



NRL/MR/6110--99-8327

Fate and Transportation of PAH and Metal Comtaminants in the Anacostia River Tidal Region

RICHARD B. COFFIN

*Environmental Quality Sciences Section
Chemistry Division*

JOHN W. POHLMAN
CLARK S. MITCHELL

*Geo-Centers, Inc.
Landover, MD*

February 12, 1999

Approved for public release; distribution unlimited.

1 9990224035

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE February 12, 1999	3. REPORT TYPE AND DATES COVERED Program Overview June 1997-June 1998	
4. TITLE AND SUBTITLE Fate and Transportation of PAH and Metal Contaminants in the Anacostia River Tidal Region		5. FUNDING NUMBERS	
6. AUTHOR(S) R.B. Coffin, J.W. Pohlman,* and C.S. Mitchell*		8. PERFORMING ORGANIZATION REPORT NUMBER NRL/MR/6110-99-8327	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Washington, DC 20375-5320		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval District Washington Washington Navy Base Washington, DC 20375		11. SUPPLEMENTARY NOTES *Geo-Centers, Inc., Landover, MD	
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE A	
13. ABSTRACT (Maximum 200 words) PAH and metal contaminant transport has been studied in the Anacostia River tidal region quarterly since June 1997. Data from this report indicates that the physical transport of total suspended solids (TSS) through the tidal region of the Anacostia River has a substantial impact on the concentrations and fate of PAHs. Result show that the upper tidal region is a source of PAHs to the lower region. To initiate an understanding of the fate of PAHs attached to TSS, sediment traps were placed through the river. Sediment deposition at the wide and deep region of the river was similar to or greater than values measured in the upper regions where TSS concentrations are elevated. This observation has been supported with the following approaches: (1) comparison of river volumes in the upper river relative to the wide and deep region, and (2) measurements in the variation of current velocity through the river. These results indicate that this segment of the river is a region of substantial sedimentation of TSS attached PAHs attached. This correlates with previous studies that report high concentrations of PAH contaminants in sediments at this region of the river.			
14. SUBJECT TERMS Contaminant Sediment Ventilation doctrine		PAH Metals Tenability	Source Transport
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	15. NUMBER OF PAGES 17 16. PRICE CODE
19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED		20. LIMITATION OF ABSTRACT UL	

CONTENTS

I. Background	1
II. Outline of Field Work to Date	1
III. Results	2
A. Current Velocity	2
B. Thermal Stratification	5
C. Total Suspended Solids	5
D. PAH Concentrations	9
IV. Summary	12
V. Objectives for Program Completion	13
VI. Other Related Research Underway	13
VII. References	14

FATE AND TRANSPORT OF PAH AND METAL CONTAMINANTS IN THE ANACOSTIA RIVER RIDAL REGION

I. BACKGROUND

To address concerns regarding contaminant input to the Anacostia River, scientists at the Naval Research Laboratory conducted an initial survey of contaminant transport during June 1997 (Coffin et al. 1997). The primary goal of this project was to determine the concentrations and transport of polycyclic aromatic hydrocarbons (PAH) and heavy metal contaminants through the tidal region of the river. This initial survey has been extended to include 4 additional sampling events and provides the ability to identify potential sources and sinks of contaminants in the river. A full description of project goals and strategies is presented in Coffin et al. (1997). Complete data interpretation from these sampling dates is currently underway. This document provides a summary of current findings. A final report will be provided April 15, 1999.

Based on results from the initial field work and reorganization in funding levels, several components of the program have been changed. These are listed below:

1. Acoustic surveys of particle transport have been omitted. Total suspended solid (TSS) concentrations were measured using standard methods for each sample site.
2. In addition to measurement of the concentrations and speciation of PAHs attached to TSS in the water column, measurements on samples from sediment traps and the nepheloid layer (active particle layer at the sediment-water column interface) were applied to increase the understanding of distribution and transport.
3. During the June 1997 sampling polychlorinated biphenyl (PCB) concentrations on TSS were below limits of detection (Coffin et al., 1997). However, considering high sedimentation rates through the Anacostia River and typically slow turnover of PCBs, trace levels of PCBs may be detected if larger amounts of TSS could be sampled.

II. OUTLINE OF FIELD WORK TO DATE

Samplings were conducted from June 24 to 27, 1997; September 14 to 17, 1997; February 24 to 27 1998; and May 27 to June 3, 1998. Parameters measured during each sampling event were: 1) current velocity through Acoustic Doppler Current Profiles (ADCP) and a hand-held velocity meter on the sampling vessel, 2) TSS in the water column and nepheloid layer, and total solids in sediment traps, 3) carbon and nitrogen content of TSS, 4) PAH concentration in all TSS samples, and 5) dissolved and particulate metals. Nepheloid and sediment trap PAH samplings were not performed on June 1997 sampling. Sampling was conducted at stations S0, S1, S4, S5, and S7 (Fig. 1). Sampling schedules through these periods were as follows:

Day 1: Set ADCP (Acoustic Doppler Current Profile) systems at S4 and S5
Set sediment traps at S1, S4, S5, and S7

Day 2: Conduct two river transects at S0, S1, S4, S5, and S7 during different tidal stages

Day 3: Conduct cross river transects at S4, S5, and S7, and repeat sampling at S0 and S1

