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13. ABSTRACT (Maximum 200 words)

The resuspension - deposition continuum plays a significant part in the distribution of fine grained sediments and associated organic pollutants in aquatic systems. The chemistry of resuspension was investigated during a year long study by submitting a variety of sediments, including relatively contaminated homogenized dredge spoils and moderately contaminated stratigraphically intact sediments, to artificial resuspension using a particle entrainment simulator. Fine grained sediments were entrained into the test cylinder under conditions that are similar to the resuspension energy that would be expected in a typical estuary. Samples of the resuspended material were collected under a variety of experimental conditions, for the evaluation of organic contaminants such as polycyclic aromatic hydrocarbons (typically associated with oil pollution as well as petrogenically derived) and PCBs (a mixture of toxic organic constituents associated with industrial pollution) as well as for geotechnical parameters such as grain size and particle number and organic carbon content. Results thus far indicate that the volume weighted resuspended sediment load is proportional to the shear stress energy applied for any given core. Moreover, each core has a relatively characteristic erodibility pattern, apparently depending upon the distinctive characteristics of the sediment, for example, grain size composition, biological density, homogeneity, etc.

14. SUBJECT TERMS
Resuspension, deposition, organic contaminants, PES, hydrocarbons, polychlorinated biphenyls, estuaries, fine sediments, shear stress energy, erodibility

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THE UNIVERSITY OF RHODE ISLAND

TO

THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

FY 1991

PURSUANT TO AFOSR AWARD NO. AFOSR-91-0304

Project Title:

THE ROLE OF RESUSPENDED SEDIMENTS IN THE TRANSPORT AND BIOACCUMULATION OF TOXIC ORGANIC CONTAMINANTS IN THE NEARSHORE MARINE ENVIRONMENT

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INTRODUCTION

Estuaries form an important linkage between land and sea. Serving as conduits of pollutants transported by rivers, they sequester, attenuate, and redistribute the contaminants. In part because of the physically dynamic nature of estuaries, the resuspension - deposition segment of the biogeochemical cycle is very important, particularly concerning hydrophobic pollutants such as those derived from oil pollution (e.g., polycyclic aromatic hydrocarbons) and industrial pollution (e.g., PCBs). Ultimately, the purpose of the first year of study was to evaluate, on a molecular level, the behavior of important hydrophobic organic pollutants during the resuspension of contaminated estuarine sediments. Specifically, the focus of the study was to consider the relationship between erosional stress energy and chemistry of resuspended sediment. The specific variables examined were: organic contaminant levels (i.e., PAHs, PCBs), sediment geotechnical data (particle size and number), and organic carbon data.

COMPREHENSIVE LIST OF OBJECTIVES

EXPLICIT OBJECTIVES - YEAR 1

Objective 1: Shear Stress Level / Contaminant Level / Geotechnical Parameters - Homogenized Sediment

Initially, sediments were obtained by the USEPA Environmental Research Laboratory - Narragansett (ERL-N) from a survey of coastal New York/New Jersey; as stated in the proposal, we planned to use these in our study; however, as detailed in the mid year progress report, personnel at the ERL-N inadvertently discarded all but two of these sediments. These samples, from two sites in the NY/NJ area, were subjected to resuspension experiments using the particle entrainment simulator (PES); however, this was during a time when the system was contaminated and as such the samples and data were discounted. Nevertheless, Dr. Wayne Davis (ERL-N) provided us with a large portion of dredge spoil sediment from Black Rock Harbor, a contaminated estuarine site in Connecticut, with which we conducted a series of resuspension experiments. This allowed us to evaluate stress energy - chemical relationships for homogenized sediment specifically called for in the year 1 objectives.

These sediments were subjected to artificial resuspension experiments using the particle entrainment simulator (PES) under three to five resuspension energy levels ranging from 0 to 5 dynes/cm^2. This involved the collection of 100 samples for organic contaminant analysis alone (including dissolved and particulate fractions, see Table 1). In addition, samples were collected for particle characteristics as well as for organic carbon detection - these amounted to an additional 100 samples. Thus, the total number of analytical determinations for just these sediments was 300.

During each experiment, after the core was mounted to the PES apparatus, the instrument was adjusted to a known oscillation magnitude (seconds/cycle) corresponding to a pre-calibrated shear stress. The shear stress levels that the PES has been calibrated at are 2, 3, 4 and 5 dynes/cm^2, corresponding to 0.16, 0.12, 0.10, and 0.08 s/c of the perforated disk. Accordingly, the core would respond to the applied energy; however, a finite passage of time was required before the rate of entrainment equaled the rate of deposition, that is, that the system was in steady state. The determination of the steady state condition was accomplished by evaluating the turbidity of the overlying water using a single beam spectrophotometer (i.e., Bausch & Lomb, Spectronic 20). If the variability in measured percentage transmitance was less than a few per cent, the system was considered to be at steady state for the given resuspension energy; samples were then taken. It was not always necessary to track the response of the system up to the steady state condition; previous experience allowed us to take samples after approximately 15 minutes and assess the variation in turbidity. Figure 1 depicts data for all three cores experimented on from the Black Rock Harbor Sediments. In a general sense, it can be seen that resuspension builds up to steady state within a few minutes of the initiation of turbulence, although at the lower shear levels, this takes longer.

Once steady state was achieved, samples for trace organics, particle size, and organic carbon were collected. Resuspended solids determinations were also obtained from the filters used for organic contaminant collection. Consistent with known principles, in general, it was observed that the greater the shear energy applied the greater concentrations of resuspended solids in the overlying water column (Figure 2). However, variables relating to the time duration of resuspension experiments (not all the experiments could be done in one day, and sometimes the completion of sampling required multiple days, between which the core and overlying water was refrigerated), the degree of compaction, degree of biological activity and other sediment characteristics caused the data to be variable.

