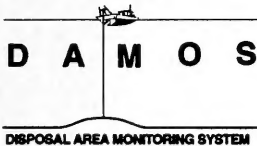


Application of *in situ* UV Spectrometry for Characterization of Harbor Sediment

DATA LIBRARY
Woods Hole Oceanographic Institution



Contribution 127
February 2000



**US Army Corps
of Engineers**
New England District

TC
187
.057
2007

REPORT DOCUMENTATION PAGE

form approved
OMB No. 0704-0188

Public reporting concern for the collection of information is estimated to average 1 hour per response including the time for reviewing instructions, searching existing data sources, gathering and measuring the data needed and correcting 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 Observations and Records, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302 and to the Office of Management and Support, Paperwork Reduction Project (0704-0188), Washington, D.C. 20503.

1. AGENCY USE ONLY (LEAVE BLANK)	2. REPORT DATE February, 2000	3. REPORT TYPE AND DATES COVERED FINAL REPORT
---	---	---

4. TITLE AND SUBTITLE APPLICATION OF IN SITE UV SPECTROMETRY FOR CHARACTERIZATION OF HARBOR SEDIMENT	5. FUNDING NUMBERS
--	---------------------------

6. AUTHOR(S) Gregory A. Tracey, Donald C. Rhoads, and Drew A. Carey

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Science Applications International Corporation 221 Third Street Newport, RI 02840	8. PERFORMING ORGANIZATION REPORT NUMBER SAIC-455
--	---

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) US Army Corps of Engineers-New England District 696 Virginia Rd Concord, MA 01742-2751	10. SPONSORING/MONITORING AGENCY REPORT NUMBER DAMOS Contribution No. 127
--	---

11. SUPPLEMENTARY NOTES Available from DAMOS Program Manager, Regulatory Branch USACE-NAE, 696 Virginia Rd, Concord, MA 01742-2751

12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited	12b. DISTRIBUTION CODE
--	-------------------------------

13. ABSTRACT <p>Polycyclic Aromatic Hydrocarbons (PAHs) are common constituents of aquatic sediments in navigable waterways. The need for maintenance dredging and concern over proper disposal of dredged sediments requires that the distribution and concentration of chemicals such as PAHs be known. This report presents preliminary findings from laboratory and field tests of a portable fluorescence imaging system for mapping PAH distribution in sediment.</p> <p>The UltraViolet-Remote Ecological Monitoring Of The Seafloor (UV-REMOTS®) instrument collects a vertical profile image of the top 6–8 cm of sediment at the sediment-water interface. Adapted from the photo REMOTS® system, it is designed to provide a two-dimensional digital image wherein each component pixel constitutes a full spectral characterization of fluorescence emission in response to a UV light source. The excitation and emission frequencies are selected to optimize for the known PAH fluorescence response to UV light. Because PAHs are composed of many different compounds, variation in intensity and spectral pattern correspond to changes in PAH concentration and composition.</p> <p>Results of the laboratory tests with spiked sediments indicate the UV-REMOTS® system can detect differences in PAH concentration and composition in the range of 10–100 ppm (ug/g dry weight) and above. Field results from the Providence River suggest measurable differences in fluorescence between sampling locations as well as small-scale variation in fluorescence within the image of a single sample. Based these results, it is concluded that UV-REMOTS® shows good promise as a tool for rapid assessment of PAH concentration, composition and spatial distribution.</p>
--

14. SUBJECT TERMS Polycyclic Aromatic Hydrocarbons (PAHs), portable fluorescence imaging system, UV-REMOTS®	15. NUMBER OF TEXT PAGES: 11
--	-------------------------------------

	16. PRICE CODE
--	-----------------------

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
---	---	--	-----------------------------------

**APPLICATION OF *IN SITU* UV SPECTROMETRY
FOR CHARACTERIZATION OF HARBOR SEDIMENT**

CONTRIBUTION #127

February 2000

Submitted to:
Regulatory Branch
New England District
U.S. Army Corps of Engineers
696 Virginia Road
Concord, MA 01742-2751

Prepared by:
Gregory A. Tracey, Donald C. Rhoads,
and Drew A. Carey

Submitted by:
Science Applications International Corporation
165 Dean Knauss Drive
Narragansett, RI 02882
and
Admiral's Gate
221 Third Street
Newport, RI 02840
(401) 847-4210



**US Army Corps
of Engineers.**
New England District

TABLE OF CONTENTS

	Page
List of Figures.....	iii
List of Tables.....	v
Executive Summary	vi
1.0 INTRODUCTION	1
2.0 MATERIALS AND METHODS	3
2.1 Laboratory Studies.....	3
2.2 Field Sampling	3
2.3 Camera Operation	3
2.4 Data Processing and Analysis.....	4
3.0 RESULTS	5
3.1 Laboratory Studies.....	5
3.2 Field Data	5
3.2.1 Horizontal Characterization	6
3.2.2 Vertical Characterization.....	6
3.3 Intensity Analysis.....	7
4.0 DISCUSSION.....	9
5.0 CONCLUSIONS	10
6.0 REFERENCES	11

INDEX

APPENDIX

LIST OF FIGURES

(Figures located in Appendix)

- Figure 1. Locations of UV-REMOTS® for characterization of harbor sediment
- Figure 2. Results of UV-REMOTS® laboratory analysis of anthracene (ANT) spiked water and sediments: A) Reference sediment in seawater; B) ANT and seawater; C) ANT and sediment; and D) Sediment PAH mix with ANT
- Figure 3. Inter-comparison of full sediment area spectra at each location for each excitation wavelength
- Figure 4. Inter-comparison of entire imaged area spectra for each excitation wavelength
- Figure 5. RGB Images at Shooters Dock, Site 2, State Pier, and Sassafras Point showing full mask (i.e., complete imaging) and spatial location of individual ROIs
- Figure 6. Inter-comparison of the six ROIs at Shooters Dock and Site 2
- Figure 7. Inter-comparison of the Middle Left ROI at the three locations for all four excitation wavelengths
- Figure 8. Inter-comparison of the Middle Right ROI at the three locations for all four excitation wavelengths
- Figure 9. Inter-comparison of the Bottom Left ROI at the three locations for all excitation wavelengths
- Figure 10. Inter-comparison of the Bottom Right ROI at the three locations for all four excitation wavelengths
- Figure 11. Inter-comparison of each ROI at the three locations for the 299 nm excitation wavelength
- Figure 12. Inter-comparison of each ROI at all three locations for the 314 nm excitation wavelength
- Figure 13. Inter-comparison of each ROI at all three locations for the 335 nm excitation wavelength

LIST OF FIGURES (continued)

Figure 14. Inter-comparison of each ROI at all three locations for the 365 nm excitation wavelength

LIST OF TABLES

(Tables located in Appendix)

- Table 1. PAH Concentrations from the Providence River (PR) and Harbor (November 1992)
- Table 2. Statistical Summary of Non-Zero Pixel Abundance by Excitation Wavelength and Region of Interest (ROI) for UV-REMOTS®
- Table 3. Statistical Summary of Non-Zero Pixel Abundance by Excitation Wavelength and Sample Location for UV-REMOTS®

EXECUTIVE SUMMARY

Polycyclic Aromatic Hydrocarbons (PAHs) are common constituents of aquatic sediments in navigable waterways. The need for maintenance dredging and concern over proper disposal of dredged sediments requires that the distribution and concentration of chemicals such as PAHs be known. This report presents preliminary findings from laboratory and field tests of a portable fluorescence imaging system for mapping PAH distribution in sediment.