Day 4: Retrieve sediment traps

Retrieve ADCP systems and download current velocity

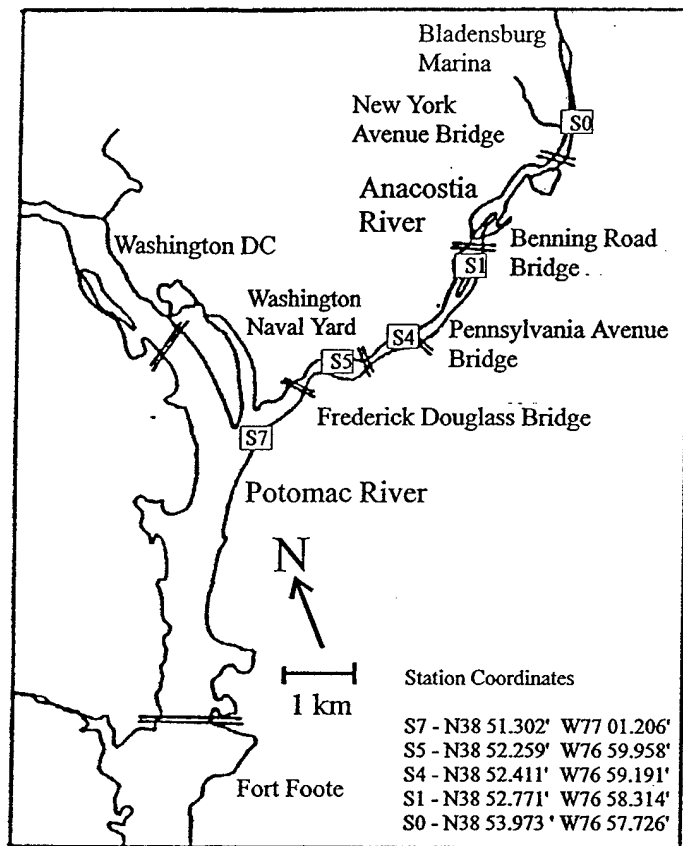


Fig. 1: Sample locations in the tidal region of the Anacostia River.

Methods for field sampling and laboratory analysis are presented in Coffin et al. (1997), with the exception of nepheloid sampling. This was accomplished by inverting a weighted nalgene funnel to the sediment-water column interface and using a pneumatic pump to draw samples. Typically, 1 L samples were obtained. In the laboratory, samples were processed with the same method described for sediment traps.

III. RESULTS

A. Current Velocity

A key component to developing an understanding of the contaminant transport through the tidal region of the Anacostia River has been to determine the factors that

control the TSS concentration and distribution. Variations in current velocities and thermal profiles are important. Current velocities were examined by using two approaches. During each sample event, an ADCP system was installed at S4 and S5 (Fig. 1) to provide continuous analysis of current velocities. In addition, a hand-held current meter was deployed from the sampling vessel at each station. Data from the ADCP system showed that flow direction was dependent on the tidal cycle. Through the water column current velocity was more rapid at S4 than at S5 (Table 1). The slower current velocity at S5, in front of the Washington Naval Yard (WNY), indicates that greater sediment deposition could occur at this point. This observation supports the preliminary conclusion (Coffin et al., 1997) that the river morphology makes this region a primary TSS sedimentation zone, possibly resulting in higher concentrations of contaminants in the sediments.

Table 1: ADCP profiles of current velocities for June 1997. Averaged velocities are presented at selected depths through the water column at stations S4 and S5.

Water Column Depth (cm)	Current Velocity (cm sec ⁻¹)	
	Station S4	Station S5
50	13.4	8.2
100	13.0	8.3
150	11.3	8.7
200	13.6	8.8
250	13.2	9.0

The ADCP system was also used to calibrate the hand-held current meter. Large spatial and temporal variations in current velocity, within and between sampling stations, were evident from the hand-held current meter (Fig. 2). This variation was a function of the volume of water transported from the upper regions of the river and tidal energy. Velocity at station S5 was consistently low, relative to S1, S4, and S7. The average current velocity for the all sample events was 0.08 ± 0.05 m sec⁻¹ (n = 113) while values for S7, S4, and S1 were 0.21 ± 0.19 (n = 115), 0.13 ± 0.08 (n = 71), and 0.22 ± 0.20 (n = 89) m sec⁻¹, respectively. The current velocity at S5 was significantly slower (Student's t-test) than for stations S7 (P < 0.01, n = 228), S4 (P < 0.01, n = 182) and S1 (P < 0.01, n = 202). The variation in current velocity at S1 is likely to result from variation in tidal energy and the narrow channel and the bridge supports in the channel. Variations at S7 occur as a result of tidal energy and convergence with the Potomac River.

Current Velocity (m sec^{-1})