Objective 2: Shear Stress Level / Contaminant Level / Geotechnical Parameters - Intact Sediment

Besides the experiments using Black Rock Harbor dredged sediments for homogenous samples (above), two sites in Narragansett Bay, one heavily contaminated (Providence River,

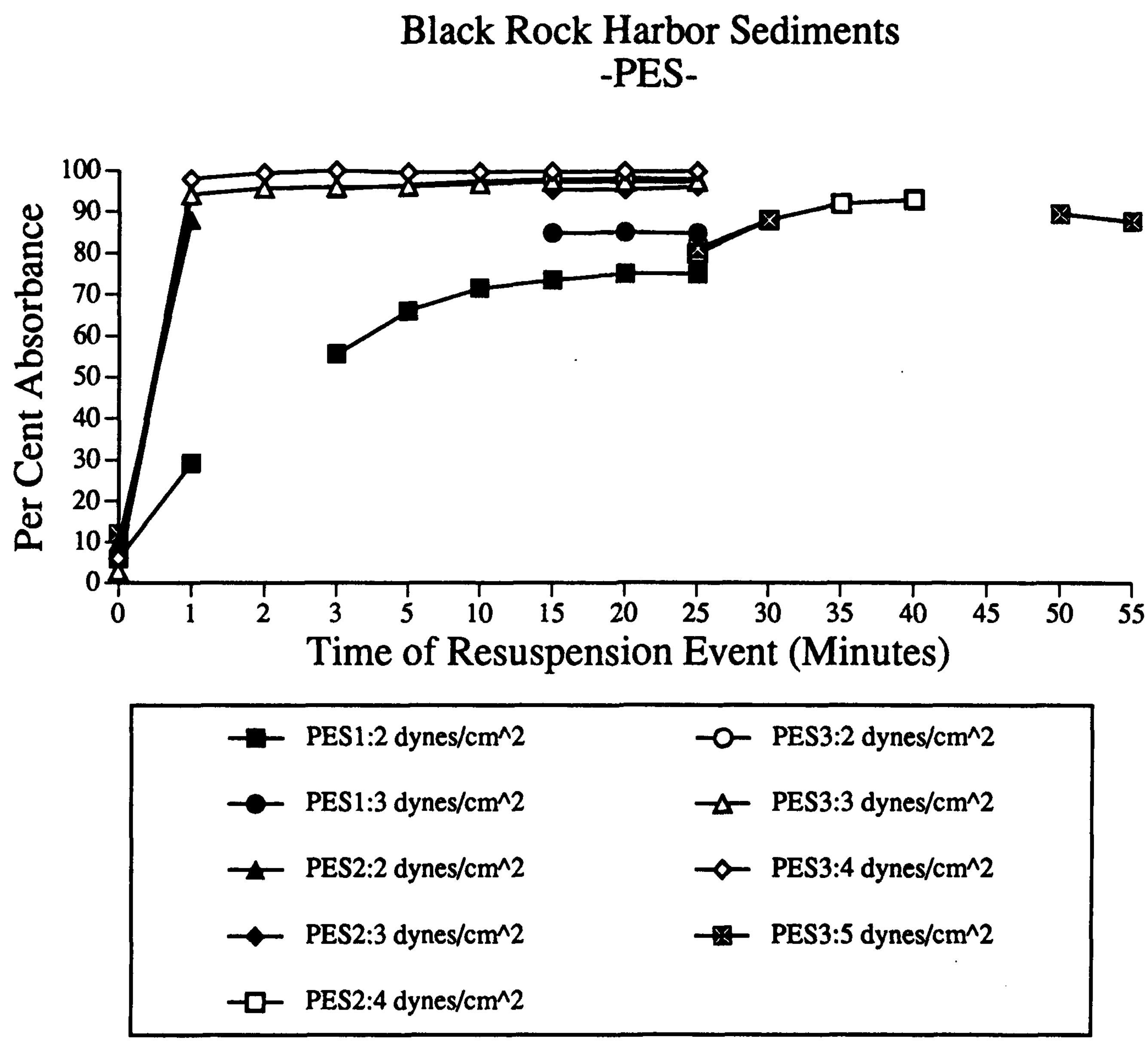

Figure 1. Turbidity of overlying water (in % Absorbance) for the Black Rock Harbor Sediment Experiments. PES 1, 2, 3 represents the three core subjected to shear stresses equivalant to 2, 3, 4, and 5 dynes/cm^2.

