data reflects PAH concentrations after 10 years of weathering since the previous work by Huggett.

The other chromatograms shown in Figure 2-12 suggest that some minor differences may exist among the specific types of creosote or creosote-tar blends found in sediments proximal to the Creosote Sites 1 and 2, Creosote Site 3, and Creosote Site 4 areas. For example, the creosote from sediment near Creosote Site 4 (ER11; Figure 2-12 D) sediment contains an exceptionally high concentration of anthracene (relative to phenanthrene and to fluoranthene or pyrene). This feature is not reasonably attributable to weathering and is more likely related to the specific nature of the creosote in the ER11 sediment (i.e., proximal to the former Creosote Site 4). In particular, excess anthracene could be attributed to the presence/blending of an anthracene-enriched liquor (a common dyestuff feedstock produced by coal tar refiners) into creosote (McNeil, 1966). Further distinctions among the specific types of creosotes from sediments throughout the study area will be better assessed using the quantitative PAH data described below (see Section 2.7.7). Due to the noted affects of weathering observed (Figure 2-12), any comparison should rely most heavily on the higher molecular weight PAH, i.e., those least affected by environmental weathering.

The third chromatographic category recognized among the sediments studied included those containing mixtures of urban background and creosote/creosote blends. These sediments appear to represent a spectrum of mixtures, mostly attributable to the amount and degree of weathering of the creosote component within the mixture. Figure 2-13 shows five examples of sediments containing different mixtures of urban background and creosote/creosote blends, the latter of which exhibit various degrees of weathering. The relative magnitude of the UCM ‘hump’ provides one measure of the relative abundance of urban background, since this petroleum-derived component is a characteristic feature of urban background (see above). With increasing abundance of creosote (or creosote-blends), the UCM ‘hump’ becomes suppressed in the chromatograms. The variable degrees of weathering of the creosote fractions (as described above) also alter the appearance of the chromatograms.

Finally, since the chromatographic characteristics of different types of petroleum products is well-established (e.g., Stout et al., 2002a), note that a few sediments exhibited evidence of the presence of petroleum in excess of what is reasonably attributable to urban background. Examples of these are shown in Figure 2-14. The first type of petroleum was observed in the SB07 sediment collected along the eastern shoal, across the channel from the Creosote Site 1 property (Figure 2-3). The SB07 sediment contained a mixture of urban background along with a trace amount of creosote (akin to SB11 in Figure 2-13 A), but it also contained a broad boiling petroleum product that contains a series of *n*-alkanes ranging from approximately $n\text{-}C_{12}$ to $n\text{-}C_{40}$ (Figure 2-14 A). Though somewhat unspecific in its character, this distribution would be consistent with a heavy fuel oil (e.g., fuel oil #6 or

bunker C) or even a weathered crude oil. The presence of the *n*-alkanes, which are relatively susceptible to biodegradation, suggests that the heavy fuel oil in SB07 is not significantly weathered. A similar broad boiling petroleum, though somewhat more weathered, was also evident in two sediments from the western shoal near the South Gate Annex (NS10 and NS16).

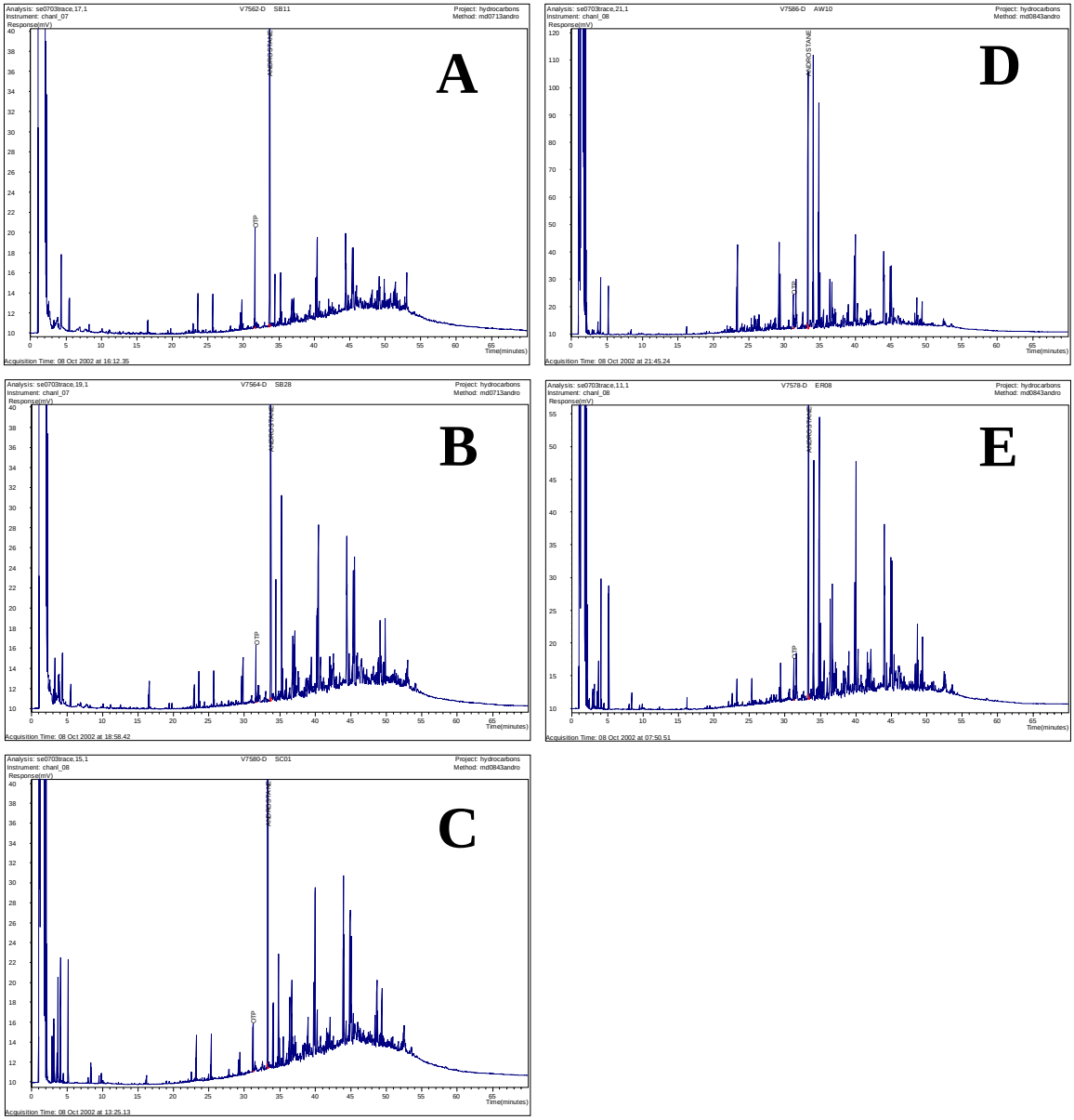

Figure 2-13. GC/FID chromatograms of extractable hydrocarbons in sediments containing mixtures of (A) urban background and trace quantities of creosote (SB-11), (B) urban background and a moderate quantity of moderately weathered creosote (SB-28), (C) urban background and a moderate quantity of severely weathered creosote (SC-01), (D) urban background and a significant quantity of moderately weathered creosote (AW-10), and (E) urban background and a significant quantity of severely weathered creosote (ER-08). * = Int. Stand. For other compound abbreviations, see Table 2-2.

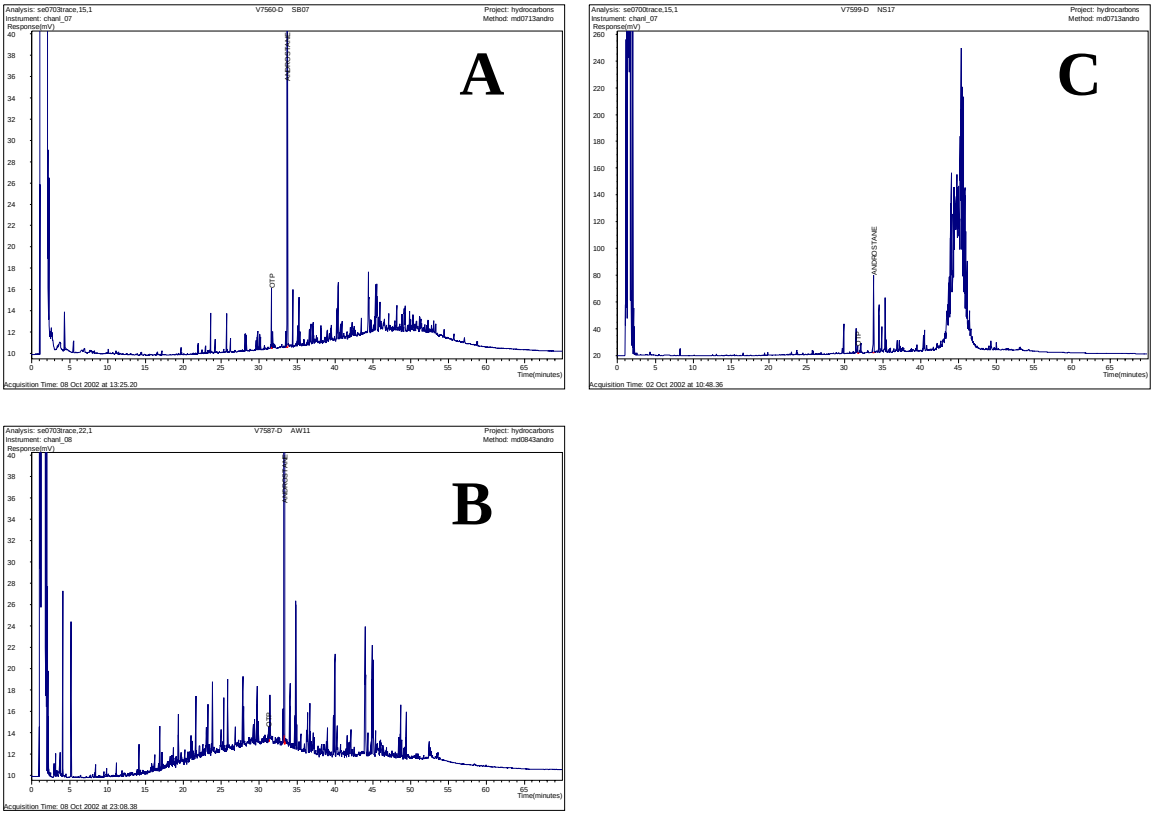

Figure 2-14. GC/FID chromatograms of extractable hydrocarbons in three sediments containing evidence of petroleum; (A) broad boiling petroleum (e.g., fuel oil #6) in SB07, (B) unweathered middle distillate (e.g., diesel fuel #2) in AW11, and (C) specialty oil in NS17.