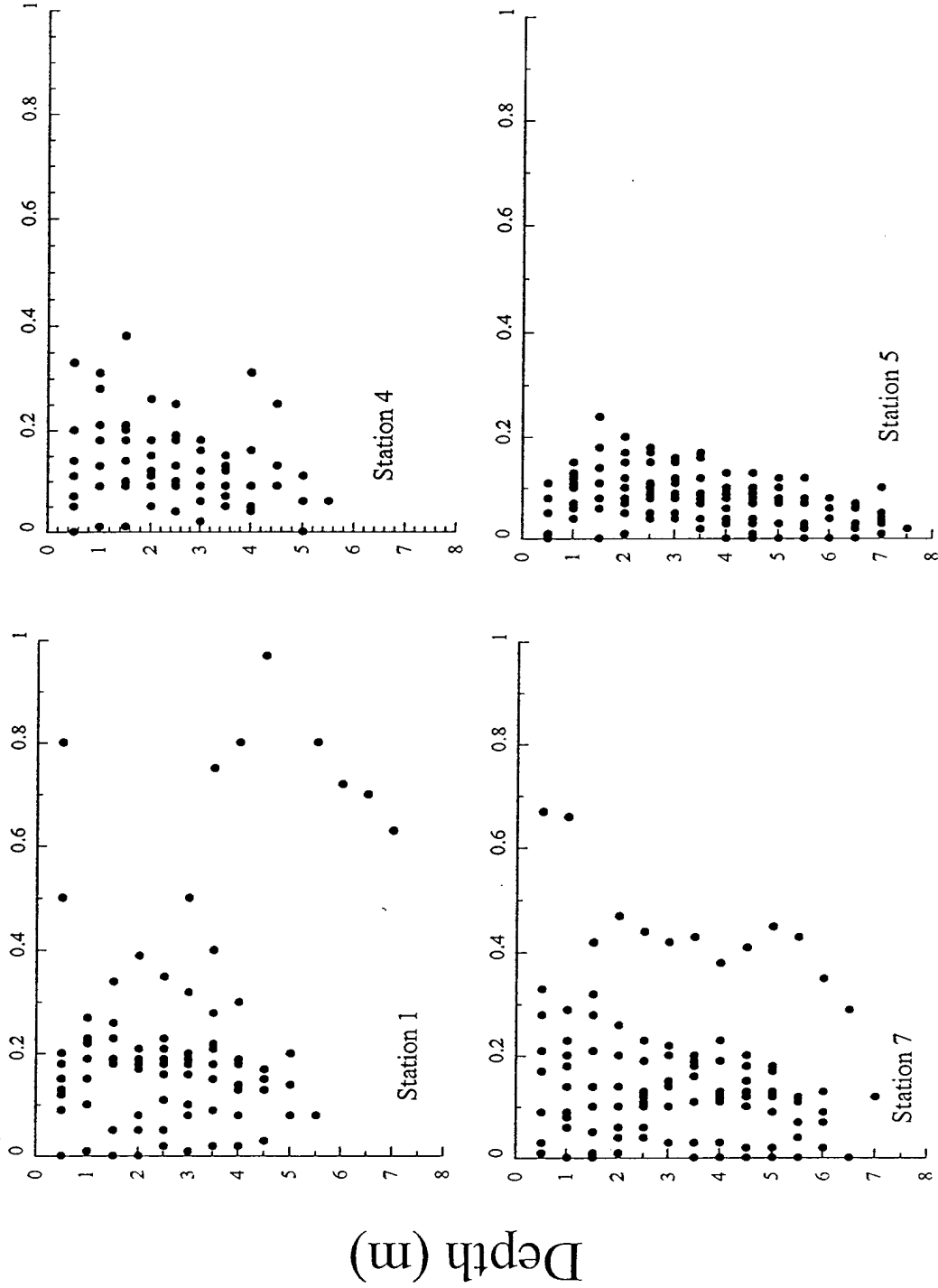


Figure 2: Summary of current velocity measured with a hand-held meter for June 1997, November 1997, and February 1998. Stations are S1, S4, S5, and S7 at 5.0, 3.6, 2.7 and 0 km from the river mouth.

B. Thermal Stratification

Thermal profiles obtained during the initial June 1997 sampling demonstrated stratification at stations S4 and S5 indicating tidal transport of colder Potomac River water into the Anacostia River (Coffin et al., 1997). Stratification at these stations was also observed during September and February, but the degree of stratification was less (0.5 C vs 1.5 C) and the stratification profile varied with depth; 1 to 4 m in June, 1.5 to 2.5 m in September, and 3 to 4 m February (Fig. 3). On some occasions thermal stratification was not observed, e.g., station S5 during September 1997. Stratification varies through different tide stages; it is greatest during the flooding tides (Fig. 4). These results again demonstrate the tidal influence of the Potomac River. The physical parameters that are likely to alter these thermal profiles include wind velocity and direction, river flow velocity, and tidal energy ranging between spring and neap tidal events. Temperature stratification may increase the upriver transport of TSS and attached contaminants or may reduce amounts of TSS deposition in certain areas. Thus it is an important parameter for the development of transport models and investigation of upstream contaminant transport.

C. Total Suspended Solids

A large seasonal variation in total suspended solids was evident through the year, ranging from 2.1 to 69.0 mg L⁻¹, with highest concentrations consistently measured in the upper reaches of the river – stations S0, S1 and S4 – as shown in Fig. 5. The TSS concentrations were significantly lower in the river at S5 than at the upper region ($P < 0.05$, $n = 66$). The lower TSS concentrations may be the result of greater sediment deposition during lower current velocities. With the data acquired to date, average TSS concentrations through the entire river were 19.4 ± 6.8 ($n = 38$), 20.0 ± 12.2 ($n = 49$), 38.8 ± 5.6 ($n = 12$) and 25.0 ± 9.6 ($n = 20$) mg L⁻¹ for June 1997, September 1997, February 1998, and May 1998, respectively. In February TSS concentrations were significantly higher ($P < 0.01$, $n = 536$) than at other sampling dates. Averaged velocities through the river measured between September 1997 and February 1998 were 0.09 ± 0.07 and 0.23 ± 0.21 m sec⁻¹, respectively, suggesting that TSS values increased with higher flow velocities in the river. However, tidal dilution with water from the Potomac River and thermal gradients will also alter TSS.

This program initially included acoustic analysis to monitor the TSS distribution in the water column. However, budget restraints prevented continuing this work. We are currently testing the calibration of a hand-held nephelometric instrument to measure TSS concentrations. Calibration of this instrument with field samples demonstrated a linear relationship between TSS and light absorption during a recent sampling ($r^2 = 0.998$, $n = 8$). Preliminary field data using the nephelometric instrument indicates a strong relationship between the current velocity and TSS concentrations (Fig. 6). This approach will be tested at different locations through time to confirm this application.