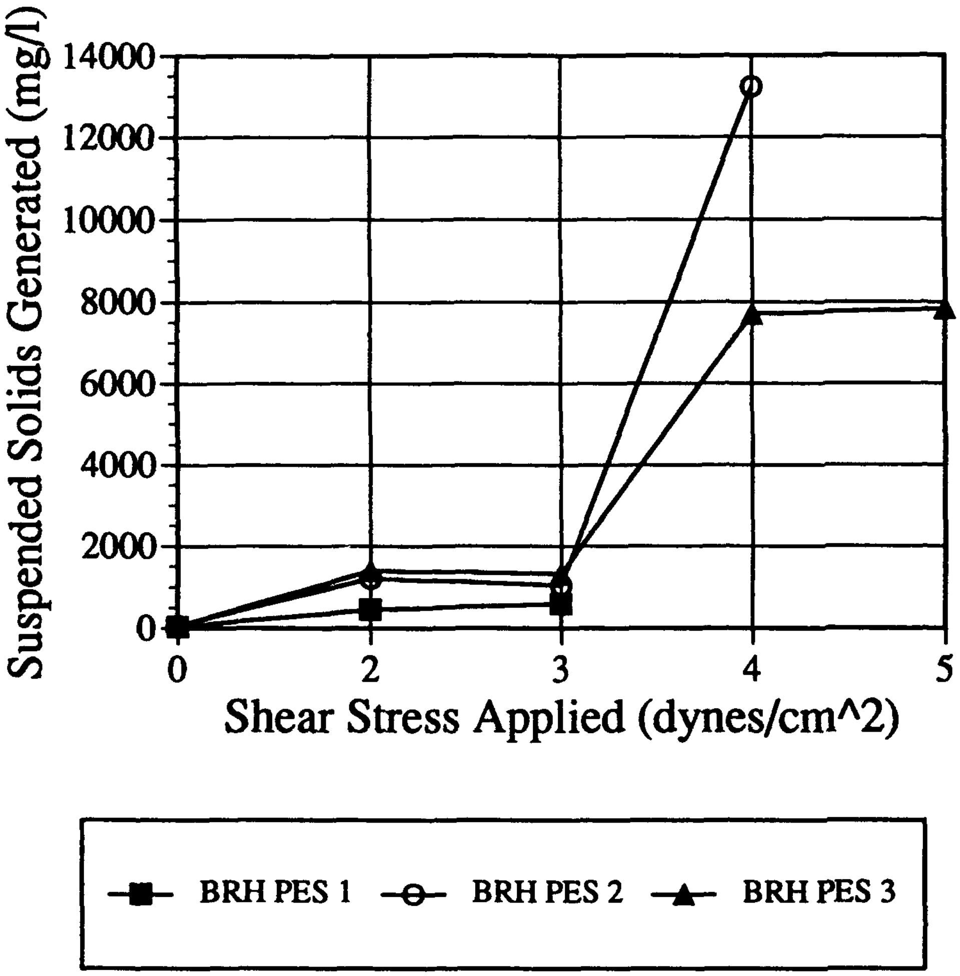

Figure 2. TSS concentrations versus applied shear stress.
BRH = Black Rock Harbor Sediment Cores;
PES 1, 2, & 3 represent three different resuspension experiments with different batches of the BRH sediments.

PRR) and the other moderately contaminated (Rocky Point, RP, in the upper portion of Narragansett Bay), were selected for coring via a cruise in April of 1992. This provided us with two types of sediments with potentially different lithologic and contaminant characteristics appropriate for the category of "intact" sediments as outlined in the year 1 objectives.

These sediments were subjected to the PES for resuspension experiments in a fashion identical to that of the homogeneous sediments, that is they were resuspended using entrainment stresses ranging from 0 to 5 dynes/cm^2. Similar to the BRH sediments analyzed, the Rocky Point (Figure 3) and the Providence River Cores (Figure 4) took approximately 15 minutes to reach steady state. Likewise, both dissolved and particulate organic samples as well as particle and organic carbon samples were collected. The TSS data have been analyzed and reveal that the amount resuspended is proportional to the shear stress applied (Figure 5).

Additional Studies on chemistry - particle interactions

<u>Geochemical distribution of organic contaminants among different particle size fractions of sediments taken from the Providence River.</u>

Briefly, this experiment involved wet sieving sediment samples from the Providence River in Narragansett Bay into several size fractions and evaluating the chemical distributions for all the various fractions. The experiment is 100% complete and the analytical data are awaiting interpretation. This will yield additional insight into the distribution of hydrophobic contaminants within intact sediments.

Objective 3: Set Up and Calibrate TLC-FID analyzer

The Iatroscan, Thin Layer Chromatography - Flame Ionization Detector (TLC-FID) instrument, was purchased and was installed in June 91. Many analytical, procedural, and methodological experiments were undertaken to ensure accurate and precise results.

Methods Development

Extraction studies using mussels, clams, worms, lobster, and flounder tissues were undertaken using a variety of analytical schemes to evaluate the extent to which lipids as well as organic contaminants were extracted. Separation protocols on the analytical chromarods (rods are used like TLC where separation takes place) were developed for both polar and neutral lipid classes. These involved the development of the rods in various solvent systems under close time and compositional tolerances to affect analytical separation before the quantification step on the TLC-FID instrument.

