Contract Report D-95-1
August 1995

US Army Corps of Engineers
Waterways Experiment Station

Dredging Operations Technical Support Program

Dredging Elutriate Test (DRET) Development

by Francis A. DiGiano, Cass T. Miller, Jeyong Yoon
University of North Carolina

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Prepared for Headquarters, U.S. Army Corps of Engineers

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Final report

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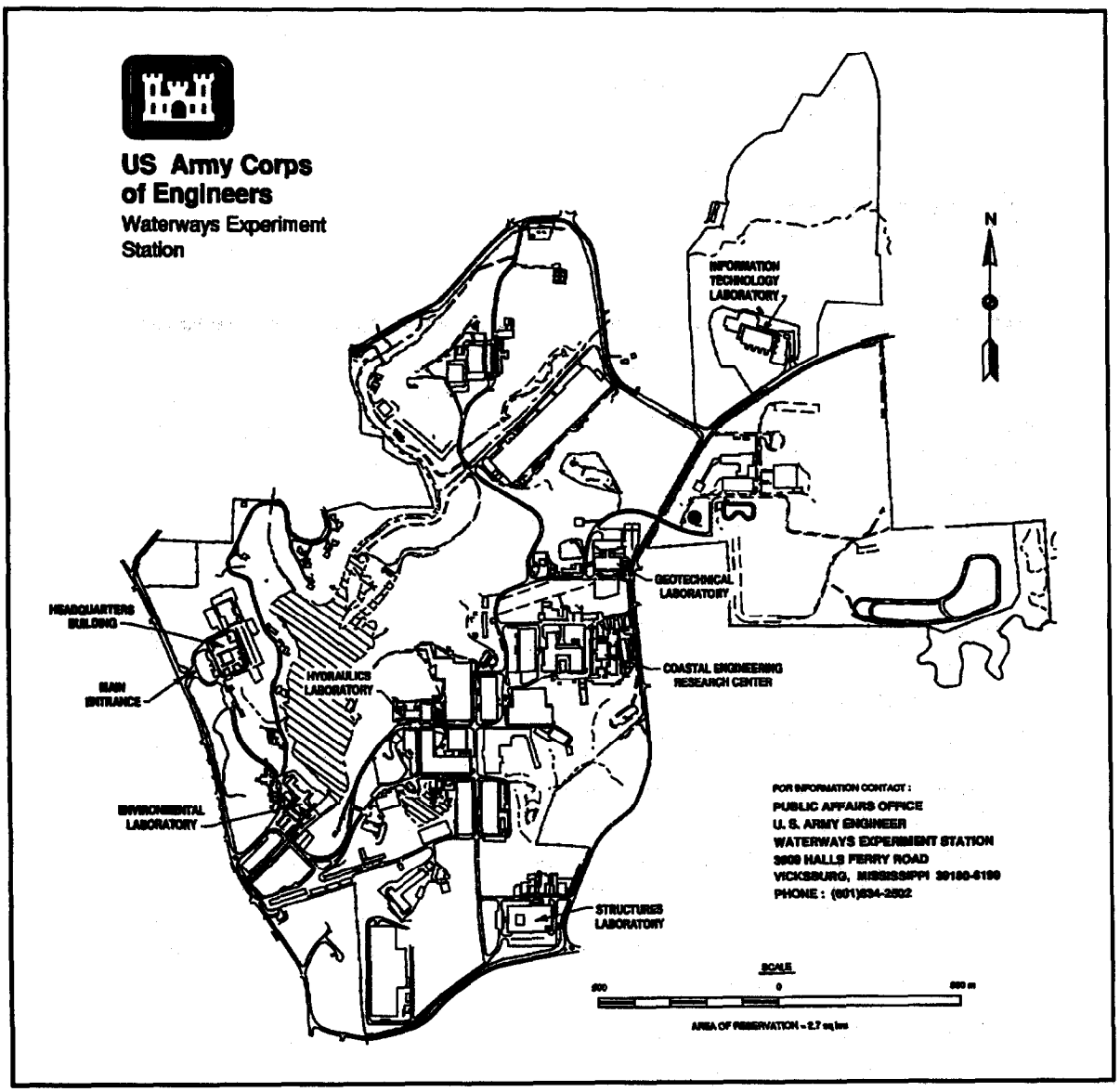
Prepared for U.S. Army Corps of Engineers
Washington, DC 20314-1000



Waterways Experiment Station Cataloging-in-Publication Data

DiGiano, Francis A.
Dredging Elutriate Test (DRET) development / by Francis A. DiGiano, Cass T. Miller, Jeyong Yoon ; prepared for U.S. Army Corps of Engineers.
79 p. : ill. ; 28 cm. — (Contract report ; D-95-1)
Includes bibliographical references.
1. Water quality — Testing. 2. Dredging spoil. 3. Marine sediments — Analysis. I. Miller, Cass T. (Cass Timothy) II. Yoon, Jeyong. III. United States. Army. Corps of Engineers. IV. U.S. Army Engineer Waterways Experiment Station. V. Dredging Operations Technical Support Program (U.S. Army Engineer Waterways Experiment Station. Environmental Laboratory) VI. Title. VII. Series: Contract report (U.S. Army Engineer Waterways Experiment Station) ; D-95-1.
TA7 W34c no.D-95-1

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Preface

The work described in this report was conducted during fiscal years 1988 through 1990 by Drs. Francis A. DiGiano and Cass T. Miller and Mr. Jeyong Yoon, Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, under contracts DACW39-88-K-0063 and DACW39-88-K-0063-P00005 with the Water Resources Engineering Group (WREG), currently the Engineering Applications Branch (EAB), Environmental Engineering Division (EED), Environmental Laboratory (EL), U.S. Army Engineer Waterways Experiment Station (WES). These contracts were supervised by Dr. Donald F. Hayes who was with WREG during the contract period and is currently with the Department of Civil Engineering, University of Utah. Funding for this work was initially provided by Work Unit #32433 entitled "Contaminant Release Control During Dredging" under the Improvement of Operation and Maintenance Techniques (IOMT) Research Program. Administrative supervision during the contract period was provided by Dr. John J. Ingram, Chief, WREG/EAB; Dr. Raymond L. Montgomery, Chief, EED; and Dr. John Harrison, Director, EL. The IOMT Program Managers were Messrs. E. Clark McNair, Jr., and Robert F. Athow, Hydraulics Laboratory, WES.

Final technical editing of this report was conducted during fiscal year 1993 by Dr. Hayes under an interagency support agreement between the University of Nebraska Water Research Center and the Environmental Restoration Branch (ERB), EED, EL, WES. The WES representative was Mr. Daniel E. Averett, ERB. Funding for the technical editing and report preparation was provided by the Dredging Contaminated Sediments: Techniques for Evaluating Resuspension and Release of Contaminants Task Area under the Dredging Operations Technical Support (DOTS) Program; managed through the Environmental Effects of Dredging Program (EEDP). Technical review of this report was provided by Dr. Michael R. Palermo, EED, EL, and Mr. Averett. Administrative supervision during the agreement period was provided by Mr. Norman R. Francingues, Chief, ERB; Dr. Raymond L. Montgomery, Chief, EED; and Dr. John Harrison, Director, EL. The DOTS Program Manager was Mr. Thomas R. Patin, and the EEDP Program Manager was Dr. Robert M. Engler.

This report should be cited as follows:

DiGiano, F. A., Miller, C. T., Yoon, J. (1995). "Dredging elutriate test (DRET) development," Contract Report D-95-1, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

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1 Introduction

The problem of sediment resuspension during dredging has been examined as part of the Corps of Engineers (CE) Improvement of Operations and Maintenance Techniques (IOMT) Research Program. Sediment resuspension, as measured by suspended solids concentration, has been assessed for various dredge types operating under a variety of conditions. Suspended solids concentrations varied widely—from 10 to 900 mg/ℓ—at distances from 100 to 400 ft from the dredge (Hayes 1987). Resuspended sediment particles have the potential to release contaminants to the water column. The extent of contaminant release depends on many factors: the characteristics of the particles, the type of contaminants sorbed, the chemistry of the water, and type of dredgehead.

Previous IOMT research has focused attention on the application of a standard laboratory test, known as the standard elutriate test (SET) that is intended to predict the release of contaminants from dredged materials at the point of disposal. This research investigates modifications to the SET as well as an equilibrium partitioning model to predict contaminant release at the point of dredging. Previous modifications to the SET for predicting contaminant release from confined disposal facilities (CDF) have proven successful (Palermo 1986). The approach builds on the experience of the U.S. Army Engineer Waterways Experiment Station (WES) with both the standard and modified elutriate tests, the former designed to predict the impact of dredged materials in open-water disposal (Lee et al. 1975) and the latter the impact in confined disposal areas (Palermo and Thackston 1988b, 1988c). Subsequent work was done using the SET for application to the point of dredging (Ludwig, Sherrard, and Amende 1989) and summarized in Technical Note EEDP-09-3 (Havis 1988).

The major difference in point-of-dredging and point-of-disposal applications of the elutriate test is the total suspended solids (TSS) concentrations, resulting from the applications. The solids-water (SW) ratio used in the elutriate test should reflect the disparity in these concentrations. The SW ratio can influence the distribution of contaminant between soluble and sorbed phases, i.e., the partitioning. At the point of disposal, the concentration of solids in the slurry can be estimated fairly well. However at the point of dredging, TSS concentrations in the plume depend upon many variables including the type of dredgehead being used and other characteristics of the dredging operation.

The maximum TSS concentration (mass of dry solids/volume of water) at the point of dredging is usually less than 10,000 mg/ℓ, which translates roughly to a solids-to-water volume ratio of 1:250 (assuming the density of solids to be 2.5 g/cm^3) instead of the 1:4 sediment-to-water volume ratio recommended in the SET; this solids concentration is also far less than used in the modified elutriate test (typical solids concentration is 150,000 mg/ℓ or a solids-water ratio of 1:17). Another important aspect of an elutriate test is characterization of the resuspended solids. Very little has been reported thus far on their size distribution and settling properties.

Objectives

The objectives of this research were as follows:

a. Use the modified elutriate test as a starting point for development of a dredging elutriate test (DRET). Consider the effects of solids concentration, aeration time, and settling time on contaminant concentrations (soluble and particulate) in the water. Compare results to field data collected by the CE at the New Bedford Harbor dredging site according to a standard, well-defined protocol.

b. Develop a DRET that can assist in accounting for the effect of different dredgeheads on contaminant release and of different dredge site characteristics.

c. Examine the application of a simple, equilibrium partitioning model as an alternative to a DRET.

d. Investigate the characteristics of the suspended particles produced in the DRET using particle size distribution analysis and settling rates.

Background

The SET is a simple, batch laboratory experiment developed in the 1970s in which sediment and water are contacted under specific conditions. The purpose of the SET was to compare the release of chemical constituents resulting from this batch test with that measured during open-water disposal operations. In the SET procedure, 20 percent (by volume) of undisturbed sediment from the dredging site is added to water from the dredging site yielding a 1:4 sediment/water ratio. The combined sample is mixed by mechanical shaking for 30 min while being aerated with compressed air. After settling for 1 hr, a sample is withdrawn from the supernatant. The SET defined the contaminant release as the soluble fraction of contaminants found in the supernatant after a prescribed settling time. The SET was found by Jones and Lee (1978) to be a conservative predictor of contaminant release observed in field conditions.

The SET procedure was later modified by Palermo and Thackston (1988a) to predict release of contaminants during disposal into a CDF. The sediment:water ratio and mixing conditions were changed to reflect those found in CDF disposal operations and both the dissolved (C_{diss}) and total (C_{total}) contaminant remaining in the supernatant were measured. Palermo and Thackston defined the contaminant fraction associated with suspended solids, F_{ss}, in milligrams/kilogram as:

$$F_{ss} = \frac{(1 \times 10^6)(C_{total} - C_{diss})}{[TSS]} \tag{1}$$

where $[TSS]$ is the total suspended solids concentration (both the contaminant and TSS concentrations are expressed in milligrams/liter). The total concentration (C_T) of contaminant for the field situation is calculated by:

$$C_T = \frac{C_{diss} + F_{ss}TSS_f}{1 \times 10^6} \tag{2}$$

where TSS_f, the final total suspended solids concentration, is estimated by a settling column (8-in diam) test, independent of the modified elutriate test (MET).

The following laboratory procedure was adopted by Palermo and Thackston (1988a) for the MET: 3.75-ℓ sample size, consisting of the average field influent concentration of dredged solids, or 150 g/ℓ if no data are available; aeration for 1 hr; and settling for up to 24 hr. These conditions were decided upon by Palermo and Thackston after they performed two factorial experiments. In the first, they investigated two levels of slurry concentration (50 and 150 g/ℓ), aeration (1 hr) versus mixing without aeration, and two levels of settling time (6 and 24 hr). The second factorial experiment provided more detail using four levels of aeration time (0, 1, 3, and 6 hr) and four levels of settling time (from 3 to 96 hr). While a comparison of the MET with field data (Palermo and Thackston 1988b) was encouraging (within a factor of two agreement for 23 out of 34 values of total pollutant concentration), the results were considered preliminary.

Palermo and Thackston (1988b) discussed mainly the total concentration of contaminants, although they presented data for the dissolved concentration and the suspended fraction (miligrams/kilograms TSS). While not stated specifically, inspection of the data suggests that most of each important contaminant remained associated with particles during elutriate tests and in field samples.

The measurements of settling in an 8-in column and in the field are given in Table 1 (Palermo and Thackston 1988c). Two observations from Table 1 are possible. First, despite the large initial slurry concentration (57 to 152 g/ℓ), the final TSS in the settling test was very low (10 to 85 mg/ℓ).

Table 1
Predicted Suspended Solids Concentration

Site	Test Slurry Concentration, g/ℓ	Column TSS mg/ℓ	Mean Field TSS, mg/ℓ
Mobile	99	33	40
Savannah	142	85	75
Norfolk	122	20	202[a] 35[b]
Black Rock	57	84	173
Hart Miller	152	10	25

[a] High wind.
[b] Low wind.

This suggests that most of the suspended material for marine sediments settles fairly rapidly (within 24 hr) leaving behind very small particles. In fact, the companion paper by Palermo and Thackston (1988b) showed that TSS declined very sharply during the first 24 hr, and furthermore that about 90 percent of these supernatant sediment particles were less than 10 μm in diameter. The second observation is that the settling test usually produced lower TSS than measured in the field. Palermo and Thackston applied a settling efficiency adjustment factor (1.5 to 2.0) to account for nonquiescent conditions in the field.

To date, only the SET has been used to predict contaminant concentrations at the point of dredging; in this test, the solids to water ratio is fixed at 1:4 by volume. Ludwig, Sherrard, and Amende (1989) obtained field data from four sites: Black Rock Harbor near Bridgeport, CT; the Calumet River in Chicago, IL; the Duwamish Waterway in Seattle, WA; and the James River near Jamestown, VA. Concentrations of various contaminants on predredged sediments were not reported. A comparison of soluble contaminant concentrations from field samples with those from replicate SETs revealed that 74 percent of the chemical constituent measurements (a total of 38) were within one order of magnitude. The remaining 26 percent of the comparisons showed that the SET overestimated the expected release, i.e., the SET is a conservative indicator of release. Despite the relative success of the SET, recommendations were to modify the SET to (a) include predictions of both the dissolved and particulate–associated contaminant concentrations (only the dissolved was examined); (b) account for dredge types; and (c) use a solids/liquids ratio and aeration time that better represents field conditions so as to reduce the tendency to overestimate release of soluble contaminants.

2 Methods

Dredging Elutriate Test (DRET)

Figure 1 depicts the major elements of the DRET for which a protocol was sought. The development of a DRET began with selection of the experimental variables to be investigated, these being based on the work of Palermo (1986). The tests were conducted in 4-ℓ graduated cylinders equipped with a magnetic stir bar for mixing and a diffuser for aeration. Air was bubbled through the solution at a flow rate of 0.5 ft^3/hr (0.24ℓ/min). Water and sediment representative of predredged conditions were obtained from a field site at New Bedford Harbor to conduct the test. These were added to a graduated cylinder to give the desired initial suspended solids concentration to begin the DRET.

The three variables are initial solids concentration, aeration time, and settling time. While Palermo (1986) recommended 150 g/ℓ TSS as the initial concentration for the MET as appropriate for CDF effluent quality prediction, field data (Havis 1987) at the point of dredging indicated that solids concentration for resuspension because of dredging was much lower. In order to cover the range of interest and to determine the effect on final concentration of contaminants after settling, four different initial solids concentrations were tested: 0.5, 1, 5, and 10 g/ℓ.

An aeration time of 1 hr was used by Palermo (1986). At the point of dredging, aeration time simulates the time that sediment is vigorously resuspended by the dredgehead to allow for oxidation and mass transfer of contaminants. In developing the DRET, a comparison was included of 1 and 6 hr of aeration time.

Settling time at a CDF has specific meaning because the configuration of the site allows for a calculation of the time particles are suspended and able to release contaminants. In contrast, settling time at the point of dredging is open-ended because once resuspended, the sediment particles may be transported away while desorbing contaminants. A nominal settling time (under quiescent conditions) of 1 hr was selected for initial testing; however, other experiments were done to determine the change in TSS with settling time from 0.5 to 24 hr as well as some investigation of the rate of desorption of polychlorinated biphenyls (PCB).

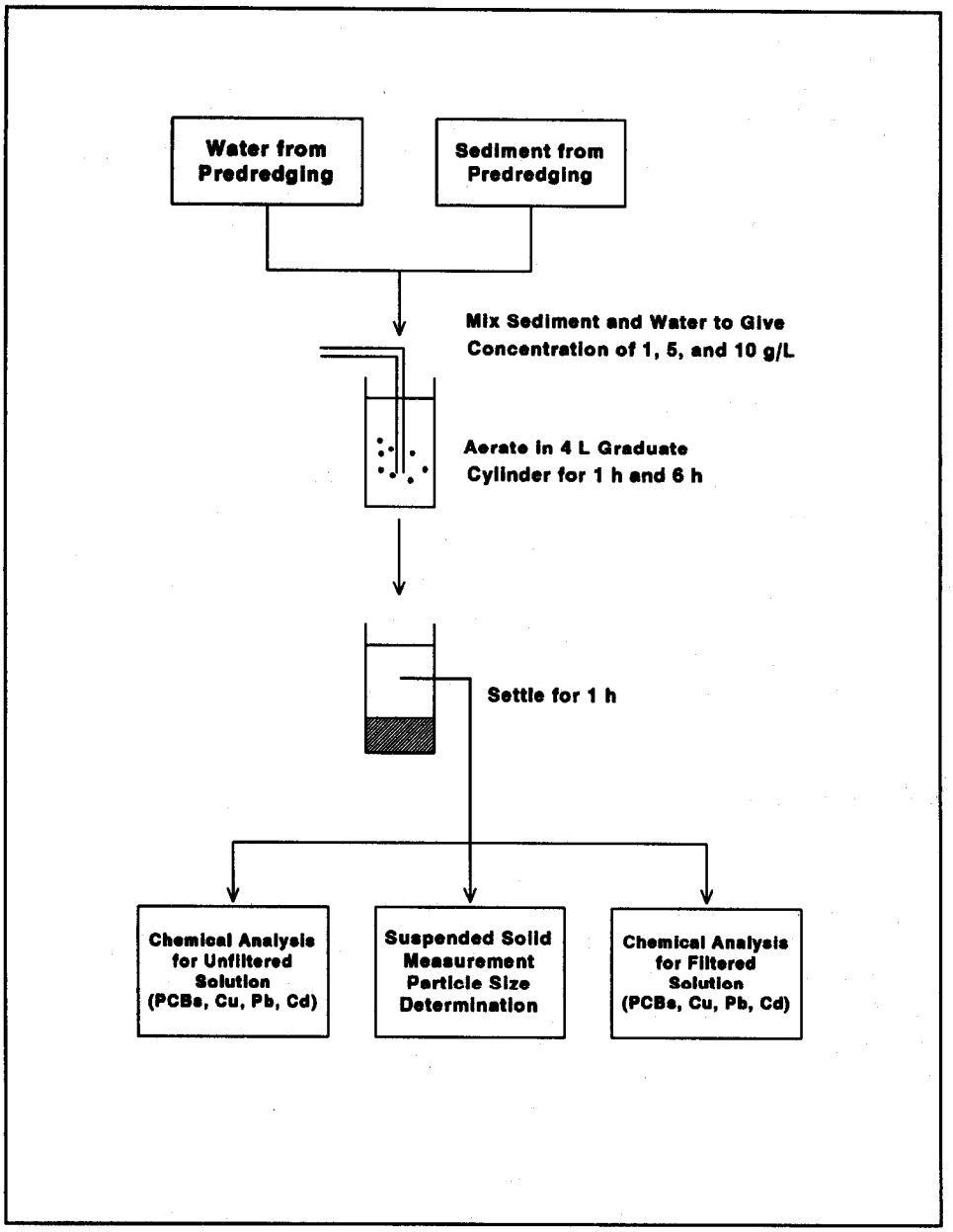

Figure 1. Steps in development of DRET protocol

A siphon was used to remove 3 ℓ of solution above the settled material from the cylinder for analyses of PCB and metals (Cu, Cd, and Pb). Two 1-ℓ samples were required for analysis of soluble and suspended PCB. The remaining 1-ℓ sample was used for analysis of metals (both soluble and suspended), TSS, and particle size distribution (PSD). Based on preliminary DRETs, it became clear that the contaminants and nature of TSS remaining in the water were very important because most of the contaminants were sorbed rather than soluble.