Temperature (C)

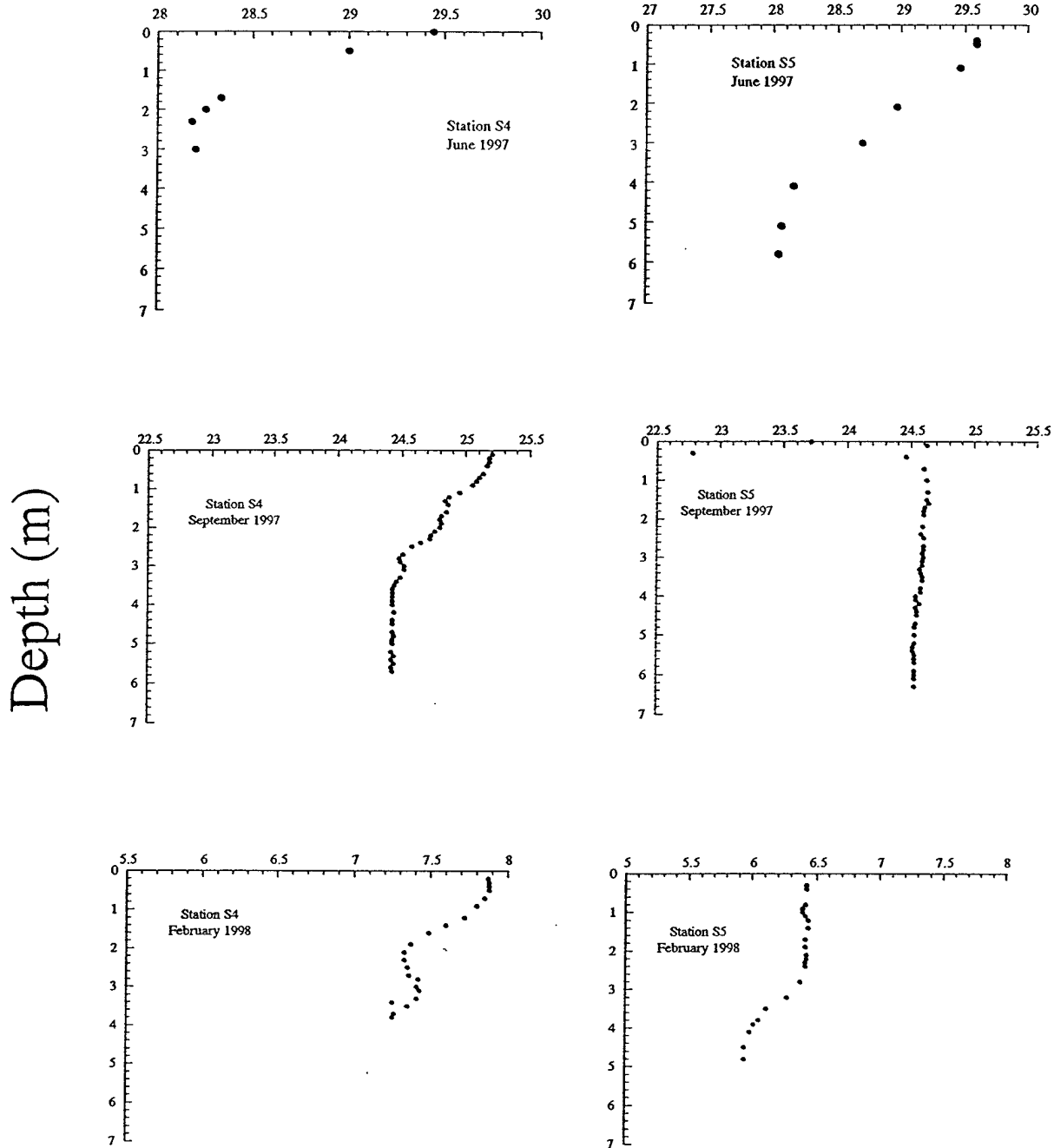


Figure 3: Seasonal variation in thermal profiles at S4 and S5 in the Anacostia River.

Temperature (C)