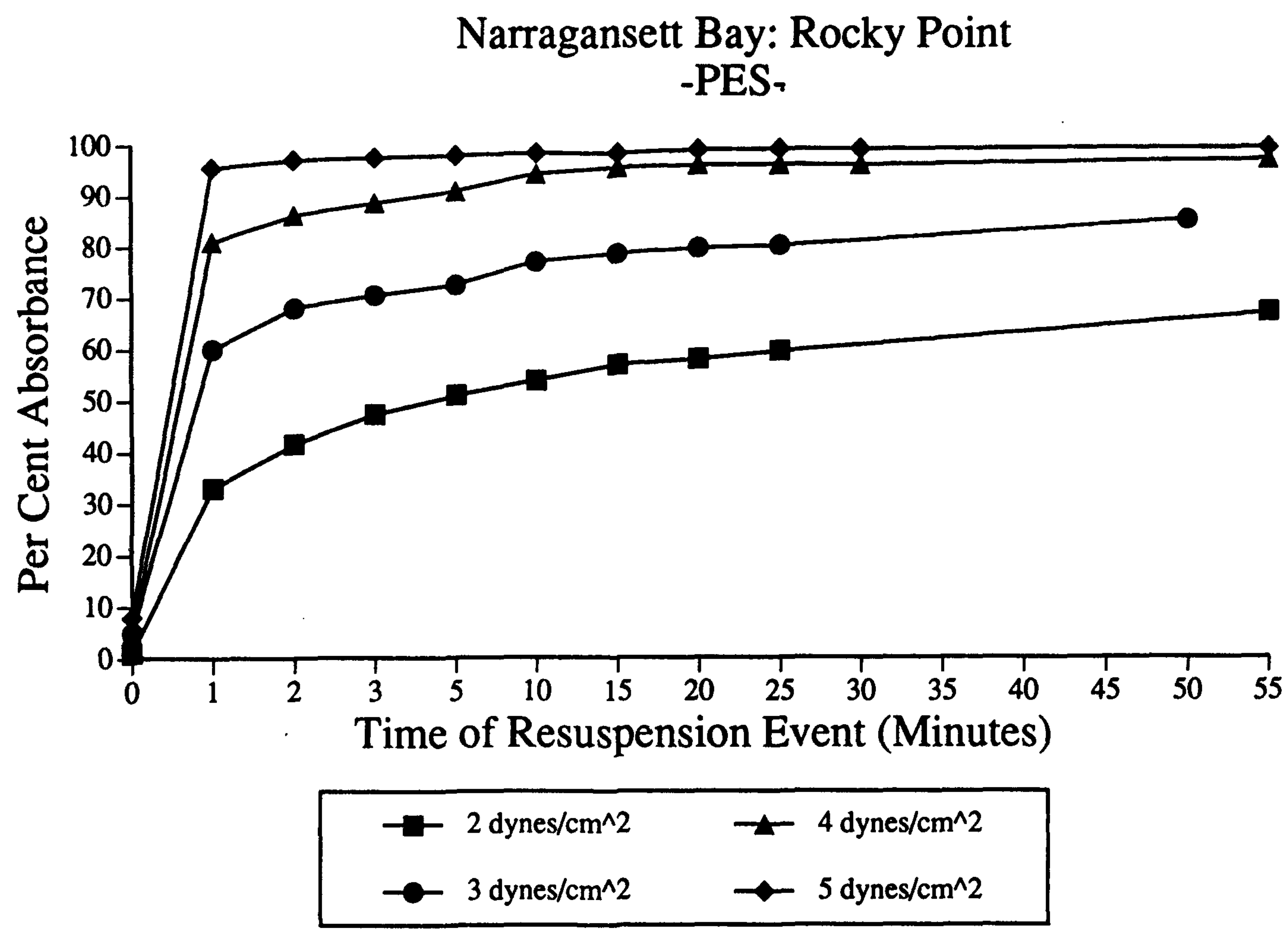

Figure 3. Turbidity of overlying water (in % Absorbance) for the Rocky Point Resuspension Experiments. Each curve represents the data resulting from applied shear stresses of 2, 3, 4, & 5 dynes/cm^2.