A distinct petroleum product was observed in a western shoal sediment just north of the Jordan Bridge Creosote Site 1 and Creosote Site 1 at AW11. This sediment clearly contained a middle distillate petroleum product consistent with marine diesel, diesel fuel #2, or fuel oil #2. This sediment also contained an abundance of *n*-alkanes, which indicates that the middle distillate fuel had not experienced a significant degree of weathering. This distillate fuel was only evident at this location. Finally, the NS17 sediment from the western shoal near Pier 17 in the South Gate Annex contained a very narrow-boiling (C_{27}-C_{30}) petroleum product. This material is quite unusual and is most likely attributable to some sort of specialty grease, hydraulic oil, or transformer oil. This product was unique to this location.

In summary, the chromatographic character of the THC for the sediments throughout the study area (described above) provides a good basis for understanding the nature of the potential PAH sources in the study area. Table 2-4 summarizes the chromatographic character interpreted for each sample and for convenience lists the THC and $TPAH_{\Sigma 43}$[12] concentrations measured. The percentage of the THC comprised of the TPAH is also reported.[13] As can be seen, the sediment samples dominated by creosote or creosote blends contained the highest concentrations of TPAH and also had the highest %THC as PAH. Oppositely, those sediments dominated by urban background contained the lowest concentrations of TPAH, and had the lowest percentages of THC attributable to PAH.

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[12] $TPAH_{\Sigma 43}$ refers to the total concentration of PAH analytes listed in Table 2-2.

[13] %TPH as PAH = [(mg/kg $PAH_{\Sigma 43}$/mg/kg TPH)] x 100

Most mixed samples exhibit intermediate features. Notably, those few sediments containing a recognizable petroleum fraction (which tends to increase the THC concentration without increasing the TPAH concentration) have lower %THC as PAH compared to similar samples that did not contain petroleum.

Table 2-4. Summary of Chromatographic Character Categories, THC and $TPAH_{\Sigma 43}$ concentrations for the sediment samples studied by ACF. Samples listed by chromatographic character.

Client Sample ID	GC/FID Chromatographic Character	THC (mg/kg)	$TPAH_{\Sigma 43}$ (mg/kg)	%THC as PAH
AW01	Creosote or Creosote Blend Dominant	3,621	867	24
AW02	Creosote or Creosote Blend Dominant	12,305	3,998	32
EX03	Creosote or Creosote Blend Dominant	13,090	4,275	33
ER01-C-1	Creosote or Creosote Blend Dominant	7,799	2,549	33
ER11-DUP	Creosote or Creosote Blend Dominant	1,247	419	34
AW03-C2-1	Creosote or Creosote Blend Dominant	8,124	3,130	39
ER11	Creosote or Creosote Blend Dominant	1,744	761	44
AW04	Creosote or Creosote Blend Dominant	5,142	2,247	44
AW03-C2-2	Creosote or Creosote Blend Dominant	3,685	1,839	50
AW03-C2-3	Creosote or Creosote Blend Dominant	9,716	7,084	73
AW05	Urban Background w/ Heavy Creosote	1,480	159	11
AW08	Urban Background w/ Heavy Creosote	2,102	247	12
AW10	Urban Background w/ Heavy Creosote	1,935	439	23
AW11	Urban Background w/ Heavy Creosote and middle distillate petroleum	3,770	227	6
ER08	Urban Background w/ Heavy Creosote	1,029	172	17
NS10	Urban Background w/ Heavy Creosote and trace broad boiling petroleum	3,559	170	5
NS16	Urban Background w/ Heavy Creosote and trace broad boiling petroleum	2,575	172	7
NS17	Urban Background w/ Heavy Creosote and specialty petroleum	3,892	165	4
SB36	Urban Background w/ Heavy Creosote	751	161	21
SB40	Urban Background w/ Heavy Creosote	979	264	27
SB51	Urban Background w/ Heavy Creosote	1,950	271	14
ER12	Urban Background w/ Moderate Creosote	634	83	13
NS09	Urban Background w/ Moderate Creosote	1,066	110	10
SB05	Urban Background w/ Moderate Creosote	674	96	14
SB20	Urban Background w/ Moderate Creosote	142	18	13
SB28	Urban Background w/ Moderate Creosote	492	55	11

Table 2-4. Summary of Chromatographic Character Categories, THC and $TPAH_{\Sigma 43}$ concentrations for the sediment samples studied by ACF. Samples listed by chromatographic character. (continued)

Client Sample ID	GC/FID Chromatographic Character	THC (mg/kg)	$TPAH_{\Sigma 43}$ (mg/kg)	%THC as PAH
SC01	Urban Background w/ Moderate Creosote	883	73	8
NS13	Urban Background w/ Trace Creosote	1,175	45	4
NS15	Urban Background w/ Trace Creosote	950	36	4
PC24	Urban Background w/ Trace Creosote	648	41	6
SB11	Urban Background w/ Trace Creosote	203	12	6
SB12	Urban Background w/ Trace Creosote	552	41	7
SB30	Urban Background w/ Trace Creosote	223	18	8
BC02	Urban Background Dominant	204	8	4
BC05	Urban Background Dominant	357	27	8
JC06	Urban Background Dominant	549	20	4
JC12	Urban Background Dominant	436	33	8
JC22	Urban Background Dominant	569	30	5
NS03	Urban Background Dominant	472	27	6
NS05	Urban Background Dominant	602	30	5
NS11	Urban Background Dominant	913	40	4
NS15-DUP	Urban Background Dominant	668	31	5
PC05	Urban Background Dominant	2,250	18	1
PC14	Urban Background Dominant	873	9	1
PC21	Urban Background Dominant	445	12	3
PC24-DUP	Urban Background Dominant	805	34	4
SB03	Urban Background Dominant	634	21	3
SB04	Urban Background Dominant	732	28	4
SB07	Urban Background Dominant w/ broad boiling petroleum	602	29	5
SB50	Urban Background Dominant	499	25	5
SC06	Urban Background Dominant	1,356	59	4
SC08	Urban Background Dominant	1,406	26	2
SC11	Urban Background Dominant	345	13	4

2.7.5 Assessment of PAH Concentrations

The tabulated $TPAH_{\Sigma 43}$ concentrations for the samples studied were presented in Table 2-4. The complete data tables including the concentrations of individual PAH analytes are in Appendix E, along with histograms of each. Some generalities regarding the PAH concentration data are described in the following paragraphs.

The $TPAH_{\Sigma 43}$ concentrations for the sediments studied (n = 53, including duplicates) ranged from 7,083 to 7.7 mg/kg (dry) and had a median concentration of 55.4 mg/kg. The population of concentrations is shown in Figure 2-15, which is color-coded based upon the predominant chromatographic character of the extractable hydrocarbons (as inventoried in Table 2-4). As might be predicted, the sediments with extractable hydrocarbons dominated by creosote or creosote blends occur at the upper end of the population whereas the sediments dominated by urban background occur at the lower end (Figure 2-15). This now obvious result shows the importance of including GC/FID fingerprinting in any assessment of PAH sources in sediments.

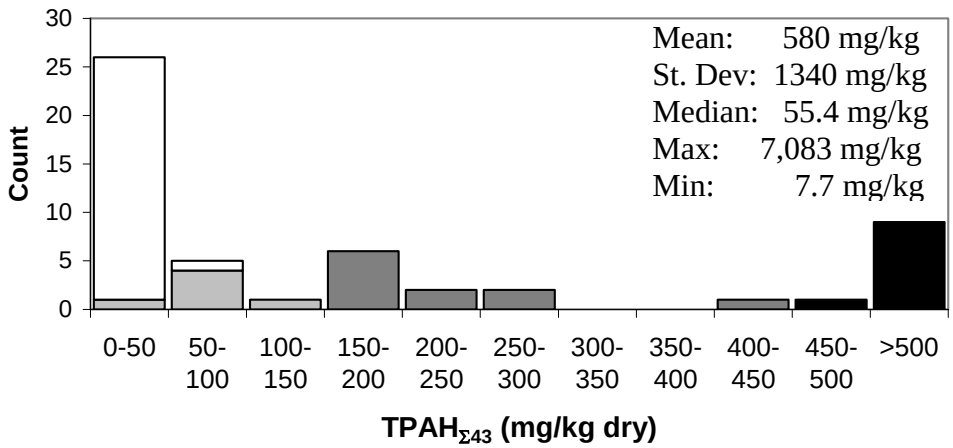


Figure 2-15. Histogram showing the distribution and population statistics of total PAH (sum of all 43 analytes; Table 2-2) in the sediments studied. Color Key based upon chromatographic character (Table 2-4). Black—creosote or creosote blend-dominant, Dark Grey—urban background with heavy creosote, Light Grey—urban background with moderate creosote, White—urban background with trace and urban background dominant.

The spatial distribution of $TPAH_{\Sigma 43}$ measured in the sediments within the study area generally is shown in Figure 2-16. The symbol size in Figure 2-16 is proportional to the measured $TPAH_{\Sigma 43}$ concentrations and thereby gives a visual assessment of where the highest and lowest THC concentrations occurred. As was evident in the THC data (Figure 2-10) and in the study of Walker and Dickhut (2001), the highest PAH concentrations also were observed in sediments proximal to the former wood treating facilities of Creosote Site 1 and Creosote Site 3 (Figure 2-16). Other sediments containing higher PAH concentrations were observed in the western shoal sediments near the South Gate Annex south of the Creosote Site 1 property, and along the eastern shoal downriver from Creosote Site 3. Notably, the PAH concentrations observed in sediments nearest the NNSY were quite low (NS03-NS05; 27-30 mg/kg $TPAH_{\Sigma 43}$).

Though low for this study area, the PAH concentrations in the sediments of Paradise Creek were highest near the head (PC05; 18 mg/kg) and remained low until reaching the mouth (PC24; 34 to 41 mg/kg), where there was an influence of a trace amount of creosote observed (Table 2-4). These low concentrations within the Paradise Creek sediments are consistent with those expected from urban runoff (e.g., Stout et al., 2001a; Stout et al., 2003), and provide no evidence of any additional source(s) of PAH associated with South Gate Annex or Paradise Creek Landfill. The concentrations of PAH in the Scuffletown Creek sediments are slightly higher than observed in Paradise Creek (SC06 and SC08; 26 and 59 mg/kg). These concentrations still are not atypical of urban runoff, but suggest that the PAH contained within the urban drainage influencing Scuffletown Creek probably exceeds that of Paradise Creek. URS (1996) had predicted variable inputs of PAH from stormwater runoff throughout the study area; therefore such variations are not unexpected. St. Juliens Creek and Blows Creek sediments contained consistent and low concentrations of PAH that appear consistent with urban background. The absence of elevated PAH concentrations in sediments within the various tributaries argue against a significant contribution from these to the elevated PAH within the Southern Branch of the Elizabeth River.