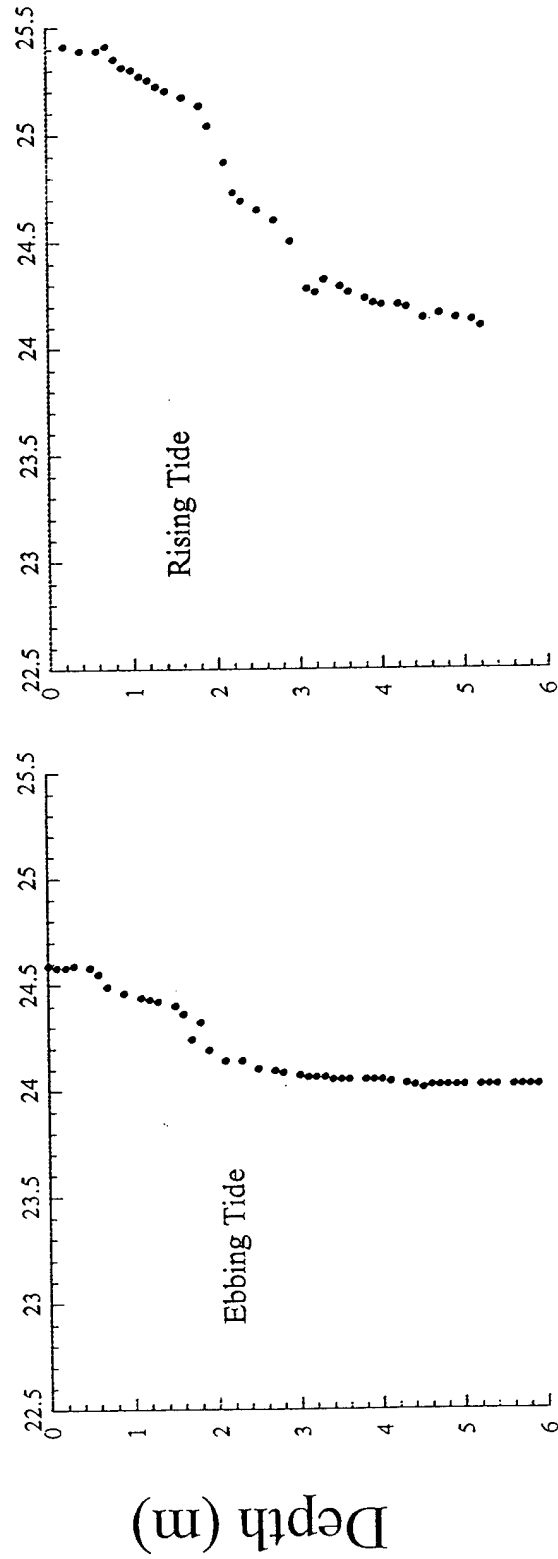
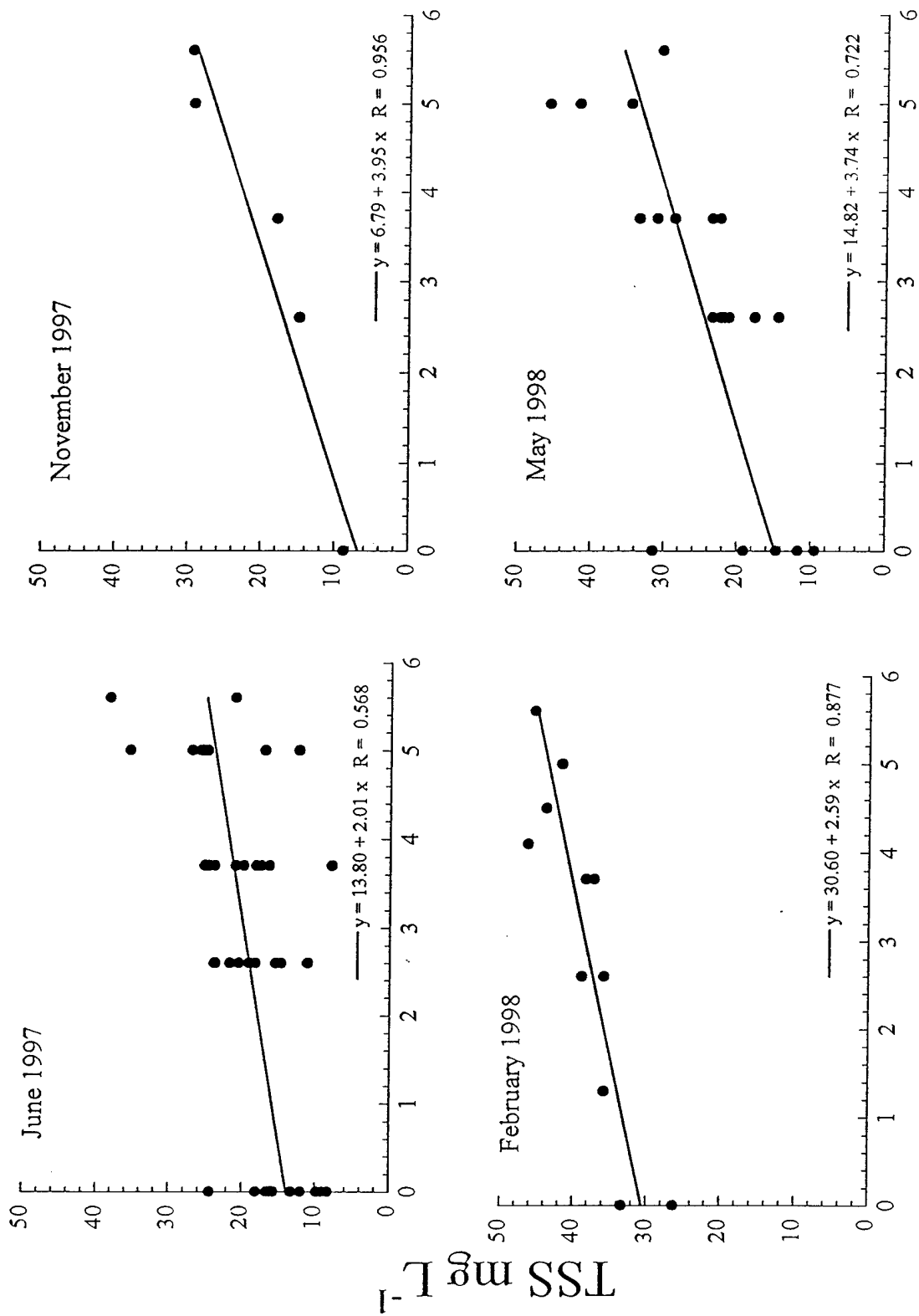


Figure 4: Thermal profiles during ebbing and rising tides in the Anacostia River at Station S5 during September 16, 1997.