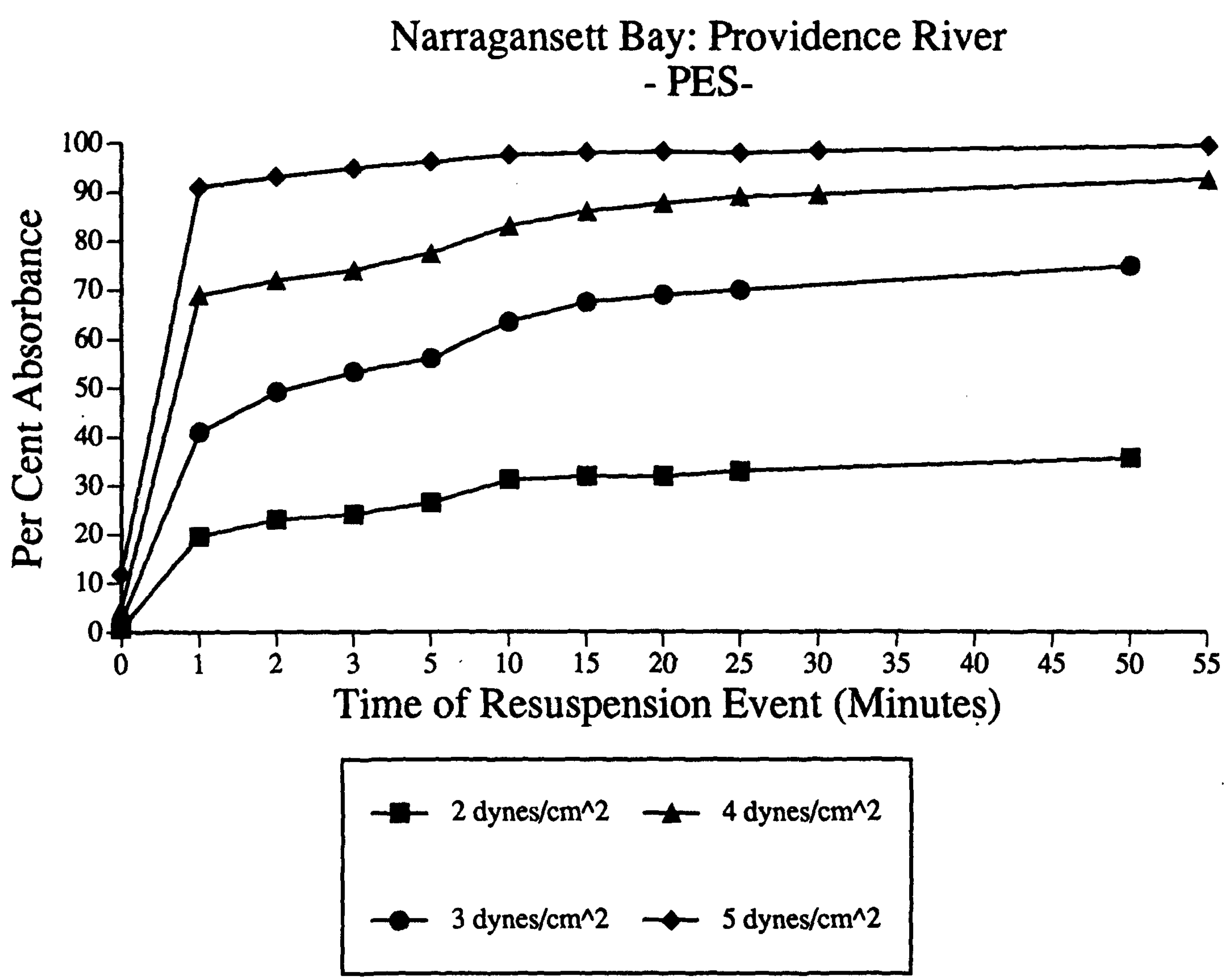

Figure 4. Turbidity of overlying water (in % Absorbance) for the Providence River Resuspension Experiments. Each curve represents the data resulting from applied shear stresses of 2, 3, 4, & 5 dynes/cm^2.

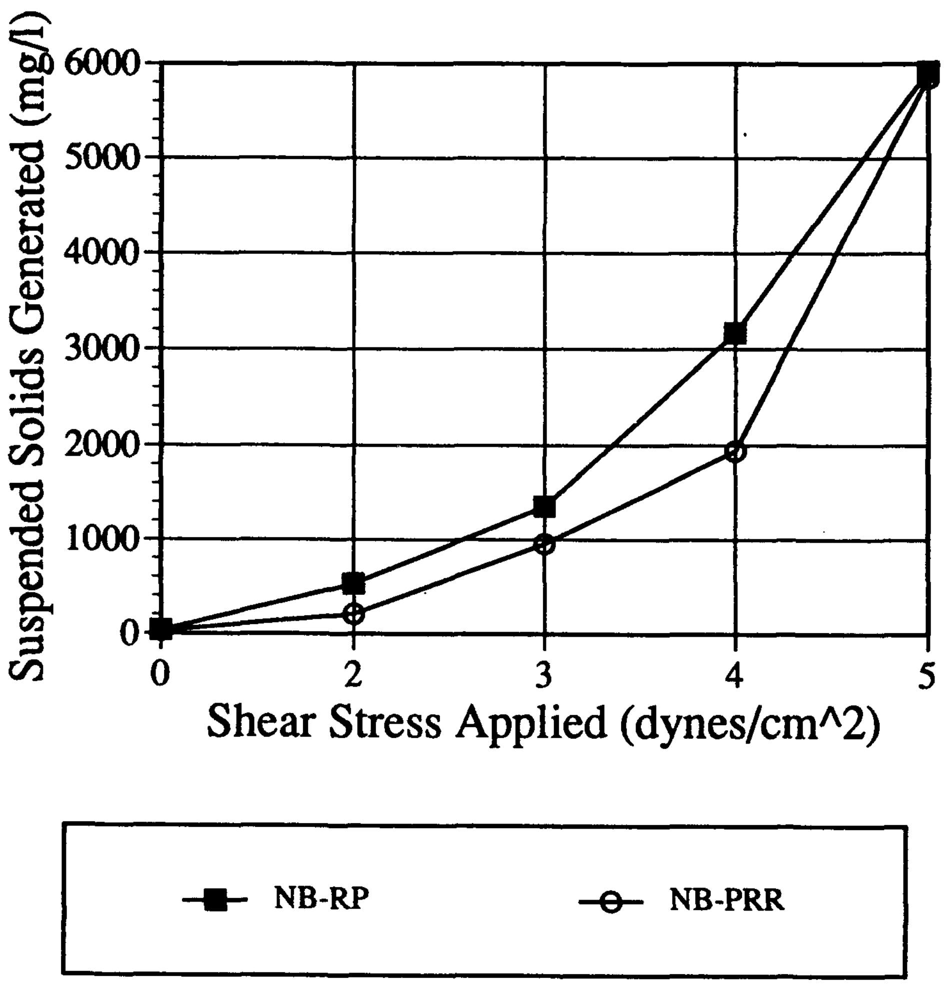

Figure 5. TSS concentration versus applied shear stress.
NB-RP = Narragansett Bay - Rocky Point Core Resuspension Experiments;
NB - PRR = Narragansett Bay - Providence River Core Resuspension Experiments.

The list of lipid classes that we are now able to separate and quantify accurately is as follows:

1. diacyl glycerides
2. fatty alcohols
3. free fatty acids
4. glycerol ether diesters
5. lysophosphatidyl choline
6. monoacyl glycerides
7. phosphatidyl choline
8. phosphatidyl ethanolamine
9. sterol esters
10. sphingomyelin
11. sterols
12. triacyl glycerides
13. wax esters
14. lysophosphatidyl choline

Calibration

Five point calibration curves were developed for each lipid class that was quantified in the samples. The working concentration range for each lipid class is from 0.3 - 1.8 μg on an absolute basis.

Detection Limits

Detection limits were evaluated by assigning a minimum area above a S/N value of 10/1 as the criterion for minimum measurements. Using this criterion, on an absolute basis, 0.1 - 0.3 μg of lipid class is the minimum amount routinely quantified; however, the detection limit can be lowered by at least a factor of two if needed. Using a typical amount of sample extracted, e.g., 1 g dry weight, yields a detection limit (concentration basis) of 10 - 30 μg/g dry weight per lipid class. However, this low a detection limit is not usually required since the tissue samples contain large amounts of lipids.

Blanks / Accuracy / Precision

All analytical rods were scanned, that is, burned to remove any contamination before they were used with samples and the associated blank signal was automatically subtracted from the analyte signal. Usually the blank signals were only 1% of the lowest analytical signal.