The spatial distribution of the %THC as PAH (Table 2-4) in each sediment reveals a similar pattern as observed in the $\%TPAH_{\Sigma 43}$ (Figure 2-17). The samples containing elevated percentages of PAH exist proximal to the former wood treatment facilities. This figure further serves to emphasize the apparent overwhelming influence that creosote and related blends that appears related to these former facilities appears to have had on the PAH within the study area.

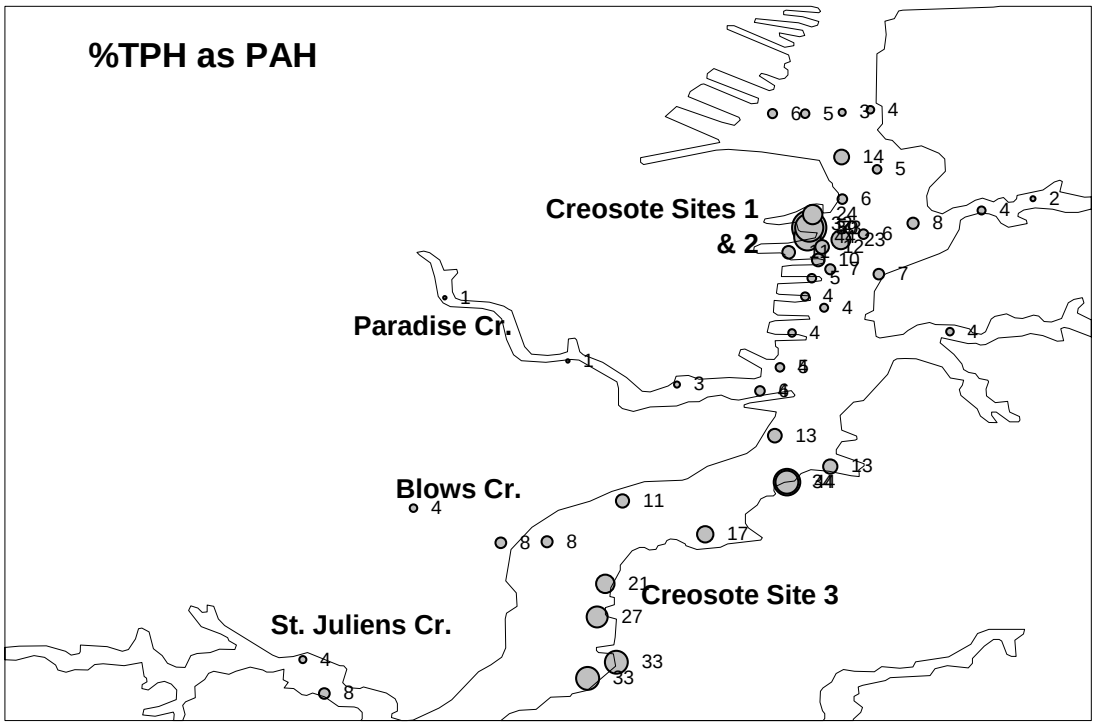


Figure 2-16. Map depicting the %THC as PAH (Table 2-4) calculated for the sediments studied. Bubble size increases with TPAH concentration, data points shown in percent mass. See text for description.

2.7.6 Characterization of PAH "Fingerprints"

Although the THC fingerprinting (Section 2.7.4) and spatial distribution of the $TPAH_{\Sigma 43}$ concentrations and %THC as PAH (Section 2.7.5) provided important evidence regarding the most likely PAH sources in the study area, a complete contaminant source study must include a detailed analysis of the individual PAH distributions (or PAH fingerprints). In the following paragraphs, a numerical analysis technique, namely, Principle Component Analysis (PCA), was used to examine these distributions or the sediments studied in an unbiased manner. PCA is described in Section 1.5.5.4 of this report. Therefore, the basis for this data analysis method is not discussed here.

Principal Component Analysis (*EinSight* Version 4.04, Infometrix, Woodinville, WA) was conducted on the PAH dataset to determine common distributions and/or trends among the sediments studied. This approach offers the advantage over selected PAH ratio cross-plots because it simultaneously considers all the PAH data. Before PCA, the individual PAH concentration data for each sample were auto-scaled to remove the effect of widely varying concentrations between samples. The data were also log-transformed before analysis to further reduce the effects of concentration. Thus, all PAH analytes were given equal weight in the PCA and the effects of low or high absolute concentrations were eliminated. (Only C4-chrysenes were excluded from the PCA due to their low abundance in only a few samples, which tended to override more substantial differences among the samples.)

Figure 2-17A shows the factor score plot resulting from a PCA of the normalized PAH for the sediments studied. This factor score plot is a cross-plot of the first and second principal components, *viz*., PC-1 and PC-2, which accounted for 92.7% and 4.5% of the variance within the data set, respectively. The spatial relationships between samples plotted in Figure 2-17A are representative of the chemical relationships that exist between samples. Samples that plot close to one another tend to have similar distributions of PAH (regardless of concentration). Conversely, the further samples plot from one another, the more distinct their PAH distributions tend to be. The dominant variance in PC-1 indicates that the horizontal variations far exceed the vertical variations.

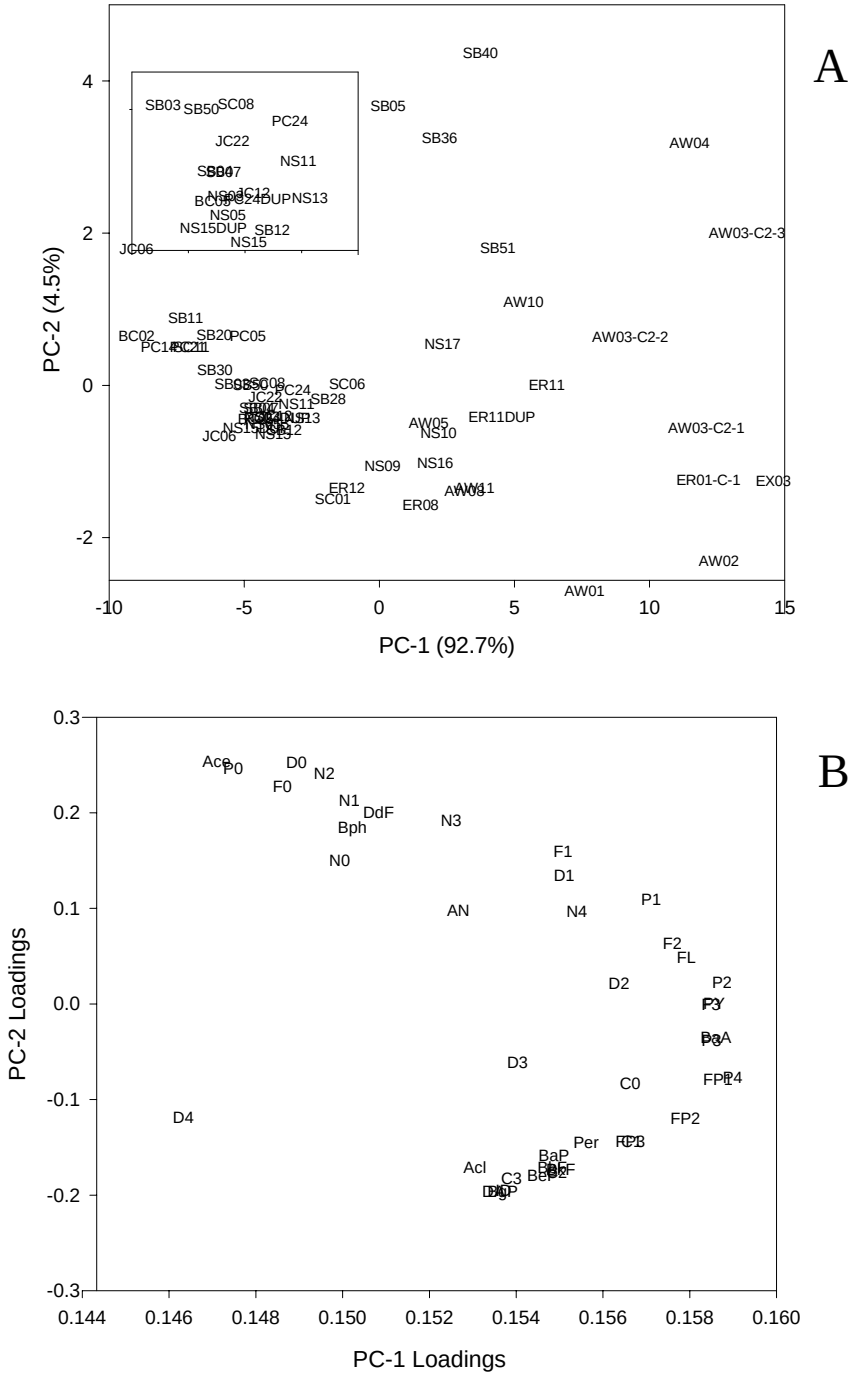


Figure 2-17. (A) Factor score plot of PC-1 *versus* PC-2 for PAH data for sediments. Inset shows expanded view of cluster of samples. (B) Factor loadings plot of PC-1 and PC-2. PAH analyte abbreviations in Table 2-2.

Interpreting the chemical reason(s) behind a sample's location in the factor score plots is achieved through inspection of the corresponding factor loadings plot (Figure 2-17 B). For example, samples that plot toward the right side of Figure 2-17A are enriched in PAH that plot toward the right side of Figure 2-17B (and *vice versa*). Visual inspection of the PAH 'fingerprints' for selected "end-member" samples identified by PCA can demonstrate the variability revealed by PCA. Figure 2-18 shows the histograms for two samples from the left and right extremes of Figure 2-17 A. Figures 2-18A and B show that samples toward the left of Figure 2-17A are enriched in high molecular weight PAH (HPAH) and contain a greater proportion of alkylated PAH. Also note the relatively low concentrations of PAH in both of these end-members. These features are consistent with those anticipated for urban background, i.e., derived from a combination of pyrogenic soot particles with a petrogenic lube-oil like component, which is consistent with the chromatographic character of these samples (Table 2-4). Figures 2-18C and D show samples toward the right of Figure 2-17A are dominated by selected, non-alkylated PAH. These end-member samples contain much higher concentrations of PAH and had exhibited chromatographic features consistent with variously weathered creosote or creosote blends. Thus, it is clear that the PC-1 in Figure 2-17A represents a mixing trend between urban background (to the left) and creosote or creosote blends (to the right).