A series of DRETs was conducted to determine the effect of initial TSS, aeration time, and settling time on final suspended solids and the PSD. For these tests, artificial seawater was prepared by mixing Instant Ocean (commercial name) with distilled water. Four initial TSS concentrations (0.5, 1, 5, and 10 g/ℓ) were tested using four aeration times (1, 3, 6, and 12 hr) and four settling times (1, 6, 12, and 24 hr). The objective of these DRETs was to determine if final TSS could be estimated for a given set of elutriate conditions, thereby providing a way of reproducing field values should such data be available.

Analytical Methods

Laboratory measurements of PCB, Cu, Cd, Pb, and TSS were done in accordance with procedures recommended by the U.S. Environmental Protection Agency (EPA) Narragansett Laboratory and Standard Methods for the Examination of Water and Wastewater (American Public Health Association (APHA) 1981). In addition, particle size distribution analysis (PSDA) was performed using a protocol developed at the University of North Carolina. Details of all procedures are found in Appendix A.

Site and Field Tests

New Bedford Harbor, as shown in Figure 2, is located in Bristol County, Massachusetts, about 50 miles south of Boston and approximately 30 miles southeast of Providence, RI. Bottom sediment in New Bedford Harbor is contaminated with PCB and heavy metals to the extent that the site is being studied by the EPA under the Federal Superfund program. PCB contamination in sediment of New Bedford Harbor ranges from a few to over 100,000 ppm (Weaver 1983). The water column in New Bedford Harbor has been measured to contain PCB in the parts per billion range.

The U.S. Army Engineer Division, New England, provided analyses of TSS, metals, and PCB during pilot dredging operations to compare with laboratory data. Pilot field tests were conducted in November 1988, December 1988, and January 1989 (U.S. Army Engineer Division, New England 1989). Three dredgeheads were used during the pilot dredging operation: cutterhead, horizontal auger, and matchbox.

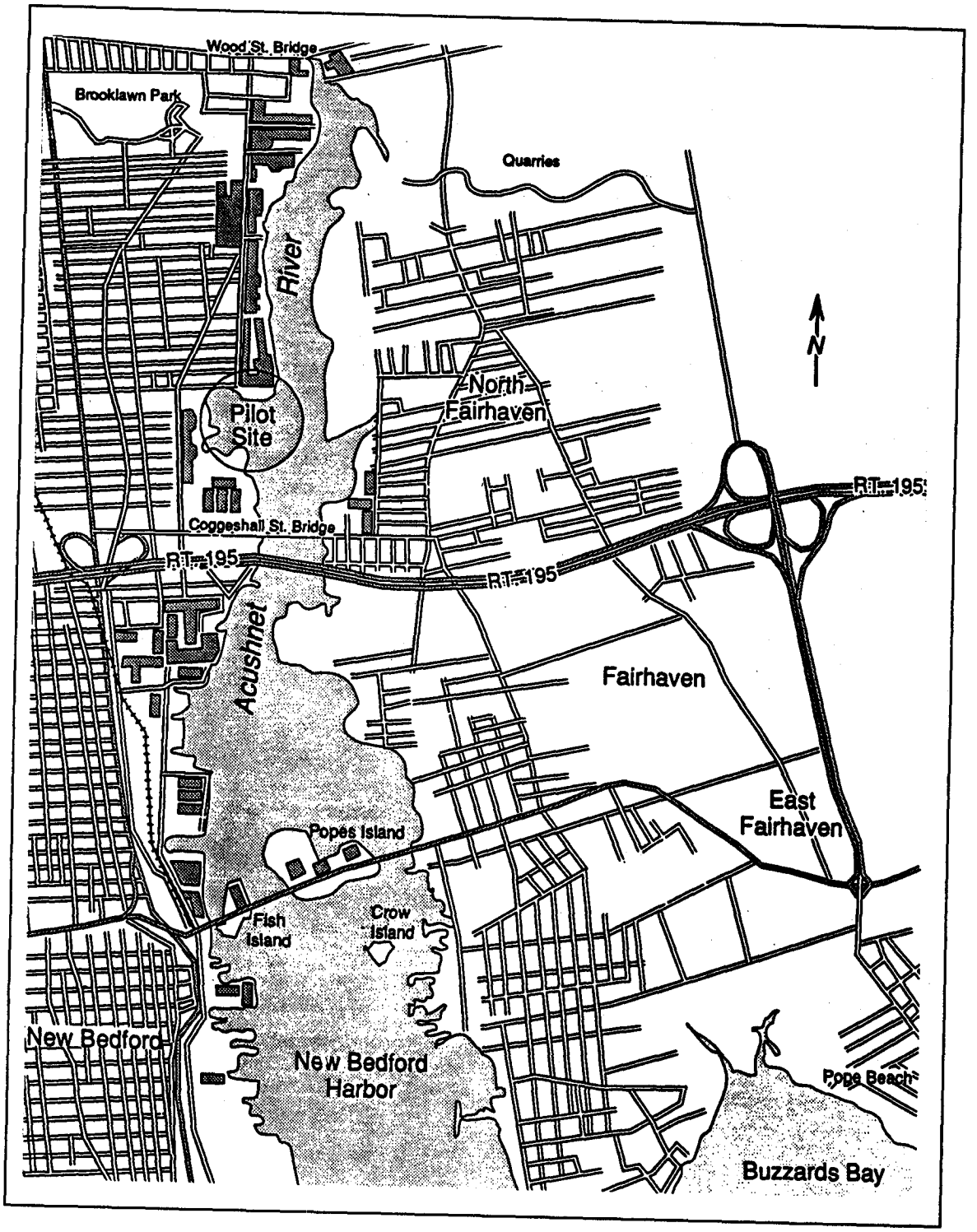

Figure 2. New Bedford Harbor area map

3 Evaluation of DRET Protocol

Volatilization of PCB During the DRET

PCB have been reported in air as well as in soil, water, sediments, and human tissue. PCB are semivolatile. Coates and Elzerman (1986) measured Henry's constants by using the characteristics of semivolatility and slight solubility. Therefore, any loss of PCB during the DRET through vaporization must be considered in an evaluation of material balance. Aqueous solutions of PCB were prepared by adding appropriate amounts of standard stock Aroclor 1242 and Aroclor 1254 solution. Distilled water was added to obtain an Aroclor concentration typically found in the DRET (about 3 $\mu g/\ell$). The spiked water sample was aerated for 4 hr in a sealed 4-ℓ graduated cylinder. The off-gas was passed through a Florisil trap, following the method of NIOSH (Eller 1984). These traps were extracted with hexane and analyzed for PCB; none was detected. Therefore, it was deduced that a significant loss of PCB by volatilization during the DRET did not occur.

Sediment and Water Characteristics

The characteristics of the sediment and water samples from the New Bedford Harbor pilot dredging site were determined before DRETs were performed. The results of these analyses appear in Table 2. These measurements provided background level concentration for PCB, Cu, Pb, and Cd. The moisture content was needed to calculate the initial TSS added to initiate a DRET, and the specific gravity was needed to calculate the final TSS at the end of an elutriate test by the PSD analyzer method.

The value for the sediment PCB concentration in Table 2 can be further clarified. The determination of initially sorbed PCB requires two steps: extraction of PCB from the sediment phase, and quantification of the extracted solute. A variety of methods are available to extract hydrophobic solutes from a solid phase. In this instance, Soxhlet extraction was used. In later work, results from a simple liquid:solid extraction procedure were compared with results from the Soxhlet extraction procedure. Similarly, a variety of

Table 2
Sediment and Water Characteristics

Media	Property	Value	Units
Sediment	Moisture content	0.65	g water/g wet sample
	Specific gravity	2.3	
	PCB	234[a]	µg/g (dry weight)
	Pb	376	µg/g (dry weight)
	Cu[b]	1246	µg/g (dry weight)
	Cd[b]	20	µg/g (dry weight)
Water	Suspended solids	<5	mg/ℓ
	PCB	<DL[c]	
	Pb	<DL	
	Cu	<DL	
	Cd	<DL	

[a] Average of two values: 242 and 226 µg/g.
[b] Obtained from U.S. Army Engineer Division, New England.
[c] Detection limit.

methods exists for quantifying the concentration of a complex mixture such as PCB. A simple four-peak method and a more sophisticated multiple linear regression method were compared.

Table 3 shows the PCB concentration of New Bedford Harbor sediment with replicate samples to verify the quantification method by complex mixture statistical reduction (COMSTAR) (Burkhard 1987); the simple liquid-solid extraction procedure was used here. The PCB concentration for sediments determined from diagnostic peaks was within 10 percent of the concentration computed using COMSTAR (Table 3) for samples analyzed using the simple liquid-solid extraction method. However, the overall peak pattern for soluble PCB was quite different from that of the Aroclor standard mixture so that quantification by the diagnostic peak method was not firmly based. The concentration of soluble PCB might be best determined by calculation of concentrations of individual congeners. Calculation of specific PCB congeners, however, was not used for this study because of time and cost constraints.

The results of both Soxhlet and liquid-solid extraction of the original sediment (two replicate samples, each yielding one PCB analysis but with multiple gas chromatography injections) are shown in Table 4. Soxhlet extraction gave a higher estimate of sorbed PCB. However, the same extraction technique should be used to compare results with those obtained in the DRET. All DRET results were obtained by the simple liquid-solid extraction procedure.

Table 3
PCB Concentration Quantification Method Comparison

Sediment Sample	Diagnostic Peak Method µg/g dry weight	COMSTAR Method µg/g dry weight	COMSTAR r^2
A	160	158	0.934
B	173	189	0.935
Average	167	173	0.934

Table 4
Comparison of Extraction Methods for Determining Sediment PCB Concentrations

Sample	Soxhlet Extraction µg/g dry weight	Liquid-Solid Extraction µg/g dry weight
1	242	160
2	226	173
Average	234	167

Therefore, the average sorbed PCB value obtained with the simple liquid-solid extraction procedure (167 µg/g) was used for analysis of DRET data.

Total Suspended Solids and PCB from DRET

Table 5 summarizes the TSS and PCB concentrations obtained in the DRETs conducted at three target initial TSS concentrations (1, 5, and 10 g/ℓ) and two different aeration times (1 and 6 hr); a replicate of the 5-g/ℓ target level actually yielded 4.7 g/ℓ because of changes in moisture content, but this for all intents was considered the same as 5 g/ℓ. The settling time in each experiment was 1 hr. The parameters measured after the DRET were TSS concentration, PCB concentration in filtered and unfiltered solutions, PCB mass on filter, and metals concentrations (Cu, Pb, and Cd) in filtered and unfiltered solution (metals will be discussed separately). The TSS concentration remaining after 1 hr of settling ranged from 60 to 172 mg/ℓ. Although TSS remaining in solution increased with initial sediment concentration for the samples with 6 hr of mixing, it was less than proportional. It should be noted that all values of PCB and TSS concentrations in Table 5 are actual values, not averages. For each DRET, 1 ℓ of sample was required for extraction of total PCB; 1 ℓ for extraction of soluble PCB; 250 ml for soluble and total metals; and 500 ml for one gravimetric determination of the TSS concentration.

Table 5
PCB Concentration Summary from DRETs

TSS_i g/ℓ (1)	Final TSS mg/ℓ (2)	PCB Concentrations: Filtered Solution µg/ℓ (3)	Unfiltered Solution µg/ℓ (4)	On Filter µg/ℓ Solution (5)	Sorbed µg/g[a] (6)	Calculated Sorbed µg/g[b] (7)
1-hr Mixing, 1-hr Settling						
1.0	63	3.0	10.2	13.1	207.9	114.3
5.0	172	1.6	15.8	14.8	86.1	82.6
5.0[c]	167	0.4	13.6	12.5	75.0	79.2
10.0	81	3.0	10.2	7.8	96.3	88.9
6-hr Mixing, 1-hr Settling						
1.0	60	NA[d]	6.3	NA	NA	NA
4.7	104	1.1	8.2	6.4	61.5	68.3
5.0	111	2.4	12.8	11.5	103.6	93.7
10.0	125	2.5	7.7	9.9	79.3	41.4

[a] Measured by liquid-solid extraction of solid captured on filter.
[b] Unfiltered PCB (column 4) less filtered PCB (column 3), i.e., F_{ss}.
[c] Duplicate sample.
[d] NA = Not available.

As shown in the Table 5, the PCB concentrations in the unfiltered solution (6.3 to 15.8 µg/ℓ) were always far greater than those in the filtered solution (0.4 to 3.0 µg/ℓ). Soluble PCB (filtered solution) showed no discernible increase with increasing initial TSS; this is expected for strongly bound compounds. Since PCB were not detectable in the water from predredged conditions, the amount of PCB found in the filtered solution came entirely from the sediment. The measurement of PCB in the filtered solutions had some bias as the result of the four-peak quantification method (see COMSTAR validation in Table 3) since the overall peak pattern did not match a standard Aroclor mixture exactly. It was clear that most of the PCB remaining in the water column were associated with TSS; nevertheless, soluble PCB may still be significant depending upon local conditions and regulations.

The sorbed PCB were obtained in two different ways. Column 6 of Table 5 shows the measured value as obtained by extraction and analyses of PCB from the solid fraction retained on the filter. Column 7 shows the calculated value obtained by subtracting the filtered PCB from the unfiltered PCB and calculation on a dry weight basis; this is equivalent to the F_{ss} calculation as presented in Equation 1 (Palermo and Thackston 1988b). A reasonable mass balance was achieved for PCB given that the difference between unfiltered and filtered PCB should equal the PCB on the filter. This can be seen by inspection of columns 3 to 5 in Table 5. The sorbed PCB were in the range 62 to 104 µg/g, with the exception of one outlier (208 µg/g). Most PCB concentrations on the filter were around 100 µg/g or less. With one exception,

these sorbed PCB concentrations were lower than the initial sediment PCB concentration (167 μg/g). The reason for the outlier is unknown. The sorbed PCB concentration calculated by the direct method and indirect method were in good agreement. Although the sediment was mixed for 15 min for homogenizing, the wide variation of sorbed PCB might arise from the heterogeneity of the sediment. The data in Table 5 suggest that increasing aeration time does not yield any significant difference in the release of PCB; statistical analysis was not warranted because of the limited amount of data.

In this work, total PCB were represented by the sum of Aroclor 1242 and Aroclor 1254. Table 6 summarizes the concentrations of Aroclor 1242 and 1254 in the DRET. For all samples, the concentration of PCB in filtered solutions was higher for Aroclor 1242 than for Aroclor 1254. This is expected based on the higher solubility of Aroclor 1242 (240 μg/ℓ for Aroclor 1242 versus 12 μg/ℓ for Aroclor 1254 at 25 °C) (Erickson 1986). Inspection of the sorbed PCB data for Aroclor 1242 and 1254 in the Table 6 shows no clear trend. The sorbed concentrations of the two PCB mixtures were usually within a factor of two.

Metals from DRET

The concentrations of Cu, Cd, and Pb in both filtered and unfiltered samples taken after 1 hr of settling in evaluation of the DRET are presented in Table 7. Unfiltered Cu ranged from 34 to 105 μg/ℓ and unfiltered Pb from 5 to 24 μg/ℓ, whereas unfiltered Cd could not be detected. Concentrations of these metals in filtered samples were typically below detection limits. These data suggest that very little of the sorbed Cu and Pb were released in soluble form for the DRET conditions evaluated (initial TSS of 1, 5, and 10 g/ℓ; aeration time of 1 and 6 hr; settling time of 1 hr). The maximum time allowed for desorption was 7 hr, this being for an aeration time of 6 hr and settling time of 1 hr. The concentration of unfiltered Cu and Pb were not proportional to the final TSS concentration (also shown in Table 7) as one would expect. This might be caused by the heterogeneity of the sediment or lack of complete metal recovery from the suspended solids by acid digestion, which is required for atomic absorption spectroscopy.

Previous research on the SET by Jones and Lee (1978) also showed that very little if any soluble metals (Cd, Cr, Ni, Pb, Cu, Hg, and As) were present. Fe and Mn present in reduced form in disturbed sediment were oxidized upon resuspension of the sediment material in the elutriate test, and it was reasoned that $Fe(OH)_3$ and $Mn(OH)_3$ could well act as sorption traps for metals. It appears that the particulate-borne fraction of the trace metals constitutes the major source of metal contaminants in the water column. The data in Table 7 indicated that increasing aeration time did not yield any significant difference in the release of Cu, Cd, and Pb.

Table 7
Metals Concentrations from DRETs

Suspended Solids		Pb		Cu		Cd	
Initial g/ℓ	Final mg/ℓ	Filtered µg/ℓ	Unfiltered µg/ℓ	Filtered µg/ℓ	Unfiltered µg/ℓ	Filtered µg/ℓ	Unfiltered µg/ℓ
1-hr Mixing, 1-hr Settling							
1.0	63	ND[a]	16	ND	78	NA[b]	NA
5.0	172	ND	19	ND	101	NA	NA
5.0[c]	167	ND	NA	14	NA	NA	NA
10.0	81	ND	5	ND	38	NA	NA
6-hr Mixing, 1-hr Settling							
1.0	60	ND	5	ND	67	ND	ND
4.7	104	ND	24	ND	71	ND	ND
5.0	111	ND	22	13	105	NA	NA
10.0	125	ND	7	ND	34	ND	ND

[a] ND = Not detectable.
[b] NA = Not available.
[c] Duplicate sample.

Batch Shaker Test

Another experiment was designed to measure the release of PCB from sediment particles by vigorous shaking rather than in the DRET. The objective was to determine the rate of release of PCB in a simple batch test wherein the effects of aeration and settling were eliminated. The experiment was conducted by adding 10 g/ℓ of sediment to artificial seawater in 2-ℓ bottles (in duplicate) and placing them on a laboratory, rotating shaker device for 1 and 6 hr after which soluble PCB concentrations were measured. The results shown in Table 8 are in the same range as the filtered solution PCB concentrations summarized in Tables 5 and 6 for the DRET conducted with an initial TSS (TSS_i) of 10 g/ℓ and mixing times of 1 and 6 hr. Although more data are needed to determine the release rate, it appears that shaking for 6 hr provides

Table 8
Release of PCB in Duplicate Batch Shaker Test (TSS_i = 10 g/ℓ)

Time of Shaking hr	Aroclor 1242 µg/ℓ	Aroclor 1254 µg/ℓ	Total PCB µg/ℓ
1.0	1.52	0.17	1.69
1.0	1.57	0.19	1.76
6.0	2.10	0.24	2.34
6.0	1.84	0.38	2.22

little if any further release of PCB than shaking for 1 hr. Further, the simple shaker test is a good estimator of the more elaborate DRET for soluble PCB.

Distribution of Sorbed PCB with Particle Size

An experimental method was sought to determine whether sorption of PCB depended on particle size. Palermo and Thackston (1988b) suggested that the F_{ss} value was always higher in the modified elutriate tests than in the field samples because of differences in settling conditions. That is, the graduated cylinder enables quiescent settling, while wind action occurs in the field, keeping some coarser particles in suspension that would otherwise settle in the elutriate test. The result is a higher mean solids concentration (F_{ss}) in the elutriate test because the fine particles have greater affinity for contaminants than the more coarse particles.

An experimental problem is in subdividing the distribution of already very small particles ($d_p < 20$ μm) into fractions so that sufficient particles can be recovered to extract and perform PCB analyses. Membrane and glass fiber filters having stated pore sizes in the range of interest were first tried. However, PSD analyses revealed that these filters could not be relied upon to isolate particles by their diameter. One practical problem is clogging of the filter. The method finally selected was wet sieve analysis in which a slurry of solids was passed first through a 10-μm sieve and then through a 5-μm sieve. It was not possible to distinguish differences by PSD analysis before and after the 5-μm sieve. However, subdividing into fractions with a diameter greater than and smaller than 10 μm was more successful. The results of PSD analysis with respect to particle number distribution before and after passage through the 10-μm sieve are shown in Figure 3. Converting from number of particles to volume of particles gave the PSD shown in Figure 4. The effectiveness of the sieve in subdividing particle size fractions is more evident when the differences in volume rather than number distributions are examined. For each PSD, the median particle diameter (d_{50}), and geometric standard deviation (GSD) were determined. These are listed in Table 9 and show that the wet sieve served to separate particles effectively into two size ranges.

The sorbed PCB present before and after the wet sieve were analyzed (same procedure described previously). The results are also presented in Table 9, being expressed both per unit of weight (μg/g) and surface area (μg/mm^2) of particles. Based on external surface area, the larger size fraction contained almost twice the sorbed PCB per unit volume as the smaller size fraction. However, the sorbed PCB were equivalent on a mass basis. This result is consistent with the notion of linear partitioning, which is a mass dependent rather than a surface area dependent phenomenon (Karichoff, Brown, and Scott 1979).