The UltraViolet-Remote Ecological Monitoring Of The Seafloor (UV-REMOTS®) instrument collects a vertical profile image of the top 6–8 cm of sediment at the sediment-water interface. Adapted from the photo REMOTS® system, it is designed to provide a two-dimensional digital image wherein each component pixel constitutes a full spectral characterization of fluorescence emission in response to a UV light source. The excitation and emission frequencies are selected to optimize for the known PAH fluorescence response to UV light. Because PAHs are composed of many different compounds, variation in intensity and spectral pattern correspond to changes in PAH concentration and composition.

Results of the laboratory tests with spiked sediments indicate the UV-REMOTS® system can detect differences in PAH concentration and composition in the range of 10–100 ppm (ug/g dry weight) and above. Field results from the Providence River suggest measurable differences in fluorescence between sampling locations as well as small-scale variation in fluorescence within the image of a single sample. Based these results, it is concluded that UV-REMOTS® shows good promise as a tool for rapid assessment of PAH concentration, composition and spatial distribution.

1.0 INTRODUCTION

One of the essential missions of the U.S. Army Corps of Engineers (USACE) is to monitor and maintain navigable waterways. Particulates originating from rivers, land runoff, and atmospheric deposition accumulate in harbors and channels. Dredging is required to restore the depth and width of these channels and harbors. A variety of chemicals of concern (CoCs) are associated with these particulates which may pose a problem for aquatic biota depending upon their concentration. One of the major classes of CoCs is Polycyclic Aromatic Hydrocarbons (PAHs). PAHs enter the environment in raw (i.e., petrogenic) form as oil and fuel products or in a combusted (i.e., pyrogenic) form such as stack ash and automobile exhaust.

As part of the regulatory requirements for dredging, the USACE must characterize the quantity and type of sediments that require dredging and determine their suitability for land or aquatic disposal. Although the ultimate determination of suitability rests on biological effects testing (e.g., EPA/USACE 1994, 1998), the measurable levels of CoCs in surface sediments provide a critical guide for project scoping and sample location.

Traditional analyses (e.g., for PAHs) in bottom sediments for purposes of contaminant characterization typically involve sample collection, chemical extraction, and instrumental analysis (e.g., UV spectrometry, gas chromatography/mass spectrometer, and/or high performance liquid chromatography). These traditional methods have the advantage of low analytical detection limits but are laborious, expensive, and time consuming. The sheer number of sediments requiring characterization as well as the long analytical time-frame and high cost per sample of chemical analysis present an increasingly formidable challenge to the USACE in executing its responsibilities for characterizing harbor sediments. As a result, the USACE has expressed a need for field instrumentation that can be rapidly and inexpensively deployed to characterize and quantify PAH concentrations in sediment.

Science Applications International Corporation (SAIC) has developed a prototype field instrument called UV-REMOTS® (UV-R) which shows great promise for the rapid evaluation of PAH composition and concentration in sediment. The basic format for the technology is based on the original REMOTS® sediment profile camera which produces a photographic image of the sediment-water interface (to 20 cm depth) such that various habitat attributes (sediment, grain-size, fabric, depth of mixture, and community structure) can be ascertained. In UV-R, the analog visible (white light) camera system of REMOTS® was replaced with a digital camera and UV-light source such that chemicals that fluoresce under UV light can be detected and quantified (Rhoads et al. 1995).

In this report, the results of the first substantial field deployment of UV-R in the Providence River of Narragansett Bay are presented. The objectives of the study were 1) to assess the operational performance characteristics of the instrument under field

conditions; 2) to evaluate the fluorescence properties of field sediments in relation to expected (laboratory-based) PAH distribution/concentration measurements; 3) evaluate the spatial patchiness of PAHs in undisturbed (i.e., *in-situ*) material sediments; and 4) evaluate the ability of UV-R to distinguish differences in PAH distribution within the sediment column. The results of the investigation will be discussed relative to these four objectives; recommendations for additional system improvements, data analysis, and data needs are also provided.¹

¹ Funding for this work was provided primarily by the USACE Waterways Experiment Station, Vicksburg, MS with supplemental funding from the NAE DAMOS Program.

2.0 MATERIALS AND METHODS

Field test objectives were evaluated in the Upper Providence River, Rhode Island at selected stations. Spectral data on PAHs in sediment were collected using UV-R and qualitatively compared with existing bulk sediment chemistry. Prior to the field test, the response characteristics of UV-R were determined in a series of laboratory bench tests in which ambient sediments were mixed with known concentrations of PAHs of interest.

2.1 Laboratory Studies

In the development of the UV-R technology, SAIC as part of its Internal Research and Development (IR&D) program, conducted a series of experiments since 1993 to evaluate PAH fluorescence properties and optimized the UV-R hardware and software systems for PAH detection and analysis. For this report, example laboratory data sets derived from anthracene-spiked water and sediment matrices are included to provide a comparison for interpretation of field results. Results of four treatments are presented:

- 1) seawater only;
- 2) seawater + 1000 ppm anthracene; and
- 3) anthracene + seawater + sediment at 1000 ppm final concentration.

2.2 Field Sampling

Field deployment of the UV-R system was carried out from November 22–26, 1997, at nine stations shown in Figure 1 including one site each at Sassafras Point, Fields Point Bulkhead, State Pier, and Station E Pipes, and two sites each at the Shooters Dock and the Hurricane Barrier. The sites were selected based on historical measurements of PAH concentration within the general study area. No traditional chemical analyses of PAH concentration were made at the time of UV-R deployment.

2.3 Camera Operation

Deployment of the UV-R camera is similar to the deployment of the white light REMOTS® camera (Rhoads and Germano 1986). The UV-R camera is lowered to the bottom and the prism descends to the seafloor, slowed by hydraulic pistons, and is allowed to penetrate the sediment. When the optical prism is in the mud, the camera first collects a digital RGB image consisting of 640×480 pixels to allow for visualization of objects in the sediment as well as the sediment/water interface. The 640×480 image is divided into “bins,” four pixels on each side. The 4×4 pixel binning is applied to increase signal strength for fluorescence detection while still providing adequate image resolution. A mercury (Hg) vapor light source sequentially emits four separate excitation wavelengths of 299, 314, 335, and 365 nm. The PAHs in the sediment absorb energy at these

wavelengths and, depending on concentration and composition, will emit “red shift” light (i.e., fluoresce) across a broad spectrum of wavelengths. Based on prior investigation and literature values, specific wavelengths were selected to measure the fluorescence response and hence characterize the PAH composition of the sample. Before the red shift light is collected for spectral measurement, a blocking filter is used to block-out all excitation light. The selected emission endpoints include 17 total narrow wavelengths including 15 wavelengths between 350–500 nm (at increments of 10 nm) and two additional wavelengths at each of 550 nm and 600 nm bandwidths. In this manner, up to 68 intensity images (17 emission \times 4 excitation bands) for each image replicate can be obtained.

Also collected on each sampling day are dark field (camera on, no light) and white field images (camera on, white surface illuminated) for the purpose of correcting internal electrical noise and variation in target illumination, respectively. The resulting data are internally stored then relayed to the surface computer after one or several samples are collected.

2.4 Data Processing and Analysis

The primary method of correcting raw image (RI) data for variance in electronic noise and sample illumination is described in Equation 1:

$$CI(i,j) = (RI(i,j) - DF(i,j)) / WF(i,j) \quad (1)$$

where CI = corrected image matrix, DF = dark field image matrix, and WF = white field image matrix, and i,j is the row and column location of pixels. In the above corrections, the DF matrix is used to remove electrical noise in the camera system, while the WF matrix permits correction of individual pixels for differences in pixel illumination across the image. Except where noted, the above corrections were applied to all data sets included in this report.