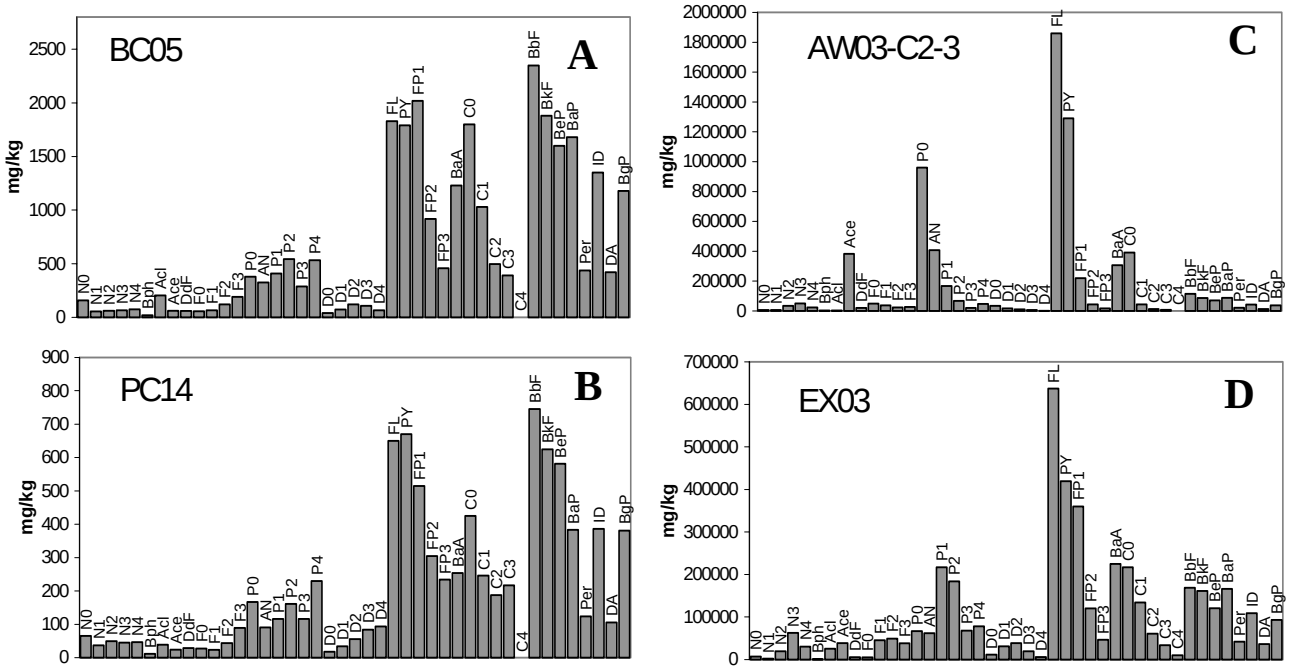


Figure 2-18. Histograms showing the distribution of individual PAH in selected sediments identified as 'end-members' in PC-1 (Figure 2-18). (A-B) PAH patterns consistent with urban background; (C-D) PAH patterns consistent with variously weathered creosote or creosote blends. Compound abbreviations are listed in Table 2-2.

The variability in the two end-member creosotes (Figures 2-18C and D) shows the differences observed in the PC-2 within the PCA factor score plot (Figure 2-18 A). To further exemplify this difference, end-members from the PC-2 extremes are shown in Figure 2-19. The SB40 sediment contains a greater proportion of lower molecular weight PAH (LPAH) and a higher relative

abundance of non-alkylated parent PAH. Conversely, the AW01 sediment is dominated by HPAH and is relatively depleted in non-alkylated, parent PAH. These differences are reasonably attributed to weathering, which tends to remove LPAH and the more susceptible (soluble and degradable) non-alkylated, parent PAH[14]. The THC in both of these sediments had been characterized as containing heavy or dominant creosote (Table 2-4). Therefore, the significant shift toward HPAH is reasonably attributable to different degrees of weathering among the creosotes (as was evident in Figure 2-12). Interestingly, some PAH isomer ratios (e.g., P0/AN, FL/PY, and BaA/C0) appear to vary with weathering; however, these ratios could also be due to the presence of different creosote 'types' (Walker and Dickhut, 2001), which is further addressed later in this section.

Figure 2-19. Histograms showing the distribution of individual PAH in selected sediments identified as 'end-members' in PC-2 (Figure 2-18). (A) moderately weathered creosote and (B) severely weathered creosote.

Based upon the interpretations described above, it is clear that the PCA revealed a combination of mixing of urban background and creosote (PC-1) and creosote weathering (PC-2) trends among PAH in the sediments studied. These trends are graphically represented in Figure 2-20. The symbols used in Figure 2-20 are based upon the chromatographic categories described in Section 2.7.4 (Table 2-4). The distribution of the chromatographic categories across the figure is remarkably consistent with the mixing trend evident in the PAH data alone. This consistency between the interpretation based upon the THC chromatograms and the PAH distributions tends to bolster the confidence in both interpretations.

In summary, those sediments containing PAH attributable to urban background appear toward the left of Figure 2-20. "Overprinting" of the urban background-derived PAH due to the presence of even trace amounts of moderately to severely creosote (or creosote blends) causes samples to spread toward the right of Figure 2-20. The degree of weathering of the creosote largely determines whether the sample plots toward the top or the bottom; being moderately weathered toward the top of Figure 2-20 (and Figure 2-18A) and severely weathered toward the bottom of Figure 2-20 (and Figure 2-18A). Based upon this result, it is evident that most of the creosote or creosote blends found in sediments studied can be considered severely weathered, having lost all or nearly all of the two- and three-ring PAH (e.g., Figure 2-19 B). The least weathered creosote was encountered in SB40 (Figure 2-19A), and even this sample demonstrates a significant loss of two-ring and three-ring PAH relative to unweathered creosote (e.g., Stout et al., 2001).

[14] D. L. Elmendorf et al. 1994. "Relative Rate of Biodegradation of Substituted Polycyclic Aromatic Hydrocarbons, S. A. Stout files.

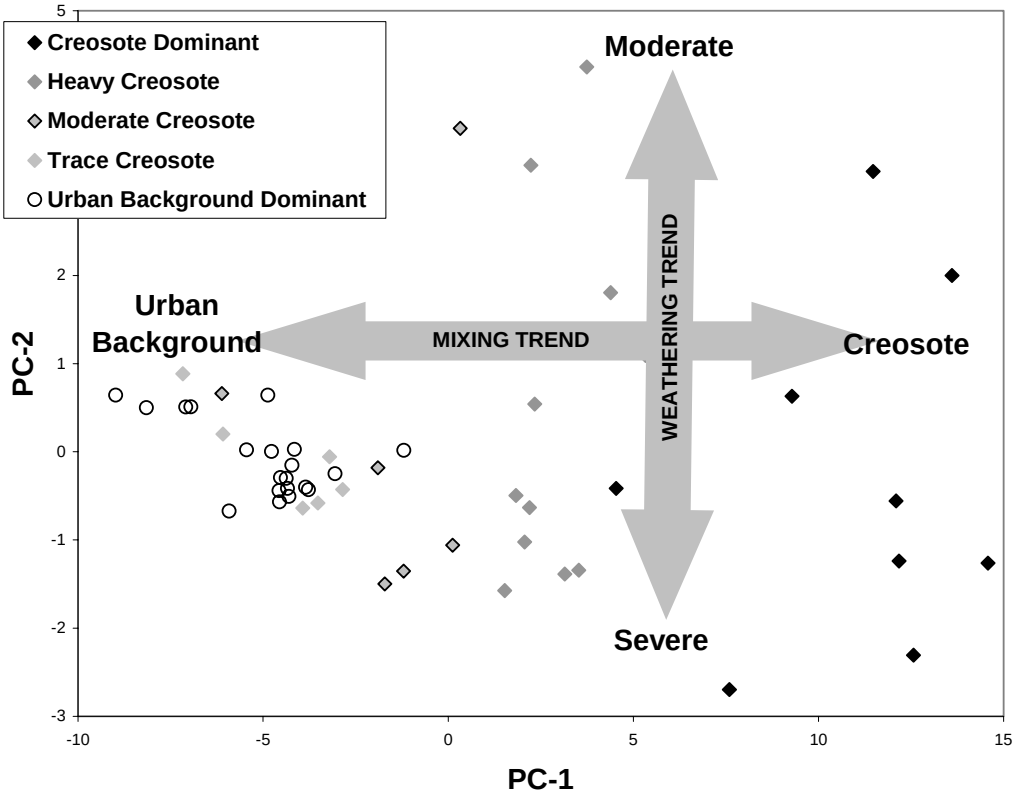


Figure 2-20. Interpreted PCA factor score plot shown in Figure 2-17A. Sample point symbols correspond to chromatographic character of THC (as per Table 2-4). See text for description.

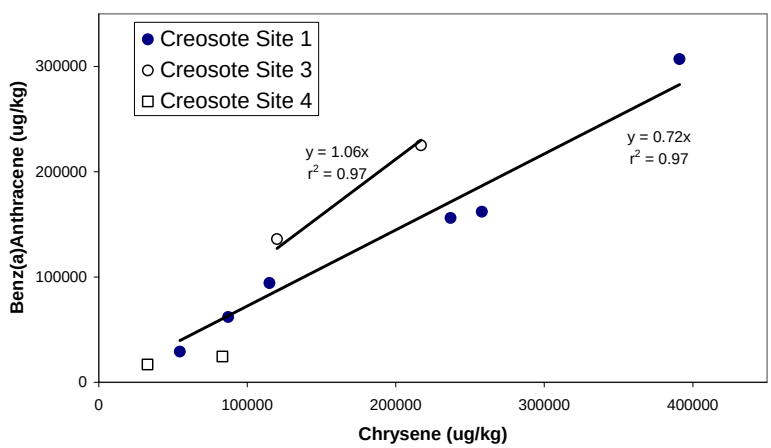
2.7.7 Distinguishing Distinct Creosote Types

As revealed by the preceding data analysis, the greatest variability evident among the creosote- or creosote blend-dominated sediments in this study was in their degrees of weathering, which ranged from moderately to severely weathered (Figures 2-19 and 2-20). There was some indication that weathering could not account for all of the observed differences. For example, the ER11 sediment collected near to the former Creosote Site 4 property contained excessive anthracene, which could only be resonably attributed to the presence of a unique material (e.g., creosote-anthracene liquor blend). This single sample provides an insufficient basis to conclude that the Creosote Site 4 discharges were equally unique. The previous work by Walker and Dickhut (2001) and Walker et al., 2002) also had suggested that the creosotes from the Creosote Site 1 area could be distinguished from those nearer Creosote Site 3 (see below). As such, this issue deserves some consideration based upon the data acquired in this study.