Known amounts of specific lipid classes from standard solutions were spotted on the rods and developed after which the lipid classes on these rods were instrumentally quantified. Comparisons of that which was applied with that calculated yielded results usually within ± 10% and no more than ± 20% of the known value.

Standards were analyzed in succession on two rods yielding between rod variabilities (rsd from mean) averaging 5%. Samples were analyzed four days apart on two rods yielding variabilities (rsd from mean) averaging 10%.

Summarizing, 100% of the planned experiments concerning objective three have been completed during year one of the project.

IMPLICIT OBJECTIVES - YEAR 1

Objective 1: Ongoing evaluation of analytical methods

Included as part of the study, a significant effort was expended in upgrading and compiling analytical QA/QC documentation for organic contaminant analysis in the laboratory. We have nearly completed much of the accuracy and precision portion of this effort. Along with multiple blank analyses, we have completed numerous analyses of Standard Reference Materials (SRM) from the National Institutes of Science and Technology (estuarine sediment and urban dust) and the National Research Board Canada (estuarine sediment). In addition, many experiments to evaluate and quantify recoveries of organic analytes have been completed. The result of this exercise will be a current, well ordered, QA/QC document that will be complete and flexible.

Summary of SRM experiments

Figures 6 and 7 are useful in evaluating the ability of the analytical methodology to obtain accurate PAH and PCB values for marine sediments. On average, the PAH concentrations, for SRM NIST 1941 "Organic Contaminants in Marine Sediment," were 13% above the published values including both certified and uncertified components. Limiting the analysis to just the certified components, our laboratory had results within 2.5% of the accepted values. There are no certified PCB data for this SRM; however, a comparison of our results with the uncertified values reveals that, on the average, our chlorobiphenyl concentrations were 35% above published values. The relatively high bias was due to coelution and contaminant problems for 3 of the 15 chlorobiphenyl congeners; excluding these, the mean concentration was within 12% of the published data.

Objective 2: Evaluation of the specific methods used for study

Blanks have not been considered yet in this report because they were not explicitly noted in the proposal; however, once the study was underway it was obvious that considerable attention needed to be expended on the cleanliness of the sample collection procedures. Before

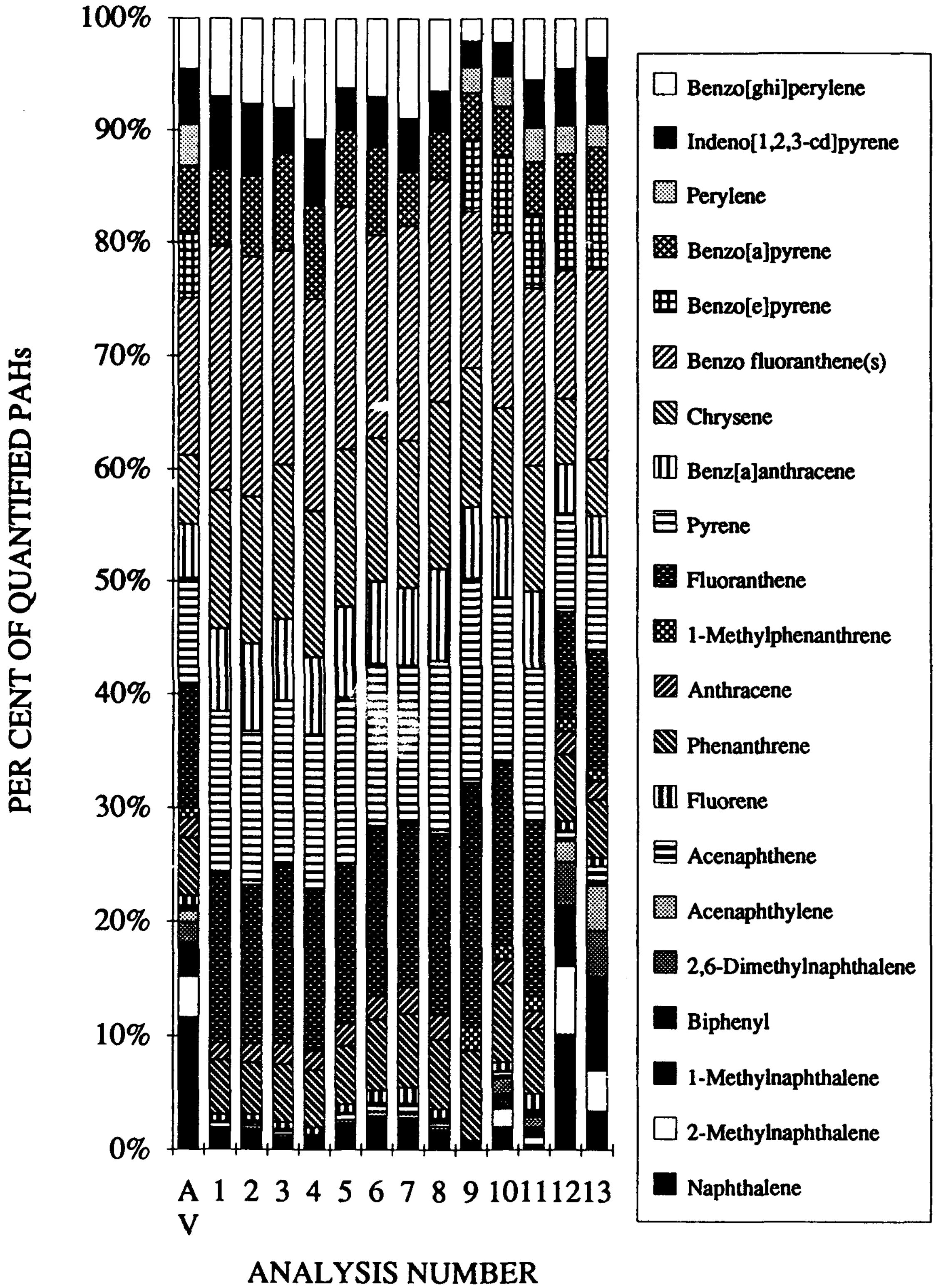

Figure 6. The relative distribution of PAHs determined from the multiple analysis of SRM NIST 1941 "Organics Contaminants in Marine Sediment." AV = Accepted Values as published in the SRM documentation, including both certified and non-certified constituents.