MATLAB programs (Mathworks, Inc.) were written to visualize the data and perform the above corrections. The program permits further examination of the data using area, intensity, and spectral quality filters for specified Regions of Interest (ROI) within the image. ROIs are selected by the user and depend on the camera penetration depth and other features readily visible in RGB images taken at the same location. For example, ROIs are used to mask out the water column part of each image and to limit the ROI to only those parts of the sediment profile that exhibit fluorescence.

3.0 RESULTS

3.1. Laboratory Studies

Laboratory investigations with anthracene in water and sediment were performed to evaluate the spectral sensitivity of the UV-R system to PAH concentration. Typical spectra of clean 'reference' sediment from Central Long Island Sound for four excitation wavelengths show corrected fluorescence intensity ranges from 10–80 units (Figure 2A). Measured anthracene concentration for this sediment was <1 ppm. In contrast, the spectra obtained when 1000 ppm anthracene is added to seawater (0 to 1200 units; Figure 2B) or sediment (0 to 1100 units; Figure 2C) show a characteristic anthracene signature (note change in intensity scale). The 365 nm excitation band (1100–1150 ADU) exhibits a strong peak at 420 nm, (i.e., dropping sharply for higher and lower excitation wavelengths) and a secondary peak at 450 nm. Little difference in the anthracene spectra is observed whether the carrier matrix is water or sediment.

The spectral signature of a PAH mixture containing approximately 500 ppm anthracene, benzo(a)pyrene and pyrene in sediment is more complex (Figure 2D). The latter two PAHs are known to have peaks at 420 nm as well as broader peaks in the 450–500 nm range. The peak for anthracene at 420 nm is retained, although apparently augmented by fluorescence at this wavelength from either benzo(a)pyrene and pyrene. These data illustrate the need for a spectral PAH library so as to permit the deconvolution (i.e., spectral unfolding) of the PAH mix spectra into its component parts.

3.2 Field Data

Preliminary analysis of the RGB images taken at the locations shown in Figure 1 indicated that only three of the locations had sufficient camera penetration to produce data for analysis. These locations included Shooters Dock site 2 (A), State Pier (C), and Sassafra Point (E), (Figure 1).

Data images from the above locations were inspected to characterize both between and within-station differences in PAH distributions. Between station characterizations were conducted to address horizontal gradients of PAH distribution which might be correlated with known PAH gradients in the Providence River. Within-station analyses focused on investigation of PAH vertical distribution in the sediment column, particularly the existence of potential "hot spot" areas which might be caused by aggregations of PAH particulates (e.g., coal tar) or bioturbation patterns. Horizontal and vertical spatial analyses are presented separately below.

3.2.1 Horizontal Characterization

To test for between station differences in PAH concentration and composition, images collected at three stations (Shooters Dock, Site 2 [A], State Pier [B], and Sassafras Point [D]) were spectrally analyzed. Results are presented by station and excitation band in Figures 3 and 4, respectively. In Figure 3, the three stations show that the 365 nm excitation wavelength generated the largest fluorescence intensities, exceeding by a factor of 3 to 4 those contributed by other wavelengths.

A comparison across stations at the same excitation wavelength is shown in Figure 4. Two notable features in the data are the peak at 314 nm excitation/400 emission band (B) at Shooters, and the higher emission for the Shooters or Sassafras Point samples relative to the State Pier sample at 299, 314, and 365 nm (A,B,D). Higher fluorescence returns for Shooters/Sassafras vs. State Pier is probably related to total PAH concentration in the sediment; the State Pier station is generally lower in Total PAH and constituent analytes than the other two locations based on 1992 analyses of PAH concentrations (Table 1). An alternative explanation is the presence of dissolved humic or chlorophyll/phaeophytin substances which exhibit a broad fluorescence emission peak centered between 420 and 460 nm. The discrimination between the two potential fluorescing agents will require further characterization. The 314 excitation/400 emission peak (B) may be explained by high pyrene in the sediment (13 ppm) (Table 1), as this compound has peak emission at 398 nm (Rudnick and Chen 1998), although a similar pyrene peak was not observed for the laboratory PAH mix discussed in Section 3.1.

3.2.2 Vertical Characterization

To test for within-station difference in PAH concentration and composition, four Regions of Interest (ROI) were selected for each of the three stations (Shooters Dock 2, State Pier, and Sassafras Point) as indicated by open circles in the RGB images of Figure 5. Possible variation may be due to the history of sediment deposition and/or localized bioturbation. The ROI locations were selected to maximize area while avoiding image edges. These ROIs have the same size (pixel population) and spatial orientation. The ROIs are designated in the results below as Middle Left (ML), Middle Right (MR), Bottom Left (BL), and Bottom Right (BR). An additional two ROIs were selected for Shooters Dock, Site 2 to characterize the water column immediately above the sediment. These ROIs were designated as Top Left (TL) and Top Right (TR).

Spectral analysis of each ROI allowed for an inter-comparison of each site and also allowed for spectral comparison of ROIs containing just water and/or just sediment. An analysis was performed on the six ROIs at Shooters Dock, Site 2, to compare the two ROIs located entirely in the water column with the sediment signals (Figure 5A). Results are shown in Figure 6. The purpose of this analysis was to determine how fluorescence returns in the water column (a shade was used to cover the camera prism's optical window

to minimize infiltration of visible light) compared with the intensities of the sediment/interstitial water. From Figure 6, it is seen that ambient light leakage intensities are similar to those found in the sediment for emission spectra of 350–450. However, emission wavelengths of 500–600 (visible light wavelength) had much larger intensities. This observation underscores the importance of having an efficient “shade” on the camera to prevent visible light contamination.

In order to exclude water column light noise in the analysis of sediment-associated PAH spectra, the remainder of the analyses focus on the Middle and Bottom ROIs as these areas encompass only sediment. Each of these ROI is presented separately by station in Figures 7–10. As found for the whole sediment samples, the 365 nm excitation band produces highest emission intensities for each of the locations.

The same data presented by excitation wavelength in Figures 11–14 do reveal some ROI-specific phenomena. For example, unique peaks are observed:

- 1) at 299 excitation /430 emission for bottom left (BL) and bottom right (BR) ROI for Sassafras and State Pier (Figure 11E,F);
- 2) at 314/380, 314/420 and 314/450 nm combinations for Middle left ROI at State Pier (Figure 12C); and
- 3) at 335/440, 335/450 combination for Middle Left and Middle Right ROI at State Pier and Sassafras Point, respectively (Figure 13 [C,D]).

Finally, the 365 nm peak for the BR-ROI is higher for Shooters/Sassafras as found previously for the whole sediment, but in the three other regions, Shooters emission was at or below State Pier (Figure 14). Hence, the bottom right portion of the spectra was dominating the return observed for the full image, possibly indicating a locally higher PAH concentration.

3.3. Intensity Analysis

The data sets presented above have been processed using the full correction algorithm (Equation 1) without regard to the intensity of the fluorescence emission. That is, the data results represent average fluorescence emission over the entire ROI. In this section, the variance of the fluorescence emission pattern are analyzed to discern whether highly localized (i.e., pixel-scale) emissions occur which may relate to small amounts of PAH materials (e.g., soot particles, oil droplets). The inspection of pixel returns within ROIs reveal that relatively few of the pixels in each ROI actually contained detectable emission data (Table 2). For example, the average number of non-zero pixels ranged about 1–9% at Shooters 2; the other two sites were found to have similar statistical distributions. It is also apparent that the number of non-zero pixels for the entire sediment

image increases proportionately with number of sampled pixels (Table 3).