The issue of distinguishing the sources of creosote-derived PAH is an important consideration relative to the liability for cleanup. In addition, understanding the source(s) of creosote may show potential for redistribution of contaminants within the Southern Branch of the Elizabeth River. Understanding this may affect decisions on any future investigation and/or remediation of sediments near naval facilities.

Intuitively speaking, the long operational histories of the different wood treatment facilities (Section 2.3.2.2) makes it unlikely that they used/produced creosote(s) or creosote blends with a unique and consistent chemical character during their entire operational history. Rather, it seems more likely that the chemical composition for the various products would have changed over time and been highly dependent upon the suppliers' sources of tar (e.g., coal tar, carbureted water gas tar, or oil tar) and how these were distilled and blended. Furthermore, local facilities were reportedly supplied by the same creosote producer during peak operations in the 1940s (Lu, 1982). The data of Walker and Dickhut (2001) suggests that the creosote(s) in sediments near Creosote Site 1 (n = 13) could be distinguished from that in sediments near Creosote Site 3 (n = 12). The basis for their distinction lay primarily with the ratios of HPAH isomers, particularly benz(a)anthracene/chrysene (BaA/C0)[15]. These authors used this distinction to evaluate a non-linear source-mixing model for the sediments throughout the study area and concluded that most sediments from the study area had been impacted by creosote from the Creosote Site 1 facility and from manufactured gas plant (MGP) residues (downriver from the study area) and from coal. The Creosote Site 3 creosote impact was contended to have been limited to the eastern shoal proximal to this property.

To investigate the potential differences between creosotes from the different facilities, we have focused on those sediments that were proximal to each facility and that contained THC and PAH dominated by creosote or creosote blends, as inventoried in Table 2-4. Although more limited with respect to the number of samples than Walker and Dickhut (2001), the sediment data collected in our study also revealed an apparent distinction in the proportions of BaA and C0 between impacted sediments near Creosote Site 1 (n = 6) and near Creosote Site 3 (n = 2; Figure 2-21). There appears to be a slight distinction with respect to the one sample near Creosote Site 4 (ER11 and ER11-dup). While this suggests that there may be a basis to distinguish different creosote sources using the ratio of BaA/C0, reliance upon this single isomer pair ratio (BaA/C0) may not be a sufficient basis to assess the source of creosotes in sediments, particularly those also influenced by urban background



(which tends to exhibit BaA/C0 ratios akin to Creosote Site 1 rather than Creosote Site 3).

Figure 2-21. Regression plot of chrysene and benz(a)anthracene in sediments containing dominant creosote (Table 2-4) proximal to Creosote Site 1, Creosote Site 3, and Creosote Site 4. Note that these data are not surrogate corrected, and therefore, absolute

[15] These authors also present other minor differences in ratios of BbF/BkF and BgP/ID, though these appear very subtle. A noted difference in molecular weight groups (Σ202/Σ252) was likely to be due to weathering rather than source. Thus, BaA/C0 provided the most defensible basis to distinguish creosote source types.

concentrations should not be compared to Walker and Dickhut (2001).

Other isomer ratios evaluated from our data do not provide good agreement with the published data of Walker and Dickhut (2001). Examples of some of these are shown in Figure 2-22A and B. These plots show the ratios of other HPAH isomer pairs (BbF/BkF and ID/BgP) *versus* BaA/C0. The current data were plotted and the previous data from Walker and Dickhut (2001) were approximated by the squares labeled AW (Creosote Site 1) and ER (Creosote Site 3). There is poor agreement in the actual values of all ratios, however, the BaA/C0 distinction (*x*-axis in each) still is evident in both datasets.

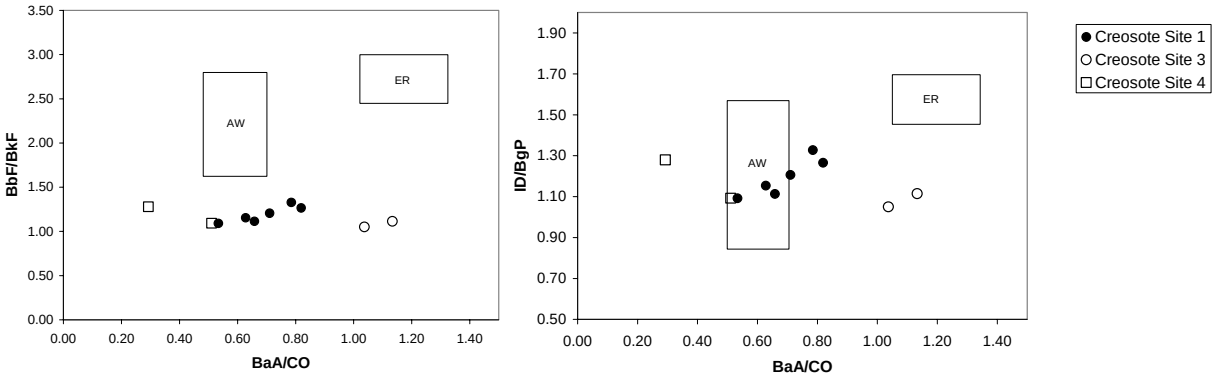


Figure 2-22. Double-ratio plots of HPAH isomer pairs for creosote dominated sediments from Creosote Site 1, Creosote Site 3, and Creosote Site 4 areas. Boxes (AW and ER) indicate data from Walker and Dickhut (2001); use of ratios allows comparison of data between these studies.

Further inspection of the current data did not reveal a reliable basis to distinguish the creosotes from the different locations. All the parameters evaluated appeared to be correlated with an expected weathering phenomenon. While PAH isomers are often argued to exhibit comparable environmental fates, and thereby their ratios (e.g., BaA/C0) should be useful in source studies (e.g., Walker and Dickhut, 2001), caution is still warranted because compound-specific weathering (e.g., degradation) is possible. In fact, the data indicated that BaA/C0 and other ratios in the creosotes could be affected by severe weathering. For example, Figure 2-24 shows that the HPAH isomer ratios of BaA/C0, BbF/BkF, and BaP/BeP in the six sediments near Creosote Site 1 containing dominantly creosote sharply decrease after reaching a certain LPAH/HPAH ratio (~0.2), a proxy for weathering. Thus, while HPAH isomer pairs may be useful in distinguishing sources of creosote, as per Walker and Dickhut (2001), they must be cautiously evaluated in light of the degree of weathering. Particular caution is necessary in using such simple parameters in developing mixing models in a PAH source allocation, also as per Walker and Dickhut (2001). This is particularly important since this study has shown the urban background is an important source of PAH in the area. When these HPAH ratios for the urban background dominated sediments are plotted along with the creosote-dominated sediments, it is apparent that they exhibit features largely consistent with Creosote Site 1-type of creosote (Figure 2-23). This result makes it impossible to use these HPAH isomer ratios to distinguish between or investigate mixing of these two dominant PAH source end-members using these simple ratios. The similar HPAH isomer ratios shared by the Creosote Site 1 population and the area's urban background population is likely to have contributed to Walker and Dickhut's (2001) conclusion that creosote exists throughout the system. Rather, the current data (which includes the detailed fingerprinting of the THC and full suite of PAH) suggest that it is the urban background signature that is persistent throughout the system.

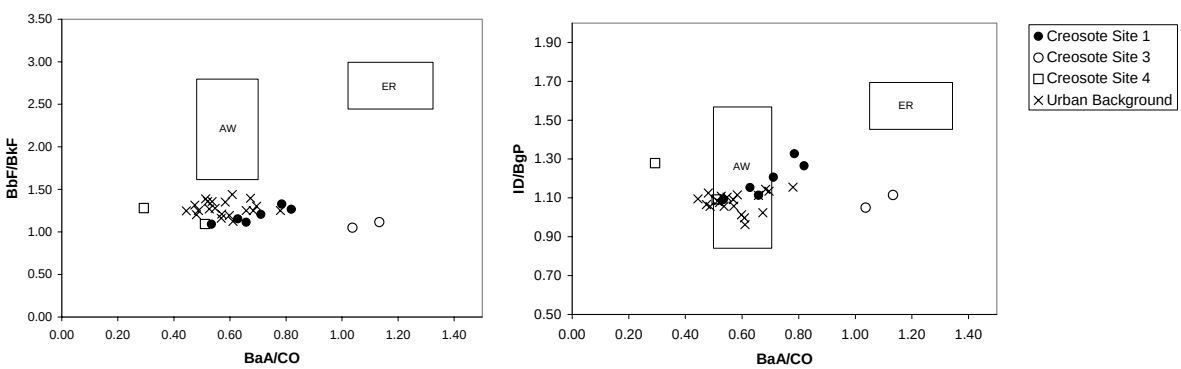


Figure 2-23. Double ratio plots of HPAH isomer pairs for creosote- and urban background-dominated sediments. Boxes indicate data from Walker and Dickhut (2001); use of ratios allows comparison of data between these studies.

Further analysis of the issue of distinguishing creosote sources within the study area on the basis of their chemistry is beyond the scope of this demonstration project. It is reasonable to expect that some differences in the nature of the creosote and related materials may exist. The most likely reason for these differences may be because the sediments nearer Creosote Site 3 may have been mostly impacted by two catastrophic inputs of creosote during discrete spill events (e.g., tank failures), whereas the creosotes and related materials apparently released nearer Creosote Site 1 may have been

more gradual, and thereby represent a population of materials with varying degrees of weathering. Future investigations that may focus on this issue may benefit from additional methods of analysis that could include (1) compounds specific stable carbon isotopes or (2) detailed analysis of the accompanying aliphatic hydrocarbons (F1 fractions), which could identify and distinguish various petroleum blending agents. In addition, further investigations of sediment dynamics would also provide a significant amount of information regarding the fate/transport and redistribution of PAH from the potential source areas.

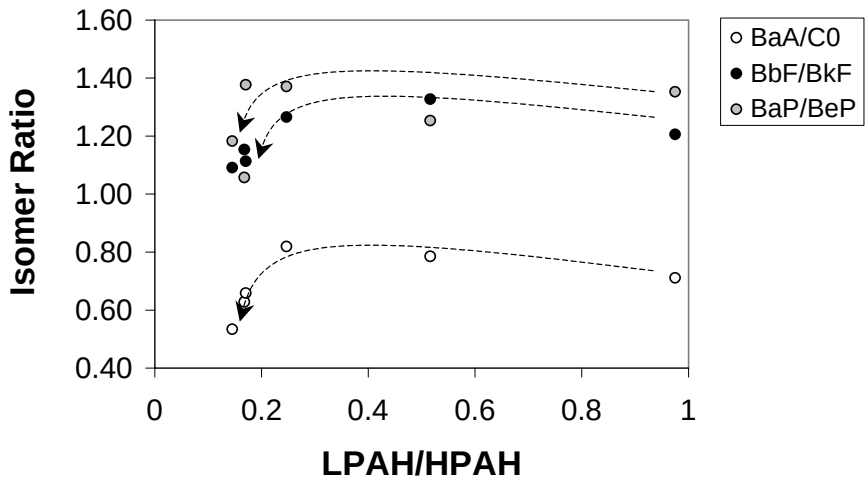


Figure 2-24. Plot showing the sharp decrease in various HPAH isomer ratios in Creosote Site 1 area creosotes after a severe degree of weathering (as measured by LPAH/HPAH).