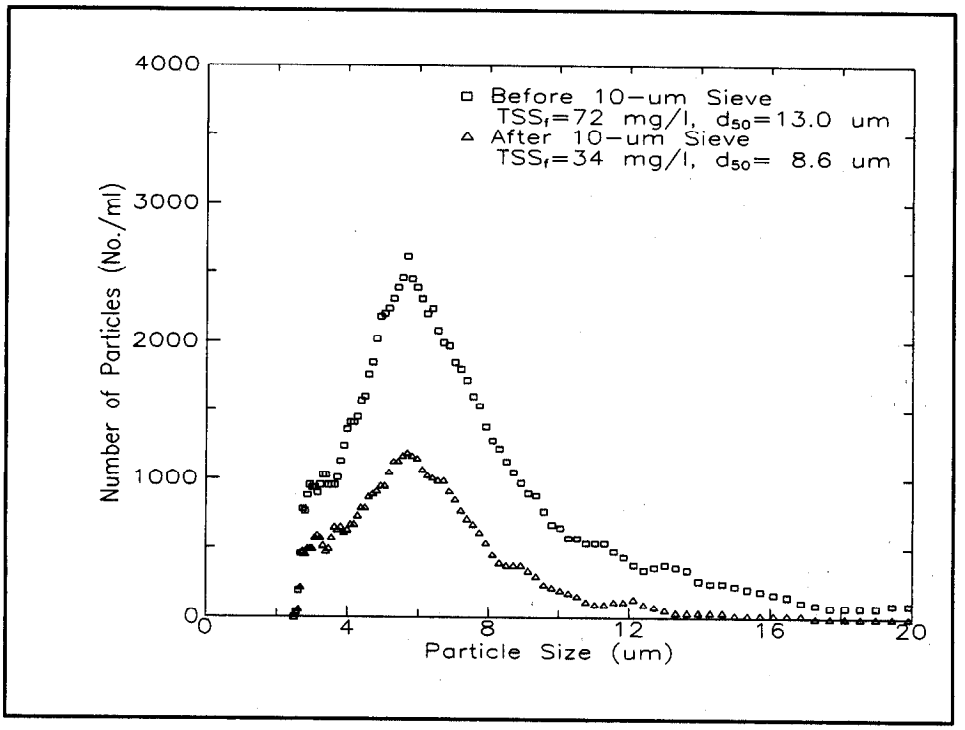

Figure 3. Number PSD for wet-sieved samples

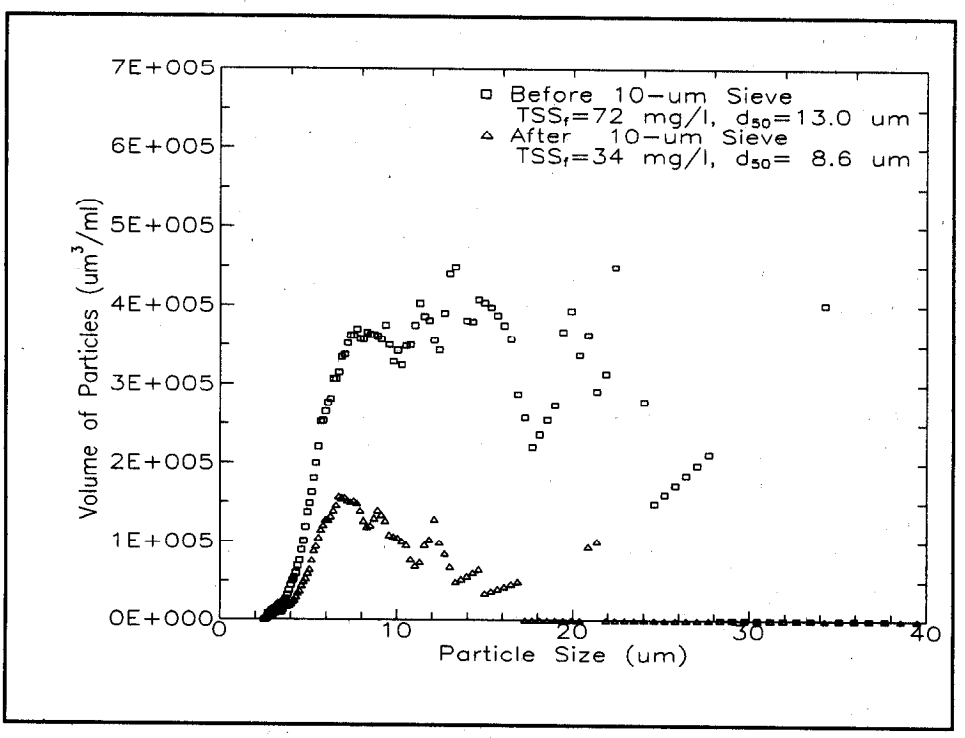

Figure 4. Volume PSD for wet-sieved samples

Table 9
Particle Characteristics Before and After Wet Sieving

Sample	Final TSS mg/ℓ	d_{50} μm	GSD	Surface Area mm²/ml	Total PCB μg/ℓ	Sorbed PCB μg/g	Sorbed PCB μg/mm² × 10⁻³
Before Sieving	72	13.0	1.98	15.30	7.0 7.1	97.4	0.46
After Sieving	34	8.6	1.94	4.96	3.7 3.6	108.5	0.74

Correlation of Final TSS and DRET Conditions

While the soluble PCB concentration and F_{ss} (i.e., sorbed PCB concentration) are of most interest in the DRET, it is also useful to understand the relationship between TSS remaining in the DRET and DRET conditions, i.e., initial SS, mixing time, and settling time. This is not necessarily a substitute for a settling column analysis to determine TSS for use with the F_{ss} value. Rather it provides information on how conditions of the test influence the TSS remaining with time and in particular, the time of settling beyond which no further substantial change in TSS, and thus total PCB, can be expected-regardless of whether a 4-ℓ graduated cylinder or larger settling column is used. It also makes sense to design a DRET that will give a TSS similar to independent measurements in the field, e.g., from pilot tests of dredgeheads, so as to account for any effect of solids concentration on the partitioning between sorbed (F_{ss}) and soluble phase contaminant.

A three-factor matrix experiment was designed (Table 10) to define the relationship between TSS remaining in the DRET and operating conditions in more detail than was provided by the experiments from which Table 5 was constructed. In particular, settling times greater than the 1 hr used in these previous experiments were of interest.

The elements of the matrices completed in Table 10 for settling times of 6, 12, and 24 hr were selected to cover the minimum and maximum aeration times and initial TSS concentration, the intent being to fill in other elements if warranted later. These elements account for 28 different experiments with each done in duplicate or triplicate. The final TSS concentration was determined gravimetrically as well as by calculation from the PSDA, the latter requiring assumptions regarding shape (spherical) and density (2.3 g/cm^3) of the particles.

Table 10
Design of Three-Factor Experiments

Settling Time hr	TSS_i g/ℓ	Aeration Time, hr			
		1	3	6	12
1	0.5	x	x	x	x
	1.0	x	x	x	x
	5.0	x	x	x	x
	10.0	x	x	x	x
6	0.5	x			x
	10.0	x			x
12	0.5	x			x
	10.0	x			x
24	0.5	x			x
	10.0	x			x

The results for TSS concentrations with settling time fixed at 1 hr and initial solids concentration and aeration time as variables are presented in Table 11. These data show that gravimetric analysis of TSS was reproducible in the duplicate elutriate tests. Moreover, good agreement was obtained between these measured values and those calculated from the PSDA. The use of PSD analysis for this purpose will be discussed in more detail in a later section. The data suggest that aeration time had no significant effect on the TSS_f concentration at any level of initial solids concentration. However, TSS_f concentration increased with initial solids concentration, albeit far less than proportionally; a ten-fold increase in initial solids concentration produced roughly a two-fold increase in TSS_f. This same trend was followed in the first series of elutriate tests shown in Table 5.

The effect of settling time on TSS_f at the two levels of aeration (1 and 12 hr) and two levels of initial solids concentration (0.5 and 10 g/ℓ) is given in Table 12. The data sets obtained for 1 hr of settling (Table 11) have been reproduced in Table 12. Aeration time had little effect on the settling properties, but, as noted above, a higher initial solids concentration produced higher TSS concentrations at least during the first 6 hr of settling. In these experiments, a 20-fold increase in TSS_i concentration only increased the TSS_f concentration by a factor of about two. As important, most of the settling occurs during the first 6 hr regardless of aeration time or the TSS_i concentration. Palermo and Thackston (1988b) noted little decrease after 24 hr, but the TSS_i concentrations were much higher (62 to 155 g/ℓ) than used in this study (0.5 to 10 g/ℓ).

Table 11
TSS_f (mg/ℓ) as a Function of TSS_i and Aeration Time; Settling Time = 1 hr

TSS_i, g/ℓ	Method	Aeration Time, hr			
		1	3	6	12
0.5	Measured[a]	87, 89	78, 84	91, 84	72, 70
	Calculated[b]	80, 81	80, 86	62, 53	58, 63
1.0	Measured	68, 69, 94	86, 81	82, 81	81, 86
	Calculated	--	99, 78	91, 94	91, 102
5.0	Measured	123, 121, 101	100, 103	150, 149	147, 136
	Calculated	--	105, 136	169, 172	177, 155
10.0	Measured	117, 125, 122	134, 152	151, 174	167, 200
	Calculated	--	164, 169	165, 179	226, 199

[a] TSS measured from gravimetric analysis.
[b] TSS calculated from PSDA.

Table 12
TSS_f (mg/ℓ) as a Function of Settling Time

TSS_i, g/ℓ	Method	Settling Time, hr			
		1	6	12	24
1-hr Aeration Time					
0.5	Measured[a]	87, 89	27, 30	34, 36	34, 35
	Calculated[b]	80,81	--	--	--
10.0	Measured	117, 125, 122	57, 51	47,48	47,39
	Calculated	--	--	--	--
12-hr Aeration Time					
0.5	Measured	72, 70	37, 42	34, 35	33, 24
	Calculated	58, 63	--	--	--
10.0	Measured	167, 200	68, 68	42, 40	36, 32
	Calculated	226, 199	--	--	--

[a] TSS measured from gravimetric analysis.
[b] TSS calculated from PSDA.

The results presented above indicated that most of the settling took place during the first 6 hr in the DRET. More definition of settling during the first 6 hr was needed. PSDA provided a convenient alternative for calculating the residual TSS at any settling time because it required that only a very small sample volume (3 ml) be withdrawn from the 4-ℓ graduated cylinder; this is

far less than the volume needed for multiple gravimetric analysis (2 ℓ); this allowed multiple analysis to be performed over a 6-hr period.

The validity of PSDA as a substitute for gravimetric analysis was first tested by correlating the TSS obtained by calculation from PSDA with that from gravimetric analysis in the three-factor matrix experiment as presented in Tables 11 and 12. Using 26 pairs of data, a good correlation was obtained (slope of 1.05 and r^2 of 0.874) as shown in Figure 5.

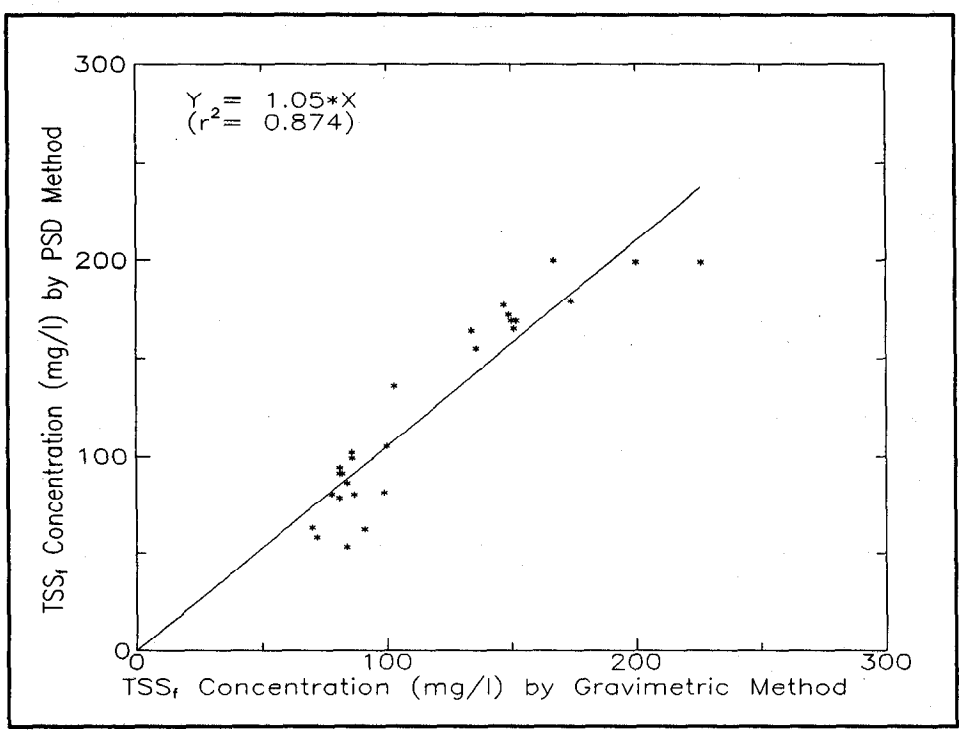

Figure 5. Comparison of TSS_f measured by gravimetric method to TSS_f measurement by PSD method

Two additional experiments were conducted to show in greater detail the pattern of TSS_f remaining with settling time. In these elutriate tests, the TSS_i were 0.5 g/ℓ and 10 g/ℓ and the aeration time was 1 hr. As indicated in Figure 6, most settling occurred within 1 hr. Therefore, this is a reasonable settling time to use in a DRET.

All the data obtained in the three-factor matrix experiments and the two follow-up experiments shown in Figure 7 were combined to search for a correlation of TSS_f concentration with TSS_i concentration, aeration time, and settling time. The form of the relationship sought had to account for two important effects: (a) TSS_f increases nonlinearly with TSS_i and (b) the TSS_f concentration decreases nonlinearly with settling time. The data did not show an effect of aeration time; thus this factor was eliminated from the regression analysis. The regression model chosen was of the form:

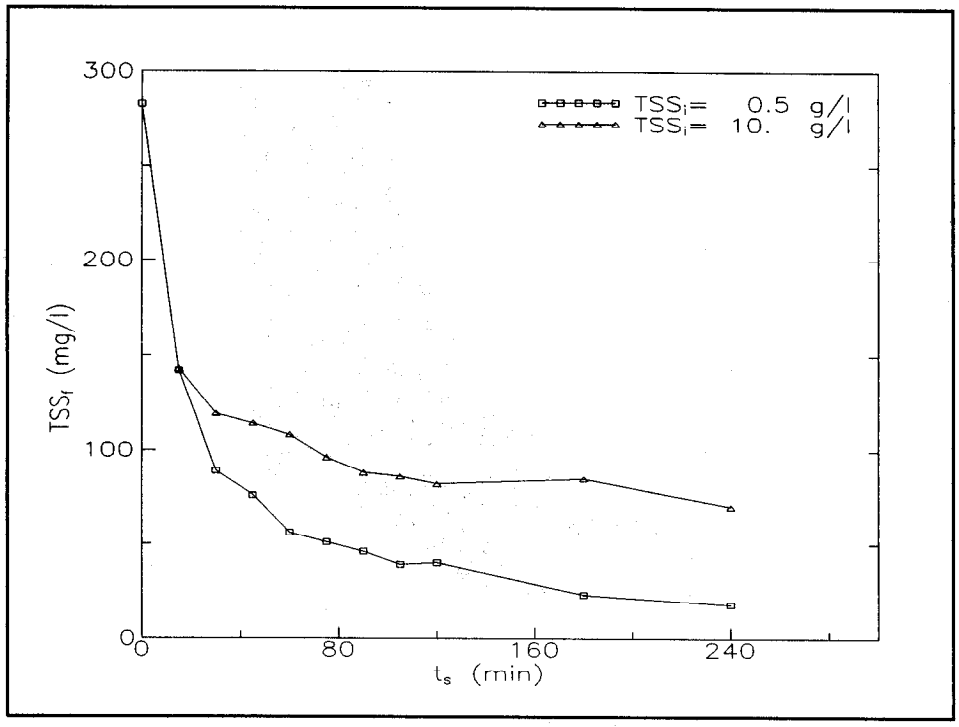

Figure 6. TSS_f as a function of time after a 1-hr aeration time

$$TSS_f = \exp(a_1 t_s)(1 + a_2 TSS_i^{a_3}) \quad (3)$$

The resulting values of the coefficients a_1, a_2, and a_3 in the regression model are presented in Table 13. A reasonably good fit was obtained as indicated by the 95-percent confidence intervals of the model parameters.

Data from the three-factor matrix experiment (Tables 11 and 12) and the follow-up experiments (Figure 6) can also be examined independently from the regression model. The dependence of TSS_f on TSS_i and settling time is depicted in a three-dimensional plot (Figure 7). It is again clear that settling

Table 13
Regression Model Parameter Estimates

Coefficient	Estimate	Standard Error	95% Confidence Interval
a_1	0.104	0.016	0.072-0.136
a_2	96.2	4.92	86.3-106.
a_3	0.203	0.027	0.150-0.256

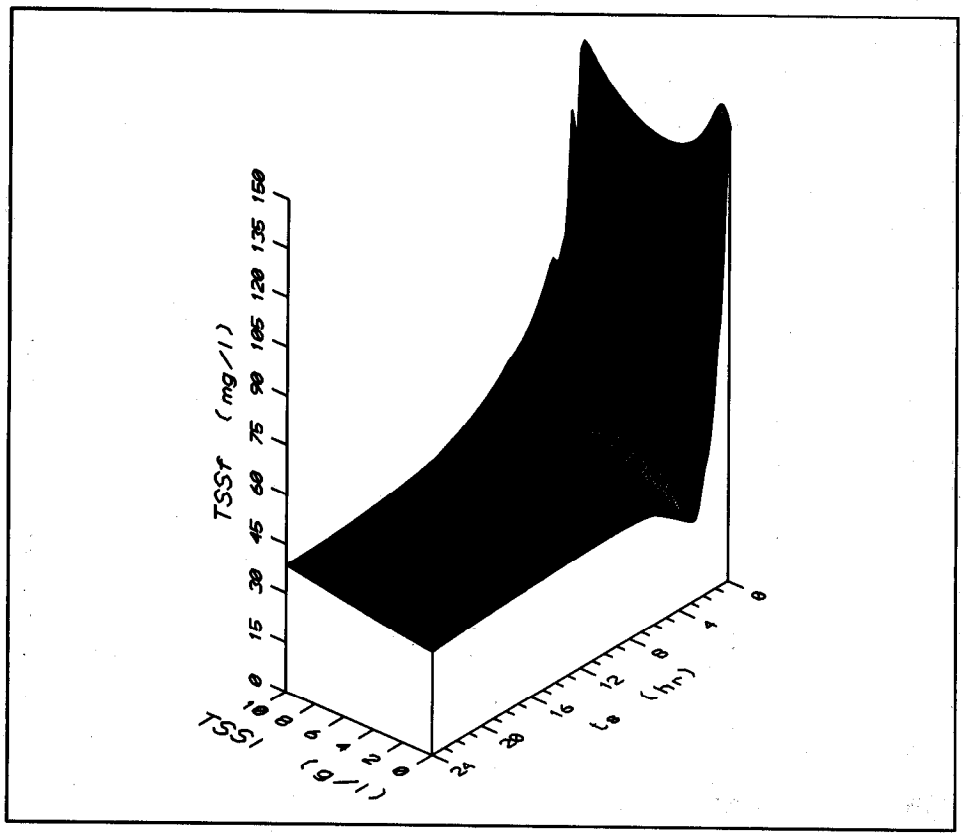

Figure 7. TSS_f surface as a function of settling time(t_s) and initial suspended solids concentration (TSS_i)

time is more important than TSS_i and that most settling occurs within the first 6 hr. Such a relationship should be used with caution because sediment material from different sites may have different settling properties.

4 Field Results

Field Data from New Bedford Harbor

Samples were collected from sampling ports attached to each dredgehead type (cutterhead, horizontal auger, and matchbox) and from the plume during various phases of the dredging operation. The location of the plume samples is shown in Figure 8. The plume data for PCB and TSS concentrations that were presented in the U.S. Army Engineer Division, New England (1989) report are average values obtained from the following stations (1-5, 6-10, and 11-15). These samples were taken within about 100 ft of the dredge site and some just inside the dredge area itself. Most samples were taken during the dredging operation and the remainder within a couple of hours after dredging had stopped. Neither the dredgehead nor the plume samples are represented by settling conditions achieved in the DRET. That is, samples from the port attached to a dredgehead are more representative of the initial sediment load added in the DRET and do not account for any sedimentation, while samples from the plume are not represented by a fixed settling time in the DRET. Therefore, the DRET may predict soluble PCB concentrations reasonably (if enough time is allowed in the field to approach equilibrium to a similar extent as in the DRET), but not predict total contaminant concentration accurately unless partitioning data from the DRET are combined with information on TSS expected in the field, as Equation 2 represents. This limitation has been noted by Palermo and Thackston (1988b) in the development of the modified elutriate test.