As seen in Tables 2 and 3, the area of emission (number of non-zero pixels) resulting from 335 nm excitation was typically 3X lower and 365 nm 2X higher than either the 299 nm or 314 nm bands. Such differences may be related to the optical density of the excitation filters and/or lamp intensity at the particular wavelength. The relatively low number of non-zero pixels is attributed to low PAH signal in comparison to camera and background noise.

4.0 DISCUSSION

Laboratory studies have demonstrated the capability of UV-R to detect various PAH analytes and quantify concentrations in the range of 10–100 ppm and higher. PAH data determined on traditional chemical analyses of grab samples, show the concentrations of total PAHs at State Pier and Sassafra Point (20 and 30 ppm, respectively) have directly proportional fluorescence intensities (365 nm excitation; 400 and 600 maximum ADU, respectively; Figure 3). This suggests a possible correlation between the total PAH field concentrations and the derived intensity spectra from the UV-R, although obviously a more rigorous experimental design is needed to establish this apparent correlation.

Spectral differences were observed between stations which may be related to the relative concentration of specific PAH analytes, particularly pyrene. Again, definitive analysis of PAH composition will require more extensive field and laboratory testing. Here, one of the primary needs is the development of PAH spectral libraries and non-parametric statistical analysis routines (e.g., signal theory) to decode the PAH signature into its component parts. In this effort, a focus on a few PAH analytes which are surrogates for overall PAH transport pathways (e.g., pyrene for pyrogenic compounds, anthracene for petrogenic compounds) may be sufficient for field reconnaissance mapping to permit characterization of Total PAH concentration.

Results of sediment column characterizations also show that ambient PAH concentrations at selected locations are near the present detection limit of the instrument. For these locations, approximately 3% of the pixels in the ROI are above internal camera noise and illumination variance. This would suggest that the selected ROI should be kept sufficiently large so as to incorporate an adequate sample size to characterize PAH composition. Increased binning and emission reading times can also increase S:N ratios. In the present data set, the full sediment image (excluding water column) had > 100 pixels for three of four excitation bands (Table 3), which should represent a large enough sample for spectral analysis. The more limited data density for individual ROI (generally < 20 pixels/ROI; Table 2) would reduce the certainty of spectral characterization. Notwithstanding, smaller ROIs used in the present investigation have permitted the elucidation of more spatially isolated spectra (e.g., “hot spots”) which would otherwise be lost in the signal obtained from a full sediment image.

5.0 CONCLUSIONS

From the results of UV-R field demonstration, the following conclusions can be drawn:

- The prototype field system shows good promise of detecting PAHs in water and sediment in the range of 10–100 ppm and above. With further development, a rapid means of assessing PAH distributions may be feasible in the next several years;
- The optical/mechanical system was proven to be field-ready;
- The system has detected station to station differences which may be related to PAH concentration and composition;
- The system has detected small sediment column spatial variations, which suggest micro scale variation in PAH distribution within the top 0-15 cm of surface sediments.

The UV-R camera system developed by SAIC is still in its experimental stages. Recommendations for improving the overall quality of the results include modifying the camera system to reduce internal noise, stray reflections, and hot spots (replacing scratched lenses, dirt on the first-surface reflecting mirror and higher quality RGB filters). The second recommendation arises in the processing of the image data. A non-parametric approach should be developed to characterize and isolate the internal noise to better permit the separation of this signal from the sample data. Such noise reduction algorithms are commonly employed in signal processing of acoustic data, for example, and could be readily applied to the UV-R data sets. At present, the parametric method for signal correction, while applicable to high PAH environments (e.g., oil spills) is too severe for lower PAH environments created by non-point sources. This system was developed for synchronous spectral analysis (i.e., emission intensity averaged over time). Future configurations might consider application of this “time-resolved” spectrometry (i.e., emission growth and decay rate) such as employed in other systems (Rudnick and Chen 1997).

6.0 REFERENCES

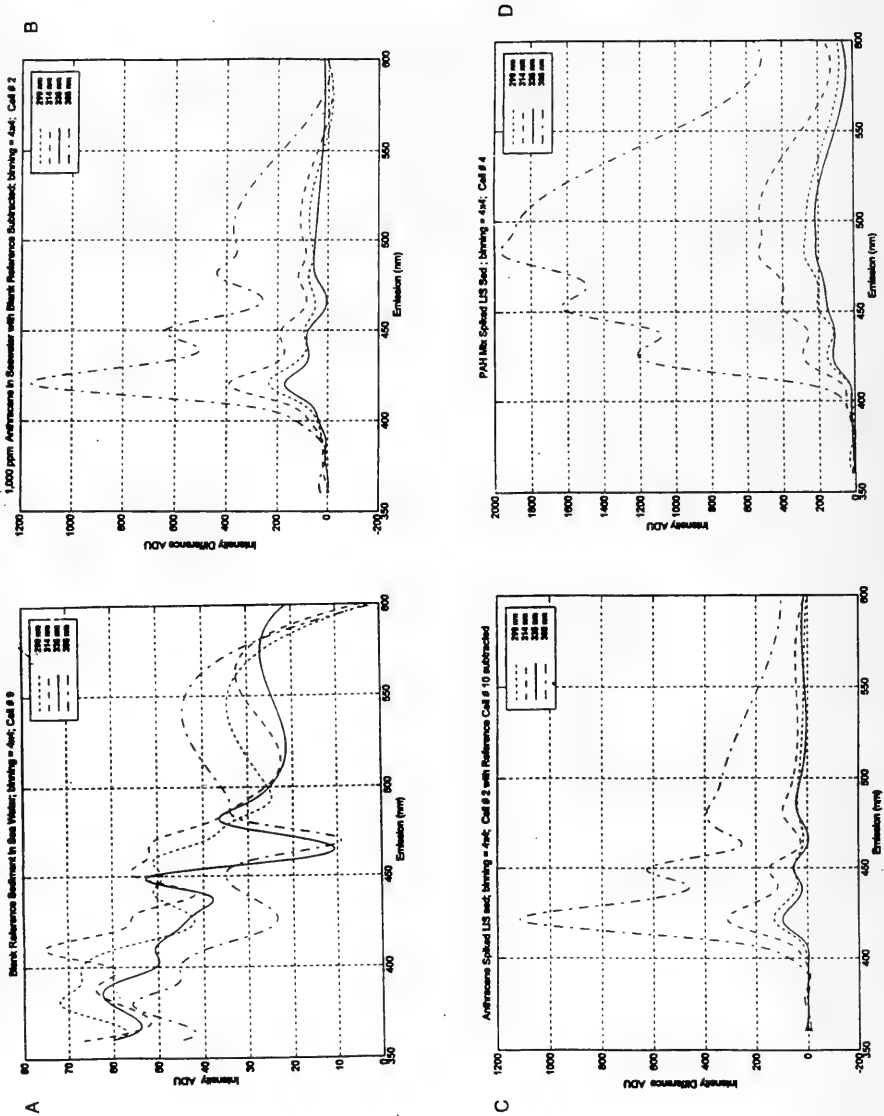
- Rhoads, D. C.; Germano, J. D. 1986. Interpreting long-term changes in benthic community structure: a new protocol. *Hydrobiologia*. 142:291-308.
- Rhoads, D. C. 1995. Measuring Hydrocarbon Contaminants on the Seafloor. *Sea Technology*. August 1995.
- Rhoads, D. C.; Muramoto, J.A.; Coyle, C.; Ward, R. H.; Anderson, R. 1996. Rapid *In-Situ* assessment of Organic Contaminants in Aquatic Sediments with the REMOTS® UV Imaging Spectrometer. Presentation. Proceedings of 'Conference on Challenges and Opportunities in the Marine Environment, Marine Technology Society.' Washington, D.C.
- Rudnick, S. M.; Chen, R. F. 1997. Real time, *in situ* instrumentation for the detection of pollutants in the coastal environment. Coastal Zone '97 Conference Proceedings, ed. M. C. Miller and J. Cogan, Vol 1:408-410, Boston, MA July 19-15, 1997.
- Rudnick, S.M.; Chen, R. F. 1998. Laser-induced fluorescence of pyrene and other polycyclic aromatic hydrocarbons (PAH) in seawater. *Talanta* 49:907-919.