2.8 STEP 7: SUMMARY AND SYNTHESIS OF RESULTS

The ACF data described in Sections 2.7.4 through 2.7.7 demonstrated that the sources of PAH in sediments within the study area are the result of mixing of variably weathered creosotes (or related creosote blends) with an urban background signature. The detailed chromatographic (GC/FID) fingerprints of the THC in each sediment were very revealing. These fingerprints were used to recognize five categories of THC in the sediments studied, namely,

1. Creosote- or related creosote-blend dominant,
2. Urban background with heavy creosote,
3. Urban background with moderate creosote,
4. Urban background with trace creosote, and
5. Urban background.

While a few sediments also contained some petroleum products (e.g., Figure 2-14), no recognizable contribution of PAH were attributable to those evident in the PAH data. This finding was not

unexpected, given the proportionately low concentration of PAH in petroleums, as compared to creosote or urban background. The THC, total PAH, and % THC as PAH of these five categories is inventoried in Table 2-4.

The same five mixing categories were substantiated based upon the mixing trend evident in the detailed distribution of the 43 PAH analytes (Table 2-2), which was developed using PCA (Figures 2-18A and 2-20). Selected statistical measures associated with the population of sediments within each category are presented in Table 2-5. Inspection of Table 2-5 revealed that some parameters are better than others in recognizing the degree of mixing; e.g., compare the boldfaced mean values in selected parameters. For example, as might be expected, the concentration of PAH ($PAH_{\Sigma 43}$) shows marked decrease as the relative amount of creosote decreases. Similarly, the percent of the THC that occurs as PAH (%THC as PAH) decreases as the relative amount of urban background, including its PAH-depleted "UCM", increases. Two measures of the degree of alkylation on PAH homologue groups [(FL+PY)/(FP2+FP3) and (BaA+C0)/(C2+C3)] also show marked changes based upon the degree of mixing. Both ratios decrease as the relative proportion of urban background increases. This decrease most likely is due to the greater contribution of a residual range petroleum component (e.g., lubricating oil) that is contained within urban runoff. Interestingly, none of the H (HPAH) isomer ratios examined (FL/PY, BaA/C0, BbF/BkF, BeP/BaP, or ID/BgP) exhibited any particular capability for distinguishing the categories. This fact serves to emphasize the difficulty in conducting PAH source studies using simple ratios available from priority pollutant (EPA Method 8270) datasets.

Table 2-5. Selected population statistics for five categories of sediments (n = 53) containing mixtures of PAH derived from creosote(s) and urban background.

		THC*	$PAH_{\Sigma 43*}$	%THC as PAH	PAH_{PP**}	%PAH as PP	FL/ PY	(FL+PY)/ (FP2+FP3)	BaA/ C0	(BaA+C0)/ (C2+C3)	BbF/ BkF	BeP/ BaP	ID/ BgP
Creosote	Mean	18391	**2716**	**40**	1987	71	1.3	**17.3**	0.7	**12.7**	1.2	0.8	1.2
Dominant	St Dev	19598	2023	14	1669	9	0.3	13.9	0.2	9.2	0.1	0.1	0.1
n=10	Median	46445	2398	36	1656	74	1.4	13.0	0.7	10.4	1.1	0.7	1.2
	Min	1247	419	24	295	57	0.9	4.2	0.3	4.1	1.0	0.6	1.1
	Max	49002	7084	73	6041	85	1.7	51.0	1.1	34.2	1.3	0.9	1.2
Heavy	Mean	2184	**223**	**13**	147	66	1.0	**7.7**	0.7	**5.3**	1.2	0.8	1.2
Creosote	St Dev	1137	84	8	62	3	0.4	4.4	0.2	1.9	0.1	0.1	0.0
n=11	Median	1950	172	12	110	66	0.9	6.6	0.7	4.9	1.2	0.8	1.2
	Min	752	159	4	108	60	0.4	2.4	0.4	2.8	1.1	0.7	1.1
	Max	3892	439	27	314	71	1.6	15.4	1.1	9.1	1.3	0.9	1.2
Moderate	Mean	649	**72**	**12**	46	64	0.9	**4.6**	0.6	**4.6**	1.2	0.9	1.1
Creosote	St Dev	320	33	2	21	1	0.3	4.2	0.2	0.8	0.1	0.1	0.0
n=6	Median	654	46	12	50	64	0.9	3.6	0.5	4.6	1.2	0.8	1.1
	Min	142	18	8	11	63	0.6	1.8	0.4	3.7	1.1	0.8	1.1
	Max	1066	110	14	72	66	1.4	13.0	0.9	6.0	1.3	1.0	1.2
Trace	Mean	625	**32**	**6**	21	65	1.0	**3.4**	0.5	**4.3**	1.3	0.8	1.1
Creosote	St Dev	388	14	2	9	1	0.2	0.6	0.1	0.9	0.0	0.0	0.0
n=6	Median	600	39	6	25	65	1.1	3.5	0.6	4.0	1.3	0.8	1.1
	Min	203	12	4	8	63	0.6	2.4	0.5	3.4	1.2	0.8	1.1
	Max	1175	45	8	29	66	1.3	4.0	0.7	5.5	1.3	9.0	1.2
Urban	Mean	735	**26**	**4**	16	61	1.0	**2.8**	0.6	**2.9**	1.3	1.0	1.1
Background	St Dev	469	12	2	8	4	0.2	0.4	0.1	0.8	0.1	0.3	0.1
n=20	Median	602	27	4	16	62	1.0	2.8	0.6	3.1	1.3	0.9	1.1
	Min	204	8	1	5	48	0.6	2.3	0.4	1.4	1.1	0.8	1.0
	Max	2250	59	8	37	65	1.2	3.5	0.8	4.3	1.4	1.7	1.1

* mg/kg (dry)
** mg/kg (dry) priority pollutant PAH only

The utility in identifying the most diagnostic parameters is that they might prove useful in developing various two-component mixing “models” (linear and non-linear) for PAH sources in sediments in the study area. The rigorous development of mixing models is beyond the scope of this demonstration study, but the basis for a mixing model using two diagnostic features from Table 2-5 is shown in Figure 2-25. This double-ratio plot shows the spread of samples between the two recognized end-members, *viz*., urban background and creosote, when two or the more diagnostic parameters from Table 2-5 are cross-plotted. With consideration given to the specific character of each end-member due to the effects of weathering (which contribute to the scatter among the creosote-dominated end-members), mathematical analysis could be used to estimate the proportional contribution that each end-member has made to the intervening (mixed) samples. Such multiple mixing “models” can be developed from the resulting percent contribution data and can be used to establish the range of contributions of different PAH sources to each sample. This information can then provide the basis for development of a cost allocation model for an impacted area.

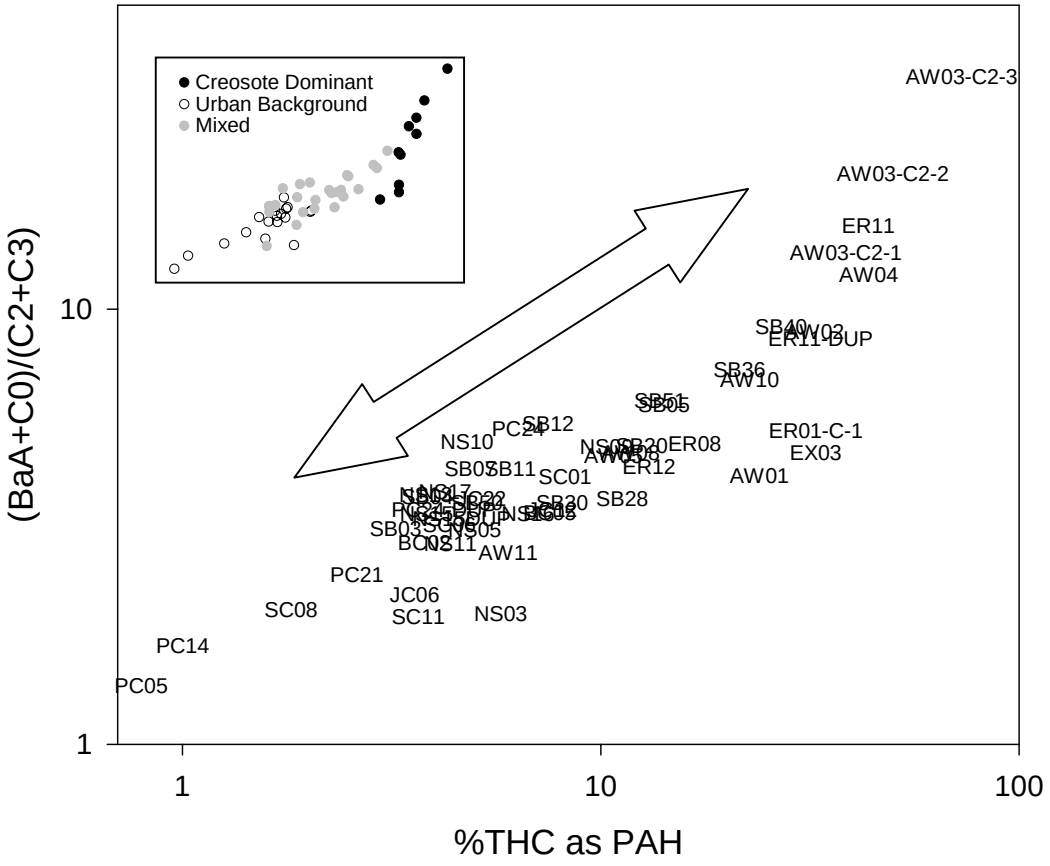


Figure 2-25. Cross-plot of diagnostic parameters useful for distinguishing PAH source end-members and mixtures for sediments in the Elizabeth River study area. Inset shows chromatographic categories.

The results presented in the preceding sections and summarized above provide a defensible basis to address the four specific questions that were the objectives of this demonstration study, namely,

1. Have PAH derived from Creosote Site 1 (and adjacent Creosote Site 2) historic tar refining and wood treatment operations impacted sediments proximal to the Main Shipyard and South Gate Annex?