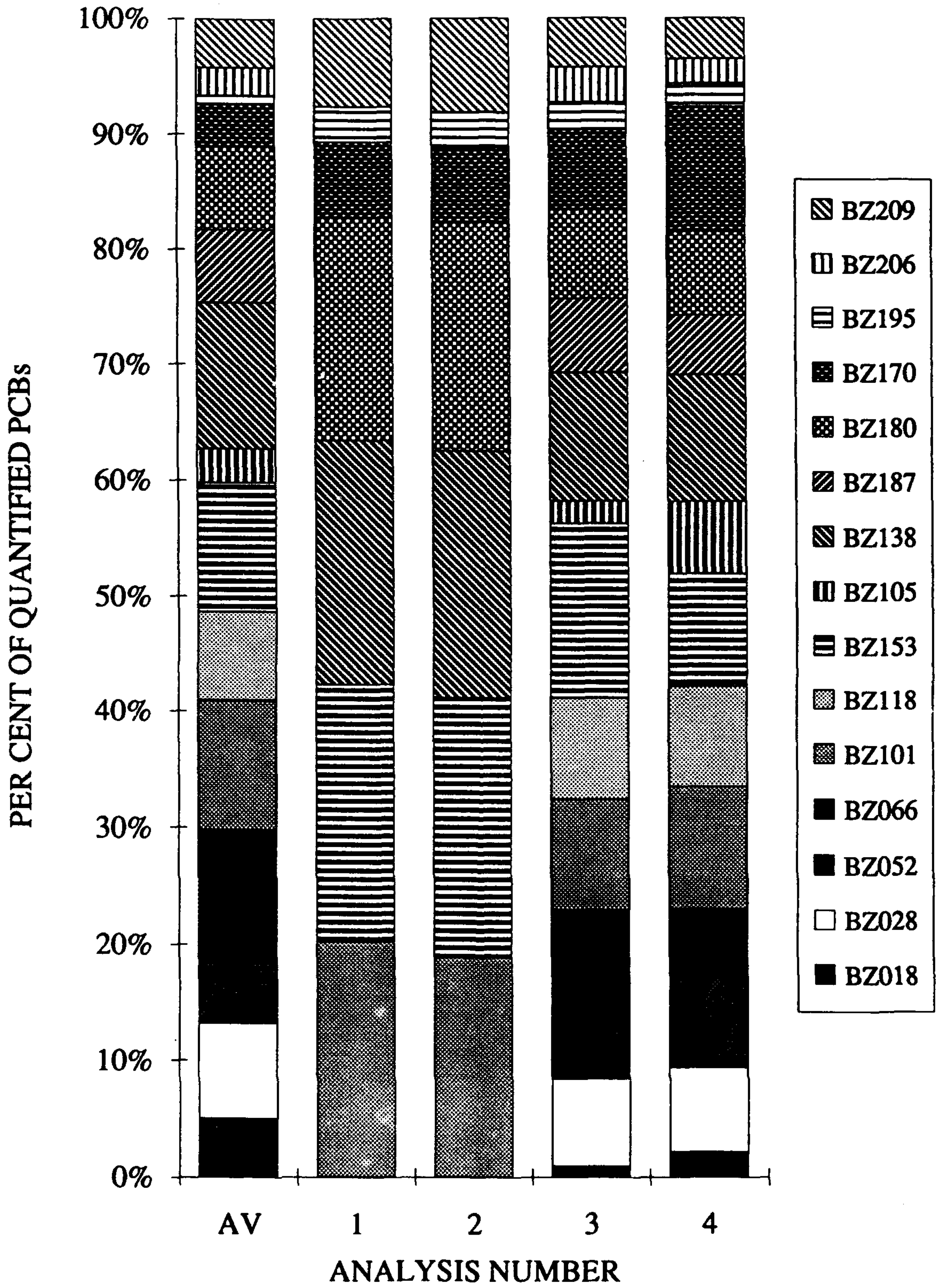

Figure 7. The relative distribution of individual chlorobiphenyls determined from the multiple analysis of SRM NIST 1941 "Organics Contaminants in Marine Sediment." AV = Accepted Values as published in the SRM documents, including both certified and non-certified constituents.

particle resuspension experiments began in earnest, it was necessary to evaluate the amount of contamination that could be expected from the resuspension apparatus itself. The PES was not created for the evaluation of trace organics; rather, it was designed to be a compact and convenient device for the determination of bulk shear stress - resuspension relationships for sediments. Extensive numbers of blanks were done and the PES was continually cleaned and reevaluated (Table 1). After nearly six months of trying to clean the system, we needed to have new chambers constructed out of borosilicate glass so that they could be subjected to our rigorous cleaning procedures, the previous resuspension chambers were made out of plastic. Moreover, we had to resurface parts of the PES with teflon and completely disassembled and cleaned the shaft - cylinder mounting mechanism before we were satisfied that adequate blanks would be achieved. The system was found to be contaminant free as of and following February 1992.