Index

bioturbation, 5, 6
contaminant, 1, 11
density, 8, 9
deposition, 1, 6
disposal site
 Central Long Island Sound (CLIS), 5
gas chromatography (GC), 1
habitat, 1
hurricane, 3
organics
 polyaromatic hydrocarbon (PAH), iii, v, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11
REMOTS®, 1, 3, 11
sediment
 chemistry, 3
sediment sampling
 grabs, 9
statistical testing, v, 8, 9

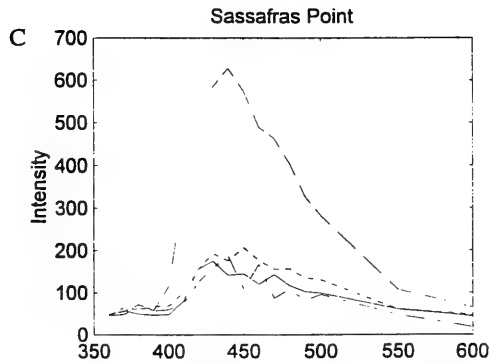
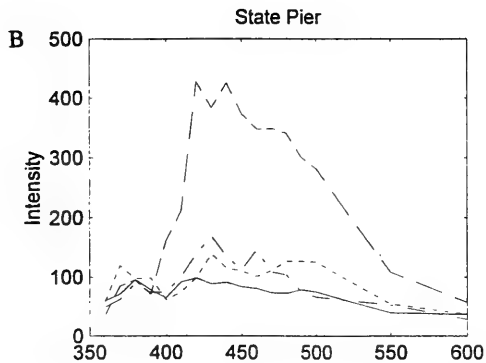
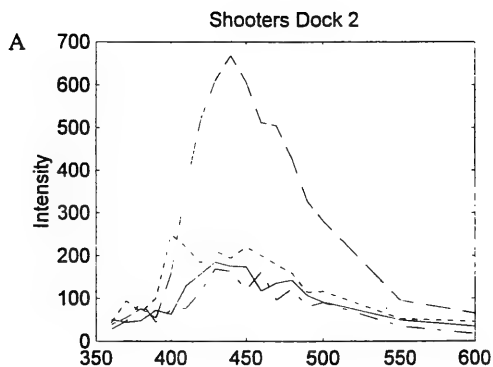
Appendix

Figure 2. Results of UV-REMOTS laboratory analysis of anthracene (ANT) spiked water and sediments:
 A) Reference sediment in seawater; B) ANT and sediment; C) ANT and seawater; and D) Sediment PAH mix with ANT.



Location : Entire Area

LEGEND
(excitation wavelengths)



emission wavelengths (nm)

Figure 3 A-C. Inter-comparison of full sediment area spectra at each location for each excitation wavelength.

Wavelength : 299 - 365

LEGEND

—— Shooters 2
- - - State Pier
- - - Sassafra Point

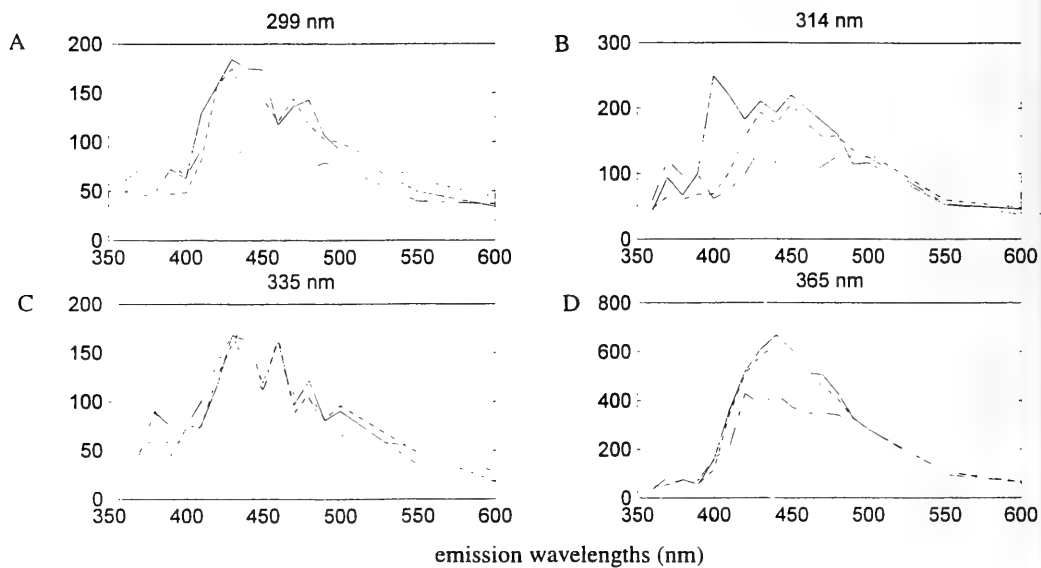
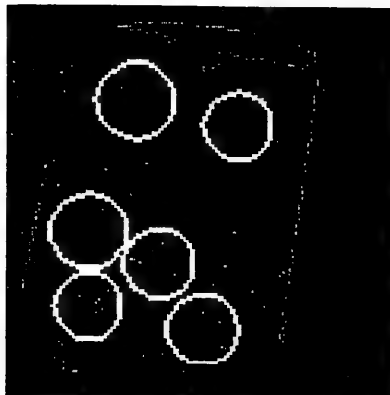


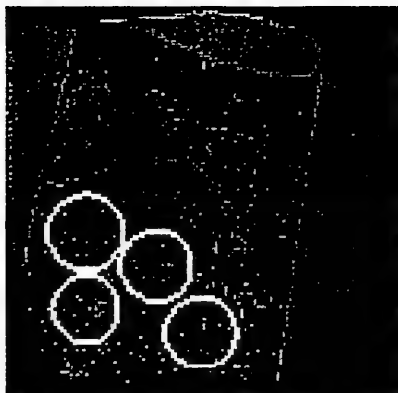
Figure 4 A-D. Inter-comparison of entire imaged area spectra for each excitation wavelength.

A



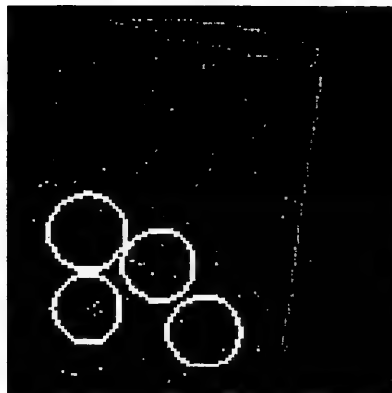
A) Shooters Dock, Site 2
Upper top ROIs (both left and right) are in the water column. Bottom four are the sediment-water interface

B



B) State Pier
All ROIs are in the sediment

C



C) Sassafras Point
All ROIs are in the sediment

Figure 5 A-C. RGB Images at Shooters Dock, Site 2 (A), State Pier (B), and Sassafras Point (C) showing full mask (i.e., complete imaging) and spatial location of individual ROIs.