PCB and TSS Data

The average and range of concentrations of PCB reported in the U.S. Army Engineer Division, New England (1989) report as total (unfiltered PCB), dissolved (filtrate PCB), and particulate (captured on the filter) for each dredgehead (at the dredgehead) are presented in Table 14. Total PCB should be slightly greater than the particulate PCB, but this was not found from inspection of the data in Table 14; the only explanation is a difference in analytical methods used to obtain these data (the determination of total PCB is an

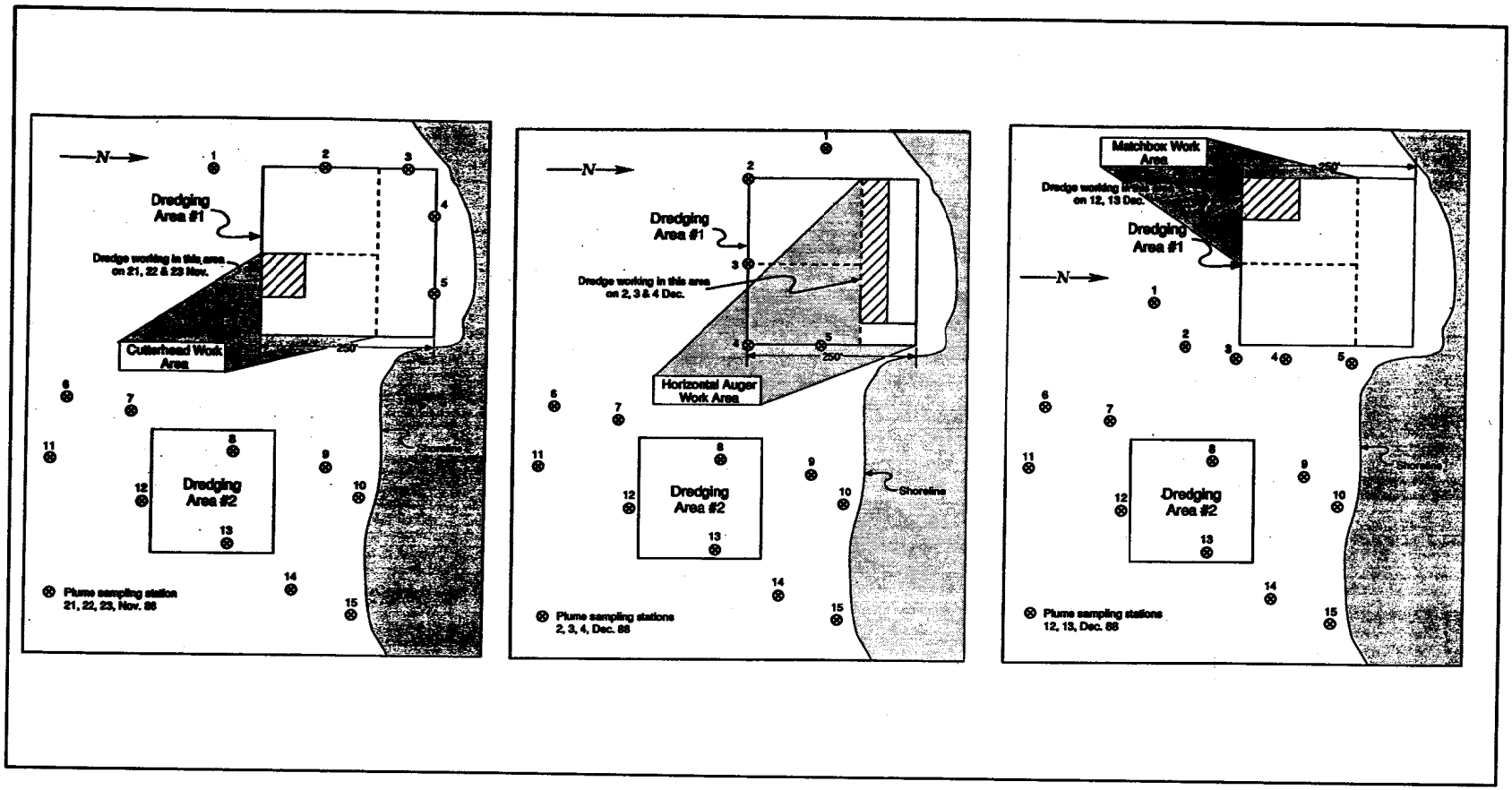

Figure 8. Field sample location map

Table 14
Summary of PCB Data from New Bedford Harbor Pilot Study[a]

Dredgehead Type	Total PCB, μg/ℓ		Dissolved PCB, μg/ℓ		Particulate PCB, μ/ℓ	
	Average	Range	Average	Range	Average	Range
Cutterhead	7.0	1.6-26.6	0.6	0.5-1.0	22.3	0.6-66.7
Horizontal Auger	54.9	12.6-133	10.1	1.0-22.9	200.3	18.2-382
Matchbox Dredge	2.6	0.2-4.5	0.5	0.3-0.6	56.9	6.7-205

[a] Data from U.S. Army Engineer Division, New England (1989), Table 5.
Other useful data are as follows:
(1) Background total PCB: 0.607 μg/ℓ at Coggeshall St. Bridge, 0.114 μg/ℓ at the Hurricane Barrier.
(2) Background TSS: 6.4-10.2 mg/ℓ at Coggeshall St. Bridge, 4.4-7.9 mg/ℓ at the Hurricane Barrier.
(3) Dredgehead sampling was from the water column adjacent to operating dredgehead.

independent procedure that does not rely on removing suspended material from a filter for analysis). The most obvious trend is that a much higher PCB concentration was produced by the horizontal auger than either the cutterhead or matchbox dredge.

The U.S. Army Engineer Division, New England (1989) report did not summarize the average values of TSS corresponding to the data in Table 14, so it is not possible to calculate the sorbed concentration of PCB (μg/g), i.e., F_{ss}. However, the report does contain data for individual samples from the dredgehead for which both particulate (or total) PCB and TSS concentration were measured. These are listed in Table 15 for each dredgehead.

The TSS ranged from 46 to 388 mg/ℓ for the cutterhead dredge; 634 to 4,037 mg/ℓ for the horizontal auger dredge; and 62 to 582 mg/ℓ for the matchbox dredge. These data show that the cutterhead dredge gave the least resuspension of sediment. The sorbed PCB concentrations were calculated and appear in the last column of Table 15. In some instances, the total PCB were used for calculation even though the particulate PCB would be more appropriate. The justification is that the data for total PCB may be more reliable than for particulate because the sample is analyzed directly with less chance for experimental error in recovery of solids from the filter. Moreover, total PCB should approximate the sorbed fraction because only a small amount is dissolved. As can be seen in Table 15, the sorbed concentration of PCB varied widely. Most of the values in Table 15 are between 25 and 100 μg/g. For comparison purposes, the sorbed PCB concentration measured on pre-dredged sediment by the simple liquid–solid extraction procedure was 167 μg/g (see Table 4).

The results of TSS and PCB (total or particulate) analyses on samples from the plume for each dredgehead are given in Table 16. Again, the sorbed PCB

Table 15
TSS and PCB Concentrations for Individual Dredgehead Samples[a]

Dredgehead Type	Sample	TSS, mg/ℓ	Total PCB µg/ℓ	Sorbed PCB µg/g
Cutterhead	519121	56	5.43	97.
	519321	88	6.87	78.
	519521	46	3.59	78.
	519522	61	3.48	57.
	521951	76	3.20	42.
	521952	388	3.39	8.7
	526222	216	4.97	23.
Horizontal Auger	519923	4,037	133.	33.
	520122	634	19.9	31.
	520323	1,083	29.6	27.
	527422	2,207	16.2	7.3
	527423	1,757	98.6	56.
	527424	2,133	108.	51.
	527425	1,665	47.4	28.
Matchbox	520521	76	4.54	60.
	526322	111	119.[b]	1,070.
	526522	62	205.[b]	3,300.
	526722	582	0.19	0.33
	526923	214	7.47[b]	35.
	526924	201	12.6	63.
	526924	121	30.4[b]	251.
	527924	68	6.72[b]	99.
Standard Elutriate Test			91.3[b]	–

[a] Data from U.S. Army Engineer Division, New England (1989), Tables 2, 11, and 17.
[b] Particulate PCB.

concentration was calculated and appears in the last column. This calculation is similar to that of F_{ss} (Palermo and Thackston 1988b), the difference being that the total PCB value was used as an approximation to the total PCB less soluble PCB because of the very small value of the latter. While the sorbed PCB concentration data are scattered, most fall between 80 and 214 µg/g, which is in rough agreement with predredged sediment values (Table 4).

Table 16
TSS and PCB Concentrations for Individual Plume Samples[a]

Dredgehead Type	Sample	TSS, mg/ℓ	Total PCB µg/ℓ	Sorbed PCB µg/g
Cutterhead	513151	37	1.41	38
	513153	4	1.41	353
	513251	16	1.65	103
	513351	5	0.66	131
	513353	5	0.54	108
Horizontal Auger	513451	7	1.45	207
	513453	8	0.71	89
	513551	13	1.74	134
	513553	3	1.85	617
	513651	24	2.19	91
	513653	10	1.90	190
Matchbox	513851	8	1.64	205
	513852	24	5.13[b]	214
	513853	11	1.13	103
	513953	32	49.4[c]	1,543

[a] Data from U.S. Army Engineer Division, New England (1989), Tables 3, 15, and 20.
[b] Particulate PCB.
[c] Suspect value; another sample on same day gave 1.2 µg/ℓ but did not include TSS data.

A comparison of the sorbed PCB calculated for each dredgehead type at the dredgehead and in the plume is given in Figures 9 and 10, respectively. The sorbed PCB should be independent of dredgehead used. This was generally shown to be the case, the exceptions being some anomalously large, sorbed concentrations from the matchbox dredgehead. One possible explanation is that different dredgeheads remove sediment to different depths; thus if sorbed PCB concentrations vary with depth, the type of dredgehead becomes important. A related possibility is that sorbed PCB concentrations are a function of particle size, and different particle sizes are associated with resuspended sediment from each dredgehead. The laboratory data presented in Table 9 suggest that sorbed PCB concentrations are not a function of particle size. Nevertheless, if the results from the matchbox dredgehead are ignored, the sorbed concentrations of PCB at the dredgehead, where coarser TSS are expected, are generally lower than those collected in the plume, where finer TSS are expected.

The field data for PCB also provide a breakdown into Aroclor 1242 and 1254 as listed in Table 17 for dredgehead samples. These again show that

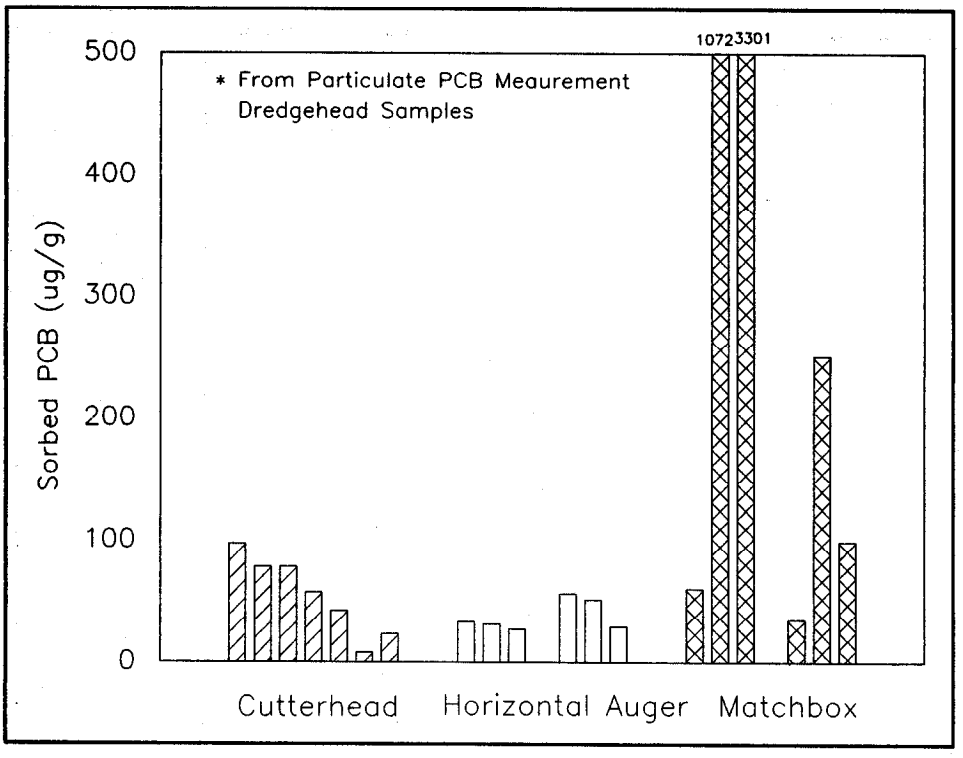

Figure 9. Comparison of sorbed PCB for dredgehead samples

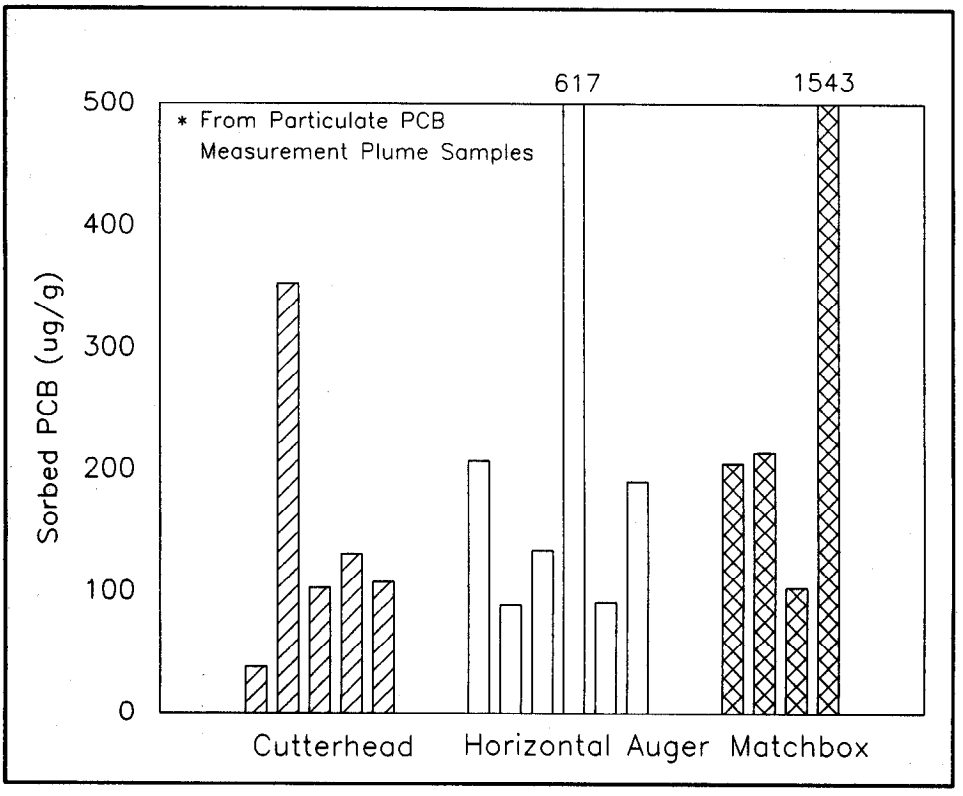

Figure 10. Comparison of sorbed PCB for plume samples

particulate PCB are much greater than dissolved. In addition, most of the values for dissolved Aroclor 1242 are greater than for dissolved Aroclor 1254 whereas the total (or particulate) are in much closer agreement. These data may be may be explained by the higher solubility of Aroclor 1242 as discussed earlier.

Metals Data

A summary of total, dissolved, and particulate concentrations of Cu, Cd, and Pb measured at each dredgehead is given in Table 18. The grab samples taken for metals analyses were different from those taken for PCB analyses but obtained during the same dredging pilot tests. As was found for the PCB data, there was poor agreement between the two methods of metals analysis, i.e., total without filtration of the sample and filtration to yield both dissolved and particulate fractions (the sum of these two fractions should equal the total metals). Also listed in Table 18 are the TSS data where available. The range of values for each dredgehead is similar to that presented in Table 17 with the PCB data.

Because the metals data were obtained at the dredgeheads, they should represent the maximum concentrations at the point of dredging. Therefore, the results would correspond more closely to the initial conditions of the DRET evaluated in this study than to the data after 1 hr of settling (Table 7). Unfortunately, metals concentrations were not available from plume samples, which would have made it possible to compare results with those of the DRET more directly.

The data in Table 18 show that the concentrations of dissolved metals, with the exception of one data point for Pb, are very low (near the detection limit of the analytical procedure), while those of particulate metals are much higher. This agrees with the findings for PCB concentrations and supports the contention that knowledge of the TSS remaining after dredging is very important when evaluating environmental impacts.

The sorbed concentrations (μg/g) of Cu, Cd, and Pb are presented in Figures 11 to 13, respectively. These were calculated from the data in Table 18 using the TSS and the concentration of particulate metals (where available) of that of the total metals (a reasonable estimate of the particulate given the low concentrations of dissolved metals). Each bar graph in the figures represents a field measurement. The sorbed concentration of Cu and Pb is one to two orders of magnitude greater than that of Cd. This is consistent with the soluble concentration of Cd also being very low (Table 18) and with results of the DRET (Table 7). Sorbed concentrations of each metal should only depend on solid-liquid phase partitioning and not on the type of dredgehead used, given that the aqueous phase concentrations are similar in all field samples. The variation in sorbed concentration from sample to sample and from dredgehead to dredgehead may be due to the effect of dredgehead type

Table 17
Aroclor Detail for Dredgehead Samples[a]

Dredgehead Type	Sample	TSS mg/ℓ	Total PCB, µg/ℓ			Dissolved PCB, µg/ℓ			Particulate PCB, µg/ℓ		
			1242	1254	Sum	1242	1254	Sum	1242	1254	Sum
Cutterhead	519121	56	3.50	1.93	5.43						
	519122					0.49	0.04	0.53			
	519123		2.43	1.33	3.76						
	519321	88	4.29	2.57	6.86						
	519322					0.51	ND	0.51	0.25	0.31	0.57
	519521	46	2.31	1.28	3.59						
	519522		2.20	1.28	3.48						
	519523					0.47	0.03	0.50	1.45	1.70	3.16
	520921		13.9	12.7	26.6						
	520923		8.44	5.89	14.3						
	520922					1.16	0.43	1.59	41.2	25.5	66.7
	521950								20.6	12.1	32.8

(Sheet 1 of 3)

[a] Data from U.S. Army Engineer Division, New England (1989).

Table 17 (Continued)

Dredgehead Type	Sample	TSS mg/ℓ	Total PCB, µg/ℓ			Dissolved PCB, µg/ℓ			Particulate PCB, µg/ℓ		
			1242	1254	Sum	1242	1254	Sum	1242	1254	Sum
	520950					0.99	ND	0.99			
	521951	76	1.80	1.40	3.20						
	521952	388	2.24	1.16	3.40						
	926222	216	2.90	2.07	4.97						
	566223					0.63	0.04	0.68	6.77	5.61	12.4
Horizontal Auger	519922					11.9	11.1	22.9	220.	142.	364.
	519923	4,037	82.4	50.1	133.						
	520122	634	12.2	7.66	19.9	5.48	3.31	8.79	10.3	7.97	18.2
	520123	1,083	18.6	10.5	29.1						
	520123		5.72	6.84	12.6	4.35	3.46	7.81	22.8	14.0	36.8
	510323		16.0	13.7	29.6						
	527421		7.73	8.46	16.2						
	527422	2,207				0.98	0.01	.99	212.	170.	382.

(Sheet 2 of 3)

Table 17 (Concluded)

Dredgehead Type	Sample	TSS mg/ℓ	Total PCB, µg/ℓ			Dissolved PCB, µg/ℓ			Particulate PCB, µg/ℓ		
			1242	1254	Sum	1242	1254	Sum	1242	1254	Sum
	527423	1,757	60.2	38.4	98.6						
	527424	2,133	67.5	40.5	108.						
	527425	1,665	23.1	24.2	47.4						
Matchbox	520521	76	2.66	1.88	4.54						
	520522					0.59	0.00	0.59	9.55	7.51	17.1
	520523		2.60	1.79	4.39						
	566322	111				0.52	0.00	0.52	6.72	52.0	119.
	526522	62	0.97	0.15	1.12						
	526722	582	0.19	0.00	0.19						
	524923	214				0.33	0.01	0.34	3.94	3.53	7.47
	526924	121				0.36	0.02	0.38	6.54	6.07	12.6
	526925								18.2	12.1	30.4
	527924					3.96	2.75	6.72			

(Sheet 3 of 3)

Table 18
Metals Data from Dredgehead Samples[a]

Dredgehead Type	Sample	TSS[b] mg/ℓ	Total, µg/ℓ			Dissolved, µg/ℓ			Particulate, µg/ℓ		
			Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd	Pb
Background	Bridge		6.5	3.4	0.22						
	Station 1		7.8	0.22	4.						
Cutterhead	519122	60							228	6	71
	519123		90.	2.	31.						
	519522	46							91	2	32
	520922					2	0.1	0.4		9	110
	520923		281.	10.	120.						
	521950	127				2	0.2	0.5	687	25	303
	521952	164	91.	3.	39.						
	527621					2	0.03	0.2	285	7	103
	527622		1,367.	127.	1,556.						

(Continued)

[a] Data from U.S. Army Engineer Division, New England (1989).
[b] Average values from dredgehead port samples.