Distance Upstream (km)

Figure 5: TSS concentration in the Anacostia River for June 1997, November 1997, February 1998, and May 1998. Stations are S0, S1, S4, S5, and S7 at 5.6, 5.0, 3.6, 2.7 and 0 km from the mouth of the river.

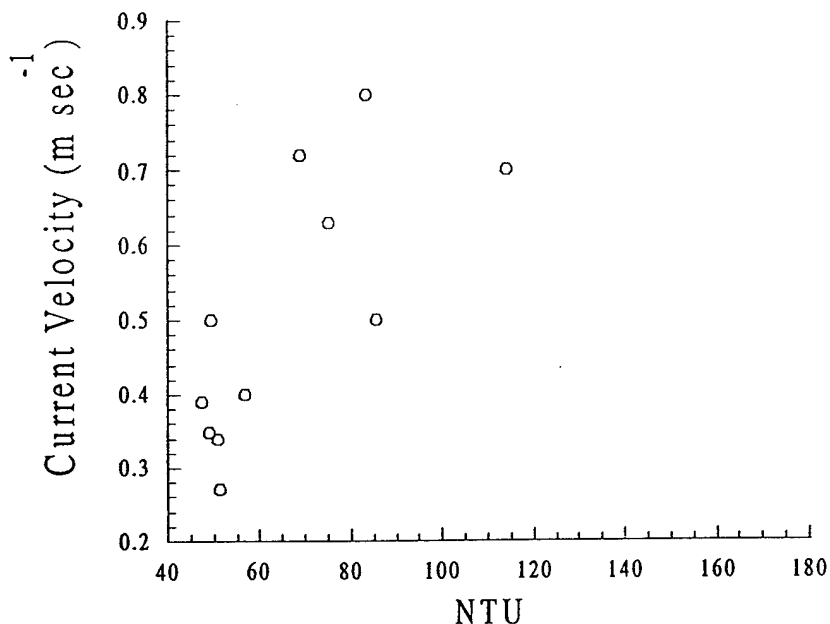
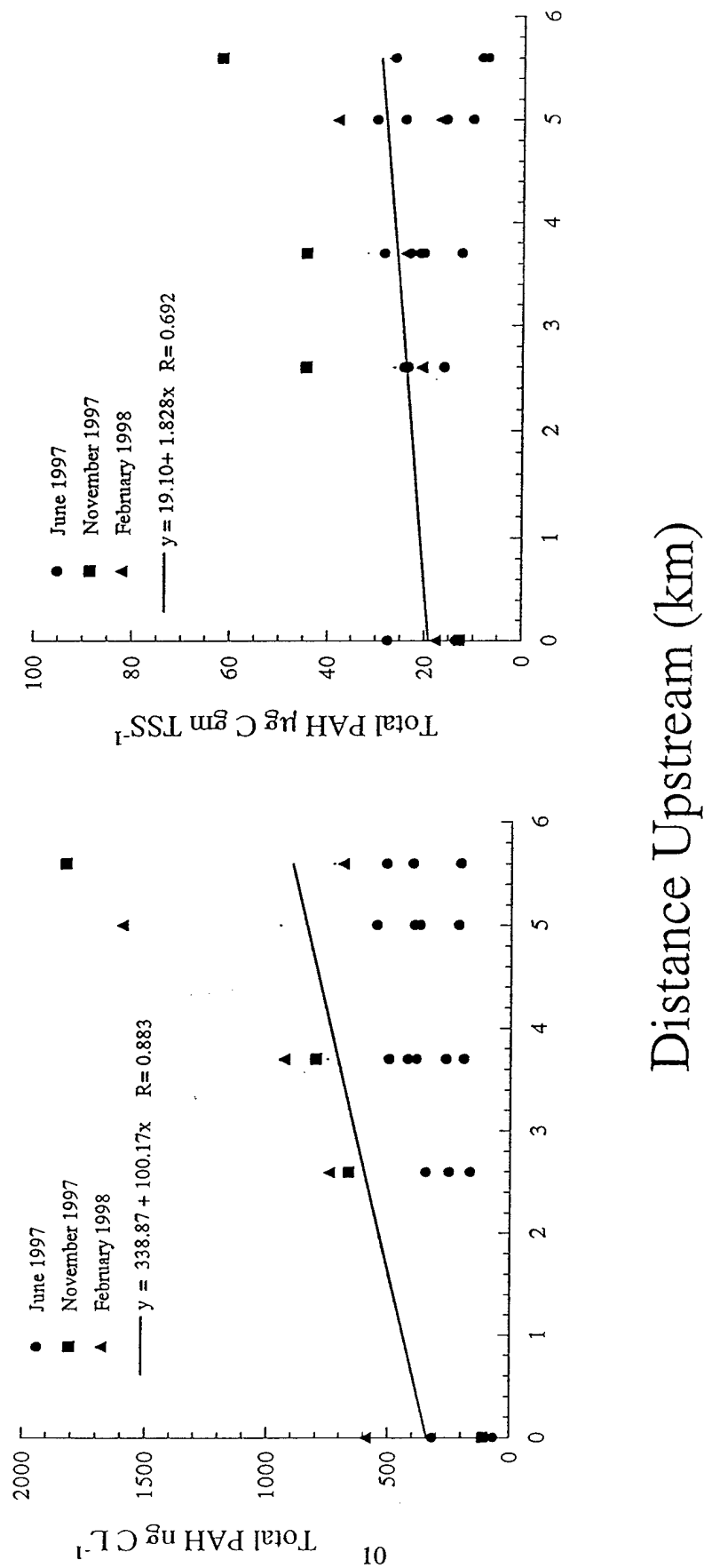


Fig. 6: Nephelometric analysis (NTU) of TSS loading relative to current velocity measured at S1 during June 1998 sampling.