2. Have PAH derived from Navy properties impacted the sediments in Paradise Creek, Blows Creek, and St. Juliens Creek and, if so, have these contributed to the sediments in the Southern Branch of the Elizabeth River?

3. What are the chemical characteristics and concentrations of PAH attributable to the ambient urban background within the study area?

4. Can the PAH associated with creosote and related materials derived from Creosote Site 1/Creosote Site 2 area be distinguished (either chemically or spatially) from the PAH associated with these materials near the Creosote Site 3 or Creosote Site 4 sites?

ACF data collected in this demonstration study is used to answer each of these questions/ objectives in the final sections of this report.

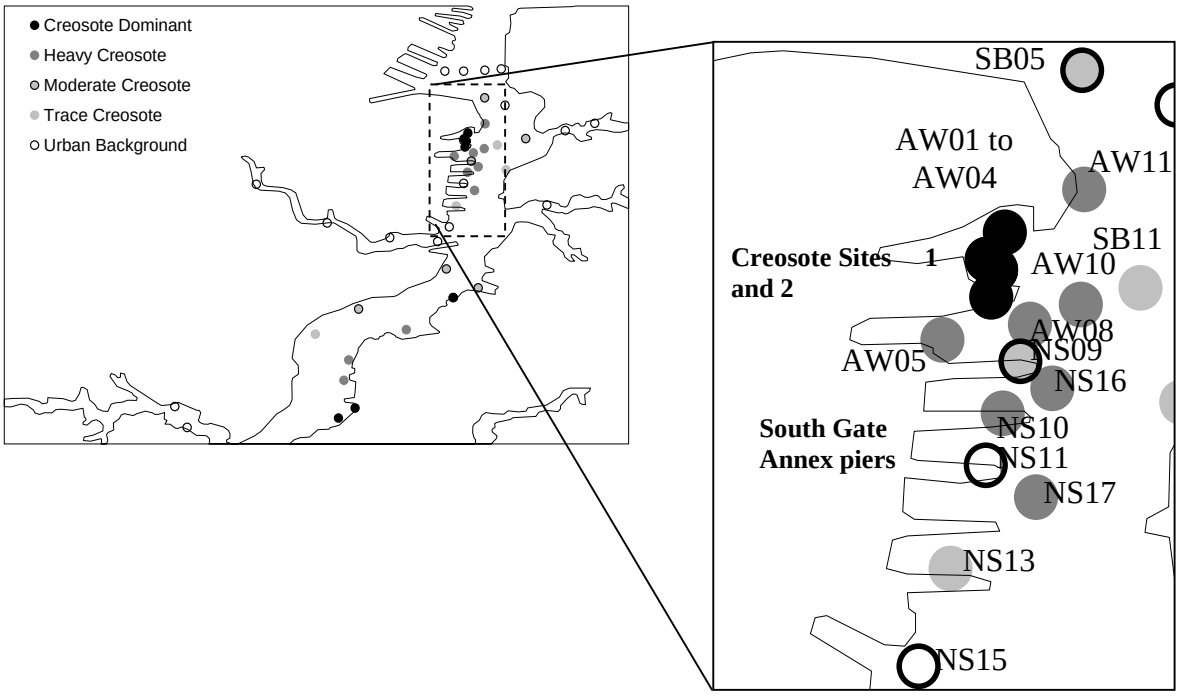


Figure 2-26. Map showing the distribution of chromatographic categories for THC in sediments from the study area (left). Expanded view of Creosote Site 1 and 2 area and Southgate Annex area (right).

2.8.1 Impact of PAH Derived from Creosote Site 1/Creosote Site 2 Operations on Sediments Proximal to Navy Property

The grain size data indicated that the sediments along the western shoal of the Southern Branch of the Elizabeth River between the NNSY and the mouth of Paradise Creek were among the finest grained sediments in the study area (Section 2.7.2). The data suggested that this region may be an area of sediment deposition, and based upon the weak correlation between the %fines and TOC (Figure 2-8), also an area of contaminant deposition. This fact appeared to be confirmed by the elevated concentrations of THCs in the sediments all along this area (Figure 2-10). The highest THC concentrations were found in the sediments immediately proximal to the Creosote Site 1/Creosote Site 2 (e.g., AW01, AW02, AW03, and AW04) properties). This observation is in agreement with previous assessments of sediments in the study area (Section 2.3.3) and was not unexpected. However, elevated concentrations of THC extended away from Creosote Site 1 into the shoal sediments proximal to the Navy's South Gate Annex piers (e.g., NS10, NS16, NS17; Figure 2-10). There was some evidence that elevated THC concentrations in sediments also extended north of the Creosote Site 1/Creosote Site 2 sites and (at least) into the sediment just north of the Jordan Bridge (AW11[16]; Figure 2-10).

Evaluation of the GC/FID fingerprints of the THC in the sediments throughout the study area revealed various amounts of creosote or related tar distillates (e.g., creosote-tar blends or coal tar; Section 2.7.4). These materials clearly exhibited variable degrees of weathering (Figure 2-12A and B), although this was not necessarily related to the concentration nor location. In the single sediment core from this area (AW03), the creosote was most weathered in the shallowest horizon (i.e., AW03-C2-1 < AW03-C2-2 < AW03-C2-3; Figures 2-18 and 2-20). Based upon the GC/FID fingerprints, the relative proportion of creosote(s) tended to decrease with increasing distance away from the Creosote Site 1 and 2 area (Figure 2-26). Taken alone, this spatial distribution demonstrates that creosote-like materials from the Creosote Site 1 and 2 area indeed have impacted the western shoal sediments proximal to the South Gate Annex piers.

The detailed PAH data described in Sections 2.7.5 and 2.7.6 further confirmed this conclusion. Elevated PAH concentrations, including the highest encountered anywhere (AW03; 7084 mg/kg $TPAH_{\Sigma 43}$), were demonstrated to occur in the sediments proximal to the Creosote Sites 1 and 2 area (Figure 2-16). As was evident in the THC data, the concentration of PAH also tended to decrease with increasing distance from the Creosote Site 1 area, thereby implicating a significant PAH source in this area. Most of the shoal sediments proximal to the South Gate Annex piers contained PAH at concentrations that were lower than those found immediately proximal to Creosote Site 1, but were well above those found in other parts of the study area. This same 'intermediate' character of these sediments in the vicinity of the South Gate Annex piers was revealed by the percentage of the THC that could be accounted for as PAH, which also tended to decrease away from the Creosote Site 1 area (Figure 2-17).

Numerical evaluation of the PAH distributions or "fingerprints" using PCA revealed that numerous shoal sediments near the South Gate Annex piers contained mixtures of weathered creosote (mostly severely weathered creosote) and urban background (Figure 2-18, see NS09, NS10, NS16, NS17). This result, obtained by the unbiased numerical assessment derived from PCA, was in strong agreement with the chromatographic interpretations of the THC. The PAH fingerprinting data also indicated that the sediments north of the Jordan Bridge had also been impacted by weathered

[16] This sample's elevated THC, in part, is due to the presence of an unweathered diesel fuel #2/fuel oil #2 component (Figure 2-14B).

creosote (Figure 2-18, see AW11). This impact of creosote appeared to extend as far north as SB05, which is located very near to the Main Shipyard (just north of the railroad bridge). Although there is no evidence of PAH impacts due to creosote or related tar distillate material within the sediments most proximal to the Main Shipyard (NS03 and NS05), the presence of creosote at SB05 suggests that some creosote from Creosote Site 1/2 may be present within some areas of the Main Shipyard.

In conclusion, there is strong evidence that creosote(s) or related tar distillates from the Creosote Site 1 and 2 area have impacted the western shoal sediments: (1) proximal to the South Gate Annex piers as far south as NS13, and (2) as far north as SB05. Any impact to the sediments within the Main Shipyard of such materials is not evident in the available data (NS03 and NS05). However, impacts of such materials between SB05 and NS03/NS05 cannot be ruled out.

2.8.2 Potential Impact of PAH Derived from Navy Properties to Sediments in Paradise, St. Juliens, and Blows Creeks

The sediments within the two major western tributaries to the Southern Branch of the Elizabeth River within the study are, *viz*., Paradise Creek and St. Juliens Creek, contained lower concentrations of THC and PAH than most sediments along the shoals of the river (Figures 2-10 and 2-16). The RSC data showed these tributaries to contain consistently low concentrations of PAH. The absence of any obvious PAH 'hotspots' within these tributaries' sediments argues against the existence of a significant source of PAH along these tributaries. This conclusion was bolstered by the ACF data.

In Paradise Creek, the concentrations of THC and PAH were highest in the uppermost reach sampled (PC05; 2250 mg/kg THC and 18 mg/kg $PAH\Sigma_{43}$). This location was proximal to the Navy's Paradise Creek landfill and to an adjacent property. However, the chromatographic character of the THC and the PAH "fingerprint" of the PC05 sediment were entirely consistent with those expected from urban background (Figure 2-11 A). The other sediments further downstream within Paradise Creek that were evaluated exhibited comparable features (e.g., Figure 2-18 B), i.e., they were also consistent with urban background. Numerous stormwater outfalls exist along Paradise Creek, which would reasonably explain the source of urban background-derived PAH in these sediments. Any Navy property contribution to the urban background source of PAH is likely to be indistinguishable from that of the surrounding urban environments. The absence of any evidence of a discrete point-source of PAH along Paradise Creek also provides a sufficient basis to conclude that the Paradise Creek landfill is not a significant and/discernable source of PAH.

In St. Juliens Creek, the concentrations of THC were also low and comparable to those observed in Paradise Creek, and still lower than most sediments along the Southern Branch (Figure 2-10). Again, the chromatographic character of the THC in the St. Juliens Creek sediments was entirely consistent with that of urban background (Figure 2-11B). Similarly, the PAH "fingerprints" for the St. Juliens Creek sediments evaluated also were consistent with urban background. Notably, the concentrations of PAH were slightly higher in the St. Juliens Creek sediments than were observed in the Paradise Creek sediments (Figure 2-16). This concentration could simply indicate a slightly different nature of the drainage areas, or perhaps the presence of an additional source of PAH proximal to St. Juliens Creek. Variation among the different tributaries is not unexpected; the urban background character of the Scuffletown Creek sediments is slightly different from Paradise or St. Juliens Creeks. Thus, it is most likely that the nature of the urban background in St. Juliens Creek is simply slightly different from that in Paradise Creek. More importantly, there is no evidence support-ing the existence of a discrete point source of PAH in the St. Juliens Creek Annex.