Table 18 (Concluded)

Dredgehead Type	Sample	TSS[b] mg/ℓ	Total, μg/ℓ			Dissolved, μg/ℓ			Particulate, μg/ℓ		
			Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd	Pb
Horizontal Auger	519922	4,037				5	0.5	22.	4,644	138	1,483
	519923		1,363.	163.	1,707.						
	520323	1,299	1,188.	31.	608.	3	0.1	1.0	832	23	392
	527422								4,219	95	1,372
	527423	1,757	3,617.	131.	1,550.						
	527424	2,133	3,932.	146.	1,592.						
	527425	1,665	1,884.	27.	642.						
Matchbox	520522	75				3	0.5	2.	99	3	32
	520523		102.	3.	39.						
	527924	68							71	2	28

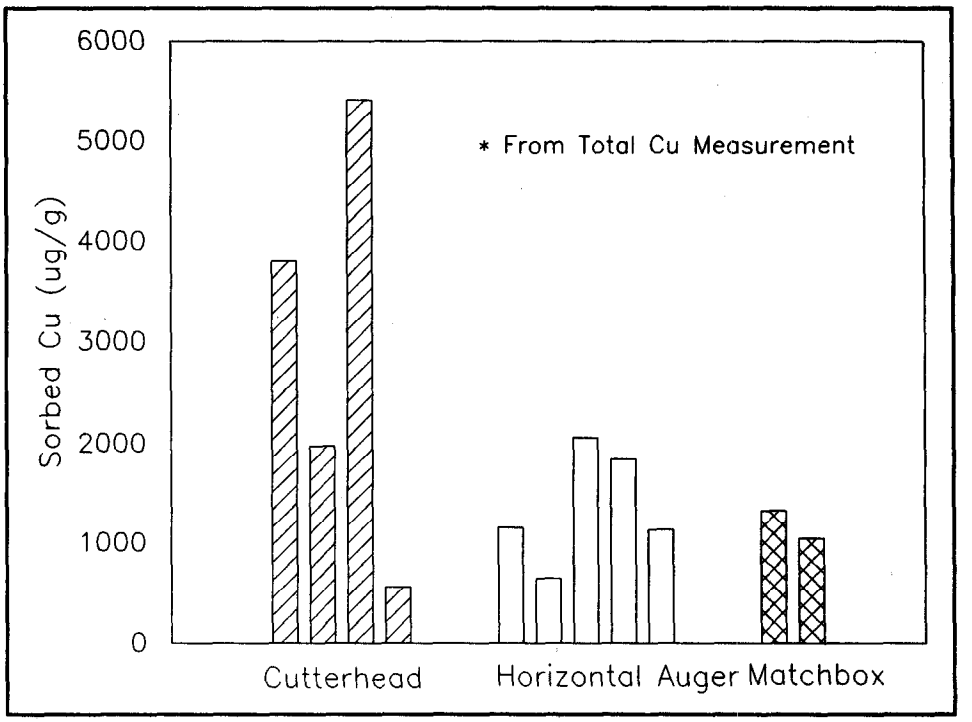

Figure 11. Sorbed Cu concentrations as a function of dredgehead type

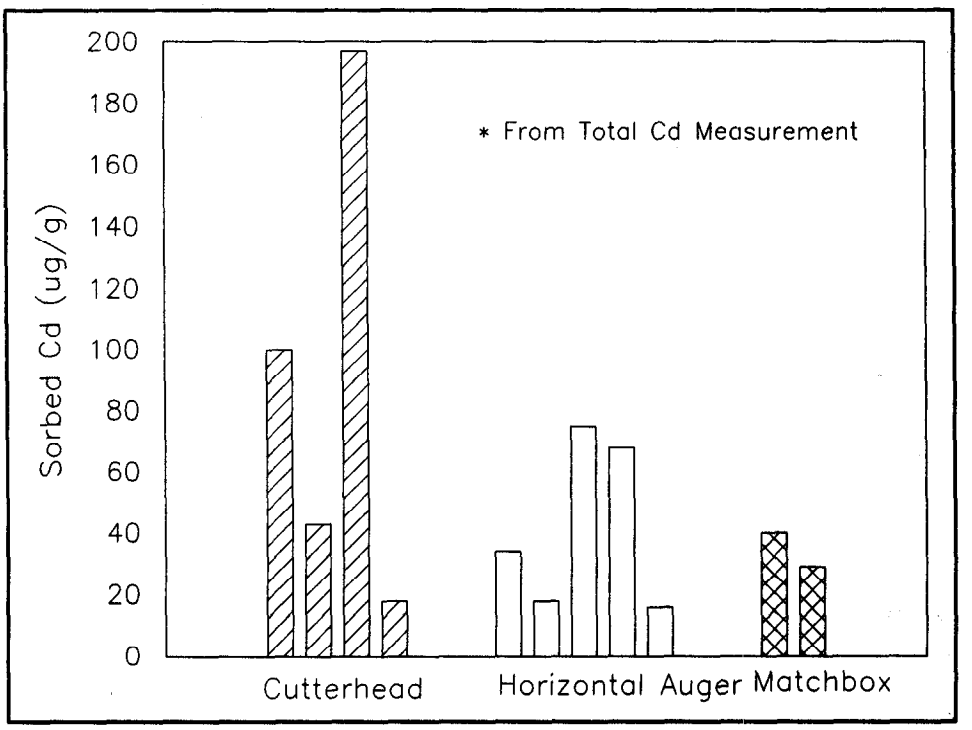

Figure 12. Sorbed Cd concentrations as a function of dredgehead type

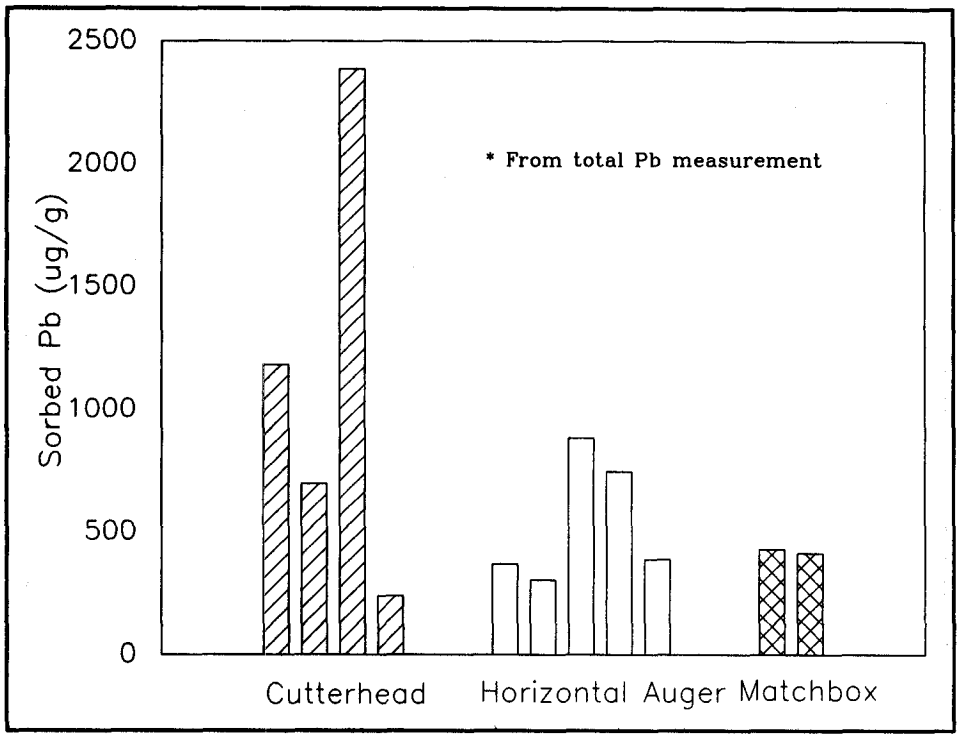

Figure 13. Sorbed Pb concentrations as a function of dredgehead type

on the depth of sediment removed or to variations in contaminant concentrations in the sediment.

Comparison of Field and DRET Results

The TSS, PCB (total, soluble, and particulate), Cu, Cd, and Pb concentrations that were measured for samples collected during the New Bedford Harbor pilot-scale test and in the DRET are compared by dredgehead type in Tables 19 to 21. In each of these tables, the field results have been separated into those obtained from the ports of the dredgehead and from the plume; the average value and the range are given for each parameter. Data from these tables were obtained from the U.S. Army Engineer Division, New England (1989) report of "New Bedford Harbor Superfund Pilot Plant Study: Evaluation of Dredging and Dredged Material Disposal." A summary of PCB concentrations (total and dissolved) at the dredgehead are shown in Table 5; individual TSS and PCB concentration values at the dredgehead are shown in Tables 2, 11, and 17; and individual TSS and PCB concentration values in the plume are shown in Tables 3, 15, and 20 of this report. The average and range of concentrations shown for the DRET were obtained in investigation of the effects of initial TSS and aeration time with settling fixed at 1 hr (Tables 5 and 7).

Table 19
Summary Comparison for Cutterhead Dredge[a]

Parameter	Dredgehead	Plume	DRET
TSS, mg/ℓ	133 (46-388)	13.4 (4-37)	110 (60-172)
Total PCB, μg/ℓ	7 (1.6-26.6)	1.133 (0.539-1.65)	10.6 (6.3-15.8)
Soluble PCB, μ/ℓ	0.6 (0.5-1.0)	0.799 (0.51-1.59)	2.0 (0.4-3.0)
Particulate PCB, μg/ℓ	22.3 (0.6-66.7)	--	10.9 (6.4-14.8)
Total Cu, μg/ℓ	457 (90-1367)	--	71 (34-105)
Total Cd, μg/ℓ	35.5 (2-127)	--	ND[b]
Total Pb, μg/ℓ	436 (31-1556)	--	14 (5-24)

[a] Data from U.S. Army Engineer Division, New England (1989).
[b] ND = Not detectable.

Table 20
Summary Comparison for Horizontal Auger Dredge[a]

Parameter	Dredgehead	Plume	DRET
TSS, mg/ℓ	1,931 (634-4037	10.8 (3-24)	110 (60-172)
Total PCB, μg/ℓ	54.9 (12.6-133.0)	1.64 (0.71-2.19)	10.6 (6.3-15.8)
Soluble PCB, μ/ℓ	10.1 (1.0-22.9)	--	2.0 (0.4-3.0)
Particulate PCB, μg/ℓ	200.3 (18.2-382)	--	10.9 (6.4-14.8)
Total Cu, μg/ℓ	2,397 (1188-3932)	--	71 (34-105)
Total Cd, μg/ℓ	99.6 (27-163)	--	ND[b]
Total Pb, μg/ℓ	1,220 (608-1707)	--	14 (5-24)

[a] Data from U.S. Army Engineer Division, New England (1989).
[b] ND = Not detectable.

The limitations of the DRET in simulating TSS of the field sample and thus the total concentration of any contaminant have been mentioned several times. Nevertheless, it is useful to compare field and DRET results to understand the extent to which agreement exists, especially in the instance where both dredgehead and plume samples are available for comparison. For the cutterhead and matchbox dredges, the TSS after 1 hr of settling in the DRET are more consistent with those obtained from the dredgehead than the plume sampling. For the horizontal auger dredge, the DRET produces much lower TSS than at dredgehead but still greater than in the plume. Thus despite the much higher TSS measured at this dredgehead than at the others, most of the

Table 21
Summary Comparison for Matchbox Dredge[a]

Parameter	Dredgehead	Plume	DRET
TSS, mg/ℓ	179 (62-582)	18.8 (8-32)	110 (60-172)
Total PCB, μg/ℓ	2.6 (0.2-4.5)	2.63 (2.13-5.13)	10.6 (6.3-15.8)
Soluble PCB, μ/ℓ	0.5 (0.3-0.6)	--	2.0 (0.4-3.0)
Particulate PCB, μg/ℓ	56.9 (6.7-205)	--	10.9 (6.4-14.8)
Total Cu, μg/ℓ	102 (--)	--	71 (34-105)
Total Cd, μg/ℓ	3 (--)	--	ND[b]
Total Pb, μg/ℓ	39 (--)	--	14 (5-24)

[a] Data from U.S. Army Engineer Division, New England (1989).
[b] ND = Not detectable.

suspended material settles very rapidly as was observed in laboratory experiments. The DRET is expected to give much lower TSS than found at the horizontal auger dredgehead where no settling time is allowed.

A comparison of the DRET and field results for soluble PCB concentrations show that the DRET overpredicts field concentrations, but values fall within an order of magnitude for the cutterhead and matchbox dredges. However, the DRET underpredicts soluble PCB by an order of magnitude for the horizontal auger dredge at the dredgehead. This could be related to the high TSS observed during dredging with a horizontal auger compared with the other two dredges.

Metals data, both from the DRET and the field, were limited. For both, soluble metals were near the detection limits. For total metals, the data in Tables 19 to 21 show that DRET results are within an order of magnitude of those for the cutterhead and matchbox dredges but two orders of magnitude lower than for the horizontal auger dredge. This should be expected given that total metals depend on TSS and that the DRET produced a TSS similar to those at the cutterhead and matchbox dredgehead but much lower than at the horizontal auger dredgehead.

Comparisons of DRET and field results for PCB (total and soluble) listed in Tables 19 to 21 are also presented graphically in Figure 14 (comparison with dredgehead field samples) and Figure 15 (comparison with plume field samples). These show again that the DRET is a reasonable predictor for the soluble PCB concentration from the cutterhead and matchbox dredges but not for the horizontal auger dredge.

Also included in Figures 14 and 15 is a comparison of the DRET with the SET, the latter being performed in conjunction with the collection of field samples by the U.S. Army Engineer Division, New England. The same data for the SET and DRET are given in both figures, the difference being only in

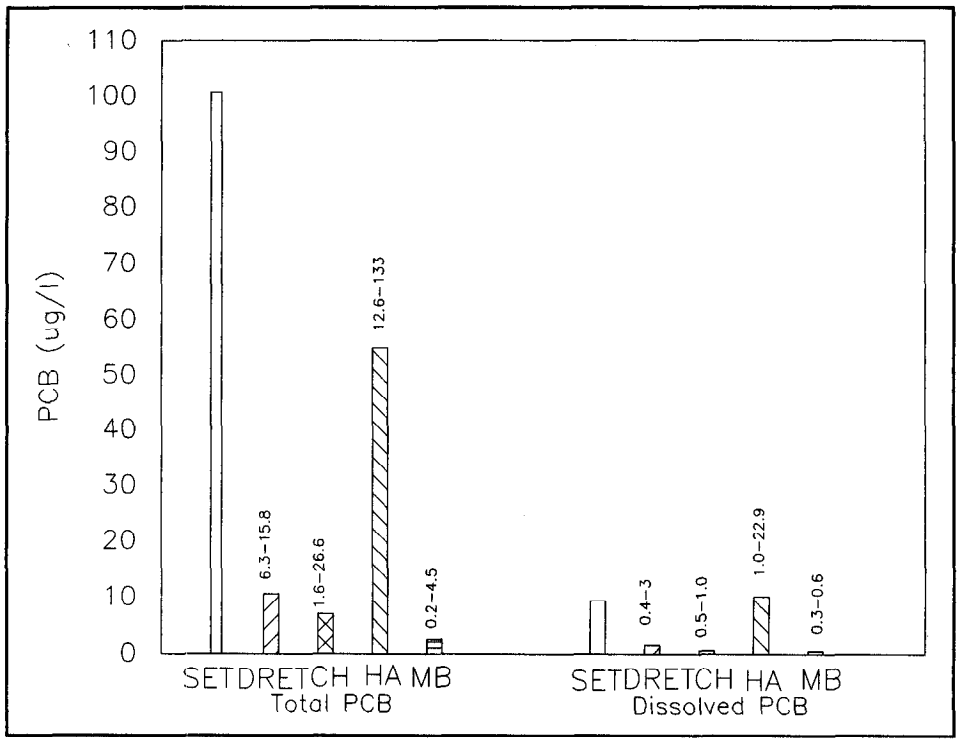

Figure 14. Comparison of PCB concentrations for field dredgehead samples (CH-cutterhead, HA-horizontal auger, MB-matchbox), DRET, and SET results

which type of field sample is being compared (dredgehead or plume). The major difference between the SET and the DRET is the initial TSS. A sediment to water volume ratio of 1:4 is used in the SET; in contrast, the maximum initial TSS in the DRET is 10 g/ℓ, which translates to a sediment to water volume ratio of about 1:226. Therefore, the initial TSS in the DRET is almost one order of magnitude lower than in the SET, and this suggests that the final TSS (1 hr of settling) and correspondingly, the total contaminant concentrations, will be lower in the DRET than in the SET. Consequently, the set overestimates the field concentrations of total and also the soluble PCB concentrations greatly for both the dredgehead and plume samples taken from the cutterhead and matchbox dredge operation. However the SET is a better predictor of the horizontal auger dredge than the DRET.

The relationship between total PCB and TSS for the DRET and field data is given in Figure 16. While all of the DRET data are presented, the range of TSS was narrowed for this comparison such that only the plume samples and some of the cutterhead dredgehead samples were included. An approximately linear relationship exists taking all three sources of data together (DRET, plume, and dredgehead). The slope of this line is on the order of 75 μg/g and represents the sorbed phase PCB concentration, or F_{ss}. The fact that both DRET and field data fit the relationship means that the DRET can describe

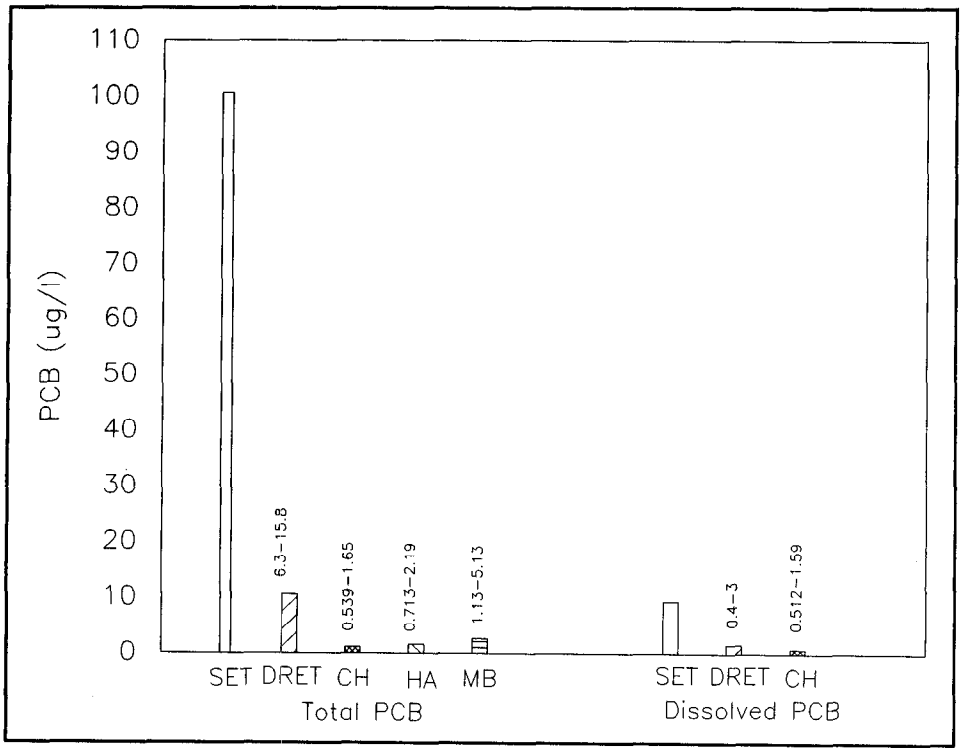

Figure 15. Comparison of PCB concentrations for field plume samples (CH-cutterhead, HA-horizontal auger, MB-matchbox), DRET, and SET results

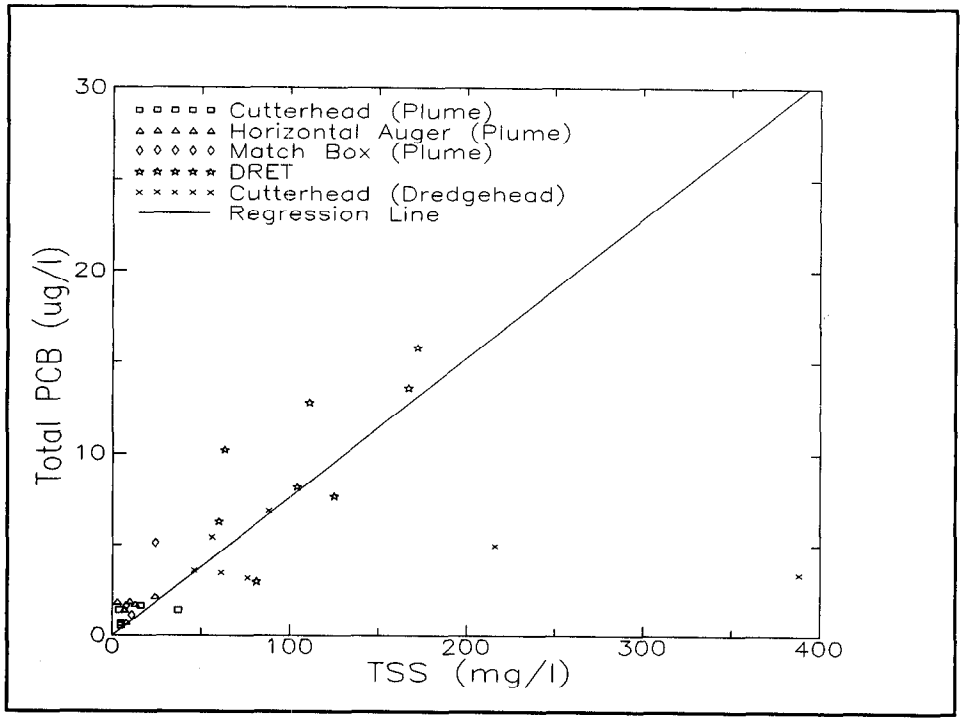

Figure 16. Relationship between total PCB and TSS concentrations

partitioning. Such information, together with an estimate of TSS (e.g., from field information or a settling column analysis), can be used to obtain the expected total PCB concentration.

5 Investigation of Particle Size Characteristics

Changes in Particle Size Characteristics During Settling in the DRET

The objective of this section is to provide detail on how the particle size characteristics change during quiescent settling in the DRET. Of particular interest is the time of settling beyond which no further significant change in particle size may be expected. This may have implications if the sorbed PCB (or F_{ss}) concentration is a function of particle size. The PSD data provide good detail on the decrease in particle size with settling time (as is shown in Figure 17). Both the total volume of particles (i.e., mass of particles) and the average diameter of particles become smaller with settling time. These experiments were performed with an initial solids concentration of 0.5 g/ℓ and were aerated for 1 hr. The distribution of particle diameter with particle mass was examined after each settling time. As shown in Figure 18, each set of data was fit by a log-normal distribution rather well—the steeper the slope, the wider the distribution of particle diameters. The median particle diameter (d_{50}) and the GSD of particle sizes are given in Table 22 for each settling time, for experiments conducted with an initial solid concentrations of 0.5 g/ℓ and an aeration time of 1 hr.

The largest change in PSD occurs during the first 30 min with the median size decreasing from 10.7 to 6.5 μm. It is not surprising that little change in d_{50} was noted after several hours given that the particles are very small and their discrete settling velocities (by Stoke's Law) would be very low. Palermo and Thackston (1988b) also found by grain size analysis that about 90 percent of the dredged sediment material has a particle diameter less than 10 μm.