Station: Shooters Dock, Site 2

LEGEND
(location of ROIs (see also Figure 5 A-C))

◇	◇ top left	*	* top right
- - -	middle left	- - -	middle right
—	bottom left	- - -	bottom right

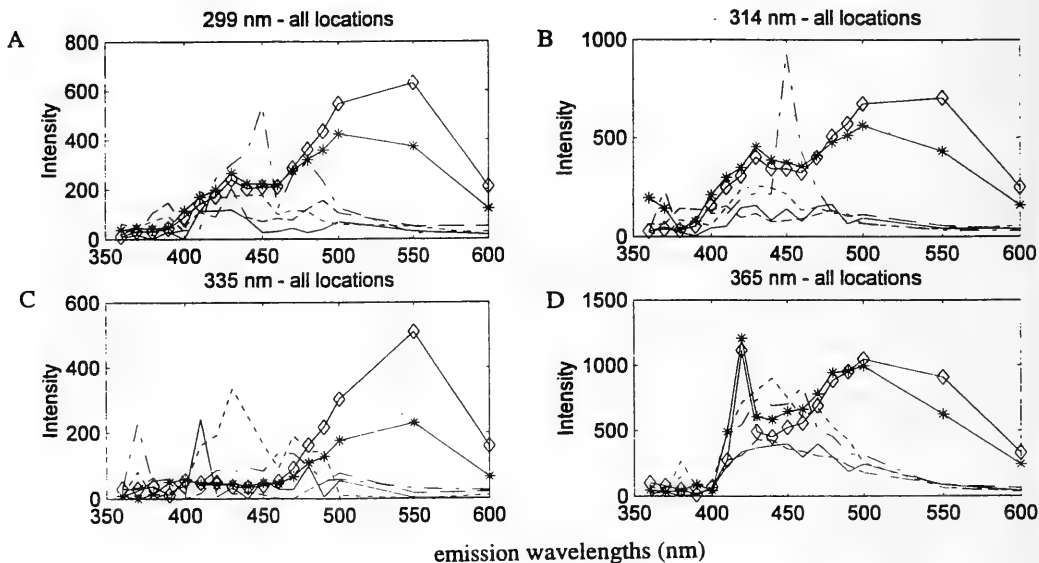
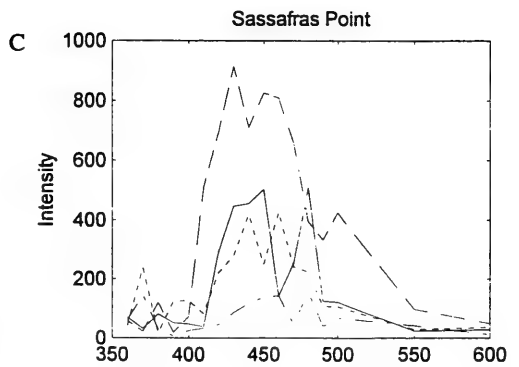
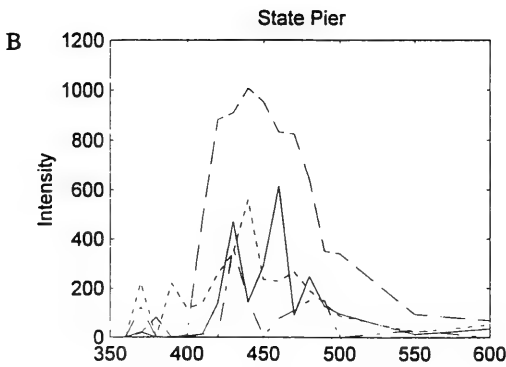
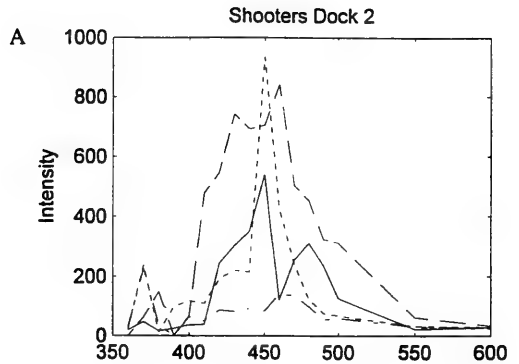
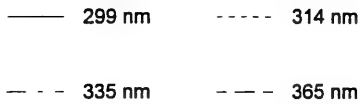


Figure 6 A-D. Inter-comparison of the six ROIs at Shooters Dock and Site 2. Note the high intensities above 500 nm present in the top ROIs due to visible light contamination from the overlying water column.

ROI Location : middle left

LEGEND



emission wavelengths (nm)

Figure 7 A-C. Inter-comparison of the Middle Left ROI at the three locations for all four excitation wavelengths.

ROI Location : middle right

LEGEND

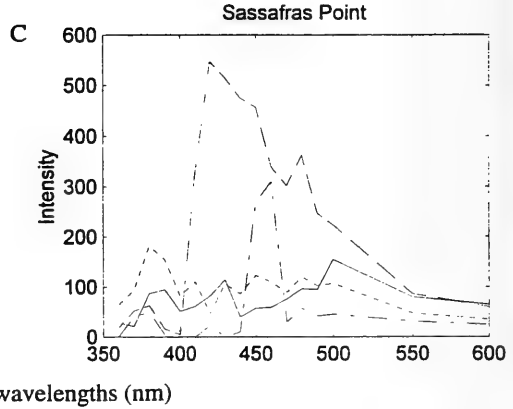
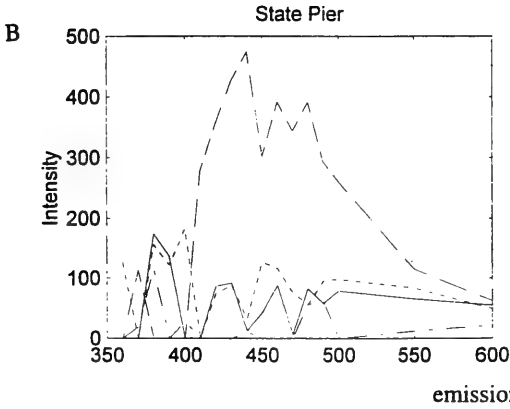
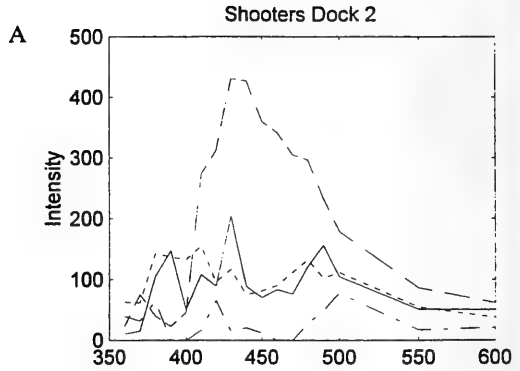
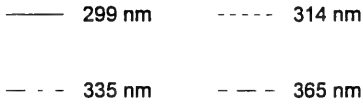
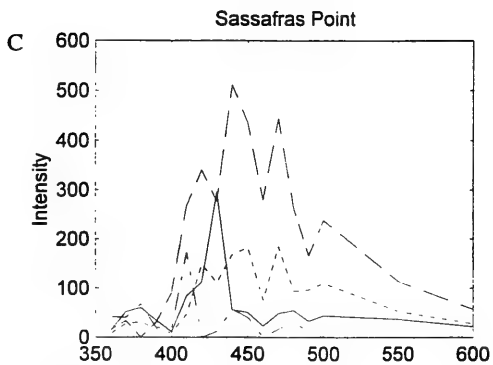
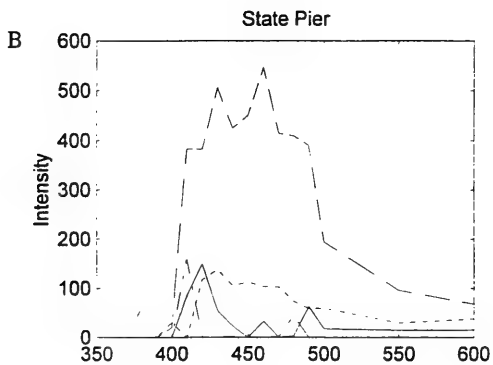
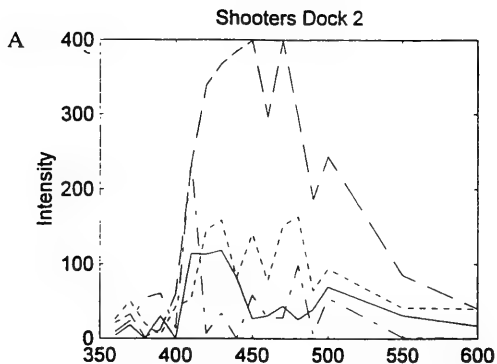
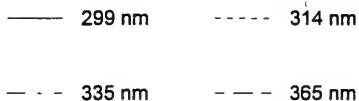