Finally, the small size of Blows Creek (and the concrete weir at its mouth) suggests that it should barely be considered a tributary to the Elizabeth River, let alone a significant source of contaminants. Nonetheless, the RSC data and the two samples evaluated in detail in this study from Blows Creek (BC02 and BC05) indicated that the sediments within the creek contain low concentrations of THC and PAH, the latter entirely attributable to urban background. Evidence was observed for a contribution of naturally occurring, plant-derived hydrocarbons (e.g., plant waxes) to the sediments within Blows Creek. This fact is not unexpected, given the abundance of vegetation that surrounds this small creek over much of its length. The presence of this modern organic matter also increased the TOC of these sediments compared to other tributary sediments (Figure 2-8). There is no evidence that Blows Creeks should be considered as a specific point source of PAH to the Elizabeth River.

In conclusion, the sediments within the western tributaries to the Elizabeth River that flank the various Navy properties in the study area contain low concentrations of PAH. The nature and concentration of these PAH (and associated hydrocarbons) are entirely consistent with a non-point source(s) of PAH, i.e., urban background. The PAH in urban background primarily result from the combination of urban runoff and direct atmospheric fallout, both of which contain partially combusted petroleum residues (soot particles) that are either washed from urban surfaces during storm events or are deposited directly into waterways. Considering the urban environment encompassing the study area, a contribution of PAH derived from non-specific sources of urban background is expected. Establishing the general characteristics and concentrations resulting from this source of PAH was the third objective of this study, which is summarized in the next section.

2.8.3 Character and Concentration of PAH Attributable to Urban Background

The ACF of hydrocarbons extracted from sediments from the southern branch of the Elizabeth River and its tributaries clearly identified the presence of PAH derived from urban background. Urban background collectively refers to a variety of non-point sources such as (1) stormwater runoff; (2) direct deposition (atmospheric fallout) of combustion particles (soot) from vehicle exhaust and factories; (3) surface runoff from proximal roadways, parking lots, and bridges; or (4) discharges from recreational, commercial, and military boat/ship traffic. In many environments, stormwater runoff is probably the largest chronic contributor of background PAH to urban sediments (Eganhouse et al., 1982). Because these PAH source materials are persistent, and have been so for decades, establishing their character and concentration in the Elizabeth River study area is important. This study provides a basis to recognize this important source of PAH in future studies in this area.

The chromatographic characters of the THC in sediments exclusively containing urban background were described in Section 2.7.4, with examples of GC/FID fingerprints shown in Figure 2-11. In each case, sediments impacted by urban background could be recognized by the presence of a residual range UCM that had various resolved peaks consistent with PAH. Among these were fluoranthene and pyrene, which often occur in a ratio of around 1 (Table 2-5). The detailed distributions of PAH in sediments impacted with urban background were equally recognizable and dominated by high molecular weight PAH (three- to six-ring PAH). Examples of representative PAH “fingerprints” for urban background were shown in Figure 2-18A and B. The combination of THC chromatograms and PAH “fingerprints” provides a strong basis to recognize those sediments dominated by urban background in any future investigations.

Statistical analysis of data for the 20 sediments recognized to contain hydrocarbons derived exclusively from urban background was performed, with some selected results presented in Table 2-5. The most relevant of these for any future work in the study area probably is the concentration of

PAH that might be attributable to an urban background source(s). The non-point source nature of urban background is pervasive throughout the study area, impacting all sediments in a relatively equal proportion. (One might expect slightly higher concentrations of PAH in sediments in the immediate vicinity of stormwater outfalls.) It is important to establish what is the "typical" concentration of PAH derived from urban background because this concentration provides a reasonable basis to assess whether there has been an additional impact from any particular point source of PAH. Unless the source(s) of urban background-derived PAH are eliminated (unlikely in our current society), the ambient background concentration of PAH in an area provides a benchmark below which there is no practical basis to remediate sediments.

Figure 2-27 shows the box and whisker plots for the total concentrations of PAH as measured in this study ($TPAH_{\Sigma 43}$) and as priority pollutant PAH ($TPAH_{16PP}$; as per Table 2-2). It is notable that the latter comprises only about 62 percent of the former on average (with a range of 47 to 65 percent; Table 2-5). Population statistics related to each of these TPAH values is given in Table 2-5. These results show that Elizabeth River sediments containing more than 50 mg/kg $TPAH_{\Sigma 43}$ or 30 mg/kg $TPAH_{16PP}$ should be considered to have been impacted by a source(s) of PAH other than is readily attributable to urban background. The opposite is not true because some sediments containing trace amount of creosote can contain less than 50 mg/kg $TPAH_{\Sigma 43}$ (Table 2-4).

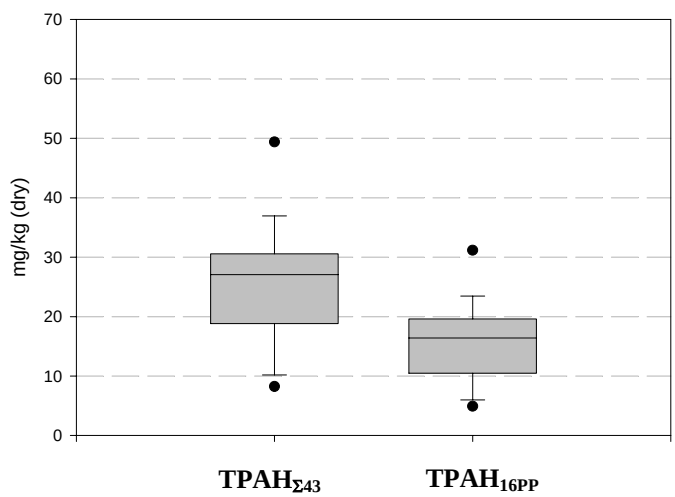


Figure 27. Box and whisker plots of $TPAH_{\Sigma 43}$ and $TPAH_{16PP}$ for the 20 sediments from the study area impacted exclusively by urban background. The boxes and the whiskers represent the 25th and 75th and 10th and 90th percentiles, respectively. Outliers are BC02 (-) and SC06 (+) and these represent the 5th and 95th percentiles. Lines = medians.

2.8.4 Distinguishing PAH from Different Wood Treatment Facilities

This topic was thoroughly evaluated in Section 2.7.7. There are two ways to address this issue, namely, (1) ACF, and (2) spatial trends and distributions. The ACF methods used in this study were able to defensibly distinguish the creosote present in the single sediment sample collected near the former Creosote Site 4 (ER11 and ER11-Dup). The ER11 sediment contained a creosote blend that had exceptionally high concentrations of anthracene, which exceeded all other PAH. This may be

explained by the presence of a unique creosote blend, probably one that included an anthracene-rich liquor. Because only one sample from this area was included in the ACF part of this study, it is not possible to determine if this sample is representative of all sediments in the vicinity of Creosote Site 4 or not.

With respect to the other creosote source areas, our data clearly indicated that the greatest chemical differences between creosotes in sediments from the Creosote Site 1 and Creosote Site 3 areas were in their degrees of weathering. At both locations, even the least weathered creosotes encountered (AW04 near Creosote Site 1 and SB40 near Creosote Site 3) were moderately weathered, each having lost most of the two-ring and three-ring PAH compared to unweathered creosote (e.g., Figures 2-18C and 2-19 A). Most other creosote-impacted samples from each area were severely weathered (e.g. Figure 2-19B), wherein even the four+ ring PAH had been affected to some degree by weathering (e.g., Figure 2-24). This high degree of weathering of the creosotes throughout the study area undermined the ability of the ACF performed herein to distinguish the different creosotes. Only the ratio of benza(a)anthracene to chrysene (BaA/C0) was consistently different in creosote-dominated sediments proximal to Creosote Site 1 and Creosote Site 3 (Figs. 2-21 and 2-22). This same distinguishing feature had been observed in an earlier study (Walker and Dickhut, 2001). However, the data for creosote-laden Creosote Site 1 sediments suggest that the ratio of BaA/C0 may be decreased after severe weathering (Figure 2-24), which may confound this simple approach. Clearly, if future studies were to address this issue more rigorously, additional methods of ACF (e.g., compounds-specific stable carbon isotope ratio analysis) would appear necessary.

The spatial distribution of creosote-dominated sediments provided a reasonable basis to distinguish between the sources of creosote and related materials in the sediments studied. High concentrations of PAH (Figure 2-16) and creosote-dominant chromatographic features were clearly evident in sediments proximal to Creosote Sites 1 and 2, Creosote Site 3, and Creosote Site 4 (Figures 2-16 and 2-26). This fact alone demonstrates that each of these sites likely has introduced PAH to the sediments nearest to them. In Section 2.8.1, the impacts of PAH from Creosote Site 1 on sediments along the western shoal south and north of the former facility was demonstrated (e.g., Figure 2-26). Throughout the study area, if the RSC PAH concentration data were considered, the apparent "impact patterns" from each site tend to reveal themselves (Figures 2-4 to 2-7). The patterns around Creosote Site 3 indicate that impacts from this site are largely limited to western shoal sediments downriver from the former site. Thus, in this study, the spatial distribution of PAH tends to reveal the impacts from the various former wood treatment sites to a better degree than the ACF alone. This fact underscores the added value of the combined RSC and ACF approach in a contaminant source study.

2.9 FURTHER STEPS RELATIVE TO NAVY SEDIMENT POLICY

The results of this contaminant source demonstration study clearly indicate that the sources of PAH to the Southern Branch of the Elizabeth River are dominated creosote-like sources. These PAH appear to be derived from suspected sources of creosote and related materials (i.e., former wood treatment facilities) that had existed along the River for decades. Concentrations of PAH attributed to creosote and related materials are highest in the sediments most proximal to these former facilities. This fact, combined with the absence of any historical records to suggest that the Navy had handled, used, or generated creosote-like materials other than creosote-treated wood pilings for bulkheads and/or piers, suggest that the predominant PAH sources are non-Navy. In addition, from the PAH concentrations, chemical fingerprints, and spatial distributions within sediments of the western

tributaries near Naval IR sites (i.e., Paradise Creek, Blows Creek, and St. Juliens Creek) indicate that they contain PAH in concentrations and distributions that are typical of urban background, a pervasive non-point source of PAH that is found throughout the study area.

Thus, in accordance with Navy policy, these findings alone necessitate further instruction from CNO before implementing any further ER,N-funded studies relative to potential PAH inputs into the Southern Branch of the Elizabeth River and/or its western tributaries. The results of this study serve as appropriate information to augment a WCSD for subsequent submittal to the regulatory authorities.

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List of Appendices to Section 2 (Available through Stacey Curtis, SSC San Diego):

A: Sample Inventory with Location Coordinates and COC Documents

B: Rapid Sediment Screening Results—Tabulated

C: TOC and Grain Size Results of Samples Selected for ACF—Tabulated

D: GC/FID Chromatograms and Tabulated THC Concentration Data for Samples Selected for ACF

E: Tabulated PAH Concentration Data for Samples Selected for ACF and Corresponding Histograms

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