Effects of initial TSS (TSS_i) concentration and aeration time (t_a) on PSD of particles remaining after 1 hr of settling are given in Figures 19 and 20, respectively. Qualitatively, the greater the TSS_i concentration, the greater the mass of particles remaining; however, the effect on median particle diameter is not clearly seen. The effect of aeration time on both final TSS and median particle diameter is also unclear. The particle diameter-mass relationship followed a log-normal distribution in all instances. The resulting distributions

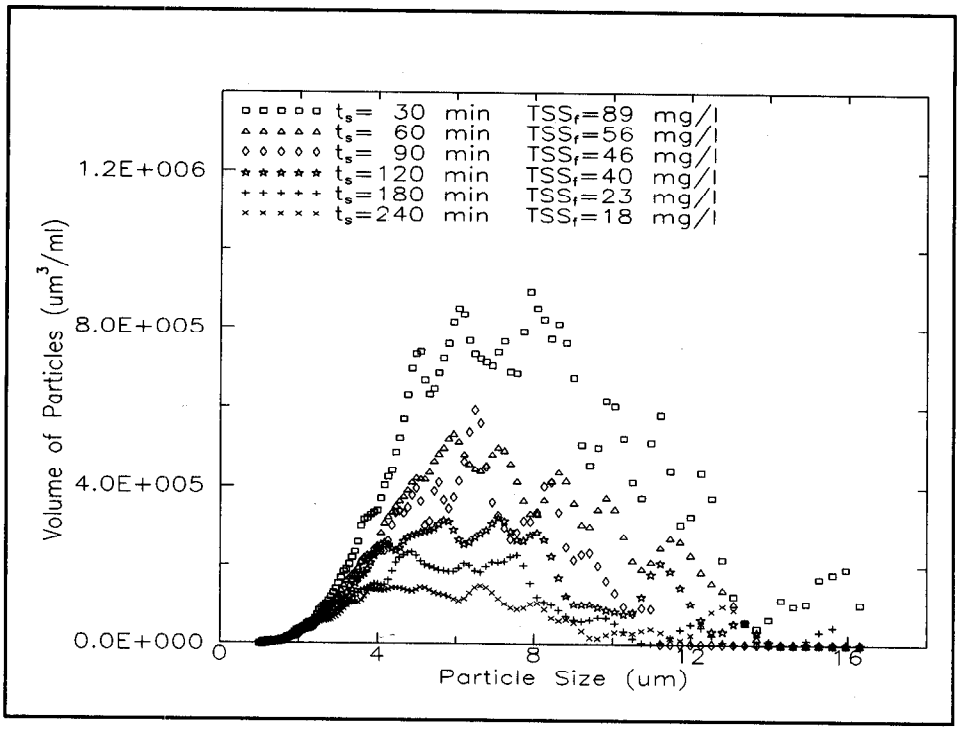

Figure 17. Volume PSD as a function of settling time

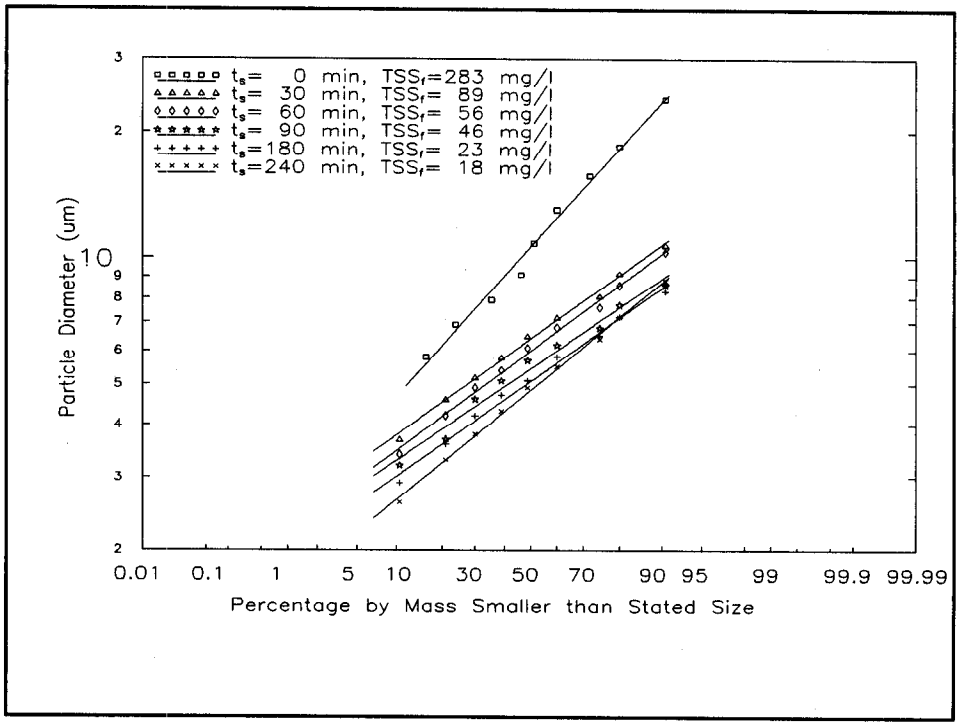

Figure 18. Log-normal PSD as a function of settling time

Table 22
Particle Size Characteristics as a Function of Settling Time; Initial Solids Concentration = 0.5 g/ℓ; Aeration Time = 1 Hr

Settling Time min	d_{50} μm	Geometric Standard Deviation
0	10.7	1.8
30	6.5	1.5
60	6.0	1.5
90	5.7	1.5
180	5.1	1.5
240	4.9	1.6

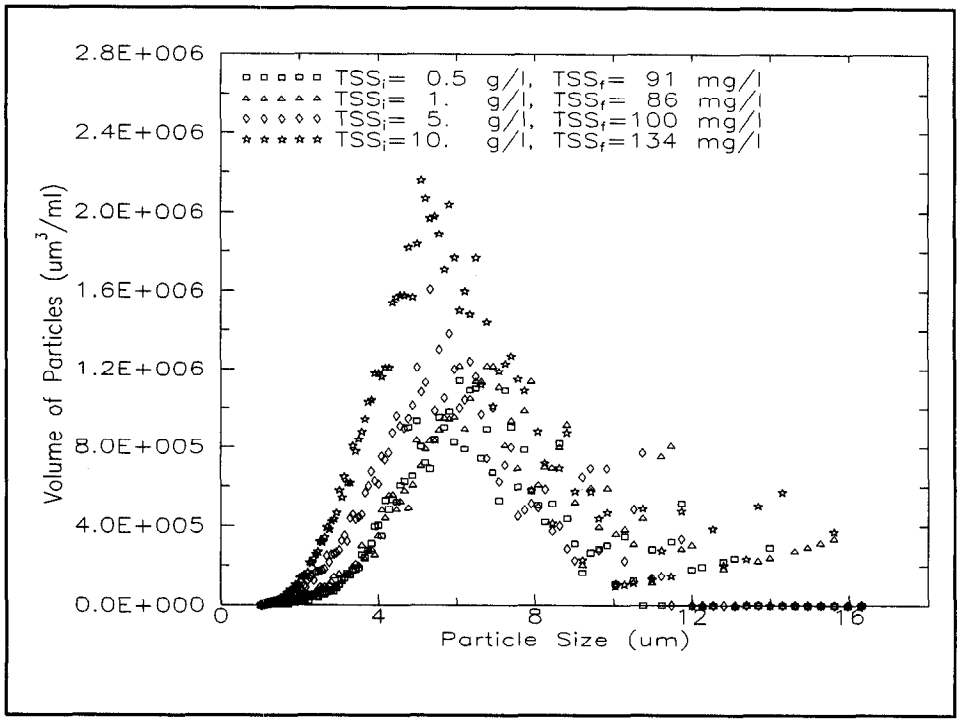

Figure 19. Volume PSD as function of TSS_i concentration

were very similar for all the data sets in Figures 19 and 20. An example from each data set where TSS_i and aeration time were varied is given in Figure 21. Neither parameter had a strong effect on the distributions. This is also apparent from the similarities of d_{50} and GSD given in Tables 23 and 24 that were obtained from log-normal distributions of each experiment.

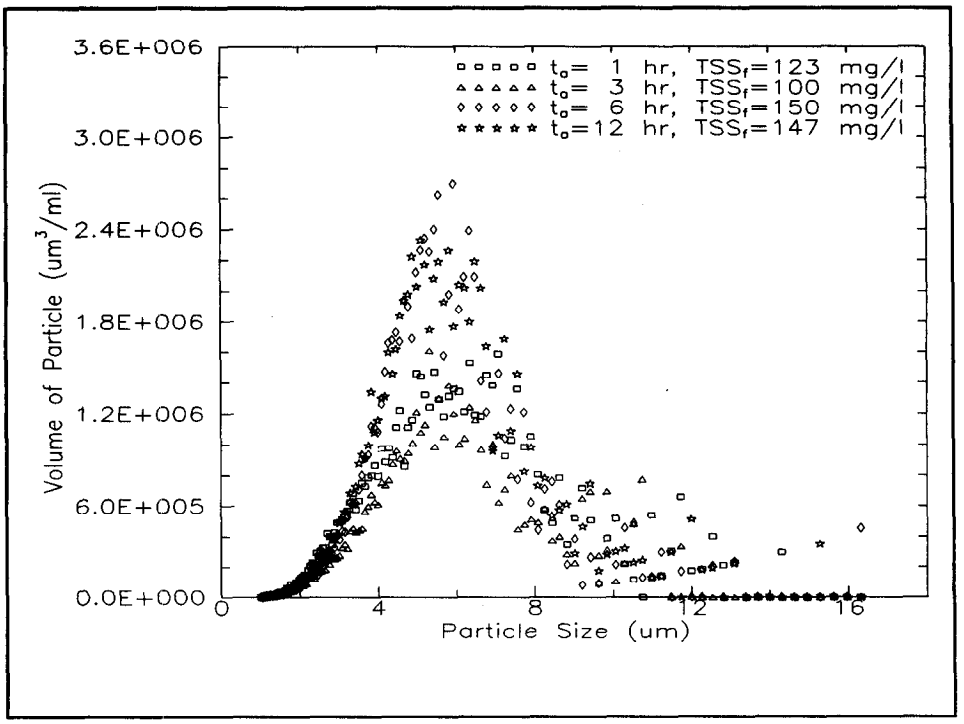

Figure 20. Volume PSD as a function of aeration time

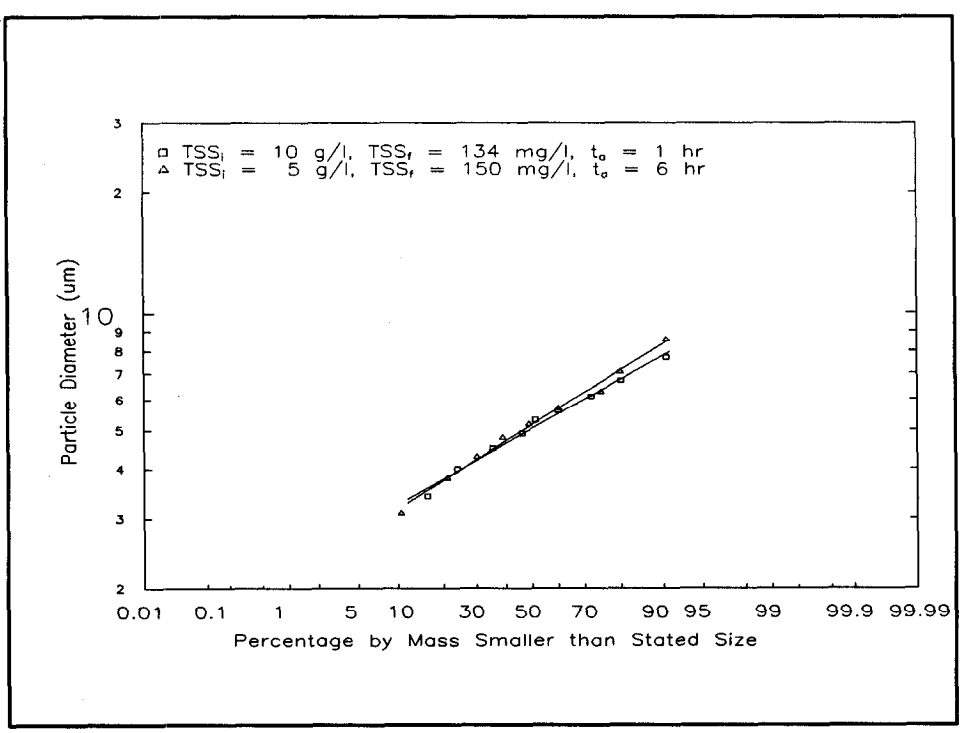

Figure 21. Log-normal PSD as a function of aeration and settling times

Table 23
Particle Size Characteristics as a Function of Initial Suspended Solids Concentration

TSS_i Concentration g/ℓ	d_{50} μm	Geometric Standard Deviation
0.5	5.9	1.44
	5.8	1.47
1	6.5	1.41
	5.9	1.44
5	5.3	1.48
	5.5	1.48
10	5.2	1.49
	5.1	1.51

Table 24
Particle Size Characteristics as a Function of Aeration Time

Aeration Time hr	d_{50} μm	Geometric Standard Deviation
1	5.4	1.56
	5.6	1.58
3	5.3	1.48
	5.4	1.48
6	5.3	1.38
	5.3	1.42
12	5.3	1.42
	5.6	1.41

Another way to interpret PSD data is with a power law expression:

$$n(d_p) = Ad_p^{-\beta} \tag{4}$$

or in linear form:

$$\log n(d_p) = \log A - \beta \log d_p \tag{5}$$

where

$n(d_p)$ = the particle size function

A = coefficient related to concentration of particles

β = constant that characterizes particle size function

A plot of the cumulative particle number concentration, N, of size less than or equal to d_p against d_p is used to calculate the slope at any d_p. This slope ($\Delta N/\Delta d_p$) is $n(d_p)$. Such analyses have been conducted in aerosol and aquasol science fields to characterize particles according to their β values. The derivation of Equation 4 was given by Lawler, O'melia, and Tobiason (1980). It shows that when $\Delta = 1$, there are an equal number of particles in each logarithmic size interval. Even distributions of surface area and of volume likewise correspond to $\Delta = 3$ and $\Delta = 4$, respectively. When $\Delta = 4$, both larger fractions of the number and surface area of particles are found in the smaller sizes. Moreover, a mechanistic interpretation is available for Δ values that accounts for the predominant mode of particle collisions affecting the distribution. For small particles, a $\Delta = 2.5$ is consistent with theory for flocculation of small particles by Brownian motion, whereas for larger particles a $\Delta = 4.75$ is consistent with flocculation by differential settling (Stumm and Morgan 1981).

The data obtained by PSD analysis for settling times between 0 and 6 hr (presented as Figure 23) were fitted to the linearized form of the power law function, Equation 5. As indicated in Figure 22, the plot of log $n(d_p)$ versus log d_p was linear down to d_p of about 3 to 4 μm, whereas the log-normal distribution of d_p with mass of particles was applicable to the whole range (Figures 19 and 22). Only the data in the linear portion of Figure 23 were used to calculate the slope, β. Values of β from this elutriate test (TSS_i of 0.5 g/ℓ) as well as another at the maximum TSS_i of 10 g/ℓ are listed in Table 25 for each settling time. Values for β in these tests range from 3.3 to 5.1. As a frame of reference, particulates found in ocean systems have β values in the range of 4 to 5 (Lal 1977). Based on the theoretical considerations discussed above, a high β value indicates that the smaller particles account for most of the number of particles and surface area, and further, that differential settling is an important mechanism for particle growth (Stumm and Morgan 1981).

Settling Characteristics of Particles

The settling characteristics of this sediment material were analyzed in a classic settling column experiment (Camp 1946). The height of the settling column was 40 cm, and samples were withdrawn at 20 cm. Particles removed by sedimentation in time t have an average settling velocity, v_s, for this experimental system of:

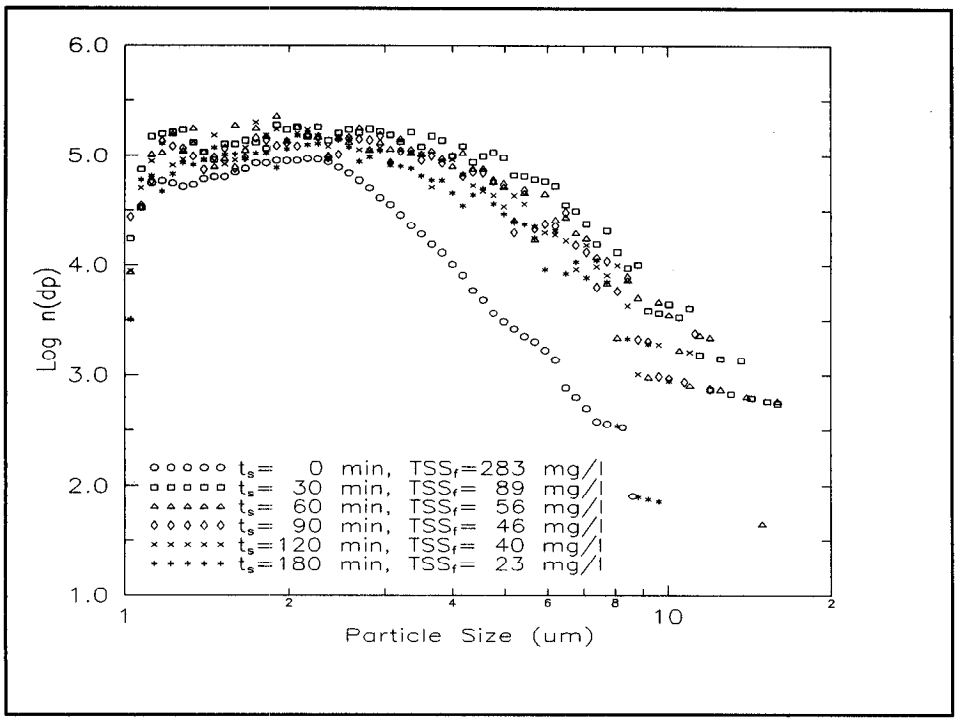

Figure 22. Log-normal PSD as a function of settling time

Table 25
β Values From Power-Law Regression

TSS_i g/ℓ	Settling Time, min					
	0	30	60	90	120	180
0.5	5.0	3.3	3.4	3.5	3.5	3.4
	(0.980)[a]	(0.895)	(0.896)	(0.915)	(0.938)	(0.907)
10.0	4.0	4.4	4.6	5.0	5.1	4.5
	(0.970)	(0.965)	(0.966)	(0.959)	(0.957)	(0.969)

[a] r_2.

$$v_s = \frac{20}{t} \text{ cm/min} \tag{6}$$

The experiments were conducted using a TSS_i concentration of either 0.5 or 10 g/ℓ and aerating for 1 hr before settling. A distribution of settling velocities for the sediment sample was obtained by plotting the fraction of solids remaining in the settling column at time, t, against the corresponding v_s. The same experiment was repeated in distilled water instead of artificial

seawater to determine the extent to which flocculent settling was enhanced by double layer compression at high ionic strength.

For comparative purposes, the distribution of settling velocities was also calculated from the PSD analysis of the TSS_i assuming that discrete settling took place and therefore Stoke's law applied:

$$v_s = \frac{(p_s - p_w)gd_p^2}{18\mu} \tag{7}$$

where

p_s = density of solids

p_w = density of water

g = acceleration of gravity

d_p = particle diameter

μ = kinematic viscosity

The PSD data provide the information needed to determine the fraction of particles having diameter, d_p. Measurements of p_s were made and reported earlier in Table 2. Thus a theoretical distribution of settling velocities was determined that assumes discrete particle settling, i.e., no change in particle size during sedimentation caused by flocculation, e.g., by differential settling.