Figure 8 A-C. Inter-comparison of the Middle Right ROI at the three locations for all four excitation wavelengths.

ROI Location : bottom left

LEGEND



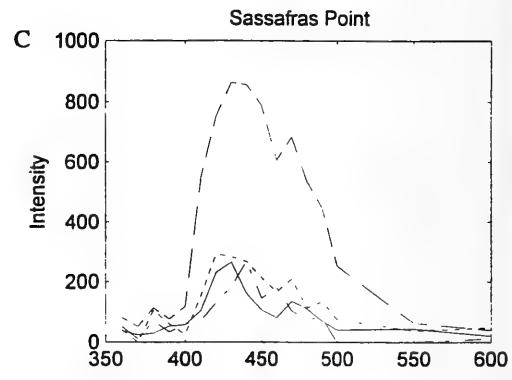
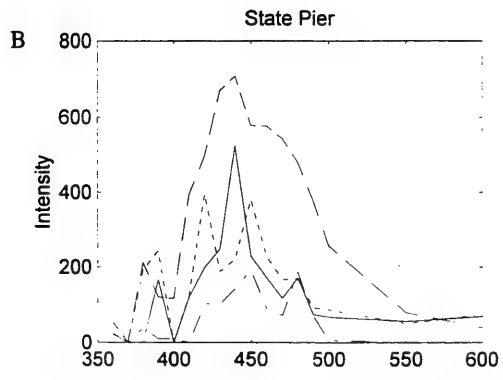
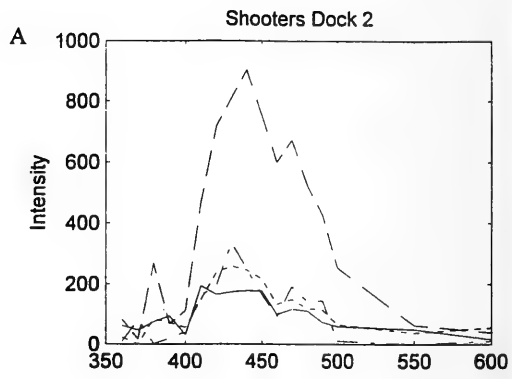
emission wavelengths (nm)

Figure 9 A-C. Inter-comparison of the Bottom Left ROI at the three locations for all four excitation wavelengths.

ROI Location : bottom right

LEGEND

- 299 nm
- - - 314 nm
- . - . 335 nm
- - - 365 nm



emission wavelengths (nm)

Figure 10 A-C. Inter-comparison of the Bottom Right ROI at the three locations for all four excitation wavelengths.

Excitation Wavelength : 299 nm

LEGEND

- Shooters 2
- - - State Pier
- · - · - Sassafra Point

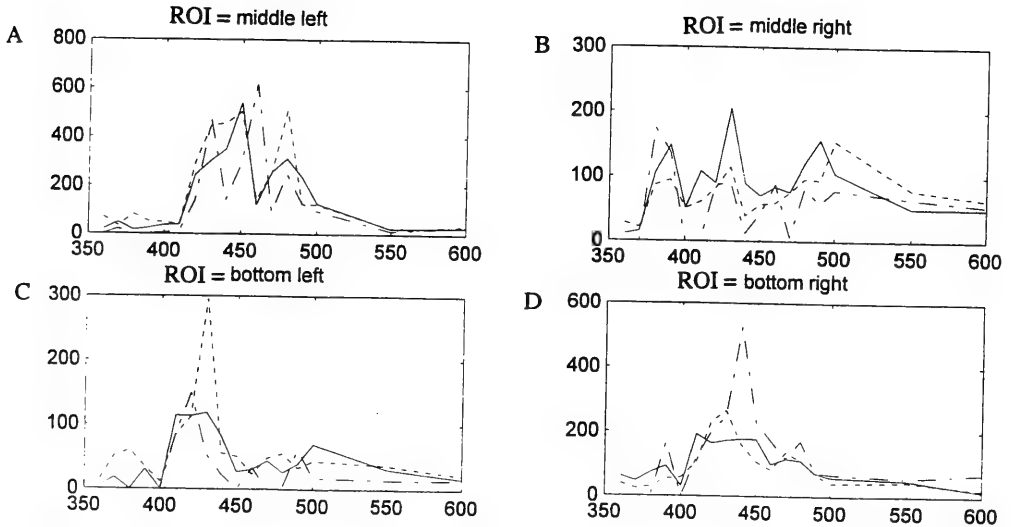


Figure 11 A-D. Inter-comparison of each ROI at the three locations for the 299 nm excitation wavelengths.

Excitation Wavelength : 314 nm

LEGEND

— Shooters 2
- - - State Pier
- - - Sassafra Point

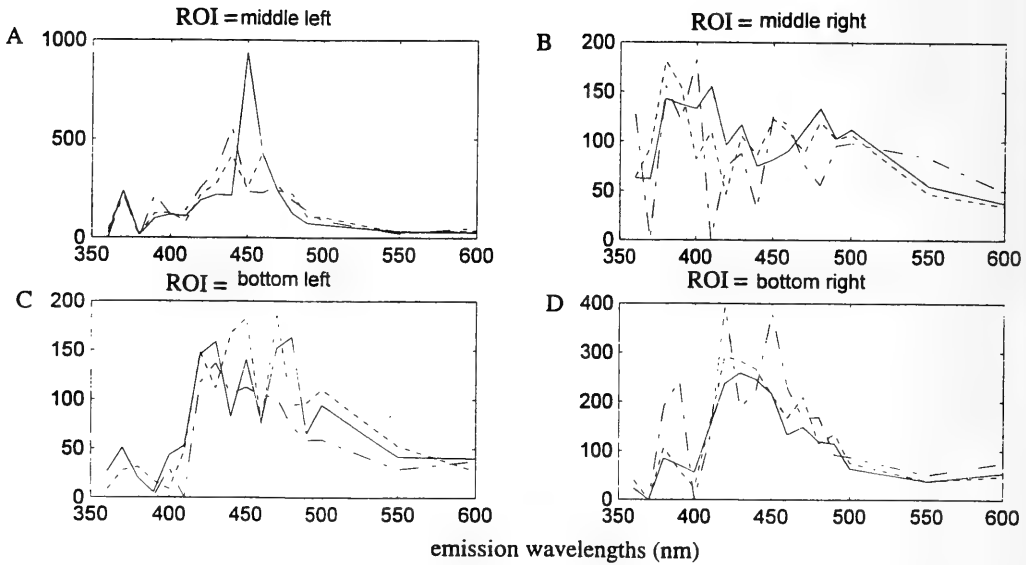


Figure 12 A-D. Inter-comparison of each ROI at all three locations for the 314 nm excitation wavelength.