D. PAH Concentrations

In the initial June 1997 sampling, significant concentrations of PAHs were found associated with particulates in the water column. This analysis was continued in subsequent samplings and, in addition, PAH concentrations on particulates in the nepheloid layer and in sediments collected in sediment traps were determined. PAH concentrations were measured in the water column in terms of TSS weight and water volume (Fig. 7). Large variations in PAH concentration throughout the river are evident and, as a result, a significant difference in PAH concentrations was not observed between S5 (high sedimentation region) and the upper river ($P > 0.05$). Variations of PAH concentration was probably the result of tidal transport and seasonal variations in current velocity.

Since there was an apparent decrease in PAH concentrations with distance down stream, slopes based on concentrations at each station S0 to S7 were compared in terms of PAH $\mu\text{g C gm}^{-1} \text{TSS}^{-1}$ and PAH ng C L^{-1} (Fig. 7). The slope is substantially greater in terms of volume. The small slope for the PAH concentration based on TSS concentrations, coupled with the observation of higher TSS in the upper river (presented above), suggests PAHs from the upper regions of the river is an important factor in the total loading to the tidal region.



Distance Upstream (km)

Figure 7: PAH concentrations in the Anacostia River, presented in terms of filtration volume and TSS. Stations referenced in the text are S0, S1, S4, S5, and S7 at 5.6, 5.0, 3.6, 2.7 and 0 km from the river mouth.

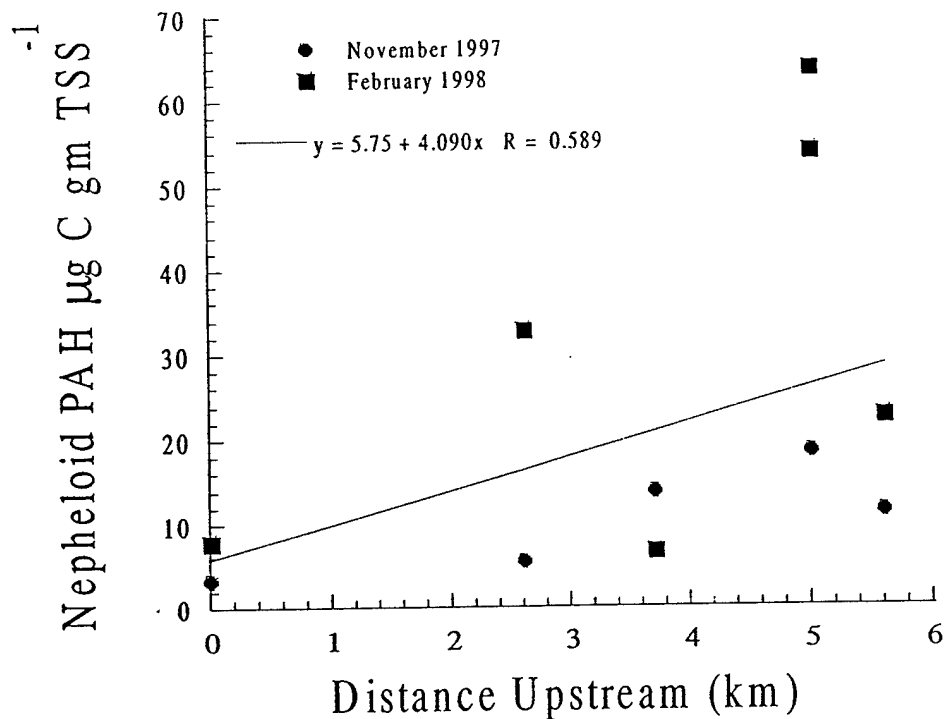


Fig. 8: PAH concentrations measured in the sediment nepheloid zone throughout the Anacostia River tidal region. Stations referenced in the text are S0, S1, S4, S5, and S7 located at 5.6, 5.0, 3.6, 2.7 and 0 km, respectively, from the mouth of the river.

PAH concentrations were measured in the nepheloid layer during the November 1997 and May 1998 samplings. Distribution of PAHs in the nepheloid mirror that of the TSS in the water column, i.e., the highest concentrations were found in the upper reaches of the tidal zone (Fig. 8). There is not a significant difference ($P > 0.5$) in PAH concentrations between the upper regions of the river and S5, the primary sedimentation region. The total quantity of PAHs in the nepheloid layer was much greater than in the water column. There is an interesting difference in the slopes of PAH concentrations in the water column and the nepheloid TSS through the river. For PAHs attached to particles in the water column, the slope of concentrations through the river was approximately 1.8 and for PAHs in the nepheloid layer, the slope was 4.1 (Fig. 7). This comparison suggests that the sedimentation of PAHs is occurring at a more rapid rate than the degradation through the river. Analysis of data from subsequent sampling events will assist in understanding the relative contribution of sedimentation, transport, and degradation of the PAHs in both phases.

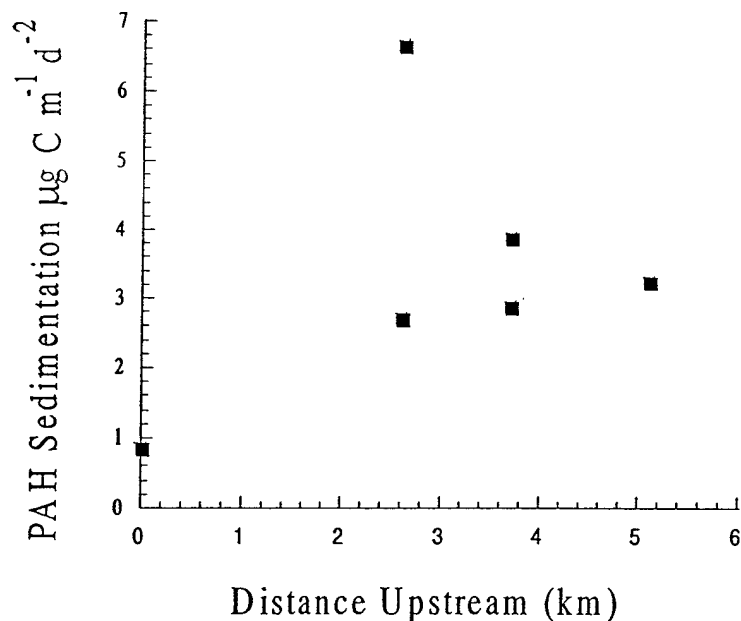


Fig. 9: PAH concentrations in sediment traps at sampling stations in the Anacostia River during February 1998. Stations referenced in the text are S0, S1, S4, S5, and S7 located at 5.6, 5.0, 3.6, 2.7 and 0 km, respectively, from the mouth of the river.

Preliminary analysis of PAH concentrations in sediment traps showed values to be higher or equivalent in sediment traps at S5 to the upper river sampling sites where TSS was substantially greater (Fig. 9). In the upper regions of the river, similar or slightly smaller concentrations of PAHs were measured in the traps. This analysis needs confirmation of sedimentation rates with an accurate elemental tracer and additional sediment trap analysis to determine statistical variations.

IV. SUMMARY

This survey of the Anacostia River is designed to afford an understanding of the transport of PAH contaminants through the tidal region. Data presented in the survey show that concentrations of PAHs attached to total suspended solids in the water column and in the nepheloid layer are significant and correspond with a previous survey of the distribution of PAHs in the sediment (Wade et al., 1994). This result necessitates understanding the physical transport and fate of particle-bound PAHs. The database outlined in this report shows that the physical transport of TSS through the tidal region of the Anacostia River has a substantial impact on the concentrations and fate of PAHs. Tidal mixing, resulting in reversed river currents and transport of TSS, makes spatial interpretation of variations in PAH concentrations in the river difficult. While there is not a large variation in concentrations of PAHs attached to TSS, there is a substantial decline in the total TSS loading from the upper tidal region to the mouth of the Anacostia River.

This result shows that the upper tidal region is a source of PAHs to the lower region of the river.

Thermal stratification is another physical parameter that can control the transport of TSS through the river. The combination of thermal stratification and tidal energy can result in the upstream transport of the TSS and associated PAHs. Thermal stratification was definitely observed in this study with variations controlled: 1) seasonally, with higher stratification during warmer months, 2) spatially as a function of river current velocity and river morphology, and 3) over short time scales that were controlled by tidal energy.

Sediment deposition at station S5 was similar to or greater than values measured in the upper regions where TSS concentrations are elevated. This observation has been supported by: 1) comparison of river volumes in the upper river relative to S5 (Coffin et al., 1997), 2) measurements in the variation of current velocity through the river with a hand-held current meter and ADCP, and 3) application of sediment traps to survey PAH deposition through the river. These results indicate that S5 is a region of substantial sedimentation of PAHs attached to TSS.

V. OBJECTIVES FOR PROGRAM COMPLETION

1. The current database shows that PAH sources originate from the regions above the tidal mixing zone. However, the large variation in PAH concentrations at stations in the tidal zone makes it difficult to delineate sources from the tidal and nontidal regions. Dye tracer studies will be conducted to analyze the tidal excursion through different segments of the river. This will assist in understanding variations in the fate and transport.
2. An accurate estimate of the sedimentation rate is needed. Sediment traps provide a maximum estimate of sedimentation because particles are fixed in the containers and not resuspended and transported. A potential tracer for sedimentation is ^7Be , which is produced in the atmosphere and actively binds with TSS in the water column. This element has a half-life of 40 days, which would provide a short time scale analysis of sedimentation.

VI. OTHER RELATED RESEARCH UNDERWAY

1. A key to determining the fate of PAHs is analysis of microbial degradation. Researchers that are involved with this program have been awarded ONR research funds to accomplish this goal. This effort includes aerobic and anaerobic PAH degradation in the sediment and water column. When additional funding is obtained, work will focus on the seasonal and spatial variation in PAH degradation. This effort will analyze the fate of PAHs through a survey of transport and degradation.
2. Immunological assays have been initiated to determine the contribution of PAHs to toxicity in the river. This is accomplished through immunoassays of sentinel species

and the bacterial assemblage. Future funding will support a long-term analysis of ecosystem health in terms of PAH toxicity.

3. Data presented in this study indicate that PAH sources originate above the Anacostia River tidal zone. Input from the nontidal zone is not known. In collaboration with Dave Shepp (MWCOCG) a program is being organized to delineate sources of PAHs. A key component of this research effort will be to use stable carbon isotope analyses to fingerprint the sources through the tidal and nontidal regions.

VII. REFERENCES

Coffin, R. B., M. Orr, E. Carey, L. Cifuentes, and J. Pohlman. 1998. Contaminant Distribution and Fate in Anacostia River Sediments: Particulate Transport Survey. NRL/MR/6115—98-8139.

Wade, T. I., D. J. Velinsky, E. Reinharz, C. E. Schlekat. 1994. Tidal River Sediments in the Washington, D. C. Area. II. Distribution and Sources of Organic Contaminants. *Estuaries* 17:321-333.