Flocculation by double layer compression can explain the increase in particle removal rate in seawater compared with distilled water as is shown in Figures 23 and 24. In these settling tests, aeration time was fixed at 1 hr, and two different TSS_i concentrations (0.5 and 10 g/ℓ) were used. Seawater, with its high ionic strength, serves to increase double layer compression greatly (Weber 1972). Further evidence of flocculent settling in seawater is provided in Figure 25. Here, the theoretical distribution of settling velocities based on Stoke's law and PSD analysis is given for each of the two TSS_i concentrations and is compared with the actual distributions obtained in sea water experiments. The Stoke's law calculations for nonflocculent, or discrete settling, show that the particles are much slower settling than observed in seawater. For example, Stoke's law predicts that 70 percent of the particles have a settling velocity equal to or less than about 1.7 cm/min, whereas in a 0.5 g/ℓ suspension in seawater only about 40 percent of the particles had this settling velocity or less. Moreover, increasing the TSS_i concentration to 10 g/ℓ further decreases the percentage of particles with this settling velocity or less. Higher

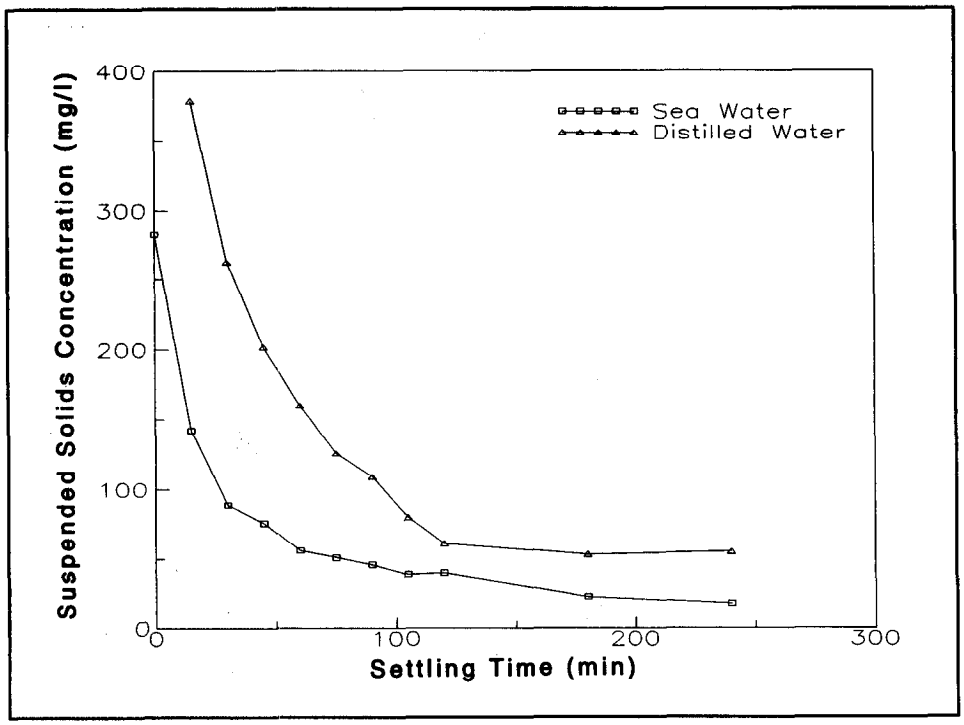

Figure 23. Settling behavior for TSS_i concentrations of 0.5 g/ℓ

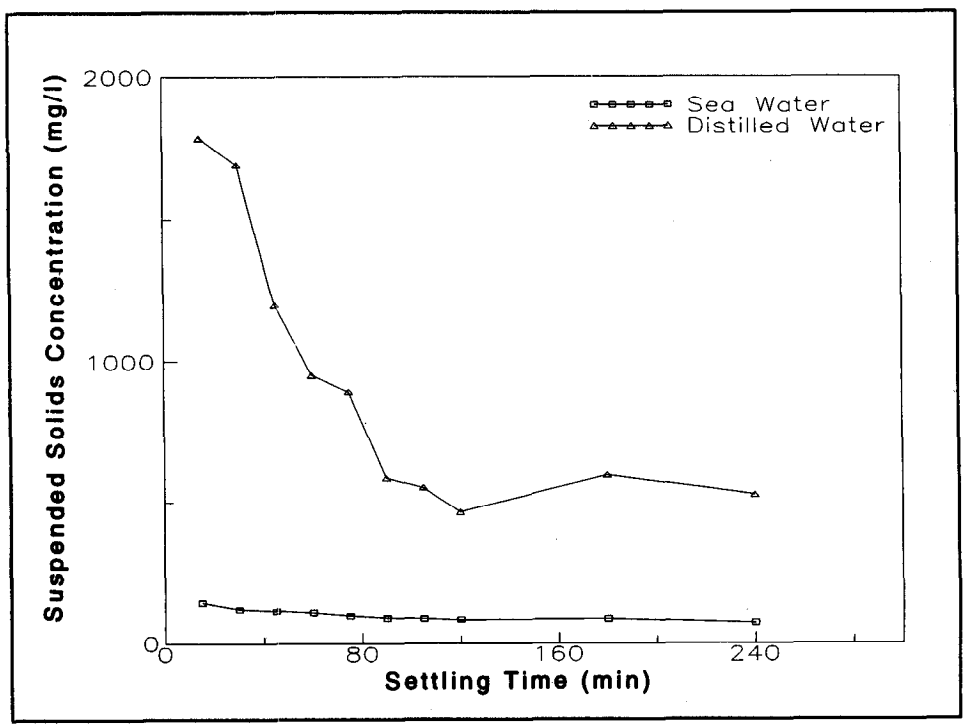

Figure 24. Settling behavior for TSS_i concentrations of 10 g/ℓ

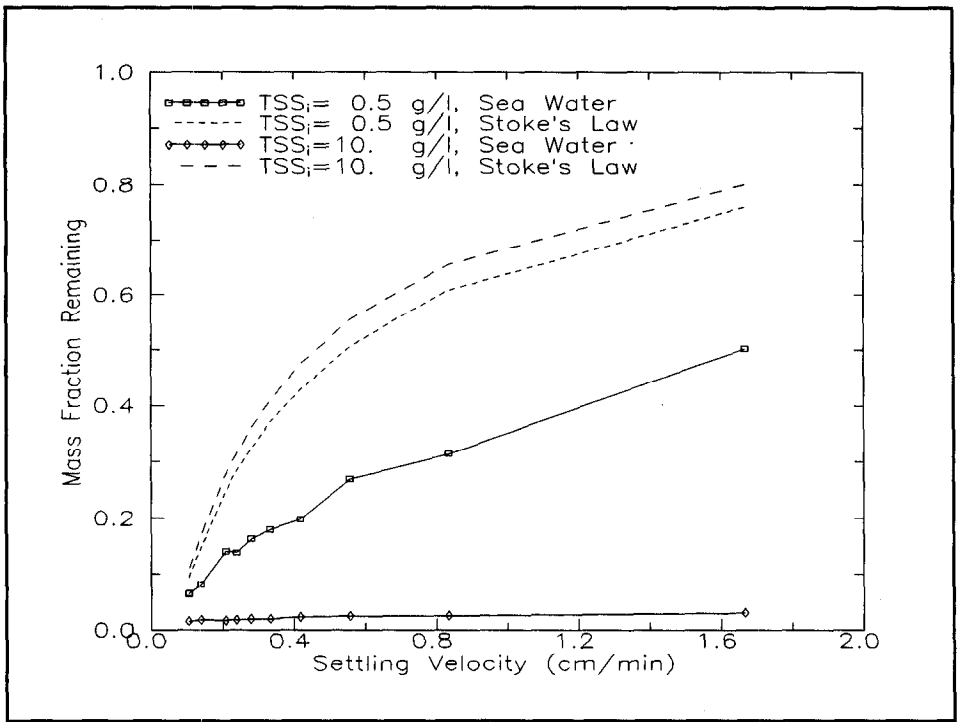

Figure 25. Comparison of observed settling characteristics and Stoke's law predictions

TSS_i concentrations promote a greater number of particle collisions that leads to greater particle growth and increased settling velocities.

Palermo and Thackston (1988a) investigated the settling properties of sediment particles in a CDF. In settling-column studies they observed flocculent settling above the zone-settling interface. Palermo and Thackston (1988a) used TSS_i concentrations of 55 to 155 g/ℓ, whereas a maximum of 10 g/ℓ was used in these experiments. Thus it is not surprising that zone settling was never observed in experiments performed at the lower TSS_i concentrations used in this work and that flocculent settling predominated.

6 Application of Equilibrium Partitioning Model

Development of the Model

A simple equilibrium partitioning model was used to predict the concentration of soluble PCB in the DRET. A mass balance for soluble and sorbed PCB in the water column at equilibrium from addition of sediment with sorbed PCB is:

$$M_s q_i = V_l C_e + M_s K_p C_e \tag{8}$$

where

M_s = mass of sediment added in the DRET, g

q_i = initial mass of sorbed PCB per mass of sediment, or mass fraction of PCB, μg/g

V_l = volume of solution, ml

C_e = equilibrium concentration of soluble PCB, μg/ml of solution

K_p = partition coefficient, ml/g

K_p is calculated by:

$$K_p = f_{oc} K_{oc} \tag{9}$$

where

f_{oc} = fraction of organic carbon in sediment

K_{oc} = organic carbon normalized partition coefficient, ml/g

Karickhoff, Brown, and Scott (1979) proposed a correlation to estimate the value of K_{oc} for neutral, nonpolar, hydrophobic solutes:

$$logK_{oc} = logK_{ow} - 0.21 \tag{10}$$

where K_{ow} is the octanol-water partition coefficient of the solute.

Solving for C_e in Equation 8, the predicted soluble PCB concentration from the DRET is:

$$C_e = \frac{M_s q_i}{V_l + M_s K_p} \tag{11}$$

Equation 11 can also be written as

$$C_e = \frac{q_i}{V_l/M_s + K_p} \tag{12}$$

For strongly sorbing contaminants (large K_{oc}), high organic carbon sediment (large f_{oc}), and solids concentrations of the range used in the DRET (M_s/V_l), $K_p \gg V_l/M_s$. This suggests that the equilibrium fluid phase concentration (C_e) is a linear function of the initial PCB concentration on the solid phase (q_i), and that C_e is relatively insensitive to the solids concentrations used in the DRET.

The predicted total PCB concentration (unfiltered PCB) is represented by:

$$C_t = (1 + TSS_f K_p)C_e \tag{13}$$

where TSS_f = total suspended solids concentration, g/ml.

To use Equations 12 and 13, several parameters must be estimated. The sediment PCB concentration (167 μg/g) is from the liquid-solid extraction. If the results of Soxhlet extractions were used instead of liquid-liquid extractions, the sediment PCB concentrations for use in Equation 12 would have been 234 μg/g. This would give higher predicted values of C_e in Equation 12. As mentioned earlier, the liquid-solid extraction result was used to be consistent with the analytical method used for analysis of the DRET data. The f_{oc}, as measured by a total organic carbon (TOC) analyzer, was found to be 0.15. The analyzer oxidizes the TOC to CO_2 with sodium persulfate and analyzes the CO_2 with an infrared detector (APHA 1981).

The PCB composition of the mixture used to select K_{ow} and thus K_{oc} in Equation 10 and K_p in Equation 9 was 1:1 Aroclor 1242 and 1254. The mass

Table 26
Composition of PCB Mixture and K_{ow} Values

Homologous Group	% Composition[a]		Log K_{ow}[b]
	1242	1254	
Monochlorobiphenyl	1.0	0.05	4.56
Dichlorobiphenyl	16.0	0.1	5.02
Trichlorobiphenyl	43.0	0.5	5.64
Tetrachlorobiphenyl	27.0	10.0	6.67
Pentachlorobiphenyl	9.0	70.0	6.38
Hexachlorobiphenyl	4.0	14.0	7.12
Heptachlorobiphenyl	--	5.35	7.93

[a] Data from Onuska, Kominar, and Terry (1983).
[b] Data from Erickson (1986) for lowest value in homologous group.

percentage of each PCB homolog of standard Aroclor 1242 and 1254 mixture is given in Table 26 (Onuska, Kominar, and Terry 1983), along with the lowest K_{ow} values within each homologous group (Erickson 1986). Since the mass percentage and K_{ow} values of every congener in standard Aroclor 1242 and 1254 were not available, the data in Table 26 were used to predict soluble PCB concentrations. This approach will give the highest predicted soluble PCB concentration (least sorption to sediment).

The mass of solids to mass of solution (M_s/V_l) is known as the solids concentration for batch reactor experiments. An inverse relationship between the solids concentration and the measured partition coefficient of hydrophobic pollutants such as DDT and Heptachlor has been observed (O'Connor and Connolly 1980). The dependence of partition coefficient on TSS concentration in aqueous suspensions has been termed the "solids effect" (Voice and Weber 1985). However, since the range of TSS in the DRET was similar to that of field samples, the solids effect was not considered. The assumption of equilibrium might be conservative because it has been reported that PCB congeners containing up to four chlorines approach equilibrium within 6 weeks and congeners with greater than 6 chlorines may require months or years to reach equilibrium (Coates and Elzerman 1986). This assumption would also serve to maximize the predicted PCB concentrations.

The predicted soluble and total PCB concentrations are shown in Table 27. The predicted amounts of soluble PCB in the filtered solution were all about 3 μg/ℓ regardless of the amount of solids added in the DRET (Table 27). PCB are so strongly sorbed to particles that very little is released to the water at equilibrium. Thus for calculation purposes, the initial sorbed PCB concentration (sediment PCB) is about equal to the final sorbed PCB concentration.

Table 27
Equilibrium Model Predictions of PCB Concentrations

TSS_i, g/ℓ	TSS_f, mg/ℓ	C_e, µg/ℓ	C_t, µg/ℓ	q_e, µg/g
1-hr Aeration Time, 1-hr Settling Time				
1.0	63	2.8	11	167
5.0	172	2.9	29	167
5.0	167	2.9	28	167
10.0	81	3.0	14	167
6-hr Aeration Time, 1-hr Settling Time				
1.0	60	2.8	10	167
4.7	104	2.9	18	167
5.0	111	2.9	20	167
10.0	125	3.0	21	167

The total predicted PCB concentrations in Table 27 ranged from 10 to 29 µg/ℓ. These predicted concentrations were proportional to TSS_f because of the dominant effect of TSS on sorbed PCB concentration. In this procedure, the sorbed PCB distribution with particle size was assumed to be mass dependent. This will be discussed in a section that follows.

Comparisons of predicted and experimental values of soluble and total PCB are given in Figures 26 and 27, respectively. The predictions were typically higher than or equal to the experimental values. Overprediction of soluble PCB concentrations may be caused by either assuming a q_i that is too high or by assuming a K_p that is too low. These figures show that the total PCB concentration is proportional to the TSS_f concentration, but the soluble PCB concentration is nearly independent of the TSS_f concentration. This makes sense considering most of the PCB are particle associated. However, contaminants that are not nearly as strongly sorbed will desorb to a greater extent and thus be associated with the soluble rather than the suspended fraction.

Usefulness of the Model

The equilibrium partitioning model was used here to predict fairly well the soluble PCB concentration obtained in the DRET. It was also able to explain the total PCB concentration if the residual TSS concentration was known after settling. The model represents, therefore, an alternative to the DRET to predict both soluble and total concentrations of PCB or other contaminants provided the following information is available: sorbed contaminant concentration on the sediment (q_i), fraction of organic carbon in the sediment (f_{oc}); TSS

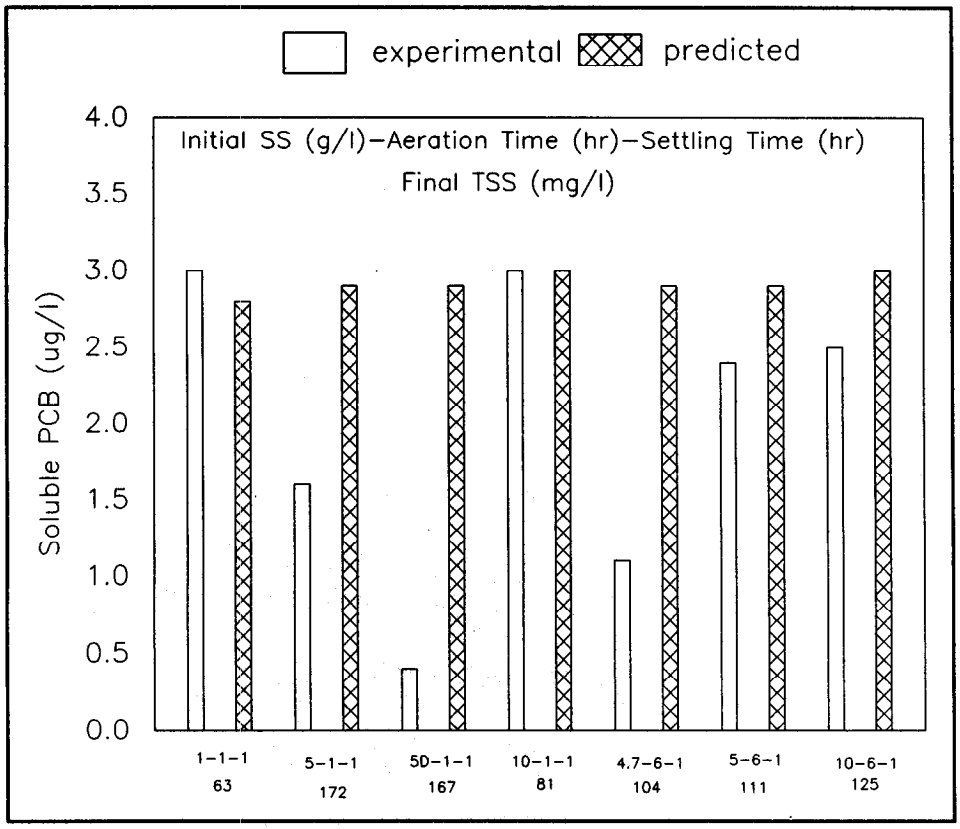

Figure 26. Comparison of measured and predicted soluble PCB concentrations

concentration initially resuspended by the dredge; and TSS remaining in the water column after particle settling.

The information needed is not extensive nor time-consuming to obtain. Experimental values of q_i and f_{oc} can be obtained relatively quickly as part of the sediment characterization procedure. Resuspension of TSS must be estimated from available data being gathered by the U.S. Army Corps of Engineers for various dredgeheads. TSS remaining after settling can be estimated from a standard settling column analysis (typically an 8-in diam column), or alternatively, particle size analysis of the sediment. In the latter method, the fraction of particles expected to remain in suspension at the field site can be estimated; based on this research, only particles of diameter less than about 10 µm remain in suspension after 1 hr of quiescent settling.

While the focus of this research was PCB release, the release of other nonpolar organic contaminants could also be predicted provided that data were available on their partition coefficients. The database for nonpolar organic compounds has been greatly expanded (Chapman 1989; Reuber et al. 1987).

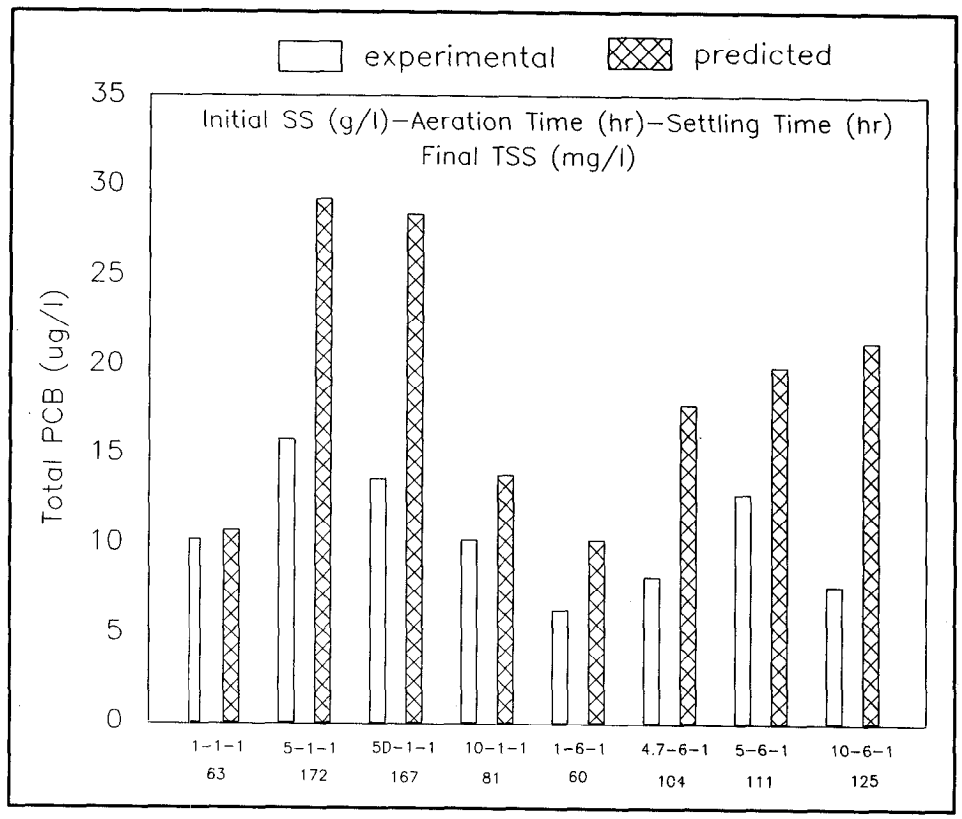

Figure 27. Comparison of measured and expected total PCB concentrations

If a DRET is still considered necessary, the equilibrium partitioning model could at the very least serve as a screening tool to estimate the release of contaminants expected for a range of DRET conditions. This could save time and expense, especially if the analytical procedures are as involved as those for PCB.

7 Conclusions and Recommendations

Conclusions

An evaluation of the DRET protocol suggests using 10 g/ℓ as the initial TSS concentration. The release of soluble PCB did not depend upon the choice of initial TSS (1 versus 10 g/ℓ). This can be explained by the strong sorption of PCB to sediment. For other less strongly sorbed contaminants, the initial TSS concentration may be more important. A value of 10 g/ℓ is well above the TSS observed in the pilot study at New Bedford Harbor and thus should give a conservative prediction of soluble contaminants, at least for the cutterhead and matchbox type of dredges.

An aeration time of 1 hr and a settling time of 1 hr should be used in the DRET. Increasing the aeration time produced no further release of soluble PCB. This was also shown in separate batch shaker experiments. A settling time of 1 hr is longer than needed to remove from suspension all but the particles less than 10 μm in diameter. Moreover, the batch shaker experiment confirmed that little further release of soluble PCB occurred by extending the time available for desorption to 6 hr.

The DRET overpredicted the soluble PCB released from cutterhead and matchbox dredgeheads in the New Bedford Harbor pilot study, although all predictions were well within an order of magnitude. However, the DRET underpredicted release of soluble PCB from the horizontal auger dredge by an order of magnitude. Notably, this dredgehead also produced TSS an order of magnitude higher than either the cutterhead or matchbox. Nevertheless, the TSS were still less than one-half the initial TSS recommended in the DRET.

A sorbed phase concentration of PCB, or F_{ss} value, on the order of 75 to 100 μg/g was found in the DRET and in the field samples (both at the dredgehead and in the plume). This is considerably lower than the sorbed PCB measured independently on the predredged sediment sample (167 μg/g), but, nonetheless, the DRET simulated the field results rather well. DiGiano, Miller, and Yoon (1993) also summarized the DRET PCB release predictions discussed in this report.

Only limited data were available for metals (Cu, Cd, and Pb) in the DRET and the pilot study (dredgehead samples only). The DRET was low in prediction of total metals concentrations but within an order of magnitude for the cutterhead and matchbox dredges; however, the DRET was two orders of magnitude too low for the horizontal auger dredge. Failure of the DRET to predict total metals for the horizontal auger dredge is in part due to the TSS concentration at this dredgehead being much higher than the TSS concentration after settling in the DRET.

A simple particle sizing experiment ($d > 10$ μm and $d < 10$ μm) showed that on a mass basis, sorbed PCB concentrations were independent of particle size. Thus, an equal mass concentration of fine and coarse particles for the sediment sample analyzed should be expected to produce a similar concentration of soluble PCB.