Objective 3: Secure, train, and certify graduate student for study

Although this aspect of the first year of the study was not explicitly stated, it nonetheless needed to be undertaken as part of the project. A Ph.D. graduate student was selected in June 1991 and began training for the analysis of organic compounds in environmental matrices as well as in the use of the Iatroscan for lipid analysis. The training was progressing, although very slowly. Subsequently, we suggested that the student change to the M.S. program. However, eventually, it became evident to all concerned that the student was not really interested in the research and finally left the project in May. This left us in the unpleasant situation of having invested significant effort and having very limited return. Looking back on the motivation of this student, it is evident to us that we ought to have dismissed the individual sooner and sought another student; however, since May we have hired technical help who are working out extremely well. Thus, our problems with the graduate student, along with considerable instrumentation and blank obstacles caused us to fall behind in the accomplishments of certain aspects the first year of the study.

STATUS OF RESEARCH EFFORT

The tasks, relating to the resuspension experiments, for year 1 of the project were broken up into various segments, each requiring a certain level of effort to complete (objectives 1 & 2). Table 1 details the effort expended as well as the fraction completed for both the sampling and collection tasks as well as the analysis tasks for all the experiments. It can be seen that all samples have been collected for the stated objectives, yet the degree of analytical completeness is relatively low. As noted above, the reasons for this are two: one concerned

Table 1. Effort Report - Resuspension Experiments.

	SAMPLE COLLECTION			CHEMICAL ANALYSIS		
Sample Name	Expected Samples	Completed Samples	% Complete	Expected Analyses	Completed Analyses	% Complete
Particulate Organic Contaminants						
Blanks	20	20	**100**	50	50	**100**
BRH PES 1	12	12	**100**	24	15	**63**
BRH PES 2	18	18	**100**	36	0	**0**
BRH PES 3	20	20	**100**	40	3	**8**
RP	20	20	**100**	40	0	**0**
PRR	20	20	**100**	40	0	**0**
Dissolved Organic Contaminants						
Blanks	5	5	**100**	5	5	**100**
BRH PES 1	12	12	**100**	24	0	**0**
BRH PES 2	18	18	**100**	36	0	**0**
BRH PES 3	20	20	**100**	40	0	**0**
RP	20	20	**100**	40	0	**0**
PRR	20	20	**100**	40	0	**0**
Particle Properties						
BRH PES 1	12	12	**100**	12	0	**0**
BRH PES 2	18	18	**100**	18	0	**0**
BRH PES 3	20	20	**100**	20	0	**0**
RP	20	20	**100**	20	0	**0**
PRR	20	20	**100**	20	0	**0**
Carbon Content						
BRH PES 1	12	12	**100**	12	0	**0**
BRH PES 2	18	18	**100**	18	0	**0**
BRH PES 3	20	20	**100**	20	0	**0**
RP	20	20	**100**	20	0	**0**
PRR	20	20	**100**	20	0	**0**

blanks, the other reflected that we had some difficulty motivating the graduate student involved. Because of these problems, the analytical completeness is significantly less than what we had hoped for. Despite these problems, projections indicate that by the end of the summer most of the organic analyses will be complete. As stated above, Objective 3, the set up and calibration of the FID-TLC methodologies, was completed during the first year of the study as proposed.

CUMULATIVE CHRONOLOGICAL LIST OF PUBLICATIONS

Quinn, J. G., R. E. Coburn and J. S. Latimer. (1992). Lipid analysis of *Nereis virens* samples from the 1991 ERL-N trophic transfer study. Final report to the Environmental Research Laboratory - Narragansett. Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, 3 pages + Tables.

Quinn, J. G., R. E. Coburn and J. S. Latimer. (1992). Lipid analysis of tissue samples from the American Lobster (*Homarus americanus*) used in the 1991 ERL-N trophic transfer study. Final report to the Environmental Research Laboratory - Narragansett. Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, 9 pages + Tables + Figures.

LIST OF PROFESSIONAL PERSONNEL ASSOCIATED WITH THE EFFORT

We have been working with various experts at the ERL-N. In particular, Dr. Wayne Davis and Mr. Darryl Keith have, and continue to, contribute significantly to the success of the study. Dr. Davis has provided us with insight into the biogeochemical aspects of the resuspension phenomena. He will be playing a key role in year 2 of the study, when the organism exposure/resuspended sediment studies begin. Mr. Keith has expertise in the geological aspects of this study and will lend his knowledge when we undertake the particle geotechnical analysis of the samples collected in year 1 of the study. In addition, we have received crucial technical and logistical help from Mr. Paul Ferri at the ERL-N under the direction of Dr. Wayne Davis.

The collection of sediment cores in Narragansett Bay was facilitated by Captain Mark S. Gustafson of the R/V Laurie Lee with help from Ms. Ellen MeCray and Dr. Robert Cairns. The fabrication of the 2 all glass PES cylinders as well as assistance in sediment coring was accomplished by Mr. Dave Butler of the URI Equipment Development Laboratory.

INTERACTIONS WITH OTHER SCIENTISTS

Papers Presented at Meetings

Latimer, J. S., L. A. LeBlanc and J. G. Quinn. 1991. "PCBs, PAHs, and petroleum hydrocarbons in the sediments of an urban estuary: historical trends and current inputs" International Conference of the Estuarine Research Federation, November 10-14, 1991. San Francisco.

Consultive and Advisory Functions

Contaminated Sediment Assessment Methods Workshop. In anticipation of the commencement of the AFOSR project I participated in a workshop sponsored by the Office of Water of the US Environmental Protection Agency from May 6-8, 1991, Narragansett, RI.

NEW DISCOVERIES

Once all the samples are analyzed insights and new understandings will be forthcoming in the form of scientific papers and in the final report for the project.