Excitation Wavelength : 335 nm

LEGEND

— Shooters 2
- - - State Pier
- - - - - Sassafra Point

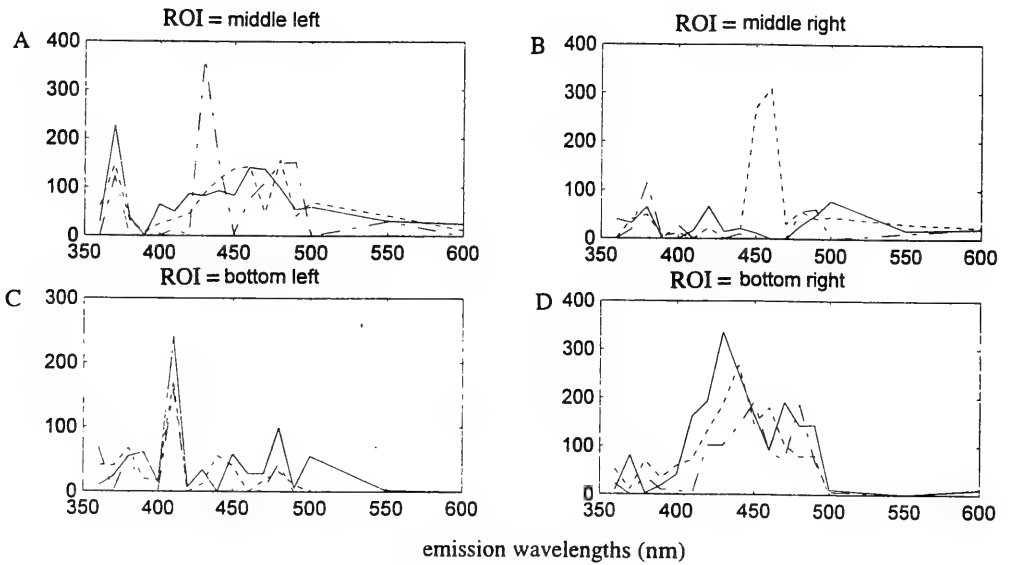


Figure 13 A-D. Inter-comparison of each ROI at all three locations for the 335 nm excitation wavelength.

Excitation Wavelength : 365 nm

LEGEND

— Shooters 2
- - - State Pier
- - - - - SassafRAS Point

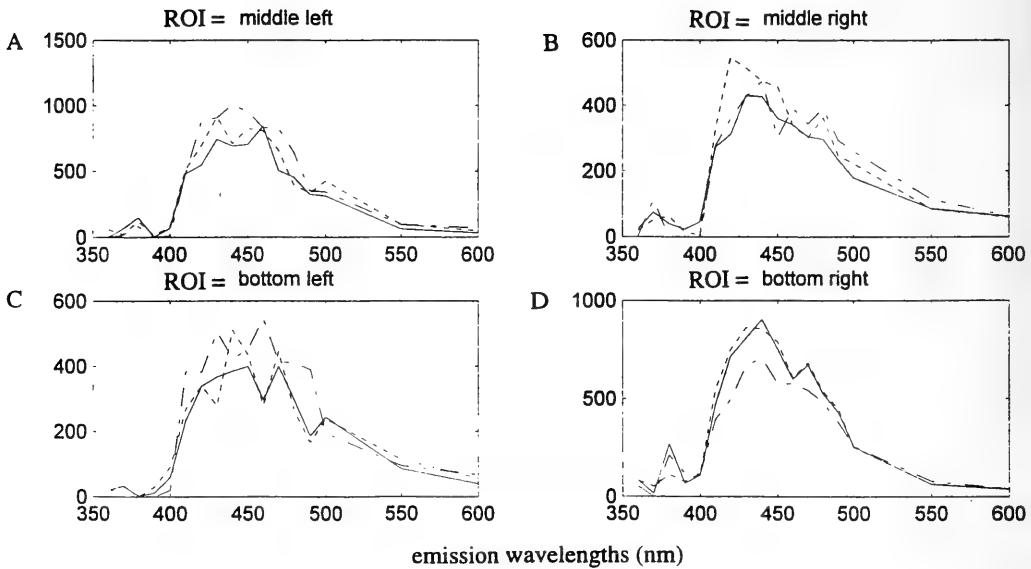


Figure 14 A-D. Inter-comparison of each ROI at all three locations for the 365 nm excitation wavelength.

Table 1. PAH concentrations from the Providence River (PR) and Harbor (November, 1992).

Analyte	Upper PR		State Pier		Sassafras Point	
	Conc	DQ	Conc	DQ	Conc	DQ
Napthalene	0.88		0.38	J	1.1	
2-Methyl napthalene	0.44	J	0.24	J	0.71	
Acenaphthylene	0.22	J	0.17	J	0.4	J
Acenaphthene	0.48	J	0.15	J	0.33	J
Fluorene	0.77		0.38	J	0.62	J
Phenanthrene	4.3	B	1.3	B	2.4	
Anthracene	0.96		0.43	J	0.77	
Fluoranthene	7.0		2.3		3.1	
Pyrene	13.0		5.8		8.9	
Benzo(a)anthracene	3.1		1.3		1.9	
Chrysene	3.8		1.6		2.4	
Benzo(a)fluoranthene	3.4		1.4		1.7	
Benzo(k)fluoranthene	3.6		1.5		1.7	
Benzo(a)pyrene	2.7		1.1		1.7	
Dibenzo(a,h)anthracene	0.29	J	0.03	U	0.06	U
Benzo(g,h,i)perylene	3.1		1.7		2.1	
Indeno(1,2,3-cd)pyrene	2.2		0.03	U	0.06	U
Total PAHs*	50.2		19.7		30.0	

units: ppm

* sum of detected values and detection limits

Data Qualifier (DQ):

U = undetected

B = analyte also detected in method blank

J = estimate value; less than Practical Quantitation Limit

Table 2. Statistical summary of non-zero pixel abundance by excitation wavelength and Region of Interest (ROI) for UV-REMOTS.

		Excitation Wavelength								
		299 nm		314 nm		335 nm		365 nm		
ROI	Total Pixels	No. Pixels	% Total	No. Pixels	% Total	No. Pixels	% Total	No. Pixels	% Total	Mean of % Total
Middle Left	450	7	1.55	7	1.55	3	0.66	17	3.77	1.88
Middle Right	388	12	3.10	15	3.86	3	0.77	20	5.15	3.22
Bottom Left	343	12	3.50	9	2.62	2	0.58	13	3.80	2.63
Bottom Right	399	17	4.26	15	3.76	4	1.00	35	8.77	4.45
Mean			3.10		2.95		0.75		5.37	

ROI - Region of Interest

Table 3. Statistical summary of non-zero pixel abundance by excitation wavelength and sample location for UV-REMOTS.

		Excitation Wavelength								
		299 nm		314 nm		335 nm		365 nm		
ROI	Total Pixels	No. Pixels	% Total	No. Pixels	% Total	No. Pixels	% Total	No. Pixels	% Total	Mean of % Total
Shooters Dock 2	4570	160	3.50	100	2.20	40	0.87	375	8.20	3.69
State Pier	8398	350	4.10	400	4.70	50	0.60	800	9.50	4.73
Sassafras Point	8398	160	1.90	100	1.20	35	0.41	375	4.40	1.98
Mean			3.17		2.70		0.63		7.37	

ROI - Region of Interest