While the main objective of the DRET is to gather data on soluble PCB and the partition coefficient (K_p), it also provides some information on particle size distribution and settling characteristics. Particles remaining after just 30 min of settling are less than 20 μm in diameter. Notwithstanding the recognized deficiencies of a 4-ℓ graduated cylinder in simulating settling rates of the field situation, the experiments showed that very little settling can be expected beyond 1 hr of quiescent conditions and further that the particles remaining were smaller than 10 μm.

The flocculent nature of particle settling observed above a region of zone settling in a CDF (Palermo and Thackston 1988a) was also found for simulation of the solids concentration at the point of dredging. These experiments differed greatly in the initial TSS (55 g/ℓ minimum for the CDF versus 10 g/ℓ maximum for the point of dredging). Far less efficient settling and thus higher total PCB concentrations may be expected in freshwater dredging operations where destabilization of particles is less effective.

An equilibrium partitioning model was shown to predict fairly well the soluble PCB of the DRET. The model (Equation 12) shows that strongly sorbed contaminants such as PCB will produce soluble PCB concentrations in direct proportion to the sorbed concentration but nearly independent of the concentration of resuspended solids. In this research, the soluble PCB concentration was only about 3 μg/ℓ regardless of whether 1 or 10 g/ℓ of solids were added in the DRET. However, the sorbed PCB concentration used in the DRET was low (167 μg/g) compared with other areas of New Bedford Harbor; thus higher soluble PCB concentrations may be expected in other areas.

The equilibrium partitioning model should be able to predict the soluble PCB at the point of dredging if the sorbed PCB concentration and fraction of organic carbon on the sediment and the concentration of resuspended solids are known. This is, therefore, an alternative to the DRET. In addition, the total PCB can be predicted if the residual TSS are known (Equation 13). This prediction approach is similar to the use of F_{ss} (Equation 2), the main

difference being that the concentration of sorbed PCB is not obtained in the DRET but is instead calculated by K_p, the partition coefficient (Equation 9).

Recommendations

If the horizontal auger dredge is to be used, more work is needed to develop a DRET that is a conservative predictor of contaminant release. This dredgehead produced much higher TSS concentrations than either the cutterhead or the matchbox dredges and seemed to have produced more contaminant release despite the weak dependency of soluble contaminant concentrations on TSS concentrations as discussed.

A simple equilibrium partitioning model that predicts soluble PCB is based on very conservative assumptions (equilibrium state). Therefore, a non-equilibrium partitioning relationship needs to be developed. The equilibrium partitioning model is also based on uniform concentration of contaminants in the sediment. However, the contaminant concentrations in the field may vary with location and depth of sediment; these variations need to be included in modeling.

The DRET test methods presented in this report are based on only one set of laboratory and field data from New Bedford Harbor, a seawater system. Additional comparisons of field releases at the point of dredging with DRET test predictions should be conducted at several sites with varying site conditions.

Even though much research has been done on dredging and disposal operations, comparison with previous research was difficult since the analysis method and quantification of contaminants are not standardized nor specified in detail. Standardization of analysis methods and detailed descriptions of methods should be included in future documents in order to facilitate comparison of results.

References

Allen, T. (1981). "Particle size, shape and distribution." *Particle size measurement*. 3rd ed., Chapman and Hall London, New York.

American Public Health Association (APHA). (1981). *Standard methods for examination of water and wastewater*. 15th ed., American Water Works Association, Water Pollution Control Federation, APHA, Washington, DC.

Burkhard, L. P. (1987). "Determination of polychlorinated biphenyls using multiple regression with outlier detection and elimination," *Anal Chem* 59(8), 1187-1190.

Camp, T. R. (1946). "Sedimentation and the design of settling tanks," *Transactions of American Society of Civil Engineering* 111, 895-936.

Chapman, P. M. (1989). "Current approaches to developing sediment quality criteria," *Environmental Toxicology and Chemistry* 8, 589-599.

Coates, J. T., and Elzerman, A. W. (1986). "Desorption kinetics for selected PCB congeners from river sediments," *Journal of Contaminant Hydrology* 1, 191-210.

Day, P. R. (1965). "Physical and mineralogical properties including statistics of measurement and sampling." *Method of soil analysis*. C. A. Black, ed., American Society of Agronomy, Inc, Publisher, Madison, WI.

DiGiano, F. A., Miller, C. T., and Yoon, J. (1993). "Predicting release of PCB's at point of dredging," *Journal of Environmental Engineering*, ASCE, 119(4), 72-89.

Eller, M. P. (1984). "NIOSH manual of analytical methods," Vol 2., 3rd ed., National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, Cincinnati, OH.

Erickson, M. D. (1986). Analytical chemistry of PCB. Butterworth Publishers, Boston, MA.

Havis, R. N. (1987). "Sediment resuspension by selected dredges," Environmental Effects of Dredging Technical Notes, EEDP-09-2, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

_____. (1988). "A preliminary evaluation of contaminant dredging at the point of dredging," Environmental Effects of Dredging Technical Notes, EEDP-09-3, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Hayes, D. F. (1987). "Guide to selecting a dredge for minimizing resuspension of sediment," Environmental Effects of Dredging Technical Notes, EEDP-09-1, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Jones, R. A., and Lee, G. F. (1978). "Evaluation of the elutriate test as a method of predicting contaminant release during open-water disposal of dredged sediments and environmental impact of open-water dredged material disposal," Technical Report D-78-45, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Karickhoff, S. W., Brown, D. S., and Scott, T. A. (1979). "Sorption of hydrophobic pollutants in sediment suspensions," *Water Research* 13, 241-248.

Lal, D. (1977). "The oceanic microcosm of particles," *Science* 198, 997-1009.

Lawler D. F., O'melia C. R., and Tobiason, J. E. (1980). "Use of particle size integral water treatment plant design from particle size to plant performance," *ACS Advances in Chemistry Series* 189, 353-388.

Lee, G. F., Richardson, J. S., Piwoni, M. D., Homer D. H., Lopez, J. M., Saleh, F., and Mariani, G. M. (1975). "Research study for the development of dredged material disposal criteria," Contract Report D-75-4, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Ludwig, D. D., Sherrard, J. H., and Amende, R. A. (1989). "Evaluation of the standard elutriate test as an estimator of contaminant release at dredging sites," *Journal Water Pollution Control Federation* 61, 1666-1672.

O'Connor, D. J., and Connolly, J. P. (1980). "The effect of concentration of desorbing solids on the partition coefficient," *Water Research* 14, 1517-1523.

Onuska, F. I., Kominar, R. J., and Terry, K. A. (1983). "Identification and determination of polychlorinated biphenyl by high resolution gas chromatography," *Journal Chromatography* 279, 111-118.

Palermo, M. R. (1986). "Development of a modified elutriate test for estimating the quality of effluent from confined dredged material disposal areas," Technical Report D-86-4, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Palermo, M. R., and Thackston, E. L. (1988a). "Flocculent settling above zone settling interface," *Journal Environmental Engineering*, ASCE, 114(4), 770-783.

_____. (1988b). "Test for dredged material effluent quality," *Journal Environmental Engineering*, ASCE, 114(6), 1295-1309.

_____. (1988c). "Verification of predictions of dredged material effluent quality," *Journal Environmental Engineering*, ASCE, 114(6), 1310-1330.

Reuber, B., Mackay, D., Paterson, S., and Stokes, P. (1987). "A discussion of chemical equilibria and transport at the sediment-water interface," *Environmental Toxicology and Chemistry* 6, 731-739.

Schlemmer G., and Welz, B. (1986). "Palladium and magnesium nitrates, a more universal modifier for graphite furnace atomic absorption spectroscopy," *Spectrochimia Acta*. 41B(11), 1157-1165.

Slavin W., Carnrick, G. R., and Manning D. C. (1982). "Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace," *Analytical Chemistry* 54, 621-624.

Stumm, W., and Morgan, J. J. (1981). *Aquatic chemistry: Introduction emphasizing in natural waters*. 2nd ed., Wiley-Interscience Publication, New York.

U.S. Army Engineer Division, New England. (1989). "New Bedford Harbor Superfund Pilot Plant Study: Evaluation of dredging and dredged material disposal," Interim Report, Waltham, MA.

Voice, T. C., and Weber, W. J., Jr. (1985). "Sorbent concentration in liquid/solid partitioning," *Environmental Science and Technology* 19, 789-796.

Weaver, G. (1983). "PCB contamination in and around New Bedford, Massachusetts," *Environmental Science and Technology* 18(1), 20A-27A.

Weber, W. J., Jr. (1972). *Physicochemical processes for water quality control*. Wiley Interscience Publication, New York.

Appendix A
Analytical Methods

Analysis of polychlorinated biphenyls (PCB)

One of the main objectives in this research was to compare laboratory data with field data for recommending experimental conditions to be used in the dredging elutriate test (DRET). Therefore, all procedures for analyses and quantification of PCB and metals were adopted from those used by the U.S. Environmental Protection Agency (EPA) Narragansett Laboratory, which conducted the analyses for the New Bedford Harbor pilot study samples. Some modifications to the EPA procedure for PCB were used in this study: a nitrogen carrier gas was used instead of a helium gas in gas chromatography (GC) analysis, and hexane was used as an extraction solvent instead of freon. Chromerge (chromic and sulfuric acid mixture) was used to clean all glassware involved in the measurement of PCB.

Two 1-ℓ aliquots were taken from the 3-ℓ sample siphoned from the graduated cylinder for PCB analyses; one aliquot was passed through a 0.45-μm glass-fiber filter. The filtered and unfiltered aliquots were spiked with about 1.4 μg of octachloronaphthalene (OCN) and refrigerated in brown glass bottles with Teflon-lined caps until extraction (within 24 hr). The water samples were collected from New Bedford Harbor before the dredging operations. The unfiltered solution and the filtered solution in the DRET were extracted three times with 65 mℓ of high-purity hexane. Water was removed by addition of sodium sulfate and concentrated to 1 to 2 ml with a Kuderna Danish apparatus.

The filter was placed in a 40-ml culture tube and spiked with an internal standard (OCN). A few drops of acetone and enough high-purity hexane were added to cover the filter. The vial was shaken manually for a few minutes and the solvent was allowed to remain in contact with the solids overnight. Water was removed by addition of sodium sulfate, after which the extract was transferred to an 80-ml micro Kuderna Danish apparatus for concentration to 1 to 2 ml.

The concentration of PCB on New Bedford Harbor sediment was analyzed by removing a 1 to 2 g subsample from the sample provided, spiking with an

internal standard (OCN), covering with acetone, extracting with hexane overnight (Soxhlet), drying with sodium sulfate, and concentrating to 1 ml. The 1-ml extract was then treated with mercury, a 50-percent solution of sodium hydroxide (1 time), and a 50-percent solution of sulfuric acid (three times).

GC with an electron capture detector (ECD) was used to measure concentrations of PCB. All GC-ECD analyses were performed with a Hewlett-Packard Model 5890A, equipped with a split/splitless, auto injection system, and a standard ^{63}Ni electron capture detector. The GC-ECD conditions used in this work were as follows:

a. A 30-m DB5 column with 0.25-μm film thickness and 0.25-mm ID.

b. Nitrogen carrier gas and make-up gas flow rates of approximately 1.5 and 45 ml/min, respectively.

c. A 275 °C injection temperature and 325 °C detector temperature.

d. A 6.0 °C/min ramp rate.

e. Averaging of results from two injections.

Quantification of PCB is not simple because the analyte is not a single compound but rather a complex mixture of 209 possible congeners. In addition, standards of all 209 congeners are not readily available for calibration. The applicability of the different quantification techniques depends on the analytical technique, the PCB concentrations, the consistency of the PCB pattern within a sample set, and the analytical objectives (Erickson 1986).[1] Quantification against an Aroclor standard by the area of selected peaks may be appropriate if the PCB pattern closely resembles that of commercial Aroclor mixtures. Since one of the objectives of this research was to compare the laboratory data with field data, the quantification method was based upon the PCB analysis method used by the EPA laboratory in Narragansett. An internal standard (OCN) was added to the sample immediately prior to the extraction procedure, and analytes were quantified using the ratio of the analytes and internal standard responses. A range of standard solution concentrations was prepared with an approximate 1:1 ratio of Aroclor 1242 to 1254 and was used to establish a multipoint calibration curve. Four chromatographic peaks were selected for quantification: two diagnostic peaks to Aroclor 1242 and two diagnostic peaks to Aroclor 1254. The quantification peaks were chosen to match the EPA-Narragansett Laboratory method. Concentrations for each Aroclor were calculated from the mean of the two diagnostic peak-to-internal standard ratios and the total reported.

A common approach in GC peak identification is to compare the patterns produced by the sample with those produced by a mixture of commercial

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[1] References cited in this appendix are located at the end of the main text.

preparations such as Aroclor or Clophen, with the contents of samples expressed in terms of Aroclor or Clophen mixture concentrations.

Degradation, biotic or abiotic, of selected compounds can cause dissimilarities and can lead to erroneous conclusions. Burkhard (1987) developed a method called complex mixture statistical reduction (COMSTAR) which is used for analysis of PCB chromatogram traces obtained from capillary-column GC separation. COMSTAR uses a multiple-peak regression analysis with outlier checking and elimination. The COMSTAR approach fits a distribution of PCB mixtures that minimize the variance among individual chromatographic peaks in a sample and a computed theoretical distribution consisting of a combination of well-characterized mixtures. The well-characterized mixture response is based upon GC calibration using test mixtures of known composition.

Analysis of Metals

All glassware and polyethylene bottles used in this metal analysis were soaked in nitric acid, rinsed with deionized water, and dried. Seawater is difficult to analyze because of the matrix effect of salt. The matrix is atomized along with the analyte and the background signal can overwhelm the signal of the sample (Slavin, Carnrick, and Manning 1982). Samples can be pretreated to remove this interference, but the pretreatment process is time-consuming and can lead to sample contamination (Slavin, Carnrick, and Manning 1982). In this work, the method of direct determination using graphite furnace atomic absorption spectrometry with a stabilized temperature platform and Zeeman background correction (Model 5100PC and Zeeman/5100PC) was used to analyze Cu, Cd, and Pb. A matrix modifier was added to samples to reduce matrix effects. Analysis conditions appear in Table A1, and the matrix modifiers were those suggested by Schlemmer and Welz (1986).

Table A1
Atomic Absorption Conditions

Metal	Wavelength nm	Matrix Modifier mg	Temperature, °C	
			Pyrolysis	Atomizer
Cu	324.8	0.015 Pd + 0.01 $Mg(NO_3)_2$	1300	2500
Pb	283.3	0.2 PO_4 + 0.01 $Mg(NO_3)_2$	850	800
Cd	228.8	0.2 PO_4 + 0.01 $Mg(NO_3)_2$	900	1600

A 200-ml aliquot of settled water from the DRET was passed through a 0.45-μm polycarbonate filter to analyze dissolved metals and a 50-ml aliquot was digested with nitric acid to analyze the total metals. The detection limit

for each metal (Cu, Cd, and Pb) was 5 μm/ℓ, 10 μg/ℓ, and 5 μg/ℓ, respectively.

Measurement of Suspended Solids and Particle Size

The measurement of total suspended solids was performed using a 500-ml aliquot according to Standard Methods for the Examination of Water and Wastewater (American Public Health Association 1981).

The particle size distribution analyzer (PSD, Model 112LSD/ADC-80XY) used in this research determines the number and size of particles in an electrically conductive liquid. This is accomplished by forcing the suspension to flow through a small aperture having an immersed electrode on either side (Allen 1981). As a particle passes through the aperture, it changes the resistance between the electrodes. The change in resistance is proportional to the volume of particles. Pulses are amplified, sized, and counted. From the derived data, the particle size distribution (PSD) can be determined. A schematic diagram of the PSD analyzer is given in Figure A1.

The reliability of PSD measurements of heterogeneous particulate suspensions is limited because of particle clogging of the sensor orifice and particle breakup. The recommended range for each orifice is approximately 2 to 40 percent of the orifice diameter (Allen 1981). Most of the particles in the sediment from New Bedford Harbor were below 20 μm. Therefore, two aperture tubes (30 and 90 μm) were used. The total volume of suspended solids was calculated by integrating the curve of particle size with respect to the number of particles, assuming spherical particles. The mass of suspended solids was calculated using the computed volume of particles and assuming a uniform particle density of 2.3 g/cm^3.

Particle Sizing

Particle sizing by several types of filters such as membrane filter (2, 5, and 8 μm), glass fiber filter (5 and 8 μm), and nylon mesh (5 and 10 μm) was attempted following the method (Day 1965). The objective was to isolate enough of a given range of particle sizes to perform analyses of sorbed PCB. Each fractionated portion was evaluated using the PSD analyzer to determine the resultant size distribution.

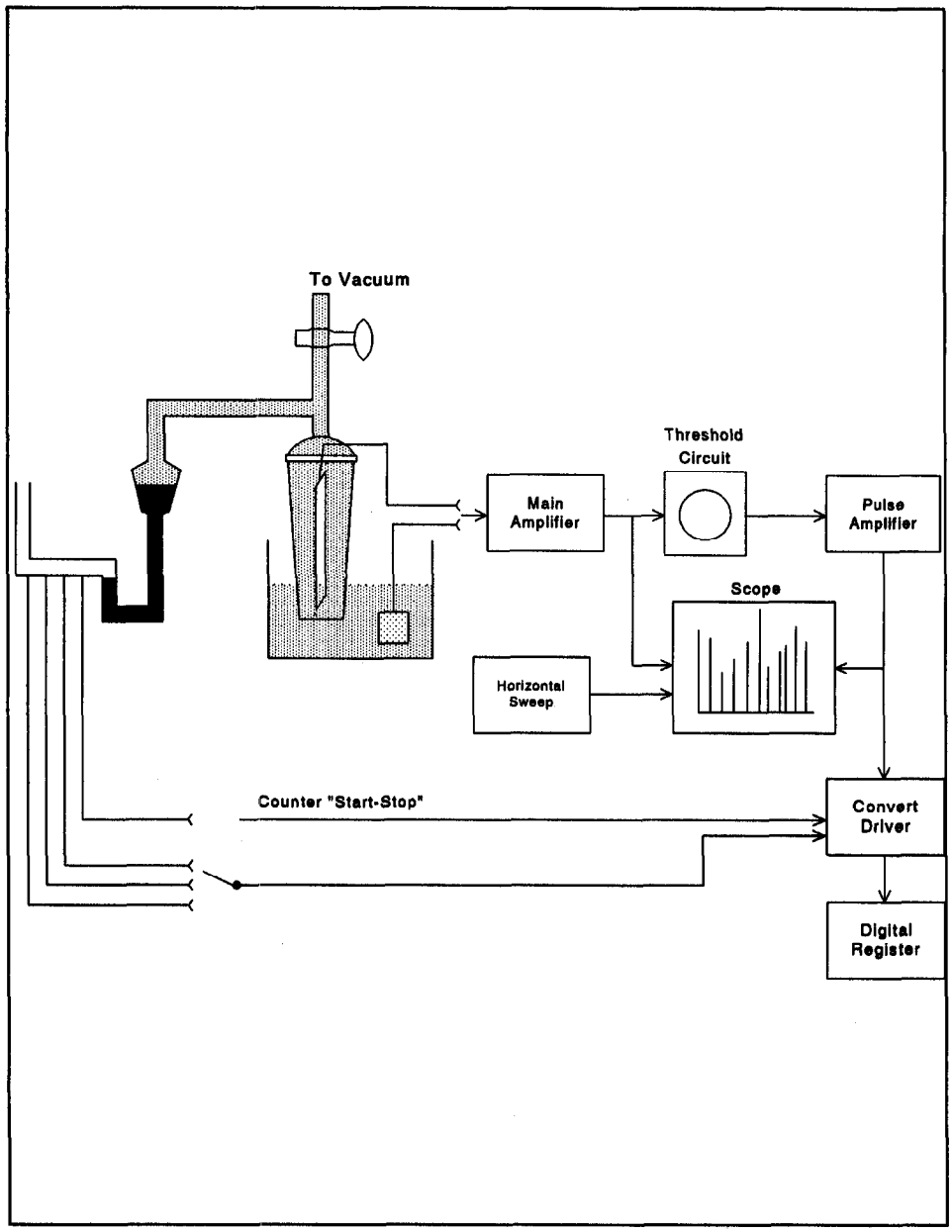

Figure A1. Schematic diagram of PSD analyzer

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
August 1995

3. REPORT TYPE AND DATES COVERED
Final report

4. TITLE AND SUBTITLE
Dredging Elutriate Test (DRET) Development

5. FUNDING NUMBERS

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Environmental Sciences and Engineering
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Corps of Engineers, Washington, DC 20314-1000;
U.S. Army Engineer Waterways Experiment Station, 3909 Halls Ferry Road, Vicksburg, MS 39180-6199

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
Contract Report D-95-1

11. SUPPLEMENTARY NOTES
Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

The removal of contaminated sediments from waterways by dredging generates concern about the release of contaminants to the water column. The ability to predict the magnitude of these potential releases during the project planning process will improve decision making in regard to water quality impacts and controls or mitigation measures for the dredging project. This report describes the development of a simple laboratory test, the dredging elutriate test (DRET), to predict the concentration of contaminants in the water column at the point of dredging. The DRET is procedurally similar to the modified elutriate test developed by the Corps of Engineers to predict the contaminant concentrations in effluent from a confined disposal facility. The test involves mixing sediment and site water, allowing the heavier solid particles to settle, sampling and supernatant, and analyzing for dissolved and particulate bound contaminants. Results of the laboratory test compared well with field data collected while dredging New Bedford Harbor sediment, which was contaminated with polychlorinated biphenyls. Most of the contaminated loading was associated with the suspended particles.

14. SUBJECT TERMS
Contaminated sediment
Dredging
Elutriate
New Bedford Harbor
PCBs
Sediment
Water quality

15. NUMBER OF PAGES
79

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT